

# Is 2-D Graphite an Ultimate Large Hydrocarbon?

## IV. Structure and Energy Spectra of Large Polycyclic Aromatic Hydrocarbons with Different Symmetry\*

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Z. Naturforsch. **58b**, 965 – 970 (2003); received June 30, 2003

The structure and energy spectra of large polycyclic aromatic hydrocarbons (PAHs) with different symmetry and edge structure have been studied by quantum chemical methods. It is shown, that if the electron correlation is taken into account, the energy gap in the spectra of the one-electron excitation  $\Delta E$  is different from zero as the number of  $\pi$ -centres of the PAHs,  $N$ , tends to infinity ( $N \rightarrow \infty$ ). Hydrocarbons with different edge structures but with the same symmetry have different energy gaps when  $N$  tends to infinity. Hydrocarbons with different symmetry but with the same edge structures have similar energy gap values.

**Key words:** Polycyclic Aromatic Hydrocarbons, Symmetry, Energy Spectra

### Introduction

The expediency of investigations of structure and energy spectra of polycyclic aromatic hydrocarbons (PAHs) is determined by the following reasons. PAHs with a large number of  $\pi$ -centres are candidates for new materials with unique electronic properties (see refs. [1, 2] and references given therein). Large planar PAH molecules are particularly interesting because they are models for two-dimensional (2-D) graphite. In the classical works of Coulson [3, 4] the first attempt of modelling of real 2-D graphite with large PAHs was made.

Studies of the energy spectra of PAHs with a large number ( $N$ ) of carbon atoms (with  $D_{6h}$  symmetry) were made by Stein and Brown [5, 6], using the one-electron Hückel method. In this approximation, the width of the energy gap (EG),  $\Delta E$ , approaches zero when  $N$  approaches infinity [5, 6].

In the earlier papers of this series [7–9] it was shown that the EG in the spectra of the one-electron excitation of planar hydrocarbons with  $\pi$ -systems in con-

jugation and with a large number of  $\pi$ -centres is different from zero when the electron correlation is taken into account. In the asymptotic case  $N \rightarrow \infty$  (2-D model of graphite) is  $\Delta E_{\infty} \neq 0$ .

In a recent work [10] of Moran *et al.*, this result has also been obtained by *ab initio* calculations at the B3LYP/6-31G(d) level of theory.

The energy spectrum of a  $\pi$ -electron system depends on the edge structure as well as on the symmetry of the  $\pi$ -system. In a previous paper of this series [11], it was shown that the width of the EG,  $\Delta E_{\infty}$ , of PAHs depends significantly on the edge structure of the hydrocarbon.

In the present work the influence of the symmetry on the energy spectra of PAHs with a large number of  $\pi$ -centres is investigated, and especially the influence on the spectra of the one-electron excitations in the asymptotic case  $N \rightarrow \infty$ .

### Objects of Investigation

We consider PAHs with two types of edge (peripheral) structures; namely acene **Ac(n)** and phenantrene **Ph(n)**, belonging to the symmetry groups  $C_s$ ,  $C_{2h}$  and  $D_{2h}$ , shown in Figs 1 and 2.

\* Part III of this series is ref. [11].

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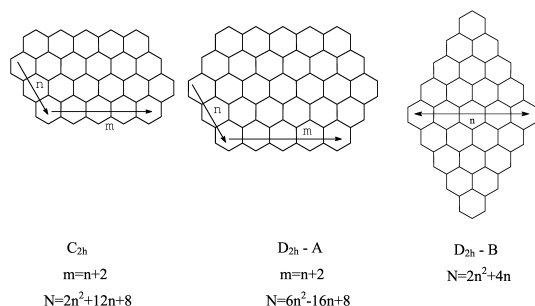


Fig. 1. PAHs with **Ac(n)** edge structures and symmetries  $C_{2h}$  and  $D_{2h}$ .  $N$  is the number of  $\pi$ -centres.

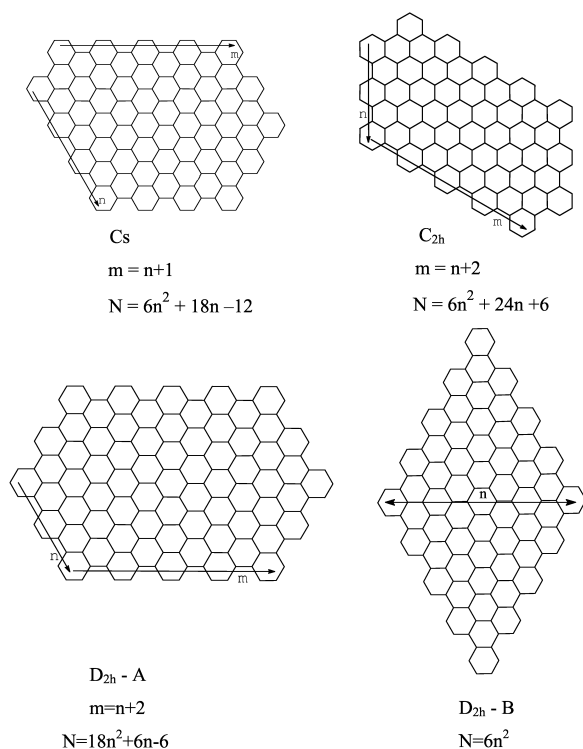


Fig. 2. PAHs with **Ph(n)** peripheral structures and symmetries  $C_s$ ,  $C_{2h}$ , and  $D_{2h}$ .  $N$  is the number of the  $\pi$ -centres.

### Methods of Investigation

The methods of investigation are described in an earlier paper of this series (see ref. [11] and references given therein), only the main relations are presented here.

#### Energy gap equation

Because the investigated PAHs are alternant systems, their energy spectra are investigated with the

AMO (Alternant Molecular Orbitals) variant of the Extended Hartree-Fock method [12]. The width of the energy gap is given by the following equation [13]:

$$\Delta E = \sqrt{\Delta_{\text{corr}}^2 + (\Delta_{\text{top}}^2 + \Delta_{\text{geom}}^2)} \quad (1)$$

where  $\Delta_{\text{corr}} = 2\delta\gamma$  is the correlation correction, and  $\gamma$  is the one-centre Coulomb integral (Hubbard parameter [14]).

The dimensionless parameter  $\delta$  satisfies the following equation:

$$M\delta = 2m = \delta \sum_k^m \gamma / \sqrt{\delta^2 \gamma^2 + \beta^2 e^2(k)} \quad (2)$$

where  $M = 2m$  is the number of  $\pi$ -electrons of the molecule.

Equation (2) has always a trivial solution  $\delta = 0$ , *i. e.*, the AMO energies are identical with the MO energies in the one-electron approximation. If  $\delta \neq 0$ , then (2) has the form:

$$M = 2m = \sum_k^m \gamma / \sqrt{\delta^2 \gamma^2 + \beta^2 e^2(k)}. \quad (3)$$

The following condition must be fulfilled for a non-trivial solution  $\delta \neq 0$ :

$$\sum_k^m \gamma / \sqrt{\delta^2 \gamma^2 + \beta^2 e_k^2} < \sum_k \gamma / |\beta e(k)|$$

or

$$|\beta|/\gamma < (|\beta|/\gamma)_{\text{crit}} = 1/2m \sum_k |\beta e(k)|^{-1}.$$

Let us denote with  $e_g = e_{g,\text{top}} + e_{g,\text{geom}}$  the HOMO energy of the hydrocarbon.

From the inequality

$$|\beta|/\gamma < (|\beta|/\gamma)_{\text{crit}} = 1/2m \sum_k |e(k)|^{-1} < 1/2e_g \quad (4)$$

$$= 1/\Delta E$$

it can be seen that if  $\Delta E \rightarrow 0$ , then  $(|\beta|/\gamma)_{\text{crit}} \rightarrow \infty$ , *i. e.*, (2) always has a non-trivial solution  $\delta \neq 0$ .

The dependence of the resonance integrals on the bond lengths  $R$  for neighboring carbon atoms is given by Mulliken's formula [15]:  $\beta(R) = \beta_0 S(R)/S(R_0)$  where  $S$  is the overlap integral and  $R_0 = 1.4 \text{ \AA}$ . The results are obtained with the following set of standard parameters [7–10]:  $\beta_0 = -2.4 \text{ eV}$ ,  $\gamma = 5.4 \text{ eV}$ .

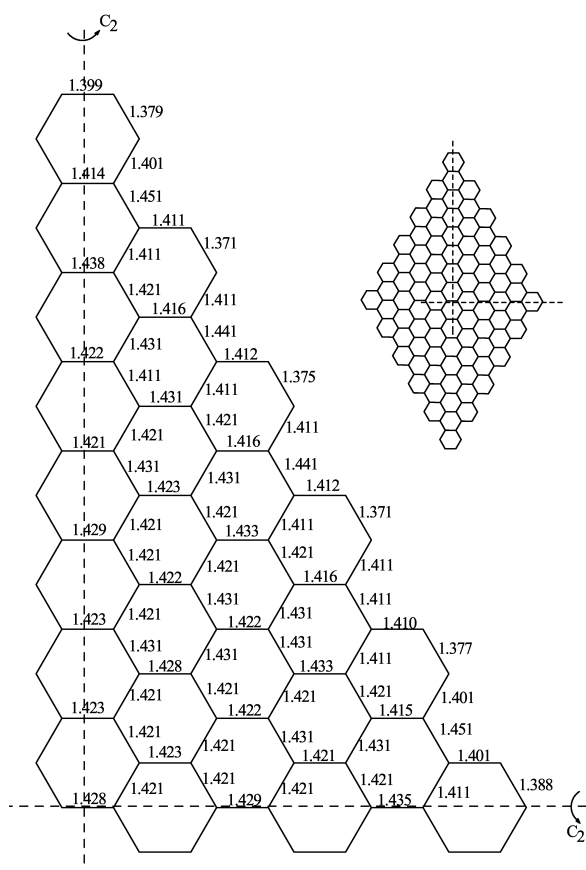


Fig. 3. Bond lengths of a PAH with **Ph(n)** edge structure, **D<sub>2h</sub> – B** symmetry and  $N = 216$  calculated with the extended SSH method.

The MO energies,  $e_k$ , and the topological and geometrical components of the EG in (1) were calculated using the HMO method.

#### Geometry of the hydrocarbons

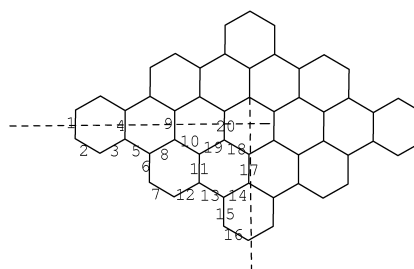
In order to estimate the bond length, and  $\Delta_{\text{geom}}$ , respectively, the extended Su-Schrieffer-Heeger (ESSH) method [16] with the following Hamiltonian can be used:

$$\begin{aligned} \mathbf{H}(\text{ESSH}) &= \mathbf{H}_{\pi} + \mathbf{H}_{\sigma} + \mathbf{H}_{\pi-\sigma} + \mathbf{H}_{\pi-\pi} \\ &= \mathbf{H}(\text{SSH}) + \mathbf{H}_{\pi-\pi}. \end{aligned} \quad (5)$$

The one-electron part of (5),  $\mathbf{H}(\text{SSH})$ , is given in terms of the original SSH model [17], whereas the two-electron part  $\mathbf{H}_{\pi-\pi}$  is approximated according to the Pariser-Parr-Pople model [18].

Table 1. Bond lengths (in Å) of PAH **D<sub>h2</sub> – B** (see Fig. 1) with  $N = 54$  C-atoms, calculated with AM1 semi-empirical method [20] and the extended SSH method, respectively. The bonds are labeled in Scheme 1.

Bond number	AM 1	ESSH	Bond number	AM 1	ESSH
1	1.400	1.385	11	1.411	1.400
2	1.384	1.365	12	1.407	1.394
3	1.412	1.391	13	1.449	1.438
4	1.413	1.399	14	1.419	1.404
5	1.449	1.438	15	1.402	1.387
6	1.407	1.394	16	1.389	1.374
7	1.370	1.393	17	1.441	1.422
8	1.412	1.400	18	1.416	1.405
9	1.441	1.424	19	1.444	1.423
10	1.422	1.407	20	1.414	1.404



Scheme 1.

The following parameterizations were used: the electron-lattice coupling constant is  $\alpha = 3.21 \text{ eV/\AA}$ , and the spring constant for C-C bonds is  $K = 24.6 \text{ eV/\AA}^2$  [15]. For the two-centre Coulomb repulsion integrals ( $\gamma_{ij}$ , necessary for the calculation of the electron-electron interaction energy) the Mataga-Nishimoto approximation [19] was used ( $\gamma = 10.84 \text{ eV}$ ):

$$\gamma_{ij} = e^2 / (e^2 / \gamma + R_{ij}).$$

The relative computational simplicity of the ESSH approach allowed us to describe hydrocarbons with up to  $N \sim 10^3$   $\pi$ -centres. Geometry optimization was carried out also with the semiempirical quantum-chemical method AM 1 [20].

#### Numerical Results and Discussions

##### Geometry of the hydrocarbons

In Fig. 3, the result for the geometry of a PAH with **Ph(n)** periphery, **D<sub>2h</sub> – B** symmetry (see Fig. 2) and  $N = 216$  C-atoms as an example is shown, calculated with the extended SSH method. In Table 1, using the hydrocarbon example of **Ph(n)** edge structure and **D<sub>2h</sub> – B** symmetry (see Fig. 2) and  $N = 54$

n	C <sub>s</sub>					D <sub>2h</sub>				
	N	$\Delta_{top}$	$\Delta_{geom}$	$\Delta_{corr}$	$\Delta E$	N	$\Delta_{top}$	$\Delta_{geom}$	$\Delta_{corr}$	$\Delta E$
4	156	1.128	0.122	0	1.250	96	1.396	0.072	0.000	1.468
5	228	0.929	0.092	0	1.021	150	1.126	0.055	0.000	1.181
6	312	0.793	0.071	0	0.864	216	0.944	0.042	0.000	0.986
7	408	0.693	0.057	0.190	0.773	294	0.812	0.034	0.000	0.846
8	516	0.616	0.046	0.264	0.713	384	0.712	0.028	0.000	0.740
9	636	0.555	0.038	0.305	0.667	486	0.635	0.023	0.000	0.658
10	768	0.505	0.032	0.326	0.628	600	0.572	0.020	0.000	0.592
11	912	0.464	0.027	0.349	0.603	726	0.521	0.017	0.000	0.538
...	#	...	...	...	...	#	...	...	...	...
16	1812	0.330	—	0.195	0.384	1536	0.360	—	0.191	0.408
17	2028	0.313	—	0.192	0.367	1734	0.339	—	0.189	0.388
18	2256	0.296	—	0.189	0.352	1944	0.320	—	0.187	0.371
$\infty$					0.239*	$\infty$				0.257*

\* Value of  $\Delta E$  calculated by means of the Aitkens formula – three point Pade approximation [22]. The results are obtained with the last three values of  $\Delta E$ .<sup>#</sup> If the number of the  $\pi$ -centres is  $N > 912$  and 726, respectively, the geometrical component to the EG is  $\Delta_{geom} \cong 0$ , and the calculations are carried out with ideal geometry of the hydrocarbons.

n	Ac(n)					Ph(n)				
	N	$\Delta_{top}$	$\Delta_{geom}$	$\Delta_{corr}$	$\Delta E$	N	$\Delta_{top}$	$\Delta_{geom}$	$\Delta_{corr}$	$\Delta E$
2	16	2.136	0.209	0.440	2.386	24	2.664	0.130	0.000	2.794
3	30	0.892	0.147	1.328	1.686	54	1.833	0.099	0.000	1.932
4	48	0.341	0.065	1.426	1.483	96	1.396	0.072	0.000	1.468
5	70	0.120	0.022	1.426	1.433	150	1.126	0.055	0.000	1.181
6	96	0.040	0.007	1.404	1.405	216	0.944	0.042	0.000	0.986
7	126	0.012	0.003	1.372	1.372	294	0.812	0.034	0.000	0.846
8	160	0.004	0.000	1.328	1.328	384	0.712	0.028	0.000	0.740
9	198	0.001	0.000	1.296	1.296	486	0.635	0.023	0.000	0.658
10	240	0.000	0.000	1.264	1.264	600	0.572	0.020	0.000	0.592
11	286	0.000	0.000	1.230	1.230	726	0.521	0.017	0.000	0.538
12	336	0.000	0.000	1.199	1.199	864	0.478	0.015	0.000	0.493
...	#	...	...	...	...	#	...	...	...	...
16	576	0.000	—	1.121	1.212	1536	0.360	—	0.191	0.408
17	646	0.000	—	1.100	1.100	1734	0.339	—	0.189	0.388
18	720	0.000	—	1.080	1.018	1944	0.320	—	0.187	0.371
...	...	...	...	...	...	...	...	...	...	...
28	1680	0.000	—	0.929	0.929					
29	1798	0.000	—	0.917	0.917					
30	1920	0.000	—	0.906	0.906					
$\infty$	$\infty$				0.785*	$\infty$				0.257*

Table 2. Comparison of the calculated values for the different components of the energy gap of hydrocarbons with **Ph(n)** edge structure of **C<sub>s</sub>** and **D<sub>2h</sub>** – **B** symmetries (see Fig. 2). All entries are in eV.

Table 3. Comparison of the calculated values for the different components of the energy gap of hydrocarbons with **D<sub>2h</sub>** symmetry and **Ac(n)-B** (Fig. 1) and **Ph(n)-B** (Fig. 2) edge structures. All entries are in eV.

\* Value of  $\Delta E$  calculated by means of the Aitkens formula – three point Pade approximation [22]. The results are obtained with the last three values of  $\Delta E$ .<sup>#</sup> If the number of the  $\pi$ -centres is  $N > 864$  and 336, respectively, the geometrical component to the EG is  $\Delta_{geom} \cong 0$ , and the calculations are carried out with ideal geometry of the hydrocarbons.

C-atoms, the good correlation between the results of the bond lengths calculated with the AM1 semiempirical quantum chemical method [20] and the extended SSH method is demonstrated.

The geometrical component,  $\Delta_{geom}$ , which contributes to the EG, (see (1)) depends on the geometry of the hydrocarbon. When the number  $N$  of  $\pi$ -centres increases, the alternation of the bond lengths exists only in the periphery of the PAH (see Fig. 3). In the central part the bond lengths are nearly equal and are close in value to the bond lengths of graphite 1.421 Å [21].

Let us denote by  $N_p$  and  $N_i$  the number of  $\pi$ -bonds in the periphery and in the inner part, respectively, of a PAH with  $N$   $\pi$ -centres. If  $N \gg 1$ , the following relation

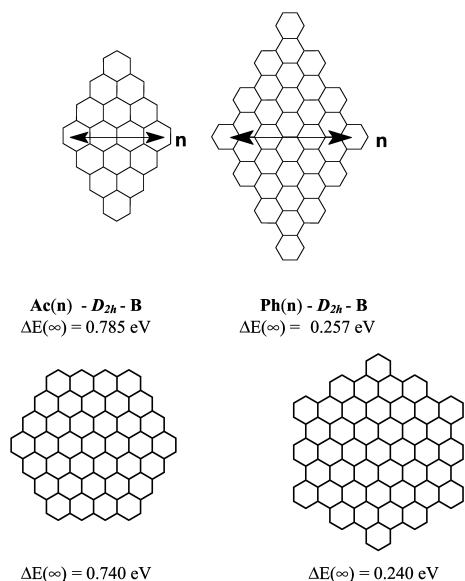
is true:

$$N_p/N_i \sim 1/N \rightarrow 0.$$

When  $N$  increases the geometrical component  $\Delta_{geom}$  decreases and tends monotonically to zero (see Tables 2 and 3).

### Energy spectra of the hydrocarbons

The dependence of  $\Delta E$  on the number of  $\pi$ -centres in PAHs was calculated for all hydrocarbons shown in Figs. 1 and 2. In Tables 2 and 3 only typical examples are compared. The conclusions given here are based on the numeric results for all hydrocarbons taken into account.



Scheme 2.

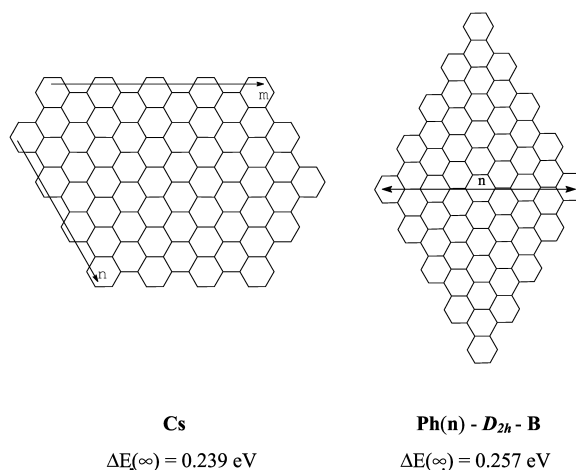
The results for the energy gap of PAHs with **Ph(n)** edge structures and symmetries **C<sub>s</sub>** and **D<sub>2h</sub> - B** are compared in Table 2 (see Fig. 2). In Table 3 are compared the results for  $\Delta E$  of PAHs with **D<sub>2h</sub> - B** symmetry and both **Ac(n)** and **Ph(n)** peripheries (see Figs 1 and 2).

For all PAHs with **Ac(n)** edge structure, the main contribution to the energy gap is the correlation correction. The geometrical and topological components give contributions for systems with a small number of  $\pi$ -centres and approaches zero with increasing number of  $\pi$ -centres. The dependence of  $\Delta E$  on the number of  $\pi$ -centres is illustrated by the results collected in Tables 2 and 3. For PAHs with **Ph(n)** edge structure, the main contributions to the energy gap are the topological and correlation components. The correlation correction, however, contributes for hydrocarbons with large number of  $\pi$ -centres ( $N > 10^3$ ).

Hydrocarbons with different edge structure but with the same symmetry have different values for the energy gap in the limit case  $\Delta E(\infty)$ . An example is given in Scheme 2 (see Table 3).

The hydrocarbons have practically the same values for the EG like the PAHs **Ac(n)**, and **Ph(n)** with **D<sub>6h</sub>** symmetry (see ref. [8]).

Hydrocarbons with different symmetries but with the same edge structure have similar values of the EG, as this follows from Table 2 and is illustrated by the



Scheme 3.

hydrocarbons **Ph(n)** with **D<sub>2h</sub>** and **C<sub>s</sub>** symmetry (see Table 2 and Scheme 3).

The numeric results for the energy gap of the investigated hydrocarbons lead to the following general conclusions:

(i) The most important characteristic of the energy spectra of the large PAHs – the width of the energy gap – is different from zero for all investigated systems:  $\Delta E(\infty) \neq 0$ . This means, that 2-D graphites modelled by PAHs with different edge structure and different symmetry with singlet ground state are semiconductors.

The estimates of the one-particle excitation energies,  $\Delta E$ , in this work concern direct – vertical electron transitions, for which the absorption of the photon is not connected with absorption or release of a phonon. The energy of the lattice distortions of a hydrocarbon with a large number of  $\pi$ -centres is of the order of magnitude  $\hbar\omega_q \sim 0.2 - 0.3$  eV [23, 24].

Denoting the energy of a phonon in PAH with  $\hbar\omega_q$ , the energy of the indirect transition,  $\Delta\epsilon_q$ , *i. e.*, the transition where along with the absorption of a photon, a phonon is absorbed or released, will be equal to [25]:

$$\Delta\epsilon_q = \Delta E \pm \hbar\omega_q \quad (6)$$

This means that if the width of the EG has a low value ( $\Delta E < 0.3$  eV), the  $\Delta E$  value becomes comparable with that of phonons:

$$\Delta E \sim \hbar\omega_q.$$

(ii) The main factor concerning the structure of PAHs, which determines the width of the energy gap, is the periphery structure of the hydrocarbons. Table 4

Table 4. Energy gap  $\Delta E$  ( $N \rightarrow \infty$ ) for PAHs with different edge structures and symmetries (see Figs. 1 and 2). All values are in eV.

Symmetry	$\Delta E$ ( $N \rightarrow \infty$ ) <b>Ac(n)</b>	$\Delta E$ ( $N \rightarrow \infty$ ) <b>Ph(n)</b>
<b>Cs</b>	—	0.239
<b>C<sub>2h</sub></b>	0.797	0.240
<b>D<sub>2h</sub> – A</b>	0.623	0.236
<b>D<sub>2h</sub> – B</b>	0.784	0.257
<b>D<sub>6h</sub></b>	0.740*	0.240*

\* The results are taken from ref. [8].

summarizes the values of the energy gap (in the asymptotic case  $N \rightarrow \infty$ ) for all systems investigated in this paper.

#### Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft (N. T.) and Deutscher Akademischer Austauschdienst (A. S.).

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