CROATICA CHEMICA ACTA CCACAA 56 (3) 451—459 (1983)

CCA-1391

YU ISSN 0011 1643
UDC 547:541.17
Original Scientific Paper

Topological Properties of Small Li Clusters and the Pariser-Parr-Pople-Type Model*

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A simple analysis of the spin multiplicity of the ground state is presented in the weakly correlated limit. The ab initio MRD-CI predictions on the small lithium clusters and the full CI results of the Pariser-Parr-Pople model for the corresponding network of centers exhibit a close parallelity which is possible to rationalize.

INTRODUCTION

The evident relevance of the topology concept for the electronic structure of molecules and the interest in the graph theory[1] as its mathematical implementation stimulates a natural question about the limits of their applicability. The formal identity of the Hückel determinants and the determinants of adjacency matrices can be considered as an indication that the topology approach essentially cannot yield more information than the simplest version of the Hückel theory. Without doubt this theory itself represents a very useful tool for some limited purposes. Moreover, it can be assumed that the conjugated hydrocarbons form the main class of compounds suitable for the successful application of this concept.

The biradical character of some unstable conjugated hydrocarbons is one of the fundamental properties which can be indicated, to some extent, by topological considerations. The more refined problem whether the biradical ground state is a triplet or singlet cannot be answered if the correlation effects are not taken into account explicitely (cf. e. g. Ref. 2). The values of occupation numbers of natural orbitals have been used in Ref. 2 as an important criterion for the biradical character of the singlet ground state of a molecule. The natural orbitals are the eigenfunctions of the one-electron density operator resulting from the correlated molecular wavefunction. If two electrons in the molecular ground state move mutually indepently, two occupation numbers of natural orbitals (say n and n′) have values near to one and the molecules exhibit biradicaloid features.

The question of the singlet-triplet splitting can be settled in the case of alternant conjugated hydrocarbons (i. e., compounds with bipartite graphs) with the help of the exact solable Pariser-Parr-Pople model.[2,3,4] For example,

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* Presented at *The IUPAC International Symposium on Theoretical Organic Chemistry,* held in Dubrovnik, Croatia, August 30 — September 3, 1982.

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*** Present address: BASF, 6700 Ludwigshafen/Rh., Germany it has been shown[2] that the ground state of alternant hydrocarbons with different numbers of centers in both classes ($n^* \neq n^0$) is a triplet. On the contrary, the alternant hydrocarbons without single Kekulé structure but with $n^0 = n^*$ as well as some structures containing 4n rings in their conjugated carbon skeleton have slightly lower lying singlet than the lowest triplet. These predictions of the PPP π-electron model have been confirmed by more sophisticated all electron ab initio calculations and by the corresponding experimental investigations. The behaviour of nonalternant conjugated hydrocarbons is less obvious.

In this contribution, a simple analysis of the problem of the multiplicity of the ground state and of the possible biradical character of the lowest singlet state is presented in the weakly correlated limit. The seemingly surprising parallelity between PPP full CI results for some conjugated hydrocarbons and properties of small Li clusters predicted by the ab initio MRD CI procedure[5] represents an example of the farreaching similarity in the behaviour of chemically completely different systems.

In addition, the importance of the correlation effects is demonstrated on an example of weakening of two different bonds in a nonalternant biradicaloid system leading to alternant biradicals of different kind (i. e. with $n^0 = n^*$ and $n^0 \neq n^*$) which are both without Kekulé structures.

THE RELATIVE POSITION OF THE LOWEST SINGLET AND LOWEST TRIPLET AND THE BIRADICALOID BEHAVIOUR OF THE LOWEST SINGLET (NEARLY UNCORRELATED LIMIT)

Let us consider Slater determinants $|a^2\rangle = |K_{in}, a\,\bar{a}\rangle$, $|b^2\rangle = |K_{in}, b\,\bar{b}\rangle$ and $^3|ab\rangle = |K_{in}, ab\rangle$ with corresponding energy expectation values E_a, E_b, E_T where K_{in} represents doubly occupied $(n - 1)$ MO's and the bar over the MO-symbol means the spin down orientation. It is advantageous to write the energy expectation value for the Slater determinant $|K\rangle$ in the form

$$E_K = \langle K|\hat{H}|K\rangle = \sum_{j=1}^{n} n_j \left(h_j + \frac{(n_j - 1)}{2} J_{jj} + \sum_{l<j} (n_l J_{jl} - K_{jl}) \right) \tag{1}$$

where the doubly occupied MO's precede the singly occupied ones. n_j is the occupation number of j-th MO, J_{jl} and K_{jl} are the Coulomb and exchange integrals, and h_j is the matrix element of the one electron part of H.

If we assume that due to the symmetry or due to the Brillouin theorem the wavefunction

$$^1|K.\,.\,ab\rangle = \frac{1}{\sqrt{2}} [(|K_{in}, a\bar{b}\rangle - |K_{in}, b\bar{a}\rangle)] \tag{2}$$

cannot interact strongly with $|a^2\rangle$ and $|b^2\rangle$, the CI between $|a^2\rangle$ and $|b^2\rangle$ yields the wavefunction

$$|\varepsilon_\pm\rangle = c_a(\pm)|a^2\rangle + c_b(\pm)|b^2\rangle \tag{3}$$

where

$$c_b(-)/c_a(-) = \Delta/K_{ab} - \left[1 + \left(\frac{\Delta}{K_{ab}} \right)^2 \right]^{1/2} \tag{4}$$

with

$$\Delta = L_b - L_a + (J_{bb} - J_{aa})/2 = (E_b - E_a)/2$$

and

$$L_x = h_x + \sum_{j=1}^{n-1} (2\,J_{jx} - K_{jx}), \quad x = a, b$$

$$L_a + L_b = (E_b + E_a)/2$$

The energy ε_- is related to the expectation value E_T of the triplet state $^3|\,ab\rangle$ in the following way:

$$\Delta E = E_T - \varepsilon_- = -\Delta\,J_{ab} + K_{ab}\left[\left(1 + \left(\frac{\Delta}{K_{ab}}\right)^2\right)^{1/2} - 1\right] \tag{5}$$

$$= \Delta - J_{ab} - K_{ab}\left(1 - \left|\frac{c_a}{c_b}\right|\right)$$

where

$$\Delta\,J = (J_{aa} + J_{bb})/2 - J_{ab}$$

In the weakly correlated limit the »biradicaloid« character of the lowest singlet can be due to the circumstance that the ratio $|\,c_b\,(-)/c_a\,(-)\,|$ is near to one or due to the fact that the energy expectation value E_s fo the wave-function $^1|K_{in}, ab\rangle$ is lower thanε_-:

$$E_s - \varepsilon_- = \Delta\,E + 2\,K_{ab} < 0. \tag{6}$$

In the special case of alternant hydrocarbons with the nonbonding orbitals $|\,a\rangle$ and $|\,b\rangle$ which can be chosen so that they are alternant conjugated

$$|\,b\rangle = |\,\tilde{a}\rangle,$$

it holds

$$\Delta\,J_{ab} = 0, \quad \Delta = L_{\tilde{a}} - L_a$$

$$\Delta\,E = K_{ab}\,[(1 + (\Delta/K_{ab})^2)^{1/2} - 1] \geq 0 \tag{8}$$

In addition, if $L_{\tilde{a}} - L_a$, the relation

$$c_b\,(-)/c_a\,(-) \cong -1 \tag{9}$$

holds as well, and $\Delta\,E = 0$.

Therefore, the Hund's rule is not valid for symmetrical alternant biradicals and for biradicals with $n^* = n^0$ but without Kekulé structure. The singlet ground state has a biradical character. On the other hand, for topological biradicals with $n^* \neq n^0$ the individual nonbonding MO's $|\,a\rangle$ and $|\,b\rangle$ are alternant self-adjoint ($|\,\tilde{a}\rangle = |\,a\rangle$, $|\,\tilde{b}\rangle = |\,b\rangle$) and the Hund rule is valid, but $|\,c_b\,(-)/c_a\,(-)\,|$ is near to one because Δ is very small and K_{ab} is not negligible. In general, in the case of alternant systems a very small energy difference between the lowest singlet and triplet ($\Delta\,E \sim 0$) or the triplet character of the ground state ($\Delta\,E < 0$) are necessarily accompanied by the biradicaloid character of the lowest singlet state. The biradicaloid character of the lowest singlet for a nonalternant system is a molecular property independent from the quantity $\Delta\,E$: On the contrary, the ground state of a nonalternant hydrocarbon can be, for example, a triplet ($E_T \langle \varepsilon_-$) and the lowest singlet state has no biradical features ($c_b^{(-)}/c_a^{(-)} \simeq 0$). The dependence of the biradicaloid character on the geometric structure for nonalternant topologies is less clear.

An example of the transition between different kinds of biradicaloid topopologies is discussed in the Appendix.

Li CLUSTERS AND THE NETWORKS OF CENTERS INTERACTING ACCORDING THE PARISER-PARR-POPLE-MODEL

The parallelism of the energy characteristics for Li clusters and topologically equivalent networks of centers interacting according to the Pariser-Parr-Pople (PPP) model is shown in Table I. In this table some typical examples of the Li_4 and Li_6 clusters and corresponding PPP networks are included. The topologies **9** and **10** with 8 centers are added because they demonstrate a surprisingly similar description of the spin splitting for the two typical hydrocarbon biradicals of different kind (**9** : n = n*) no Kekulé structure, **10** : n* ≠n⁰ on one side, and for the hypothetic Li-clusters with the same topology on the other side.

TABLE

Comparison of the Lowest Singlet ($E_{S,PPP}$) *and Triplet Energies of Pariser-Parr-Pople Networks with the Lowest Singlet* ($E_{S,Li}$) *and Triplet* ($E_{T,PPP}$) *Energies of Li-clusters Calculated with the MRD-CI Method*

Topology[1]	$E_{S,PPP}$ (eV)[2]	$E_{T,PPP}$ (eV)[2]	ΔE_{PPP} (eV)[3]	$E_{S,Li}$ (a. u.)[4]	$E_{T,Li}$ (a. u.)[4]	ΔE_{Li} (a. u.)[4]
1	—8.04	—7.75	0.29	—29.570	—29.575	—0.005[5]
2	—9.23	—7.03	2.20	—29.573	—29.554	0.019
3	—9.46	—8.01	1.45	—29.591	—29.573	0.018[5]
4	—14.82	—13.23	1.59	—44.378	—44.358	0.020
5	—15.48	—15.44	0.04	—44.380	—44.384	0.004
6	—15.66	—11.74	3.92	—44.383	—44.363	0.020
7	—17.06	—14.82	2.26	—44.399	—44.371	0.028
8	—17.86	—13.70	4.16	—44.405	—44.355	0.046
9	—16.18	—16.13	0.05	—59.130	—59.117	0.013
10	—17.25	—17.64	—0.59	—59.120	—59.124	—0.004
11	—12.03	—12.41	—0.38	—	—	—
12	—11.55	—11.48	0.07	—44.349	—44.347	0.002
13	—11.13	—11.79	—0.60	—	—	—

1) See Figure 1.

2) Calculated with the full CI PP method ($\beta = -2.6$ eV, electron repulsion integrals parametrized with the Michl-Karwovski approximation (cf. Ref. 14).

3) $\Delta E_{PPP} = E_{T.PPP} - E_{S.PPP}$, $\Delta E_{Li} = E_{T,Li} - E_{S,Li}$

4) Applied for the MRD-CI procedure with the basis set *F* of Ref. 6. The Li—Li distances are taken equal 5.8654 a. u. The number of reference configurations is chosen so that their weight in the final correlated wavefunction is greater than 80%.

5) With the AO basis *D* MRD-CI yields for the compound 1 the $E_{,SLi} = -29.847$, $E_{T,Li} = -29.839$, $\Delta E_{Li} = 0.008$ and for the cluster 3 $E_{S,Li} = -29.863$, $E_{T,Li} = -29.842$, $\Delta E_{Li} = 0.021$ for the optimized geometries. The larger basis *D* inverses the sign of ΔE_{Li} for the Li cluster 1.

The energies ($E_{S,LPP}$ and $E_{T,PPP}$) of the lowest singlet and the lowest triplet of PPP networks with the edges of equal lengths result from the exact solution of the PPP model.[2-4]

The energies of the lowest singlet and the lowest triplet of the Li clusters ($E_{S,Li}$ and $E_{T,Li}$) have been obtained employing the ab inition MRD-CI method[5] with a relatively small AO basis set *E* (Ref. 6) of the double-zeta quality [*6s1p/2s1p*].

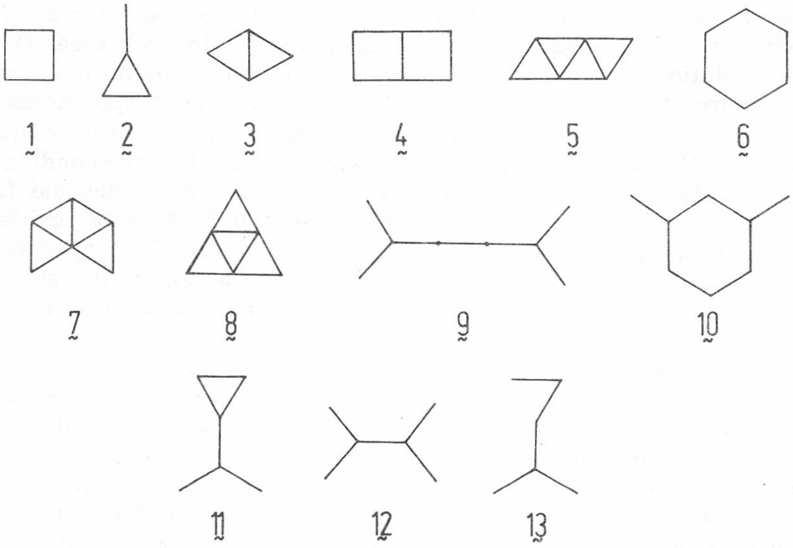

Figure 1. The graphs **1**—**13**

The most stable Li_4 and Li_6 clusters are such planar geometries which exhibit high compactness and have the singlet ground state (cf. Ref. 7). Good measure of the compactness is the average number of nearest neighbors.[6,7]

Some of PPP networks (e. g. structures **5**, **7** and **8**) are not allowed as topologies of conjugated unsaturated hydrocarbons with sp^2 hybridization present at carbon atoms but they are useful for model considerations of Li clusters. Furthermore, the absence of the spatially strongly directed σ-bonds in Li clusters broadens the applicability of the PPP model to the topologies with small rings which would exhibit large strains in the case of conjugated unsaturated hydrocarbons. The pronounced difference in the character of the π-bonds in hydrocarbons and binding in the Li clusters is demonstrated also by the small energy increase which accompanies certain deviations from the planarity of the lithium clusters.[7,8] On the other hand, some of topologies which are favorable from steric reasons for the π-electron systems are not compact enough to exhibit large binding energies for Li clusters (e. g. clusters **9** and **10**).

The sequence of the MRD-CI energies for Li_4 and Li_6 clusters and the sequence of the corresponding energy characteristics of the PPP networks with the identical topologies is in all considered cases the same. The only discrepancies between both approaches has been found in the case of clusters **1** and **5** where the signs of the very sensitive quantity ΔE_{Li} ($\Delta E_{Li} = E_{T,Li} - E_{S,Li}$) are different. Nevertheless, the sign of ΔE_{Li} is inversed when the more flexible AO basis set *D* [*6s2p*/*6s2p*] is employed in the MRD-CI treatment and when the lengths of the square sides are optimized (cf. Ref. 9). The similar effect can be expected for the larger cluster **5** as well.

The energy $E_{S,Li}$ of the cluster **3** is closer to the $E_{S,Li}$ of the square Li_4 (**1**) than to the $E_{S,Li}$ of the rhombus Li_4 (**3**). The relatively small stability of the »T-form« Li_4 with all equal interatomic distances obtained with the smaller

AO basis *F* contradicts the result with better AO basis sets for a »T-form« of Li_4 cluster with optimal interatomic distances.[10,11] In both cases (**1** and **2**) the exact solutions for the PPP networks yield better qualitative agreement with the more flexible versions of sophisticated ab initio approaches.

When various changes in geometries of small lithium clusters are investigated with the MRD-CI method, the appearance of corresponding »nonalternant« topologies leads to surprising changes in the biradicaloid features of the systems. Because the results employing the PPP model exhibit far-reaching similarities with some features of the electronic properties of Li clusters calculated with ab initio methods, the variations of the spin characteristics resulting from the changes in topology of PPP networks are described in the Appendix employing the PPP full CI procedure.[4]

In order to understand why the exact solutions of PPP networks and the MRD-CI results on Li cluster exhibit quite similar feature, it is appropriate to emphasize some essential features of the PPP model Hamiltonian (cf. e. g. Ref. 12, 13). In its one-electron part the couples of centers between which the electron hopping occurs are determined and therefore, in this manner includes the topological characterization. In its two electron part the Coulombic electron-electron interaction between the atomic centers is described in a semiclassical manner because it depends only upon the number operators of electrons localized at the interacting centers. This combination of topological description of the covalent bond network and the semiclassical Coulombic interaction is evidently sufficient to yield some characteristic information relevant for alkali metal clusters. Surprisingly enough, the parametrization in the semiempirical PPP approximation chosen for the purpose of description of the π-electron properties in conjugated unsaturated hydrocarbons does not describe wrongly the relevant energetic properties of Li clusters.

The reason for the relevance of the PPP model is evidently a formal similarity between the interaction of 2*s* orbitals in the small planar Li clusters and the interaction of the p_z orbitals in a planar network of the PPP model of conjugated unsaturated hydrocarbon.

CONCLUSIONS

Various properties of the ground state of unstable systems can be partly understood in the weakly correlated limit but the detailed prediction of the spin multiplicity depends on the details of the implemented procedure. The considerations of topology alone can reveal only the possible spin behaviour of the unstable systems but the proper consideration of the electron correlation is necessary for more detailed predictions of the spin multiplicity of the molecular ground state.

The surprising parallelity between the ab initio MRD CI results for the small planar Li cluster and some features of the corresponding network of centers described with the exact solable Pariser-Parr-Pople model is due to the topological characterization of the bonds and to the simple but sufficient description of the electron-electron interaction in this model.

Acknowledment. — The work has been supported by the Deutsche Forschungsgemeinschaft in the framework of the Sonderforschungsbereich 6 »Structure and

APPENDIX

The Transition between the Representatives of Three Classes of Biradicaloids. (The Full CI Treatment of the PPP Model).

The deap changes in the electronic structure during the transition between three representatives of three different classes of biradicals can be followed when the resonance integral β_{24} or β_{34} in the structure **11** is gradually weakened (compare Figures 2 and 3 for numeration). When β_{24} in the nonalternant biradicaloid **11** becomes zero, the alternant topological biradical **13** with $n^* \neq n^0$ appears. If β_{34} vanishes the alternant biradicaloid **12** with $n^* \neq n^0$ but without a Kekulé structure is formed.

The Hückel MO energies are shown in Figure 2. The compounds **12** and **13** have two Hückel nonbonding orbitals, but the structure **11** exhibits only one nonbonding orbital which should be doubly occupied according the *Aufbauprinzip.* The changes in the energies of the lowest singlet and lowest triplet obtained from the exact solution of the Pariser-Parr-Pople model with the weakening of the bond between centers 2 and 4, and 3 and 4 in the scheme **11** is shown in Figure 3.

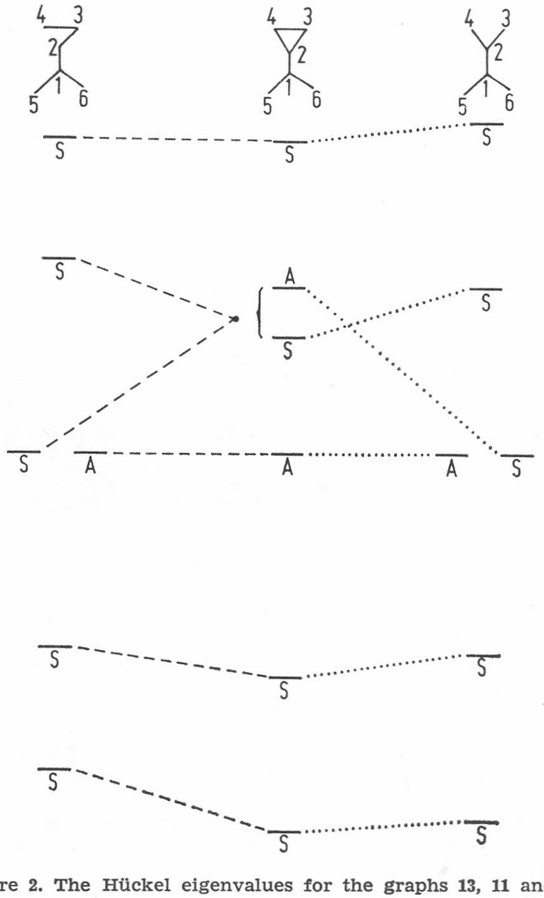

Figure 2. The Hückel eigenvalues for the graphs 13, 11 and 12.

The energy of the triplet drops strongly with increasing value of β_{34} in transition from **12** to **11** and crosses the energy of the lowest singlet. The hypothetic compound **11** should have a very stable triplet ground state. It is necessary, of course, to take into account a very large strain in the three member ring which makes this topology at the end unfavorable as a structure for a real conjugated hydrocarbon. The intercore repulsion is underestimated in the PPP expression for the total π-electron energy as well. The occupation numbers n and n′ of natural orbitals which are nearest to the value 1 are found to be equal one (n = n′ = 1) for the lowest singlet state of topological alternant biradical **13** with $n^+ \neq n^0$. For the biradicaloid **12** with no Kekulé structure n = 1.02, n′ = 0.98 but for the non-alternant biradicaloid **11** n = 1.67, n′ = 0.33.

This example shows the large variety in the behaviour of unstable molecules which can be well indicated with the exact solutions of the relevant PPP models. The topology is a very important and an interesting property. However, only a method which allows to take into account the electronic correlation at least in a simple manner can distinguish between some important characteristics of the ground state of such compounds.

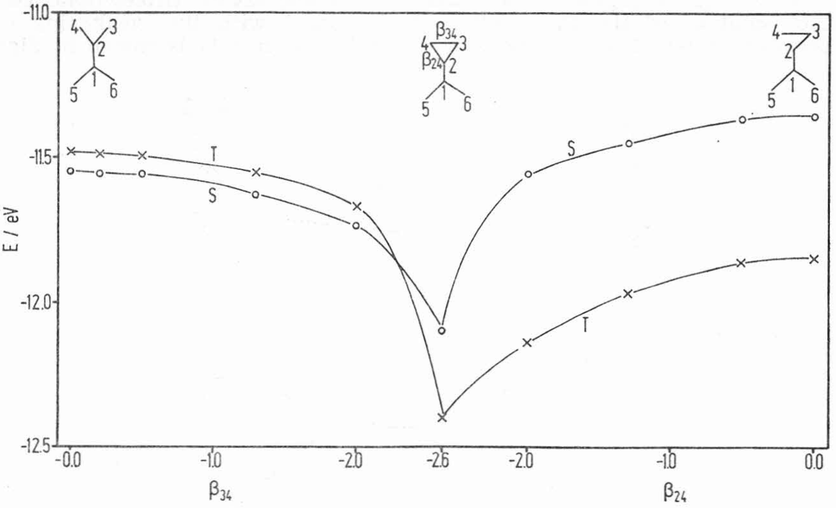

Figure 3. The changes in the energies of the lowest singlet (S) and of the lowest triplet (T) with decrease of the resonance integrals β_{24} or β_{34} in the compound **11**. The full CI PPP method has been employed with resonance integrals β_{ij} equal —2.6 eV for the usual not weakened conjugated bonds and with the electron-electron repulsion integrals γ_{ij} evaluated according to the Michl-Karwovski formula (cf. e. g. Ref. 14).

REFERENCES

1. A. Graovac, I. Gutman, and N. Trinajstić, *Topological Approach to the Chemistry of Conjugated Molecules, Lecture Notes in Chemistry, Nr. 4,* Berlin--Springer-Verlag, 1977.
2. D. Döhnert and J. Koutcký, *J. Amer. Chem. Soc.* **102** (1980) 1789.
3. R. G. Parr, *The Quantum Theory of Molecular Electronic Structure,* Benjamin, New York, 1963.
4. J. Paldus, *J. Chem. Phys.* **61** (1974) 5321.
5. R. J. Buenker and S. D. Peyerimhoff, *Theor. Chim. Acta* **35** (1974) 33; R. J. Buenker, S. D. Peyerimhoff, and W. Butscher, *Mol. Phys.* **35** (1978) 771.
6. H.-O. Beckmann and J. Koutecký, *Surface Science* **120** (1982) 127.
7. G. Pacchioni, D. Plavšić, and J. Koutecký, *Ber. Bunsenges. Phys. Chem.,* submitted.
8. D. Plavšić, J. Koutecký, G. Pacchioni, and V. Bonačić-Koutecký, *J. Phys. Chem.,* submitted.
9. H.-O. Beckmann, J. Koutecký, and V. Bonačić-Koutecký, *J. Chem. Phys.* **73** (1980) 5182.
10. J. Flad, H. Stoll, and H. Preuss, *J. Chem. Phys.* **71** (1979) 3042.

11. H.-O. Beckmann, J. Koutecký, P. Botschwina, and W. Meyer, *Chem. Phys. Letters* **67** (1979) 119.
12. J. Koutecký, *Chem. Phys. Letters* **1** (1967) 249.
13. J. Linderberg and Y. Öhrn, *Propagators in Quantum Chemistry*, Academic Press, London 1973.
14. E. W. Thulstrup and J. Michl, *J. Amer. Chem. Soc.* **98** (1976) 4533.

SAŽETAK

Topološka svojstva i model Pariser-Parr-Pople tipa za male Li klastere

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Jednostavna analiza spinskog multipliciteta u osnovnom stanju prikazana je u slabo koreliranom ograničenju. *Ab initio* MRD-CI predviđanja o malim litijevim klasterima i potpuni CI rezultati Pariser-Parr-Pople modela za odgovarajuću mrežu centara pokazuju bliski paralelizam koji je moguće racionalizirati.