THE TOPOLOGICAL SPIN HAMILTONIAN - A NEW PERSPECTIVE FOR
THE CHEMICAL GRAPH THEORY ?

J.Cioslowski

Department of Chemistry , Georgetown University ,
Washington , D.C. 20057 , USA

Abstract: Well-known failures of the Hückel topological
Hamiltonian prompt us to develop an alternative approach to
correlation between the topological features and electronic
structure of molecules. The topological spin (TS) Hamilto-
nian appears to be one of those alternatives. The applica-
tion of the connected moments expansion (CMX) makes the cal-
culations tractable even for large molecules. Major differ-
ences and similarities between the Hückel and TS methods are
pointed out and pathways for further development are under-
lined.

I. WHY ANOTHER TOPOLOGICAL HAMILTONIAN ?

The failures of the topological Hückel Hamiltonian can be

classified into those we know the reason precisely and those

we do not now exactly what is going on. The first class

comprises difficulties associated with the fact that the

eigenfunctions of the Hückel Hamiltonian are antisymmetrized

products of spinorbitals and therefore they not allow for

the electron correlation. Because of that we can expect

everything but a proper description of the states with a

different multiplicity. Being more explicit , we should not

be surprised at the troubles with the topological resonance

energy when applied to radicals [1] as well as at the fact

that the topological predictions , even if usually confined to the ground state , can provide incorrect state multiplicities [2]. In the light of that the incorrect prediction of a vanishing singlet - triplet splitting in the absorption spectra appears obvious.

The second class of invalid results from the Hückel theory is even more troublesome. The most notorious example is the 1.4-divinylbenzene / 2-phenylbutadiene pair of isospectral molecules with the same spectrum of Hückel eigenvalues , but pretty different PE spectra [3]. In this case it is of course easy to suspect that this is another manifestation of the breakdown of the Koopmans theorem , but in fact the reason for such a dramatic difference between theoretical predictions and the realm of experimental data remains more or less unaccountable.

Bearing in mind the above facts we realize that another alternative for a topological Hamiltonian is badly needed. There is also another aspect of the whole problem : having another topological Hamiltonian derived we would be able to verify the (correct) predictions of Hückel theory.

We believe that the topological spin (TS) Hamiltonian , although not perfect , can serve as a valuable alternative for the standard Hückel one.

II. THE TS HAMILTONIAN

Suppose we deal with a molecule possessing N carbon atoms and M carbon-carbon bonds. From p_z atomic orbitals we

construct the Slater determinants assigning a spin α to [N/2] electrons and a spin β to N - [N/2] of them. There are $C_N^{[N/2]}$ such determinants and this set forms our basis. Using the quasi-degenerate perturbation theory , Maynau and Malrieu [4,5,6,7] were able to show that the matrix element of the effective pi-electron Hamiltonian between the determinants |P> and |Q> reads :

$$H_{PQ} = -\sum_{i-j}' g_{ij} <P|i\bar{j}><i\bar{j}|Q> + <P|\bar{i}j><\bar{i}j|Q>$$

$$- <P|i\bar{j}><\bar{i}j|Q> - <P|\bar{i}j><i\bar{j}|Q> \quad . \tag{1}$$

In eq. (1) the sum runs over all bonds i-j. For P = Q , the bond i-j contributes to the sum with factor g_{ij} only if the determinant |P> has a spin alternation on this bond. For P $\neq$ Q , there is a contribution of $-g_{ij}$ only when the determinants |P> and |Q> differ exactly by a spin alternation on the i-j bond. The factor g_{ij} is always positive and depends on the bond length between atoms i and j. The choice $g_{ij} = -1$ results in a purely topological Hamiltonian having a positively valued ground state energy.

There are several definite differences between the Hückel and TS topological Hamiltonians. We list in Table 1 some of them. First , in the Hückel picture , the total pi-electron energy (E_{pi}) is a sum of appropriate eigenvalues , whereas in the TS picture , E_{pi} is equal to the smallest eigenvalue. This means that standard methods used in the chemical topology to approximate E_{pi} are useless in the case of the TS Hamiltonian. Second , the TS Hamiltonian always provides us with correct ground state multiplicities. Actually , we

TABLE 1. COMPARISON BETWEEN THE HÜCKEL AND THE TS
TOPOLOGICAL HAMILTONIANS

PROPERTY	HÜCKEL HAMILTONIAN	TS HAMILTONIAN
electron correlation	included partially through effective Hamiltonian	included explicitly
basis functions	atomic p_z-orbitals	Slater determinants constructed from atomic p_z-orbitals
dimension of the basis set	N	$C_N^{[N/2]}$
eigenvectors	molecular pi-orbitals	valence bond (VB) wavefunctions
eigenvalues	orbital energies	energies of the neutral electronic states
the ground state wavefunction	the Hartree product of molecular spinorbitals	the eigenfunction with the lowest energy
the ground state multiplicity	from the Hund rule incorrect predictions very common	directly from calculations or from the Ovchinnikov rule
the total pi-electron energy (E_{pi})	a sum of eigenvalues over the occupied orbitals	the smallest eigenvalue
a fundamental inequality for E_{pi}	the McClelland upper bound [9] $E_{pi} \leqslant (2MN)^{1/2}$	$E_{pi} > M$

(N - the number of the carbon atoms , M - the number of the carbon-carbon bonds)

TABLE 1. (continued)

approximations for E_{pi}	inequalities [10] integration of the model function [11] approximate numerical integration [13] moments of the adjacency matrix [14] spectral density [15] additive nodal increments (ANI) [16] others [17]	the connected moments expansion (CMX) [12]
ionization potentials	related to the eigenvalues via a linear correlation	not available
electronic transition energies	only qualitatively from differences between orbital energies	related to the eigenvalues via a linear regression
bond orders	related to the bond lengths	related to the bond lengths
partial atomic charges	substantially overestimated	always zero
major deficiencies	electron correlation not included and therefore incorrect predictions for state multiplicities , transition energies and bond orders in excited states	only two-body interactions taken into account and therefore invalid results for four membered rings molecules only neutral states included explicitly and therefore zero partial atomic charges predicted

even need not pursue any calculations. There is a simple Ovchinnikov rule that enables us to find a correct value of multiplicity by direct counting of "starred" and "unstarred" vertices in the molecular graph [8]. On the contrary , the MO predictions based on the Hund rule notoriously give

incorrect answers (the cyclobutadiene molecule is a typical example) [2]. Third , the effective Hamiltonian (1) was derived neglecting several many-body contributions and therefore is inappropriate for systems possessing four - membered rings. For more specific information about various the reader should consult the original literature [4-7].

Taking equation (1) into account , direct correspondence between the TS Hamiltonian matrix elements and the topology of molecule is easily demonstrated by the equation [12] :

$$H_{PQ} = A_{ij}U_{PQ}^{ij} \quad , \tag{2}$$

where $\underline{A}$ is the adjacency matrix and the four indices tensor $\underline{U}$ is defined by its components :

$$U_{PQ}^{ij} = <P|i\bar{j}><i\bar{j}|Q> + <P|\bar{i}j><\bar{i}j|Q>$$

$$- <P|i\bar{j}><\bar{i}j|Q> - <P|\bar{i}j><i\bar{j}|Q> \quad . \tag{3}$$

Note , that the tensor $\underline{U}$ depends solely on N and is independent of the topology of molecule. The whole information about topology is comprised in the adjacency matrix.

III. THE CMX APPROXIMATIONS

The Hamiltonian (1) appears to have a very serious disadvantage that is a huge number of the basis functions needed to construct the secular problem. For example , for the system possessing 20 atoms (N=20) there are $\binom{20}{10}$=184756 determinants. This fact disables us from calculating the molecular properties without assistance of powerful computers. Because of that we seek approximate methods that can provide estimates for the ground state energy with the knowledge of

some graph invariants. It is well known that such method are quite successful in the case of Hückel Hamiltonian. Unfortunately, as pointed above , all the standard tricks that work for the Hückel method are useless for the TS Hamiltonian.

Very recently we have developed the connected moments expansion (CMX) techniques [12] that allows us to express the ground state energy of any quantum-mechanical systems in terms of the Hamiltonian moments :

$$\langle H^k \rangle = \langle \emptyset | \hat{H}^k | \emptyset \rangle \ , \tag{4}$$

where $|\emptyset\rangle$ is any trial function having a non-zero overlap with the ground state ket. The explicit formula reads [12]:

$$E = I_1 - I_2^2/I_3 - (1/I_3)(I_2 I_4 - I_3^2)^2/(I_3 I_5 - I_4^2) - \ldots \ , \tag{5}$$

where :

$$I_1 = \langle H \rangle \ ; \tag{6}$$

$$I_2 = \langle H^2 \rangle - \langle H \rangle^2 \ ; \tag{7}$$

$$I_3 = \langle H^3 \rangle - 3 \langle H^2 \rangle \langle H \rangle + 2 \langle H \rangle^3 \ ; \tag{8}$$

$$I_4 = \langle H^4 \rangle - 4 \langle H^3 \rangle \langle H \rangle - 3 \langle H^2 \rangle^2 + 12 \langle H^2 \rangle \langle H \rangle^2 - 6 \langle H \rangle^4 \ ; \tag{9}$$

$$I_5 = \langle H^5 \rangle - 5 \langle H^4 \rangle \langle H \rangle - 10 \langle H^3 \rangle \langle H^2 \rangle + 20 \langle H^3 \rangle \langle H \rangle^2$$
$$+ 30 \langle H^2 \rangle^2 \langle H \rangle - 60 \langle H^2 \rangle \langle H \rangle^3 + 24 \langle H \rangle^5 \ . \tag{10}$$

Appropriate choice of $|\emptyset\rangle$ is a delicate matter , even if it is known that the series (5) is always convergent. First, the trial ket should enable us to compute the moments , (4), in a feasible way. Second , the trial ket should not substantially deviate from the exact ground state wavefunction, if we wish a fast convergence of (5). In the case of TS Hamiltonian the following choice seems to offer a good compromise between those two requirements.

For a given molecular graph we assign $[N/2]\, \alpha$ and $N-[N/2]$ β spins to the vertices in the way that minimizes the number of adjacent vertices having the same spin assigned. Then the resulting maximal spin alternation determinant gives rise to the largest diagonal matrix element of the TS Hamiltonian. Usually there are several such determinants and , as has been pointed out in ref. [6], they have a major contribution to the ground state wavefunction. Let us consider the case of alternant , singlet ground state hydrocarbon. There are two maximal spin alternation determinants with the diagonal matrix element equal to the number of edges (M) in the molecular graph. Each of these determinants itself is not an eigenfunction of the spin $\hat{S}^2$ operator , whereas their linear combinations are. Interesting enough , there is not a big difference in the convergence of the CMX series , when only one determinant instead of a linear combination is taken as $|\emptyset>$ (Table 2).

Considering the context of Table 2 some details have to be pointed out. The CMX(n) approximation corresponds to truncation of the series after n first terms. Thus , for example , eq.(5) represents CMX(3) approximation. A general algorithm for generation of higher terms of CMX can be find in ref. [12b]. Fortunately , as was shown in ref. [12a] , there is no need to go beyond the CMX(3) level , when the approximate energies are scaled through the formula :

$$E_{pi} \approx 1.032\ E_{CMX(3)} + 0.411 \ . \tag{11}$$

Such approximate energies reproduce exact ones within 0.3 %.

TABLE 2. TWO EXAMPLES OF CONVERGENCE OF THE CMX SERIES FOR
TWO DIFFERENT TRIAL FUNCTIONS USED

3-METHYLENE-1.4-PENTADIENE			1.2-XYLYLENE		
	CMX(n) approx. energy			CMX(n) approx. energy	
n	one det.	two det.	n	one det.	two det.
1	5.00000	5.00000	1	8.00000	8.00000
2	7.50000	11.25000	2	11.20000	11.20000
3	6.80624	6.16154	3	10.37151	10.87519
4	7.11610	8.74736	4	10.65167	11.03037
5	7.08732	6.76927	5	10.62475	11.02959
6	7.15363	8.02424	6	10.67441	11.04834
7	7.14491	7.09833	7	10.66543	11.06819
8	7.22024	7.71837	8	10.72923	11.05048
9	7.04322	7.27388	9	10.44771	11.05081
10	7.33280	7.57735	10	10.82155	11.04968
11	7.59520	7.36324	11	10.93007	11.06151
12	7.43379	7.51077	12	10.88588	11.04272
13	7.47650	7.40748	13	10.90783	11.02953
14	7.46383	7.47899	14	10.90728	11.03472
15	7.47094	7.42910	15	10.92108	11.03358
16	7.47034	7.46372	16	10.90890	11.03383
17	7.47221	7.43961	17	10.95848	11.03376
	exact: 7.44949			exact : 11.03380	

IV. PERSPECTIVES OF THE TS HAMILTONIAN

The TS total pi-electrons energies exhibit several
properties which parallel closely those associated with the
Hückel energies. The branching of molecular graph decreases
E_{pi}. Among benzenoid hydrocarbons the phene isomers are
predicted to be more stable than the acene analogues. There
are , however , some differences. In particular , we studied
several cases of the "isospectral" molecules and always
found that they have definitely different TS Hamiltonian
spectra and thus different E_{pi}. Therefore we conjecture here
that "TS isospectral" molecules do not exist.

Another point that requires further clarification is the calculation of the connected moments. For one - determinant function , the three first I's are given by [12a] :

$$I_1 = I_2 = M \tag{12}$$

and

$$I_3 = -4M +2N - 2v_3 \quad , \tag{13}$$

where v_3 is the number of vertices of degree three (branching points) in the molecular graph. However , the general formula for I's is still unknown. Knowledge of such a formula would open a route to calculation of the TS resonance energy (TSRE). For this purpose one would have to evaluate several connected moments with and without contributions from cyclic conjugation and then calculate the respective energies from CMX. The calculated TSRE would probably reflect stabilities of (poly)radicals much better that TRE does.

Eventually , it is obvious that there should be several approximate or exact relations between the eigenvalues of the TS Hamiltonian and topological invariants. Another problem worthwhile to investigate is relation between the bond orders calculated within TS and Hückel frameworks.

REFERENCES

[1] I.Gutman and B.Mohar , Chem.Phys.Lett. 69 (1980) 375

[2] D.Döhnert and J.Koutecky , J.Amer.Chem.Soc. 102 (1980)
    1789

[3] E.Heilbronner and T.B.Jones , J.Amer.Chem.Soc. 100
    (1978) 6506

[4] M.Said , D.Maynau , J.P.Malrieu and M.A.Garcia-Bach ,
    J.Amer.Chem.Soc. 106 (1984) 571

[5] M.Said , D.Maynau and J.P.Malrieu , J.Amer.Chem.Soc.
    106 (1984) 580

[6] D.Maynau and J.P.Malrieu , J.Amer.Chem.Soc. 104 (1982)
    3021
    J.P.Malrieu and D.Maynau , J.Amer.Chem.Soc. 104 (1982)
    3029

[7] D.Maynau , M.Said and J.P.Malrieu , J.Amer.Chem.Soc.
    105 (1983) 5244

[8] A.O.Ovchinnikov , Theor.Chim.Acta 47 (1978) 297

[9] B.J.McClelland , J.Chem.Phys. 54 (1971) 640

[10] see for example : J.Cioslowski and I.Gutman ,
    Z.Naturforsch. 41a (1986) 861

[11] I.Gutman , J.Chem.Phys. 66 (1977) 1652

[12a] J.Cioslowski , Chem.Phys.Lett. , 134 (1987) 507

[12b] J.Cioslowski , Intern. J. Quant. Chem. Symposia , in
    press
    J.Cioslowski , Phys.Rev.Lett. , 58 (1987) 83
    P.Knowles , Chem.Phys.Lett. , 134 (1987) 512

[13] J.Cioslowski , Z.Naturforsch. 40a (1985) 1169

[14] Y.Jiang , A.Tang and R.Hoffmann , Theor.Chim.Acta <u>66</u> (1984) 183

J.Cioslowski , Chem.Phys.Lett. <u>122</u> (1985) 234

[15] J.Cioslowski , MATCH , <u>20</u> (1986) 95

J.Cioslowski and O.E.Polansky , Theor.Chim.Acta , submitted

[16] J.Cioslowski , Theor.Chim.Acta , <u>68</u> (1985) 315

[17] I.Gutman and S.Petrovic , Chem.Phys.Lett. <u>97</u> (1983) 292