# MOLECULAR MODELING TO CIRCUMVENT CANCER DRUG RESISTANCE ASSOCIATED WITH ABCG2

<u>Sachiko AIDA-HYUGAJI</u><sup>1</sup>, Hiroshi NAKAGAWA<sup>2</sup>, Jumma NOMURA<sup>2</sup>, Minoru SAKURAI<sup>2</sup>, Umpei NAGASHIMA<sup>3</sup>, Toshihisa ISHIKAWA<sup>2</sup>

<sup>1</sup>Tokai University, 1117 Kitakaname, Hiratsuka 259-1292, Japan <sup>2</sup>National Institute of Advanced Industrial Science & Technology, 1-1-1 Umezono, Tsukuba, Ibaraki 305-8568, Japan <sup>3</sup>Tokyo Institute of Technology, Nagatsuta, Yokohama 226-8501, Japan

#### Background:

Irinotecan (7-ethyl-10-[4-(1-piperidino)-1-pieridino]-carbonyloxycamptothecin: CPT-11) is a widely-used potent antitumor drug that inhibits mammalian DNA topoisomerase I (Topo I). However, overexpression of ABCG2 (BCRP/MXR/ABCP) can confer cancer cells resistance to SN-38, that is, the active form of CPT-11. In the present study to develop a platform for the molecular modeling to circumvent cancer drug resistance associated with ABCG2, we have characterized a total of fourteen new SN-38 analogues by some typical properties, which were evaluated by molecular orbital (MO) calculations and neural network (NN) QSAR technique.

#### Methods and Results:

The NN was first applied to estimate hydrophobic properties (LogP) of the analogues. Thereafter, the electrostatic potential (ESP) and the solvation free energy (DG) were evaluated by MO calculation. The LogP and DG values respectively represent the hydrophobicity and the hydrophilicity of the SN-38 analogues. These indexes were found to be well correlated with the drug resistance ratio experimentally observed in ABCG2-overexpressing cells (Fig.1). It is suggested that hydrophilic analogues carrying OH- or NH2-groups at positions 10 or 11 in the A ring are good substrates for ABCG2 and therefore exported from cancer cells. In contrast, SN-38 analogues with Cl or Br atom at those positions have similar LogP values and high affinities toward the putative active site of ABCG2, however they were not substrates of ABCG2. From these results, it is strongly suggested that hydrogen bond formation with OH- or NH2-groups at positions 10 or 11 in the transport mechanism of ABCG2.

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## COMPUTING THE WIENER INDEX OF SOME NANOTORI

Ali Reza ASHRAFI

Department of Mathematics, Faculty of Science, University of Kashan, Kashan, Iran

The Wiener index of a graph G is defined as  $W(G) = \frac{1}{2} \sum_{\{x,y\} \subseteq V(G)} d(x,y)$ , where V(G) is the

set of all vertices of G and for  $x, y \in V(G)$ , d(x, y) denotes the length of a minimal path

between x and y.<sup>1</sup> In this paper, we calculate the Wiener index of some nanotori.<sup>2</sup>

Key words: nanotori, Wiener index

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#### FRAMES FOR HILBERT SPACES AND HILBERT C\*-MODULES

Ljiljana ARAMBAŠIĆ

University of Zagreb, Department of Mathematics, Bijenička c. 30, HR-10000 Zagreb, Croatia

A finite or countable sequence of vectors  $\{f_i : i \in I\}$  in a separable Hilbert space  $(H, (\cdot, \cdot))$  is said to be a *frame* for *H* if there are constants C, D > 0 such that

$$C ||x||^2 \le \sum_{i \in I} |(x, f_i)|^2 \le D ||x||^2$$
, for every  $x \in H$ .

To a frame  $\{f_i : i \in I\}$  we associate the *analysis operator*  $T : H \to \ell_2(I), T(x) = ((x, f_i))$ . Its adjoint operator is defined by  $T^* : \ell_2(I) \to H, T^*((c_i)) = \sum_{i \in I} c_i f_i$  and it is called the

synthesis operator. The reconstruction formula holds

$$x = \sum_{i \in I} (x, (T * T)^{-1} f_i) f_i, \text{ for every } x \in H.$$

Hilbert space frames have been used in signal processing, image processing, data compression, wireless communication, etc.

A Hilbert C\*-module is a generalisation of a Hilbert space for which the inner product takes its values in a C\*-algebra instead of complex numbers. The concept of frames has been extended to the situation of Hilbert C\*-modules. It turns out that many results from Hilbert space case are also valid in this more general situation.

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# (HCl)<sub>2</sub> AND (HF)<sub>2</sub> IN SMALL HELIUM CLUSTERS: QUANTUM SOLVATION OF HYDROGEN-BONDED DIMERS

Zlatko BAČIĆ

New York University, New York, NY, USA

Nanodroplets of helium doped with molecules or molecular clusters offer a unique opportunity to investigate the intriguing properties of finite-size extremely quantummechanical systems, the ways in which quantum solvation modifies the dynamical properties of the solute molecule or cluster, and their evolution with the size of the solvent cluster. We will review the results of our theoretical investigations of the HF and HCl dimers in small helium clusters. The quantum mechanical ground-state energies and vibrationally averaged structures of  $He_n(HCl)_2$  and  $He_n(HF)_2$  (n=1-14, 30) clusters have been calculated exactly using the diffusion Monte Carlo (DMC) method. In addition, the interchange-tunneling splittings of these clusters were determined using the fixed-node DMC approach. The results revealed that the solvation by just four He atoms reduces the interchange tunneling splitting of the HF dimer by 30% relative to the gas phase, by virtue of their occupying the equatorial ring which encircles the transition state of the tunneling pathway. In contrast, helium solvent was found to have virtually no effect on the tunneling dynamics of the HCl dimer.

# ON THE USE OF THE TOPOLOGICAL INDICES FOR STUDYING OF ALKANES

Abdolhamid BAMONIRI<sup>1</sup>, Ali Reza ASHRAFI<sup>2</sup>

<sup>1</sup>Department of Chemistry, Faculty of Science, University of Kashan, Kashan 87317-51167, Iran <sup>2</sup>Department of Mathematics, Faculty of Science, University of Kashan, Kashan 87317-51167, Iran

The Padmakar–Ivan (PI) index of a graph G is defined as  $PI(G) = \sum [n_{eu}(e|G) + n_{ev}(e|G)]$ , where  $n_{eu}(e|G)$  is the number of edges of G lying closer to u than to v,  $n_{ev}(e|G)$  is the number of edges of G lying closer to v than to u and summation goes over all edges of G. The PI index is a Szeged-like topological index developed very recently. The PI and Szeged indices are applied to the structure boiling point modeling of alkanes. We are also comparing the results with the case of Wiener index. In this study the saturated hydrocarbons are selected because there are several structure boiling point models of these compounds.

Keywords: alkane, boiling point, PI index, Szeged index

## PREDICTION OF TISSUE PARTITION COEFFICIENTS USING MATHEMATICAL STRUCTURAL DESCRIPTORS VERSUS EXPERIMENTAL PROPERTIES

Subhash C. BASAK, Denise MILLS, Brian D. GUTE

Natural Resources Research Institute, University of Minnesota Duluth, 5013 Miller Trunk Hwy., Duluth, MN 55811, USA

QSAR models for rat and human tissue:air partition coefficients were developed utilizing experimentally determined partition coefficients for 131 chemicals obtained from the literature and mathematical molecular descriptors. The descriptors were partitioned into four hierarchical classes, including topostructural, topochemical, 3-dimensional, and *ab initio* quantum chemical. Three types of regression methodologies—ridge regression, principal components regression, and partial least squares regression—were used comparatively in the development of the structure-based models. The results indicate that many of the structure-based models are comparable or superior to their respective property-based models. It was also found that ridge regression outperformed principal components regression and partial least squares regression, with respect to the structure-based models, and that generally the topochemical descriptors alone produced models of good predictive ability.

# PROTON TRANSFER ASSISTED BY 2-ACETYLPYRIDINE-4-PHENYL–3-THIOSEMICARBAZONE ACROSS WATER /1, 2-DICHLOROETHANE INTERFACE

<u>Ali BENVIDI<sup>1</sup></u>, Shah Nawaz LANJWANI<sup>2</sup>, Zhifeng DING<sup>2</sup>

<sup>1</sup>Department of Chemistry, Yazd University, Yazd, Iran <sup>2</sup>Department of Chemistry, University of Western Ontario, London, Ontario N6A 5B7, Canada

The assisted transfer of proton by interfacial complexation with 2-acetylpyridine-4-phenyl-3-thiosemicarbazone (APPT) was studied at the micro interface of two immiscible electrolyte solution (ITIES). Thermodynamic of proton transfer was investigated by cyclic voltammetry. The dependence of half wave potential of the ligand concentration suggests that the equilibrium is effectively displaced towards an 1:1 (proton : ligand) stoichiometry, with a formation constant of log  $K_f = 12.1$ . The formal Gibbs energy of proton transfer and the diffusion coefficient of proton in aqueous solution and diffusion coefficient of HAPPT<sup>+</sup> in organic phase were evaluated.

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### MOLECULAR DYNAMICS AND RANDOM EXPULSION MOLECULAR DYNAMICS SIMULATIONS OF AUXIN BINDING PROTEIN1 AND ITS AUXIN COMPLEXES

Branimir BERTOŠA, Sanja TOMIĆ

Ruđer Bošković Institute, HR-10002 Zagreb, POB 180, Croatia

Auxins are the first identified plant hormones that control and regulate plant growth and development. It is known that Auxin Binding Protein1 (ABP1) binds auxins with high affinity and it is a strong candidate for an auxin receptor. In order to understand molecular mechanism of auxin binding to ABP1, a series of molecular dynamics (MD) simulations of ABP1 and its complexes with auxin-related compounds have been made. Beside the standard MD simulations at room temperature, simulations in which temperature was shortly increased on 500 K in order to induce conformational change have also been performed (altogether 70 ns of MD simulations were accomplished). Possible pathways for entrance and exit of auxin-related compounds from the ABP1 auxin binding pocket have been investigated using random expulsion molecular dynamics (REMD) simulations. MD simulations revealed two different conformations of ABP1, however, auxin binding stabilizes one of them. REMD simulations traced two the most probable routes for an auxin molecules to enter or to leave the ABP1 binding site. According to the previous knowledge about the orientation of ABP1 towards a membrane, one of the routes leads to a membrane and the other one to the lumen of ER or to citosol (depending on the ABP1 location). In all simulations the same hydrogen bonding network of water molecules from the bulky water to the ABP1 active site was created. Hydrogen bond network is involved into proposed active site mechanism, which can work via the replacement of a water molecule coordinated to zinc with the carboxyl oxygen of the auxin ligand.

# MOLECULAR RECOGNITION AND SECONDARY STRUCTURE OF ACTH (1-24) AND ITS ANTISENSE PEPTIDES

Vladimir BLAGAIĆ<sup>1</sup>, Nikola ŠTAMBUK<sup>2</sup>, <u>Paško KONJEVODA<sup>2</sup></u>, Alenka BOBAN-BLAGAIĆ<sup>3</sup>, Biserka POKRIĆ<sup>2</sup>

<sup>1</sup>Department of Obstetrics & Gynecology, General Hospital "Sveti Duh", Sveti Duh 64, HR-10000 Zagreb, Croatia <sup>2</sup>Ruđer Bošković Institute, Bijenička cesta 54, HR-10002 Zagreb, Croatia <sup>3</sup>Department of Pharmacology, Zagreb University School of Medicine, Šalata 4, HR-10000 Zagreb, Croatia

Molecular Recognition Theory is based on the finding that peptides specified by the complementary RNAs bind to each other with higher specificity and efficacy. We investigated ACTH (1-24) and its antisense peptides structure with with SSpro and SSpro8 methods. The properties of ACTH (1-24) are discussed considering its structure-function relationship, and possible ligand-receptor binding predicted by means of the Molecular Recognition Theory.

## **ON NUMERICAL CHARACTERIZATION OF PROTEOMIC DATA**

Sol BOBST<sup>1</sup>, <u>Milan RANDIĆ</u><sup>2</sup>, Marjana NOVIČ<sup>2</sup>, Marjan VRAČKO<sup>1,2</sup>

<sup>1</sup>Ceratox Consulting, Houston, Texas, USA <sup>2</sup>National Institute of Chemistry, Ljubljana, Slovenia

Characterization of 2D gels with numerical descriptors is appealing for archival organization of large databases and comparative analysis of experimental results. Recently an approach based on consideration of a nearest neighbor (NN) in order of abundance, which is viable for the development of unique molecular invariant descriptors, was further improved by restricting NN to a sequential order of appearance. This study presents the application of this sequential neighbor (SN) approach to a previously published data set. The SN method requires as input for construction of SN distance matrix the coordinates and the abundance of protein spots in 2-D gel. It follows with calculation of the sequential distances between spots, computes the average row sums of SN distance matrix as one component and the abundance as the other component of a 2 component vectors that characterize individual proteomic maps. All calculations were performed by an in-house computer program PROMISE (PROteomics Map Invariant SEarch). Analysis carried out by PROMISE yielded results that produced useful descriptors with respect to dose-response characterization of 2D gels. High correlation was found when at least three SN components were considered (in ordered fashion in the range NN  $\{1,2,3,\ldots,6\}$ . Also, plotting the difference of the 2 Component Vector from the control set provides data that could be useful for analysis with possible 3D graphical representation of map characterization. In conclusion, the presented data provides support that PROMISE analysis of abundance and coordinate data from 2D gels with Sequantial Neighbor (SN) methodology can provide useful molecular descriptors that retain high correlation with dose-response analysis of 2D gel proteomic data.

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#### THIELE CUMULANTS AND THE FREE ENERGY DECOMPOSITION

<u>Matevž BREN</u><sup>1,2</sup>, Urban BREN<sup>3</sup>

<sup>1</sup>University of Maribor, Faculty of Organizational Sciences, Slovenia <sup>2</sup>Institute of Mathematics, Physics & Mechanics, Slovenia <sup>3</sup>National Institute of Chemistry, Slovenia

The partitioning of the free energy into additive contributions originating from groups of atoms or force field terms has a potential to provide free energy based relationships between structure and biological activity of molecules and has been used as a background for many new methods of Bioinformatics like scoring functions or QSAR. Whether such decomposition is justified has been a subject of vigorous debate in the molecular modeling society. We address this question in terms of the free energy perturbation (FEP) method, which represents the most robust methodology for calculations of the free energy differences.

The starting point is the standard expression for the calculation of the free energy difference by FEP<sup>1</sup>:

$$\Delta G_{i \to i+1} = -\beta^{-1} \ln \langle \exp(-\beta \Delta E) \rangle_i, \qquad (1)$$

where  $\Delta G_{i \to i+1}$  denotes the free energy difference between states i and i+1.  $\Delta E = E_{i+1} - E_i$  represents corresponding potential energy difference.  $\beta^{-1} = k_B T$ , where k<sub>B</sub> stands for the Boltzmann constant, and T is the thermodynamic temperature. Notation  $\langle \cdots \rangle_i$  indicates averaging over the ensemble of configurations generated by a MD simulation on the potential energy surface of the state i. If we expand exponential function into a Taylor series we get:

$$\Delta G_{i \to i+1} = -\beta^{-1} \ln \left( 1 - \beta \left\langle \Delta E \right\rangle_i + \frac{\beta^2}{2} \left\langle \Delta E^2 \right\rangle_i - \cdots \right)$$
(2)

The series expansion of the logarithmic function gives us a double power series, which reordered in increasing powers of forms:

$$\Delta G_{i \to i+1} = -\beta^{-1} \sum_{n=1}^{\infty} \frac{\mu_n}{n!} \beta^n$$
(3)

The coefficients  $\mu_n$  are the so called *Thiele cumulants*. We will express these cumulants in the form of potential energy differences.

Potential energy can originate from different groups of atoms or force field terms. Every dissecting of the free energy into such components possesses an inherent error (termed the nonadditivity error) arising from coupling between corresponding potential energy contributions. We will explain this nonadditivity error with the appearance of mixing potential energy terms in the equation (3).

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# CHEMICAL REACTIVITY AS A TOOL TO STUDY CARCINOGENICITY

Urban BREN, Janez MAVRI

National Institute of Chemistry, Hajdrihova 19, SI-1001 Ljubljana, Slovenia

Chloroethylene oxide, an ultimate carcinogen of vinyl chloride, reacts with DNA giving rise to 7-(2-oxyethyl)guanine adduct in a nearly quantitative yield. This reaction represents an initial step of carcinogenesis associated with vinyl chloride. From experimental data for this reaction we calculated the second-order rate constant of 0.049 s<sup>-1</sup>M<sup>-1</sup>, which corresponds to the activation free energy of 19.5 kcal/mol. We also performed a series of medium high ab initio and density functional theory simulations. Effects of hydration were considered in the framework of the Langevine dipoles solvation model and the solvent reaction field method of Tomasi and co-workers. In silico calculated activation free energies are in a very good agreement with the experimental value. This fact presents strong evidence in favor of the validity of the proposed reaction mechanism and points to the applicability of quantum-chemical methods to studies of other reactions associated with carcinogenesis. Insignificant stereoselectivity of the studied reaction was also predicted.

# HIGH THROUGHPUT *in silico* SCREENING IN THE PHARMACEUTICAL INDUSTRY

Darko BUTINA

ChemoMine Consultancy Limited, 201 Icknield Way, Letchworth Garden City, Herts SG6 4TT, UK

Ability to generate millions of virtual chemical structures using computer has revolutionised ability to analyse the profiles of those structures and make better decisions which structures to make in the laboratory. The structures could be profiled in terms of activity (any 2D or 3D models), physico-chemical properties like clogP or solubility, and most importantly, in terms of drug-like properties like ability to cross human intestinal wall or blood brain barrier, metabolic stability or any relevant in vitro screen.

However, there are some problems associated when dealing with millions of chemical structures using computers, like storage and exchange of those structures across the network, registration of those structures, visualisation and creating the tables of the calculated properties (software like excel has serious problem in storing large number of columns and rows). In addition, it is not a trivial task to analyse problems that can have thousands of columns with millions of rows.

This talk will attempt to highlight all those issues and answer some of them.

## PROBLEMS IN QUANTIFICATION OF FLAVONOID ACTIVITY

Vjera BUTKOVIĆ<sup>1</sup>, Saša P. KAZAZIĆ<sup>1</sup>, Nenad KEZELE<sup>1</sup>, <u>Leo KLASINC<sup>1,2</sup></u>, William A. PRYOR<sup>2</sup>

<sup>1</sup>*Ruđer Bošković Institute, HR-10002 Zagreb, POB 180, Croatia* <sup>2</sup>*Department of Chemistry, Louisiana State University, Baton Rouge, USA* 

Flavonoids are a broad class of biologically active compounds found in nearly every plant where they have key functions in growth, development and defence, as well as interaction with other plants (allelopathy). Because a considerable part of our food is of plant origin it is no surprise that flavonoids are also active in humans as antioxidants, radical scavengers, and metal chelators. Indeed, when referring to their biological activity it is the activity in humans that is actually meant. There are numerous methods for testing it, e.g. quenching of reactive oxygen species, reactions with synthetic radicals, enzymatic and non-enzymatic measurement of lipid peroxydation inhibitors and interaction with metal ions. Because these properties develop in environments under conditions that are difficult to determine and control the activities determined by various methods correlate poorly thus making theoretical prediction impossible in any reliable way. Some of the reasons will be discussed.

# SATELLITE IMAGERY FOR MAPPING TERRESTRIAL CARBON SOURCE AND SINK DISTRIBUTIONS: METHODOLOGIES AND A CASE STUDY IN CANADA\*

#### Jing M. CHEN

Department of Geography, University of Toronto, 100 St. George Street, Toronto, Ontario, Canada M5S 3G3

The heterogeneous nature of terrestrial ecosystems presents a major challenge in our effort to improve regional and global carbon cycle estimation, and yet the ecosystem carbon budget information not only has significance in understanding the global climate change, but has also become a major knowledge gap in formulating policies related climate change, given the options of including sinks in national greenhouse gas inventory under the Kyoto Agreement. To address the need of mapping the carbon source and sink distribution in terrestrial ecosystems for various science and policy purposes, satellite remote sensing can play a critical and indispensable role. Optical remote sensing imagery can be used to retrieve the following land surface parameters that are useful for carbon cycle modeling:

- (1) land cover type,
- (2) leaf area index,
- (3) fire scar age,
- (4) clumping index,
- (5) biomass,
- (6) wetland area, and
- (7) leaf pigment contents.

In this presentation, a brief review of the methodologies for retrieving these parameters will be provided and a case study in Canada will be introduced. In our regional carbon modeling in Canada, the first three parameters have been used, while progresses are being made to produce and use the other parameters' maps. In addition to these remotely sensed land surface parameters, soil texture and organic carbon maps, gridded monthly climate data from 1901 to 2000, large fire polygon data since 1959, and forest inventory data are used to produce annual spatial distributions of carbon sources and sinks in Canada's forests and wetlands at 1 km resolution for the period from 1901 to 2000. Through this case study, it is unequivocally demonstrated that remote sensing imagery has provided the critical information for mapping carbon source and sink distribution and improving regional carbon budget estimation.

\*The following people have contributed significantly to the case study to be presented:

W. JU, A. ŠIMIĆ, L. ZHANG, B. CHEN, at University of Toronto,

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- D. PRICE, B. AMIRO, at the Canadian Forest Service, Edmonton,
- K. HIGUCHI, D. CHAN, D. WORHTY, at the Environment Canada, Toronto,

over 20 scientists in Fluxnet Canada Research Network

# **EXACTLY SOLVABLE COULOMBIC MODELS FOR CALIBRATION AND BENCHMARKING OF ELECTRONIC STRUCTURE METHODS**

Jerzy CIOSLOWSKI

Department of Physics, University of Szczecin, Wielkopolska 15, 70-451 Szczecin, Poland

It is well known that electrons subject to weak confinement fields form strongly correlated systems in which spatial localization takes place due to the phenomenon of Wigner crystallization. Such systems are described by wavefunctions that follow from simple electrostatic considerations and consequently can be written explicitly in closed forms. This property makes them highly suitable for calibration and benchmarking of electronic structure methods and testing their performance in the strongly correlated regime.

Unfortunately, because of the intervening autoionization, Wigner crystallization does not occur in ordinary atoms and molecules. On the other hand, the two commonly mentioned examples of Wigner crystals, namely the low-density homogeneous electron gas, and atoms and molecules in an infinitely-dimensional Cartesian space, do not constitute realistic representations of chemical species.

Harmonium atoms, also known as quantum dots, consist of electrons held together by central harmonic attraction to a fixed point. At the weak-confinement limit, these atoms undergo Wigner crystallization, forming "Wigner molecules" in which the quasi-localized electrons are analogous to nuclei in molecules described with a fixed rather then rotating frame of reference.

Explicit formulae for natural orbitals of the ground-state two-electron Wigner molecule and their occupancies are given for the first time. The occupancies are shown to exhibit quite unusual, albeit regular, dependencies on the angular momentum.

The newly derived wavefunctions of the doublet and quartet states of the three-electron Wigner molecule are presented together with the corresponding one-electron densities. The corresponding three-particle bosonic system is also analyzed for the sake of comparison.

Demonstrating a beautiful synergy between mathematics and physics in solving quantumchemical problems, the algebraic derivations of these expressions employ a wide range of techniques, including the saddle-point approximation, some lesser-known properties of orthogonal polynomials, differentiation of elliptic functions, and the theory of modular identities and q-sums.

# THE BRAIN NATRIURETIC PEPTIDE (BNP) AND OPERATIVE RISK ASSESSMENT IN PATIENTS WITH CORONARY ARTHERY BYPASS GRAFTING

<u>Vedran ČORIĆ<sup>1</sup></u>, Paško KONJEVODA<sup>2</sup>, Davor MILIČIĆ<sup>1</sup>, Nikola ŠTAMBUK<sup>2</sup>

<sup>1</sup>University Hospital Rebro, Kišpatićeva 16, HR-10000 Zagreb, Croatia <sup>2</sup>Ruđer Bošković Institute, Bijenička cesta 54, HR-10002 Zagreb, Croatia

*The European System for Cardiac Operative Risk Evaluation* (EuroSCORE) is a standard score system for operative risk assessment in patients with coronary arthery bypass grafting. However, its efficacy, measured as area under the receiver operator curve (AUC) is only 0.743 (95% confidence interval 0.721-0.765). We present a new operative risk assessment system based on serum values of N-terminal segment of pro-BNP. The system is based on algorithm derived with *rpart* program for recursive partitioning inside the R software. It is simple, cheap and with better predictive value in comparison to EuroSCORE.

### A MODEL OF tRNA STRUCTURE FROM A GRAPH AND QUANTUM THEORETICAL PERSPECTIVE

Edgar E. DAZA C.<sup>1</sup>, Clara I. BERMÚDEZ S.<sup>1,2</sup>, Johan F. GALINDO C.<sup>1</sup>

<sup>1</sup>Grupo de Química Teórica, Universidad Nacional de Colombia, Bogotá, D.C. Colombia <sup>2</sup>Grupo de Biología Molecular Teórica y Evolutiva, Universidad Nacional de Colombia, Bogotá, D.C. Colombia

Two major problems can be recognized when chemical and biological phenomena are considered from a molecular perspective. The first one is related with the very concept of what molecular structure is. The second one arises when molecules are compared, because of the lack of good approaches to assert how similar or different two molecules are. Both questions become severe when we consider biomolecules as proteins or nucleic acids. If we intend to establish models conceptually more rigorous, better suited to perform comparison between molecules, we consider that it is necessary to go a step further in the interpretation of what the molecular structure is, i.e. to go beyond the simple model of a geometrical distribution of nuclei. Therefore a new model encompassing most of the knowledge about chemical structure is required.

We have developed a model to characterize families of tRNAs using simultaneously graph theory and weighting factors from quantum mechanical calculations.<sup>1</sup> However, to study molecules with a very similar pattern of binding (like tRNAs) and having a set of vertices apparently small (four nucleotides) it is necessary to revisit the graph definition and the method of assigning weighting factors, in such a way that its construction reveals finer details in the structure, such as the nature of each nucleotide (vertex) with respect to its first neighbors. Therefore we suggested an alternative way of constructing tRNAs graphs. Our model embraces, in addition to molecular connectivity, other concepts like stacking interactions and some molecular interactions that are of the utmost importance to double helix stability. Besides we have proposed new graph theoretical indices which, used as structural descriptors, allowed us to compare the tRNAs. Some examples are provided.



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### STRANGE FULLEROIDS BY MAP OPERATIONS

<u>Mircea V. DIUDEA</u><sup>1</sup>, Monica ȘTEFU<sup>1</sup>, Alexandru E. VIZITIU<sup>1</sup>, Csaba L. NAGY<sup>1</sup>, Damir VUKIČEVIĆ<sup>2</sup>, Ante GRAOVAC<sup>2,3</sup>

 <sup>1</sup>Faculty of Chemistry & Chemical Engineering, "Babes-Bolyai" University, 400028, Cluj, Romania
 <sup>2</sup>Faculty of Science, Mathematics & Kinesiology, University of Split, Nikole Tesle 12, HR-21000 Split, Croatia
 <sup>3</sup>RuđerBošković Institute, POB 180, HR-10002 Zagreb, Croatia

New strange fulleroids are built up by using the three classical composite map operations:<sup>12</sup> tripling (leapfrog *Le*), quadrupling (chamfering *Q*) and septupling (capra *Ca*) on the trivalent Platonic solids. These transforms belong to the tetrahedral, octahedral and icosahedral symmetry groups and show interesting mathematical and (possible) physico-chemical properties.<sup>3</sup> Kekulé structure count (see Figs. 1 to 3) has been obtained by applying a *divide et impera* strategy.



E(Q(D)); 140 vertices

E(Q(D)); 140 vertices

Kekulé count = 287 738 150 948



Figure 1. The open Le(D) and its capped (by dodecahedron halves Dh) transform (Schlegel projection).

Kekulé count = 3 515 625 000 000



Figure 2. The open Q(D) and its Dh transform (Schlegel projection).

Kekulé count = 28 275 919 171 875 000



*Figure 3*. The open *Ca*(*D*) and its *Dh* transform (Schlegel projection).

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# COMPUTING BIPARTITE EDGE FRUSTRATION OF FULLERENE GRAPHS

Tomislav DOŠLIĆ<sup>1</sup>, Damir VUKIČEVIĆ<sup>2</sup>

<sup>1</sup>Department of Informatics & Mathematics, Faculty of Agriculture, University of Zagreb, Svetošimunska c. 25, HR-10000 Zagreb, Croatia <sup>2</sup>Faculty of Sciences, University of Split, N. Tesle 12, HR-21000 Split, Croatia

Bipartite edge frustration of a graph is defined as the smallest number of edges that have to be deleted from the graph to obtain a bipartite spanning subgraph. We show that for fullerene graphs this quantity can be computed in polynomial time and obtain explicit formulas for the icosahedral fullerenes. We also report some computational results and discuss a potential application of this invariant in the context of fullerene stability.

### SUPPORTED METHYLTRIOXORHENIUM AS A CATALYST FOR OLEFIN METATHESIS

Jürgen ECKERT

Materials Research Laboratory & Department of Chemical Engineering, University of California, Santa Barbara CA, 93106, USA

Olefin metathesis is a powerful method for forming new C=C bonds. However, the full potential of heterogeneous metathesis catalysts has yet to be exploited, because supported metal oxides show low rates of activation and rapid deactivation. The deposition of CH<sub>3</sub>ReO<sub>3</sub> onto the dehydrated surface of amorphous silica-alumina does generate a catalyst for olefin metathesis, although CH<sub>3</sub>ReO<sub>3</sub> itself is not active. The nature of the interactions between the silica-alumina surface and the grafted organometallic complex were probed by DFT calculations in conjunction with extensive experimental studies using solid-state NMR, IR, and EXAFS. Chemisorption of the intact molecular complex occurs via interaction of one oxo ligand with an Al site, resulting in significant elongation of this Re=O bond. A second surface-organometallic interaction arises by coordination of an adjacent bridging oxygen atom (AlOSi) to the Re center. We have also investigated by a combination of DFT and experimental studies a variety of other properties of this system, such as the observation that only a small fraction of the CH<sub>3</sub>ReO<sub>3</sub> deposited onto the silica alumina surface is found to be active, and the molecular role of organotin promoters. The latter confer functional group tolerance on supported Re catalysts for olefin metathesis, and we were able to demonstrate by our analysis, as well as kinetic studies, the reasons why a completely Sn-free catalyst performs metathesis as efficiently as the organotin-containing perrhenate catalyst. Initial computational studies of possible pathways to the formation of an active carbene species will also be described. Our insights represent a first step towards understanding the role of solid oxide supports in conferring metathesis activity to CH<sub>3</sub>ReO<sub>3</sub> and related heterogeneous catalysts.

The work described in this presentation was carried out in collaboration with my UCSB colleagues S. L. SCOTT, C. RAAB, A. W. MOSES, N. A. RAMSAHYE, H. LEIFESTE, S. CHATTOPADHYAY and B. F. CHMELKA, and was supported by the Office of Science, U. S. Department of Energy.

# SPHERICITIES OF ORBITS, CYCLES, AND DOUBLE COSETS. THEIR APPLICATIONS TO COMBINATORIAL ENUMERATION OF STEREOISOMERS

#### Shinsaku FUJITA

#### Department of Chemistry & Materials Technology, Kyoto Institute of Technology, Matsugasaku, Sakyoku, Kyoto, 606-8585 Japan

Although Pólya's theorem<sup>1</sup> has been widely used in the enumeration of isomers, it is not applicable to stereochemical problems in which pseudoasymmetry and *meso*-compounds should be taken into consideration. We have proposed the concept of **sphericities of orbits** (or coset representations) and developed the USCI (unit-subduced-cycle-index) approach, which is capable of solving such stereochemical problems.<sup>2</sup> Moreover, we have modified the sphericity concept to a slightly different form, i.e., **sphericities of cycles**, which gives a basis of the proligand method for enumerating stereoisomers.<sup>3,4</sup> This presentation is devoted to the proposal of the third sphericity concept, i.e., **sphericities of double cosets**, as well as to its application of chemical combinatorics.

Let us consider an allene molecule of  $D_{2d}$ -symmetry as an example. The eight operations of  $D_{2d}$  are numbered sequentially as follows:

$$\mathbf{D}_{2d} = \{\underbrace{I}_{1}, \underbrace{\sigma_{d(1)}}_{2}, \underbrace{S_{4}}_{3}, \underbrace{C_{2(1)}}_{4}, \underbrace{C_{2(3)}}_{5}, \underbrace{\sigma_{d(2)}}_{2}, \underbrace{S_{4}^{3}}_{3}, \underbrace{C_{2(3)}}_{5}\}$$
(1)

After making the right coset decomposition by C<sub>s</sub>, the resulting cosets are numbered sequentially.

$$\mathbf{C}_{s} \setminus \mathbf{D}_{2d} = \{\underbrace{\mathbf{C}_{s}I}_{1}, \underbrace{\mathbf{C}_{s}S_{4}}_{2}, \underbrace{\mathbf{C}_{s}C_{2(3)}}_{3}, \underbrace{\mathbf{C}_{s}S_{4}^{3}}_{4}\} = \{\underbrace{\{1,2\}}_{1}, \underbrace{\{3,4\}}_{2}, \underbrace{\{5,6\}}_{3}, \underbrace{\{7,8\}}_{4}\}$$
(2)

The sequential number denotes the four positions of the allene molecule. The right cosets are further modified by  $C_s$  to give double cosets as follows:

$$\mathbf{C}_{s} \backslash \mathbf{D}_{2d} / \mathbf{C}_{s} = \{\underbrace{\mathbf{C}_{s} I \mathbf{C}_{s}}_{\mathbf{A}}, \underbrace{\mathbf{C}_{s} S_{4} \mathbf{C}_{s}}_{\mathbf{D}}, \underbrace{\mathbf{C}_{s} C_{2(3)} \mathbf{C}_{s}}_{\mathbf{D}}, \underbrace{\mathbf{C}_{s} S_{4}^{3} \mathbf{C}_{s}}_{\mathbf{D}}\}$$
(3)

$$= \left\{ \underbrace{\left\{ \underbrace{\{1,2\}}_{1} \atop \{2,1\}}_{A} \right\}}_{A}, \underbrace{\left\{3,4\}}_{\frac{2}{8},7\}}_{p} \\ \underbrace{\{8,7\}}_{p} \\ B \\ \underbrace{\{6,5\}}_{3} \\ B \\ \underbrace{\{4,3\}}_{p} \\ \underbrace{\{4,3\}}_{p}$$

They correspond to the subduction of right coset representation. This correspondence is used to define the sphericity of double cosets. Thus, the double cosets A and B in eq. 4 are homospheric distinctly, while p and p(bar) construct a single enantiospheric double coset, Thereby, the resulting allene ABpp(bar) belongs to  $C_s$  symmetry. This idea can be applied to give an alternative proof of the proligand method.<sup>3,4</sup>

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### ELECTRONIC STRUCTURE OF 2-HALOSUBSTITUTED 1,2-DIPHENYLETHANONES

Petra GALER<sup>1</sup>, <u>Leo KLASINC</u><sup>2</sup>, Berta KOŠMRLJ<sup>1</sup>, Branka KOVAČ<sup>2</sup>, Boris ŠKET<sup>1</sup>

<sup>1</sup>University of Ljubljana, Faculty of Chemistry and Chemical Technology, Aškerčeva 5, Ljubljana, Slovenia <sup>2</sup>Ruđer Bošković Institute, Bijenička 54, HR-10002 Zagreb, Croatia

The molecular and electronic structure of 2-halo and 2,2-dihalo-1,2-diphenylethanones [or benzoins] has been investigated by UV photoelectron spectroscopy, high level ab initio calculations [density functional theory calculations, *ab initio* outer valence Green's function calculations, tddft method] and comparison with the spectra of related molecules. The aim of the study is to analyse the effect of carbonyl group lone pair orbital interaction with halogen lone pair and with benzene  $\pi$ -orbitals. Results are expected to give insight into the

possible mechanism of their biological activity as photolabile protective groups for amino acids, nucleosides other biologically important and molecules. Namely, benzoins are important representatives of 'caged' compounds, inert in the dark but which upon exposure to light are converted to active species that are able to participate in chemical or biochemical processes.



Figure 1. HeI photoelectron spectrum of PhCOCFBrPh

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# SOME RESULTS ON SYMMETRY AND NON-TRANSITIVE CHEMICAL GRAPHS

Ahmad GHOLAMI

Department of Mathematics, Faculty of Science, University of Kashan, Kashan 87317-51167, Iran

An Euclidean graph associated with a molecule is defined by a weighted graph with adjacency matrix  $M = [d_{ij}]$ , where for  $i \neq j$ ,  $d_{ij}$  is the Euclidean distance between the nuclei *i* and *j*. In this matrix  $d_{ii}$  can be taken as zero if all the nuclei are equivalent. Otherwise, one may introduce different weights for distinct nuclei. Balaban introduced some monster graphs and then Randić computed complexity indices of them.<sup>1-6</sup>

In this paper, using the Computer Algebra System GAP, with a simple method, we calculate the automorphism group of some weighted graphs.<sup>7</sup>

Key words: Weighted graph, Euclidean graph, automorphism group

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# CONFORMATIONAL ANALYSIS VIA CHIROTOPE GENERATION

#### Ralf GUGISCH

University of Bayreuth, Department of Mathematics, D-95440 Bayreuth, Germany

There is an approach of A. Dreiding and A. Dress using oriented matroids (also known as chirotopes) as a tool for presenting conformational information of chemical molecules. Thus, the computer-based construction of (feasible) chirotopes can give an overview over the conformation space of a given molecule.

We designed a generator of chirotopes fulfilling the special requirements and the necessary flexibility for this application. It can be seen as the first step towards a generator of conformers, a reasonable and needed supplement to the molecule-(configuration)-generator MOLGEN.

#### RATIONALIZATIONS OF THE SOLID-STATE REACTION MECHANISMS

Ivan HALASZ, Ernest MEŠTROVIĆ, Hrvoj VANČIK

Department of Chemistry, Faculty of Science, University of Zagreb, Horvatovac 102A, HR-10000 Zagreb, Croatia

Chemical reactions in solid state are in different ways more or less accompanied and coupled with phase transitions in the crystal lattice.<sup>1</sup> Since both the processes, i.e. the change in covalent topology (chemical reaction) and conversion of supramolecular self-organization (e.g., phase transition) occur in the rigid condensed systems, our concept of the reaction mechanism ought to be extended such a way that it includes both processes. At least two limiting cases could be postulated:

(1) *synchronous one step mechanism* with simultaneous occurrence of chemical reaction and phase transition, and

(2) *consecutive two step mechanism*, where chemical reaction precedes phase transition, and the last is slow rate determining step. In the case of addition reaction we can label the synchronous mechanism as  $Ad_s$ , and consecutive one as  $Ad_c$ , respectively.

To find out how these two processes (chemical reaction and phase conversion) are coupled, it is appropriate to measure chemical process and corresponding phase changes by different and independent experimental methods. While the rate of chemical reaction can be best determined by spectroscopy, the solid-state phase transition kinetics can well be studied by the time resolved X-ray powder diffraction methods, and the diffraction reflections were assigned to corresponding crystal planes by the single crystal structure determination.

Models for such a mechanistic study we found in dimerization/dissociations of nitrosobenzene derivatives.

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#### NEW SCHIFF BASES AS CORROSION INHIBITOR FOR COPPER OBJECTS TO ASSIST CURATORS IN TREATMENTS OF RELATED ARTWORKS: THEORETICAL STUDIES

Masood HAMADANIAN<sup>1</sup>, Mohsen BEHPOUR<sup>1</sup>, <u>Gholam Reza VATANKHAH<sup>2</sup></u>

<sup>1</sup>Department of Chemistry, Kashan University, Kashan, Iran <sup>2</sup>Faculty of Conservation, The Art University of Isfahan, Isfahan, Iran

Corrosion is an electrochemical process by which the metallic objects are destroyed gradually through anodic dissolution.<sup>1,2</sup> One of the most important metals in conservation science is copper because of the huge cultural heritage which is made from copper or its alloys like bronze and they have been corroded during the years or are still corroding. Therefore, various attempts must be employed to prevent or retard this destructive process. Inhibitors are chemical compounds containing hetero-atoms (O, N, S, ) or a delocalized pair of  $\pi$  electrons. Application of inhibitors is one of the most practical and economical methods. The corrosion inhibition efficiency of compounds is connected with their adsorption properties. The adsorption depends mainly on certain physico-chemical properties of the inhibitor molecules such as functional groups, aromaticity, electron density at donating atoms,  $\pi$ -orbital character of donating atoms, and electronic structure of the molecules.<sup>3-5</sup> Therefore, a knowledge of inhibition mechanisms is important both from industrial and scientific points of view. Many experimental researches investigated several Schiff bases as corrosion inhibitors for various metals and alloys in acidic media.<sup>6-8</sup> Theoretical studies based on quantum chemical calculations have predicted some molecular parameters of chemical compounds and found its relation to corrosion inhibition.<sup>9,10</sup>

This work attempts to calculate the interaction energies of three Schiff bases on the surface of face-centered cubic (fcc) copper were determined via a cluster model and ab initio quantum chemical calculations at density functional theory level (Fig. 1). The cluster model has been applied, previously, to the adsorption of molecules on the surface of catalysts.<sup>11,12</sup> These Schiff bases have shown inhibition effects for corrosion of metal in HCl aqueous solution.<sup>13</sup>



*Figure 1.* Structural formula of molecules (a) 2-[{-1-methyl-3-[(2-sulfanylphenyl) imino] butylidene} amino)-1-benzenethiol (SB<sub>1</sub>), (b) 2-({-1,2-diphenyl-2-[(2-sulfanylphenyl) imino] ethylidene} amino)-1-benzenthiol (SB<sub>2</sub>), (c) 2-[{-1-methyl-3-[(2-phenoxy) imino] butylidene} amino)-1-phenol (SB<sub>3</sub>).

The interaction of the corrosion inhibitor molecule with the metal surface is considered locally. Thus, the quantum chemical study is restricted to the calculation of interaction energies between the molecule and metallic atoms upon which the adsorption is directly taking place. The B3LYP method includes a mixture of HF with Density functional theory (DFT) exchange terms associated with the gradient-corrected correlation functional. Although the three semi-empirical parameters are fitted to produce thermo-chemistry of a set of small organic molecules, but it has been shown that performs exceptionally well on transition metal systems as well, and has much less convergence problems than those commonly found for pure DFT methods. In this work, the LANL1MB basis set includes the scalar, mass velocity and Darwin relativistic effects are used. The geometry of inhibitor Schiff bases were optimized via the B3LYP/ 6-31G\*\* method. The electronic energies of these isolated copper models and Schiff bases were obtained via the B3LYP/LANL1MB method  $(E_{iso}^{inhibitor} and E_{iso}^{copper})$ . Three types of adsorption may take place in the inhibition process at the metal-solution interface by the above Schiff bases: 1) electrostatic attraction between charged molecules and the charged metal surface, 2) interaction of unshared electron pairs on the N and S atoms in the molecule with the metal surface, and 3) interaction of  $\pi$ electrons of the aromatic rings and C=N groups with the metal surface or a combination of the above interactions. The total interaction energies of the inhibitor Schiff bases-copper in each model were calculated as a function of inhibitor distance from the copper surface and the minimum energy values (E (r<sub>min</sub>)) are given of it. The interaction of the inhibitor Schiff bases with the copper surface is known as  $E_{int}$  and calculated by equation 1.

$$E_{\rm int} = E(r_{\rm min}) - (E_{iso}^{inhibitor} + E_{iso}^{copper})$$
(1)

In most cases studied, molecule SB<sub>3</sub> is a best inhibitor and inhibitor SB<sub>2</sub> is better than SB<sub>1</sub> because it has a more negative  $E_{int}$  value.

# COUNTING THE NUMBER OF HETERO FULLERENES $C_{n-k}X_k$ , FOR n = 180, 240, 260, 320, 540

Masood HAMADANIAN, Modjtaba GHORBANI, Ali Reza ASHRAFI

Institute of Nanoscience and Nanotechnology, University of Kashan, Kashan 87317-51167, Iran

The most famous starting point for enumeration under group action is an important paper of Pólya in which he not only describes cycle index techniques for determining the numbers of orbits under finite group actions, but he demonstrates how to apply these methods for the chemical problem of isomer enumeration as well.

Hetero fullerenes are fullerenes where some of the carbon atoms are replaced by other atoms. Fripertinger applied SYMMETRICA<sup>1,2</sup> to write some codes for computing the number of  $C_{60-k}B_k$  molecules, where B is a hetero-atom such as Si.<sup>3</sup> In this paper, the number of all  $C_{n-k}B_k$  molecules are computed for n = 180, 240, 260, 320, 540.

Keywords: fullerene, hetero fullerene, cycle index, permutation group

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# INVESTIGATION OF EXPLOSIVE PERFORMANCE OF MONO-, BI- AND TRI-CYCLIC NITRAMINES BY *ab initio* COMPUTATIONAL METHODS

Masood HAMADANIAN<sup>1</sup>, Mohsen OFTADEH<sup>2</sup>, Reza HABIBPOUR<sup>2</sup>

<sup>1</sup>Department of Chemistry, Faculty of Science, Kashan University, Kashan, Iran <sup>2</sup>Department of Chemistry, Faculty of Science, Payam-Noor University, Isfahan, Iran

Cyclic nitramines are members of a great group named "propellants" as energetic materials. RDX and HMX are two of the famous propellants, which are employed in rockets and some guns. HMX also applied in implode materials in nuclear fission.<sup>1-4</sup> In our research, three groups of cyclic nitramines including some of one, two and three cyclic nitramine compounds are investigated. They are designed by substitution of  $-NO_2$ , -F, and -H on their rings. The related computations are carried out by *ab initio* (RHF) and DFT (B3LYP) methods. The basis sets 6-31G\*\* and 6-311++G\*\* (Gaussian 98 software) have been used in calculations.

Specific impulse has a direct relationship with two parameters ratio of gas products coefficients per molecular weight, n/M, and heat of detonation,  $\Delta H_{detonation}$ . Fluorine can increase the heat of detonation in mono-cyclic nitramines. The reverse results are obtained for bi- and tri-cyclic nitramines, what can be used in synthesis of these compounds as propellants. In unsubstituted nitramines the ratio of n/M is greater than in substituted nitramines. The results have shown that a good combination of these factors and molecular geometry effects can be applied in order to predict the explosive performance factor.

In this study, better results were obtained by DFT rather than RHF method. However, the basis sets variation had no effect on the results of the two methods.

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#### **MOLECULAR IDENTIFICATION FROM GRAPHS**

Ray HEFFERLIN, Ken LUK, Rebecca CHUNG

Southern Adventist University, Collegedale, Tennessee United States of America

Molecules containing transition-metal atoms can be incredibly complicated; nevertheless we seek to apply the methods of previous investigations on global molecular identification, based on the rule of 8, <sup>1-3</sup> to the simplest species among them. We seek first to characterize neutral transition-metal (TM) diatomic molecules, and second to characterize species containing one central TM atom with non-TM ligands. As before, we use Diophantine algebra as opposed to other methods such as the beautiful set theory of Vukičević and Graovac.<sup>4</sup> In stellar and other high-temperature environments, TM diatomics are common.<sup>6</sup> In analyzing them we assume:

(A) that the bonding is covalent, van der Waals, and/or dative,

(B) of integer orders 0 to 4, (C) selected so as to fulfill the rule of 18 on each group 8 to 12 atom or

(D) to have an even number of valence electrons on each group 3 to 7 atom.

In analyzing the TM molecules more familiar in chemistry, we began with an exhaustive search of the literature on their structures, on oxidation states,<sup>5</sup> on valences,<sup>6,7</sup> and on bonding preferences across the TM groups.<sup>8</sup>

We assume:

(a) that TM species obey rules of 8 (have closed-shell configurations  $4s^03d^04p^0$ ), 2 ( $4s^23d^04p^0$ ), 12 ( $4s^23d^{10}4p^0$ ), and 18 ( $4s^23d^{10}4p^6$ ),

(b) that the ligands obey rules of 2 (group 1 atoms), 4 (group 2), 6 (group 13) or 8 (groups 14 to 18),

(c) that ionic bonds (with up to 3 electrons donated by the TM atom) connect ligands to the central atoms of groups 3 and 4,

(d) that two-center two-electron covalent bonds and dative bonds (up to a total of 3), and van der Waals bonds, connect ligands to atoms of groups 5 to 12,

(e) that the electrons in a dative bond are allocated by more electronegative p atoms, and

(f) that the coordination number of the central atom is unrestricted (a major difference from previous work).<sup>1-3</sup>

It will be shown with numerous examples how the algebra applies. Of course, not all of the molecules satisfy the rules, and some of them that do may be stable only in exotic environments. Aside from molecular characterizations, the mathematical formulae to be presented—and improvements to come—should prove useful in designing software to forecast TM molecule structures.

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# MATHEMATICAL MEANING AND IMPORTANCE OF THE TOPOLOGICAL INDEX Z

Haruo HOSOYA

Ochanomizu University (Emeritus), Bunkyo-ku, Tokyo 112-8610, Japan

My first graph-theoretical paper, Topological Index. A Newly Proposed Quantity Characterizing the Topological Nature of Saturated Hydrocarbons,<sup>1</sup> was published in 1971. Since then I have been working in mathematical chemistry for more than thirty years. If the essence of all my papers is to be abstracted, one may say that many chemical problems and phenomena can be described and analyzed mathematically, and then interpreted chemically by using proper counting polynomials. Although the topological index was coined by myself for the Z-index, this term has now become the general name for topological descriptors.<sup>4</sup>

Good correlation is observed between the boiling point of alkanes and Z, which is the sum of the non-adjacent numbers, p(G,k)s, of graph G representing their carbon atom skeleton. For tree graphs those p(G,k) values are identical to the absolute values of the characteristic polynomial of G, while for non-tree graphs some correction terms become necessary. Then one can systematically analyze the graph-theoretical meaning of Z and then the chemical meaning of the observed correlation. Later the Z index was found to be utilized for analyzing the graph theoretical meaning of the aromatic stability of conjugated hydrocarbons,<sup>3,4</sup> and also for the classification and coding of hydrocarbons.

Possibly due to its mathematically naïve definition, the p(G,k) and Z values of several series of typical graphs were found to be closely related to several series of numbers and the related mathematical objects. For example, the Z's of path and monocycle graphs are nothing else but the Fibonacci and Lucas numbers, respectively, which have the same recursion relation, as  $f_n = f_{n-1} + f_{n-2}$ .<sup>1,4</sup> Moreover, the whole families of p(G,k) numbers of these two series of graphs form Pascal's and asymmetrical Pascal's triangles, respectively.<sup>5</sup> This means that by using the Z-index one can obtain new graph-theoretical meaning of the well known algebraic concepts and theorems. Quite recently various series of graphs were discovered whose Z-indices are closely related to fundamental concepts and theorems in elementary mathematics as follows.

(1) Pell numbers, 1, 2, 5, 12, 29, *etc.*, which recur as  $f_n = 2 f_{n-1} + f_{n-2}$ . (2) Solutions of Pell equation,  $x^2 - D y^2 = N (N = \pm 1 \text{ etc.})$  for special values of D and N.

(3) Pythagorean triangles (a, b, c) composed of all integers with  $a^2 + b^2 = c^2$ .

(4) Heronian triangles (a, b, c) composed of all integers with integral area.

A very important role of the Z-index in elementary mathematics has thus been verified.

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### A NEW VIEW OF HYBRIDIZED ATOMIC ORBITALS FROM *n*-DIMENSIONAL WORLD

Haruo HOSOYA<sup>1</sup>, Fuyuko KIDO<sup>2</sup>, Sumio TOKITA<sup>2</sup>

<sup>1</sup>Ochanomizu University (Emeritus), Bunkyo-ku, Tokyo 112-8610, Japan <sup>2</sup>Department of Applied Chemistry, Saitama University, Shimo-Okubo 255, Saitama 338-8570, Japan

We have been studying algebraic structure of *n*-dimensional atomic orbitals (AOs), and have shown that the number of degeneracy of the angular part of them can be obtained from the Pascal's triangle.<sup>1,2</sup> The periodic table of the hypothetical 4-dimensional world was also predicted and discussed.<sup>3</sup> In this paper algebraic structure of the hybridized sp<sup>*n*</sup> and sp<sup>*n*</sup>d<sup>*n*-l</sup> type AOs is clarified. Namely, the relations among these hybridized AOs appearing in the discussion of electronic structure of molecules in 3-dimensional real world are globally understood, if both sp<sup>*n*</sup> and sp<sup>*n*</sup>d<sup>*n*-l</sup> type are inherent to an atom in *n*-dimensional world. The general expression of *m*th lobe of sp<sup>*n*</sup> hybridization in *n*-space is given by

$$\chi_{n,m} = \frac{1}{\sqrt{n+1}} s - \sum_{k=1}^{m-1} \frac{1}{\sqrt{(n+2-k)(n+1-k)}} p_k + \frac{\sqrt{n-(m-1)}}{\sqrt{n-(m-2)}} p_m.$$

$$(n = 0, 1, 2, \dots; m = 1, 2, 3, \dots, n, n+1)$$

These orbitals span the *n*-simplex, or the smallest regular geometrical object in *n*-space as summarized in the following table.

п	sp <sup>n</sup>	$x_1$	Geometrical Structure	cos θ	θ
1	sp	$\frac{1}{\sqrt{2}}s + \frac{1}{\sqrt{2}}p_x$	Line segment	$-\frac{1}{1}$	180°00′
2	sp <sup>2</sup>	$\frac{1}{\sqrt{3}}s + \sqrt{\frac{2}{3}}p_x$	Regular triangle	$-\frac{1}{2}$	120°00′
3	sp <sup>3</sup>	$\frac{1}{\sqrt{4}}s + \sqrt{\frac{3}{4}}p_x$	Regular tetrahedron	$-\frac{1}{3}$	109°28′
4	sp <sup>4</sup>	$\frac{1}{\sqrt{5}}s + \sqrt{\frac{4}{5}}p_x$	Regular 5-cell	$-\frac{1}{4}$	104°29′

Another set of typical hybridized orbitals,  $sp^n d^{n-1}$  type, are found to correspond to the cross polytope and *n*-cube in *n*-space. Namely, in each dimension *n* pairs of hybridized orbital lobes are directed from the origin toward the both ends of *n* coordinate axes.

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#### SOME TOPOLOGICAL INDICES OF TUC4C8(R) NANOTUBES

#### Ali IRANMANESH, B. SOLEIMANI

Department of Mathematics, Tarbiat Modarres University P.O. Box 14115-137, Tehran, Iran

A graph G = (V, E) is a combinatorial object consisting of an arbitrary set V = V(G) of vertices and set E = E(G) of unordered pairs  $\{x, y\} = xy$  of distinct vertices of G called *edges*. For any pair of vertices x, y we define the *distance* d(y, x) to be the length of the shortest path between x and y. If there is no (finite) path, we define  $d(y, x) = \infty$ . Let e be an edge of the graph G connecting the vertices u and v. Define two sets  $N_1(e|G)$  and  $N_2(e|G)$  as:

$$N_1 = N_1(e|G) = \{x | x \quad V(G), \ d(x, u) < d(x, v)\}$$
$$N_2 = N_2(e|G) = \{x | x \quad V(G), \ d(x, v) < d(x, u)\}$$

and denote by  $n_1(e|G) = |N_1(e|G)|$  and  $n_2(e|G) = |N_2(e|G)|$ . In other words,  $n_1(e|G)$  is the number of vertices closer to *u* than to *v* and equidistant to *u* and *v* are not counted. The Szeged index is defined as:

$$Sz = Sz(G) = \sum_{e \in E(G)} n_1(e|G) n_2(e|G)$$

where the summation goes over all edges of the graph G.

A  $C_4C_8$  net is a trivalent decoration made by alternating squares  $C_4$  and octogons  $C_8$ . It can cover either a cylinder or a torus.

In this paper, we compute the Szeged index of  $TUC_4C_8(R)$  nanotube. Also, we compute Padmakar-Ivan index, abbreviated (*PI*) index, of  $TUC_4C_8(R)$  nanotube where *PI* index of a graph *G* is defined as:

$$PI(G) = \sum [n_{eu}(e|G) + n_{ev}(e|G)]$$

where  $n_{eu}(e|G)$  is the number of edges of *G* lying closer to *u* than to *v*,  $n_{ev}(e|G)$  is the number of edges of *G* lying closer to *v* than to *u* and summation goes over all edges of *G*.

# CALCULATION OF CONFINED FLUID MEAN DENSITY WITH INTERACTION OF YUKAWA

Mohammad Reza JALALI

Isfahan Payam Noor University, Isfahan, Iran

To study the fluid structure, using computer simulation method, it is necessarily to calculate the mean density of fluid to determine the number of particles in each cell. In this paper we used Kim approximation method, which contain two approximation methods, namely, weighted density approximation of Tarazona and modified hyper netted chain approximation proposed by Rickayzen and Augousti in theory of density functional. Mean density of Yukawa fluid confined between two parallel plane walls for hard walls and attractive Yukawa walls were calculated using this approximation and compared with other methods at different temperatures. Further results, according to these calculations, are that the mean density of confined fluid such as a solvent in colloidal system depends on the temperature of the fluid, interaction between fluid molecules, their interaction with the walls and separation of the walls.

Keyword: mean density, density functional, Yukawa potential

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# THE CONSTRUCTION OF HOSOYA MATRICES

Dušanka JANEŽIČ<sup>1</sup>, <u>Sonja NIKOLIĆ<sup>2</sup></u>, Ante MILIČEVIĆ<sup>3</sup>, Nenad TRINAJSTIĆ<sup>2</sup>

<sup>1</sup>National Institute of Chemistry, Hajdrihova 19, SI-1000 Ljubljana. Slovenia <sup>2</sup>Ruđer Bošković Institute, P.O.B. 180, HR-10002 Zagreb, Croatia <sup>3</sup>Institute of Medical Research & Occupational Health, P.O.B. 291, HR-10002 Zagreb, Croatia

The step-by-step graphical construction of Hosoya matrices for a selected acyclic graph, cycle-containing graph, edge-weighted graph and multigraph is given.

# **ON HOSOYA MATRICES**

Dušanka JANEŽIČ<sup>1</sup>, Sonja NIKOLIĆ<sup>2</sup>, Ante MILIČEVIĆ<sup>3</sup>, <u>Nenad TRINAJSTIĆ<sup>2</sup></u>

<sup>1</sup>National Institute of Chemistry, Hajdrihova 19, SI-1000 Ljubljana. Slovenia <sup>2</sup>Ruđer Bošković Institute, P.O.B. 180, HR-10002 Zagreb, Croatia <sup>3</sup>Institute of Medical Research & Occupational Health, P.O.B. 291, HR-10002 Zagreb, Croatia

Hosoya matrices are formulated in terms of Hosoya indices.<sup>1</sup> They are square  $V \times V$  matrices. Initially Hosoya matrices were introduced for acyclic molecular graphs<sup>2</sup> and then were extended to cycle-containing graphs, edge-weighted graphs and multigraphs.<sup>3,4</sup> We present the sparse and dense Hosoya matrices for several classes of these graphs and in the related poster we give the step-by-step construction of Hosoya matrices.

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#### **APPROXIMATE SOLUTION OF DENSE LINEAR SYSTEMS**

Željko JERIČEVIĆ<sup>1,2</sup>

<sup>1</sup>Department of Molecular & Cellular Biology, Baylor College of Medicine, Houston, TX 77030, USA <sup>2</sup>Department of Biology & Medical Genetics, Medical School Rijeka, HR-51000 Rijeka, Croatia

A novel numerical approach for approximate solution of large linear systems of a dense type based on the Fourier transform has been recently developed.<sup>1</sup> In order to make the method applicable to broader range of problems, the effects of partitioning the system matrices and applying piecewise transforms of different length and type were studied. The basic idea behind the methodology remains the same, namely to use unitary, orthogonal transforms which concentrate energy in a small number of coefficients. The transformed system is reduced in size by pruning off non-significant information (in digital signal processing fashion) before solving the reduced system in transform domain and generating the transform of approximate solution. Inverting the transform of approximate solution yields the approximate solution of the original system. The results indicate that partitioning and reshuffling of matrices before applying the transforms increase flexibility and numerical efficiency of the method.

$$\mathbf{B}\mathbf{Q} = \mathbf{Q}\mathbf{\Lambda} \qquad (\mathrm{E}q\ 1)$$

The eigenvalue problem in Eq 1 is transformed using the Fourier transform matrices F

 $\mathbf{FBF}^{-1}\mathbf{FQ} = \mathbf{FQA} \qquad (\mathrm{Eq}\ 2)$ 

By partitioning into submatrices and applying piecewise Fourier transform we get:

$$\mathbf{B} = \begin{bmatrix} \mathbf{b}_{1,1} & \mathbf{b}_{1,2} \\ \mathbf{b}_{2,1} & \mathbf{b}_{2,2} \end{bmatrix} \qquad \mathbf{F} = \begin{bmatrix} \mathbf{f}_{1,1} & \mathbf{0} \\ \mathbf{0} & \mathbf{f}_{2,2} \end{bmatrix} \qquad \mathbf{F}^{-1} = \begin{bmatrix} \mathbf{f}_{1,1}^{-1} & \mathbf{0} \\ \mathbf{0} & \mathbf{f}_{2,2}^{-1} \end{bmatrix}$$
$$\mathbf{Q} = \begin{bmatrix} \mathbf{q}_{1,1} & \mathbf{q}_{1,2} \\ \mathbf{q}_{2,1} & \mathbf{q}_{2,2} \end{bmatrix} \qquad \mathbf{\Lambda} = diag(\lambda_1, ..., \lambda_N)$$

Substituting into Eq 2

$$\begin{bmatrix} \mathbf{f}_{1,1} & \mathbf{0} \\ \mathbf{0} & \mathbf{f}_{2,2} \end{bmatrix} \begin{bmatrix} \mathbf{b}_{1,1} & \mathbf{b}_{1,2} \\ \mathbf{b}_{2,1} & \mathbf{b}_{2,2} \end{bmatrix} \begin{bmatrix} \mathbf{f}_{1,1}^{-1} & \mathbf{0} \\ \mathbf{0} & \mathbf{f}_{2,2}^{-1} \end{bmatrix} \begin{bmatrix} \mathbf{q}_{1,1} & \mathbf{q}_{1,2} \\ \mathbf{q}_{2,1} & \mathbf{q}_{2,2} \end{bmatrix} = \begin{bmatrix} \mathbf{f}_{1,1} & \mathbf{0} \\ \mathbf{0} & \mathbf{f}_{2,2} \end{bmatrix} \begin{bmatrix} \mathbf{q}_{1,1} & \mathbf{q}_{1,2} \\ \mathbf{q}_{2,1} & \mathbf{q}_{2,2} \end{bmatrix} \Lambda$$

Yields the application of transforms on partitioned matrices:

$$\begin{bmatrix} \left(\mathbf{f}_{1,1} \ \mathbf{b}_{1,1} \ \mathbf{f}_{1,1}^{-1}\right) & \left(\mathbf{f}_{1,1} \ \mathbf{b}_{1,2} \ \mathbf{f}_{2,2}^{-1}\right) \\ \left(\mathbf{f}_{2,2} \ \mathbf{b}_{2,1} \ \mathbf{f}_{1,1}^{-1}\right) & \left(\mathbf{f}_{2,2} \ \mathbf{b}_{2,2} \ \mathbf{f}_{2,2}^{-1}\right) \end{bmatrix} \begin{bmatrix} \left(\mathbf{f}_{1,1} \ \mathbf{q}_{1,1}\right) & \left(\mathbf{f}_{1,1} \ \mathbf{q}_{2,1}\right) \\ \left(\mathbf{f}_{1,1} \ \mathbf{q}_{2,1}\right) & \left(\mathbf{f}_{1,1} \ \mathbf{q}_{2,2}\right) \end{bmatrix} = \begin{bmatrix} \left(\mathbf{f}_{1,1} \ \mathbf{q}_{1,1}\right) & \left(\mathbf{f}_{1,1} \ \mathbf{q}_{1,2}\right) \\ \left(\mathbf{f}_{2,2} \ \mathbf{q}_{2,1}\right) & \left(\mathbf{f}_{2,2} \ \mathbf{q}_{2,2}\right) \end{bmatrix} A$$

The procedure is easily generalized for higher number of partitions.

Numerical experiments illustrating feasibility of the method and quality of the approximation for eigenvalue problem in chemical graph theory are presented. Further developments in combination with other methods are also discussed.

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# AN EIGENVALUE CONJECTURE OF P. C. MÜLLER (UNIVERSITY OF WUPPERTAL)

Peter E. JOHN

Instute of Mathematics, Ilmenau Technical University, D-98684 Ilmenau, Weimarer Str. 25, PSF 10 05 65, Germany

Let A = (a\_ij) denote a nxn-matrix with entries  $a_i, j = -1$  (j = n-i),  $a_i, j = -1$  (j = n+1-i), a\_i, j = 1 (j = n+1-i) and a\_i, j = 0 otherwise. Conjecture: For i = 1, 2,.., n the eigenvalues of matrix A are {(-1)^(k-1)}.k, for k = 1, 2,.., n.

A simple proof is given.

# VOLATILE ANESTHETIC-PROTEIN INTERACTION: NMR STRUCTURE OF CaM/HALOTHANE COMPLEX IN SOLUTION

<u>Nenad JURANIĆ</u><sup>1</sup>, Slobodan MACURA<sup>1</sup>, Alan R. PENHEITER<sup>2</sup>, Keith A. JONES<sup>2</sup>, John H. STREIFF<sup>2</sup>

<sup>1</sup>Department of Biochemistry & Molecular Biology, Mayo College of Medicine, Rochester, MN, USA <sup>2</sup>Department of Anesthesiology, Mayo College of Medicine, Rochester, MN, USA

Anesthetic mechanisms are not clearly understood, but many hypotheses invoke direct interactions of anesthetics with proteins. Thus, the study of anesthetic-protein interactions could have an impact on the numerous health related effects of anesthetics and anesthesia. In addition, studies of low affinity interactions of proteins are of general interest to other areas of study, such as protein signaling and pharmaceutical design. Only a small number of three dimensional structures of volatile anesthetic-protein complexes have been determined to date, and all have been done with x-ray crystallography. We report here on the solution structure of a volatile anesthetic-CaM complex, obtained by the NMR method. Preliminary, low-resolution structure, of the complex (see Figure 1) shows that halothane binds to the hydrophobic pocket in both lobes of CaM. The overall structure is close to CaM, except that the region of the central linker appears less flexible. The majority of structural contacts between halothane and CaM involve the side-chain methyl-groups of methionines inside the hydrophobic pockets.



*Figure 1.* Assembly of NMR derived backbone conformations of CaM/halothane complex using molecular simulation program XPLOR/Quanta. Halothane molecules are given in black.

# THE STUDY OF LASER ABLATION EFFECTS ON PMMA AND POLYCARBONATE POLYMERS

Masoud KAVOSH TEHRANI

Malek Ashtar University of Technology, Shahinshahr, Iran

PMMA and polycarbonate polymers have been put under radiation of laser beam in our experiments. The related thresholds and the fluxes have been calculated and corresponding

absorption coefficient were measured.

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# GAS PHASE INTERACTION OF TEMPO-RADICALS WITH Cr<sup>+</sup> AND Fe<sup>+</sup> IONS

Leo KLASINC<sup>1</sup>, Bogdan KRALJ<sup>2</sup>, Marko ROŽMAN<sup>1</sup>, <u>Dunja SRZIĆ<sup>1</sup></u>, Dušan ŽIGON<sup>2</sup>

<sup>1</sup>*Ruđer Bošković Institute, Zagreb, Croatia* <sup>2</sup>*Jožef Stefan Institute, Ljubljana, Slovenia* 

The interaction of 2,2,6,6-tetramethyl-piperidyl-1-oxyde (TEMPO) radicals (<u>1</u>) and its 4-hydroxy-, 4-methoxy- and 4-acetamido-derivatives (<u>2</u>, <u>3</u> and <u>4</u>, respectively) with  $Cr^+$  and  $Fe^+$  ions was investigated within a Fourier transform ion cyclotron resonance mass spectrometer (FT ICR MS). The reaction products formation between the laser generated mass selected <sup>52</sup>Cr<sup>+</sup> or <sup>56</sup>Fe<sup>+</sup> ions and the neutral radical molecules <u>1</u> - <u>4</u> present in the instrument's gas phase was monitored by recording "snapshot" mass spectra at various delay times starting from the ion selection.

In agreement with the marked difference in both electronic structure of the ions (Cr<sup>+</sup> 3d<sup>5</sup>; Fe<sup>+</sup> 3d<sup>6</sup>4s) and ionization energies of the neutral metals (Cr 6.8 eV; Fe 7.9 eV) and radicals (<u>1</u> - <u>4</u> ~ 7.3 eV) obvious differences in reactivity and products formation are observed and discussed. Thus, Fe<sup>+</sup> prefers charge exchange with the radicals R<sup>•</sup> according

 $Fe^+ + R^{\bullet} \longrightarrow Fe^0 + R^+$ 

and reacts much faster by ligating consecutively up to three of them, i.e.

 $\operatorname{Fe}^{+} + \operatorname{R}^{\bullet} \longrightarrow \operatorname{FeR}^{+} \xrightarrow{+\operatorname{R}^{\bullet}} \operatorname{FeR}_{2}^{+} \xrightarrow{+\operatorname{R}^{\bullet}} \operatorname{FeR}_{3}^{+}$ 

The ligation of  $Cr^+$  is much slower and if existent at all stops with the second ligand R<sup>•</sup> because  $Cr^+$  wants to preserve its half-filled stable d<sup>5</sup> electronic structure.

# *k*-DOMINATING SETS ON THE ASSOCIATIVE AND COMMUTATIVE PRODUCTS OF TWO PATHS

Antoaneta KLOBUČAR

Department of Mathematics, Faculty of Economics, University of Osijek, Gajev trg 7, HR-31000 Osijek, Croatia

In this paper I first present some my earlier results, on the *k*-dominating sets of Cartesian products and cardinal products of two paths, and then new results about the k-dominating sets of strong product and equivalent product of two paths. (*k*-domination number of strong and equivalent product of  $P_m X P_n$  for *m* and *n* arbitrary.)

## PREDICTING PROTEIN INTERACTIONS WITH SURFACE DESCRIPTORS

Janez KONC, Dušanka JANEŽIČ

National Institute of Chemistry, Hajdrihova 19, SI-1000 Ljubljana, Slovenia

Interactions between proteins are mediated through their surfaces. A protein exhibits on the surface a set of physical properties of its amino acid functional groups. The characteristics of the surfaces are known to be conserved among proteins, which otherwise share little sequence identity. Binding sites are the most conserved areas on the proteins surfaces. A computer program is developed, which compares surfaces of different proteins encoded by descriptors, and superimposes the similar areas. This program is then used to search for areas on the surface, where the protein may interact with other proteins.

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## **CONSTRUCTION OF NANOTUBE JUNCTIONS**

István LÁSZLÓ

Department of Theoretical Physics, Institute of Physics & Center for Applied Mathematics & Computational Physics, Budapest University of Technology & Economics, H-1521 Budapest, Hungary

Carbon-nanotube-based electronics offers significant potential as a nanoscale alternative to silicon-based devices for molecular electronics technologies. Using nanotube junctions a truly nanoelectronic architecture can be realized where both devices and interconnects are based on carbon nanotubes. Although there are various theoretical propositions for nanotube junctions, all of them are applied for non chiral nanotubes.

We have recently presented an algorithm for constructing junctions between single wall nanotubes of any chirality and diameter.<sup>1</sup> This method is based on Geometric Intersection of Cylinders and it can describe most of the Y and T junctions obtained by the To-Doped Vapour Catalyst method. Namely in this method new nanotube branches are attached to already developed nanotubes. In the present work a new method will be presented for constructing nanotube junctions between three nanotubes of any chirality.

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### **AROMATICITY OF CARBON NANOTUBES**

István LUKOVITS, Franciska H. KÁRMÁN, Peter M. NAGY, Erika KÁLMÁN

Chemical Research Center, H-1525 Budapest, POB 17, Hungary

Carbon nanotubes (CNTs) are composed of  $sp^2$  carbon atoms being arranged in a hexagonal pattern. Therefore CNTs are special cases of peri-condensed benzenoids. Benzenoids are unsaturated aromatic hydrocarbons, meaning that despite the fact that there are unsaturated bonds, it is rather difficult to saturate these bonds by using addition reactions. Aromaticity can be explained in terms of the number of Kekulé structures (K), the greater K is the more aromatic is the molecule. In this study the hypothetical (2,2)<sub>m</sub> CNTs and (m,4) and (m,3) planar graphene sheets have been compared, where m denotes the number of hexagonal strips in the CNTs and the number of "columns" in planar graphene sheets. Enumeration of Kekulé structures is a mathematical problem. The Kekulé count in planar structures was obtained by using an algorithm proposed recently,<sup>1</sup> whereas it was calculated by the transfer matrix technique in the (2,2)<sub>m</sub> tubes.<sup>2</sup> The aromatic character of the structures was found that CNTs are more aromatic than their planar counterparts, therefore it is more difficult to saturate (functionalize) CNTs than the corresponding planar graphene sheets.

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#### THE SIX (OR SEVEN) BRIDGES OF KALININGRAD: A PERSONAL EULERIAN WALK, 2006

Roger B. MALLION

#### The King's School, Canterbury, CT1 2ES, England, United Kingdom

The 18<sup>th</sup>-century problem of the Bridges of Königsberg was solved in a memoir dated 1736 and written by the Swiss mathematician Leonard Euler (1707–1783) soon after he had been appointed to the senior Chair of Mathematics at the St. Petersburg Academy of Sciences. Not long after the Conferences of Yalta and Potsdam had assigned the region to the Soviet Union after World War II, Königsberg came to be known as the city of Kaliningrad [Калининград], capital of the Kaliningrad Oblast, which, since the early 1990s, has found itself as an exclave of the present-day Russian Federation, isolated from mainland Russia by the newly independent republic of Lithuania (and, beyond that, Latvia and Belarus). Furthermore, the Kaliningrad Oblast's only other adjoining neighbour is Poland which, like Lithuania, has been a Member of the European Union since May 1<sup>st</sup>, 2004. This state of affairs thus determines that the Kaliningrad Oblast is, these days, *doubly* anomalous, in that it is not only an *exclave* of the Russian Federation but (simultaneously) it is also a foreign enclave within the European Union. It was into this intriguing and unique area that I ventured, last February, in order to investigate what the current situation is with regard to 'Eulerian Walks' in the Kaliningrad of 2006, precisely 270 years after Euler considered the problem as it applied to the Königsberg of 1736. This talk will evaluate how the disposition of the Bridges has varied over the years. Until 1875, the configuration of the Bridges was precisely what it was in Euler's time, and an Eulerian Walk was thus still not then feasible; by the 1930s, however, the original seven Bridges had increased in number to ten, and careful examination shows that an Eulerian Walk was at that time possible. It will be demonstrated that, only a few years ago - at the beginning of the present millennium - an Eulerian Walk was again not feasible. In fact, though, thanks to the rebuilding, only last year, of the (1905) Kaiserbrücke - which was reconstructed in order to commemorate the 750th anniversary of the founding of the city (in 1255) - an Eulerian Walk is once again now possible in present-day Kaliningrad. This claim will be demonstrated both by use of the conventional Graph-Theoretical equivalent of Euler's original algorithm and by describing the specific Eulerian Walk that I (and my intrepid Polish travelling companion. Paweł Skrzyński) actually executed in practice, on Sunday, February 26<sup>th</sup>, 2006.

# ENTROPY PRODUCTION IN A SYSTEM OF COUPLED NONLINEAR DRIVEN OSCILLATORS

Mladen MARTINIS, Vesna MIKUTA-MARTINIS

Theoretical Physics Division, Ruđer Bošković Institute, HR-10002 Zagreb, Croatia

We study the time evolution of a classical system of coupled nonlinear oscillators, undergoing a process of entropy production due to the environmental influence. How to define precisely the entropy production rate in a classical system in a stationary state, under external nonconservative forces, is in general an open problem. Entropy in both physics and chemistry is an exact measure of the rate of heat dissipation in a closed thermodynamic system. This precision is lost when an open thermodynamic system, exemplified in the biological and social sciences, is considered. Main attention will be paied to the time dependence of the Shannon entropy of the system. Entropy production rate employed in this talk measures energy cost to maintain, at steady-state, dissipative structures (structures preserving functions). It can be applied to thermodynamic-closed mechanical systems as well as to thermodynamic-open systems of self-organizing structures (i.e., living systems).

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# CHARACTERIZATION AND SIMILARITY/DIVERSITY STUDY OF PROTEOMIC MAPS

Andrea MAURI, Viviana CONSONNI, Roberto TODESCHINI

Milano Chemometrics & QSAR Research Group, Department of Environmental Sciences, University of Milano-Bicocca, P.za della Scienza 1, 20126 Milano, Italy

The evaluation of complex therapeutic and toxic behaviour of chemicals from their effects on simpler biological systems such as cells is among the most interesting trends in drug discovery, environmental safety studies, molecular pharmacology and hazard assessment.

In this field special attention has been payed to the cellular proteome which characterizes the different abundance of thousands of proteins belonging to the same cell, where toxicological studies on proteomic maps consist in perturbing the control cell with a chemical and evaluate the resulting differences in the abundance of protein expressions with respect to the control cell.<sup>1</sup>

A very interesting mathematical challenge is to understand the complexity of cellular events, and then describe and characterize changes in proteomic maps.

The theory of the partial ordering is used to characterize proteomic maps, their fingerprints resulting in a matrix called "Hasse matrix".<sup>2-4</sup>

The similarity/diversity between two proteomic maps is obtained by the definition of a distance between the corresponding Hasse matrices. This distance – weighted standardized Hasse distance - has some useful properties and seems to show a high sensitivity to changes in protein abundances.

This distance measure can be naturally standardized, thus allowing the interpretation of the distances as absolute values (e.g. percentage) and deriving simple similarity and correlation indices.

The proposed measure has been evaluated on some proteomic maps taken from literature.<sup>5,6</sup>

A sensitivity analysis has been also performed showing the high capability of this measure to taking into account small modifications of the proteomic maps.

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# APPLICATION OF CHEMOMETRICS METHODS IN DIMERIZATION REACTION OF A DYE IN WATER AND WATER-NON AQUEOUS SOLVENTS MIXTURE

Mohammad MAZLOUM ARDAKANI<sup>1</sup>, Jahanbakhsh GHASEMI<sup>2</sup>, S. LOTFI<sup>3</sup>

<sup>1</sup>Department of Chemistry, Faculty of Science, Yazd University, Yazd, Iran <sup>2</sup>Department of Chemistry, Faculty of Science, Razi University, Kermanshah, Iran <sup>3</sup>Department of Chemistry, Ardakan Payam Noor University, Ardakan, Iran

Spectrophotometric methods are frequently used to analyze chemical equilibria. If the components involved can be obtained in pure form, or if their spectral responses do not overlap, such analysis is, in general, trivial. This is not the case for many systems, particularly those with similar components, which are difficult to analyze. In 1993, Scarminio and Kubista introduced an algorithm for analyzing correlated spectral data by procrustes rotation, which eliminated the need for referent samples.<sup>1</sup>

In this work, the dimerization constants of methylene green (MG) have been determined by studying the dependence of their absorption spectra on the temperature in the range of 20 - 90 °C at different total concentrations of MG ( $9.85 \times 10^{-5}$  to  $2.98 \times 10^{-4}$  M) and different concentration of NaCl as supporting electrolyte. The equilibrium parameters of the dimerization of NG have been determined by chemometrics refinement of the absorption spectra obtained from thermometric titrations performed at different ionic strengths. The dimerization constants are varied by changing the ionic strength: The degree of dimerization are increased by the ionic strengths of the medium. The enthalpy and entropy of the dimerization reactions were determined from the dependence of the equilibrium constants on the temperature.

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# **RELATIONSHIP BETWEEN THE INTERNAL BODY CLOCK AND SOME BODY FUNCTIONS: STATISTICAL APPROACH**

<u>Vesna MIKUTA-MARTINIS<sup>1</sup></u>, Ljubica MATIJEVIĆ-MAŠIĆ<sup>2</sup>

<sup>1</sup>Theoretical Physics Division, Ruđer Bošković Institute, HR-10002 Zagreb, Croatia <sup>2</sup>Department of Clinical Immunology & Rheumatology, Clinical Hospital Dubrava, HR-10000 Zagreb, Croatia

All activities in biosystems are observed to show cyclic behavior on the level of cells, tissues, organs and the whole organisms. **Chronobiology** is the branch of science that examines these time – related phenomena in living organisms and quantifies mechanisms of biological time structure ( circadian, circavital and circannual rhythm ).

In mammals, physiology and behaviour are subject to daily oscillations that are driven by an endogenous clock. In the absence of external time cues this internal clock generates cycles of approximately but not exactly 24 hours – circadian rhythms.

Many important oscillating phenomena in the human body like the blood pressure, temperature and the heart frequency are influenced by circadian rhythm. The haematopoetic and immune systems in all their components are also characterized by multifrequency oscillations with a dominant rhythms of proliferation and cell functions within circadian, circannual and circavital frequency ranges. We have studied the influence of the chronobiologic rhythms on these oscillating phenomena in humans.

In this research we have explored the influence of the circadian rhythm on some very important oscillating parameters like the number and function capability of immunocompetent cells, cell proteins, immunoglobulines (IgA. IgG, IgM), components of complement, hormons (cortisol) as well as the blood pressure and the heart frequency.

The study was performed on the group of 22 young men in the age between 20 and 23 and experimental results were analysed using ANOVA (ANalysis Of VAriance) and some other tests.

Our analysis suggests the significant influence of chronobiologic oscillations on some physiologic, immune and hormonal parameters. It could be very important in the application of drugs in therapy.

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# RETRIEVAL OF BIOPHYSICAL/STRUCTURAL CANOPY PROPERTIES FOR AGRICULTURE AND FORESTRY APPLICATIONS USING AIRBORNE IMAGING SPECTROMETRY

#### John R. MILLER

Earth Observations Laboratory, Department of Earth and Space Science and Engineering, York University, 4700 Keele Street, Toronto, Canada M3J 1P3

Imaging spectrometry data is increasingly being put to use in managed ecosystems as in agriculture and forestry as well as in natural ecosystems by exploiting and evaluating linked leaf-canopy models to retrieve quantitative estimates of leaf biochemical contents of total chlorophyll and water as well as canopy parameters such as crown or canopy leaf area index, fractional vegetative cover or soil moisture content and residue content. Retrieval accuracies for estimated biophysical/structural canopy variables as determined by comparison with intensive field data collection are typically 10% of nominal values under normal field conditions and therefore are making imaging spectrometry an effective tool being evaluated for a range of specific applications. This progress toward provision of a vegetative state mapping tool can be primarily attributed to

*(i)* the wide availability of well-calibrated airborne imaging spectrometers with software to deliver good atmospheric correction and virtual turn-key generation of above-canopy reflectance imagery,

*(ii)* wide availability of robust and understood leaf and canopy models for a range of canopy types that can be coupled and used to infer canopy biophysical/structural variables, and

*(iii)* airborne, satellite and field data collection protocols and strategies that have allowed the assessment of the variable retrieval accuracy as well the appropriateness/limitations of models to be evaluated.

This paper provides a summary of research results recently obtained by the Earth Observations Laboratory at York University using such approaches and strategies. Examples of applications of imaging spectrometry described in this paper include:

*(i)* mapping the spatial heterogeneity in cereal crops and tracking seasonal change of canopy green leaf area index, green biomass, vegetative cover, and leaf pigment content,

*(ii)* tracking seasonal change and intersite differences in needle pigment content in coniferous trees crowns in the boreal forest region as a measure of stand condition and species, and

*(iii)* deriving leaf pigment content in structured canopies as in vineyards and olive groves and linking this to local growth conditions.

The paper will described how success achieved in canopy or leaf property retrievals has been found to be often critically dependent on spatial resolution of the hyperspectral imagery due to the spatial heterogeneity of most vegetated targets. Assessment studies of the applicability of specific leaf-canopy models has therefore required careful attention to:

*(i)* study sites which encompass a sufficiently wide variation in the properties to be retrieved to allow for an unambiguous estimate of retrieval accuracies,

*(ii)* detailed laboratory measurements at the leaf level to determine optical properties and biochemical constituents,

*(iii)* image data at selected target areas with sufficient resolution to enable vegetation crown and background areas to be sampled and the canopy model assumptions to be assessed.

Such strategies have permitted leaf/canopy property retrievals in cereal crops from emergence through maturity, in closed deciduous forest canopies, in open conifer stands, and in open canopies as in olive groves and vineyards.

# *Ab initio* RHF & DENSITY FUNCTIONAL THEORY STUDIES OF SOME CYCLIC ORGANODIBORANES

Seyed Nezamoddin MIRSATTARI,<sup>1</sup> Mirabdullah Sed SADJADI<sup>2</sup>

<sup>1</sup>Department of Chemistry, Shahreza Branch, Islamic Azad University (IAU), Shahreza, Iran <sup>2</sup>Research & Science Branch, Islamic Azad University (IAU), Tehran, Iran

Molecular structure and bonding, thermochemical stability and vibrational spectra of 1,2-tetra methylene diborane(I), 1,2:1,2-bis (tetramethylene) diborane(II), 1,1-tetra methylene diborane(III) and 1,1:2,2-bis (tetramethylene) diborane(IV), have been studied employing quantum computational *ab initio* RHF and density functional theory (B3LYP and B3PW91 methods) using  $6-31G^*$ ,  $6-31G^{**}$  and  $6-31++G^{**}$  basis sets. NBO analyses have been carried out to study in detail the nature of the B-C, C-C, B-H bonds in these molecules. The results showed that these compounds are thermodynamically stable in the gas phase, but bicyclo structures are more stable than monocyclic structures.

Key words: alkylborane, ab initio calculation, DFT, vibrational spectra

# SOME MATHEMATICAL METHODS FOR COMBINATORIAL ENUMERATIONS

Ghorban Ali MOGHANI

Color Control & Color Reproduction Department, Iran Color Research Center (ICRC), Tehran, Iran

The Group Theory is strong and useful tool for working with chemical graphs for instance, enumeration, symmetry and so on. Enumeration of compounds in chemistry is one of the most important fields to which Pólya's theorem has been applied.

It is necessary to generate the automorphism group of a chemical graph in computer-aided structure elucidation. An Euclidean graph associated with a molecule is defined by a weighted graph with adjacency matrix  $M = [d_{ij}]$ , where for  $i \neq j$ ,  $d_{ij}$  is the Euclidean distance between the nuclei i and j. In this matrix  $d_{ij}$  can be taken as zero if all the nuclei are equivalent. Otherwise, one may introduce different weights for distinct nuclei.

In this paper we go on our works to find the automorphism group as well as compute Q-Conjugacy Character Table for some chemical molecules such as fullerenes, nanoclusters and in general we provide theorems for all Q-Conjugacy Character Table of groups for which their symmetry groups are dihedral.

Keywords: symmetry, Q-conjugacy character table, dihedral groups, fullerene

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# Q-CONJUGACY CHARACTER TABLES OF SOME FULLERENS AND MOLECULES: AN APPLICATION OF COMBINATORIAL ENUMERATION OF ISOMERS

Ghorban Ali MOGHANI,<sup>1</sup> A. R. MIRHABIBI,<sup>1</sup> <u>Hamid MESGARANI</u><sup>2</sup>

<sup>1</sup>Department of Nano-Materials, Iran Color Research Center (ICRC), Tehran, Iran <sup>2</sup>Department of Mathematics, Rajaey University, Tehran, Iran

Enumeration of compounds in chemistry is one of the most important fields to which Pólya's theorem has been applied. The Group Theory is strong and useful tool for working with chemical graphs for instance, enumeration, symmetry and so on.<sup>1-7</sup>

It is necessary to generate the automorphism group of a chemical graph in computer-aided structure elucidation. An Euclidean graph associated with a molecule is defined by a weighted graph with adjacency matrix  $M = [d_{ij}]$ , where for  $i \neq j$ ,  $d_{ij}$  is the Euclidean distance between the nuclei i and j. In this matrix  $d_{ij}$  can be taken as zero in the case that all the nuclei are equivalent. Otherwise, one may introduce different weights for distinct nuclei. Combinatorial enumerations by means of Unit Subduced Cycle Indices (USCIs) is discussed by using the point groups as examples. Several properties of USCIs are discussed by clarifying the relationship between double cosets and the subduction of the USCIs.

In this paper at first we present our results<sup>8-11</sup> with some MATLAB and GAP programs in order to find the automorphism group and then compute Markaracter Table and Q-Conjugacy Character Table for some molecules such as the big fullerene  $C_{80}$  and tetraammine platinum (II).

Keywords: automorphism group, USCI method, Q-Conjugacy Character Table, tetraammine platinum (II), fullerene

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# SOME COMPUTATIONAL METHODS FOR CALCULATING ISOMERS OF FULLERENES AND MONSTER MOLECULES

Ghorban Ali MOGHANI, Soroor NAGHDI

Color Control & Color Reproduction Department, Iran Color Research Center (ICRC), P.O. BOX 16765-654, Tehran, Iran

Enumeration of compounds in chemistry is one of the most important fields to which Polya's theorem has been applied. The Group Theory is strong and useful tool for working with chemical graphs for instance, enumeration, symmetry and so on.

It is necessary to generate the automorphism group of a chemical graph in computer-aided structure elucidation.

In this paper at first we introduced some useful scientific programs to obtain automorphism group of some molecules such as fullerenes and nanoclusters and then we will find their isomers-counting matrices by using USCI method which are applied for combinatorial enumerations.

Keywords: symmetry, isomers, nanocluster, fullerene

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# NEW APPROACHES TO THE LIQUID-SOLID PHASE TRANSITION OF LENNARD-JONES FLUIDS. II. MONTE CARLO SIMULATION IN THE ISOBARIC-MULTITHERMAL ENSEMBLE

Chizuru MUGURUMA<sup>1</sup>, Yuko OKAMOTO<sup>2</sup>

<sup>1</sup>Faculty of Liberal Arts, Chukyo University, Toyota, Aichi 470-0393, Japan <sup>2</sup>Department of Physics, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Aichi 464-8602, Japan

The generalized-ensemble algorithms have been introduced as the methods to overcome the multiple-minima problem. The algorithms are based on artificial, non-Boltzmann weight factors. The multicanonical (MUCA) algorithm performs a free one-dimensional random walk in potential energy space, which allows the simulation to avoid getting trapped in states of energy local minima. We applied the algorithm to the Lennard-Jones fluids and reported that the algorithm is suitable for analyzing the transition state of the first-order phase transition.<sup>1</sup> In the present study, we expand the method to the isobaric-multithermal (MUTH) ensemble and investigate the liquid-solid phase transition of the Lennard-Jones fluids.<sup>2</sup>

The isobaric-multithermal Monte Carlo (MUTHMC) simulations were carried out with the system of 108 argon particles in a periodic cubic cell to determine the MUTH weight factors at initial pressure  $P_0$  of 1 atm and 3000 atm, and the long production runs were performed with these MUTH weight factors. By applying the reweighting techniques, we can obtain probability distributions  $P_{NPT}$ 

and thermodynamic quantities as expectation values  $\langle g \rangle_{_{NPT}}$  at any temperature T and pressure P:

$$P_{NPT}(E,V;T,P) = \frac{P_{MUTH}(E,V;P_0)w_{MUTH}^{-1}(E;P_0)\exp\left[\frac{P_0V}{k_BT_0}\right]\exp\left[-\frac{E+PV}{k_BT}\right]}{\int dV \int dEP_{MUTH}(E,V;P_0)w_{MUTH}^{-1}(E;P_0)\exp\left[\frac{P_0V}{k_BT_0}\right]\exp\left[-\frac{E+PV}{k_BT}\right]}$$
(1)  
$$\left\langle \mathcal{G} \right\rangle_{NPT} = \frac{\int dV \int dE\mathcal{G}(E,V;P_0)P_{NPT}(E,V;T,P)}{\int dV \int dEP_{NPT}(E,V;T,P)}$$
(2)

For the MUTH weight factors, we found a change in the curvature around 6.6 kJ/mol, which does not depend on the pressure. The thermodynamic properties calculated by the reweighting techniques exhibit the characteristics of the first-order phase transition under constant pressure, and the snapshots show that the phase transition corresponds to the liquid-solid phase transition. The transition temperatures are around 82 K for 1 atm and 120 K for 3000 atm. We will describe the results of further investigation at the conference.

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# MOLECULAR ORBITAL CALCULATION FOR LARGE MOLECULE WITH SAKURAI-SUGIURA METHOD ON GRID COMPUTING ENVIRONMENT

<u>Umpei NAGASHIMA</u><sup>1,4</sup>, Yuichi INADOMI<sup>2,4</sup>, Hiroaki UMEDA<sup>1,4</sup>, Toshio WATANABE<sup>1,4</sup>, Takayoshi ISHIMOTO<sup>1,4</sup>, Tetsuya SAKURAI<sup>3,4</sup>

<sup>1</sup>Research Institute for Computational Science, National Institute of Advanced Industrial Science & Technology, 1-1-1 Umezono, Tsukuba, Ibaraki 305-8568, Japan

<sup>2</sup>Computing & Communications Center, Kyushu University, 3-8-33-710 Momochihama, Sawara-ku, Fukuoka 814-0001 Japan

<sup>3</sup>Institute of Information Sciences & Electronics, University of Tsukuba, 1-1-1 Ten-nodai, Tsukuba, Ibaraki, Japan

<sup>4</sup>Core Research for Evolutional Science & Technology (CREST), Japan Science & Technology Agency (JST), Kawaguchi Center Building, 4-1-8, Honcho, Kawaguchi, Saitama 332-0012, Japan

We have been developing the computational tool to obtain the molecular orbitals for large molecules such as proteins and molecular clusters without excessive calculation costs. In our method, the entire Fock matrix is generated by the technique based on the fragment molecular orbital method,<sup>1</sup> which is applicable to large systems and suitable for the parallel processing. To solve the large scale generalized eigenproblem, we use the Sakurai-Sugiura method.<sup>2</sup> Because this method solves several number of liner equation which has a large granularity and master-worker type of execution, the method is sufficient for parallel processing on the computers of the distributed memory parallel architecture. The method is favorable to calculate only a small number of eigenvalues and corresponding eigenvectors of the large scale matrix. Our method has high parallelization efficiency and the communication cost is negligible to the total calculation costs. Thus, this is one of the right applications for using the Grid technology. Elapsed time of Hartree-Fock calculation of Lysozyme (129 amino-acid residues and solvent molecules, total 8258 atoms) with FMO/HF/STO-3G (20758 basis functions) is listed in Table 1. Molecular structure of Lysozyme is depicted with HOMO (lower left) and LUMO (center) in Fig. 1. Performance of the method was improved drastically by parallel processing.

		CPU type	# proc.	E-time
FMO calculation		Opteron <sup>a</sup>	128	6.3 hr
Flock matrix generation		Opteron <sup>a</sup>	64	42.3 hr
eigenvalue and eigenvector of Flock matrix	Cholrsky decomposition + householder + bisection	Opteron <sup>a</sup>	1	4.1 hr
	Sakurai-Sugiura method	Xenon <sup>b</sup>	1	44.5 min
		Xenon <sup>b</sup>	128	1.9 min

Table1. E-time for FMO-MO calculation of Lysozyme

<sup>a</sup>Opteron: model 246, 2.0GHz; <sup>b</sup>2.0GHz Xeon: 3.06GHz



Figure 1. Position and shape of HOMO/LUMO of Lyzozyme

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## ELECTRONIC AND MAGNETIC STRUCTURE OF CARBON NANOTUBES WITH TOPOLOGICAL LINE DEFECT

<u>Kyoko NAKADA</u><sup>1</sup>, Kei KUWABARA<sup>1</sup>, Kota DAIGOKU<sup>1</sup>, Takazumi KAWAI<sup>2</sup>, Susumu OKADA<sup>3</sup>

 <sup>1</sup>Department of Chemistry & Biological Science, College of Science & Engineering, Aoyama Gakuin University, 5-10-1 Fuchinobe, Sagamihara 229-8558 Japan
<sup>2</sup>Fundamental & Environmental Research Laboratories, NEC Corporation, 34 Miyukigaoka, Tsukuba 305-8501 Japan
<sup>3</sup>Center for Computational Sciences & Institute of Physics, University of Tsukuba, Tennodai, Tsukuba 305-8571 Japan

We propose a new category of carbon nanotubes having topological line defects. Our tight-binding band calculations showed that a series of nanotubes having a single armchair line as a defect (Fig. 1(a), denoted by  $(n,n)_D$ ) exhibit a flat band at E=0. By expressing the non-bonding orbital in an analytic form, we identified the localized state of the  $(n,n)_D$  nanotubes as the edge states of the zigzag graphite ribbons.<sup>1</sup> The localized states of another nanotubes having a line defect made of five armchair lines are identified as the edge states of Klein's ribbon.<sup>2</sup>

Our first-principles total-energy calculations showed that the ground state of the  $(n,n)_D$  nanotubes is ferromagnetic showing a spin ordering along the tube axis. The net spin moment is small but finite irrespective to the tube radius. We also showed that the  $(n,n)_D$  nanotubes are energetically stable comparable to the intact (n,n) nanotubes. Our tight-binding molecular-dynamics (TBMD) simulations supports the energetic stability of the  $(n,n)_D$  nanotubes as well.

Our TBMD calculations show that the reaction barriers of sequential  $C_2$  implantations is about 2eV, indicating the possibility of synthesis. We also show that the aggregates of atomic divacancies can easily transform into the line defect of the  $(n,n)_D$  nanotubes, which indicates another synthetic pathway to the  $(n,n)_D$  nanotubes by annealing defective CVD nanotubes.



*Figure 1.* (a) The structure, (b) the energy dispersion and density of states within the TB scheme and (c) the spin density distribution of the  $(6,6)_D$  nanotube.

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# DESCRIPTOR THINNING AND PROPER CROSS-VALIDATION IN QSAR

<u>Ramanathan NATARAJAN</u><sup>1</sup>, Subhash C. BASAK<sup>1</sup>, Jessica J. KRAKER<sup>2</sup>, Douglas M. HAWKINS<sup>2</sup>

<sup>1</sup>University of Minnesota Duluth, Natural Resources Research Institute, 5013 Miller Trunk Hwy., Duluth, MN 55811, USA <sup>2</sup>University of Minnesota Twin Cities, Schools of Statistics, 224 Church Street SE, Minneapolis, MN 55455, USA

The number of molecular descriptors available for QSAR modeling continues to increase, and therefore subset selection (variable selection) is commonly used. The methodology applied by many researchers involves variable selection *followed by* the application of cross-validation. With this approach, the cross-validation step does not include the descriptor selection, and the resulting "naïve  $q^{2}$ " is always higher than the "true  $q^{2}$ " leading to overestimation of the predictive ability of the model. Application of proper cross-validation that includes descriptor thinning is very important for developing QSAR models with reliable predictive ability. Results obtained by statistical simulation as well as from a few data sets will be presented to highlight the importance of including descriptor selection within the cross-validation step.

# FREE AND RIBOSOME-BOUND STRUCTURES OF MACROLIDE ANTIBIOTICS: THE ROLE OF NMR AND CONFORMATIONAL ANALYSIS IN LIGAND DESIGN

#### Predrag NOVAK

#### Faculty of Science, Department of Chemistry, Horvatovac 102a, HR-10000 Zagreb, Croatia

Macrolide antibiotics are therapeutically important molecules that are effective inhibitors of bacterial protein biosynthesis. They bind to the large 50S ribosomal subunit at or near the peptidyl transferase center and block the elongation of the peptide chain. Understanding the mechanism by which macrolides exert their activity is crucial for the design of novel molecules possessing bioactivity. Recently available crystal structures of some ribosome-macrolide complexes have thrown new light on the binding mechanisms and hence provide a good basis for the design of new ligands and inhibitors.<sup>1,2</sup> However, when analysing solid state structures of ribosome-macrolide complexes one should keep in mind the discrepancies between structures obtained for halophilic archeon *H. marismortui*<sup>2</sup> and *D. radiodurans*.<sup>1</sup> Therefore, important steps in the process of drug design should also include elucidation of the solution-state structures of free and bound ligand molecules since the structural features of the complex may not be exactly the same in solution and in the solid state.

One and two-dimensional NMR techniques have proven usefull in conformational analysis and structure-based inhibitor design. Here, an approach which combine NMR parameters such as spin-spin coupling constants, nOe and relaxation times coupled with molecular modelling is employed to study free conformations of macrolide antibiotics such as azithromycin, telithromycin and oleandomycin.<sup>3</sup> Furthermore, an application of transferred nOe and STD (saturation transfer difference) NMR experiments provides information on the bound state conformation and binding epitopes.<sup>4</sup> The knowledge gained from these studies can serve as a platform for the design of novel compounds with an improved biological profile.

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# EXPERIMENTAL AND DFT STUDIES OF HYDROGEN BONDS IN SALICYLALDEHYDE-4-PHENYLTHIOSEMICARBAZONE

<u>Katarina PIČULJAN</u>, Predrag NOVAK, Tomislav BILJAN, Tomica HRENAR, Mirta RUPČIĆ, Marina CINDRIĆ, Zlatko MEIĆ

Faculty of Science, Department of Chemistry, Horvatovac 102a, HR-10000 Zagreb, Croatia

Thiosemicarbazones and their metal complexes have attracted much interest nowdays owing to their chemical and biochemical significance. It was demonstrated that they exhibited biological activity as anti-cancer, anti-viral, anti-bacterial and anti-fungal agents. Salicylaldehyde-4-phenylthiosemicarbazone (SALTSC-4Ph) posseses several proton-donor and proton-acceptor groups and therefore can form both intra- and inter-molecular hydrogen bonds. Exploring H-bond structure of SALTSC-4Ph makes a significant contribution to understanding of its bioactivity.

The results of H-bonding interaction studies in both protonated and deuteriated (OH and OD) SALTSC-4Ph are reported. A combination of experimental and theoretical methods enabled a straightforward assignment of vibrational modes in IR and Raman spectra and elucidated the nature of H-bonds in solution. Investigation of deuterium isotope effects in NMR spectra gave further insight into these interactions. Quantum chemical calculations at the B3LYP/6-31G\* level including the explicit solvent molecule were performed. Apart from intramolecular H-bonds, SALTSC-4Ph was also found to form stable complexes with acetone and DMSO molecules.

# EINSTEIN: FROM SPECIAL THEORY OF RELATIVITY (1905), THROUGH GENERAL THEORY OF RELATIVITY (1916), UNTIL COSMOLOGICAL TERM (1917)

#### Krunoslav PISK

#### Ruđer Bošković Institute, POB 180, HR-10002 Zagreb, Croatia

1905 – Special Theory of Relativity (STR)

About uniform motion in empty space and relative motions with uniform translations among frames of reference. The speed of light is constant in inertial frames. A new concept of space and time: space-time continuum as an integral entity. Lorentz transformations as coordinate links among different frames. Relations among observables. Relativity of lengths and time intervals. Equations which express physical laws are form-invariant (covariant) against Lorentz transformations. A new relation between mass and energy,  $E = mc^2$ , emerges naturally.

#### 1916 – General Theory of Relativity (GTR)

Extension of STR by imposing that equations of law of physics are form-invariant against general space-time transformations (general covariance), which also include coordinate relations among accelerated frames. Accelerated frames and gravitational fields (principle of equivalence). Gravitation and curvature of space. Equations of GTR:

a) Einstein's field equations - energy (mass) – distribution and corresponding pressures, as a source of curved space;

b) Einstein's equations of motion – motion of material particle in gravitational field. GTR and Newton's laws of motion and gravitation.

#### 1917- Cosmological Term

When applied to the Universe, solution of field equations of GTR are not static. Einstein modifies original equations by introducing a cosmological term (cosmological constant today) -  $\lambda$ , which is consistent with relativity postulates. Now, a quasi-static distribution of matter in Universe is possible. The Universe appears a 3-dimensional curved space (with constant radius of curvature *R*) and finite volume of  $2\pi^2 R^3$ , with  $\lambda = 1/R^2$ .

#### Epilogue

Thirteen years ago (1930), after Hubble's discovery of Universe expansion Einstein said that introduction of cosmological term was "the biggest blunder of my life".

Recent measurements indicate that Universe accelerates and abandoned cosmological term could play important role – "dark energy"<sup>4</sup>.

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# MODELING OF BIOTRANSFER FACTORS OF ORGANOCHLORINE COMPOUNDS

Matevž POMPE, Gregor ARH

University of Ljubljana, Faculty of Chemistry & Chemical Technology, Aškerčeva 5, 1000 Ljubljana, Slovenia

Our study will focus on organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs), which may have neurotoxic and immunological effects. Their use is regulated in many European countries but nevertheless they can contaminate many environments and food products. Their levels in foodstuffs from animal origin tend to decrease, but several regions of new Member States and Associate countries were severely polluted with these compounds. Only very limited studies have focused on the levels of transfer between animal feeds and livestock products, e.g. transfer from animal feed to milk and meat products. Even more, there is no study about the proliferation of these compounds along the food processing chain to the final product. The investigation is a part of FP6 EU integrated project TRUEFOOD. This year we will present our initial results about the modelling of the literature data on biotransfer coefficients of OCPs and PCBs from the environment to pork meat will be used for the creation of theoretical prediction models that will be able to estimate these coefficients for the compounds where experimental values are not yet available.

The following methodologies will be used to perform this part:

• several different structural representations will be tested to obtain suitable computer readable representations of the chemical structure,

• modelling performance of multiple linear correlation and artificial neural networks will be tested to find a quantitative correlation between chemical structure and biotransfer factors,

• a proper estimation of the prediction capabilities of the obtained models will be done by using external test set procedures.

# ON THE DISTANCE MATRICES OF POLYCYCLIC GRAPHS AND THEIR SPANNING TREES

Sarah Michele RAJTMAJER, Nenad TRINAJSTIĆ

Ruđer Bošković Institute, P.O.Box 180, HR-10002 Zagreb, Croatia

The relationship between distance matrices of a polycyclic graph G and the related spanning trees of G is examined. In particular, we examined the highest eigenvalue of the spectra of these distance matrices. It is discovered that branching increases this highest eigenvalue while symmetry decreases it. A rigorous definition of *increases* and *decreases* is attempted.

# **ON CHARACTERIZATION OF 2-D MAPS**

Milan RANDIĆ

National Institute of Chemistry, Hajdrihova 19, SI-1000 Ljubljana, Slovenia

Various experimental measurements and theoretical computational have been displayed as discrete 2-D maps, such as the 2-D NMR data or proteomics data. We will briefly review several currently employed methods for numerical characterization of such 2-D maps, pointing to the advantages and limitations of some of the approaches. We will also examine the effects of limiting input information on 2-D map to a subset of spots on the map and will report on the minimal number of proteins in proteomics maps and proteome which suffices for reliable characterization of 2-D maps. Finally we will report on use of partial ordering for development of canonical labels for 2-D maps that will facilitate cataloguing of such maps.

# **ON NUMERICAL REPRESENTATION OF DNA AND PROTEINS**

Milan RANDIĆ<sup>1</sup>, Marjana NOVIČ<sup>1</sup>, Dražen VIKIĆ-TOPIĆ<sup>2</sup>, <u>Dejan PLAVŠIĆ<sup>2</sup></u>

<sup>1</sup>National Institute of Chemistry, P.O.Box 3430, SI-1001 Ljubljana, Slovenia <sup>2</sup>Ruđer Bošković Institute, NMR Center, P.O.Box 180, HR-10002 Zagreb, Croatia

We have introduced a novel numerical representation of DNA, which is simple and characterizes DNA uniquely. This representation is given as a sequence of real numbers based on a unique graphical representation of DNA codons. The approach is illustrated with the coding sequences of the first exon of  $\beta$ -globin gene of a dozen species including human. The method can be extended to proteins as is exemplified by humanin, a 24-residue polypeptide that protects against neural cell death.

# THE INFLUENCE OF THE FORM OF MOLECULAR GRAPH ON THE SUCCESS OF ESTIMATION OF STABILITY CONSTANTS OF COORDINATION COMPOUNDS

Nenad RAOS, Ante MILIČEVIĆ

Institute for Medical Research & Occupational Health, Ksaverska c. 2, POB 291, HR-10001 Zagreb, Croatia

The estimation of stability constants of coordination compounds by using the topological analysis<sup>1-4</sup> is dependent not only on the topological indices chosen but, as well, on the constitutional formula, i.e. graph representing chemical species which determine the chemical equilibria.

In the lecture will be discussed the influence of the form of chemical graph in calculations aimed at estimation of stability constants of copper(II) and nickel(II) mono- (ML) and bis-chelaes (ML<sub>2</sub>) with 1,2-diaminoethanes, amino acids, and their derivatives. It will be shown that fairly good estimates ( $\Delta \log K < 0.5 \log K$  units) should be obtained from graphs of the ligands (L), and graphs of ML and ML<sub>2</sub> complexes, former for the estimation of stability constants of both ML and ML<sub>2</sub> chelates. An improvement were obtained by proposing additional binding of water molecules, as well as writing the molecular graph in an unusual way, i.e. by drawing additional bonds due to secondary ligation or hydrogen bonding.

There are no substantial differences between the various models, but the results clearly show that more realistic graphs lead to better estimate of stability constants.

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# α-PHENYLHYDRAZATION OF HETEROCYCLIC SYSTEMS UNDER SOLVENT FREE CONDITIONS

Zahra SADEGHI, Javad SAFARI

Department of Chemistry, Faculty of Sciences, University of Kashan, Kashan, P. O. Box: 87317-51167, I. R. Iran

2-ketomethylquinolines are important component in organic chemistry because of the applications of these compounds in heterocyclic synthesis and chemical transformations.<sup>1-4</sup> Different kinds of 2-ketomethylquinolines (1) were subjected to the  $\alpha$ -phenylhydrazation reaction in the presence of sodium nitrite, derivatives of aniline and silica modified sulfuric acid (I) (Scheme 1).  $\alpha$ -phenylhydrazation reaction were perform under mild and completely solvent free condition and gave moderate to excellent yields. When reactions occur at the methylene group, the azo-compound formed initially rapidly rearranges to form the  $\alpha$ -hydrazokethones (3).<sup>4</sup>



#### Scheme 1.

The reported  $\alpha$ -phenylhydrazation reaction can be readily carried simply by placing sodium nitrite, derivatives of aniline; silica modified sulfuric acid (I), 2-ketomethylquinoline (1), in conditions without solvent at room temperature for 30 min under abrasion. The initial azo-products were converted to the corresponding  $\alpha$ -hydrazokethones immediately and the products can be isolated by simple filtration and evaporation of the solvent.

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# THERMODYNAMIC THEORETICAL CALCULATION, SYNTHESIS AND LIQUID PHASE OXIDATION OF CYCLOHEXANOL USING *tert*-BUTYLHYDROPEROXIDE OVER HOST/GUEST NANOCOMPOSITE MATERIALS

Masoud SALAVATI-NIASARI, Masood HAMADANIAN, Elham ZAMANI

Institute of Nano Science & Nano Technology, University of Kashan, Kashan, Iran

Thermodynamic properties of 12- and 13-membered diaza dioxa Schiff-base copper(II) complexes were theoretically calculated and then 12- and 13-membered diaza dioxa Schiff-base copper(II) complexes have been prepared in nanocavity microreactor by the one-pot template synthesis of (1,8-diamino-3,6-dioxaoctane)copper(II) using bifunctional diketone within the pores of zeolite-Y. The copper(II) complexes were entrapped in the supercage of Y-zeolite by a two-step process in the liquid phase:

(*i*) inclusion of a copper(II) precursor complex,  $[Cu(1,8-diamino-3,6-dioxaoctane)]^{2+}$ -NaY, and

(*ii*) template condensation of the copper(II) precursor complex with the bifunctional diketone.

Encapsulated copper(II) complex is catalytically very efficient as compared to other neat complexes for oxidation of cyclohexanol with *tert*-butylhydroperoxide (TBHP) as oxidant and is stable to be recycled without much deterioration.

Keywords: theoretical calculation, nanocomposite, copper(II), Schiff-base macrocycle, oxidation

# AN IMPROVED MNEMONIC DIAGRAM FOR THERMODYNAMIC RELATIONSHIPS

Mohemmed Taghi SALEHI

Payame Noor University, Esfahan Center, I.R.Iran

It is the purpose of the present paper to illustrate that a number of the most important expressions in thermodynamics of simple systems, between the state functions such as P,V,S,T,A,G,H and U, which represent pressure, volume, temperature, Helmholtz free energy, Gibbs free energy, enthalpy, and internal energy, respectively, may be developed directly from a mnemonic diagram. This paper discusses a variation of a mnemonic first introduced by König<sup>1</sup> and further developed by Callen.<sup>2</sup> Philips<sup>3</sup> has recently presented a three-dimensional version of mnemonic diagram. The differential forms of the potentials and the Maxwell relations could have been obtained by this rules.

The material that follows is limited to simple systems that are defined to be macroscopically homogeneous, isotropic, uncharged and chemically inert. Thus we see that the mnemonic diagram allows us to write the essential equations relating the eight thermodynamic properties in a straightforward manner.

Acknowledgment. The valuable and helpful discussions with Dr. M.R. Jalali are greatfully acknowledged.

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# NUMERICAL REPRESENTATION OF STEREOCHEMICAL ENVIRONMENTS BY USING FRAU

#### Hiroko SATOH

#### National Institute of Informatics, Japan

Stereochemistry is essential information for discussing property, activity and reactivity based on chemical structures. We developed methodologies for representation of stereochemistry named CAST<sup>1,2,3</sup> and FRAU<sup>4</sup> and implemented to our chemical software. CAST is a canonical coding method for stereochemistry and was implemented to a <sup>13</sup>C NMR chemical shift prediction system CAST/CNMR,<sup>5,6</sup> which ensures highly accurate prediction by considering stereochemistry that can be practically utilized in structural analysis studies such as structural revision.<sup>7</sup> The FRAU system numerically characterizes molecular-fields based on electrostatic and steric interactions and was applied to classification and prediction of typical reagents' functions. In order to know further applicability of FRAU to detecting more detailed similarities and differences in reagents and also to predicting stereo- and regio-selectivity, I have investigated whether the 3D-stereochemical environments can be distinguished with the FRAU's descriptors, this is the issue of this paper. Correlations were analyzed between the FRAU's descriptors and stereochemical environments around oxygen atoms of cyclohexanediol, and quercitol (1,2,3,4,5-cyclohexanepentaol), all of which in

chair-form conformation. Two kinds of the FRAU's descriptors, which are steric and field features (FF-steric and FF-field) were used in the investigation. Hydrogen atoms in the hydroxyl groups were not taken into account for neglecting differences of orientations of the hydrogen atoms. As a result, good correlations were found between the features and stereochemical environments.

For example, the results of quercitol is shown in Fig. 1, where horizontal and vertical axes are FF-steric and FF-field, respectively, and all of the 100 oxygen atoms of the diastereo isomers in two types of chair-form conformation of quercitol are plotted. This shows that the oxygen atoms clearly made clusters according to the stereochemical environments, namely, axial, 1,3-diaxial, 1,3,5-diaxial oxygen atoms were grouped for axial atoms, respectively, and more detailed similarities were also distinguished within each of the clusters and also within the equatorial oxygen atoms group. The results demonstrated possibilities of FRAU to numerically detect the similarities and differences of 3D stereochemistry.





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# A SIX DIMENSIONAL PERSPECTIVE TO DEFINE SPACE BASED ON THE TETRAHEDRON

James SAWYER

President Six Dimension Design, Buffalo, New York, USA

The intitial purpose of this paper is to define the geometry of atomic space using vectors with a real number system. A line is a set of real numbers. This elaborate geometry has an order based on the six unique vectors of the tetrahedron. This tetrahedral base system is a transformation of our perception of real space. The high renaissance artists' three dimensional reality of space is based on the 90 degree angle that man stands in relationship to the earth. Now, drawing equally spaced lines parallel to man and parallel to earth creates a two dimensional grid. Projecting that same two dimensional grid onto the plane of earth is three dimensional coordinate system. Comparing the two systems is the only way to clearly see the advantages in re-defining space.

(1) Atoms do not bond only at 90 degree angles, in crystals. Atoms bond based on triangular, tetrahedral, and octahedral patterns, in crystals.

(2) The higher level platonic solids which follow the same vectors as the tetrahedron and octahedron are the cuboctahedron and truncated octahedron.

This paper shows in descriptive geometry a system of perspective to draw these geometric shapes based on a six dimensional system that an engineering student could use.
## COMPLEX SYSTEMS AND MEASUREMENTS OF VAGUE AFFINITIES

Lech P. SCHULZ

Department of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland

A search for general approaches useful across disciplines, such that relationships between systems investigated could be assessed in a precise way, is a serious challenge needing a generic consideration. Phenomena in the micro- and macro- world constitute diversified varieties consisting of individual objects. Such collections can mutually overlap and split in various degrees depending on the common and different properties of the individuals involved. The universal tools employed herein admit measurements of sophisticated relationships between varieties of individuals of the physical world such as elementary particles, molecular systems, nano- and bio-systems, as well as areas underlain, e.g., by natural events like seismic or meteorological phenomena. This is due to the special treatment of complex systems (grounded mathematically<sup>1</sup>), which are supported by properties of objects endowed by the information of interest.

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#### FUZZY SET BASED ALGORITHMS AND EFFICIENCY IN THE OPTIMIZATION OF NON-LINEAR PARAMETERS FOR MANY-ELECTRON EXPONENTIALLY CORRELATED GAUSSIAN FUNCTIONS

Lech P. SCHULZ, Jacek KOMASA

Department of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland

Finding wave functions suitable for decreases of energy is a first class problem in the Explicitly Correlated Gaussian functions approach (ECG) combined with the variational method.<sup>1</sup> Employing Powell's concept, the species with up to six electrons have been calculated with a highest accuracy. However, in the case of many electrons involved, further progress is limited by the time of computations, even if powerful modern computers are used. Also, extrapolations, genetic algorithms, etc. have not approved their efficiency in the relation to the hard challenge of the energy descent predictions. In this work, fuzzy set and resemblance based modifications of wave functions received by means of the Powell's method have been investigated. The concept is aimed to skip computer time consuming cyclic procedures of randomly determined non-linear coefficients of wave functions. Such a skipping turns out possible by the assumption that decreases of energy constrain an implicit structure of parameters. Thence, certain transformations of wave functions with optimal changes of structured non-linear coefficients should diminish the energy as well. This has really been confirmed in the example of ECG computations for helium atom. Moreover, competitions between fuzzy set based modifications and original Powell's descents were assessed to find the most robust conditions for passing over time consuming procedures.

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#### VINDICATING THE PAULING-BOND-ORDER CONCEPT

Jelena SEDLAR<sup>1</sup>, <u>Ivana ANĐELIĆ</u><sup>2, 4</sup>, Ivan GUTMAN<sup>3</sup>, Damir VUKIČEVIĆ<sup>4</sup>, Ante GRAOVAC<sup>2,4</sup>

 <sup>1</sup>Faculty of Civil Engineering, Matice Hrvatske 15, HR-21000 Split, Croatia
<sup>2</sup>Ruđer Bošković Institute, Bijenička c. 54, HR-10002 Zagreb, Croatia
<sup>3</sup>Faculty of Science, University of Kragujevac, P. O. Box 60, 34000 Kragujevac, Serbia & Montenegro
<sup>4</sup>Faculty of Natural Sciences, Mathematics & Kinesiology, Nikole Tesle 12, HR-21000 Split, Croatia

In the Pauling-bond-order concept it is assumed that all Kekulé structures of a benzenoid molecule contribute equally to the  $\pi$ -electron contents of the carbon-carbon bonds. We modified the Pauling bond order

(a) by increasing the weight of a Kekulé structure proportional to the number of Fries-type hexagons, and

(b) by increasing the weights of the Kekulé structures that are compatible with Clar aromatic sextet formulas.

Improvements in reproducing experimental carbon-carbon bond lengths are insignificant, implying that equal weighting of Kekulé structures is more justified than one could anticipate.

#### HYBRID HATCHING-SHADING METHOD FOR DEPICTING OF RELIEF IN MODERN MAPS

Marjan SIKORA

Faculty of Electrical Engineering, Mechanical Engineering & Naval Architecture, University of Split, R. Boškovića bb, HR-2100 Split, Croatia

Today, in modern cartography, it is common to present not only thematic layers but also the underlying relief. The development of the computer technology has enabled several forms of relief depicting. The most common methods are the contour mapping, and shaded relief. The contours are lines that connect the points of same height on terrain. The shaded relief is the method that shades the areas oriented toward the source of the sun in brighter color, and those oriented opposite in darker.

The advantage of the contour mapping is that the height differences can be perceived easily, and also the correct height detection is possible. Disadvantage is that relief can not be experienced intuitively – one has to make conscious effort to read map.

The shaded relief map is just the opposite – one can immediately perceive the shape of the terrain. Problem is that the dark areas cause that other map elements – annotations, lines, symbols – are not readable. Recently these two techniques are often combined, and shades are also faded in order not to interfere with other map elements.

Beside these two methods, there is another relief depicting method, which was used before 20<sup>th</sup> century. This method could in some applications be interesting and good alternative for existing methods. This is the hatching method first developed by German major J. G. Lehmann (1765-1811). This method is based on hatching – the hatches are drawn according to the slope of the terrain. They are drawn perpendicular to contour lines, and they vary in length and width. The bigger the slope of the terrain. Also, the hatches are perpendicular to contour lines, and that is the direction of the flow of the water. By the force of the abrasion water often creates the canals in the real world, so when one reads the map drawn with this method, it easily perceives the form of the terrain. The disadvantage of this method is that doesn't take into account the direction from which the light comes – so one cannot easily perceive the orientation of the terrain.

In order to overcome this shortcoming, the combined hatching-shading method was developed. This method works in a following way: hatches are drawn with their midpoint on the contour, and their direction is perpendicular to the contour. The width of hatch-lines doesn't depend on the slope of the terrain – instead it depends on the orientation of the terrain, same as with shaded-relief map. In this way, the combined hatching-shading method encapsulates advantages of above mentioned three relief depicting methods. Since the hatches are drawn in the place of contours, the height of terrain can be accurately determined; the direction of hatch-lines shows the direction of the water flow lines; and finally the width of hatch lines gives the impression of shading, and depicts the orientation of the relief.

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#### EXPLICIT CIRCUMRADIUS EQUATIONS FOR CYCLIC HEPTAGONS AND OCTAGONS

Dragutin SVRTAN

Department of Mathematics, University of Zagreb, Bijenička c.30, HR-10000 Zagreb, Croatia

Finding formulas for the area or circumradius of polygons inscribed in a circle in terms of side lengths is a classical subject.<sup>1</sup> For the area of a triangle we have the famous Heron's formula and for cyclic quadrilaterals we have the Brahmagupta's formula. A decade ago D. P.Robbins<sup>3</sup> found the minimal equations, of degree 7, satisfied by the squared area of cyclic pentagons and hexagons by a method of undetermined coefficients and he wrote the result in a nice compact form. For the circumradius of cyclic pentagons and hexagons he did not publish the formulas because he was not able to put them into a compact form. The method he used could hardly be used for heptagons due to computational complexity of the approach (leading to a system with 143307 equations). In another approach with two collaborators<sup>2</sup> a concise heptagon/octagon area formula was obtained recently (not long after D.P.Robbins premature death) in the form of a quotient of two resultants (the quotient still hard to be written explicitly because it would have about one million terms-who wants to be a millioner). This approach uses covariants of binary quintics. It is not clear if this approach could be effectively used for cyclic polygons with nine or more sides. A nice survey on this and other Robbins conjectures is written by I. Pak.

In the MCC2005 talk we have presented an intrinsic proof of the Robbins formulas for the area (and also for the circumradius and area times circumradius) of cyclic hexagons based on an intricate direct elimination of diagonals (the case of pentagon was treated in Ref. 5) and using a new algorithm from Ref. 6. In the early stage we used computations with MAPLE (which sometimes lasted several days!).

In this talk we shall explain a simple quadratic system, which seems to be new, for the circumradius and area of arbitrary cyclic polygons based on a Wiener-Hopf factorization of a new Laurent polynomial invariant of cyclic polygons. Explicit formulas, of degree 38, for the squared circumradius (and less explicit for the squared area) of cyclic heptagons /octagons are obtained. By solving our system in certain algebraic extensions we found a compact form of our circumradius heptagon/octagon formulas with remarkably small coefficients.

Acknowledgement. I would like to thank Igor Urbiha for helpful discussions.

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# CARBON $sp^2$ SHAPES, VIRUSES AND THEORY OF ELASTICITY

Antonio ŠIBER

Institute of Physics, Bijenička c. 46, HR-10001 Zagreb, Croatia

I shall present a particularly efficient application of the elasticity theory<sup>1</sup> to energetics and geometry of carbon shapes and viruses. It shall be shown that a deep insight in these objects can be acquired by studying the pentagonal disclinations in otherwise planar, hexagonally coordinated crystalline membrane. It has been demonstrated<sup>2</sup> that a single pentagonal disclination leads to buckling of the surrounding membrane in a conical shape whose energy scales as a logarithm of the membrane radius. This can be profitably applied to viral<sup>3</sup> and carbon  $sp^2$  shapes<sup>4</sup> since both classes of shapes are characterized by a pentagonal disclination in otherwise hexagonal crystalline lattice (pentagonal carbon ring in (generalized) fullerenes vs. pentameric capsomer in viral protein coatings<sup>5</sup>, see Fig. 1).



*Figure 1.* Panel (a): Turnip yellow mosaic virus. Panel (b): Icosahedral (giant) fullerene. The pentagonal disclinations are denoted.

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#### HYPERSPECTRAL ALGORITHMS FOR FORESTRY APPLICATIONS

<u>Anita ŠIMIĆ<sup>1,2</sup></u>, Jing CHEN<sup>1</sup>, David GOODENOUGH<sup>3</sup>

<sup>1</sup>University of Toronto, Department of Geography, Toronto, ON, Canada <sup>2</sup>G-ECO Research Inc., Mississauga, ON, Canada <sup>3</sup>Pacific Forestry Centre, Victoria, BC, Canada

Main purpose of this study is to present a new top-down approach of estimating leaf reflectance and chlorophyll content based on hyperspectral remote sensing data. The intermediate objectives are:

(1) to show performance of the geometric-optical 5-Scale model, emphasizing the importance of canopy architecture and multiple-scattering scheme in simulations of canopy reflectance. Validation of the 5-Scale model was carried out for a forested area in the Greater Victoria Watershed District (GVWD), British Columbia (BC),

(2) to introduce and validate a new concept of inversion of the canopy reflectance model to compute foliage (leaf) reflectance,

(3) to correlate measured chlorophyll content with reflectance indices derived based on the estimated leaf reflectance, and

(4) to develop two Look-Up-Tables (LUT) that can be applied to conifer forests. The first LUT provides the fractions (probabilities) of viewing each of four canopy scene components (sunlit and shaded foliage and ground) as a function of leaf area index (LAI) and solar zenith angle (SZA). The second LUT is a result of the inversion of the 5-scale model and provides the multiple-scattering (M) factor as a function of wavelength, LAI and SZA. The primary purpose of these LUTs is to invert the hyperspectral remote sensing data in each pixel (treated as a stand) into leaf area reflectance. This approach allows for estimation the leaf level information in the absence of leaf spectra field measurements and simplifies further applications of hyperspectral imagery at regional scale. Good agreement between AVIRIS data and modeled reflectance was found for all ground plots. Validation of the measured and estimated leaf reflectance based on the LUTs exhibited good agreement for most of the points. More research is needed to use chlorophyll data in larger ranges and to use leaf model inversion methods. The ability to estimate leaf chlorophyll content based on remote sensing data will be useful for other applications such as ecosystem health assessment, resources management and carbon cycle estimation.

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## **MOLECULAR RECOGNITION OF THE ANTISENSE PEPTIDES**

Nikola ŠTAMBUK<sup>1</sup>, Paško KONJEVODA<sup>1</sup>, Nikola GOTOVAC<sup>2</sup>, Biserka POKRIĆ<sup>1</sup>

<sup>1</sup>Ruđer Bošković Institute, Bijenička cesta 54, POB 180, HR-10002 Zagreb, Croatia <sup>2</sup>Department of Radiology, General Hospital Požega, Osječka bb, HR-34000 Požega, Croatia

Molecular Recognition Theory of the interacting antisense peptides is investigated with respect to the side chain polarity of the amino acids, secondary protein structure and genetic code table. This theoretical concept will be discussed in the context of the protein structure-function relationship.

#### CESIUM ION-SELECTIVE ELECTRODE BASED ON DIBENZOPYRIDINO-18-CROWN-6

Nahid TAVAKOLI

Department of Chemistry, Payame Noor University, Esfahan, Iran

A PVC membrane cesium ion-selective electrode has been constructed using dibenzopyridino-18-crown-6 as a membrane carrier. The sensor shows a Nernstian response for  $Cs^+$  ions over a wide construction range ( $1 \times 10^{-6}$  to  $1 \times 10^{-2}$ ). It has a fast response time and can be used for more than 5 months without any considerable divergence in potentials. The proposed sensor exhibits comparatively good selectivities with respect to alkali, alkaline earth and some transition and heavy metal ions.

*Keyworde:*  $Cs^+$ , *electrode* 

#### INVESTIGATION OF THE ROLE OF COORDINATION NUMBER IN THE LENNARD-JONES-DEVONSHIRE THEORY

Gholam Reza VAKILI-NEJAD

Department of Chemical Engineering, Faculty of Engineering, University of Kashan, Kashan 87317-51167, Iran

The theory of Lennard-Jones-Devonshire (LJD) has been studied for more than six decades by many researchers. Recently, Magee and Wilding have shown that the original LJD cell theory critical point for the 12-6 potential terminates a line of pseudo solid-liquid coexistence, rather than a liquid-gas transition as originally postulated and that the model exhibits a further first order transition. In this work the effect of coordination number on the pressure-volume-temperature behavior of systems represented by the LJD-based equation of state has been investigated. We have found that by varying the value of coordination number (C), different curves of  $P^*$  (dimensionless pressure) versus  $v^*$ (dimensionless volume) can be obtained for a specific  $T^*$  (reduced temperature). Consequently, it is possible to obtain improved representations of the experimental data by taking advantage of this characteristics of the P\*-v\*-T\*-C relationship. As a final point we can say that the revised LJD theory, as a completely molecular theory, produces excellent results in comparison with the experimental data. Moreover, a few powerful cubic equations of state such as SRK and PR could be recast in this new theory to find a sound theoretical basis.

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## QUANTUM CHEMICAL PREDICTION OF ADME-Tox PROPERTIES

Sofie VAN DAMME,<sup>1</sup> Wilfried LANGENAEKER,<sup>2</sup> Patrick BULTINCK<sup>1</sup>

<sup>1</sup>Department of Inorganic & Physical Chemistry, Ghent University, Krijgslaan 281 S-3, B-9000 Gent, Belgium <sup>2</sup>Silicos NV, Wetenschapspark 7, B-3590 Diepenbeek, Belgium

ADME-Tox properties are very important in pharmaceutical research, determining the fate of many molecules in the drug design sequence. Knowledge of ADME-Tox properties in the earliest stages of drug design is therefore highly desirable. The aim of this investigation is to construct low throughput in *silico models* in which ADME-Tox properties of single compounds are predicted with high accuracy using quantum chemical descriptors.

A new program was developed that meets the requirements to select stable, robust and interpretable models with a great predictive power. The program can systematically select the optimal subset of a user specified number of descriptors among a large set of descriptors or use a genetic algorithm. All necessary regression and internal and external validation techniques are available. The only constraint on the obtained models is that we can attach a physico-chemical meaning to the model, in order to get chemical insight into the key features that determine whether a molecule is active or not.

With this program, we were able to obtain a satisfactory model for the blood-brain barrier

problem using quantum chemical descriptors.<sup>1,2</sup>

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### THORNY GRAPH

Damir VUKIČEVIĆ

Faculty of Science, University of Split, Nikole Tesle 12, HR-21000 Split, Croatia

Software *Thorny Graph Calculator* will be presented. This software analyzes weather there exists thorny graph with prescribed one of the following properties:

(1) valence connectivities

(2) Randić index and number of vertices

(3) Zagreb index and number of vertices

(4) Modified Zagreb index and number of vertices

It also analyzes if there is thorny graph with the prescribed any combination of the following properties:

(1) Number of vertices with prescribed valencies

(2) Zagreb vertex index

(3) Modified Zagreb vertex index

(4) Randić vertex index

The following thorns are allowed: methyl-thorns, ethyl-thorns, propyyl-thorns, isopropyl-thorns, butyl-thorns, (2-methyl-propyl)-thorns, (1-methyl-propyl)-thorns, and (1,1-dymethyl-ethyl)-thorns.

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#### ON THE SYMMETRY OF A POLYHEX CARBON TORUS

Morteza YAVARI<sup>1</sup>, Ali Reza ASHRAFI<sup>2</sup>

<sup>1</sup>Faculty of Science, Islamic Azad University, Kashan, Iran <sup>2</sup>Department of Mathematics, Faculty of Science, University of Kashan, Kashan, Iran

An Euclidean graph associated with a molecule is defined by a weighted graph with adjacency matrix  $M = [d_{ij}]$ , where for  $i \neq j$ ,  $d_{ij}$  is the Euclidean distance between the nuclei *i* and *j*. In this matrix  $d_{ij}$  can be taken as zero if all the nuclei are equivalent. Otherwise, one may introduce different weights for distinct nuclei.

In this paper we present some MATLAB and GAP programs and use them to find the automorphism group of a polyhex carbon torus.

Key words: Euclidean graph, symmetry, polyhex carbon torus

#### STRONGLY CORRELATED THERMOELECTRICS

Veljko ZLATIĆ

Institute of Physics, Bijenička c. 46, HR-10001 Zagreb, Croatia

Intermetallic compounds with Ce, Yb or Eu ions often exhibit anomalous thermoelectric properties which, at the first sight, appear quite complicated. Some of these intermetallics have a huge thermoelectric power S(T) below 150 K, which makes them attractive for cooling devices. We shell explain the behavior of S(T) in intermetallic compounds with Ce, Yb or Eu ions in very simple terms, using Kondo scattering on the magnetic states with internal structure.<sup>1,2</sup> This internal structure is due to the crystal field splitting of 4f states in Ce and Yb or to the Hund's rule coupling of 4f and 5f states in Eu or U compounds. The band-structure effects will also be discussed, because the proximity of the chemical potential to the band-gap modifies drastically the thermoelectric response.<sup>3</sup> However, the thermoelectric figure of merit, ZT, is never very impressive in bulk systems with rare earth ions, due to the large overall thermal conductivity. Thus, it is not clear if strong correlations in bulk intermetallics can lead to useful devices. This might change in multilayers with correlated metals sandwiched between normal metals. A particularly interesting behavior is expected when correlated layer is close to the metal-insulator boundary. We shall also discuss briefly the attempts to calculate the non-linear charge and heat currents of correlated systems.<sup>4</sup>

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#### THE HOSOYA-WIENER POLYNOMIAL ON WEIGHTED TREES

Blaž ZMAZEK<sup>1,2</sup>, Janez ŽEROVNIK<sup>1,2</sup>

<sup>1</sup>*FME*, University of Maribor, Smetanova 17, SI-2000 Maribor, Slovenia <sup>2</sup>*IMFM*, Jadranska 19, SI-1000 Ljubljana, Slovenia

The Hosoya-Wiener polynomial<sup>1,2</sup> of a graph G is defined as:

$$H(x) = H(G; x) = \sum_{u, v \in V(G)} x^{d(u,v)} \text{ or } \hat{H}(x) = \hat{H}(G; x) = \sum_{u, v \in V(G); u \neq v} x^{d(u,v)}$$

Obviously,  $H(x) = \hat{H}(x) + |V(G)|$ .

We can generalize the Hosoya-Wiener polynomial to weighted graphs as follows. Let *G* be a edge and vertex weighted graph, defined by two weighting functions *w* and  $\lambda$ . *H*( $\lambda$ ,*w*;*x*) is defined as:

$$H(\lambda, w; x) = H(G, \lambda, w; x) = \sum_{u, v \in V(G)} w(u) w(v) x^{d(u,v)},$$

where d(u,v) is the graph distance between u and v. Clearly, the new definition is equivalent to original definition if all vertex weights are equal to 1. Note that  $H(\lambda,w;x)$  is in general not a polynomial if arbitrary edge lengths are allowed.

It is known that the unweighted Wiener number<sup>4</sup> is the value of the first derivative of the Hosoya-Wiener polynomial at x=1, W(G) = H'(G;1). Analogous result can easily be proved for weighted Wiener number, i.e.  $W(\lambda, w, G) = H'(G, \lambda, w;1)$ .<sup>3</sup>

We will discuss an algorithm for efficient computation of  $H(\lambda, w; x)$  on trees.

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#### HOW TO OPTIMISE USEFUL INFORMATION DERIVED FROM EXPERIMENTAL DATA?

Tomislav P. ŽIVKOVIĆ

Ruđer Bošković Institute, P.O.B. 180, HR-10002 Zagreb, Croatia

On January the first 1801, on the done of the nineteen century, first planetoid Ceres was detected. After few days of observation Ceres disappeared near the Sun. The observations were published and many astronomers tried to calculate the trajectory of Ceres from the scarce data in order to determine its position in more favorable conditions. All those predictions differed substantially from that of Gauss. After approximately one year Ceres was observed precisely at the time and on the place predicted by Gauss. By this single prediction Gauss became immediately famous. In order to determine Ceres orbit he invented at that time completely new mathematical method known today as a least square fit. It was known that Ceres orbit should be an ellipse. Mathematically, the problem was to find the best ellipse to fit published experimental data.

The problem treated by Gauss is a special case of a more general problem how to find the best curve consistent with given experimental data. There are two aspects of this problem. First, one may know general analytical form of this curve. In this case the problem is to find optimum parameters that determine this curve. For example, an exponential decay has the form  $y(t)=A^*exp(-bt)$  where A and b are unknown parameters and where t is time. In the case of such a decay the problem is to find best parameters A and b to fit experimental data. Second, the analytical form of this curve may be unknown. For example, in a study of some chemical reaction it may be unknown whether this is a first order reaction, a second order reaction, or something else. Each possible reaction type has different analytical form. In this case one has to determine which reaction type agrees in an optimal way with given experimental data. From this point of view main purpose of experimental data is to determine reaction type.

Above problems are usually treated by first linearising the curve that describes experimental data. For example, in the case of an exponential decay one can transform the curve that describes this decay to the form ln y(t)=lnA-bt. This formula describes a straight line and mathematically the problem is to find the best line that in the sense of a least square fit agrees with experimental data. In some cases such a linearization may be achieved in several ways and besides one can also devise various nonlinear methods in order to solve the same problem<sup>1</sup>. All such methods produce generally different results. It is therefore highly important to asses in some quantitative way reliability of various possible methods and to devise a general approach how to obtain an optimum method. General strategy how to achieve this goal will be described.

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