

C. Trindle

The Hierarchy of Models in Chemistry

Criteria for useful models in chemistry are given. A number of prevalent and bonding models are briefly discussed. The possibility of encoding chemists' non-numerical conceptual models by the methods of Artificial Intelligence is described. . . .

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B. Kirtman and
W. E. Palke

Factors Governing Nuclear Geometry and Bond-Orbital Directions in Second Row AH_2 Molecules

A number of simple rules which govern the molecular geometry and bond-orbital directions in AH_2 systems are explained in terms of VB orbital characteristics and energy decomposition. . . .

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D. Cremer and
E. Kraka

A Description of the Chemical Bond in Terms of Local Properties of Electron Density and Energy

Salient features of chemical bonding are considered in terms of the saddle points r_p of the one-electron density $\rho(\mathbf{r})$ in the regions between the bonded nuclei and local energy density $H(r_p) = G(r_p) + V(r_p)$. Information about the concentration and depletion of electronic charge at r_p is stored in $\nabla^2 \rho_p$. It was found, however, that the $\nabla^2 \rho_p$ criterion does not suffice for detecting weak covalent bonds. . . .

1259—1281

W. L. Luken

Properties of the Fermi Hole in Molecules

The shape of the Fermi hole in molecules is discussed. If the wavefunction is given in the form of a single Slater determinant, the Fermi hole is determined by a square of the Fermi orbital. A set of Fermi orbitals can be used to transform a set of canonical SCF MOs into localized MOs. . . .

1283—1294

Z. B. Maksić,
M. Eckert-Maksić,
and K. Rupnik

Model Description of Some Molecular Properties by the Modified-Atom-in-a-Molecule (MAM) Approach

Conclusive evidence is presented which shows that the concept of modified atoms in a molecule (MAM) is a viable model for the description of numerous molecular properties. Modification of an atom in a chemical environment can be decomposed into isotropic and anisotropic components. Isotropic (monopole) part is responsible for the changes of σ_A^d , χ^d and ESCA shifts. Extramolecular electrostatic potentials require inclusion of higher (anisotropic) local multipoles. Special attention is devoted to the description of atomic anisotropy by hybrid AOs. The latter explain various relationships existing between directional features and properties which can be termed as »local«. It is argued that atomic monopoles and hybridization indices represent pseudo-observables *par excellence*.

1295—1353

S. K. Kang,
T. A. Albright,
and J. Silvestre

The Bonding of P_4 to d^8 — ML_3 Complexes

Structure and Stability of η^1 , η^2 , and η^3 complexes of P_4 to $Rh(PH_3)_2Cl$ are studied by the EHT method. It is found that η^1 -square planar and η^2 complexes with C_{2v} symmetry are the most stable. d^{10} η^1 -tetrahedral complexes of P_4 are expected to be quite stable. The best candidate for an η^3 mode of bonding is the trimer $Fe_3(CO)_9$.

1355—1370

H. Nakatsuji
and M. Hada

Interaction of the Hydrogen Molecule with the Palladium Atom. A Force Theoretic Study

The interaction between the H_2 molecule and $^1S(4d^{10})$ and $^3D(4d^95s^1)$ states of the Pd atom were considered as a model for chemisorption phenomenon. The force and density origins of the interactions were clarified. The former was calculated by using the Hellman-Feynman Theorem. The singlet Pd(1S)- H_2 system provides stable ground state, whilst the interaction bet-

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**E. Ortoleva
and M. Simonetta**

A Theoretical Study of the Influence of Surface Structure on Chemisorption of Nitrogen on Iron Single-Crystal Faces

Fe_n clusters (where *n* = 9, 10, 13, 15, 18) were used in a process of modelling of 111, 100 and 110 surface planes of an iron single-crystal. The calculations were performed within the EHT framework. The ordering of reactivity of surfaces is determined. Reactivity decreases as follows: 111 > 100 > 110. 1387—1393

**M. Persico
and J. Tomasi**

An Evaluation of Solvent Effects on Isomerization Mechanisms in Diimide and Methylenimine

Inversional and rotational isomerization mechanism in N₂H₂ and CH₂NH in solution have been studied by an *ab initio* approach. The reaction potential of a solvent was mimiced by a dielectric continuum and included in the solute hamiltonian. It was found that the solvent effect is mainly dependent on the hybridization state of the nitrogen atoms and the relative orientation of their lone pairs. . . . 1395—1409

**G. Klopman and
M. R. Frierson**

The Alpha-Effect. A Theoretical Study Incorporating Solvent Effects

Experimental observations unambiguously show that OOH⁻ anion has a higher nucleophilic character in solutions than the OH⁻ anion. This finding was rationalized by the model of frontier MOs (FMO). Namely, it was shown that splitting of the FMO energy levels strongly depends on the solvent. 1411—1415

**H. O. Villar,
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R. E. Cachau,
and E. A. Castro**

Some Comments on the Nucleation Phenomena

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M. V. Basilevsky,
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Where is the Limit to which the Qualitative Theory of Chemical Reactivity can be Extended? Study of Dienophilic Activity of Cyanoethylenes

The mechanism and kinetic regularities observed in Diels-Alder reactions of cyanoethylenes with cyclopentadiene and phenylcyclopropane were studied by a qualitative quantum-chemical approach. Polar effects predominated over the localization effect in the former reaction series. Experimental data can be understood as a result of the charge transfer from diene to dienophile in a synchronous transition structure (TS). The inversion of the regular activity sequence found in the latter reaction series is ascribed to localization effects in asynchronous TS. . . . 1423—1444

P. N. Skancke

A Molecular-Orbital Study of the Thermal Walk Rearrangement of Bicyclo-[2.1.0]pent-2-ene

Ab initio MO calculations involving geometry optimization indicate that in the walk rearrangement of bicyclo[2.1.0]pent-2-ene the reaction path going via inversion of the migrating center is slightly preferred. It was found that the transition structure (TS) has a diradical nature. 1445—1449

W.-K. Ip and
W.-K. Li

MNDO Study of the Dimerization of Borane

The dimerization of borane was investigated by the MNDO method. Three pathways of least-motion, C_{2h} and C_1 symmetries were examined. The activation energies are 31.5, 3.8 and 2.7 (in kcal/mol) respectively. Since the MNDO procedure exaggerates the energies of transition structures, the results indicate that the borane dimerization has no, or a very small, energy barrier. . . . 1451—1460

F. Volatron,
Y. Jean, and
Nguyễn T. Anh

The Role of Lone Pairs in Heteroatomic Chemistry. Graphical Analysis and *Ab Initio* Calculations of Oxirane and Aziridine Ring Opening

Notion of the »overlap graph« is introduced and applied in analysis of energy barriers in thermal electrocyclic openings of oxirane and aziridine rings. It was found that oxygen and nitrogen lone pairs affect differently the activation energies. Qualitative conclusions are supported by the *ab initio* (STO-3G, 4-31G)+ +CI calculations.

1461—1474

J. B. Moffat

Partitioning and Additivity of the Chemical Bond

Changes in the electronic energies of various molecules on substitution of a hydrogen atom by various groups were analysed. It is shown that the substitution energy for cyano and isocyano groups can be successfully correlated with the charge on the substituent group in the substituted molecule.

1475—1483

C. Petrongolo

Non Adiabatic Effects and Radiationless Transitions

Ab initio methods for computing stationary molecular states and radiationless probabilities between nonstationary states were examined. The expansion methods, the molecular hamiltonians, the adiabatic and diabatic representations, and symmetry aspects are briefly discussed. As a specific example, nonadiabatic effects in the V—N spectrum of C₂H₄ and the corresponding V-Ry radiationless transitions are elaborated.

1485—1495

A. Julg

The Problem of Enantiomers: Support for a New Interpretation of Quantum Mechanics

The problem of enantiomers is a typical case which illustrates the difficulties of quantum mechanics in interpreting the geometric structure of molecules. A so-

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**M. Kibler
and T. Négadi**

On the Use of Nonbijective Canonical Transformations in Chemical Physics

Three quadratic transformations are considered: The Levi-Civita, the Kustaanheimo-Stiefel and a new original transformation. Applications of the Kustaanheimo-Stiefel transformation are reviewed and further developed. It is applied to the hydrogen atom, the Stark and Zeeman effects in H-like ions and briefly discussed for other potentials of interest in chemical physics and quantum chemistry. . . . 1509—1523

K. Balasubramanian

Recent Applications of Group Theoretical Generators to Chemical Physics

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T. P. Živković

The Splitting Theorem and Properties of Alternant Systems

The notion of alternant systems, as employed in semiempirical π -electron theories of planar hydrocarbons, is generalized to arbitrary symmetric hamiltonians. A CI space X_n , generated by n electrons distributed over $2n$ orthonormal orbitals, is considered. It is shown that wavefunctions $\Psi \in X_n$ of alternant hamiltonians lie in two complementary subspaces X_n^+ and X_n^- of CI space X_n . Each state $\Psi^\pm \in X_n^\pm$ has properties which characterize the eigenstates of neutral alternant hydrocarbon systems. 1553—1573

T. P. Živković

Antialternant Perturbations of Alternant Systems

The effect of the antialternant perturbation λV on the alternant hamiltonian H_0 is considered by the Rayleigh-Schrödinger expansion. A number of interesting conclusions are drawn. For example, the expectation values of alternant operators are even functions of the perturbation operator λ . The opposite is true for anti-alternant operators. Their average values can be developed in series involving only odd powers of λ

1575—1593

A. Graovac and
O. E. Polansky

Topological Effect on Molecular Orbitals. Part 8. A Study of Two Further Classes of Topologically Related Isomers

The family of isomers exhibiting topological effects on molecular orbitals (TEMO) is enlarged by two new classes. The inversions in TEMO and the predicted HOMO-LUMO separation of topologically related isomers are discussed for different central fragments.

1595—1619

L. v. Szentpály
and W. C. Herndon

A Comparison of Pencil and Paper Procedures. PMO, Free-Electron PMO, and Structure-Resonance Theory Calculations for Proton Affinities

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1621—1628

M. Grzonka,
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L. Klasinc, and
N. Trinajstić

Theoretical Studies on Small Ring Heteropropellanes. Oxapropellanes

Oxa(1.1.1)propellane, dioxa(1.1.1)propellane, trioxa(1.1.1)propellane and the parent hydrocarbon compound (1.1.1)-propellane are considered by the *ab initio* 6-31G* technique. Structural properties, particularly the central bonds, are discussed.

1629—1632

T. Hirano and
E. Ōsawa

On the Correspondence between Molecular Orbital Energies and Empirical Force Field Potential Terms

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V. Kvasnička

Second-Quantization Formalism for Geminals

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V. Kellö, I. Hubač
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and V. Špirko

***Ab Initio* MBPT(4) Calculations of the Inversion Potential Function of NH₃**

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