

be size-consistent. Effective hamiltonian formalism furnishes a very natural framework of studying systems of arbitrary complexity and offers a powerful tool for a quantitative modelling of molecular electronic structure. Till very recently, it had been generally accepted that size-extensivity and size-consistency of an effective hamiltonian H_{eff} would be maintained only for a complete valence model space, which is too restrictive a choice and is not generally very practical. We shall argue and show that the size-extensivity of H_{eff} is in no way predicated by this choice. The essential requirements are: (i) the use of a wave-operator Ω that is valid for all the n -valence sectors (valence universality of Ω); (ii) the use of an exponential structure for Ω , [$\Omega \sim \exp(s)$] that ensures asymptotic multiplicative separability; (iii) the use of a normalization that is compatible with (ii); and (iv) if truncations have to be made for a model, then it should be performed on the cluster operator S rather than on Ω . Maintenance of these leads to an open-shell coupled cluster formalism for a general model space. Size-consistency with respect to dissociation into specific channels can then be guaranteed by a careful selection of the model space functions. Several numerical examples will be discussed to illustrate the workability of the formalism, using pair-cluster model ($S \sim S_2$): (a) the interpretation of outer and inner valence ionization potentials where strong correlation effect leads to a breakdown of the orbital picture and to the emergence of satellite structure; (b) prediction of Auger spectrum with satellite features; (c) prediction of excitation energies from closed-shell ground states; (d) generation of potential surfaces where correlation effects lead to avoided crossing, conical intersection or binding behind a Coulombic barrier (as in dicationic species).

Novel Electronic Effects in Radicals and Radical Ions
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Ab initio and semiempirical molecular orbital methods have been used to make several predictions concerning unusual structural and electronic features associated with radicals and radical ions. A few representative examples follow.

(a) Distonic radical ions, which have their formal charge and radical sites on different atoms are predicted to be more stable than their classical isomers, especially when the electronegativities of

the distal atoms differ substantially. Thus, the silicon based distonic radical cation $H_2Si \cdot - O^+H_2$ is calculated to be preferred over classical SiH_3-OH^+ . The magnitude of this preference in silicon systems is consistently greater than in the corresponding carbon isomers. Stable distonic radical anions are also predicted to exist. The most favourable system for experimental observation would be organoborane radical anions.

(b) The combined stabilizing effect of a donor and an acceptor at a radical is greater than that anticipated from additivity considerations. The additional stabilization, termed the captodative effect, is much larger in radical ions than in neutral radicals. The course of several mass spectral fragmentations is determined by this electronic effect.

(c) In the complexes $Li(C_2H_4)_n$ ($n = 2, 3$), the unpaired electron is delocalized over the π^* orbitals of the ligands. The preferred structures display a Hückel arrangement of interacting π^* orbitals. Möbius topology leads to less stable Jahn-Teller distorted structures.

Theory of Reactions in the Absence of an Activation Barrier by Biman Bagchi, *Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560 012, India.*

Recent picosecond and subpicosecond laser spectroscopy experiments have revealed several chemically and biologically important reactions in solution, in which the reaction potential surface does not present a barrier to the motion along the reaction coordinate¹. The dynamics of these reactions display diverse and interesting behaviour. They include the dependence of relaxation rate on the solvent viscosity, on the solvent polarity, on temperature and on wavelength of the exciting light. Recent developments in the theoretical description^{2,3} of activationless processes in solution is reviewed and compared with the available experimental results.

1. Bagchi, B., *Int. Rev. Phys. Chem.*, 1987, **6**, 1.
 2. Bagchi, B., *Chem. Phys. Lett.*, 1987, **135**, 553, 558; **138**, 315; **139**, 119.
 3. Bagchi, B., *J. Chem. Phys.*, 1987, **87**, 5393.
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