SPHERICALLY CONFINED COULOMB SYSTEMS: SOME RECENT RESULTS

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We shall present a review of our recent work dealing with (a) the soft Coulomb core potential

\[ V(r) = -\frac{Z}{\left(\frac{r}{a}\right)^{\beta}} \]

(b) the sum of Coulomb and harmonic potential

\[ V(r) = -\frac{a}{r} + br^2 \]

both with and without the spherically confined impenetrable boundary wall of radius R; (c) the derivation of a new expression for the expectation value integral of Hermitian operators for spherically symmetric states as derived in elliptical coordinates for the Helium atom confined in a cavity of radius R with infinite potential barrier walls, and (d) the application of the accurate computational method based on the B-spline basis which leads to the most accurate calculations on the electronic properties of the confined N-electronic atoms within the third-order Douglas-Kroll method.

References


4 B-Spline basis set calculations of confined atoms, K.D. Sen, [In Preparation]
K.D.Sen (PhD, IIT-Kanpur) F.A.Sc., F.N.A. joined University of Hyderabad in 1977 where he is now the senior most professor. His collaborative research in electronic structure theory with scientists from Belgium, Cameroon, Canada, Chile, China, Germany, Greece, Japan, Mexico, Nigeria, Spain, Turkey, UK and USA has led to the publication of 8 monographs and 185 research papers. A recipient of Humboldt, Fulbright, and NSERC Canada Research Fellowship, he has been recently awarded the DAAD Research Professorship, Indo-US Professor of Physics of the American Physical Society and the J.C. Bose National Fellowship.
In cells, biological molecules function in an aqueous solution of a large number of electrolytes and small molecules. However, the effects of cosolvents/cosolutes on the structure and dynamics of liquid water are far from fully understood. We discuss the molecular mechanisms through which cosolvents and cosolutes affect protein structure formation and hydration. For example, the addition of NaI to the aqueous solution caused denaturation and significantly weakened hydrogen bonds of the polypeptide. Na₂SO₃, a “kosmotropes,” strengthened the hydrophobic interactions and increased hydrogen bonding of the polypeptide. Preferred binding of Na⁺ to the backbone carbonyl groups of BBA5 occurred in the NaI solution, consistent with the weakened protein backbone hydrogen bonds, whereas Na⁺ ions are excluded from the vicinity of protein backbone in the Na₂SO₃ solution. We suggest that the chaotropic NaI affects protein structure mainly through a direct binding of Na⁺ to the backbone and I⁻ to the protein surface, whereas the main effect of Na₂SO₃ manifests in strengthening the hydrophobic interaction and consequently the hydrogen bonding of the protein. We will also discuss the effects of different alcohols on the structure of BBA5 and elucidate the molecular mechanism through which monohydric methanol and TFE denature BBA5, whereas polyhydric glycol and glycerol protect the polypeptide structure.

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DOMINO-RING-OPENING-CYLIZATION (DROC) OF ACTIVATED SMALL RING N-HETEROCYLES

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Ring-opening transformations of small ring aza-heterocycles provide excellent routes for the construction of important synthetic targets. We have demonstrated that Lewis acid (LA) mediated/catalyzed nucleophilic ring-opening of enantiopure 2-aryl-N-tosylazetidines and aziridines takes place through an $S_N2$ pathway. This chemistry successfully delivered a wide range of non-racemic products in high enantiomeric excess by exploiting the vulnerability of aziridines and azetidines towards several nucleophiles.

By extending the protocol under optimum conditions domino-ring-opening-cyclization (DROC) reactions of aziridines and azetidines with appropriate nucleophiles provide a number of non-racemic targets of immense synthetic and pharmacological interest. Those compounds include imidazolines, tetrahydropyrimidines, oxazolidines, oxazinanes, morpholines, polyhydroxylated-pyrrolidines, piperidines, γ-lactams, dihydropyrroles, tetrahydropyridines, tetrahydroquinolines, tetrahydroquinoxalines, tetrahydroquinolines etc. Recent advances of this chemistry in terms of further mechanistic investigations, enhanced enantio- and diastereoselectivity and important applications in asymmetric organic synthesis will be presented.

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Scheme 1. Domino-ring-opening-cyclization of 2-aryl-N-tosylaziridines (n = 1) and azetidines (n = 2).
Manas K. Ghorai obtained his M. Sc. (Chemistry) from IIT, Kharagpur in 1991. He received his Ph.D. in synthetic organic chemistry from the National Chemical Laboratory, Pune (Pune University), in 1998. He held post-doctoral positions at the University of Wuerzburg (Germany), University of Siegen (Germany) and MIT, USA before joining IIT Kanpur in 2002. His research interests lie in the area of i) synthetic and mechanistic investigation of small ring aza-heterocycles, ii) enolate and dianion chemistry, iii) asymmetric synthesis including natural products and drugs employing memory of chirality and organocatalysis.