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Editorial

Atoms and molecules in a confined environment

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1 Introduction

Soon after the discovery of quantum mechanics, several model systems were developed. One of them, perhaps the simplest, was the particle-in-a-box problem. Solutions of this model confined system revealed several aspects of a quantum mechanical system. The more confined a particle in space is, the higher is its energy. The uncertainty in its position and the uncertainty in its momentum are in keeping with the Heisenberg's uncertainty principle. That a quantum mechanical system could have a nonzero energy even at 0 K was its consequence.

Subsequent to solving the hydrogen atom problem and accounting for the hydrogen atom spectrum by quantum mechanics, the problem of confining a hydrogen atom to a sphere of finite radius was solved. It became apparent that the energy of the bound states of the confined system increased beyond the energy of a free hydrogen atom indicating that a proton and an electron could coexist in the confined space and yet may not constitute a hydrogen atom. Similar results followed for hydrogen molecule ion inside a cylinder. It also became clear that atoms and molecules under pressure could behave differently. The possibility of forming hydrogen metal under high pressure was anticipated.

That imposition of symmetry constraints could result in lifting the degeneracy of energy and angular momentum states of a system became an important quantum mechanical feature that went beyond atoms and molecules. The consequent Jahn–Teller effect has been used to explain superconductivity of metals too. Properties of atomic and molecular systems under the influence of electrical, magnetic and electromagnetic fields could be understood.

The subject of atomic and molecular systems under constraint is vast. Implications range from the formation of white dwarfs and neutron stars on the one hand to insulators turning into metals and graphite turning into diamond on the other. Recent years have witnessed a phenomenal growth in the study of restricted dimensional systems, like two-dimensional graphene sheets and their modifications that exhibit hitherto unknown properties that are quantum mechanical in nature.

For a mathematician, the problem gets modified with the imposition of the boundary conditions and the solutions change. However, for a physicist, it is the right model to examine the basics of the right problem. Chemists and physicists deal with real-life materials. There are no hard boundaries between systems. Host molecules like fullerenes are "soft" cages that interact with the guest molecules electronically and otherwise.

Spectroscopists use matrix isolation techniques to study atoms and molecules in "isolation." Photochemists investigate cage effects. Nature has given us zeolites to trap and study the behavior of atoms and molecules under confinement. Organic and inorganic chemists go about synthesizing metallo-organic frameworks with the hope of trapping hydrogen, carbon dioxide and other gases. The list of theoretical and practical confined systems is endless. It does not matter what the constraints are. Properties of atoms/molecules/materials change under confinement. To understand them is to be able to make the best use of the myriad opportunities they provide.

2 Special issue

Thanks to the support of the Editorial Board of EPJD and the willingness of several authors, we have put together a special issue on "Atoms and molecules in a confined environment." The articles therein cover a wide range of topics: hydrogen atom in a modified ring-shaped potential, two-dimensional hydrogen atom, muonic hydrogen atom under confinement, hydride ion under confinement, helium atom confined by a spherical box, confined lithium atom, rubidium clusters in helium nanodroplets, ammonia inversion inside fullerene cages,

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fullerenes confined in nanotubes, carbon dioxide inside carbon nanotubes, drug molecules inside carbon nanotubes, confinement effects on stretching frequencies of molecules in an inert gas matrix and so on. How does confinement alter the ionization potential and electron affinity of atoms and other thermodynamic properties and how to apply various theoretical tools to study and predict the behavior of atoms and molecules under different confinements are some of the other topics covered in this special issue.

The number of articles in this special issue reflects the timeliness of the subject covered and the interest of fellow colleagues working in this area. There are lots of other articles that have appeared in EPJD in recent months that could have been easily included in this special issue. We take this opportunity to thank the Chief Editor and the colleagues in the editorial team for encouraging us to edit this special issue, and we are grateful to all the contributing authors for their readiness to contribute and the cooperation in bringing out this special issue.

3 Dedication to V. I. Pupyshev

We are particularly pleased to dedicate the special issue to the memory of Vladimir Ivanovich Pupyshev PhD (6 August 1949–16 June 2020), Leading Scientific Researcher in the Department of Chemistry, Lomonosov Moscow State University (MSU). Vladimir earned the PhD degree at MSU in 1975 and immediately joined the chemistry faculty there. He largely shaped the course of theoretical research at the Department from 1975 until his death in 2020. He established the "11th group" of the Chemistry Department, a specialized group for students in theoretical and physical chemistry. He started his professional career as a student in the 11th group and was part of it until the last months of his life.

Vladimir's first steps in science began with development of the foundations of the self-consistent field (SCF) method related to the analysis of convergence and multiple solutions of the SCF equations. This was the focus of his PhD thesis in physics and mathematics. In the same period (1970s–1980s), his joint work with other researchers in the MSU Chemistry department (N.F. Stepanov, A.A. Safonov and V.F. Khrustov) developed SPUSH, MSU's first in-house quantum chemistry package.

Largely influenced by his students, T.Yu. Mikhailova and A.V. Scherbinin in the late 1980s and early 1990s, he pursued new directions. This work was stimulated by the progress of G.M. Zhislin, Barry Simon, Michael Reed and Tosio Kato in obtaining rigorous results in the theory and simulation of the electronic structure and dynamics of atomic and molecular systems. During that time, Vladimir studied the evolution of quantum states and decay of metastable states. He later began his theoretical journey into describing confined atomic and molecular systems. In those areas, Vladimir developed the mathematical foundations for approximating a time-evolution operator using the techniques of Lie algebra and for describing resonance states of model one-dimensional systems on a discrete grid. He described the states of one-electron atoms in a spherical cavity and obtained rigorous results for the behavior of energy levels and their systematic degeneracy at unique values of the cavity radius. These results were later explained in terms of a special observable, an additional (apart from the energy and the angular momentum) integral of the motion, the Lenz vector, representing the integral of motion for a free hydrogen-like atom, and it partially retained the properties for an atom in a spherical cavity with the Dirichlet boundary condition. He also explored more general cases of boundary conditions (Neumann, Robin, etc.). He used the Kirkwood–Buckingham variational method to study the behavior of the energy levels of a system confined in a cavity during deformation of the cavity boundaries and under its unlimited expansion.

Further development in the field of confined atomic systems considered cavities of more general shape (cylindrical, cubic and polyhedral of various symmetry) as well as analysis of the stability of atomic nucleus positions in a cavity for systems in various electronic states. This work was done together with his former students, M. Changa, P. Yurenev and M. Kretov. This area of research was also closely related to joint work with V. Bobrikov on vibrational–rotational states of a diatomic molecule in a spherical cavity and with Vladimir's own work devoted to alternative proofs of the Jahn–Teller theorem and to the Hellmann–Feynman theorem near a threshold.

Beginning in 1989, Vladimir volunteered as an instructor in the residential summer camp in chemistry called "Chimera," led by Vyacheslav Viktorovich Zagorsky. There he taught basic quantum mechanics for the high school students. Later, in the 1990s, he assisted in development of introductory chemistry courses for middle school and even elementary school students. The central idea was to teach students about chemical substances around us, gradually introducing some basic concepts (before the students' interest was extinguished by the formal approach common in standard school education). Many of the Chimera graduates later studied in MSU's Chemistry and Materials Science Departments.

In recent years, Vladimir actively collaborated with foreign professionals (H.E. Montgomery, K.D. Sen and others) on confined atomic and molecular systems. The most significant results included analysis of changes in the structure of electronic states of one- and two-electron atomic systems in impenetrable cavities of small size, for example, in the cavity of a crystal defect or inert matrix. Analytical statements were proven concerning the behavior of wave functions and mean values for one-electron systems in an impenetrable cavity under changes in the boundaries of the cavity and in one-particle potentials. Dipole polarizabilities and screening constants were calculated based on

these results, and their values were validated for few-electron systems in an impenetrable cavity. In particular, numerically stable methods were developed for calculating energy states of systems with spherical (or circular) layers. A consistent description of the changes in the properties of such systems under variation of the dimensionality of the problem was developed. Rediscovery of a method developed by Hassè in 1930 facilitated calculation of the dipole polarizability of two-electron systems in Hylleraas coordinates. Unfortunately, his untimely death in June 2020 did not allow his further ideas and plans in these directions to be realized. As a leading Russian scientist, he brought up more than one generation of theoretical chemists, who now work around the world.

He was a brilliant lecturer who could explain complicated ideas even to undergraduate students, always providing beautiful examples to illustrate challenging problems while maintaining the highest level of mathematical rigor. He revealed the beauty of quantum chemistry, and many of his students became quantum chemists after his courses. He taught not only the physics, but also the entire history behind the development of quantum mechanics including the fortunate and unfortunate events in the lives of its creators. He was always eager to discuss the latest theater performances in Moscow or his love for the novels of Charles Dickens and Kurt Vonnegut, and he did so with the same enthusiasm that he brought to scientific problems. What will be missed most are his sharp mind and his thoughtful assistance to his colleagues and students.

Vladimir I. Pupyshev (1949–2020)

4 Selected papers of V. I. Pupyshev

1. Yu.N.Pachenko,V.I. Pupyshev, A.V. Abramenkov, M.Traetteberg, S.J. Cyvin "Potential function of internal rotation for isoprene from ab initio calculations and experimental data" J. Mol. Struct. 130, 355 (1985)
2. V.I Pupyshev, A.V Scherbinin, N.F. Stepanov "The Kirkwood–Buckingham variational method and the boundary value problems for the molecular Schrödinger equation" J. Math. Phys. 38, 5626 (1997)
3. T.Yu. Mikhailova, V.I. Pupyshev "Algebraic method for the evolution operator approximation" J. Phys. A 31, 4236 (1998)
4. V.I. Pupyshev, A.V.Scherbinin "The Lenz vector in the confined hydrogen atom problem" Chem. Phys. Lett. 295, 217 (1998)
5. T.Yu. Mikhailova, V.I. Pupyshev "Symmetric approximations for the evolution operator" Phys. Lett. A 257 1 (1999)
6. M.E. Changa, A.V. Scherbinin, V.I. Pupyshev "Perturbation theory for the hydrogen atom in a spherical cavity with off-centre nucleus" J. Phys. B. 33, 421 (2000)
7. V.I. Pupyshev "Simplest proof of the Jahn–Teller theorem for molecular systems" Int. J. Quantum Chem. 107, 1446 (2007)
8. K.D. Sen, V.I. Pupyshev, H.E. Montgomery "Exact Relations for Confined One-Electron Systems" Adv. Quantum Chem. 57, 25 (2009)
9. H.E. Montgomery, V.I. Pupyshev "On lower bounds for polarisability" Eur. Phys. J. H 38, 519 (2013)
10. H.E. Montgomery, V.I. Pupyshev "Dipole polarizability for confined two-electron atomic systems: simple approximations" Phys. Scr. 95 015402 (2020)

Author contributions

All the authors have contributed to the design and writing of this Editorial.

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