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Recent progress in confined atoms and molecules: Superintegrability and symmetry breakings

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This review article has the antecedents of Jaskolski's 1996 Physics Report on "Confined Many-electron Systems", the fifteen chapters on the "Theory of Confined Quantum Systems" in Vols. 57 and 58 of 2009 Advances in Quantum Chemistry, and the nine chapters of the 2014 Monograph "Electronic Structure of Confined Quantum Atoms and Molecules". In this contribution, the last two sets of reviews are taken as points of reference to illustrate some advances in several lines of research in the elapsed periods. The recent progress is illustrated on the basis of a selection of references from the literature taking into account the confined quantum systems, the confining environments and their modelings; their properties and processes, emphasizing the changes due to the confinement; the methods of analysis and solutions, their results including confiability and accuracy; as well as applications in other areas. The updated and current works of the Reviewer are also presented. The complementary words in the title apply to the simplest atom in its free configuration and to the harmonic oscillator quantum dot, because they admit more exact solutions than the number of their degrees of freedom; and to their many-electron and confined counterparts, due to their additional interactions and changes in boundary conditions.

Keywords: Confined quantum systems; confining environments; changes in physical properties and processes; modelings of confinements; methods of analysis and solution; confiability and accuracy; applications.

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1. Introduction

This invited review article is written against the background of W. Jaskolski´s 1996 Physics Report on "Confined many-electron systems" [1], the fifteen chapters of "Theory of Confined Quantum Systems" in Advances in Quantum Chemistry (AQC) 2009 Vols. 57 [2-10] and 58 [11-16], with S.A. Cruz as Special Editor, and the nine chapters of "Electronic Structure of Quantum Confined Atoms and Molecules" [17-25] edited by K. A. Sen in 2014. It is interesting to contrast [1] a review of the state-of-the-art in that year by a single author, with the two sets of reviews of specific topics in the field, twenty two and twenty six years later, illustrating advances and the diversification of the field in the respective periods.

The readers can get an idea on the physical systems and confinement conditions in each review from their respective titles in the references. Notice that [2-8] are restricted to one and two electron atoms, [9] and [11] to many-electron atoms, while [10] treats confined atoms as open systems, [12] reports on the photoionization of atoms encaged in spherical fullerenes while [13] a Density Functional Theory Study of Molecules confined inside fullerene and fullerene-like cages, [14] deals with the Spectroscopy of Confined atomic Systems: Effect of Plasma, [15] characterizes the Energy Level Structure of Low-dimensional Multi-electron Quantum Dots, and [16] is about Engineering Quantum Confined Silicon Nanostructures: Ab-Initio Study of the Structural, Electronic and Optical properties. We may add that in [2,3], [5-8] and [12] the atoms or molecules are confined inside spheres, while in [4] the confining boundaries are conoidal, and in [9] they are spherical, prolate spheroidal, and plane.

In the Monograph, its Editor pointed out in the Preface that, *it deals with the simplest among the quantum confined model systems, recording the significant developments in the field subsequent to the two published volumes of Advances in Quantum Chemistry* . The titles and authors can be identified in [17-25], recognizing common topics and Contributors in [17-20] and [24] from the previous set of reviews; here we spell out the other titles [21] "Confined Quantum Systems Using the Finile Element and Discrete Variable Representation Methods", [22] "Bound and Resonant States in Confined Atoms", [23] "Spatial and Shell-Confined One Electron Atomic and Molecular Systems: Structure and Dipole Polarizability", and [25] "Study of Quantum Confinement of H_2^+ Ion and H_2 Molecule with Monte Carlo. Respective Role of the Electron and Nuclei Confinement", illustrating new methods of solution, new physical effects, and new ways of modeling the confinement.

Concerning the use of the words superintegrability and symmetry breakings in the title of this contribution, the reader may find in [4], and in [26] of [17] these respective uses for the one-electron hydrogen atom and quantum dot, in their free and confined configurations. In fact, the Schrödinger equation for the hydrogen atom can be separated and integrated in spherical, spheroconal, prolate spheroidal and parabolic coordinates; and for the harmonic oscillator modeling one-electron quantum dots in cartesian, cylindrical and also spherical and spheroconal coordinates. That situation extends to the respective quantum systems confined by natural boundaries corresponding to fixed values of the respective coordinates. For the free systems, their solutions in the different coordinate systems share the same degeneracies; due to their respective O(4) and SU(3) symmetries. In contrast, the systems confined in the successive natural boundaries exhibit the corresponding symmetry breakings due to the changes in the boundary conditions, with different energy eigenvalues and eigenfuctions, and reduced degeneracies. The title and contents of [18] also illustrate these effects.

In the case of the hydrogen atom, the superintegrability is subject to the condition of the position of the nucleus at the center of the sphere, at one of the foci in the prolate spheroid, at the common focus of the paraboloids, each one with their respective set of constants of motion; if the nucleus occupies other positions, the separability of the Schrödinger equation does not hold any longer: the original constants of motion, energy eigenvalues and eigenfunctions. cease to be such.

In going from the one-electron systems to the many-electron counterparts, the presence of the additional electron-electron Coulomb interaction breaks the respective O(4) and SU(3) symmetries. Upon confining them, there are additional symmetry breakings dependent on the characteristics of the confinement.

In the process of planning the writing of this contribution, the author has considered the alternatives of reviewing the field at large a la Jasholski, or following the example of the AQC and Monograph individual reviews. Given the time constraints of the invitation, the decision has been to make a conceptual and connecting review, which is intended to serve the readers as a guide to become familiar with the variety of works in the literature illustrating the progress in recent years; and also sharing the recent results of our own work, and the problems which we are currently investigating.

This article is organized as follows: Section 2.1 identifies some connections between the different reviews in AQC dealing with the same physical systems one-electron, two-electron and many-electron atoms, and harmonic oscillators, under the same or different confinement conditions, taking into account their respective methods of solution, and their results, on specific properties. Section 2.2 starts by analyzing the further advances in the common topics in the reviews of the Monograph and those of AQC, and goes on to the remaining four new topics. Section 3 includes a selection of references from the literature illustrating recent progress in the field, taking into account the novelty of the confined quantum systems, the confining environments and their modelings, the properties of such systems, and their connections with other fields of materials science. In Section 4, the Author updates the progress in his own and collaborators' works, and gives a preview on current investigations. Section 5 consists of a discussion on the reviewed recent progress.

2. Background Reviews

This section includes brief comments about the Reviews in AQC2009 and in the Springer Monograph 2014, in 2.1 and 2.2 respectively. The first set identifies the key concepts and methods in each Review, recognizing some connections and differences among some of the Reviews, thus establishing the points of reference and the threads guiding the writing and reading of this contribution. The second set follows the same ideas, connecting first the contributions with common topics or Authors from the previous set, and going on with the new ones.

2.1. Theory of Confined Quantum Systems 2009

This section identifies some common features and differences in the reviews in Advances in Quantum Chemistry [2-16] in order to illustrate the diverse ways of modeling and analyzing the confined quantum systems, and how the results on some of their properties compare. The identification follows the order of the references covering the atoms with increasing number of electrons. Their common features and differences are some of the elements to follow in the successive sections in order to recognize the further advances and recent progress.

2.1.1.

"Properties of Confined Hydrogen and Helium Atoms" [2] analyzes the solutions for the Schrödinger equation for the hydrogen atom confined in a spherical box with the boundary condition of vanishing at the radius of the box R, as well as the polarizability of the atom. In this way model wave functions are constructed for the entire range of $R \quad [0,\infty]$ interpolating between those of the free atom for $R \to \infty$ and those of the free electron in a box for $R \to 0$, providing energy eigenvalues. The concept of the critical radius for which the energy eigenvalue vanishes: $E(R = R_c) = 0$, and the eigenfunctions are spherical Bessel functions, is also analyzed and approximated with a WKB approach, and numerically illustrated by Eq. (3.58).

Table 1 provides a comparison of the energies of the confined hydrogen atom in the state $1s, 2s, 2p, 3p, 3d$ and the polarizability of the ground state from numerical calculations, model wave functions and the simple approximation of Eq. (3.39) for confining radii [.2,10]. The agreement between the first two entries is quite good for all states and radii, while the differences of the third entry increase as the radius is decreased and the excitations are higher.

The helium atom confined in a spherical box is analyzed in terms of the effective Hamiltonian of Eq. (3.65) using screening factors $S(R)$ depending on the radius of confinement, and also interpolating between its asymptotic and small values for the states $(1s^2)\,{}^1S$, $(1s2s)\,{}^3S$, $(1s2p)\,{}^1P$ and $(1s2p)^3P$. Table 2 illustrates the results for the energies from Eqs. (3.72), (3.77) and (3.79), respectively, for $R = [1, 6]$, reported previously by the authors, compared with those of high accuracy from its Refs. [29] and [39].

There are also two sections on the hydrogen atom, centered in a sphere and at a focus in prolate spheroidal coordinates, confined by a centered harmonic oscillator potential, respectively.

2.1.2.

"Exact Relations for Confined One-Electron Systems" [3] deals with the spherical confinement of the hydrogen atom in Sections 1-6, the isotropic harmonic oscillator in Section 7, and information theoretical uncertainty-like relations in Section 8. Its bibliography is very detailed and complete, proving very useful for the reader. Additionally, some of its results are very graphical and their validity goes beyond the specific topic. Since its Section 2 has a good overlap with the previous chapter, we go on to its Section 3 on "Commutation Relations and Hypervirial theorems". In order to connect some of the basic concepts, we start by pointing out the difference between the boundary conditions of the Dirichlet, Neumann and Robin types of vanishing wavefunction, vanishing normal derivative of the wavefunction and logarithmic derivative of the wavefunction equal to a real-valued function $P(\vec{r})$, respectively; the last one becomes the second one for $P = 0$, and the first one in the limit $P \rightarrow \infty$. Also, the energy functional defined in Eq. (2.1) as the matrix element of the Hamiltonian between an initial state ψ and a final state φ includes a surface integral term involving P and the same functions. While the constants of motion commute with the Hamiltonian, a dynamical quantity $\hat{A}$ not commuting with the Hamiltonian, leads via their commutator $[H, A] = B$ to another dynamical quantity, $\hat{B}$. The virial theorem is generalized to hypervirial theorems when the expectation value of B is calculated and the proper boundary conditions of the eigenfunctions are taken into account. The section under consideration goes on to consider scaling transformation and to obtain the Kirkwood-Buckingham relation, including illustrations of their applications. Sects 4) "Energy and Region Modifications", 5) "The system in an external potential", and 6) "On Mean Values and Other Properties of Confined Systems" illustrate specific results for the different properties of the confined systems for the different conditions of confinement.

Section 7 explains the degeneracy of the confined D-dimensional harmonic oscillator and also the density at the equilibrium point as investigated in its Ref. [105]. From the properties of the confluent hypergeometric functions, the interdimensional state degeneracy under the transformation given by $(n, \ell, D) \rightarrow (n, \ell \pm 1, D \mp 2)$ can be also established.

Section 8 defines the one-electron Shannon information entropy S_r of the electron density in coordinate space, and the corresponding momentum space entropy S_p, respectively. A stronger version of the Heisenberg uncertainty principle was derived in its Ref. [109]. The total entropy as the sum of $S_T = S_r + S_p$ in D-dimensions is larger than or equal to $D(1 + \ln\pi)$ according to its Ref. [110]. Figure 5 illustrates $S_T(R)$ versus R for the confined hydrogen-like atoms.

2.1.3.

The hydrogen atom confined in semi-infinite spaces limited by Conoidal boundaries [4] is different from the other chapters in the open versus closed regions of confinement and the respective boundaries of confinement. As already mentioned in the Introduction, most of the chapters deal with confinement inside a sphere or spheroid, and one of them in a semi-infinite space with a plane boundary. This chapter reports on a series of works with paraboloidal, hyperboloidal, and circular conical boundaries confining the hydrogen atom. The review led to recognize the complementary possibilities of confinement by dihedral angles and by elliptical cones. Exact solutions of the Schrödinger equation in spherical, spheroidal, paraboloidal and spheroconal coordinates for the free hydrogen atom are known; the presence of the natural boundaries with a fixed value of the respective coordinates lead also to exact solutions for the hydrogen atom confined in the corresponding closed or open space. The latter exhibit symmetry breakings in comparison with the free system; the confinement by open boundaries has served to study surface effects on atoms and molecules.

2.1.4.

"The Hydrogen and Helium Confined in Spherical boxes" [5] overlaps in contents and methodologies with the previous chapters. Here we emphasize the review of the complementary methods of solutions and the higher accuracies attained in the numerical calculations. Its bibliography is also very complete and recommendable. For the hydrogen atom the exact solutions are products of the factors removing the singularity at the origin and at infinity, and the regular Kummer hypergeometric functions. Perturbation theory for very small boxes using the free particle confined in a spherical box as the non perturbed system and the nucleus-electron Coulomb energy as the perturbation leads to a series of powers of the confining radius for the energy of the ground state. The method of linear variational functions applied in its Ref. [12] uses the superposition of ns hydrogen orbitals with $n = 1, 2, 3$ imposing the boundary condition that the eigenfunction vanishes at the radius of confinement; the author himself in its Ref. [13] used the basis of the spherically confined isotropic harmonic oscillator; he also reports the variational boundary perturbation theory, on its Ref. [86], using B-splines functions. Other variational methods include the variational boundary perturbation theory Refs. [14,15], and variational trial functions with a linear cut-off factor ($r = r_0$) in order to satisfy the boundary condition [16-18].

Concerning the increasing accuracy of the computed results, Tables 5-8, Figs 1-2, with their associated discussions and references are very illustrative and impressive.

The investigations on the helium atom confined in a spherical box started fifteen years later after those on the hydrogen atom. Ref. [49] did it by using a Hylleraas trial wave function for the ground state $(1s)^2$, and Refs. [101], [103], [105], [108], [117] and [118] followed in the successive decades. Table 10 illustrates the comparison of their respective results for $R[2,7]$ and the free atom. The last two References also included the lowest triplet state 1^3S, Ref. [105] was one of the pioneering applications of the Diffusive Monte Carlo type, including those for H^- and Li^+. Correlation energies could also be evaluated by comparing with the Hartree-Fock results in Refs. [102], [104], [16], [18], and others illustrating simple variational calculations.

2.1.5.

"Exact solution for Confined Model Systems Using Kummer Function" [6] shows applications to the hydrogen atom in 3 and 2 dimensions, and to the Harmonic Oscillator in 2 dimensions; as well as to the constant potential, for the free particle inside an impenetrable spherical wall, and for the exterior solutions for soft confinement. Section 2 presents the different forms of the Kummer confluent hypergeometric functions in their M and N forms, regular near the origin and in the U form regular at infinity; including their relationships Eq. (20), other alternatives Eq. (23), for the first two; and also the last one, Eq. (41) and its alternatives Eq. (58). The derivative of M Eq. (19) and that of U Eq. (43) lead to the same type of functions with their parameters shifted by one unit are also important. The analysis of the exceptional solutions, and the examples of taking the limits to arrive at two independent solutions Eqs.(39) and (40), are also illuminating. The applications to the K-dimensional hydrogen atom in its free configuration lead to its polynomial eigenfunctions and eigenvalues Eqs. (65) and (66), and likewise for the harmonic oscillator, Eqs. (70). In the case of the constant potential, the situation for the solution in Eq. (73) is different, because the M function does not truncate for the good behavior at both $r \to 0$ and $r \to \infty$, however, for the example of the potential confined in the interval $[0, R]$, the eigenfunctions and eigenvalues follow from the solutions of Eq. (74) for M.

Section 3 defines the confinement in terms of boundary conditions, including examples of exterior confinement, Eqs. (75) and (76). Another exterior confinement with reduction of the dimensionality of the system, Eq. (77), describes a 3-dimensional system which is separable in its transverse and axial components, Eqs. (78) and (79); the transverse potential $V(x, y)$ confines the electron to the interval $0 < z < R$, and the solutions of Eq. (78) via its eigenvalues λ convert Eq. (79) into that of the one-dimensional hydrogen atom. The removal of the singularity at infinity in Eq. (80), with the changes of the parameters and variable of Eqs. (81) leads to the Kummer equation of Eq. (82) [TYPO CORRECTION: second derivative with respect to u], with $a = -1/\alpha$, $b = 0$.

The boundary condition of $\phi(r = 0) = 0$ cannot be satisfied by M, but N in Eq. (83) using Eq. (20) does. The other boundary condition of vanishing at $r = R$ leads to Eq. (84), from which α and the energy eigenvalue can be evaluated. For the free atom, the series must truncate and the eigenenergy with integer quantum numbers of Eq. (86) are obtained. The interior confinement involves a short range potential for $0 < r < R$ and a Coulomb potential for $R < r < \infty$, with the matching of the interior solution and the asymptotically well behaved hydrogenic wave function involving the U Kummer function and their derivatives at the boundary.

Sections 4, 5 and 6 give examples of the different confinements for the successive potentials.

2.1.6.

"Perturbation theory for a Hydrogen Atom Confined Within an Impenetrable Spherical Cavity" [7] is implemented for large, small and intermediate values of the radius of the cavity evaluating accurately the energies, oscillating strengths, dipole polarizabilities and nuclear shielding factors for the different eigenstates. The asymptotic expansions for the energy, Eqs. (24), for the eigenfunctions in terms of the oscillator strengths, Eq. (28), were developed by the Author in its Ref. [25]. Table I shows the comparison of the precise numerical and asymptotic values of the energies of the states 1s, 2s and 2p for [4,40], illustrating their improved agreement for larger radii. On the other hand, the same Author in its Ref. [31] obtained expressions for the oscillator strength f_{1s-2p}, the ground state polarizability, Eqs. (29)-(30), and the nuclear shielding factor, Eq. (31). Tables 2 and 3 report these asymptotic values compared also with precise numerical values and others by authors dealing with the same topics in the previous subsections 2.1.1, 2.1.2, 2.1.4 and 2.1.5, and its Refs. [12], [29], and [33-37]. The small size boxes are based on perturbation theory taking the free electron in the spherical box as the unperturbed system and the nucleus electron coulomb energy as the perturbation Tables 4, 5, 6 show the comparisons of the small-box perturbation and precise numerical energies for the ns, np lower energies and for the 3d, 4d, 5d and 4f, 5f, 6f eigenstates for the successive ranges of the confining radius and the respective estimated radius of convergence. Table 7 shows the perturbation theory expansion coefficients for the expansion of energies in powers of the confining radius for the 1s, 2p, 3d, 4f and 5g levels to order 31.

We go on to discuss the intermediate box size perturbation theory implemented around the radial nodes of the free hydrogen atom radial eigenfunctions. The Author in its Ref. [25] derived the first order approximations to energy of Eqs. (89)-(91) in the vicinity of the indicated radius. Higher order corrections can naturally be also evaluated, as illustrated by Eqs. (98)-(99). Correspondingly, Eqs. (100)-(101) give the corresponding expansions for the polarizabillity and nuclear shielding factors, and Tables (14) and (15) illustrate their numerical values, compared to precise values for the different radius of confinement.

2.1.7.

"Comparative Study Between the Hartree-Fock and Kohn-Sham Methods for the Lowest Singlet and Triplet States of the Confined Helium Atom" [8] investigated the same physical system and states as in 2.1.4, in two alternative formalisms. Section 2 contains the basic Hartree-Fock equations for the energy of the helium atom in its ground state, considered as a close-shell system, and for its first excited state considered as an open-shell system with the difference that the latter contains the additional exchange integral contribution. The Kohn-Sham (K-S) equations are also presented for the respective states, and with the choice of the OEP-KLI exchange-correlation functional for the open shell system. The Hartree-Fock (H-F) and K-S Eqs. (15) and (18) for the closed-shell system are the same. The corresponding comparison of Eqs. (17) and (19) for the open-shell system shows a difference. The results of the Table II of a previous work, in the common Ref. [19] here and [117] in 2.1.7, show that for the closed-shell system there are discrepancies between the HF and KS-SIC-OEP-KLI methods. The aim of [8] is two-fold: 1) recompute the ground state results by using an optimized basis set and 2) compute the lowest triplet HF state by the HF method, and compare its results with those of the KS method. In this way a reliable comparison between HF and KS is made for the confined He atom in both states.

Table 1 shows the total energy and the exchange energy for the singlet state as functions of the confining radius in KS-LDA, KS-LDA-SIC and HF including a comparison for the latter in Ref. [4]. The comparison of the respective entries in the last three shows a fairly good agreement among them, while those of the first one are different in the first decimal figures.

Table 2 shows the correlation energies estimated as the difference between the precise values of the energy, based on wave function expanded in a 40 Hylleraas basis set, and the HF energies of this work and its Refs. [30] and [31], as functions of the confining radius. The first two entries show that the correlation energy does not show appreciable changes in the third decimal figure. The Authors conclude that these results can be used as bench marks for other correlated methods.

Table 3 contains the corresponding results for the confined helium atom in the lowest triplet state. Their respective entries differ significantly compared with the ground state.

The Authors conclude that this work shows the importance of exponent optimization in the Roothan approach to solve the H-F equations for the singlet and triplet ground states of the confined helium atom. The comparison of the HF results and the KS-SIC-OEP-KLI results exhibits that the latter is inadequate for the description of the unpaired electrons.

2.1.8.

"Thomas-Fermi-Dirac-Weizsäcker Density Functional Formalism Applied to the Study of Many-electron Atoms" [9] provides references on calculations using ab-initio Hartree-Fock [67,63] and Dirac-Fock [61] procedures, density functional theory [4,60] and Thomas-Fermi-Dirac-Weizsäcker (TDFλW) statistical atomic model [64,65], for confined atoms. The first three have been restricted to confinement in a spherical box with an impenetrable wall, while the fourth one has been applied also to spherical boxes with penetrable walls, prolate spheroids with impenetrable walls, and an open space with a plane hard wall boundary. Section 2 describes the details of the calculations for confinement by closed boundaries with illustrative results for different atoms: 1) Spherical hard box. Figure 2 for ground state energy of Neon versus HF values [4] in very good agreement. Table 1 for Carbon and Neon, also compared with [4], and values reported in [64] including values of optimized orbital parameters ζ_{1s}, ζ_{2s} and ζ_{2p}. For oxygen, neon, silicon and germanium ground state energies in Table 2 and Figure 3. 2) Soft spherical box involving a constant potential for radial distances larger than the radius of confinement. For neon confined by barrier of height $V_0 = 0$ and selected values of confinement radius Table 3 reports the ground state energy and orbital parameters compared with the results of [65] using exact electron-electron interaction versus Poisson solution. This type of confinement allows the escape of the electrons through the box when the energy equals the height of the barrier [46,65]. Table 4 shows the corresponding informations for oxygen, silicon, and germanium for a barrier of height $V_0 = 1$. 3) Hard prolate spheroidal box. Figure 5 illustrates the ground-state energy for the helium atom confined in such a box when the nucleus occupies the position of a focus, as function of the volume of the box. Tables 5 and 6 show the information for the ground states of the carbon and neon atoms in the corresponding situations of confinement as functions of the eccentricity parameters and different focal distances.

Section 3 deals with the confinement in the presence of a plane hard wall boundary using prolate spheroidal coordinates, corresponding to the equatorial plane $\eta = 0$, for an atom with its nucleus placed at one focus. Results for the carbon, neon and helium are illustrated in Figs 6-10 and Table 7 including discussions in the text and comparisons with results in Refs. [46,75]. This model is important for the atom-surface interactions.

2.1.9.

"Confined Atoms Treated as Open Systems" [10] is conceptually methodologically, and content-wise different from the other chapters. The system of interest is bounded by surfaces it shares with the atoms of the confining material: matter and momentum can be transfered across the surfaces. This is a problem of quantum mechanics of a proper open system Ω bounded by a surface $S(\Omega;\vec{r})$ of zero flux gradient vector field of the electron density, Eq. (1). This approach takes into consideration the interaction of the system of interest with its environment; to what extent are the exchanges in the pressure volume product of the open system mediated by changes in the atoms of the confining surfaces? The gradient vector field of the electron also provides a definition of the structure in terms of both paths, lines of maximum density linking neighboring atoms. Thus, the open system approach deals with the structure of the system and of its interactions with the surrounding, and these change with changes in the pv product. Section 2 describes the mechanics of an open system, defining the properties of an open system Ω by Heisenberg's equation of motion obtained from the variation of the state vector within the system and on its boundaries, as determined by Schwinger's principle of stationary action. Equations (2), (3) and (4) apply for a stationary state, describing the motion for an observable $\hat{G}$, the current for property G and its density property, respectively. Section 2.1 deals with atomic expressions of the Ehrenfest and virial theorems for the observables $-i\hbar\nabla$ and $\vec{r}\cdot\vec{p}$, respectively. The commutator of the Hamiltonian and the momentum yields $-\nabla_R V$ which is the force $\hat{F}$ exerted on an electron at $\vec{r}$ by the other electrons and by the nuclei at fixed positions. Equation (5) gives the expectation values of the force as the negative of the surface integral of the momentum density or stress tensor of Eq. (6). In turn, the commutator of the virial operator yields twice the atom's electronic kinetic energy $T(\Omega)$ plus the virial of the Ehrenfest force exerted over the basin of the atom $\nu_b(\Omega)$. In a stationary state these contributions are balanced by $\nu_s(\Omega)$, the virial of the Ehrenfest force acting over the surface atoms Ω. Equation (7) is the virial theorem in terms of the total virial for the atom as the sum of $\nu_s(\Omega)+\nu_b(\Omega)=\nu(\Omega)=-2T$. Equations (8) and (9) are the expressions for the atom and surface virials as the respective integrals of the force and the stress tensor. Equations (10) and (11) are the local forms of the virial theorem and the virial field. Equations (21) and (22) describe the expectation value of the pv operator and its proportionality with the surface virial respectively.

Section 4 deals with calculations of the pressures in terms of the surface virial. Calculation of the pressure in terms of the surface virial is illustrated in 4.3 for atomic pressures in diatomic molecules, 4.4 pressure exerted on atom confined in adamantane cage and 4.5 compression of hydrogen molecules in a neon vise.

In 4.3 the diatomic molecules N_2, CO and LiF cover the range from shared, polar and ionic bonding, respectively. The pressure exerted by A on B is determined by the nature of the interatomic surface which is characteristic for shared, polar and ionic interactions. Figure 1 illustrates such surfaces for the respective molecules in the ground state, the electron density distributions and the bond paths. The paraboloidal surface in LiF is characteristic of an ionic interaction, the combination of a small paraboloidal and plane surfaces in CO of a polar interaction, and the plane surface in N_2 of a shared interaction. Each interatomic surface intersects the bond path at the position of the bond critical point. The classification of the interactions is based on the values of the electron density and its Laplacian at the bond critical point. For shared interactions $\rho(\vec{r}_c)<0.2$ and $\nabla^2\rho(\vec{r}_c)<0$, while for the closed-shell interactions $\rho(\vec{r}_c)<2$ and $\nabla^2\rho(\vec{r}_c)>0$ and is small in values as are the individual curvatures. The polar interaction occurs in systems with significant charge transfer in which the donor atom retains nonbounded valence density. Thus $\rho(\vec{r}_c)>0.2$, as for the shared interactions, and $\nabla^2\rho(\vec{r}_c)\rightleftharpoons 0$ for the polar interaction. Because of the remaining valence density in the donor atom, this interatomic surface does not follow its initial paraboloidal shape found in the region of the donor core, as significant of a large charge transfer, but instead straightens out as a plane characteristic of a shared interaction.

Table I gives the properties for the AB representative molecules: binding critical point charge of A, surface virial of A and B, volumes of A and B, and pressures of A and B. Data for the diatomic hydrides AH ground states, A=Li, Be, B, C, N and F are illustrated in Fig. 2. The zero-flux interatomic surfaces with the proton at the fixed position labeled H. The bond critical point for Li is located 1.67 a,u, from the proton, and are increasingly smaller for the other atoms. Table 2 illustrates the same properties as in Table 1. Figure 3 contains the atomic pressures for the successive molecules; the highest one on H is in BH. Data for the diatomic fluorides AF (A=Li,Be,B,C,N,O) in the ground state are shown in Fig.4 for the atomic pressures in the successive molecules; the highest one on F is in the polar molecule CF. Table 3 illustrates the same data as Tables 1 and 2 for the fluorides.

In 4.4 data on atoms and ions $\mathrm{X}=\mathrm{He},\mathrm{Be}^{+2}$, Li and Ne inside an adamantane molecular cage $C_{10}H_{16}$, represented as $X@C_{10}H_{16}$ and designated as complexes are illustrated in Fig. 5 and Tables 4-9. In the Figure molecular graphs for the cage and for the complex with $X=$ He are shown side by side. The atom is shown encased by its four interatomic surfaces. In the cage, a methine carbon is labeled C1 and its bonded H by H1; a methylene, carbon is labeled C2 and its two bonded atoms H2. Critical points are represented by dots: red for bond, yellow for ring and green for cage. The reader may appreciate the changes due to the presence of the confined helium atom and its interactions. Table 4 illustrates the pressure acting on the atom X in the complex and the associated energy change for the successive atoms, including their values of the volume, the surface virial, the pressure and the changes in the basin virial and in the energy. Table 5 illustrates the atomic pressures on C1, C2, H1 and H2 in adamantane together with the values of their volume and surface virials. Tables 6, 7, 8 and 9 give the changes in the adamantane atomic properties in forming the successive complexes for C1, C2, H1 and H2 with the values of $\Delta N(\Omega),\Delta E(\Omega),\Delta\nu(\Omega)$ and $\Delta P(\Omega)$. The reader may follow the discussion of these results in the text.

In 4.5 The system used to introduce the quantum definition of pressure consists of a linear chain of hydrogen molecules compressed between a pair of Ne atoms. Figure 7 illustrates the case of five H_2 molecules for the Ne$|H_{10}|$Ne vise, showing contour maps of the electron density at pressures of 2.6, 73 and 123 GPa; the intersections of the interatomic surfaces with the plane of the diagram are shown for the left half of each molecule, as are the atomic interaction lines. There is a (3,-1) critical point in the density at each intersection of an interaction line with an interatomic surface. The indicated structures are invariant to an increase in the pressure.

2.1.10.

"Modelling Pressure Effects on the Electronic Properties of Ca, Sr, and Ba by the Confined Atoms Model" [11] uses the confinement inside a sphere with an impenetrable wall and the spin-polarized version of Density Functional Theory. The methodology described in Sec. 2 covers the pressure as the negative rate of change of the total atomic energy with respect to the volume, Eq. (2), and the SP-DFT framework, in which the total energy changes according to its dependence on the number of electrons N and the spin number N_s as the natural variables, Eq. (3). For the atoms under consideration, in the free configurations there are singlet-triplet transitions for the valence electrons s^2, and in the transition the two electrons are unpaired to produce the triplet. However, the number of electrons is unaltered $\Delta N = 0$ in the process. In Eq. (3) only the term ΔN_s is important and its coefficient in Eq. (4) is the spin potential μ_s expressed as the partial derivative of the energy with respect to N_s for N and v fixed Eq.(5), where v is the external potential. The change in the spin number is $\Delta N_s = 2$, and $\Delta E = 2\mu_s$, Eq. (6). Ref. [32] gives the μ_s^+ for the increase of the spin as half the difference of the energies of the Lowest Unoccupied α Molecular Orbital and the Highest Occupied β Molecular Orbital, leading to a change of energy expressed by that difference. The Perdew-Wang exchange correlation functional of Ref. [33] in the LDA [34] is used in this work. The results are presented and discussed in Sect.3 under the following headings:

1) *Transition pressures for Ca, Sr and Ba*. Figure 1 illustrates the orbital energies $3p$, $3d$ and $4s$ for the confined Ca atom decreasing as functions of the increasing radius of confinement, the last two ones show a crossing around $R = 5$. Figure 2 gives the total energy as a function of the pressure for the confined Ca atom in the configurations [Ar]$4s^2$, [Ar]$4s^1 3d^1$ and [Ar]$3d^2$ with successive crossings among them between 80 and 100 GPa, showing that the ordering of the configurations change with pressure. The free energies G are displayed in Fig.3 for the respective electronic configurations. Table 1 displays the transition pressures for Ca, Sr and Ba for their most stable configurations in the intervals of the decreasing confinement radii, their multiplicities, and the comparison with experimental values from Refs. [14] and [15]. The comparison is favorable for Ca, but not for the heavier atoms.

2) *Electronic transitions as functions of pressure*. According to Fig. 3 the possibilities of excitations energies are three: $5s^2 \to 5s^1 4d^1$, $5s^1 4d^1 \to 4d^2$, $4d^2 \to 5s^1 4d^1$. Figure 4 illustrates their pressure dependences for low and increasing pressures, respectively. Table 2 reports the values of the spin-potential μ_s^+, the LUMO$^\alpha$-HOMO$^\beta$ gap and the singlet-triplet excitation energy for Ca, Sr and Ba as functions of the confinement radius. Figure 5 is the plot of ΔE versus μ_s^+ exhibiting fairly linear relationships.

2.1.11.

"Photoionization of Atoms Encaged in Spherical Fullerenes" [12] discusses in its Section 2 The Modeling of Doped Fullerenes. In its first subsection on Preliminaries, it is explained that the atom is confined with its nucleus at the center of the cage and that the radius of the cage is significantly larger than the radius of any $n\ell$ subshell of the ground state of the atom. Thus, to a good approximation, the ground state encaged atom is only perturbed insignificantly by the cage: both the atom and the cage preserve their respective structures. Furthermore, when the wavelength of the $n\ell$ photoelectron significantly exceeds the bond length between the atoms of the C_n cage, the latter can be replaced by an effective spherical, attractive, continuous, homogeneous medium acting on the photoelectron. For this, the $n\ell$ photoelectron must be slow, corresponding to near threshold $n\ell$ photoionization of the encaged atom. Thus, the slow photoelectron will perceive the fullerene cage as an unstructured semi-transparent spherical shell that generates a reflected electronic wave inside the sphere and a transmitted wave outside.

On the other hand, the cages may be neutral, charged or multilayered. Their following subsections describe modelings, successively.

2) *The $\Delta-$potential model: Neutral doped fullerenes $A@C_n$*. In this case, the cage is modeled by a spherical, short-range, attractive potential of depth -U_0 for $R_n < r < R_n + \Delta$, and zero otherwise. This model has been applied for noble gas atoms and group-V atoms, fulfilling the conditions of being centered in the cage without any charge transfer. The Van der Waals forces are responsible for the atom occupying the centered position. Since those forces are very weak compared to the Coulomb forces, they do not alter the ground state wave function of the encaged atoms appreciably. Electronic wave function and binding energies of the N electron encapsulated atom are obtained by incorporating the Δ-potential into the HF equations for the free atom. The orbital radial functions must satisfy the boundary conditions of continuous logarithmic derivatives at $r = R_n$ and $r = R_n + \Delta$. The parameters U_n and R_n are described for n=60, 240, 540 , and the thickness parameter Δ is determined by the carbon atom, taking a common value.

3) *The $\Delta-$potential model: charged doped fullerenes* $A@C_n^{\pm Z}$ combines the potential in 2) and adds the electrostatic potential of the charged shell, assuming that the extra charge Z is evenly distributed over the entire outer surface of C_n, turning out to be constant $Z/(R_n + \Delta)$ inside $0 < r < R_n + \Delta$ and Coulombic Z/r outside.

4) *The $\Delta-$potential model: multiwalled doped fullerene onions*. For neutral doped fullerene onions A@C^{60}@C^{240}@C^{540} the confining potential is the superposition of those of the single-well potential

$$V_n \rightarrow \text{a}V_{60} + \text{b}V_{240} + \text{c}V_{540} + ... \qquad (1)$$

with a, b, c,...either 1 or 0 for the successive layers.

5) *The $\delta-$potential model of single-walled doped fullerenes* was initially developed in photoionization studies of A@C$_{60}$ involving a Dirac delta function at the radial position R_c. It is also the limiting situation of the Δ potential with $\Delta \rightarrow 0$, ignoring the thickness of the carbon cage. The model is applicable only to the deep inner subshells of the encaged atom. The role of the carbon atoms is only to modify the radial part of the electronic wavefunction in the continuous state with the orbital quantum number ℓ and electron momentum with the proper boundary condition at $r = R_c$. The results are manifested as phase shifts.

2.1.12.

"Spectroscopy of Confined Atomic systems: Effect of Plasma" [14] reviews the experimental techniques, Theoretical Development, Interpretation of Spectral Properties and Atomic Data of atoms under Liquid Helium. In the Introduction it is recognized that atoms or ions embedded in a plasma also form a class of confined systems. Their atomic structural properties may change drastically depending on the coupling strength of the plasma with the atomic electrons.

The coupling constant of a plasma is defined as the ratio of the average Coulomb energy to the average kinetic energy of the plasma particles. For plasma particles obeying classical statistics, the average kinetic energy per particle is kT in terms of Boltzmann's constant and the temperature. For a one-component plasma with N particles in a volume V, the characteristic volume V/N is that of a sphere with the so-called ion-sphere radius or Wigner-Seitz radius a. The Coulomb energy per particle is $(Ze)^2/a$. Equation (1) gives the coupling constant for the plasma obeying classical statistic, proportional to the square of the particle charge and to the cubic root of the density, n, and inversely proportional to the temperature. Typical examples of weakly and strongly coupled plasmas are characterized by $\Gamma < 1$ and $\Gamma \approx 1$ to $>> 1$, respectively, with their (T, n) corresponding values.

Concerning the theoretical modeling of the plasmatic confinement in the respective coupling limits, Eq. (10) describes the Debye screening model potential as a Coulomb potential with an exponentially radial decreasing factor, and Eq. (17) the ion-sphere model for the interaction of an ion with a bound electron as the superposition of the electron-nucleus Coulomb energy and the electron-(Z-1)electron charge uniformly distributed in the volume of a sphere of radius a electrostatic repulsion energy.

2.1.13.

"The energy level structure of Low-dimensional Multi-electron Quantum Dots" [15] reviews the Computational Methodology, Quasi-one-dimensional Quantum Dots and Quasi-two-dimensional Quantum dots investigations.

In the Introduction, Quantum dots are identified as confined quantum systems of a finite number of electrons bound in a fabricated nanoscale potential, 1-100 nm, with a discrete energy-level structure following Hund's rules. Their properties can be changed by controlling the size and/or shape of the fabricated potential. The energy-level structure and optical properties of quantum dots and atoms are qualitatively different because of the differences in their respective confining harmonic and Coulomb potentials, apart from their sizes and dimensionalities.

The computational methodology based on the quantum chemical molecular orbital theory allows the calculations of the ground or low-excited states of multielectron quantum dots for a specific value of the strength of the confinement. The results vary depending on the strength of the confinement, due to a strong variation of the relative importance of the electron-electron interaction with respect to that strength; consequently, it is necessary to develop a unified method of interpreting the complicated energy-level structure of quantum dots for the whole range of the strength of confinement.

Previous studies allowed the identification of the polyad quantum number, defined by the total number of nodes in the leading configuration of the configuration interaction, CI, wavefunction, as approximately conserved for harmonic oscillator quantum dots.

In the present contribution the interpretation of the energy-level structure of quasi-one-dimensional quantum dots of two and three electrons is reviewed in detail by examining the polyad structure of the energy levels and the symmetry of the spatial part of the CI wave functions due to the Pauli principle. The interpretation based on the polyad quantum number is applied to the four-electron case, and is shown to be applicable to the general multi-electron cases. The qualitative differences in the energy-level structure between quasi-one-dimensional and quasi-two-dimensional quantum dots are briefly discussed by referring to differences in the structure of their internal space.

2.2. Electronic Structure of Quantum Confined Atoms and Molecules 2014

In this section, the further advances in the period 2009 to 2014 are illustrated by connecting and comparing the respective pairs of reviews [1-18], [4-17], [5-19], [2-20], [11-24] with common coauthors on related topics; and also by describing and analyzing the other reviews in the monograph [21-23], [25].

2.2.1.

"Surface Effects in the Hydrogen Atom Confined by Dihedral Angles" [17] presents the updating of [4], reporting mainly the results of the described confinement which is illustrated here in two parts: with the titles of the articles reviewed in its Section 2, and its main body in Section 3 on the topic of the title.

In fact, its Refs. [20] *Comment on the electron in the field of an electric dipole moment*, [21] *Ground-state energy shift of He close to a surface and its relation with the scattering potential: a confinement model*, [22] *The hydrogen atom in a semi-infinite space with an elliptical cone boundary*, [23] *Lamé spheroconal harmonics in atoms and molecules*, [24] *Rotations of asymmetric molecules and the hydrogen atom in free and confined configurations*, [25] *Ladder operators for Lamé spheroconal harmonic polynomials*, [26] *Ladder operators for quantum systems confined by dihedral angles*, [27] *Complete pure dipole spheroidal electrostatic fields and sources*, [28] *Surface current distribution on spheres and spheroids as sources of pure quadrupole magnetic fields* were reviewed in Sections 2.1-2.5, illustrating further advances previewed in [4].

The exact solutions for the hydrogen atom confined by dihedral angles were constructed in spherical, prolate, spheroidal and parabolic coordinates. The energy levels share common degeneracies identified in Sect. 3.1 and illustrated in Table 1 in terms of the respective quantum labels of their eigenstates (n_r, n_θ, μ), (n_ξ, n_η, μ) and $n_u, n_v, \mu)$, as functions of the confining angle. The O(2) symmetry breaking is manifested in several effects: Sec. 3.2 In each state, the atom acquires and electric dipole moment. Sec. 3.3 The electron exerts a pressure distribution on the confining plane meridian defining the dihedral angle. Sec. 3.4 In the hyperfine structure, the Fermi contact interaction vanishes; and the anisotropic quadrupole contributions, axial is μ-dependent, and the transverse one is μ and ϕ_0 dependent. Sect 3.5 The Zeeman effect must be dealt with degenerate perturbation theory, and was not implemented for lack of time.

2.2.2.

"Symmetry Reduction and Energy Levels Splitting of the One-Electron Atom in an Impenetrable Cavity" [18] is methodologically connected with [3]. The Reviewer singularized this chapter since the Introduction to illustrate the ideas of superintegrability and symmetry breaking. Here we elaborate some more on the basic idea of symmetry, which in quantum phenomena manifests itself in the degeneracy of the eigenstates with a common eigenenergy; correspondingly, the reduction of the symmetry leads the reduction of the degeneracy with the consequent splitting of the energy levels. Concerning the confinement in polyhedral cavities, the reader's attention is directed to: Sect. 2.3, Fig. 1 Energy levels for hydrogen at the center of the cavity formed by joint symmetrical truncation of both the cube with the edge of $4au$ and the octahedron; and Fig. 2 Energies of isotropic harmonic oscillator with the force constant $k = 1$ placed at the center of the tetrahedral cavity with the edge $5.65au$ $(\chi = 0)$ truncated to octahedron $(\chi = 0.5)$. Sect. 4.2 Table 2.1 Energy splittings of the hydrogen atom states with $n = 3$ in some large polyhedral cavities: Cube, Octahedron and Tetrahedron. Sect. 5.4 The polyhedral deformation of the sphere into the family of cube, octahedron and tetrahedron cavities, Eqs.(45)-(46), illustrated by Fig. 4 in solid lines, and the state 3d in the tetrahedrons in dashed line.

2.2.3.

"The Confined Hydrogen Atom Revisited" [19] is connected with the first part of [19], and the second Author describes the first one as a continuation of the second. It is based on two of their own recent References, reviewed in Sec. 3 *Variational and Perturbative Treatments of the Confined Hydrogen Atom with a Moving Nucleus*, and in Sec. 4 *Shannon and Fisher Entropies for a Hydrogen Under Soft Spherical Confinement*, illustrating the elements of the novelty in their respective contents.

In Sec. 3, the conclusions in the moving nucleus versus the fixed nucleus modeling are the following. The increase in the kinetic energy due to the moving nucleus is comparatively larger than the energy difference between the Coulomb interactions for each scheme and all the values of the confining radius. The average nuclear position compared with the average electron position is closer to the origin by a factor of 34% for $r_c = 0.1$ up to 67% for $r_c = 10$. As the confining radius increases the variational ansatz ψ, and average relative distances $< r >_{mov}, < r >_{fix}$ steadily approach the exact wave function and average electron-nucleus distances, respectively, corresponding to the free hydrogen atom. For all the values of r_c, the radial densities show that the nucleus remains close to the center of the cavity, due to its greater mass and localization. In contrast, the electron densities in both schemes are very similar to each other and for very small values of r_c the electron shows a free particle behavior.

In Sec. 4, the Shannon and Fisher entropies were calculated in the position (S_r, I_r) and momentum (S_p, I_p) spaces for the hydrogen atom spherically confined in soft and impenetrable boxes, and also the free particle inside an impenetrable sphere, as functions of the cavity radius r_c and the potential barrier height V_0. The entropies show a monotic behavior for the impenetrable boxes. In contrast, they show important changes for soft confinement over small radial intervals in the vicinity of $r = r_c$, reflecting the degree of the spatial charge localization associated with the potential V_0. The occurrence of negative values of the Shannon entropy in the position coordinate is explained on the grounds of a pronounced space localization, with its associated locally large density.

2.2.4.

"Variational Perturbation Treatment for Excited States of Confined Two-Electron Atoms" [20] is connected with the second part of [5], and [8]. The Authors report Hylleraass-Scherr-Knight variational perturbation theory (HSK-VPT) calculations of the energies of the 1s 2s ^1S and 1s 2s ^3S states of confined two-electron atoms ions for $Z = 1 - 4$. These are the first two excited states of the two-electron system and serve as bench marks for excited state calculations. The data reported in Table 4.2 and 4.3 support the hypothesis that HSK-VPT is a viable approach to the excited states in confined systems. Preliminary investigations of the 1s 2s ^1S and 1s 3s ^1S states indicate that the approach can be readily extended to higher excited states. The Authors also considered the extension of Knight's work to 3-10 electron atoms to their confined versions.

2.2.5.

"Confined Quantum Systems Using the Finite Element and Discrete Variable Representation Methods" [21] is a review of its Refs. [9,11,17,50,58,62,63,68,74,76,89,90,91,117,124] by the same Authors, in which they have developed and applied the methods in the title to a variety of quantum systems under different situations of confinement. Section 4 illustrates some of these specific applications showing numerical results matching favorably the most accurate in the literature.

4.1 *One-dimensional harmonic oscillator confined by a modified Wood-Saxon potential*, Eq. (5.27) and Fig. 1, was investigated in [11] in order to simulate the confinements in 1) The Zicovich-Wilson square tangential potential, Eq. (5.28) and in 2) A constant infinite barrier. The intensity and slope parameters of the Wood-Saxon potential are optimized to an optimum fit to the respective potentials, and the eigenenergies were calculated using 300 equality spaced points between [-5,5] and [-4,4] to build the Discrete Variable Representations. Table 1 shows the comparison of the results from [11] and [10], and Table 2 those fron [11] and those from [94] and [95].

4.2 *Confined Hydrogenic Atom/Ion*. This section illustrates of the theoretical and computational methodology based on the variational formalism for the bounded states and the p-version of the Finite Element Method, applied to the hydrogen atom confined in 1) an impenetrable spherical box and 2) in a C_{60} cage, and 3) hydrogen-like ions in plasmatic confinement.

1. This case was investigated in [9] and its results for the energies of the 1s and 3s states, respectively, as functions of the confining radius are illustrated in Table 5 compared with those by Varshni, Zicovich-Wilson, Saha, Joslin and Aquino, and in Table 5.4 compared with Varshni, Goldman and Aquino. Table 5.5 illustrates the results on the polarizability for the 1s state compared with those of Dutt, Banerjee, Saha and Laughlin.

2. The endohedral confinement of the hydrogen atom was modeled in [17] by adding a Gaussian potential attractive wall to the Coulomb potential, Fig. 5.6, fitting its parameters to approximate the potential of Connerade *et al* [15]. Figure 5.7 shows the energies of the 1s, 2s, 3s and 4s states of H@C$_{60}$ from the p-FEM calculations compared with those from [15], as functions of ω_0 in the Gaussian potential. Figure 5.8 displays the radial wave functions $n\ell$ from 1s to 4d for H@C$_{60}$ for $\omega_0 = 0.683$. Figure 5.9 shows the corresponding energies $E_{n\ell}$ as functions of ω_0.

3. The plasmatic confinement of ions is modeled by Debye exponentially screened Coulomb potential, Eq.(5.38), in the weakly coupled plasma $\Gamma << 1$; and with the ion-sphere model in the case of one component spatially homogeneous strongly coupled plasma $\Gamma \approx 1$. For a hydrogenic ion with a nuclear charge Z and a single bound electron immersed in a homogeneous plasma with electronic charge density n within a sphere of radius R such that exactly $Z - 1$ of the central positive charge is neutralized; the interaction potential is given by Eq. (5.39) as the superposition of the Coulomb energy $-Ze^2/r$ and the parabolically decreasing contribution $[(Z-1)e^2/2R][3-(r/R)^2]$ from the negative uniformly distributed charge. Results from [117] obtained with self-consistent FEM are illustrated in Table 5.6 for the ground state energy ($-E_{1s}$) for Ar^{17+} with different Debye parameter and screening radius for Temperature of 1 eV, and also compared with [19]. Figure 5.10 illustrates the energy levels, -E, against the radius R of the ion-sphere for the hydrogenic ion He$^+$ $n\ell = 1s$, 2s, 3s, 2p, 3p ,3d, and also the 1s without a surrounding.

Section 4.3 contains the results of the energy spectrum for two types of quantum dots: 1) an impurity located in a parabolic quantum dot, and 2) a two-electron quantum dot. The spectrum is computed using the DVR method.

1. The Hamiltonian includes the kinetic energy, the electron-nucleus Coulomb energy, the harmonic oscillator energy and a Wood-Saxon potential. Table 5.8 illustrates the optimized Wood-Saxon parameters and binding energies for the quantum dot using the DVR method [11] compared to Varshni's [118] exact values.

2. The Hamiltonian includes the kinetic energy and the harmonic oscillator potential for the two electrons confined in the quantum dot with an effective mass m*, and the Coulomb e-e repulsion in the medium with dielectric constant ϵ, Eq. (5.42). The motions of the center of mass and the relative one between the electrons

can be separated. The first one for the anisotropic confinement has the spectrum of Eq.(5.43) for the corresponding transverse and axial oscillators $|N, M, N_z\rangle$.

The relative motion equations (5.44-5.47) were solved in [50] using a variational scheme based on the DVR method, using the spherical harmonics and radial function expansions. The calculations included 30 spherical harmonics and 100 radial basis functions. The solutions for the latter were obtained from 2500 DVR basis functions equally spaced in appropriate intervals of the pairs of transverse and axial frequency parameters. The energy spectra have a precision of at least 6 significant digits.

For the isotropic case, the center of mass energy spectrum is degenerate, Eq. (5.48), with the combination $(2N + L + 3/2)$ of the radial N and angular momentum L quantum numbers.

Table 5.9 illustrates the three dimensional two-electron quantum dot energies for different values of the confining parameter and different configurations (NL,nl) from [50] based on DVR method and compared with results from [120]. Figure 5.11 illustrates the corresponding energy spectrum of the same two-electron quantum dot $E_{N,L,n,\ell}/\omega$ for $\omega = 0.1, 0.25, 0.5, 1.0$ and 4.0 compared with the degenerate spectrum without the electron-electron repulsion [50].

Figure 5.12 illustrates the relative motion energy levels of anisotropic two-electron quantum dots for $\omega_\perp = 0.5$ and $\omega_z = 0.1, 0.25, 0.5, 1, 4,$ also compared with the cases without the e-e repulsion, [50]. Figure 5.13 illustrates the total energies E_{NMN_z}, n, m, n_z for $\omega_\perp = 0.5$ and $\omega_z[.1, 1]$, including some of their crossings [50].

2.2.6.

"Bound and Resonant States in Confined Atoms" [22] is an investigation of the bound and autoionizing resonant states of two-electron Quantum Dots (QD) with He^{2+} impurity based on the Rayleigh-Ritz variational and complex-scaling methods, respectively. The Helium atom in the QD is modeled by confinement in a finite oscillator potential. Section 1. Introduction to the QD confinement discusses succesively the rectangular, harmonic oscillator, attractive Gaussian potential and in particular the Finite Oscillator (FO) potential $V_{FO} = -V_0(1 + kR)exp(-kR)$. Section 2. Theoretical Method includes 2.1 One-electron QD with the Schrödinger equation for the atomic impurity in the FO potential and a variational function expressed as a superposition of Slater-type orbitals. 2.2 Two-electron QD: Configuration Interaction Basis. The Hamiltonian is the sum of two one-electron QD Hamiltonians plus the electron 1 - electron 2 Coulomb repulsion energy. The trial wavefunction involves the antisymmetrization operator for the identical electrons, and the superposition of products of Slater-type orbitals, electron orbital angular momentum coupled states $|\ell_a, \ell_b, L, M\rangle$, and total spin eigenstates, $S(\sigma_1, \sigma_2)$. 2.3 Two-Electron QD: Hylleraas Basis. The Hamiltonian Eq. (6.16), and the trial wavefunction Eqs. (6.13-6.15), must be written in the Hylleraas coordinates $[r_1, r_2, r_{12}, \Omega_1, \Omega_2]$. 2.4 Complex-scaling Method transforms the radial coordinate $r \to re^{i\theta}$ with the corresponding changes in the Hamiltonian and each of its terms Eq. (6.18), as well as in the parameter $B' = Be^{i\theta}$ in the FO potential. Since both the CI-basis and the Hylleraas basis are not orthogonal, the eigenvalue problem appears in the form of the variational Galerkin approach, Eq. (6.20), involving both the matrix elements of $H(\theta)$ and the overlaps $\langle\Psi_i|\Psi_j\rangle$. The resonance poles are determined by finding the positions where the complex energy eigenvalues exhibit the most stabilized characters with respect to the changes in the rotational angle θ and the scaling parameter α Eqs. (6.23) leading to $E_{res} = E_r - (1/2)i\Gamma$.

Section 3 presents the succesive results and discussions. 3.1 *One-electron QD state*. 3.2 *Two-electron QD Bound states*. 3.3 *Two-electron Resonant States*. Section 4 contains concluding remarks.

2.2.7.

"Spatial and Shell-Confined One Electron Atomic and Molecular Systems: Structure and Dipole Polarizability" [23] investigates comparatively the confinement of the hydrogen atom in an impenetrable spherical box and in a spherical shell $(R_c, R_c+\Delta)$ potential, their counterparts for the hydrogen atom and the hydrogen molecular ion in an impenetrable spheroidal box and in a spheroidal shell potential, a well as for the hydrogen atom in a cylindrical cavity. The focus is on the energy levels and the static and dynamic polarizabilities of the confined systems as functions of the confining parameters. The methodology is based in B-spline expansions for the wavefunctions and the Variational Galerkin Approach. The solutions for the Schrödinger equation in the succesive geometries of confinement are constructed and applied for the evaluation of the respective polarizabilities.

The results are presented, illustrated and favorably compared with those in the literature in the following order. 3.1 *Electronic energies and polarizabilities of hydrogen molecular ion spatially and endohedrally confined in spheroidal boxes*. 3.2 *Energies and polarizabilities of endohedrally confined centered Hydrogen atom*. 3.3 *Energies of spatially confined centered hydrogen atom*. 3.4 *Energies of spatially and endohedrally confined off-center hydrogen atom*. 3.5 *Dynamic polarizabilities of spatially confined centered and off-centered hydrogen atom*. 3.6 *Energies and polarizabilities of cylindrically confined hydrogen atom*.

2.2.8.

"Density Functional Theory Applied on Confined Many-Electron Atoms" [24] is connected with [9] and [11], some of those connections allow us to concentrate here on Section 3 Modified Thomas-Fermi Model and Section 4 Kohn-Sham Model.

In Section 3 the starting point recognizes the unphysical divergent behavior of the electron density at the position of the nucleus in the Thomas-Fermi Model. The modification that Parr and Gosh proposed, Eq. (8.26) as a restriction in the minimization process, combined with the cusp condition on the derivative of the electron density and the electron density itself at the nucleus Eq. (8.27), lead to the well-behaved electron density of Eq. (8.28). The authors develop their own method to solve the equation in terms of the series expansion in Eq. (8.34). Table 8.1 shows the lower coefficients from their recurrence relations. Table 8.2 shows the values of the electron density at the nucleus for the noble gases $Z = 2, 10, 18, 36, 54, 86$ and their scaled values divided by Z^3, compared with those reported by Parr and Gosh using the iterative approach. The agreement is good to the fourth decimal.

In order to estimate the pressure according to the Slater and Krutter proposal, the Poisson equation is sufficient, and Eq. (8.41) expresses the proportionality of the derivative of $Q(\omega)$ with respect to $Q(\omega)$ at the surface of the sphere $\omega = \omega_c$, Fig. 2 illustrates the electron density at the confining spherical surface as a function of the confining radius for the noble gases in a log-log plot. The description of Fig. 3 is not clear for this Reviewer, unless $\rho(0)_{inf}$ means $\rho(0)$ for the free atom.

In Section 4, the Kohn-Sham formalism with different exchange-correlation functionals is applied to Na and K atoms under central spherical and impenetrable confinement. In Section 4.1, Table 3 illustrates the numerical values of the total energies for Na($[\mathrm{Ne}]3s^1$) and K($[\mathrm{Ar}]4s^1$) as the functions of the radius of confinement as well as the average rate of change of the energy with respect to the radius, using the PBE exchange-only functional. Fig. 4 illustrates the orbital energy for the K atom as function of the confining radius with the ordering 3s, 3p, 3d, 4s for $4.5 < R_c < 8$, showing the crossing of the two higher ones with the inversion of their ordering 4s, 3d, for $R_c < 4.5$. The pressure depends on the individual orbital energy contributions to the total energy, evaluated as the rate of change of the total energy with respect to the confining volume. Table 4 illustrates the energies for $[\mathrm{Ar}]4s^1$ and $[\mathrm{Ar}]3d^1$ and their difference as functions of the confining radius, and Fig. 5 gives the total energy as a function of the pressure for the two electronic configurations, illustrating the transition of their inversion.

2.2.9.

"Study of Quantum Confinement of H_2^+ Ion and H_2 Molecule with Monte Carlo: Respective Role of the Electron and Nuclei Confinement" [25] incorporates the nuclear motion in contrast with the familiar Born-Oppenheimer approximation with nuclei in fixed positions; additionally, the calculations are based on the variational and diffusive versions of Monte Carlo. Sections 2.1 and 2.2 deal with the theory for both molecules starting from their respective 1. Schrödinger equations, with three and four particles and their interactions, including the confining potentials for electrons and nuclei. By using Jacobi coordinates, the motion of the center of mass is removed and the Schrödinger equations in terms of relative positions and reduced masses are obtained, Eqs. (9.5) and (9.30). 2. Trial wavefunctions for the free molecular ion as the product of the nuclear vibrational and rotational function $F(\vec{R})$ and an electron nuclear wave function $\phi(r_A, r_B, R)$ are proposed, Eq. (9.7).

For the lowest vibrational rotational level, $F(R)$ is chosen as a Gaussian function with a coefficient δ in the quadratic exponent $(R - R_0)^2$, δ and R_0 becoming variational parameters. The electron nuclear wavefunction is chosen to have the Guillemin-Zener form, Eq. (9.9). The electron nucleus radial positions r_A and r_B are written in terms of prolate spheroidal coordinates (ξ, η, ϕ), Eqs. (9.10-9.11), leading to the separable form in Eq. (9.12), as the product of a decreasing exponential in ξ with coefficient $(Z(R)+a)R/2$ and a $\cosh$ function in η with coefficient $(Z(R) - a)R/2$.

When the nuclei are fixed, their separation R is a parameter as in the B-O approximation. The variational optimization of $Z(R)$ and a for $R_c = R_0 = 2$ leads to $Z(R_e) + a = 1.36$ and $Z(R_e) - a = .092$ and an energy $E_{GZ} = -0.60244$ to be compared with $E_{B0} = -0.60263$.

When the nuclei are allowed to move, $Z(R)$ is a function of the nuclear separation, such that $Z(R \to \infty) \to 1$. Eq. (13) proposes $Z(R) = 1 + \gamma/R$ and the reparametrizations $\alpha = \gamma/2$, $\beta = (1 + a)/2$, as in Eq. (9.16).

3. Trial wavefunctions for the confined H_2^+ Molecular-Ion as the product of that for the free system multiplied by electron and nuclear cut-off factors for both electron and the relative nuclear separation, Eq. (9.23).

The trial wave function for the free molecule H_2, Eq. (9.31),

$$\begin{aligned}\Phi_t &= (\vec{r}_1, \vec{r}_2, \vec{R}) \\ &= F(R)\phi(\xi_1, \eta_1, R)\phi(\xi_2, \eta_2, R)J(r_{12}) \qquad (9.31)\end{aligned}$$

involves the same nuclear vibrational rotational function with their respective coordinates, and a Jastrow correlation factor, Eq. (9.35),

$$J(r_{12}) = \exp\left(\frac{br_{12}}{1 + cr_{12}}\right).$$

Section 2.3 and 2.4 describe the implementation of the Variational and Diffusion Monte Carlo calculations for Dirichlet boundary conditions.

Section 3 presents the results and discussion for 1. Hydrogen atom located at one of the foci confined by a hard spheroidal surface, with comparisons with its Refs. [20] and [9]. 2. Clamped nuclei H_2^+ molecular ion by a spherical surface compared also with [20] and [9]. 3. Confined three-body H_2^+ molecular ion by a spherical surface. 4. Confined four-body H_2 molecule by a spherical surface, 5. Consideration of confinement in active site of enzymes. 6. Decreasing the Coulomb barrier for the fusion of protons by electronic confinement.

3. Recent Progress in the Literature up to January 2018

The literature in this section has been selected with the criteria of elements of novelty in some of the key words in the Abstract, which have been illustrated in Sec. 2 for the reviews in Advances in Quantum Chemistry, and also in the two types of review in the Monograph. The recent progress in the background of the set of those reviews is presented also by going from the simpler to the more complex confined quantum systems. Additionally, the new electromagnetic toroidal interactions and the new force approach to the old radiation reaction problem are also included.

3.1. Hydrogen-like Atoms

The common confined element in the twenty references reviewed here is the hydrogen atom or hydrogen-like systems. The readers may appreciate the recent progress along this line by comparing with [2-7] and [17-19].

“Tunable Excitons in Biased Bilayer Graphene” [26] involves electron-hole excitations between the two layers. They open a pathway for possible nanoelectronic and nanophotonic devices operating at room temperature. The binding energy of the excitations may be tuned with the external bias going from zero to several tens of milielectron volts. The novel strong excitonic behaviors are associated with a one-dimensional Van Hove singularity joint density of states and a continuously tunable band gap based graphene layer. The excitonic electronic structure is markedly different from that of 2D hydrogen atom.

“Confinement approach to pressure effects on the dipole and the Generalized Oscillator Strengths of atomic hydrogen” [27] is based on the constant barrier outside model. The Schrödinger equation is solved by a finite differences method for the fixed values of the spherical radius and the barrier height. The GOS momentum transfer distribution for $1s \rightarrow n\ell$ transitions is enhanced in amplitude and width as pressure increases. There is a critical pressure indicating the approach to the limit of the confining capacity of the system to hold the $n\ell$ state. The corresponding DOS values provide an useful way to characterize the critical pressures for the fading and ultimate bleaching of the spectroscopic emission lines.

“The hydrogen atom confined in both Debye Screening potential and impenetrable spherical box: [28] used the linear variational method based on B-splines basis functions to calculate the ground state and some low lying state energies and oscillator strengths. Comparisons with results in the literature for confined and free configurations are presented and discussed.

“High-harmonic generation and spherically confined hydrogen atom” [29] presents the investigation of the dynamics of the atom under the action of strong infrared femtosecond laser. The spherical box is introduced to model collisions of ionized electrons with neighboring atoms to model their influence on higher harmonic generation. The physical situation appropriate for such application is systematically analyzed.

“Static polarizability of an atom confined in a Gaussian potential” [30] uses the finite basis set method based on B-splines to calculate the energy spectrum, and the optical properties: dipole, quadrupole and octupole oscillator strengths and polarizabilities as functions of the depth and width parameters of the confining potential. The maximum uncertainty in the reported numerical results is estimated to be about $10^{-4} au$.

“Energy-level structure of the hydrogen atom confined by a penetrable cylindrical cavity” [31] reports the bound-state energy spectrum and its evolution for the atom located along the axis of the cavity, with penetrable and impenetrable boundaries based on the solution of the Schrödinger equation using a finite difference approach. New results are presented for a nuclear centered position for the penetrable case as the barrier height and cavity size change. Then special attention is given to the energy level evolution of states from the nuclear centered position (centered states), up to the cylinder cap (cap states), while the corresponding state evolution for intermediate nuclear positions (intermediate states) remains consistent with node conservation and symmetry. The energies of a given state increase as the nucleus moves up. The evolution as the barrier height and cavity size are reduced consists of the progressive extinction of the bound states in the order of cap, intermediate and centered states. A predominance of cavity size over barrier-height effects on the energy level shift is found.

“Endohedrally confined hydrogen atom with a moving nucleus” [32] studied the hydrogen atom as a system of two quantum particles in different confinement situations: a spherical impenetrable wall cavity and a fullerene molecule cage. The motion is referred to the center of spherical cavities and the Schrödinger equation is solved by means of a generalized Sturmian function expansion in spherical coordinates. The solutions present different properties from the ones in the literature, in which the proton is fixed in space and the electron is a quantum particle. The position of the proton is found to be very sensitive to the confinement condition.

“Confinement effects on the electron transfer cross section: a study of He^{2+} colliding on atomic H” [33] analyzes the pressure effects on the target and the physical process of interest by using the model of spherical confinement of the target at the center. The electron transfer probability is obtained by a time dependent solution of the Schrödinger equation by means of a finite difference approach and the Crank-Nicolson propagation method. Results are presented for the benchmark system $\mathrm{He}^{2+} + \mathrm{H}(1s)$ under different conditions of confinement.

“The hydrogen atom confined by one and two hard cones” [34] studies the bound states of the system is a semi-infinite space. The solutions when the nucleus is at the apex of the conical boundaries and the electron is confined outside one or two symmetric of such boundaries can be evaluated exactly. The third case assumes the position of the nucleus as the origin of the coordinate system and the apex of one conical boundary at a distance h along its axis; the solution can be evaluated by the variational Monte Carlo Method. The latter is applied to calculate the force in an Atomic Force Microscope as the negative of the rate of change of the energy with respect to h.

"Benchmark Calculation of Radial Expectation Value $\langle r^{-2}\rangle$ for Confined Hydrogen-Like Atoms and Isotropic Harmonic Oscillators" [35] recognizes that for those physical systems numerous physical quantities have been established with very high accuracy. However, the expectation values in the title of practical importance in many applications has significant discrepancies among calculations by different methods. In this work the basis expansion method with cut-off Slater-type orbitals is used to investigate the two confined systems. Accurate values for several low-lying bound states were obtained by carefully examining the convergence with respect to the size of the basis. A scaling law for $< r^n >$ was derived and is used to verify the accuracy of numerical results. Comparisons with other calculations show that the present results establish benchmark values for this quantity.

"Sum rules and the role of pressure on the excitation spectrum of a confined hydrogen atom by a spherical cavity" [36] investigates the effects of pressure induced by a soft spherical cavity on a centered atomic hydrogen impurity, on the dipole oscillator strength sum rule S_k, and its logarithmic version L_k, by means of a numerical finite-difference solution of the Schrödinger equation. The information on the energy spectrum and the eigenfunctions in the sum rules and their closure relations are analyzed as functions of the size and barrier height of the confining potential. The results are relevant in electron-impurity excitations affecting optical transitions in semiconductor nanostructures.

"Monotonicity in confined system problems" [37] is concerned with the changes in the electron density when an atom is confined at the center of an impenetrable confining sphere. The work presents four simple theorems that facilitate understanding the behavior of the electron density of the ground state with variations in the potential or in the radius of the impenetrable spherical cavity.

"Exact solution for the hydrogen atom by a dielectric continuum and the correct basis set to study many-electron atoms under similar confinements" [38] introduces a new model of confinement, alternative to the polarization potential of Jortrer and Coulson, and an alternative basis set to construct the exact solution of the corresponding Schrödinger equation, distinguishing between the solute and the solvent. Results are reported for the total energy, electron density, charge in the dielectric medium and Shannon entropy, as functions of the radius of confinement and of the dielectric constant $\epsilon \quad [2.1, 80]$, where the extreme values correspond to Teflon and water, respectively.

The two-electron atom and ions H^-, He and Li^{3+} are also investigated with the same model of confinement using the Hartree-Fock equations and implemented with the MEXICA-C code. Results are illustrated for the Highest Occupied Orbital Energies divided by Z and for the total energies divided by Z^2, $Z =, 1, 2, 3$ and $\epsilon = 80$ as functions of the confining radius.

"Fine structure in the hydrogen atom boxed in a spherical impenetrable cavity" [39] reports the relativistic corrections of the kinetic energy, the spin-orbit coupling and the point interaction Darwin term to the non relativistic familiar system based on the nucleus-electron Coulomb interaction only. The first one is negative; the second one couples the orbital and spin angular momenta to a total one with $j = \ell \pm 1/2$, and eigenstates $|\ell\, s\, j\, m_j\rangle$: for initial $n\ell$, the energy levels split following the order of the values of j; the third one occurs only for the state with $\ell = 0$. High precision numerical results of the effect of the confinement on each correction, in first order perturbation theory, are reported.

"Confinement of Atoms with Robin's Condition: Spontaneous spherical symmetry breaking in atomic confinement" [40] and Spontaneous spherical symmetry breaking in atomic confinement [41] are commented together, pointing out their use of the "not going out" Robin's boundary condition, and their identification of a symmetry breaking effect.

The boundary condition corresponds to the logarithmic derivative of the wave function at the confining surface being a real function $\lambda(\vec{r})$, representing the contact interaction of the particle with the cavity boundary; $\lambda \rightarrow 0$ leads to the Neumann and $\lambda \rightarrow \infty$ leads to the Dirichlet familiar boundary conditions. The energy functional for the Schrödinger equation and the Robin boundary condition includes a surface integral of the probability density at the boundary multiplied by λ. It is this term that makes the difference.

"Fisher information in confined hydrogen-like ions" [42] presents an investigation of Fisher information for the CHA-like systems in conjugate r and p spaces, compared with the, I, case of the free atom. Systematic results on I as a function of the confining radius are presented, with emphasis on the non-zero-(ℓ, m) states. Inferences in CHA are significantly different from the free counterpart: i) dependence on (n, ℓ) quantum numbers, ii) appearance of maxima in I_p plots for $m \neq 0$. The role of atomic number and atomic radius is discussed.

"Derived properties from the dipole and generalized oscillator strength distributions of an endohedral confined hydrogen atom" [43] uses two alternative potentials, square-well and Woods-Saxon, to model the concentric spherical shell Δ-potential wall in $H@C_{60}$. The electronic properties of the confined hydrogen atom: hyper-fine splitting, nuclear magnetic screnning, dipole oscillator strength, static and dynamic polarizability, mean excitation energy, photoionization and stopping cross section, are reported as functions of the depth of the wall V_0 for chosen shells $[R_0, \Delta]$. The values from the two modelings of the Δ potential are compared. A clear discrepancy is found between the square-well and Woods-Saxon models on the GOS, due to the square well discontinuity. These differences are reflected in the stopping cross section for protons colliding with H@C_{60}.

"Relativistic two dimensional H-like model atoms in an external magnetic field" [44] are investigated on the basis of Klein-Gordon and Dirac equations solved by the power expansion method. For a given magnetic field B the approximate solutions are determined by imposing boundary conditions at a finite radius R. For particular values of B, exact polynomials solutions are obtained. The dependence on the effective coupling constant $\gamma = B/Z^2$ and on the atomic number Z of the energy eigenvalues for several states is studied.

"Atoms confined by very thin layers" [45] provides a mathematical justification for the interest in the two-dimensional atoms with the three-dimensional Coulomb potential. The Hamiltonian of an atom with N electrons and a fixed nucleus between two parallel planes is considered in the limit when the separation between the latter tends to zero. It is shown that the Hamiltonian converges in the norm resolvent sense to a Schrödinger equation acting effectively in $L^2(\mathbb{R}^{2N})$ whose potential part depends on the separation. Moreover, it is proven that after an appropriate regularization this Schrödinger operator tends, again in the norm resolvent sense, to the Hamiltonian of a two-dimensional atom (with the 3D Coulomb potential) as the separation tends to zero.

3.2. Diatomic Hydrogen-like Ion and Neutral Molecules, and Two-electron Atoms

This section reviews seven articles on molecules and one on He-like atoms.

The article "H_2^+ embedded in a Debye Plasma: electronic and vibrational properties" [46] has the background of [14] and the works of its second author [3,20]. The embedding in a hot dense plasma is modeled by multiplying the Coulomb potential interactions with a Debye screening exponential radial factor with a decay distance D. The analysis of the problem is made within the Born-Oppenheimer approximation and in prolate spheroidal coordinates with the protons at the positions of the foci. The solution is based on the variational trial function of Eq. (6) for the $1s\sigma_g$ and $2p\sigma_u$ states, including an exponential decaying function in the spheroidal coordinate and a series expansion in Legendre polynomials of order l in the hyperboloidal coordinate and powers of the ratio of the spheroidal coordinate minus one to the spheroidal coordinate plus one. The gerade and ungerade states involve only even and odd values of l, respectively. The expansion coefficients c_{lm} and energy eigenvalues are determined by solving the secular equation and the coefficient α in the exponential factor was optimized to give ten digit convergence for each value of the nuclear separation and the Debye length. In the limit of very large values of D when the Debye screening factor becomes one, the exact energies obtained in a previous work of the same Author for the free ion are matched through $1 \times 10^{-9} E_h$. The results are reported graphically in Figs. 1 and 2 for the energies and for the potential energy curves of the ground state Eq. (12), respectively, as functions of the nuclear separations and higher energy values as D takes smaller values. Tables 1 and 3 illustrate the numerical values of the energies for the respective states and their variations with the two distance parameters, including the positions of the minima R_e, $E(R_e)$ and the dissociating energy D_e. Table 2 reports the numerical results of the $1s\sigma_g$ energy and dipole polarizability for different Debye lengths including comparisons with those from its Refs. [11], [10], [25], and [26]; the energies and the polarizabilities are consistently lower from the other reported values. Table 4 illustrates the expectation values for the potential energy, z^2 and x^2. Table 5 contains the numerical values of the parallel and perpendicular dipole polarizabilities, Eqs. (9), compared with their Kirkwood approximation lower bounds Eq. (8), their average, Eq. (13), and the anisotropy, Eq. (14). Table (56) shows the Dunham parameters fitting the potential energy curves, Eqs. (10)-(11), the harmonic force constant and the harmonic frequency.

"The Effect of Confinement on the Electronic Energy and Polarizability of a Hydrogen molecular Ion" [47] is based on the simplest variational trial function consisting of the linear combination of two $1s$ hydrogen atom orbitals, reporting numerical values of the $1\sigma_g$ and $1\sigma_u$ states molecular energies below those of the exact and a variational five-term James-Coolidge trial function, in its respective Refs. [7,10], with the claim that their results are better than those of the references. The Comment on the article [48] points out and clarifies numerical errors in its presentation and Tables, which obviously violate the variational principle. The authors in their Response [49] do not address the specific inconsistencies pointed out in the Comment, but include one page of the print outs of Mathematica® for the one electron integrals for the non perturbed Hamiltonian of two hydrogen atoms with nuclei at the foci, A and B, for the Coulomb interaction of the orbital centered in A with the nucleus in B and the orbital centered in B with the nucleus in A, for the Coulomb exchange interaction, and for the overlap of both orbitals; as well as an APPENDIX of commands of Mathematica® of one page and a half for the calculation.

This Reviewer included in [4] and [17] sections on comments to works in the literature, inviting the readers to do their own readings of the respective articles. Here, he reiterates such an invitation and makes his own specific comment: According to the Variational Principle, a variational result for the energy below the exact value is not better, it is wrong.

In "The hydrogen molecule and the H_2^+ molecular ion inside padded prolate spheroidal cavities with arbitrary nuclear positions" [50], a variational approach has been proposed for the nonseparable Schrödinger problem of the molecules in the title, in their ground states, confined by soft cavities and the nuclei not in the foci positions. The role of barrier height potential and cavity size and shape on the ground state energy of both confined molecules has been analyzed showing their importance in defining equilibrium bond lengths and energies by allowing full nuclear relaxation, consistent with the confinement conditions. The variational wave function for the H_2^+ molecular ion inside and outside are based on the Dickinson-Weinhold ansatz for the free ion, involving a superposition of $1s$ and $2p$ atomic hydrogenic orbitals centered at each nucleus, with the proper factors to satisfy the boundary conditions at the surface of the spheroidal cavity and at infinity, Eqs. (13)-(15). For the H_2 molecule the variational function is the product of the same one-electron variational functions for electrons 1 and 2, Eqs. (11)-(12), inside and outside. The energy functional of Eq.(21) is valid for both molecular systems depending on their numbers of electrons $K = 1, 2$ for H_2^+ and H_2, respectively.

Figure 2 illustrates the variations of the total energy for H_2^+ $1s\sigma_g$ with the nuclear separation for barrier potential height and eccentricity $V_0 = 0.5$ and $1/\xi_0 = 0.5$ varying sizes $D\xi_0$ in terms of focal distances $D = 1, 1.5, 2, 3$ in a), and for a fixed size $D\xi_0 = \xi$ and varying heights $V_0 = 0.25, 0.5, 2, 4500$ in b).

Table I provides the numerical values of the total energies for $V_0 = 0.25, 0.5, 2$ and nuclear separations $[0.5, 2.4]$ from this work, including comparisons with the exact one for nuclei coinciding with the foci, which are systematically below.

Table 2 illustrates the total energies E_{eq} at the equilibrium nuclear separation for a selected set of cavity sizes $(D\xi_0)$, fixed eccentricity $1/\xi_0 = 0.5$ and barrier heights $V_0 = 0.25, 0.5, 2, 4500$, with their corresponding numerical values of the variational parameters in the trial wave function. Table 3 is the counterpart of Table 2 for the ground state of the H_2 molecule.

Figure 3 illustrates a) the equilibrium electronic energy, and b) the equilibrium bond length, as functions of the size of the cavity $(D\xi_0)$, for $\xi_0 = 2$ and $V_0 = 0.25$, for both confined H_2^+ and H_2 molecules. The crossing of the curves at around $D\xi_0 \approx 1.48$ and $V_0 = 0.5$ is to be noted. The reader is invited to follow the explanations in the text.

This model adds more flexibility for the treatment of the electronic and vibrational properties of one and two-electron diatomics when subjected to spatial confinement allowing for a more realistic comparison with experiment.

"Spherically confined H_2^+: ${}^2\Sigma_g^+$ and ${}^2\Sigma_u^+$ states" [51] presents a study of the molecular ion H_2^+ under strong confinement conditions produced by a spherical barrier centered in the gravity center of the molecule. Results for the potential curves are obtained by diffusion Monte Carlo methods for the ground state $\left(X\,{}^2\Sigma_g^+\right)$ and the first excited state $\left(A^2\Sigma_u\right)$, and reported as functions of the internuclear distance d for different values of the confinement radius. Results show that the compressed states corresponding to both $\left(X\,{}^2\Sigma_g^+\right)$ and $\left(A^2\Sigma_u\right)$ present deep minima in the potential energy curves, due to the increased space for electron wave function when the protons are displaced from the barrier surface.

"Quantum states of confined hydrogen plasma species: Monte Carlo calculations" [52] implements the diffusion Monte Carlo method with symmetry-based state selection to calculate the excited states ${}^2\Pi_u$ and ${}^2\Pi_g$ of H_2^+ ions under spherical confinement. Special solutions are employed, permitting to obtain satisfactory results with rather simple native code. The results are interpreted using the correlation of H_2^+ states to atomic orbitals of H atoms lying on the confining surface and perturbation calculations. The method is straightforwardly applied to cavities of any shape and different hydrogen plasma species (at least one-electron ones, including H) for future studies with real crystal symmetries.

In "Ritz variational calculation for the singly excited states of compressed two-electron atoms" [53], a detailed analysis on the effect of spherical impenetrable confinement on the structural properties of two-electron ions in S-states has been performed. The energy values of $1sns\,{}^3S^e$, $[n = 2-4]$, states of helium-like ions $(Z = 1-5)$ are estimated within the framework of Ritz variational method using explicitly correlated Hylleraas-type basis sets. The correlated wave functions used here are consistent with the finite boundary conditions due to spherical confinement. A comparative study between the singlet and triplet states originating from a particular electronic configuration show incidental degeneracy and the subsequent level-crossing phenomenon. The thermodynamic pressure felt by the ion inside the sphere pushes energy levels toward the continuum. Critical pressures for the transition to strong confinement regime (where the singly excited two-electron energy levels cross the corresponding one-electron threshold) as well as for the complete destabilization are also estimated. This reference is connected with [5,8,20].

3.3. Many-electron Atoms

The articles to be reviewed in this subsection have antecedents and common Authors in [8,11,24] and illustrate some of their recent advances from their previous reviews.

The article "Implementation of the electron propagator to second order of GPUs to estimate the ionization potentials of confined atoms" [54] considers the confinement in spherical boxes with impenetrable walls, and The Electron Propagator Technique in the second order approximation EP2 to evaluate the energy to remove one electron from an orbital, Eq. (2), in the Hartree-Fock formalism. The use of the GPUs for the faster evaluations of two-electron integrals and four index integrals Transformations to implement EP2, were incorcoprated in the original MEXICA-C code via CUDA Kernels 1 and 2, respectively, Fig. 1. The calculations of the ionization potential were performed for the free atoms with $Z = 3, \ldots, 18$ using the same basis sets as in Ref. [30], including the predictions of Koopman's Theorem and the EP2 rules. The comparisons of the results of [30], the calculations from MEXICA and the experimental values in eV [31] show average derivatives of 0.50 to KT and 0.36 and 0.34, respectively. The authors attribute their smaller derivation to the use of the Gaussian functions in [30] to their own use of Slater type orbitals. The calculations for the confined atoms are reported for helium in Table 2, beryllium in Table 3, and neon in Table 4, for boxes of different radius; their general trends including those of other references is that they diminish as the radii became smaller, including vanishing values for different radius in the successive calculations. The differences between EP2 and KT values are also included; for He differences exhibit negative values for large radii and positive values for the smaller ones, for Be they are all positive, and for Ne they are all negative for the $2s$ orbital ionization, and all negative except for the smallest radius of one for the $2p$ orbital ionization. The authors argue that KT values provide good estimates for the ionization potentials but EP2 corrects them in the case of confined atoms; however, they recognize that such correlations do not reveal a trend for the confined atoms, since the differences are negative or positive as illustrated in the Tables. They also explain the overestimates or underestimates of the KT ionization potentials in terms of the orbital crossings between unoccupied orbitals: if the lowest unoccupied orbital (LUMO) crosses a virtual orbital the differences change sign.

The other three articles: "Roothaan's approach to solve the Hartree-Fock equations for atoms confined by soft walls: Basis set with correct asymptotic behavior" [55], "Solution of the Kohn-Sham equations for many-electron atoms confined by penetrable walls" [56], and "Electron-density delocalization in many electron atoms confined by penetrable walls: A Hartree-Fock study" [57] assume spherical confinement with a constant potential barrier outside, accounting for the soft and penetrable walls, as well as the radial basis sets inside and outside with the correct behaviors for very small and very large distances from the nucleus, taken from the common Ref. [27], [4] and [30]. The progress in these three articles, compared with the counterparts for impenetrable confinement in their previous works cited and reviewed in the first half of this section, are described next.

In [55] the atoms investigated were H, He, Be, Ne and K with the following conclusions, taking as a reference that for impenetrable confinement in which the energies increase monotonically as the radius diminishes: A) The shell structure is drastically modified, and a delocalization effect may occur for a certain barrier height, B) inner orbital energies do not necessarily go up when the radius diminishes, C) the ionization of many electron atoms is confirmed for a finite potential, and D) the asymptotic behavior of the electron density changes with the height of the potential.

In [56] the Kohn-Sham formalism was applied to study five closed shell atoms: He, Be, Ne, Mg and Argon for two heights U=0, 0.5 of constant confining potential barrier, using four exchange-correlation functionals. Tables 1 and 2 illustrate the results for the free atoms including HF values for comparison of the total energies evaluated with Gaussian and STO-CAB functions and the respective exchange correlation functionals. Table 3 shows the comparison of the exchange energy of He in the two situations of confinement from HF and KS in two of the exchange-correlation functionals. Table 4 includes the exchange and correlation energies, and their difference, for Mg in the two situations of confinement and for the fourth exchange- correlation functional. Table 5 shows the Highest Occupied Molecular Orbital energies for Mg in the two situations of confinement, comparing the results from HF and KS with the four functionals. The comparisons indicate the need to explore other exchange and correlation functionals.

In [57], HF calculation for the atoms H, He, Li, Be, N, Na, Mg, P and Ar confined in a sphere with a constant potential barrier of heights 0 and 0.5 were performed. The corresponding results were the basis to evaluate the Shannon entropy of the respective atoms as a function of the radius of confinement. The results for H are illustrated graphically in Fig. 1 for a barrier height of 0.5 displaying the Coulomb potential and constant potential energies as well as the radial distribution function for A) with a radius 0.65, B) with a radius 1.1, and C) with a radius 4, and horizontal dotted lines for the corresponding orbital energies of 0.4908, 0.1583 and -0.4945, respectively. In B) the electron density is localized between 0 and 3.5, while in C) a minor localization is recognized. Figure 2 displays the orbital energies in squares and Shannon entropies in circles as functions of the confining radius, in the respective intervals [-0.5,0.5], [2,7] and [0,5]. While the energy increases monotonically as the radius is reduced, the entropy starts at about 4 for a radius of 5 decreases to a minimum of less than 3 for a radius of about one, and shows a marked increase to close to 7 as the radius is reduced to 0.65; the first interval corresponds to localization of the electron and the second one to its delocalization as the orbital energy approaches the height of the barrier. Table 1 shows the HF total energy and the occupied orbital energy for Li, Be, N, Na, Mg and P in the three situations of confinement for five different values of the radius. Table 2 shows the corresponding information for the noble gases He, Ne and Ar. The readers may ascertain the systematic changes of decreasing energies for the confined atoms as the radius of confinement increases approaching their free atom values for a radius of 30, independently of the barrier height; and also their increasing values for a fixed radius and increasing barrier heights. The changes in the orbital and total energies are more pronounced for Li and Na, diminishing successively for Be and Mg, N and P, and He, Ne and Ar. The radial distribution defined in Eq. (16) is illustrated in Fig. 3 for Mg, zero barrier height and confining radii of 2, 3 and 30, as functions of the radial distance; the respective curves show intersections. Specifically, in the last pair the second one for its own confining radius goes below the curve for the free atom and vanishes for a distance of about 8 exhibiting a localization. On the other hand, for the confinement at the radius 2 something different happens: Table 1 shows that the orbital energy is approaching zero for smaller distances and Fig. 3 shows that the first curve goes above that of the free atom at a radial distance of around 6, exhibiting the delocalization effect like in the case of H.

Fig. 4 shows the Shannon entropy versus radial distance for Mg confined in constant potential barriers of heights 0, 0.5 and ∞; all the curves entries are in the lower right quadrant, the first two show minima and the third with impenetrable boundary show a monotomic increasing. For zero height and $R_c = 3$ the entropy is close to its lowest value corresponding to the localized state identified in Fig. 3; in the same curve for $R_c = 2$ the entropy has its highest value above that of the free atom and is delocalized as also identified in Fig. 3.

Table 3 gives the values of the Shannon entropies for the free atoms, with positive values for the lighter ones and negative values for the heavier ones, taking decreasing values for the heavier elements. Figures 5 illustrate the Shannon entropies of confined H, Li and Na referred to the entropy of the free H for A) 0, B) 0.5 and C) ∞ barrier heights, versus the confining radius. The curves in A) and B) exhibit steep changes on their left reaching a minimum followed by a monotomic increasing and approaching zero from below. The curves in C) exhibit only the monotomic increasing and approaching zero from below also. This contribution shows that the Shannon entropy is a useful tool to measure the delocalizations for many electron atoms.

3.4. Many-electron Molecules

This section reviews four articles involving the rotational properties of molecules and four more on the electronic and vibrational properties of molecules.

"Orientation of the absorbed dipolar molecules: A conical well model" [58] is a theoretical investigation on the orientation of single and two coupled polar molecules irradiated by a single laser pulse under a conical-well model. The orientation of a single hindered rotor shows a periodic behavior. In particular, the amplitudes of the oscillation are sensitive to the degree of the alternation of the field. Crossover from field-free to hindered rotation is observed by varying the hindering angle for different heights of the conical walls. For a small hindering potential and angle, the time-averaged orientation differs greatly from that behavior under strong dipole-dipole interaction. Entanglement induced by the dipole-time averaged entropy increases monotonically as the hindering angle is increased. To the competition between the confinement effect and dipole interaction is found to dominate the behavior of the coupled-rotor system.

"Anticrossing-mediated entanglement of the adsorbed polar molecules" [59] studies the entanglement of two adsorbed polar molecules in static electric fields. The concurrence is estimated to quantify the entanglement. The absorbed molecules reveal a significant rotational characteristic, such as anticrossing features, due to the influences of the electric field and quantum confinement. Numerical results demonstrate that these rotational properties dominate the amount and profile of concurrence. At zero temperature, an enhaced concurrence is obtained near the anticrossing in the ground state. Additionally, the analysis of the effect of the temperature on the concurrence shows that the temperature-dependent concurrence displays a suppresed behavior especially at the anticrossing.

"Orientation and heat capacity of horizontally absorbed molecules in electric fields" [60] presents the evaluation of the energy spectrum and the wave function to probe the rotational characteristic of the molecule. Numerical results indicated that the electric field and the effect of quantum confinement lead to anticrossing behaviors in the energy levels. The orientation reveals a stepped feature due to the anticrossig ground state. Moreover, the heat capacity displays two peaks near the anticrossing. By means of comparison, each peak of the heat capacity corresponds to a particular degree of orientation.

"Inelastic electron tunneling mediated by a molecular quantum rotator" [61] presents a basic theoretical framework of Inelastic Electron Tunneling (IET) that explicitly takes into consideration quantum angular momentum, focusing on a molecular H_2 rotator trapped in a nanocavity between two metallic electrodes as a model system. It is shown that the orientationally anisotropic coupling imposes rigorous selection rules in rotational excitation. Additionally, rotational symmetry breaking induced by the anisotropic potential lifts the degeneracy of the energy levels of the degenerated rotational state of the quantum rotator and tunes the threshold voltage that triggers rotational IET. The theoretical results provide a paradigm for physical understanding of the rotational IET process and spectroscopy, as well as molecular level design of electron-rotation coupling in nanoelectronics.

"The effect of spatial confinement on the noble gas HArF molecule: structure and electronic properties" [62] presents a systematic study on the dipole and hyperpolarizabilities of the confined argon hydroflouride molecule. Detailed analysis of the confinement induced charges in the structures of HArF is also presented. In order to render the influence of chemical compression on the properties in question, a two-dimensional harmonic oscillator potential, mimicking a cylindrical confinement, was applied. By comparing the results obtained for HArF and HF, the effect of Ar insertion on the above properties was discussed. A hierarchy of ab initio methods, including HF, MP2, CCSD and CCD(T), has been employed to investigate the effect of orbital compression on the electron correlation contributions to the studied electric properties. It was observed that the external confining potential modifies the electronic contributions to the dipole moment and (hyper) polarizabilities of HArF. In particular the first hyperpolarizability of the confined molecule is remarkably smaller than that of the free molecule.

"On the nonlinear electrical properties of molecules in confined spaces: From cylindrical harmonic potential to carbon nanotube cages" [63]. The effect of spatial confinement on the linear and nonlinear electric properties of LiF, LiH, HF and HCl is analyzed based on the results of ab initio quantum chemical calculations. Central to this study is the comparison of different models of confinement. The harmonic oscillator potential of cylindrical symmetry as well as a more sophisticated model, based on the supermolecular approximation, are applied in order to establish the correspondence between the real chemical environment and their approximate representation in the form of an analytical potential. In the case of super molecular approach, the molecular cages are represented by carbon nanotubes and nanotube-like Helium clusters. The results of calculations show that spatial confinement strongly influences the electric properties of the investigated molecules.

“About diverse behavior of the molecular electric properties upon spatial confinement” [64] reports on the influence of spatial restriction on the static electric properties of two π-electron molecules, namely carbonyl sulfide and chlorocetylene. A two dimensional harmonic oscillator potential has been applied in order to mimic that effect of orbital compression. All the components of the studied tensorial quantities were obtained using the finite-field-method. Among others, the nanoatomic changes of the first hyperpolarizability, observed for the spatially limited OCS molecule, are described for the first time in the literature. Moreover, it has been found that upon embedding in cylindrical potential the behavior of the dipole moment is different for each of the investigated molecular systems. In order to explain the obtained diverse trends, the Hirshfelder technique as well as the concept of hyperpolarizability density have been adopted.

“Vibrational nonlinear optical properties of spatially confined weakly bound complexes” [65]. This study focuses on the theoretical description of the influence of spatial confinement on the electronic and vibrational contributions to (hyper)polarizabilities of two dimeric bonded systems, namely, HCN$\cdots$HCN and HCN$\cdots$HNC. A two dimensional analytical potential is employed to render the confining environment (*e.g.* carbon nanotubes). Based on the results of the state-of-the-art calculations, performed at the CCSD(T)/aug-cc-pvtz level of theory, it is established that: i) the influence of spatial confinement increases with increasing order of the electric properties, ii) the effect of spatial confinement is much larger in the case of the electronic than the vibrational contributions, for each order of the electric properties, and iii) the decrease in the static nuclear relaxation first hyperpolarizability upon the increase of confinement strength is mainly due to changes in the harmonic term; however, for nuclear relaxation second hyperpolarizability the anharmonic terms contribute more to the drop of this property.

3.5. Quantum Dots

This section has the antecedents of [15,22] reviewing the progress in six recent articles.

“On the symmetry of three identical interacting particles in a one-dimensional box” [66] studies the quantum mechanical physical system in the tittle with two-particle harmonic interactions. The symmetry of the system is described by the point group D_{3d}. Group theory greatly facilitates the application of perturbation theory and the Rayleigh-Ritz variational method. A great advantage is that every irreducible representation can be treated separately. Group theory enables us to predict the connection between the states for the small and large box regimes of the systems. The crossing and avoided crossing of the energy levels and other interesting features of the spectrum are illustrated and discussed.

“The effects of intense laser on nonlinear properties of shallow donor impurities in quantum dots with Woods-Saxon potential” [67] presents a theoretical study of the title using the matrix diagonalization method and the effective mass approximation. This methodology enables confinement energies by varying the two parameters in the potential. The intense laser effects are included via the Floquet method, modifying the confining potential associated to the heterostructure. From the computed energies and wave functions, the optical absorption coefficients and the respective index between the ground $(\ell = 0)$ and first excited $(\ell = 1)$ states are obtained and examined. Several configurations of the barrier height, the dot radius, the barrier slope of the confining potential and the intense incident laser radiation have been considered. The results suggest that all these factors can influence the nonlinear properties strongly.

“Impurity position effect on optical properties of various quantum dots” [68] is an investigation of the effect in the tittle for a pyramid and a cone like quantum dots. First, the energy levels and wave functions in the presence of the impurity are calculated using the finite element method. Then, the influence of the impurity location on the refractive index changes and absorption coefficients for the two quantum dots was studied. It was found that: 1) there is a maximum value for the optical properties at a special impurity position, and 2) the values of the optical properties of a cone like quantum dot are larger than those of a pyramid quantum dot of the same volume and height. The conclusion is that their impurity location plays an important and considerable role in the electronic and optical properties of both quantum dots.

“Calculation of the hyperfine interaction in spherical quantum dot” [69] presents the results of unperturbed wave functions and energy eigenvalues of the ground and excited states of spherical quantum dot, $\mathrm{GaAs/Al_xGa_{1-x}}$ by using quantum genetic algorithm and Hartree-Fock Rootham method. The hyperfine coupling constant and hyperfine energies of 1s, 2p, 3d and 4f levels are evaluated as functions of quantum dot radius. The results show that both hyperfine properties change rapidly in the strong and medium confining regimes as the radius decreases. It is pointed out that dot radius, impurity charge and angular momentum have a strong influence on the hyperfine energy. Another finding is that the hyperfine energy and the hyperfine splitting vary with the aluminum concentration ratio x.

“Computation of hyperfine energies of hydrogen, deuterium and tritium quantum dots” [70] uses the same QGA and Roothan HF methodology as the previous entry by the same Authors. The results show that in the medium and strong confinement regimes the hyperfine energy and the hyperfine constant are strongly affected by dot radius, impurity charge, electron spin orientation, impurity spin and impurity magnetic moment. Additionally, for all dot radii, the hyperfine splitting and hyperfine constant of the confined hydrogen and tritium atoms are approximately equivalent to each other, and they are greater than those of the confined deuterium atom.

“Type-II quantum-dot-in-nanowire structures with large oscillator strength for quantum gate applications” [71] presents a numerical investigation of the exciton energy and oscillator strength in the quantum dots in the title. For a single quantum dot, poor overlap of the electron part and the weakly confined hole part of the excitonic wave function leads to a low oscillator strength compared to type-I systems. In order to increase the oscillator strength, a double quantum dot structure is proposed featuring a strongly localized exciton wave function and a corresponding four fold relative enhancement of the oscillator strength, paving the way towards efficient optically controlled quantum gate applications in the type-II-nanowire system. The simulations are performed using a computationally efficient configuration-interaction method suitable for handling the relatively large nanowire structure.

3.6. Confined atoms treated as open quantum systems

This subsection borrows the title of [10] and illustrates its basic idea with the series of articles [72-78] on “Endohedral confinement of molecular hydrogen”, “The atomization process of endohedrally confined hydrogen molecules”, “Pressure and size effects in endohedrally confined hydrogen clusters”, “Thermal behavior of a 13-molecule hydrogen cluster under pressure”, “Thermodynamic states of Nanoclusters at low pressures and low temperature: the case of $13\mathrm{H}_2$”, “Evolution of the vibrational spectra of doped hydrogen clusters with pressure”, “Pressure Induced metallization of Li^+-Doped Hydrogen Clusters”. The series has also common features with [12] considering hydrogen fullerene cages instead of the familiar ones with Carbon, and also different species of confined systems and different processes. The main difference between the series and the last reference is in their methodologies: while the latter models the doped fullerenes with the spherical Δ and δ potentials, the first includes the dynamical interactions between the confined systems and the atoms of the confining cage. More specifically, the series uses density functional theory for molecules applied to the supermolecule formed by the cage and the confined molecule.

In [72], the first problem investigated involved a single H_2 molecule inside a H_{20} cage leading to the pressure dependence of the ground state energy and internuclear distance of the confined molecule as a function of the cage volume: Figure 2 illustrates the results of this work compared with other model calculations and specially experimental values, with which they agree better. The second problem involved 30 hydrogen atoms allowed to relax inside a H_{60} cage of radius 4Å, reaching a minimum energy configuration: the hydrogen atoms self-assemble into a $(\mathrm{H}_2)_{15}$ stable molecular cluster characterized by two coaxial six-fold symmetry ring structures, illustrated in Fig. 3.

In [73], the confinement of thirteen H_2 molecules in a H_{60} cage was investigated. The reduction of the size of the cage leads to different compression rates with the consequent evolution of the molecular structure, energy, electron density, Mulliken populations, HOMO-LUMOS gap and ionization potential.

In [74], the investigation consist of a systematic study of zero-temperature structural and energy properties of H_{60} endohedrally confined hydrogen clusters as a function of pressure and cluster size. For low pressures, the most stable structural forms of $(\mathrm{H}_2)_n$ possess rotational symmetry that changes from C_4 through C_5 and C_6 as the cluster grows from $n = 8$ through $n = 12$ to $n = 15$, Fig. 1 The equilibrium configurational energy of the clusters increases as the pressure increases. However, the rate of this increase, on a per atom basis, is different for different cluster sizes. In consequence, the size dependences of the configurational energies per atom at different fixed values of the pressure are non monotomic functions, Fig. 4. On the other hand, for high pressures the molecular $(\mathrm{H}_2)_n$ clusters become gradually atomic or dominantly atomic, Fig. 3. The pressure-induced changes in the HOMO-LUMO cluster gaps indicate a finite-size analog of the pressure-driven metallization of the bulk hydrogen. The ionization potentials of the clusters decrease as the pressure on them increases.

In [75], the thermal behavior of a thirteen molecule hydrogen cluster under pressure was investigated using a combination of trajectory and DFT simulations. The analysis is based on characteristic descriptors: caloric curve, root-mean-square bond length fluctuation, pair correlation function, velocity auto correlation function, volume thermal expansion, and diffusion coefficients. The discussion is focused on the peculiarities of the transition ordered-to-disordered states as exhibited by the cluster under different pressures, 65 to 75 GPa, and temperatures, 10 to 600 K . These ranges correspond to the conditions of an envelope of Jupiter’s interior. The results for the successive descriptors are illustrated in Figs. 1-5 and in numerical values in Section IV. In the Section V of Conclusions, it is stated that “The results point out a smooth transition of the molecular cluster from an ordered solid state to an intermediate thermodynamic state as a precursor of a possible liquid state of the cluster”. It is the confinement of the cluster which extends the persistence of the intermediate state of temperatures (above 100 K and up to 500 K). They suggest the existence of hydrogen clusters in Jupiter’s envelope.

In [76], an equation of state is presented based on a confinement model of finite-size systems. The temperature and pressure of the system are obtained from the positions and velocities of the enclosed particles via a number of molecular dynamics simulations. The pressure has static and dynamic contributions, extending the Mie-Grüneisen equation of state to include weakly interacting anharmonic oscillators. The model consist of thirteen H_2 molecules under low-pressure and low-temperature conditions in the classical regime, inside a confining spherical hydrogen cavity. The Born-Oppenheimer molecular dynamics in conjunction with DFT are used for the time evolution of the particle system. The hydrogen molecules form a noncrystalline cluster structure with icosahedral symmetry that remains so in the whole temperature range investigated. The fluctuations of the interatomic distances increase with temperature, while the orientational order of the enclosed system of molecules fade out, suggesting a gradual order-disorder transition.

In [77], "Endohedrally encapsulated hydrogen clusters doped with inert helium $H_{24}He$ and ionic lithium $H_{24}Li^+$" were investigated. The confinement model is a nanoscopic analogue of the compression of solid hydrogen. The structural and electronic properties of the doped hydrogen clusters under pressure are determined, and compared with those of the isoelectronic pure hydrogen H_{26} counterpart. The insertion of helium or lithium lead to pressure increase rates of approximately 1.1 with respect to H_{26}, The changes of geometrical structures and HOMO-LUMO gap energies with pressure indicate the pressure-induced metallization of the Li^+ doped cluster, for which the energy gap is abruptly reduced, reaching a value of $0.21eV$ at around $511GPa$. There is a pressure domain where the metallization may be achieved faster by doping hydrogen with lithium.

In [78], the "evolution of the vibrational spectra of the isolectronic hydrogen clusters H_{26}, $H_{24}He$ and $H_{24}Li^+$ with pressure" was investigated. The vibrational modes with collective character common to the clusters were frequency shifts in the GPa region were discussed. The results are of interest to identify the dopings elements as inert He, and ionic Li^+ in hydrogen under confinement or, conversely, establish the pressure of doped hydrogen when the vibrational spectrum is known. At high pressure, the spectra of the nanoclusters resemble the spectrum of a solid, and the nanoclusters may be considered crystals of nanometer size. The computations were performed at the gradient-corrected level of DFT. The importance of this work consists in the characterization of matter at the nanoscopic level in environments different from a void.

The results for a low pressure 20 GPa compare well with measurements for the crystal. For moderate pressures 184 GPa the molecules self-assemble into a stable cluster. For high pressures 520 GPa molecular dissociation appears due to a high population in an antibinding orbital. The Figures illustrate the systematic changes in the different properties of the confined molecular/atomic system. These results are of interest in the search to achieve the metallic state of hydrogen under pressure.

3.7. Connections with Reviews in other fields of Materials Science

This section is limited to Reviews in surface science, and on toroidal dipole moments and interactions in metamaterials and in nanophotonics, in which some of our works have been cited.

The Review Article "Auger neutralization and ionization processes for charge exchange between slow noble-gas atoms and solid surfaces" [79] in Progress Surface Science, in its Ref. [147] cites our work: "Ground-state energy shift of He close to a surface and its relation with the scattering potential: a confinement model" [80]. Both articles have also the respective common Refs. [152-153] and [3-4] by Wethekam and Winter reporting evidence on the ground state evolution of the He atom close to an $\mathrm{Al}(111)$ surface deduced from He^+ grazing-scattering experiments after Auger neutralization.

The familiar electric multipole $E\ell$ and magnetic multipole $M\ell$ electromagnetic moments and their interactions have a complementary family of magnetic toroidal moments and interactions, as illustrated by our work "Complete electromagnetic multipole expansion including toroidal moments" [81]. Any three-dimensional vector field may be expressed in terms of its longitudinal component; and two transverse components: one toroidal and one poloidal with parallel circle lines and closed lines in meridian planes, respectively. They may be expressed as gradient, angular momentum and rotational of the angular momentum operators acting on scalar Debye potentials, which may be chosen as multipole ℓm solutions of the Helmholtz equations. The simplest examples for dipoles $\ell = 1$, correspond to a longitudinal, a circular loop and a toroidal solenoid currents as sources of the respective $E1$, $M1$ and $T1$ electromagnetic fields with their poloidal electric field, poloidal magnetic field and toroidal magnetic field, respectively. The toroidal current has a zero magnetic moment and its toroidal moment is the total moment of the magnetic moments of each loop in the solenoid $\vec{T} = \sum_i \vec{r}_i \times \vec{\mu}_i$. The dipole selection rules of angular momentum $l'_f = l_i \pm 1$ are common for the three types of dipole interactions $E1$, $M1$, $T1$; those of parity $\pi_f \pi_i = -, +, -$ are common for $E1$ and $T1$; the angular distribution of their radiation fields are also common for the three; their polarization states are common for $E1$ and $T1$, and different for $M1$; while $E1$ and $M1$ share the Rayleigh ω^4 frequency dependence of their radiation power, in $T1$ it becomes ω^6. These rules generalize for all l multipoles. Reference [81] is cited in the Reviews below.

A selected sample of toroidal dipole moment interactions and their novel physical effects is illustrated by the titles of Refs. [82-91] for metamaterials: "Observation of ferrotoroidic domains" [82], "On the aromagnetism and anapole moment of anthracene nanocrystals" [83], "Gyrotropy of a metamolecule: wire on a torus" [84], "Toroidal dipolar response in a metamaterial" [85], "All-optical Hall effect by the dynamic toroidal moment in a cavity-based metamaterial" [86], "Resonant Transparency and Non-Trivial Non-Radiating Excitations in Toroidal Metamaterials" [87], "Toroidal dipolar excitation and macroscopic electromagnetic properties of metamaterials" [88], "Planar superconducting toroidal metamaterial: a source for oscillating vector-potential?" [89], "Toroidal circular dichroism" [90] and "Nonradiating sources, dynamic anapole, and Aharonov-Bohm effect" [91].

"Theory and applications of toroidal moments in electrodynamics: their emergence, characteristics, and technological relevance" [92] is a review article in Nanophotonics. Its sucessive sections illustrate the place of the toroidal moments: in Sec. 2 Families of multipoles in electrodynamics: 1) Multipole expansions for potentials and fields, 2) Classification of multipoles according to symmetry rules, under space and time inversions, in electric E associated with polarization $(-,+)$, magnetic M associated with magnetization $(+,-)$, toroidal T associated with density of toroidal moments, or toroidization, $(-,-)$ and axial toroidal G associated with axial toroidization $(+,+)$. Section 3. Characteristics, interaction, and radiation of toroidal moments in materials includes: 1) Toroidization and Magnetoelectric effect, a spontaneous magnetization (polarization) induced by an external electric (magnetic) field in a variety of materials, 2) Interaction of optical waves with toroidized materials, 3) Dynamic toroidal moments in artificial metamolecules and dielectric nanostructures, 4) Electromagnetic fields and radiation patterns associated with toroidal moments. Section 4. Excitation of toroidal moments can be achieved by 1) External light and 2) Relativistic electrons. Section 5. Coupling of toroidal moments to other classes of moments includes 1) Formation and discovery of anapoles and 2) toroidal metamaterials. Section 6. Applications of toroidal moments. Section 7. Conclusions and Outlook.

4. Reviewer's and Collaborators' Work

This section updates the work of the Reviewer and his collaborators in two lines of research: One- electron diatomic molecular ions confined by dihedral angles and Many-electron atoms in the same situation of confinement in 4.1; Theory of Angular Momentum in Bases of Lamé Spheroconal Harmonics and its applications in 4.2. It also contains in 4.3 a preview of ongoing investigations along those two lines, and on toroidal moments and their interactions, as well as on the Force Approach to Radiation Reaction.

4.1. Confinement of Atoms and Molecules in Dihedral Angles

Reference [17] in its Section 1.4.3 and 1.4.2 anticipated the investigations on the one-electron diatomic molecular ions and the filling of electronic shells in atoms under dihedral angle confinement. The two next subsections describe the updating of results on both problems.

4.1.1. *The H_2^+ and HeH^{2+} molecular ions confined in dihedral angles*

The authors of [17] were invited to participate in the Workshop on Concepts of Mathematical Physics in Chemistry in honor of Professor Frank Harris in December 2014. In the oral presentation preliminary results on the H_2^+ molecular ion were presented, and results on the HeH^{2+} ion were also included in the written version [93].

The updating of the chapter under consideration starts by calling the attention of the reader to its references [1-12] dealing with the hydrogen molecule and molecular ion confined in prolate spheroidal boxes, and the last one in cylindrical harmonic confinement; [13-14] on the hydrogen atom and harmonic oscillators confined in dihedral angles; and the remaining ones [15-25] on the exact solutions for the free molecules, including the heteronuclear $\mathrm{HeH2}^+$, in the Born-Oppenheimer approximation. Naturally, the Schrödinger equations for the respective molecules are common for the free ones and for the ones confined by natural boundaries in confocal prolate spheroids or hyperboloids, or dihedral angles. The separability of the equation and the integration of the ordinary differential equations in the respective coordinates are also common. It is the change of boundary condition in the chosen confining geometry which determines the changes in the eigenvalues of the energy and the other constants of motion, and in the eigenfunctions. Our works in [8-9] involved confinement in impenetrable and penetrable prolate spheroidal boxes, respectively, with rotational invariance around the axis of the spheroid and $e^{im\varphi}$ eigenfunctions. In contrast, for confinement in a dihedral angle the $0(2)$ symmetry is broken and the eigenfunctions $\sin \mu\varphi$, where $\mu = n_\varphi \pi/\varphi_o$ for $n_\varphi = 1, 2, 3$ may no longer be integer, as discussed in detail in [13-14], including the breaking and restoration of the parity symmetry in the Legendre polynomials with associativity μ in the hyperboloidal coordinate for the homonuclear H_2^+ molecule. The separated equations (5-6) in the hyperboloidal $\eta = (r_1 - r_2)/R \in [-1, 1]$ and spheroidal $\xi = (r_1 + r_2)/R \in [1, \infty]$ coordinates, where r_1 and r_2 are the distances of the electron from nuclei 1 and 2 with the separation R, share the same structure involving the square of the angular momentum Legendre operator, linear terms with different coefficients $(Z_1 - Z_2)\rho\eta$ and $(Z_1 + Z_2)\rho\xi$, where $\rho = R/a_0$, quadratic terms with the same coefficient $-p^2\eta^2$ and $p^2\xi^2$, where $p^2 = -\rho^2 W > 0$ in terms of the electronic energy $W = 2a_0E/e^2 - 2Z_1Z_2e^2/\rho$ in units of $e^2/2a_0$, as the difference between the energy of the molecule E and the Coulomb repulsion energy between the nuclei, and the common constant of separation K.

For the molecular ions confined in dihedral angles, in the homonuclear case $Z_1 = Z_2$, the linear term in η vanishes. The eigenfunctions have a definite parity, gerade and ungerade. Their classification is made via the number of nodes of the spheroidal and hyperboloidal coordinates and the azimuthal quantum numbers $(n_\xi, n_\eta, n_\varphi)$ and parity. Since μ

is no longer integer the usual classification based on $m = 0, 1, 2, \ldots, \sigma, \delta, \pi, \ldots$ is no longer valid, but their equivalents are $n_\varphi = 1, 2, 3, \ldots$ with $0, 1, 2, \ldots$ nodal meridian planes between the two defining the confining dihedral angle. The lower states $(0,0,1)_g$, $(0,1,1)_u$ and $(0,2,1)_g$ are evaluated by constructing the matrix representation of Eq. (5) in the basis of Legendre polynomials with associativity μ and definite parities. The matrix elements of η have the selection rules $n'_\eta = n_\eta \pm 1$, with nonvanishing elements on the diagonals above and below the main diagonal of the matrix. The matrix elements of η^2 have the selection rules $n'_\eta = n_\eta - 2, n_\eta, n_\eta + 2$, with non vanishing elements on the main, and two above and below diagonals. Equation (12) gives the explicit form of the pentadiagonal matrix, with its entries evaluated in the Appendix by using mathematical induction and ladder operators identified in its Ref. [14]. For the homonuclear molecule, the matrix becomes tridiagonal because the entries in the first diagonals above and below vanish. For chosen values of the nuclear separation ρ and the electronic energy parameter p^2, the diagonalization of the matrix leads to the eigenvalues of the separation constant K_η, and the eigenvectors $a_{n_\eta}(K_\eta)$ as the coefficients in the expansion in the basis of Legendre polynomials with associativity μ and definite parity. The size of the matrix is changed to test for convergence and accuracy.

Equation (6) in the spheroidal coordinates ξ is solved by Jaffé's method using the ansatz of Eq. (13) with the removing singularity factors $(\xi^2 - 1)^{\mu/2}\, e^{-\rho\xi}(\xi + 1)^\sigma$ and a Taylor series in the variable $(\xi - 1)/(\xi + 1)$ where $\sigma = (Z_1 + Z_2)p/2\rho - (\mu + 1)$. The coefficients in the series satisfy a three-term recurrence relation with the parameters μ, ρ, σ, K, Eqs. (14) and (15); the recurrence relations can be recast into a matrix form for the eigenvalue problem following its Ref. [18]. The matrix is tridiagonal and nonsymmetric, the eigenvectors contain the coefficients in the Taylor series and the eigenvalue is $K + p^2$. The diagonalization of the matrix yields the separation constant K_ξ, and the eigenvectors $b_{n_\xi}(K_\xi)$ for the chosen values of ρ and p^2. The test of convergence and accuracy for large enough matrices can also be implemented.

The eigenfunctions of the molecule must involve common values of ρ, p^2 and the separation constants from the solutions of the Eqs. (5) and (6): $K_\eta(R, W) = K_\xi(R, W)$. The matching of this condition for different values of the nuclear separation and the electronic energy provides the information on the relationship between these two quantities for each electronic state and each angle of confinement. Figure 1 illustrates the variations of $W(R)$ for A) the ground state $(001)_g$ and B) the excited state $(021)_g$, for $R\,[0.1, 100]$ in logarithmic scale $W[-2, 0]$ and $W\,[-.45, -0.5]$ in a linear scale, respectively; and $\varphi_0 = 2\pi, 3\pi/2, \pi$ and $\pi/2$ with the respective values of $\mu = 1/2, 2/3, 1, 2$ from lower to higher values of the energy. In A) for very small nuclear separations, the electronic energy curves approach the united atom limit with a nuclear charge of $Z_1 + Z_2 = Z$ in the confined situation and energy $-4/\left(\mu+1\right)^2 = -16/9, -36/25, -1, -4/9$ for the respective angles at the positions with the dots on the left vertical scale. Each energy curve increases monotonically as the nuclear separation increases, and on the right-hand side at the vertical the values of the dissociated molecule has the electronic energy of the hydrogen atom with $Z = 1$ with the values of one fourth of those for the united atoms: $-4/9, -9/25, -1/4, -1/9$, to which the energy curves approach from below. For comparison in B) the electronic energies show minimum values in the vicinity of $R \approx 10$, showing increments for both smaller and larger nuclear separations; to the left they become horizontal for small separations approaching their united atom limits $-4/\left(\mu+3\right)^2 = -16/49, -36/121, -1/4, -9/25$ also indicated by the dots on the left vertical; to the right they increase noticeably, but for $R = 100$ are still below their dissociating limits $-1/\left(\mu+2\right)^2 = -4/25, -9/64, -1/9, -1/16$, respectively; for even larger separations they keep increasing and for $R \approx 300$ are approaching those values from below. Notice that the latter do not have the $1/\left(\mu+3\right)^2$ dissociating unlike the situation for the ground state.

Figure 2 illustrates the difference between the free molecular ion and the quasi-free molecular on with $\varphi_0 = 2\pi$. Differences are expected, because the first one has all the directions in φ available $[0, \pi]$, but the confined one is excluded from $\varphi = 0$ and $\varphi = 2\pi$ which is the meridian half plane $(x = 0, y, z)$.

The free ion states are $(000)_g$ $(010)_u$ and $(020)_g$ with the united atom energies $-4, -1, -4/9$ interlaced with those of the confined one from Fig. 1 and the ungerade state $(011)_u$, at $-16/25$. Notice the similar behaviors of the pairs of electronic energy curves of the corresponding ground and excited states for the free and confined configurations, monotomically increasing for the first and with minimum values in the other two. Notice also the crossing of the ground state energy curve of the confined ion and the ungerade state energy curve of the free ion, with different parities at around $R \approx 2$. For larger separations the free $(000)_g$ and $(010)_u$ approach their common dissociation limit at -1, while their confined counterparts parts $(001)_g$ and $(011)_u$ do it at $-4/9$; the second excited states free $(020)_g$ and confined $(021)_g$ have their dissociation limits at $-1/4$ and $-4/25$, respectively.

The total energy of the molecule is the sum of its electronic energy and the Coulomb nuclear repulsion energy. Figures 3 follow from Figures 1 by adding the positive value and inversely proportional to the nuclear separation of the latter. Remember that the horizontal scale is logarithmic. Additionally, the energy curves for the extra angles of confinement $\varphi_o = 11\pi/6, 5\pi/3, 8\pi/9, 7\pi/9$, and $2\pi/3$, and their respective values of μ are included.

The reader may appreciate the similarity of the curves and their systematic changes with the nuclear separation and with the confining angle for each state: they show a well defined minimum which shifts to larger nuclear separations and higher energies as the angle diminishes from its larger value below to smaller ones above. The differences between the curves for A) the ground state and B) the excited state of the same parity are quantitative with the minima more to the right and higher. Remember also the different vertical scales. Since the nuclear energy approaches zero for large separations, the total energy curves approach the dissociation energies asymptotically, from below as the electronic energy does. Table 1 illustrates the variations of the total energy $E\left(R,\varphi_0\right)$ for the ground states.

Each molecular energy curve is also characterized by the position of its minimum (R_e, E_e) in terms of the equilibrium nuclear separation and its variations from there $R-R_e$, $E(R)-E(R_e)$. Dunham's parametrization does it in terms of a harmonic oscillator approximation plus asymmetries of higher order $E(R) = E(R_e) + A_o z^2\left(1+A_1 z+A_2 z^2\right)$, where $z = \left(R-R_e\right)/R_e$. In turn, the rotational constant B_e, the vibrational frequency ω_e, the anharmonicity constant $\omega_e x_e$ and the Raman frequency ω_R can be determined for each energy curve as reported in Tables 2 and 3 for the ground and excited states, respectively. The corresponding values for the free molecule are also included, and the reader may appreciate the significant changes in the rotational vibrational properties of the molecule due to the confinement in the dihedral angles.

Figure 4 also follows from Fig. 2 by adding the Coulomb nuclear repulsion energy, for the ground and excited states of the molecule for $\varphi_o = 2\pi$, illustrating their total energy curves together. The reader may recognize the curves for the gerade states $(001)_g$ and $(021)_g$, below and above from Figs. 3A and 3B, respectively. The first excited state $(011)_u$ of opposite parity shows a monotonic decreasing as the nuclear separation increases and approaches asymptotically the dissociation limit form above, as the ground state does it from below, as their electronic energies did in Fig. 2. Notice that the shallow minimum of the ungerade state in Fig. 2 disappears in Fig. 4 due to the dominant Coulomb repulsion energy. The gerade states of the molecule are binding, but the ungerade state is antibinding.

Figures 5 and 6 also show the comparisons between the hyperboloidal wave functions of the free molecular ion $(000)_g$, $(010)_u$ and $(020)_g$ states and the dihedrally confined in $\varphi_0 = 2\pi$ $(001)_g$, $(011)_u$, and $(021)_g$ states, in their respective A, B and C entries. In Fig. 5: A) is symmetric and has no nodes, B) is antisymmetric and has its node at $\eta = 0$, and C) is symmetric and has two symmetrically located nodes in the interval $(-1,1)$ and for different nuclear separations. In Fig. 6: They share the nodes at $\eta = -1$ and 1 associated with the singularity removing factor $\left(1-\eta^2\right)^{\mu/2}$, A) is symmetric and has no node, B) is antisymmetric and has its node in $\eta = 0$, and C) is symmetric and has two symmetrically located nodes in the open interval $(-1,1)$ and for the same different nuclear separations; the approaching to the nodes at the extremes is preceded by a sharp maximum or minimum. The differences arise from the values of $m = 0$ and μ due to the confinement in the dihedral angle.

The confined molecular ion also acquires an electric dipole moment in the equatorial plane $\eta = 0$ and in the direction from the center of charge of the electron in the meridian plane bisecting the confining dihedral angle to the center of the molecule, which is the center of charge of the two nuclei. The evolution is explained in Eqs. (16) and (17) and the results reported in Table 4 for different angles of confinement for the H_2^+ molecular ion its ground state. Their values range from 1.145, 3.502 and 9.158 in units ea_0 for $\varphi_0 = 2\pi, \pi, \pi/2$, increasing as the angle diminishes. Here we include the corresponding values for the hydrogen atom in the respective situations of confinement in its ground state in spherical coordinates, Table 1.2 [17]: 1.27307, 3.75000, 9.2807 which are slightly larger.

Concerning the HeH^{++} molecular ion, the proton is located in the lower focus $(\xi = 1, \eta = -1, \varphi)$ and the He nucleus in the upper one $(\xi = 1, \eta = 1, \varphi)$. For its confinement in dihedral angles the azimuthal eigenfunctions and eigenvalue μ are the same as for the homonuclear molecular ion. Since now $Z_1 - Z_2 = -1$, the linear term in ρ in the matrix eigenvalue equation of Eq. (12) must be included, and the solution involves the diagonalization of pentadiagonal matrices. Parity is not conserved and the classification in g and u states is not valid. The eigenvalue equation for the spheroidal degree of freedom, Eq. (6) with $Z_1 + Z_2 = 3$, accepts Jaffé solutions of Eq. (13). The methodology to obtain the molecular ion electronic eigenfunctions, eigenenergies and constant of separation, for each nuclear separation, is the same.

The results for the ground (001) and first excited (011) states are reviewed next in the same order as in the homonuclear molecular ion. Figure 7 shows their electronic energies for $\varphi_0 = 2\pi$ as functions of the nuclear separation in the interval $[0.1, 100]$ in logarithmic scale and their own values in the vertical scale in the interval $[-4, -0.5]$. The ground state shows a monotonically increasing variation interpolating between the Li $(Z = 3)$ united atom hydrogen-like atoms limit at -4, and the dissociation limit of He$^+$, $Z = 2$, at $-16/9$. On the other hand, the first excited state starts from $-36/25$, exhibits a minimum at about $R \approx 2$ and increases approaching the dissociation limit in the excited state at $-16/25$.

Figure 8 shows the total energies for the same states and the same situation of confinement on a vertical scale in the interval [-1.7,1], in the interval of nuclear separations [0,20] in a linear scale. Both exhibit the divergent Coulomb nuclear repulsion energy for vanishing separations. The ground state total energy curve is monotonically decreasing and is identified as an antibinding state. The excited state exhibits a shallow minimum at about $R \approx 6$ followed by a small increase and continuous monotomic decreasing.

Figure 9 is the set of total energy curves in the interval $[-0.65, -0.1]$ versus nuclear separation in the interval $[1, 100]$ in logarithmic scales for the values of $\varphi_0 = 2\pi, 11\pi/6, 5\pi/3$, π and their corresponding values of μ for the first excited states. The change of the horizontal scale enhances the occurrence of the minimum, the small increase and the monotomic decreasing for the lower states; the first two characteristics disappear for $\varphi_0 = \pi$ and smaller, and even for the two previous ones. Their monotomic decreasing in the entire range of nuclear separations allows to identify them as antibinding. For the lower energy curves and larger angles of confinement, the presence of a minimum followed by a maximum and then a monotonic decreasing can be quantitatively established; for $\varphi_0 = 2\pi$, $R_{\min} \approx 7$ and $R_{\max} \approx 10$. The corresponding well may bind the molecule, which may also tunnel through the barrier and dissociate. Thus, the state is identified to be metastable.

Bates and Carson in [21] of the chapter under review studied the exact wave function of HeH^{2+} in its free configuration in the Born Oppenheimer approximation, identifying for the first time the metastable character of its (010) excited state in 1956. References [22] and [23] by Ben-Itzhak *et al* reported the experimental evidence for the existence of the $2p\sigma$ bound state of HeH^{2+} and its decay mechanism in 1993, and the mean lifetime of the bound $2p\sigma$ state of HeH^{2+} in 1994. Here we must point out that the metastability of the corresponding state (011) under dihedral confinement is still present for the angles $2\pi > \varphi_0 > 3\pi/2$.

Figure 10 illustrates the electronic hyperboloidal coordinate function for the ground state of the HeH^{++} molecular ion for $\varphi_o = 2\pi$ and $R = 7$ with its two nodes at $\eta = -1$ and $\eta = 1$, no nodes in between and a pronounced extreme near $\eta = 1$ where the He is located. The preference of the electron to be close to the He nucleus is related to the antibinding nature of the state.

In contrast, Fig. 11 with the corresponding eigenfunction for the excited state shows the common nodes at $\eta = -1$ and $\eta = 1$, with large amplitudes to be between the proton and the He nucleus, allowing for some binding; and also an extreme near $\eta = 1$ but of fairly small amplitude. Figure 12 shows the companion eigenfunction exhibiting the node at $\xi = 1$ with a large maximum nearby, no other node and an exponential decrease with vanishing amplitudes for $\xi > 3$.

Figures 13 A and B, and 14 A and B compare the hyperboloidal eigenfunctions for the A) free and B) confined in $\varphi_0 = 2\pi$ molecular ion in the respective ground and excited states, (000) and (001), and (010) and (011), for nuclear separations of 0.2, 10 and 20, and others. Apart from the nodes at $\eta = \pm 1$ in B the behaviors in between are very similar for each nuclear separation. Such common behaviors are behind the antibinding and metastable characters of the respective states in the free and confined configurations.

4.1.2. *O(2) Symmetry Breaking in Dihedrally Confined Atoms and Consequent Modifications of the Periodic Table*

The authors also participated in the International Colloquium of Group Theoretical Methods in Mathematical Physics $G31$ in June 2016, with the contribution having the same title as this subsection. The written contribution for the proceedings [94] is focused on the evaluation of the electron-electron Coulomb repulsion multipole component matrix elements between hydrogenic wave functions needed for Hartree-Fock calculations for the atoms in dihedral angle confinement.

The introduction of this contribution describes the symmetry breaking, in the hydrogen atom confined in dihedral angles as reported in [17]: i) it acquires an electric dipole moment, ii) its Fermi contact term in the hyperfine structure vanishes, iii) its Zeeman effect in first order perturbation theory vanishes and degenerate state perturbation theory is needed for its analysis, iv) the degeneracies of the energy levels D as functions of the confining angle are identified, with the consequent anticipation that v) the filling of the electron shells in the successive atoms and periodicity in their properties are different form those of the free atoms. Quantitative answers about the latter require Hartree-Fock calculations for the atoms confined in dihedral angles, specially for those with a nucleus with a charge Z, and Z and $Z - 1$ electrons. The remaining sections: 2) deals with the evaluation of the matrix elements of the Coulomb electron-electron repulsion in the basis of the hydrogen like orbitals with non integer associativity and definite parity, for which 3) shift operators and recurrence relations have been identified, and discussed in 4) in order to implement the Hartree-Fock calculations.

The hydrogenic wave functions under dihedral confinement [93] are presented in Eqs. (1) in their azimuthal sine and cosine dependence and $\mu = n_\varphi \pi/\varphi_o$ eigenvalues, Eqs. (2) in their polar angle Legendre polynomial dependence with noninteger associativity μ and restored parity Eq.(3), and their radial dependence is the same as for the free atom except that the angular momentum label is $\lambda = n_\theta + \mu$, also noninteger.

The electron-electron Coulomb repulsion is given in Eq. (4) in its multipole expansion form involving their harmonic radial $\left(r_<^l / r_>^{l+1}\right)$, polar angle $P_l^m(\eta_1) P_l^m(\eta_2)$ and azimuthal $(\cos m\varphi_1 \cos m\varphi_2 + \sin m\varphi_1 \sin m\varphi_2)$ functions. The corresponding matrix elements take the multipole expansion form of Eq. (5) involving the radial integrals of Eq. (16) of the same form as for the free hydrogen atom radial functions, the azimuthal integrals Eq. (7) with the closed forms and selection rules of Eqs. (9-13), and the polar angle integrals of Eqs. (8) and (14), for electrons $i = 1, 2$. The polar angle integrals involve the powers $\mu/2$ of $\left(1 - \eta^2\right)$ and s of η from the associated Legendre polynomials in Eq. (4); their evaluation is based on the shift operators and recurrence relations identified in 3) and discussed in 4).

In Ref. [26] of [17], we reported the identification of Ladder operators for quantum systems confined by dihedral angles, which also have their counterparts for the hydrogen molecular ion in the same situation of confinement. There, it is illustrated how multiplication by $\eta = \cos\theta$ of $|n_\theta, \mu\rangle$ leads to the superposition of $|n_\theta - 1, \mu\rangle$ and $|n_\theta + 1, \mu\rangle$ with the same associativity and polar angle excitations one unit below and above, respectively. The derivative with respect to η has the same effects.

Here, the Legendre polynomials within the multipole expansion with integer associativities $m = 0, 1, 2\ldots$ require the identification of shift operators changing the associativities of the polar angle eigenfunctions. Starting from Eqs. (8.5.2) and (8.5.4) and (8.5.5) in [95], we have identified that multiplication by $\left(1-\eta^2\right)^{1/2}$ of such eigenfunctions leads to other eigenfunctions with lower associativities Eq. (16) and higher associativities Eq. (17) of one unit, respectively; notice also the changes in the polar excitation and the multiplication by η in the second term in Eq. (16), and the corresponding double deexcitation in the second term in Eq. (19). Equations (18-21) illustrate the results of the recursive applications of Eqs. (15-17) involving multiplications by additional factors of the η or $\left(1-\eta^2\right)^{1/2}$ type, leading to superpositions of states with different polar excitations and associativities.

The matrix elements of $\left(1-\eta^2\right)^{m/2}\eta^s$ acting on an initial state $|n_\theta, \mu\rangle$, and written as a superposition of states of different polar excitations and associativities, are obtained by the multiplying by the bra $\langle n'_\theta, \mu'|$ which will project into the state matching its excitation and associativity with a well defined amplitude. The selection rules and numerical values of the matrix elements are thus determined.

4.2. Angular Momentum Theory in Bases of Lamé Spheroconal Harmonics

In the same Workshop in honor of Professor Frank Harris, the authors of the contribution with the title of this subsection and its written version [96] a review of the key concepts of angular momentum theory in bases of spheroconal harmonics. Such an alternative had already been contemplated in [4] for the rotations of free asymmetric molecules and free quantum systems with central potentials, and their counterparts confined in elliptical cones as natural boundaries in spheroconal coordinates. The implementations of the latter for asymmetric molecules, the free particle, the hydrogen atom and the harmonic oscillator were reported in the 50th Sanibel Symposium and its Proceedings, as well as in an invited review chapter in AQC61. The corresponding references were reviewed in [17] Subsection 1.2.3. The updating of this line of research starts with [96], includes the application in [97] of interest in magnetic resonance imaging and neutral atom traps, and [98] reporting a new class of shift operators and recurrence relations for individual Lamé polynomials at the G31.

4.2.1. Concepts of Mathematical Physics in Rotations of Asymmetric Molecules

The main sections in [96] had the headings: 2. *Symmetries in the rotations of Asymmetric Molecules* and 3. *Actions of Operators of Angular Momentum and Linear Momentum on Rotational Eigenstates*. In this updating the review of [98] is limited to a characterization of the Lamé spheroconal harmonics as common eigenfunctions of the square of the angular momentum and asymmetry distribution Hamiltonian operators, Eq. (7), commuting with each other, Eq. (8). In this way, the review of Sect. 3 can be done more in detail with emphasis on the structure of the respective operators, their relationships, and their matrices in spheroconal harmonic bases.

The readers interested in the mathematical details are referred to the Appendix, which includes the cartesian and spheroconal coordinate transformations Eqs. (A1), the linear momentum operators Eqs. (A8), the angular momentum operators Eqs. (A12), and the simultaneous separations of the eigenvalue equations (A18) of the square of the angular momentum and (A19) of the asymmetry distribution Hamiltonian, provided the asymmetry coordinate parameters $k_1^2 + k_2^2 = 1$ and the asymmetry dynamical parameters $e_1 + e_2 + e_3 = 0$, $e_1^2 + e_2^2 + e_3^2 = \sqrt{3}/2$ are related by Eq. (A16).

The respective eigenvalue equations can be separated into ordinary Lamé differential equations (A21) in the respective elliptical cone coordinates, because the operators commute with each other. The spheroconal harmonics are products of Lamé functions in both elliptical cone coordinates Eq. (A24) with matching asymmetry parameters $k_1^2 + k_2^2 = 1$; matching species of their singularity removing factors connected with states of definite parities $[A, B] = [1, x, y, z, xy, xz, yz, xyz]$ and numbers of nodal planes $n^1 = 0$, $n^x = n^y = n^z = 1$, $n^{xy} = n^{xz} = n^{yz} = 2$, $n^{xyz} = 3$; matching numbers of total numbers of nodes $n^{AB} + n_1 + n_2 = \ell$, for a given value of the angular momentum label $\ell = 0, 1, 2, \ldots$ with a square of the angular momentum eigenvalue $\ell(\ell+1)$, where n_1 and n_2 are the respective numbers of elliptical cone nodes; matching separation constants $h^A_{n_1}(k_1^2) + h^B_{n_2}(k_2^2) = \ell(\ell+1)$ and $e_1 h^A_{n_1}(k_1^2) + e_3 h^B_{n_2}(k_2^2) = 2E^*$, Eqs. (A23), connected with the eigenvalues of the respective operators, where e_1, e_2, e_3 are the alternative set of asymmetry parameters.

The spheroconal coordinates (r, χ_1, χ_2) are written in terms of Jacobi elliptical integrals of the types $\mathrm{sn}(\chi_1|k_1^2)$, $\mathrm{cn}(\chi_1|k_1^2) = \sqrt{1-\mathrm{sn}^2(\chi_1|k_1^2)}$, $\mathrm{dn}(\chi_1|k_1^2) = \sqrt{1-k_1\mathrm{sn}^2(\chi_1|k_1^2)}$.

The spheroconal harmonics of lower order and monomial forms are identified in the following table, using only the symbols of the functions for $i = 1, 2$ in the successive powers.

ℓ	0	1	1	1	2	2	2	3
A	1	dn	cn	sn	cnsn	dnsn	dncn	dncnsn
B	1	sn	cn	dn	cndn	sndn	sncn	sncndn
$r^\ell\, AB$	1	x	y	z	yz	xz	xy	xyz

The derivatives of each Jacobi elliptic integral involves the products of the other two with the coefficients $1, -1$ and $-k^2$. The derivatives of the square of each one of them is the product of the three of them with the respective coefficients $2, -2$ and $-2k^2$. The derivative is odd under the exchange $\chi_i = -\chi_i$, and so is the sn function, while the other two cn and dn are even. The general form of the individual Lamé polynomials involves the singularity removing factor and a polynomial of degree n_i in sn$^2(\xi_i|\chi_i^2)$. The individual Lamé polynomials of the different species and excitations are characterized by the quantum labels $|n_1\ell[A]\rangle$ and $|n_2\ell[B]\rangle$ for $i = 1, 2$, respectively. Their product corresponds to the Lamé spheroconal harmonics represented by $\Psi^{l[AB]}_{n_1n_2}$, as characterized in the previous paragraphs.

The spheroconal coordinates in Eq. (A4) are defined in terms of Jacobi elliptical integral functions connected by Eqs.(A2) and derivatives in Eqs.(A3). They are useful to obtain the displacement $d\vec{r}$, in terms of the orthogonal radial and elliptic cone unit vectors $(\hat{r}, \hat{\chi_1}, \hat{\chi_2})$ Eqs. (A6) and Eqs.(A4), the scale factors $h_r = 1$ and $h_{\chi_1} = h_{\chi_2}$, Eqs.(A5).The gradient vector in Eqs. (A7) leads to the identification of the linear momentum cartesian components in Eqs.(A8); notice that under the exchange $1 \rightleftharpoons 2$ of the elliptical cone arguments: $P_x \rightleftharpoons P_z$ and $P_y \rightarrow P_y$ similar to the coordinate exchanges $x \rightleftharpoons z$ and $y \rightleftharpoons y$. The angular momentum operator follows from the vector product $\vec{r} \times \vec{p}$, in the spheroconal bases in Eqs. (A.11) and in the cartesian component in Eqs. (A12). The momentum operator has radial components with the respective partial derivatives and the common scale factors; its cartesian components have the respective partial derivatives with the direction cosines of the respective radial and elliptic cone unit vectors along $\hat{i}, \hat{j}$ and $\hat{k}$ and their respective coefficients; those for the radial derivative involve one Jacobi elliptic integral function in each variable; the other ones involve two of such functions in the variable of the derivative and one in the other, because the derivatives of each Jacobi elliptic integral function involves its two companions. The cross product of the radial position vector and the linear momentum operator leads to the angular momentum without a radial derivative component, and cartesian components with the coefficients of the partial derivatives with respect to χ_1 and χ_2 exchanged and a possible change of sign, from those in the cartesian components of $\vec{p}$. Now, the exchange $1 \rightleftharpoons 2$ leads to: $\hat{L_x} \rightleftharpoons -\hat{L}_z$ and $\hat{L_y} \rightleftharpoons -\hat{L}y$.

The successive actions of the cartesian components of the radial position vector, linear momentum and angular momentum vectors on the singularity removing factors are in Table 4 for [AB], in Table 5 and 6 for the terms with the derivatives with respect to χ_1 and to χ_2 respectively, and in Table 7 and 8 also for the corresponding operations, including the distinction of their actions on the successive factors depending on one variable or the other, as well as the resulting species [AB] with definite cartesian parities. In Tables 5 and 6 the reader may notice the differences in the entries in the respective rows for χ_1 and χ_2, which nevertheless lead to the same values of [AB]. Additionally, they coincide with the respective entries of their counterparts in Table 4. The reason for this coincidence is that both $\vec{r}$ and $\vec{p}$ are vectors and share the same negative parity, they can only connect rotational eigenstates of different parity and angular momentum with the selection rule $\ell^{'} = \ell \pm 1$. In Tables 7 and 8 the reader may notice the differences in the entries in the respective rows and their spheroconal compositions, which nevertheless lead to their common cartesian species [AB], just like in the case of linear momentum. However, for the angular momentum, the connection is between states of the same parity. This is directly connected with the exchange of the coefficients of the respective derivatives in χ_1 and χ_2, between the angular momentum and linear momentum operators in their cartesian components. Since the rotational eigenstates are eigenstates of L^2, which commutes with L_x L_y and L_z, the latter can only connect with states with the same eigenvalue ℓ. The entries in the Tables 5-8, containing factors of the squares of sn, cn and dn are polynomials of the respective orders of sn^{2t}, which can be rewritten as a linear combinations of the connected rotational eigenstates. The natural way to display the actions of the respective operators on the spheroconal harmonics and the connections among them, is by constructing their matrices in the spheroconal harmonic bases. Section 3.3 illustrates the structure of the angular momentum L_x, L_y, L_z matrices in such bases for $\ell = 1, 2, 3, 4$. For $\ell = 1$ the basis has three eigenstates x, y, z. L_x transforms y in z and viceversa, L_y does likewise for z in x, and L_z for x and y. The matrices are hermitian with entries $\pm i\hbar$ in the elements (2, 3) and (3, 2), (1, 3) and (3, 1), and (1, 2) and (2, 1), respectively, and zeros for the remaining entries. For $\ell = 2$ the basis has five eigenstates $\Psi^{2[1]}_{02}$, xy, zx, yz, $\Psi^{2[1]}_{20}$ and the nonzero entries in the respective matrices are six. For L_x: (1, 4) and (4, 1), (2, 3) and (3, 2) of $\pm i\hbar$, and (4, 5) and (5, 4). For L_y: (1, 3) and (3, 1), (2, 4) and (4, 2) of $\pm i\hbar$, and (3, 5) and (5, 3). For L_z: (1, 2) and (2, 1), (2, 5) and (5, 2), and (3, 4) and (4, 3) of $\pm i\hbar$. Table 9 shows the explicit entries for the other connections. For $\ell = 3$ the basis has seven eigenstates $[x]_{0,2}, [y]_{0,2}, [z]_{0,2}, [xyz]_{0,0}, [x]_{2,0}, [y]_{2,0}, [z]_{2,0},$ and there are twelve connections among them. For L_x: (1, 4) and (4, 1), (2, 3) and (3, 2), (2, 7) and (7, 2), (3, 4) and (4, 3), (4, 5) and (5, 4), (3, 6) and (6, 3), and (6, 7) and (7, 6); For L_y: (1, 3) and (3, 1), (1, 7) and (7, 1), (2, 4) and (4, 2), (3, 5) and (5, 3), (4, 6) and (6, 4), (5, 7) and (7, 5); For L_z: (1, 2) and (2, 1), (1, 6) and (6, 1), (2, 5) and (5, 2), (3, 4) and (4, 3), (4, 7) and (7, 4), (5, 6) and (6, 5). Table 10 gives the expressions for the explicit entries. For $\ell = 4$ the basis contains nine eigenstates $\Psi^{4[1]}_{n_1n_2}$ $\Psi^{4[xy]}_{n_1n_2}$ $\Psi^{4[xz]}_{n_1n_2}$ $\Psi^{4[yz]}_{n_1n_2}$ with n_1n_2=04, 22, 40 and $n_1n_2 = 02, 20$ for the species 1 and the other three, respectively. They are ordered and interlaced species increasing by the order of excitation of χ_1 with the corresponding decreasing of the order of excitation of χ_2. The reader may see twenty positions in the respective matrices in the reference under review. In this case, Table 11 contains the numerical entries in the respective matrices for the special case of the most asymmetric molecules with $k_1^2 = k_2^2 = \frac{1}{2}$ and $e_1 = -e_3 = \sqrt{3}/2$ and $e_2 = 0$.

Since the numbers of non zero entries in the matrices for the explicit lower values of ℓ are 2, 6, 12, 20, we can state by mathematical induction that they correspond to $\ell(\ell + 1)$. The three matrices have zero entries in the main diagonal and the positions with non zero entries are symmetric with respect to the diagonal. The L_y matrix is also symmetric in its positions with non zeros entries with respect to the other diagonal; L_x and L_z do not have such a symmetry, but get their positions exchanged under reflection relative to that diagonal. For those rows and columns with a single entry the connection is unique, occurring only for the monomials in $\ell = 1$ and 2; the multiplicity of entries in each row or column counts the number of connections with the companion states of the other species, and the relative values of the entries are the probability amplitudes of the connections.

From the individual matrices L_x, L_y and L_z, their squares can be evaluated as well as their sum or their linear combination with the e_1,e_2 and e_3 coefficients yielding the square of the orbital angular momentum and twice the asymmetry distribution Hamiltonian, respectively. Both matrices are diagonal, the first with the common entry $\ell(\ell+1)\hbar^2$ and the second one with twice the energy eigenvalues $E^{*\ell[AB]}_{n_1 n_2}$.

4.2.2. *Family of Lamé spheroconal quadrupole harmonic current distributions on spherical surfaces as sources of magnetic induction fields with constant gradients inside and vanishing asympotically outside*

Constant gradient magnetic fields play key roles in magnetic resonance imaging and in neutral atom traps. Reference [28] in [17] reported our work on spherical and spheroidal quadrupole harmonic current distributions, on the respective surfaces, and the constant gradient magnetic induction fields in their interiors, as well as the exterior asymptotically vanishing companion fields.

Our work with the title of this section [97] is an example of the application of the Lamé spheroconal harmonics, providing an alternative family of solutions from the same problem. We start out by pointing out that of the five quadrupole harmonics $\ell = 2$, $[1]n_1 n_2$ with $n_1 n_2 = 02$ and 20, $[yz]_{00}$, $[xz]_{00}$ and $[xy]_{00}$, the last three coincide with their spherical counterpart, and our analysis is based on the first two.

The solution of the equations of magnetostatics, in order to identify the quadrupole harmonic current distributions and their constant gradient magnetic induction fields, take into consideration the solenoidal character of the latter and Ampere's law. Thus, the magnetic induction field can be written as the rotational of the magnetostatic vector potential. The potential itself is also solenoidal and we write it as the generator of rotations operator $\vec{r} \times \nabla$ acting on the spheroconal quadrupole harmonic $\ell = 2[AB]_{n_1 n_2}$, inside and outside a sphere of radius $r = a$, with the respective radial dependences $A_0 r^2/a^3$ and $A_0 a^2/r^3$, guaranteeing its continuity at the radius of the spherical surface $r = a$. The spheroconal harmonic is the product of two matching Lamé binomials in $\mathrm{sn}^2\left(\chi_i|k_i^2\right)$, $i = 1, 2$, as described in 4.2.1.

The potential does not have a radial component, and its components along the unit vectors $\hat{\chi}_1$ and $\hat{\chi}_2$ involve their own Lamé binomial and the derivative of its companion.

The magnetic induction field inside and outside the spherical boundary are evaluated as the rotational of the magnetostatic vector potential. Their radial components are different because they are directly inherited from their respective potentials, and they share the same dependence in χ_1 and χ_2 involving two terms with the product of one of the Lamé binomials and the second derivative of its companion; however, at the boundary $r = a$ both radial components are also continuous, as expected by Gauss' law. On the other hand, their components in the directions of $\hat{\chi}_1$ and $\hat{\chi}_2$ involve the radial derivatives of r^3/a and a^4/r, inside and outside respectively, and multiplied by the other binomial; now the tangential components at the boundary are discontinuous due to the difference in the radial derivatives. This difference is also expected by Ampere's law and gives the measure of the surface current distribution, which is the quantity of our interest, Eq. (11) in the reference under review.

In Eqs. (9) for the magnetic induction field inside and outside the sphere there appears the common scale factor in the square form in the denominator leading to the linear dependence r and $1/r^4$, respectively. They account for their respective characterizations in terms of constant gradient and asymptotically vanishing.

The current field lines on the spherical surface follow from Eqs. (11) via the condition of tangentiality of Eq. (12) and its integration leading to Eq. (13), which is equivalent to the constancy of the scalar potential from which the magnetostatic vector potential was constructed.

While Eq. (9) uses the unit vectors $\hat{r}, \hat{\chi}_1, \hat{\chi}_2$, the latter can be written in the cartesian basis. The magnetic induction field inside in the familiar cartesian coordinates takes the form of Eq. (16).

Figure 1 illustrates the quadrupole harmonic current distributions on the spheres for different values of the asymmetry parameter. The extreme values $\sigma = 0^\circ, 60^\circ$ correspond to the spherical case with an axis of rotational symmetry.

Table I corrected in an Erratum [97] illustrates the values of the gradients in the x, y and z directions according to Eq. (16), for the different asymmetries. Notice that their sum is zero associated with the solenoidal character of the magnetic field.

4.2.3. *Shift Operators and Recurrence Relations for Individual Lamé Polynomials*

The authors' oral contribution to the Group 31 Meeting had the title ”Review of the development and application of the spheroconal theory of angular momentum”. It consisted of a presentation of our then recent results of the previous two subsections, as well as our preliminary results of our then ongoing development on the topic with the title of this subsection. The written contribution for the Proccedings [98] is focused on reporting our new results on this topic.

Our previous work has been focused on the spheroconal harmonics as eigenfunctions of the square of the angular momentum and the asymmetry distribution operators. While in [8] of the reference under review, an article by the common authors in ”SIGMA Ladder Operators for Lamé Spheroconal Harmonic Polynomials” were identified as the angular momentum operators $L_x,\, L_y,\, L_z$ connecting the eigenstates of a given angular momentum, different species and excitations; in [96] the actions of the linear momentum operators $P_x,\, P_y,\, P_z$ on the spheroconal harmonics consist of different species and different excitations. In the present review the emphasis is on the shifting operators for the individual Lamé polynomials and the recurrence relations among them.

The following Table illustrates the changes in the species of the corresponding polynomials under the derivative operation:

$[A]$	1	cnsn	dnsn	dncn	dn	cn	sn	dncnsn
$\frac{d}{d\chi}\Lambda_{n_1}^{\ell[A]}$	dncnsn	dn	cn	sn	cnsn	dnsn	dncn	1

The reader may notice in the first row the four species with an even number of factors, followed by the other four with an odd number; as well as the exchanges under the derivative in the second row. The shifting actions of the derivative operators are proven by mathematical induction. Eq. (6) illustrates its connecting the three $\ell = 1$ monomial states, with one Jacobi elliptic integral each, to their monomial counterparts with $\ell = 2$ and the products of the other two such integrals, all of them without any elliptical cone nodes.

Equation (7) illustrates the actions of the derivative on the five Lamé polynomials with $\ell = 2$, the three from the previous case and the two of species 1 with $n_1 = 0,\, 2$ elliptical cone nodes, leading to the seven states with $\ell = 3$, as a monomial the one of species scd, and the three superpositions of species [s], [c], [d] in their two $n_1 = 0,\, 2$ states. The respective raising coefficients $R_n^{e_i}$ are determined by comparing the coefficients of the powers of sn^{2t} in the respective rows. Equation (8) also illustrates the possible lowering and raising alternatives with superpositions of $\Lambda_0^{2[e_i]}$ and $\Lambda_n^{2[e_i]}$, $n = 0,\, 2$ involving different sets of coefficients.

The generalizations of the raising action of the derivative on the $\ell = 2N$ even and species [1], [cd], [sd], [cs] to the $\ell = 2N + 1$ odd [scd], [s], [c], [d] species, and on the next $\ell = 2N + 2$ even with the respective species, is illustrated by the two following sets of equations. In the first case, the degree of the polynomial of species [1] in sn^2 is $\ell/2 = N$, and it is $(\ell/2) - 1$ for those of species $[e_i e_j]$; and their derivatives are respectively of species [scd] and degree $(\ell/2) - 1 = [(2N + 1) - 3]/2$, and of species $[e_i]$ and degree $(\ell/2) - 1 = [(2N + 1) - 1]/2$, justifying their identifications as superpositions of Lamé polynomials with $\ell = 2N + 1$ of the different species and excitations. In the second case, the initial states have just been characterized, and their derivatives are of species [1] and $[e_i e_j]$ with polynomials of degrees $(2N + 1 - 3)/2 + 2 = [2N + 2]/2$ and $[(2N + 1) - 1]/2 = [(2N + 2) - 2]/2$, thus justifying also their identification as Lamé polynomials with the common value $\ell = 2N + 2$ even for all four species. There are also additional superpositions of lowering and raising states, for each species and different excitations.

The multiplication of two individual Lamé polynomials with labels e_1 and e_2 leads to other polynomials with other values of ℓ. Equation (9) gives the example of $\Lambda_0^{1[e_i]}\Lambda_0^{1[e_j]}$ becoming $\Lambda_0^{2[e_i e_j]}$ for $i \neq j$. While for $i = j$, Eq.(10) recognizes that e_i^2 can be written as a superposition of $\Lambda_0^{2[1]}$ and $\Lambda_2^{2[1]}$, and also as the alternative superpositions of $\Lambda_0^{0[1]}$ and $\Lambda_n^{0[2]}$ for $n = 0, 2$. Equation (11) shows the product of $\Lambda_0^{[e_i e_j]}$ with itself which is $e_i^2 e_j^2$ and its superposition of $\Lambda_n^{4[1]}$ for $n = 0, 2, 4$. Equation (12) shows the alternative product $\Lambda_0^{1[e_i]}\Lambda_0^{3[e_i e_j e_k]} = e_i^2 e_j e_k$ as a superposition of $\Lambda_n^{4[e_j e_k]}$ with $n = 0, 2$ also. Equation (13) identifies the product $\Lambda_0^{2[e_i e_j]}\Lambda_0^{3[e_i e_j e_k]} = e_i^2 e_j^2 e_k$ as a superposition of $\Lambda_n^{5[e_k]}$ states with $n = 0, 2, 4$. In Eq.(14) the product $\Lambda_0^{1[e_i]}\Lambda_n^{4[1]}$ becomes another superposition of $\Lambda_n^{5[e_i]}$ with $n = 0, 2, 4$. Equation (16) expresses the product of $\Lambda_n^{3[scd]}$ with itself $s^2c^2d^2$ as the superposition of $\Lambda_n^{6[1]}$ with $n = 0, 2, 4, 6$. In the cases above, there are also other alternatives of superpositions with additional polynomials of the same species and with lower values of l, like in Eq.(10). Specifically, in Eq.(11) superpositions with $\Lambda_n^{2[1]}$, $n = 0, 2$, or $\Lambda_0^{0[1]}$; in Eq.(12) with $\Lambda_0^{2[e_j e_k]}$; in Eq.(13) with $\Lambda_n^{3[e_k]}$, $n = 0, 2$, or $\Lambda_0^{1[e_k]}$; in Eq.(14) with $\Lambda_n^{3[e_i]}$, $n = 0, 2$; in Eq.(15) with $\Lambda_n^{4[1]}$, $n = 0, 2, 4$, $\Lambda_n^{2[1]}$ and $\Lambda_0^{0[1]}$.

In the generalization in the ket notation, implying orthonormality and completeness of the basis, the product of two of them can be written as the superposition of the connected states

$$\begin{aligned} &|l_1[A_1]n_1\rangle\, |l_2[A_2]n_2\rangle \\ &\qquad = \sum_{l'[A']n'} |l'[A']n'\rangle\, \langle\, l'[A']n'\rangle\, l_1[A_1]n_1; l_2[A_2]n_2 \end{aligned}$$

as allowed by the addition of their angular momentum operators $\hat{\vec{L}}_1 + \hat{\vec{L}}_2 = \hat{\vec{L}}'$; the superposition coefficients are identifiable from the comparisons of the powers of sn^2 after the common species factor $[A']$ is removed. The application of the derivative is also associated with the addition $\hat{\vec{1}} + \hat{\vec{\ell}}_i = \hat{\vec{\ell}}_f$

4.3. Preview of Ongoing Investigations

This section outlines some of the problems which we have been investigating along the lines of 4.3.1 *the Hydrogen atom confined in a dihedral angle*, 4.3.2 *applications of the angular momentum theory in bases of Lamé spheroconal harmonics*, as well as 4.3.3 *toroidal moments and interactions*, and 4.3.4 *radiation reaction in the force approach*. Preliminary reports about their formulations, advances and results have been presented in the VIII Workshop on the Structure and Dynamics of Matter and Optics, and the LIX and LX Mexican National Physics Meetings.

4.3.1. *SO(2) Symmetry Breaking in the Hydrogen Atom Confined in Dihedral Angles: manifestation in the Zeeman Effect*

This problem was formulated in Sect. 1.3.5 of [17], but at that moment time did not allow the implementation of its solution. Equation (1.17) in that section describes the interaction between the magnetic moment of the electron with its orbital and spin contributions and a uniform magnetic field in the direction of the edge of the confining dihedral angle. While in the free hydrogen atom, the z-component of the angular momentum is a constant of motion leading to the familiar $m\hbar$ equally spaced Zeeman splittings of the energy levels, the situation for the atom in dihedral confinement is radically changed. In fact, the boundary conditions of vanishing wave functions at the meridian planes, $\varphi = 0$ and $\varphi = \varphi_0$, break the rotational symmetry around the z-axis: the eigenfunctions become $\sin\mu\varphi$, where $\mu_\varphi = n_\varphi \pi/\varphi_0$ and $n_\varphi = 1, 2, 3, ...$ instead of $\mathrm{e}^{im\varphi}$. The degeneracies D of the hydrogen atom depend on the angle of confinement as illustrated by Table 1.1 in [17]. The diagonal matrix elements of the z-component of the angular momentum in the basis of eigenfunctions $\sin\mu\varphi$ vanish, so that first order perturbation theory is not applicable. The problem must be solved by using perturbation theory for degenerate states.

Equations (1.18) and (1.19) give the general forms of the matrix elements of ℓ_z in the confined hydrogen atom eigenfunction basis and in the $\sin\mu\varphi$ basis, respectively. The latter defines the selection rules: $n'_\varphi \pm n_\varphi$ even lead to vanishing values, and odd to finite values. The overlap integrals in the radial and polar angle factors of the eigenfunctions $k(n'_r n'_\theta n'_\varphi \mid n_r\ n_\theta\ n_\varphi)$ in Eq.(1.18) were not analyzed at that time. Our recent analysis has led us to recognize that the polar angle eigenfunctions with different parities have vanishing overlaps, and overlaps different from zero require equal parities. Degenerate states have common values of the principal quantum label $\nu = n'_r + n'_\theta + \mu' + 1 = n_r + n_\theta + \mu + 1$ For each choice of n'_φ, n_φ and $n'_\theta, n_\vartheta,$ the choices of n'_r and n_r are also limited. In this way the entries for the $D \times D$ hermitian matrices vanishing and non-vanishing are identified.

The spin contributions to the magnetic moment are readily incorporated via its diagonal elements with eigenvalues $m_s = 1/2, -1/2$, and doubling the size of the matrices $2D \times 2D$. The diagonalization of the finite matrices leads to the eigenvalues of the Zeeman split energy levels and their respective eigenfunctions.

The evaluation of the radial and polar angle eigenfunction overlaps can be done numerically, but we are also exploring alternative ways by using ladder and/or shift operators.

4.3.2. *Applications of Angular Momentum Theory in bases of Lamé Spheroconal Harmonics*

In 4.2.2 an application of Lamé spheroconal quadrupole harmonics in Magnetostatics has already been reviewed. Here we describe three additional applications under investigation, two of them for electromagnetic fields, and the third one for scattering in quantum mechanics.

Indeed, the first one is about Lamé Vector Spheroconal Harmonics, our contribution to the Meeting on Selected Topics of Mathematical Physics in honor of Professor Natig Atakishiyev as a tool to construct solutions of Maxwell's equations for electromagnetic fields with a harmonic time dependence. These solutions are alternatives to the familiar vector spherical harmonics [99], with the advantage that they come in families depending on the value of the asymmetry distribution parameter σ, like in 4.2.2. The longitudinal and transverse characteristics of the sources, electric intensity and magnetic induction fields are guaranteed by using the scalar spheroconal harmonic solutions of the Helmholtz equations with radial spherical Bessel functions, as Debye potentials. The longitudinal components follow from the application of the gradient operator to the Debye potentials. The first family of transverse vector spheroconal harmonics of our interest are constructed by applying the generator of rotations operator $\overrightarrow{r} \times \overrightarrow{\nabla}$ to the Debye potentials, a second family is obtained by applying the rotational operator to the solutions of the first family. By construction both families are solenoidal. The first one is characterized as a toroidal field, and the second one as a poloidal field.

The second application was presented in the LIX Congreso Nacional de Física Session MID12 with the title: "Complete Electromagnetic Multipole Expansion in bases of spheroconal harmonics". The starting point is the multipole expansion of the scalar outgoing wave Green function for the Helmholtz equation in the complete and orthogonal bases of spheroconal harmonics multiplied by the respective spherical Bessel functions in the radial coordinate $r_<$ and $r_>$, the smaller and the larger of the field and source points r and r'. By using such a function as a Debye potential, the successive applications of the operators $\overrightarrow{\nabla}$, $\overrightarrow{r} \times \overrightarrow{\nabla}$, and $\nabla \times (\overrightarrow{r} \times \overrightarrow{\nabla})$ yields the complete expansion of the title in its respective longitudinal, toroidal and poloidal components. The expansion is complete also in the sense that it provides harmonic well-behaved solutions inside and outside a spherical surface of radius $r' = a$. For a given choice of surface charge and current distributions the solutions of the inhomogeneous Helmholtz equation are the surface integrals of the outgoing wave Green function weighted by the respective source distributions. Each term in the expansions selects the respective longitudinal or transverse, as well as spheroconal multipolarity components of the sources. Specifically, the scalar potential is the outgoing wave Green function integral transform of the surface charge density, and the vector potential is the same integral transform of the surface current density. If the sources have a well-defined direction and multipolarity, the potentials share the same properties inside and outside, and are continuous at the boundary. For the electric intensity field, its sources are the gradient of the charge density and the partial time derivative of the current density; and the magnetic induction fields' source is the rotational of the current density. They can also be evaluated as the integral transforms of the respective sources, or from the derivatives of the respective potentials. They also satisfy Maxwell's equations in the boundary condition forms: the normal components of the electric intensity field are discontinuous at the spherical charged boundary, and its tangential components are continuous; the magnetic induction field has continuous normal components, and its tangential components are discontinuous at the boundary yielding the surface current. This formalism lends itself to a unified treatment of the electromagnetic radiation of El and Ml multipole antennas and resonant cavities.

The third application: "Scattering by Asymmetric Targets in Spheroconal Harmonic Bases", M1E035, LX Congreso Nacional de Física, is explained next. It is an alternative to the familiar quantum theory of scattering in spherical harmonics, sharing the same radial spherical Bessel functions in the expansions of the plane wave and of the outgoing wave Green function for the free particle, as well as being eigenfunctions of the square of the angular momentum. The difference is that the respective harmonics are also eigenfunctions of the asymmetry distribution Hamiltonian and parity operators versus the z-component of the angular momentum. Correspondingly, the concept of phase shifts and their values are also common, but the angular distributions for the different angular momentum eigenstates $|\ell[AB]n_1 n_2\rangle$ and $|\ell\, m\rangle$ are different; notice that the asymmetry of the target is incorporated dynamically via the asymmetry distribution Hamiltonian depending on a single parameter $0 < \sigma < 60^\circ$. While in the spherical harmonic formalism the incoming plane wave is assumed to be in the z-directions and the rotational symmetry around the z-axis leads to the scattering amplitudes to depend only on the polar angle, the situation in the spheroconal harmonic formalism is different; the incoming plane waves along the x, y and z-axes scatter differently, and the amplitudes depend on both elliptical cone angular coordinates.

4.3.3. *Electromagnetic Green Function Toroidal Moment Expansion in Circular Cylindrical Coordinates*

The work in this section was reported in the contributions: "Electromagnetic multipole expansion in circular cylindrical geometry" Session M2D08 in the LIX Congreso Nacional de Física, "Normal TM modes in a toroidal cavity" in VIII Workshop on the Structure and Dynamics of Matter and Light, and "Unified treatment of toroidal antennas and resonant cavities", M1E10 in the LX CNF.

Our previous work: Complete electromagnetic multipole expansion including toroidal moments, cited by the groups that have identified toroidal dipole moments and interactions in metamaterials [85] and nanomaterials [92], was done in spherical coordinates. Since the toroids with rectangular cross sections are more common, our work has been focused in the alternative geometry.

The first contribution started from the outgoing wave Green function in circular cylindrical coordinates as a Debye potential. A poloidal current on the surface of a toroid with inner and outer radii $\rho = a$ and $\rho = b$, and lower and upper circular rings at positions $z = -h/2$ and $z = h/2$ are assumed. The magnetic induction field satisfies Helmholtz equation with the rotational of the poloidal current as its source; such a source is toroidal. The magnetic induction field is evaluated as the scalar Green function integral transform of its toroidal vector source for a current with a frequency ω and amplitude I, inside and outside the toroidal surface. The magnetic induction field inherits the alternating time dependence, the toroidal vector character of its source for each of its circular cylindrical multipole components (k_ρ, k_z, m). The one with $m = 0$ is invariant under rotations around the axis of the toroid and corresponds to the toroidal dipole. The other values of $m = 1, 2, 3...$ correspond to higher multipoles with eigenfunctions $\cos m\varphi$ and $\sin m\varphi$ of definite parity and periodicity. The electric intensity field can be evaluated as the rotational of the magnetic induction field via their Maxwell connection. Both fields are well defined inside and outside the toroidal surface, including the near and far away zones for each multipole. The electromagnetic radiation field of each toroidal multipole antenna is well-characterized in terms of polarization and angular distribution. In the case of the toroidal dipole, it shares the same properties as the electric dipole; their difference resides in their ω^6 versus ω^4 radiated power. That difference extends to the other multipoles $\omega^{2\ell+2}$ versus $\omega^{2\ell}$.

The second contribution follows from the first one upon demanding the boundary conditions for the Transverse Magnetic modes in the resonant cavity namely the vanishing of the tangential components of the magnetic induction field outside the toroidal surface. In fact, the magnetic induction field is discontinuous at such a boundary without any normal components; the discontinuity is determined by the tangential surface current consistent with Ampere's law. The boundary condition and the vanishing external electromagnetic field imposes the boundary conditions on the scalar multipole Debye potentials, which in turn define the respective resonant frequencies.

The combination of the previous paragraphs connects with the third contribution about a unified treatment of both antennas and resonant cavities, for each toroidal multipole.

4.3.4. *Analytical Solutions for the Radiation Reaction in the Force Approach*

The radiation reaction problem was analyzed by Abraham and Lorentz starting from the Larmor formula for the power radiated by a charged particle with a mass m, a charge q and an acceleration $\vec{a}$, which is proportional to the square of the last two quantities and $2/(3c^3)$ is the proportionality constant. The conservation of energy and momentum of the accelerated charge, before and after the emission of the radiation, are the basis for the identification of the radiation reaction force on the particle and its recoil due to the energy and momentum carried by the radiation. The Abraham-Lorentz radiation reaction force turns out to be proportional to the time derivative of the acceleration with the proportionality constant $2q^2/(3c^3m^2)$. In the case of an electron $e^2/m_ec^2 = r_e$ is the classical radius of the electron and $2r_e/3c = \tau = 6.3 \times 10^{-24}$ s is the time that it takes light to move 2/3 of that radius. Consequently, the equation of motion for an electron under the actions of the radiation reaction force and an externally applied force $\vec{F}$ becomes:

$$\vec{a} = \tau \frac{d\vec{a}}{dt} + \frac{\vec{F}}{me}. \tag{2}$$

Its solutions involve several nonphysical features: 1) run away solutions exponentially divergent $\vec{a} = \vec{a}_0 e^{t/\tau}$, 2) it requires knowing the acceleration at the initial time $t = 0$, for which 3) preaccelerations in the earlier interval $-\infty < t < 0$ are included in order to have this initial value at $t = 0$, with its consequent 4) acausal effects, even if there is no external force, $\vec{F} = 0$. The ills of the above formulation stem from the identification of the radiation reaction as the time derivative of the acceleration.

The force approach to the radiation reaction was proposed by G.V. López two years ago with the following conditions: it must depend on the applied force, vanishing if the applied force vanishes; in such a case the particle does not accelerate and does not radiate [100].

The identification of the radiation reaction force in the force approach also starts from the Larmor formula for the radiated power with the acceleration written as the applied force divided by the mass. It also imposes the conservation of energy and momentum, distinguishing between the cases of linear motion and circular motion. In the first case, the energy lost by the particle in a small time interval is

$$-\Delta U = -\frac{2F^2q^2}{3m^2c^3}\Delta t = \vec{F}_{rad} \cdot \Delta\vec{r}$$

and equal to the work done by the radiation reaction force while producing the small displacement $\Delta\vec{r}$. Since $\Delta\vec{r}/\Delta t$ is the velocity of the particle it follows that the radiation reaction has a magnitude proportional to the squares of the applied force and the charge, and inversely proportional to the square of the mass and to the magnitude of the velocity, and its direction is opposite to that of the velocity vector, Eq. (6).

For the circular motion including relativistic effects the radiated power includes the square of the time dilation factor in the denominator, Eq. (13), and the resulting radiation reaction force has the same characteristics as in the previous paragraph, and is also inversely proportional to the square of the time dilation factor, Eq. (15).

In both cases, if the applied force vanishes, the radiation reaction vanishes, the particle does not accelerate and does not radiate, satisfying the imposed conditions, and consistent with the observations.

The specific examples analyzed in [100] were those of relativistic motion in a straight line under a constant force, Eq. (8); and of circular motion for the charge under a constant magnetic field Eqs. (17-19) and their cartesian components Eqs. (20a,b).

For the linear motion, for Eq. (9) the first order derivative of the velocity with respect to time equation is separable with singularities in $\beta_s = 2q^2F/3m^2c^4$ and 1, and integrable, Eqs. (10) and (11a,b). This is an exact relativistic solution. The author chose to take the non relativistic limit, Eq. (12), and illustrate the graphical behavior of the difference between the motions with and without radiation reaction.

For the circular motion no analytic solutions of Eqs. (20a,b) were constructed. The graphical solutions in Fig. 2 illustrate the differences between the trajectories without and with radiation reaction for increasing values of the applied force evaluated by numerical integration.

Our own analysis of the linear and circular relativistic motion equations has allowed us to construct exact solutions for the entire range of velocities $0 < \beta < 1$ when the radiation reaction is included, in both cases.

For the linear case, to begin with we have identified some typographical errors in the solutions of Eqs. (11a) where the first factor in the numerator is simply 1, instead of the binomial, and in Eq. (11b) where the binomial in the denominator of the first factor is missing the exponent 2 in the second term. We prefer to plot directly the variations of the speed for the motion with the radiation reaction included as given by the correct form of Eq. (10), by choosing the values of β in the vertical axis and evaluating the corresponding values of the time from (Eq. (10) for an initial value of β_0 on the horizontal axis. It is necessary to distinguish between the two situations starting from the point $(t = 0, \beta = \beta(0))$ for $\beta(t) < \beta(0)$ as t takes increasing values to the right and $\beta(t)$ decreasing values illustrating the damping effect of the radiation reaction, and for $\beta(t) > \beta(0)$ as t takes increasing values to the left and $\beta(t)$ also increasing values under the dominating action of the applied force over the radiation damping with the consequent acceleration of the charge. In the respective cases, the speed goes asymptotically to their limiting values $\beta \to \beta_s$ and $\beta = 1$ of the singularities in Eq. (9). Additionally, in the non relativistic limit the graphs in the form β/β_s versus $t/[F/mc]$ have a universal behavior for the different values of F. On the other hand, the differential equation for the position shares the same singularities as that of the velocity and its solutions have the same structure.

In the circular motion under a uniform magnetic field, the applied force is proportional to the velocity, and so is the radiation reaction, apart from the dependence in the time dilation factor. The equations of motion (20a, 20b) also admit analytic solutions, which we are in the process of completing for the velocities and the trajectories.

The availability of analytical solutions allows us to formulate a physical interpretation of the radiation damping effects, which will hopefully contribute to test the force approach. Its author has also developed it further in [101] for any type of motion and in an electronic undulator application [102].

5. Discussion and Concluding Remarks

This section includes summarizing and connecting discussions about the contents of the successive sections in the article. It also contains some concluding remarks about the recent progress in the field.

Section 2 includes descriptions and illustrations of the contents in the chapters in Advances in Quantum Chemistry and the Monograph, as points of the reference to appreciate the further advances in the period between their publications, and on to the subsequent recent progress from the literature.

Section 3 is presented in its successive Sections: 1. *Hydrogen-like atoms* [26-45], 2. *Diatomic Hydrogen-like Ion and Neutral Molecules and Two-electron Atoms* [46-53], 3. *Many-electron atoms* [54-57], 4. *Many-electron Molecules* [58-65], 5. *Quantum Dots* [66-71], 6. *Confined Atoms as Open Quantum Systems* [72-78], and 7. *Connections with Reviews in other fields of Materials Science* [79-92]. Some comments about them are appropriate as a guide to the reader to appreciate the recent progress. There is still a great proportion of investigations for the simpler systems, as the natural trend from the background reviews. However, there are also qualitative changes as illustrated next.

In 1, we can follow some of the keywords in the titles: tunable excitons, biased bilayer graphene, dipole oscillator strengths, generalized oscillator strengths, Debye confinement, high harmonic generation, Gaussian potential confinement, penetrable cylindrical confinement, endohedral confinement, moving nucleus confinement, confinement effects on electron transfer cross sections, confinement by cones, benchmark calculations, sum rules, monotonocity, confinement in dielectric continuum, symmetry breaking, Fisher information, relativistic two-dimensional hydrogen atom, confinement by very thin layers. Hopefully, this list will stimulate the readers to study the original references of their specific interests. It is also illuminating to follow the set of references [27,31,33,36,43] with a common Author.

In 2, seven of the references deal with the hydrogen molecular ion and the eighth with the helium-like atoms. Debye embedding is investigated in [46]. References [47-49] involve confinement in an impenetrable prolate spheroidal box and a variational solution with the simplest trial wave function in the original article, a Comment about it, and the response. Reference [50] investigates the molecular ion inside padded prolate spheroidal cavities with arbitrary nuclear positions. References [51,52] by the same authors investigate the spherically confined molecular ion in the ${}^2\Sigma_g^+$ and ${}^2\Sigma_u^+$ states, and in the ${}^2\Pi_g$ and the ${}^2\Pi_u$ states, respectively, using the Monte Carlo approach.

The investigation of the singly excited states $1sns\,{}^1S^e$ and ${}^3S^e$ of the Helium-like isoelectronic sequence $Z = 1, 2, 3$ is based on the Ritz variational calculation with Hylleraas basis sets, providing benchmark results [53].

In 3, the set of references [54-56] with common authors have the antecedents of [8,11,24] on many-electron atoms. The work in [54] on the implementation of the electron propagator to second order GPUs to estimate the ionization potentials of (hard sphere) confined atoms was anticipated in [24]. The other works, "Roothan's approach to solve the Hartree-Fock equations for atoms confined by soft walls: Basis set with correct asymptotic behavior" [55], "solution of the Kohn-Sham equations for many-electron atoms confined by penetrable walls" [56], and "Electron density delocalization in many-electron atoms confined by penetrable walls: A Hartree-Fock study" [57], share the spherical confinement with a constant barrier outside; this feature is crucial for the analysis of ionization potentials. See also their connections with [38].

In 4, the first four references deal with rotations of molecules, and the last four with the confinement effects on the structure and electric and optical properties of a variety of molecules.

References [58-60] with a common Author also share the orientation of adsorbed polar molecules in a conical well model, in anti-crossing mediated entanglement, and in electric fields and their effects on heat capacity, respectively.

Reference [61] investigates the inelastic electron tunneling mediated by a molecular quantum rotator.

References [62-65] have common Authors, investigating the "effect of spatial confinement on the noble gas HArF molecule: structure and electric properties", "On the nonlinear electric properties of molecules in confined spaces-from cylindrical harmonic potential to carbon nanotube cages" [The latter is investigated as a supermolecule including the confined molecules and the cage], "About diverse behavior of the molecular electric properties upon spatial confinement", and "Vibrational nonlinear optical properties of spatially confined weakly bound complexes".

In 5, Ref. [66] investigates the symmetry of three identical interacting particles in a one dimensional box, with harmonic oscillator interactions using group theoretical methods.

Reference [67] investigates the effects of intense laser on nonlinear properties of shallow donor impurities in quantum dots with the Wood-Saxon potential.

Reference [68] investigates the impurity position effect on optical properties of various quantum dots, pyramidal and conical specifically.

References [69,70] by the same authors implement Calculation of hyperfine interaction in spherical quantum dot, and computation of hyperfine energies of hydrogen, deuterium and tritium quantum dots, respectively.

Reference [71] investigates Type-II quantum-dot-in-nanowire structures with large oscillator strength for optical quantum gate applications.

In 6, the subsection borrows the title of [10] and illustrates its basic idea with the series of articles [72-78] on "Endohedral confinement of molecular hydrogen", "The atomization process of endohedrally confined hydrogen molecules", "Pressure and size effects in endohedrally confined hydrogen clusters", "Thermal behavior of a 13-molecule hydrogen cluster under pressure", "Thermodynamic states of Nanoclusters at low pressures and low temperature: the case of $13\mathrm{H}_2$, Evolution of the vibrational spectra of doped hydrogen clusters with pressure", "Pressure Induced metallization of Li^+-Doped Hydrogen Clusters". The series has also common features with [12] considering Hydrogen fullerene cages instead of the familiar ones with Carbon, and also different species of confined systems and different processes. The main difference between the series and the last reference is in their methodologies: while the latter models the doped fullerenes with the spherical Δ and δ potentials, the first includes the dynamical interactions between the confined systems and the atoms of the confining cage. More specifically, the series uses density functional theory for molecules applied to the supermolecule formed by the cage and the confined molecule.

In [7], the connections of some of our works with other fields of Materials Science are illustrated. Specifically, the Review Article "Auger neutralization and ionization processes for charge exchange between slow noble-gas atoms and solid surfaces" [79] in Progress Surface Science, in its Ref. [147] cites our work: "Ground-state energy shift of He close to a surface and its relation with the scattering potential: a confinement model" [80]. Both articles have also the respective common Refs. [152-153] and [3-4] by Wethekam and Winter reporting evidence on the ground state evolution of the He atom close to an $\mathrm{Al}(111)$ surface deduced from He^+ grazing-scattering experiments after Auger neutralization.

On the other hand, the series of papers on Metamaterials and the Review Article in Nanophotonics, and their novel physical effects [82-91], cited our article: "Complete electromagnetic multipole expansion including toroidal moments" [81].

Section 4 contains the updating of the Reviewers' and collaborators' works along the lines of 1) Confined Atoms and Molecules in Dihedral Angles and 2) Development and Applications of Spheroconal Theory of Angular Momentum. New results in the first one were reviewed for the H_2^+ and HeH^{2+} molecular ions, as well as for shift operators and recurrence relations for Legendre polynomials with non integer associativity needed for HF calculations of many-electron atoms confined in dihedral angles. In the second line the theory is an alternative to the familiar one based on the spherical harmonics as eigenfunctions of the z-component of the angular momentum operator, using instead the Hamiltonian of the asymmetry distribution of molecules as the alternative constant of motion. The spheroconal harmonics depend on one asymmetry distribution parameter, and form a family which includes the spherical harmonics as a special case. An application, of interest in Magnetic Resonance Imagenology and in Quadrupole Magnetostatic Traps for Neutral atoms, is the identification of surface current distributions on a spherical surface producing magnetic induction fields with a constant gradient in its interior. Shift operators and recurrence relations for the individual Lamé polynomials have also been identified, as counterparts of those for the familiar Legendre polynomials.

The same section contains a Preview of on going investigations: 1) Zeeman effect in the Hydrogen atom confined in dihedral angles. 2) Vector spheroconal harmonics needed for the analysis and construction of solutions of Maxwell's equations and their applications; quantum theory of scattering using spheroconal harmonics to incorporate asymmetries in the target. 3) Multipole Toroidal moments and interactions in circular cylindrical geometry, and their applications in radiating and resonant cavity systems with a unified treatment. 4) Radiation Reaction in the Force Approach.

The penultimate paragraph in the Introduction included the intention to make this a conceptually connecting review. Here the attempts to implement that intention are underlined.

In Section 2.1 the concepts of confinement in quantum systems, from simple to complicated, were identified and connected for the chapters in AQC. Section 2.2 illustrated the subsequent extensions in the chapters in the Monograph with common Authors, identifying further advances in the elapsed period; and also in the other chapters incorporating their new topics, concepts and methods.

The recent progress in Section 3 is guided by the same idea following the conceptual connections and extensions in the Literature for the successive types of quantum systems. In 3.1 for the hydrogen-like atoms the titles and their keywords may help the readers to decide which references to study more in depth according to their interests. For some references, specific connections have been pointed out, but each reader may identify others. In 3.2 the seven articles on the hydrogen-like diatomic molecules have the connection with [25] and references therein, as well as with [93]. Section 3.3 illustrates the recent progress for many-electron atoms from [11-24] to [54-57], and specifically in going from impenetrable to penetrable spherical confinement. Section 3.4 on many-electron molecules involves investigations associated with different degrees of freedom: rotational motions in the first four with new forms of confinement and new physical effects; and in the last four, with common Authors, electronic structure, and also connected with [10] and [13]. Section 3.5 on Quantum dots contains one work on the symmetry of three identical particles in a box; three works on optical properties: in donor impurity quantum dots under an intense laser field, in impurity pyramidal and conical quantum dots depending on their positions, and in Type-II quantum-dot-in-a wire structures; and two works on hyperfine structure in a spherical quantum dot, and in hydrogen isotope quantum dots. Section 3.6 contains a series of seven articles on hydrogen cages confining hydrogen molecules, with common Authors, treated as supermolecules and connected with [10], [12] and [63]. Most important, the successive investigations report results on atomization, clusterization, metallization of Li^+-doped hydrogen clusters, etc. including their pressure and temperature dependences. In Section 3.7 the connections with the Reviews in Surface Science, recent articles on Toroidal Dipole interactions and novel physical effects in Metamaterials, and in Nanophotonics were recognized via their citations of our works [80] and [81].

Concluding conceptual and connecting remark: the interactions among the components of matter at the atomic, molecular, nanomaterial and metamaterial levels, are basically electromagnetic and due to their respective basic electric and magnetic individual properties. It is these properties and those interactions that determine the structure and the physical processes in their aggregates. The identification of new such properties and their new associated interactions leads to novel physical and chemical phenomena. Confinement of the aggregates, by other neighboring aggregates or by geometrical design, bring in additional elements of novelty in those phenomena or are responsible for them.

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