Chapter 1
Atomic Structure and Quantum Mechanics

Abstract Like most books dedicated to structural chemistry, we start with a short recall of the long history leading to current theories of the atomic constitution of matter and the structure of atoms, mentioning Bohr's crude model and, subsequently, the quantum mechanics frame. A brief introduction to quantum theory, operator and matrix techniques is provided, with annotations explaining the intriguing puzzle of the facts and non-intuitive reasons that contoured this paradigm. The story of Schrödinger's cat is retold, where the animal is not hurt, replacing the dead or alive states with a sleep versus awake scenario, making the probabilistic paradox quite clear, as a legitimate mixing of wave functions symbolizing the state of the system. The quantum structure of the atom is presented in an original way, i.e. by putting a special emphasis on the effective role in chemistry of Spherical Harmonics functions, grasping the concepts in an intuitive manner, with the help of heuristic symmetry reasons. Taking variable transformations as artifices in the Schrödinger equation of the hydrogen atom, the spectrum of orbital energies unfolds without following through to a complete solution. The chapter offers picturesque descriptions and explanatory artifices which are original, not met in other textbooks. An incursion into the even more mysterious world of relativistic quantum mechanics is made, bringing electron spin into sight, along with related consequences, important for understanding further topics, such as atomic and molecular magnetism. The complexity of the theorization is increased by incorporating the Feynman path integral method, bringing pictures from a territory less often visited by chemists, for the sake of a complete cross-border perspective. Finally, while introducing specific particle and wave representations, as well as their ratio, in quantifying the wave-to-particle quantum information, the basic Heisenberg Uncertainty Relationship (HUR) is recovered for a large range of observable particle-wave Copenhagen *duality*, although with the dominant wave manifestation, while registering its progressive modification with the factor $\sqrt{1-n^2}$, in terms of magnitude $n \in [0, 1]$ of the quantum fluctuation, for the free quantum evolution around the exact wave-particle *equivalence*.

M.V. Putz et al., *Structural Chemistry*, https://doi.org/10.1007/978-3-319-55875-2_1

Keywords Quantum numbers · Quantum operators · Schrödinger equation · Hamiltonian · Matrix method · Perturbation theory · Atomic shells · Spherical harmonics · Electronic spin · Relativistic quantum chemistry · Dirac equation · Path integrals · Heisenberg uncertainty · Wave-particle duality

1.1 The Long Road from Democritus to Bohr

1.1.1 Arcadian Antiquity

Humankind has been doing science as it is currently understood for only a few centuries, which represents an infinitesimal portion in the horizon of the history of the civilization and of the species itself. A multitude of social and cultural factors have contributed to the present stage of scientific knowledge, in both pure and applied forms, coupling material needs and pragmatism with the impetus for knowledge. However, the intellectual power of our ancestors, as individuals, was, in anatomical terms, the same as ours and demonstrated its own strength of insight. Therefore, it is right to pay tribute to the ancient roots of a field, even though the distance between the modern version of accepted truth and the old models, often mixed with myths and beliefs, may seem large. Thus, with no condescension to an apparently naïve picture, one should start with Democritus' atomic theory. A picture of Democritus (460–370 BCE) and his symbolized idea is shown in Fig. 1.1. It can be considered as a thought experiment, *avant la lettre*. His idea was that, whether with mechanical tools one can divide different sorts of matter, beyond instrumental limitations, a conceptual ultimate level of smallness must exist. One can see that his argument is not completely free of experimental reasoning, extrapolating a fact that could be perceived in everyday practice.

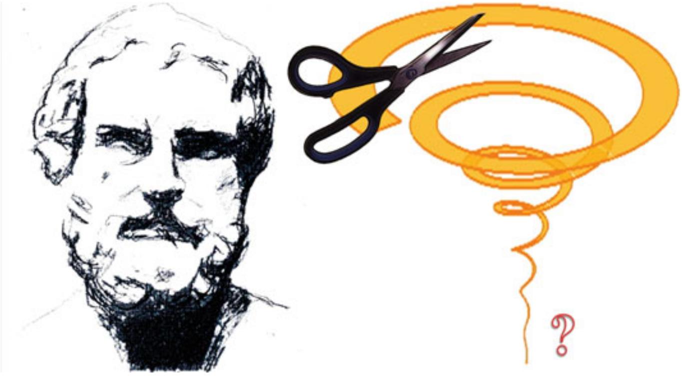


Fig. 1.1 Democritus and a representation of the idea of the finite divisibility of matter, ending with the primordial atomic concept

Etymologically, the term of atom was coined joining the prefix for negation "*a*" with the Greek word for being chopped, "*tomos*", yielding "*atomos* = without cut". Many ancient mythological or philosophical speculations addressed the idea of a primordial substance. Thales proposed water as that substance. The four elements mentioned in Plato's *Timaeus* dialogue (earth, water, air, and fire), inherited from Empedocles's constructs, contain the empirical seeds for states of matter (solid, liquid, gas, and plasma). From this, a theory was constructed, equating earth = cube, water = icosahedron, and air = octahedron. In terms of Platonic solids, the dodecahedron represented the whole Cosmos. In the *Phaedo*, Plato quoted Anaxagoras, who proposed the idea of an ordering principle that organizes things in optimal ways. Such perspectives shared much from the Pythagorean paradigm that mathematics can explain the world, this method being ennobled with the virtue of beauty. Some of these theories became obsolete, or received criticism from rival schools. For instance, Aristotle accused Pythagoras and Plato of confusing form and matter, casting doubt on the view that entities like dots, lines, and numbers can explain objects and their properties, such as heaviness.

However, the idea of primordial substances was a valuable contribution from these early thinkers. It encapsulates the same spirit that guided the development of modern chemistry, of finding that the huge variety of compounds is made up of relatively few species of atoms. One may continue this line of thought by pointing to the fact that atoms themselves are built from a limited number of particles (just three—proton, neutron, and electron—if we ignore the details of subatomic particle physics) and actually only one, the electron, is responsible for the whole chemistry.

It would be an exaggeration to link Platonic ideas with the principles of theoretical molecular geometry, but a tiny trace of common conceptual background may be supposed. We used ancient Greek thought as the conventional landmark of modern thinking, but we should acknowledge that the Pythagoreans inherited, and further transmitted (to Plato's world-view, for instance) some oriental influences. Theories about the duality of body and soul (which can be regarded as precursors of wave-particle conceptual bi-functionality) and Zeno's paradoxical constructs (*aporia* = conceptual difficulty) about possible conflicts in conceiving movement and steadiness, were a sort of primary habituation with the puzzling nature of ultimate matter. Such philosophical difficulties capture the spirit of quantum mechanics breakthroughs, by having the courage to advance ideas which are perplexing to common sense.

Roman civilization retained and enriched with further details these early proto-atomic ideas, for instance, described in tableaus from the extended poem *De rerum natura* (On the Nature of the Things) by Titus Lucretius Carus (99–55 BC). Very imaginative scenarios of atom "structure" and dynamics were constructed, which, although seen as poetic license, may be regarded as the beginnings of a structural causal explanation of the world. Thus, the sour taste of vinegar correlates with atoms wearing stings. As a collection of structures with all sorts of shapes and decorations, Lucretius's objects resemble molecules rather than atoms.

1.1.2 Along the Centuries, to the Positivist Era

During the Middle Ages, the promising line of speculative philosophy was broken and diverted in other directions. The celebrated theory and practice of alchemy, among many mystical traditions, contributed somewhat to the corpus of experimental techniques of chemistry, but had little to add to the incipient theories of matter. This is not to blame alchemy: it was in the spirit of the times. Let us recall that Isaac Newton (1643–1727), a very rigorous thinker, apostle of modern physics, and the author of *Mathematica Principia*, lost himself for many years in the study of alchemical works (experiment and "theory"). Although not entirely valuable, the alchemists' idea of the mutual affinities of substances can be regarded as parallel with the modern concepts of chemical affinity, suggesting electronegativity equalization and hard and soft acids and bases theory. Unlike antiquity's recourse to geometry as an explanatory framework, and its occasional further appearance in other branches of science, e.g. Kepler's ideas on planetary orbits as a superposition of Platonic solids, the alchemists of the Middle Ages, Renaissance, and Baroque eras did not employ geometry to advance toward the idea of structured matter. Hidden, mystical, variables and strange substances such as phlogiston (proposed by Johann Joachim Becher and Georg Ernst Stahl in the mid-seventeenth, in books such as Becher's *Physica subterranea*) were assumed, instead of the idea of geometrically structured matter. Phlogiston theory is usually regarded as a negative stage in the history of chemistry, and sure the theory was a doubtful one, but with an indulging eye, in an era still far from the outskirts of positivist sciences, it can be taken as a proto-theory of redox processes. Phlogiston does almost what electron flow performs, when passing between atomic or molecular centers (if we overlook the point that phlogiston was assigned with negative mass, while the idea of charge was not an ingredient of the construct).

It was perhaps the philosophy of Immanuel Kant (1724–1804), drawing attention to space as an essential category of thought and empirical experience, which opened up new approaches at the dawn of modern science. Kant's philosophy was influential in the age of the European Enlightenment, which gave rise to a generation of physicists and mathematicians (Lagrange, Laplace) who rearranged in very elegant ways the Newtonian and Galilean beginnings of mechanics. At about the same time, John Dalton (1766–1844) rediscovered atomic theory from the ancient sources. There is a fascinating history about how chemistry, step by step, came to work with formulas and bonding ideas, but we leave that aside here, focusing instead on atomic theory.

The firm foundations of the idea of atomic inner structure were provided by investigations revealing the electrons, as building charged particles, emerging in different experiments, as well as the discovery that the light absorbed or emitted in spectroscopy has to do with the internal dynamics of the parts constituting the atoms and molecules. Ernest Rutherford (1871–1937) discovered that the counterpart of electron charge was confined in a smaller space, the atomic nucleus, whose structure is less important for chemistry itself, at least not in a direct manner.

In the pre-quantum stage, a remarkable guess, since 1888, was the Rydberg formula for the lines observed in the spectrum of hydrogen:

$$\frac{1}{\lambda} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right), \tag{1.1}$$

where λ is the wavelength of the spectral line, $n_1 < n_2$ are integers, and R the Rydberg constant ($R = 1.097373156 \times 10^7\ \mathrm{m}^{-1}$ in the International System; $R = 13.605$ eV or $R = 1.097373156 \times 10^5\ \mathrm{cm}^{-1}$—in units customary in spectroscopy, and $R = 1/2$ in atomic units—Hartree). Equation (1.1) is perfectly in line with the Bohr atomic model; it is remarkable that early experimenters saw a numeric pattern in the yet mysterious nature of the line spectra, in advance of a proper theory. A first correlation was observed by Johann Balmer (1825–98), in 1885, for the $n_1 = 2$ case, explaining the series with the same name, that begins invisible. Here we already have the empirical path to the quantum paradigm. Some properties appear as tuned by integers, in a discontinuous manner, instead of the customary view on the continuous constitution and rules of the world, expressed in Leibniz's precept "*natura non facit saltus*" (nature does not make jumps), in line with differential calculus ideas.

1.1.3 Bohr's Atomic Model: Natura Facit Saltus!

The Bohr model interprets the lines as transitions from lower level n_1 to higher n_2, in absorption, or reversed—as relaxation—in emission. Inspired from the planetary model, with the electrons orbiting around the nuclei, the Bohr model was stated eluding, in a manner similar to Alexander the Great cutting the Gordian knot, the rules of already well-established electromagnetism. Namely, an electron on a circular orbit (as on a macroscopic scale is enforced in a coiled conductor) will produce an electromagnetic radiation, this being the principle on which radio-emitters work. Emitting radiation means energy loss. Therefore, the charged particles cannot be stable, like planets on the cosmic scale, on circular or elliptical orbits, tending to spiral down onto nuclei. Niels Bohr (1882–1965) famously said that the electrons are not obeying the mandatory rule of radiation release, since there are privileged quantified orbits. Assuming such a discontinuity, Niels Bohr built on previous hypotheses by Max Planck (1900) and Albert Einstein (1905) about the quantification of light energy, $h\nu$, in elementary bits of Planck constant h, proportional to its ν frequency. Conversely, he proposed the quantification of the angular momentum along the perimeter of circular motion, $2\pi|L| = 2\pi r{\cdot}p = nh$, or $|L| = n\hbar$ (where p is the impulse, n is an integer, and $\hbar$ the reduced Planck constant $\hbar = h/2\pi$ in Bohr's theory). We will not discuss here the well-known derivation of Bohr's model.

We present directly the result for the energy of the orbit characterized by the quantum number n, for an atom with one electron and a fixed nucleus with charge Z:

$$E_n = -\frac{Z^2}{n^2}\frac{m_e e^4}{8h^2\varepsilon_0^2} = -\frac{Z^2}{n^2}R, \tag{1.2}$$

where m_e is the electron mass, e is the electron charge, ε_0 is the vacuum permittivity, and h the Planck constant (working in the international units convention). The radius of the orbit is:

$$r_n = \frac{n^2}{Z}\frac{\varepsilon_0 h^2}{\pi m_e e^2} = \frac{n^2}{Z}a_0, \tag{1.3}$$

the factor a_0 being the radius of the first orbit of the hydrogen atom (at $n = 1$, $Z = 1$), $a_0 = 0.529177$ Å (where 1 Å = 10^{-10} m). The model accounts admirably for the spectrum of hydrogen, in the pattern of formula (1.1), assimilating the emission or absorption lines with the differences between orbit energies $E_{n_2} - E_{n_1}$, for two quantum numbers $n_1 < n_2$. Figure 1.2 shows the radii of several Bohr orbits, at proportional scale, and the schemes of the first lines from the Lyman, Balmer, and Paschen series, related to the respective $n_1 = 1$, 2, and 3 as lower energy level. Only the Balmer series falls into visible spectrum, the transition arrows from Fig. 1.2 being colored according to the wavelength. The Lyman series is placed into ultraviolet, while Paschen ($n_1 = 3$), Brackett ($n_1 = 4$), and Pfund ($n_1 = 5$) are going into infrared and far infrared.

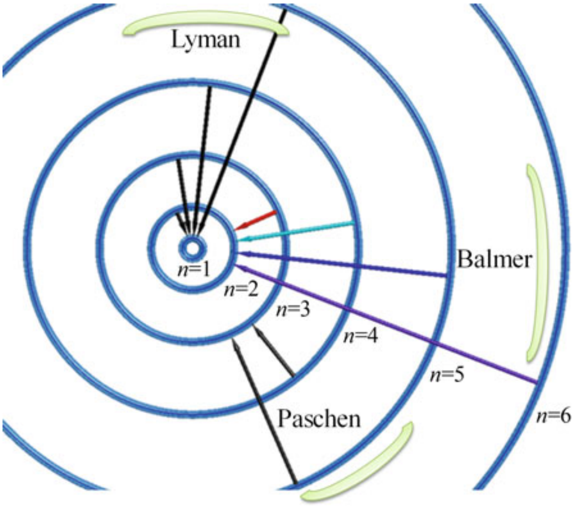


Fig. 1.2 The orbits with $n = 1$–6 quantum numbers in the Bohr model, represented at proportional radial scale altogether with the first spectral series, considered as emission: Lyman (from $n_2 = 2$, 3, etc., to $n_1 = 1$); Balmer (from $n_2 = 3$, 4, etc., to $n_1 = 2$), Paschen (from $n_2 = 4$, 5 etc., to $n_1 = 3$). The lines falling in visible (Balmer series) are rendered in corresponding colors. The ultraviolet (Lyman) and infrared (Paschen) are drawn in black

At very large n quantum numbers the energy gaps become negligible, meeting the so-called correspondence principle, assuming that quantum mechanics retrieves the classical continuum. Since the high quantum number orbits are close to each other, the "interdicted space", that was the specific of quantification disappears, resembling the classical continuum.

The Bohr model appeared in 1913, quite late in comparison with other significant discoveries at the beginning of the twentieth century (quanta ideas from 1900 to 1905 and restricted relativity in 1905). However, it had to wait for the decisive experiment with gold foils, almost transparent to alpha particle fluxes (done in 1909 by Hans Geiger and Ernest Marsden at Manchester, under the guidance of Ernest Rutherford who proposed in 1911 the interpretation of the small space occupied by the positive charge). This gave the green light for conceiving the atom, on an experimental basis, in terms of a planetary model. Prior to this, there was no firm reason to dismiss other imagined atomic structures, such as the "plum-pudding model" of Joseph John Thomson (1856–1940), with negative electrons rotating in a sphere of positive diffuse charge. In addition to giving Thomson the credit for the discovery of electrons, we should also acknowledge that his atomic model was rational. It included the basic intuition about the sphericity of the atoms, although the hypothesis of uniform positive charge was a disputable view, in the absence of other information. About the existence of electrons, as distinct particles, the cathode rays experiments were sufficiently convincing. Then, without experimental information on the positive charge, it would have been completely unreasonable to assume its concentration in a small volume, against strong electrostatic repulsion forces.

Bohr's quantum mechanics generated many conundrums, such as the question: where is the electron during the transition, if only the quantified orbits are allowed? An answer to this was offered by the next generation of quantum scientists, denying the sense of trajectory and introducing the uncertainty relationships that generated, in turn, further puzzling statements. Although his model became obsolete relatively soon, because of the new quantum mechanics of Heisenberg and Schrödinger (from 1925–26), Bohr was not outside of the further evolution of the domain, establishing the "Copenhagen interpretation" of quantum mechanics at his institute, in his home city, Copenhagen.

The Bohr atomic model has drawbacks and limitations. Although it was used to set the so-called Bohr magneton, μ_B, i.e. the quantized unit of the magnetic moment, the model predicts the wrong magnetism for the hydrogen atom, since 1 μ_B is not in agreement with experimental data. As will be revealed later, both in this text and also in the time line of science history, it turns out that the ground orbital movement of hydrogen does not produce any magnetic moment (although the orbit looks like a coil of electric current), while the measurable projections, with ±1/2 μ_B, are carried by the electron itself. The derivation of the Bohr magneton is historically and formally related to the assimilation of the $n = 1$ hydrogenic orbit with a coil of current. In classical electromagnetism, the induced magnetic moment is proportional with the product between the area of a coil and the passing current intensity. Assigning the current intensity to the frequency of the electron around the orbit (replacing number electrons in definition of intensity with the number of circular tours) and having the speed (or impulse) and area (via radius) quantized, the moment results with the absolute value:

$$\mu_{\mathrm{B}} = \frac{|e|\hbar}{2m_{\mathrm{e}}}, \tag{1.4}$$

in International System units. Actually, this value was correctly calculated two years in advance of Bohr model, in 1911, by the Romanian physicist Stefan Procopiu (1890–1972), based on Planck quantum modeling. Several other scientists fiddled around of the topic, proposing values that were either smaller (Pierre Langevin) or larger (Pierre-Ernest Weiss) than the now accepted μ_{B} unit.

A strange aspect of the Bohr model is that it seems to be two-dimensional. As suggested in Fig. 1.3, showing three superposed equivalent orbits with different inclinations, the plane of the trajectory is arbitrary. By conserving the mechanical momentum, the hydrogen atoms should behave as small gyroscopes, keeping the plane of the trajectory. On the other hand, there is no reason to propose a preferred orbit, inducing a non-natural space anisotropy. A collection of hydrogen atoms should then have arbitrary oriented orbits, so that the averaged picture of the trajectories creates spheres. One may imagine that interaction with different environment factors, or even random genesis, determines the tumbling of the orbit planes, but this sort of reasoning goes beyond the model's own controls.

An extension of Bohr's reasoning was made in 1915 by Arnold Sommerfeld (1868–1951), who allowed elliptical trajectories, at the expense of a secondary quantum number, k, varying from 1 to n, the last index being the main quantum number. The ellipse is characterized by long and short half axes, a and b, whose ratio is decided by the $n/k = a/b$ regularity. At $k = n$ the orbit is a circle, the smaller values making more eccentric ellipses, with the nucleus in a focal point. The focal

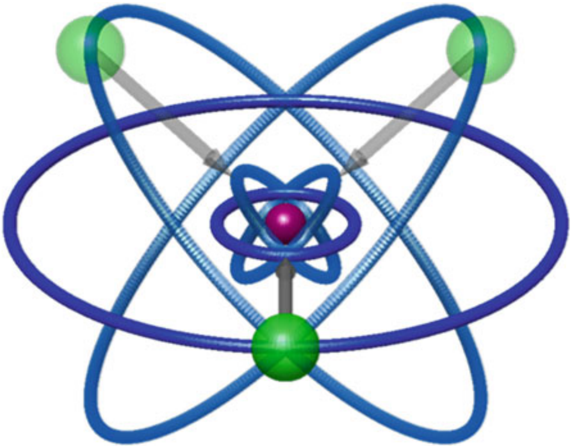


Fig. 1.3 The pictorial suggestion that the two-dimensional Bohr orbits can be arbitrarily placed in space. We superimposed three sets of $n = 1$ (inner circles) and $n = 2$ (outer circles) orbits, as well as the first Lyman emission transition, taking place from the three different space orientations. Representations of this sort are chosen frequently as the icons for topics related to quantum theory or as logos of agencies dealing with atomic or nuclear activities

points are placed on the long axes, at the $\pm(1/2)(a^2 - b^2)^{1/2}$ positions from the symmetry center of the ellipse. The energies of all the orbits with a given n have the same expression like in the Bohr model, being independent on the k quantum number. The secondary quantum number k results from the quantization condition for an angular parameter, while the principal index n results from a radial component. A representation of various Sommerfeld orbits is given in Fig. 1.4.

In spite of their apparent simplicity and relative familiarity to common sense, since they have for a long time been known as the orbits of the planets, the ellipses are tricky things. Thus, while the area has a simple expression, πab, looking like splitting of circle area, πr^2, into the product of semi-axes, the perimeter does not have a closed formula, but an infinite series expansion, or several possible approximations.

In fact, the Sommerfeld model is an unnecessary complication, since it does not advance in the conquering of new true physical regularities, although the finding that there are secondary quantum numbers and multiple orbits with the same energies goes somewhat toward the complete quantum solution of the hydrogen atom, reached by Schrödinger's and Heisenberg's quantum mechanics. However, the name of Sommerfeld deserves to be recognized among the contributors to quantum mechanics, because his mathematical knowledge, disseminated to his

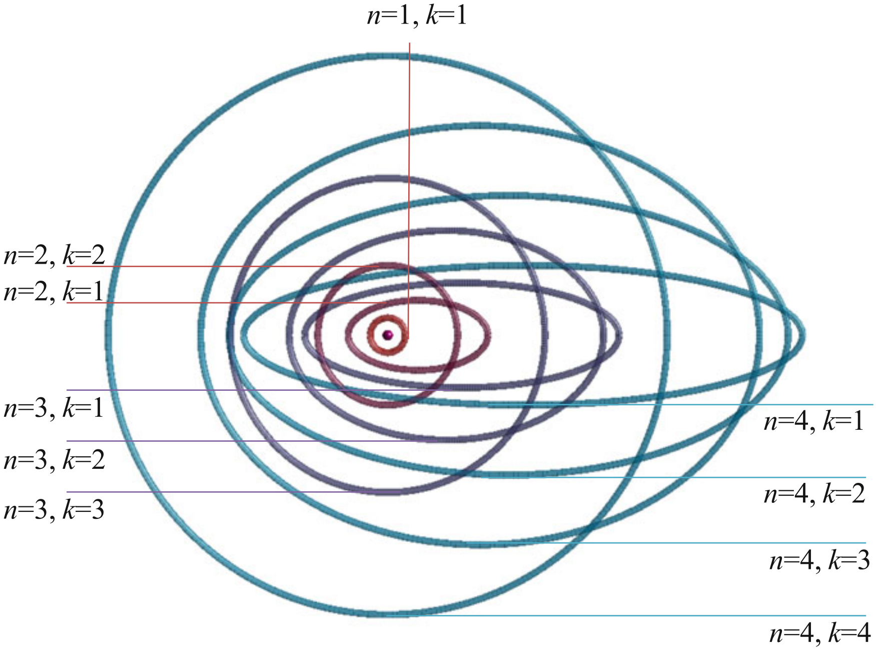


Fig. 1.4 The representation at relative scale of several orbits from the Sommerfeld atomic model, characterized by quantum numbers n = 1, 2, 3, etc. and k = 1 to n. The smaller the k index, the larger is the eccentricity of the elliptical trajectory. At k = n the orbits become circular, Bohr-type

pupils, helped to seed this revolution of humankind. A list of his doctoral and postgraduate students contains names of great importance for theories of quanta, atomic, and molecular structure: Heisenberg, Pauli, Debye, Bethe, Heitler, Ewald, Laporte, Lenz, Landé, Brillouin, Pauling, von Laue, Rabi, Condon, and Morse. Seven of Sommerfeld's apprentices won the Nobel Prize. One may say that he was an integer character, a fact measurable by his supportiveness to his students. For instance, Sommerfeld's intervention during the doctoral examination of Werner Heisenberg was essential, because the evaluators found the apprentice to be at fault with bad knowledge in some issues of experimental optics.

The Bohr and Sommerfeld models were in a difficult position in further accounts of atomic and molecular species. The atom with many electrons was not tractable, neither were the molecules. A suggestion of an attempt made by Pauli, in 1922, to solve the hydrogen molecule ion, H_2^+, into the Bohr–Sommerfeld paradigm, is represented in Fig. 1.5. Various possible orbits were found, such as a simple pendulum along the axis between nuclei, orbits around a single nucleus, lemniscata lines, circulating in a two-lobe profile around both nuclei and passing through the symmetry center, or ellipsoidal paths. The last ones were guessed as the most stable, but the numerical account proved to be cumbersome and unsatisfactorily correlated with spectroscopy data. Soon after, a better theory appeared and changed the paradigm fundamentally.

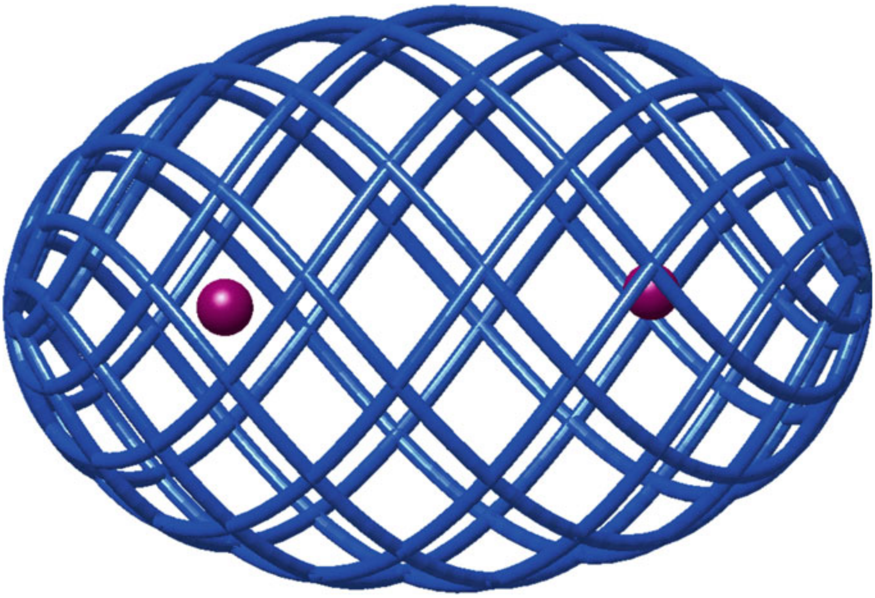


Fig. 1.5 Representation resembling one type of orbit proposed by Pauli's early treatment of H_2^+ (hydrogen molecule ion), in 1922, with a quantization of elliptic coordinates similar to the Bohr–Sommerfeld conditions.

1.2 The Dawn of Quantum Theory and the Founding Fathers

1.2.1 The Revolutionary Milieu and Quantum Mechanics

Lord Kelvin (William Thomson, 1824–1907, a revered scientist knighted in 1866) opined in 1900 that physics was a clear sky, shadowed by only a few minor clouds, the so-called ultraviolet catastrophe being one. It turned out that those apparently small dilemmas were crisis points, leading to quantum mechanics. The laws of atomic and molecular structure are the subject of this particular field of physics, a rather tricky one, since the intuition that guides us in the macroscopic world does not operate in the microcosm. The audacious reconsideration of physics began at the beginning of the twentieth century (e.g. the first idea of quanta, by Max Planck, in 1900, to cure the ultraviolet catastrophe of black body radiation, followed by Einstein's quantum-like interpretation of the photoelectric effect, an idea arising from his relativity papers, from 1905, his *annus mirabilis*).

The dark years of World War I overshadowed the impact of the Bohr model, released in 1913. However, the quantum paradigm continued with a new peak between the two world wars. Such fresh spirit was reflected more widely in the interwar revolutionary climate, from arts and philosophy to politics and social theory. Particularly, the spirit of the Weimar republic, replacing the crushed German empire in the aftermath of World War I, occasioned a partial melting of rigid conventions in academic life too, the scientists becoming unafraid to venture exciting new hypotheses, shaking the apparently well-established edifice of a mechanical interpretation of the world (von Meyenn 1994).

It was the time when cubist plastic artists rebelled against the boring rules of spatial perspective and created virtual worlds that needed new operators to decrypt their message. It was also an age of enjoying the postwar peace and the "rebirth" of human nature, with large numbers of people experiencing new forms of happiness, epitomized in the exuberance of the Charleston dance (which emerged in 1923 in South Carolina). While the Charleston has acquired by now a dated and "vintage" feel, the energized spirit of the 1920s and 1930s generated a new physics that shaped knowledge for the rest of the century, still bearing the stamp of the modern, to the present day.

In this milieu, scientists discovered in quantum mechanics a new field in which to play games of knowledge, partly for art's sake (*ars gratia artis*). After all, scientists are not logical automata; accordingly, their work appears to be influenced by, and to reflect, the trends of the époque and their own cultural position within it. We can recall here the speculation of the Romanian philosopher Lucian Blaga (1895–1961), a lesser-known figure, but somewhat comparable with Oswald Spengler, in his glittering original rethinking of world mechanisms in terms of subtle cultural parameters. Blaga took the example of quantum statistics theories and correlated them with the cultural frame of their creators. Thus, Blaga (1943) argued that Fermi and Dirac, having Western and European cultural backgrounds, based on individual self-projection, were more inclined toward the statement of a statistics giving to every state not more than one particle. By contrast, Bose and Einstein, coming, in principle, from more collectivistic oriental cultures (Indian and Semitic), were more able to imagine and accept that many particles may occupy the same place in the energy scheme.

In 1924, the duke Louis de Broglie developed the idea of wave-particle dualism in his PhD thesis (under Paul Langevin). In 1925, Werner Heisenberg established the grounding principles of so-called matrix mechanics, in cooperation with Max Born and Pasqual Jordan. According to his memoirs, he got the illuminating key during a trip to Helgoland Island, on the North Sea. In 1926, Schrödinger published his equation (Schrödinger 1926), about which the famous American physicist Richard Feynman said that seemed to have come from nowhere. Sommerfeld categorized it as the most stunning among all the dazzling discoveries of the twentieth century. Max Planck appreciated the beauty of the equation. Schrödinger's and Heisenberg's approaches made the quantum mechanics of Planck, Bohr, and Sommerfeld—still new and non-orthodox at that time—become quickly the "old theory".

Although a demonstration of Schrödinger's formula free of heuristic inserts and conceptual persuasion is probably not possible, the equation did not appear from thin air. On the other hand, the Schrödinger formula worked in innumerable tests and problems. Like several other basic hypotheses of physics, it can be conceived in terms of symmetry (Sundermeyer 2014). A ground for building hypotheses (Joas and Lehner 2009) was the optical-mechanical analogy due to Hamilton, since 1833, making a connection between geometrical optics and analytical mechanics. It put in comparison the Fermat principle for the shortest route of a ray of light passing spaces with different refractivity and Maupertuis's hypothesis of minimal action for a material particle. Since, on the other hand, the light can be treated as wave, the link between mechanics and wave theory, as mathematical apparatus, was foreseen, Schrödinger being interested in Hamilton's works in 1920. He aimed at an ambitious unification between waves and relativity, although ended with a non-relativistic wave function. At the same time, de Broglie spotted the analogy between the Fermat and Maupertuis principles, as inspiration for his hypothesis of material waves. The relativistic Wave Function Theory was established in 1928, by Dirac, not long after Schrödinger's discovery from 1926 (Fig. 1.6).

1.2.2 Modus Operandi*: Waves and Operators*

The quantum mechanical systems are described by the so-called wave functions, which encipher all the physical properties, from where these can be "decoded" using operators consisting in appropriate "recipes" of mathematical operations (multiplication, derivation), able to render the desired information.

In principle, the operator should keep the same definition, independent of the wave function at which it has to be applied. Later on, we will see that, for technical

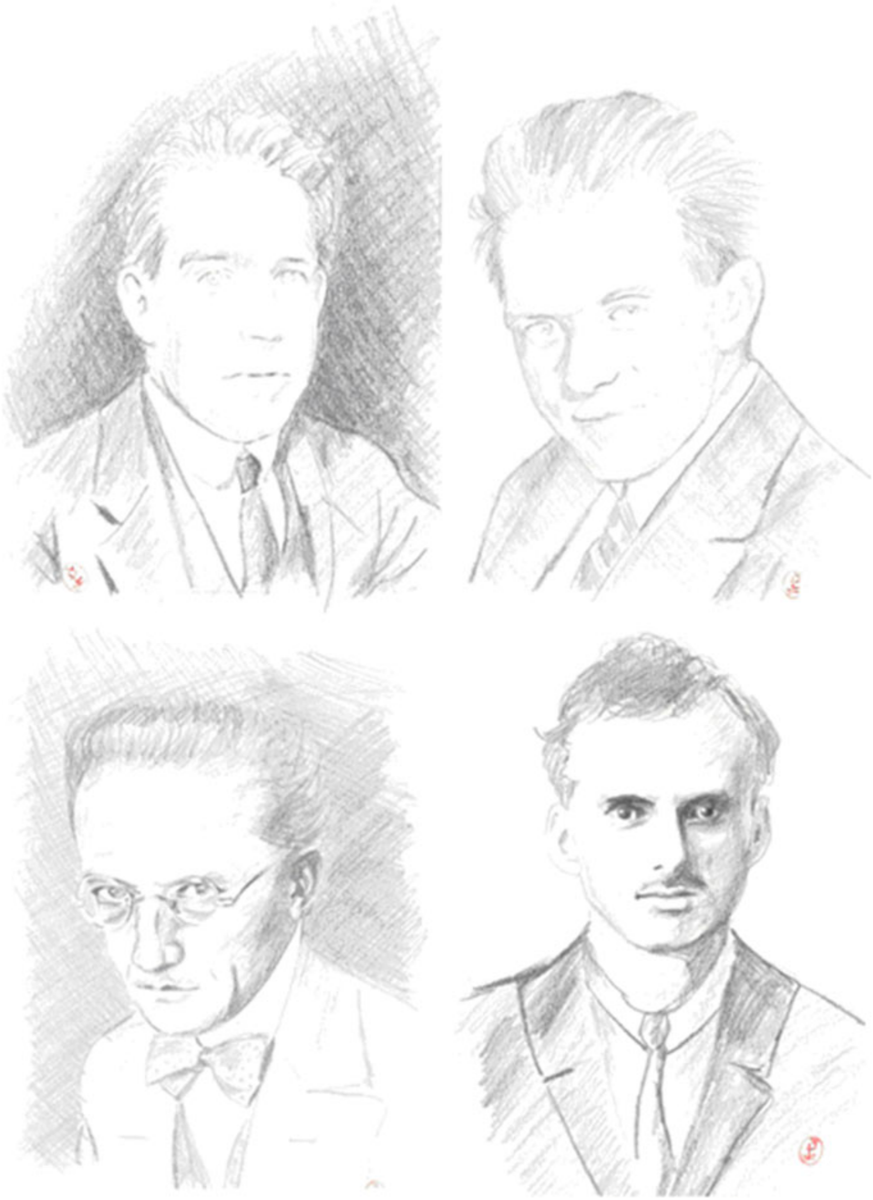


Fig. 1.6 The coryphées of quantum theory: Top: Niels Bohr (left), Werner Heisenberg (right); Bottom: Erwin Schrödinger (left), Paul Adrien Maurice Dirac (right)

reasons, in order to approximate the complicated problems without analytical solutions, we must build operators that depend on the wave function of interest, namely self-consistent procedures, as strategy in iterative approaches. After acting on a wave function, an operator produces, in general, a linear combination of numbers factoring other functions (whose full set is regarded as a basis of a space). There is a particular situation in which the operator $\hat{f}$ returns the same function with a numerical factor f, called an eigenvalue, Ω being of the eigenfunction:

$$\hat{f}\,\Omega = f\,\Omega. \tag{1.5}$$

The "eigen" prefix, from the German word "own", marks the special link between the elements of the right side, belonging to each other, as solution to the given operator problem. The hat placed on the symbol denotes its quality as operator. The fact that the algebraic machinery of the operator leaves the adequately selected wave function unchanged, up to a real factor, suggests a symmetry-like problem. Specifically, a symmetry operation is an act that leaves an object unchanged. In several cases, the eigenfunction equations have symmetry reasons. Even the justification of the generic equation of Schrödinger can be grounded on symmetry of impulses with respect of the isotropic space and of the energy related with the time flow. This reasoning is the quantum version of Noether's general theorem from mechanics (Noether 1918). Thus, momentum conservation is a consequence of the homogeneity of space (translational symmetry). Conservation of angular momentum is a consequence of spatial isotropy (rotational symmetry). Energy conservation is an expression of translation symmetry in time. These nice findings were outlined by Emmy Noether (1882–1935), a woman strongly dedicated to science at a time when such a life was quite difficult and almost forbidden for women. She worked (without payment) in the mathematical department of the University of Göttingen, a city which produced many personalities who contributed significantly to modern scientific theories. They include David Hilbert (1862–1943), a mathematician whose constructs shaped the new quantum mechanics, and Hermann Weyl (1885–1955) another mathematician, who contributed to relativity and quantum theories. Weyl embraced the paradigm drawn by Noether, generalizing it in a heuristic belief that all the basic physical rules must be rooted in symmetry.

Compressing quantum mechanics in a nutshell, we must first point out that a basic importance is given to the operator that renders the energy, called the Hamiltonian operator. In systems whose state does not depend directly on time, the generic Hamiltonian equation is:

$$\widehat{H}\,\Psi = E\,\Psi. \tag{1.6}$$

The equation of energy eigenvalues is the very core of quantum physics and computational chemistry, in a wide range of approaches, with varying degrees of approximation. For the most general form of Schrödinger's equation, including explicit dependence on time, the quantum Hamiltonian is:

$$\widehat{H}\ \Psi(t) = -\frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial t}\Psi(t). \tag{1.7}$$

Here $\hbar$ is the reduced Planck constant and "i" is the imaginary unit. To be distinguished from "*i*" used as index, in italics, the imaginary unit "i" is presented in plain text format. The name "Hamiltonian" stands in honor of the man who, one century in advance of Schrödinger, devised tools for handling the energy in analytical mechanics and produced the seeds of ideas that led Schrödinger to his iconic equation.

When the energy does not depend explicitly on time, i.e. the system is placed in a definite state and no perturbation arises from outside, Eqs. (1.6) and (1.7) can be linked proposing an exponential factor for the formal time evolution: $\Psi(t) = \exp(\mathrm{i}E\,t/\hbar)\ \Psi$. Indeed, applying the derivation from the right side of the general Schrödinger equation (1.6) one retrieves its stationary form (1.7). To make things a bit clearer, let us observe that if we associate the energy with a frequency, $h\nu$, or equivalently, $\hbar\omega$ considering the angular speed ($\omega = \nu/2\pi$), then the factors take the $\exp(\mathrm{i}\omega t)$ form, familiar from classical periodical wave equations.

Other useful operators are the impulses, which, in Cartesian components are:

$$\hat{p}_x = \frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial x}; \quad \hat{p}_y = \frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial y}; \quad \hat{p}_z = \frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial z}. \tag{1.8}$$

On this occasion we can see the "pure" form of an operator, without specifying a function on which it has to work. For instance, $\hat{p}_z\Psi$ has to perform coordinate derivative and a certain multiplication with quantum constants: $-\mathrm{i}\hbar\partial\Psi/\partial z$. In vector notation, the impulse is ascribed with the Nabla symbol:

$$\hat{p} = \frac{\hbar}{\mathrm{i}}\nabla. \tag{1.9}$$

The Nabla symbol (the Hebrew name for harp, whose shape is suggested by the ceiling-pointing tip) is also called Del in English technical literature. The impulse operator form is not obvious in relation to customary classical mechanics, where the impulse is a product of mass of the particle and velocity, the last being derivative of a coordinate with respect of time, e.g. $p_z = m\ \mathrm{d}z/\mathrm{d}t$. However, it may be suggested by formulations of analytical mechanics, where the definition of the Lagrange operator (kinetic minus potential energy) and the Hamilton principle of minimized action (a path integral of the Lagrangian) implies the use of generalized coordinate derivatives, $\partial/\partial q$, associated to the space parameters, q. The somewhat strange form of the impulse in quantum mechanics suggests, from the beginning, that it is not usable in constructing something like trajectories. The absence of mass in the impulse operator says that this sort of information has to be contained implicitly somewhere in the wave function, while the imaginary factor suggests that the impulse is a sort of half-prepared ingredient, not suitable to be used alone in setting a problem (because the physical measurables must yield real numbers).

Other operators, such as the potential energy components, are expressed simply as factors coming from the classical definitions. For instance, the potential energy of a harmonic oscillator along x axis will be proportional to x^2, while the electrostatic potential between two particles will be a factor related to the $1/r_{12}$ classical Coulomb formula. In general, the potential operator V is a multiplicative one.

The kinetic energy of a particle with mass m is formed with the help of the $p^2/(2\ m)$ classical analogy, applying twice each operator of the $\hat{p}$ set and adding them up:

$$\begin{aligned}\widehat{T} &= \frac{1}{2m}\left(\hat{p}_x^2+\hat{p}_y^2+\hat{p}_z^2\right)\\ &= -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right) \equiv -\frac{\hbar^2}{2m}\nabla^2 \equiv -\frac{\hbar^2}{2m}\Delta.\end{aligned} \tag{1.10}$$

The last parts suggest other notations, as square of Nabla symbol, or by capital Greek letter Delta. In case of many particles, the total kinetic operator is the sum of each particle component. In the cases implying circular or spherical symmetry, the transformation from Cartesian (x, y, z) to polar coordinates (r, θ, φ) is convenient. Then, the angular moments are replacing the description by impulses. The quantum moments are obtained putting the above defined impulse operators into the components of $\vec{l} = \vec{r} \times \vec{p}$ classic angular momentum components:

$$\hat{l}_x = \frac{\hbar}{\mathrm{i}}\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) = -\frac{\hbar}{\mathrm{i}}\left(\sin\ \varphi\frac{\partial}{\partial\theta} + \frac{\cos\theta}{\sin\theta}\cos\ \varphi\frac{\partial}{\partial\varphi}\right), \tag{1.11}$$

$$\hat{l}_y = \frac{\hbar}{\mathrm{i}}\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) = +\frac{\hbar}{\mathrm{i}}\left(\cos\ \varphi\frac{\partial}{\partial\theta} - \frac{\cos\theta}{\sin\theta}\sin\ \varphi\frac{\partial}{\partial\varphi}\right), \tag{1.12}$$

$$\hat{l}_z = \frac{\hbar}{\mathrm{i}}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) = \frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial\varphi}. \tag{1.13}$$

The transformation between Cartesian and polar coordinate operators is based, obviously, on the well-known relationships: $x = r\cos\varphi\ \sin\theta$, $y = r\sin\varphi\ \sin\theta$, $z = r\cos\theta$.

The impulse operators in spherical coordinates imply derivatives on vectors along the radial axis, and tangent to spherical surfaces, along the meridians of a globe ($\mathrm{d}/\mathrm{d}\theta$) or along the parallels ($\mathrm{d}/\mathrm{d}\theta\varphi$). Readers, with the help of the above, may realize the conversion to spherical coordinates defined angular momentum vector set:

$$\hat{p} = \frac{\hbar}{\mathrm{i}}\frac{\vec{r}}{r}\frac{\partial}{\partial r} - \frac{\vec{r}\times\hat{l}}{r^2}. \tag{1.14}$$

The total energy operator, $\hat{H}$, is the sum of kinetic energy and potential operators, $\widehat{T} + V$, the latter one having a simple multiplicative nature, a case for which we dropped the use of upper hat.

1.2.3 The Schrödinger Equation and Schrödinger's Cat

The Hamiltonian eigenvalue problem for a collection of particles with generally different masses, m_k, without making explicit the nature of the potential V is:

$$-\sum_{k=1}^{N} \frac{\hbar^2}{2m_k} \left(\frac{\partial^2 \Psi}{\partial x_k^2} + \frac{\partial^2 \Psi}{\partial y_k^2} + \frac{\partial^2 \Psi}{\partial z_k^2} \right) + V(x, y, z)\ \Psi = E\ \Psi. \tag{1.15}$$

This is the explicit form of the time-independent Schrödinger equation. In most of the cases, the atomic or molecular problems, where the particles are electrons and nuclei, the nuclei system may be considered fixed and not entering in the kinetic operator.

It is instructive to consider the equation for a free particle in the whole universe. Its form can be guessed in terms of heuristic symmetry reasons. Thus, it has to be periodic, for which we can take sine or cosine functions, or better, the imaginary exponential function, that comprises both options. The free particle can be everywhere in the empty space and it can adopt an infinite number of solutions with the same energy, which is entirely kinetic. Exploiting the correspondence principle, one may imagine that a free particle is reaching the classical limit. Therefore, the quantum kinetic operator should retrieve the $p^2/(2m)$ classical formula. An $\exp(\mathrm{i}\ \mathbf{p}\cdot\mathbf{r}/\hbar)$ function will do it. Making explicit the impulse-coordinate scalar product, $\mathbf{p}\cdot\mathbf{r} = p_x x + p_y y + p_z z$, one observes that applying the second-order coordinate derivatives from definition of kinetic operator (1.10), one obtains the $p^2 = p_x^2 + p_y^2 + p_z^2$ quantum form that resembles the classical kinetic energy. Adding the $\exp(-\mathrm{i}E\ t/\hbar)$ factor, discussed previously (after Eq. 1.7), as appropriate to express stationarity with respect of time evolution, the Schrödinger wave function for a free particle can be taken as follows:

$$\Psi_{\text{free}} = \exp\left(\frac{\mathrm{i}}{\hbar} (\mathbf{p} \cdot \mathbf{r} - E\ t) \right). \tag{1.16}$$

In quantum mechanics, the waves are ways to process information, the square modulus, $|\Psi|^2$, having the signification of probability of density. Not to take the form of square of modulus as pleonastic, must indicate that, in general, the wave function Ψ is complex-valued, having a conjugated companion Ψ^*. Therefore, the square is the product of the function with its conjugate $|\Psi|^2 \equiv \Psi^*\Psi$. The probability meaning refers primarily to the location in space of particles, having then, instead of trajectories, a cloud of possible positions in space.

Since it is quite famous, we will recall the Schrödinger's cat imaginary (thought) experiment, that expressed the turmoil in the face of the wave function concept. The initial setting conceived a random event that can kill the cat caged in a box without communication with the exterior, so that it was impossible to know the situation. A detector was set to receive (or not, this being the random switch) a particle coming from a possible radioactive decay, triggering (or not) the release of a poisonous gas. As long the box was sealed, there existed the equal probability for the cat to be dead or alive, this being the expressed dilemma: the wave function for the cat's state seeming a non-physical object. The opening of the box, associated with the observation perturbing the system, brings the case to a conceivable mode, deciding if the cat was alive or dead. With all respect for the original story, we would like to consider Schrödinger's cat in a different setting, more acceptable in terms of care for animals in experiments, even imaginary ones. Thus, we will consider a softer antinomy—the awake or asleep cat. The illustration of the story appears in Fig. 1.7. Assume that there is no need for an external trigger to control this (as cats can sleep any time of the day or wake in the middle of the night). If the cat has a comfortable apartment (not a box), not necessarily free of humans, but not

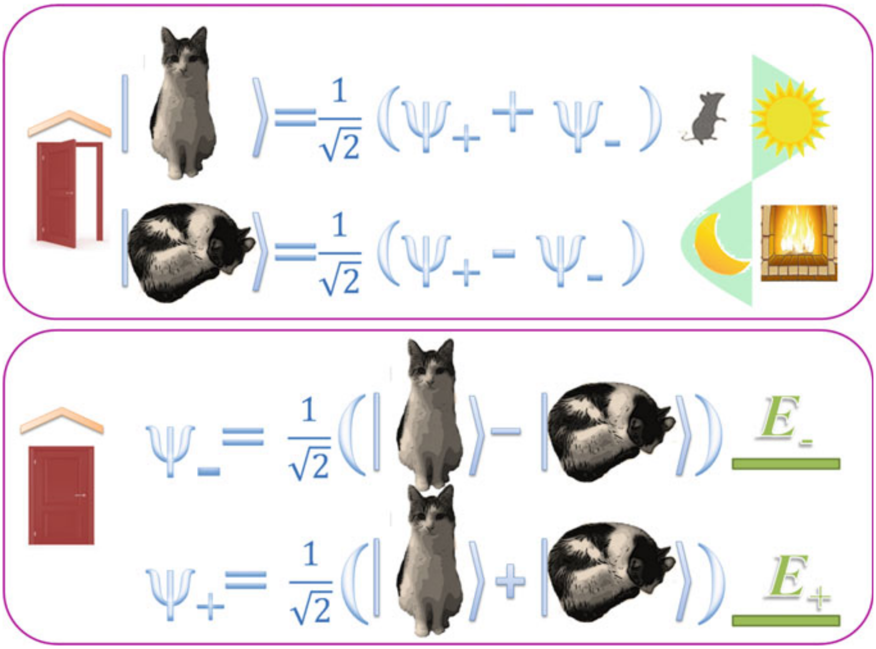


Fig. 1.7 Cat in a "ket". The Schrödinger's cat thought experiment, slightly modified: awake versus asleep cat (not alive or dead!). As function of "closed door" versus "open door" proposed operators (note the hat symbol beneath the door's icon), the solutions are of "delocalized" versus localized types. Note that functions with equal probability of awake or sleeping cat are two: ψ_+ = in-phase and ψ_- = out-of-phase. This couple has no intuitional meaning, but their remixing (sum and difference, as represented in the top half of the figure) gives rise to "measurable" states of awake or sleeping cat

in contact with the observers, then we assume that the cat spends half of the time in one of the states. One may accept that the cat state is unrelated to diurnal cycles, as just pointed out. The door is taken as the operator constructing our wave functions. Then, for a closed door, we have equal probabilities for an awake or a sleeping cat.

What is not usually observed in this cat story is that we shall have two functions driving the equal probability: the sum (awake) + (asleep) and the difference (awake) - (asleep). These are decided "by symmetry", in the condition of closed door as active operator. Of course, the sum and difference of "wave functionalized" cat do not have a common-sense equivalent, but this is how quantum mechanics is. We will even assume that the in-phase function (with summed cat states) is more stable. This assumption is not strictly needed, but brings a bit more concreteness. The states can be degenerate if the awake or sleeping cats do not interact. However, one may take as "non-diagonal" element between the cat states the beneficent feeling acquired when the cat is stretching at awakening. In this way, we evasively persuaded for a preferred "in-phase function". The symmetrized wave functions are shown in the bottom panel of Fig. 1.7. The awake or asleep cat can be obtained by the proper recombination of in-phase and out-of-phase time-independent wave functions (see the upper panel from Fig. 1.7). The opening of the door means the change of the operator, practically to a time-dependent format, bringing a perturbation that was only averaged previously (all sorts of stimuli that were not accounted before: daylight on night mysteries, a running mouse, a sleep-tempting warm chimney, and so on). The cat responds to light, noises, and other factors, while the observer is using the same channels to acquire the information about the cat status. It may seem now acceptable that the real world can be made by combination of wave functions (the state delocalized cat), which taken in themselves, are puzzling but valid in the mathematical sense, as a basis of description.

1.2.4 The Heisenberg Equations: Uncertainty and Matrix Mechanics

The handling of the operator and wave function equations is not practical, more tractable being the matrix version of quantum mechanics. The Schrödinger equation is equivalent with matrix mechanics developed by Werner Heisenberg, with essential further help from Max Born and Jordan Pasqual, in figuring the meaning and methodologies. Born gave the probabilistic interpretation and Jordan settled the matrix formalisms. The key role of Heisenberg was the revealing of the famous indetermination relationships. These signaled, from another perspective, what Schrödinger and de Broglie said, namely that the mechanics of the microcosm differ from those verified in the scales ranging from the current life objects up to the celestial bodies.

The conversion from Schrödinger to what we can generically call the Heisenberg formulation (to which many others contributed) implies the integration of the wave function over the space of coordinates. The spatial ones, with position of particles, are usually taken as primary variables, but an equivalent formulation in the impulse space is also possible.

Relying now on the statistical interpretation of the wave functions, we can put an integral equation in the form:

$$\int\limits_{\text{all } V \text{ space}} \Psi^{*}\Psi \, \mathrm{d}V = 1, \tag{1.17}$$

namely the so-called normalization condition. This means that the sum of the probabilities on all events, or its integral in continuous cases, must give unity, or the tackled particles should be somewhere in the space of considered coordinates.

The solutions of the Schrödinger equation are in general not unique. Several operator equations of type (1.6) or (1.15) can be satisfied for different eigenvalues, with different functions, or even distinct eigenfunctions can be found for the same eigenvalue, in the case of states called degenerate, representing multiplets determined by symmetry factors.

Assuming various solutions, Ψ_I, then we submit arbitrary linear combinations of them, either to the general Hamiltonian operator form (1.5), or the wave-type equations (1.15), and this mixing will yet satisfy the equality of left and right members of the formulas. This may give rise to some ambiguity which can be cleared by the following integral conditions:

$$\underbrace{\langle\Psi_I}_{''\text{bra}''} \mid \underbrace{\Psi_J\rangle}_{''\text{ket}''} = \int\limits_{\text{all } V \text{ space}} \Psi_I^{*}\Psi_J \mathrm{d}V = \delta_{IJ}, \tag{1.18}$$

$$\underbrace{\langle\Psi_I|}_{''\text{bra}''} \underbrace{\widehat{H}}_{''\text{operator}''} \underbrace{|\Psi_J\rangle}_{''\text{ket}''} = \int\limits_{\text{all } V \text{ space}} \Psi_I^{*}\widehat{H}\Psi_J \mathrm{d}V = \delta_{IJ}E_I. \tag{1.19}$$

where δ_{IJ} is the Kronecker symbol, equal to 1 when $I = J$ and to zero for different indices, $I \neq J$. With this occasion we introduced the "bra"-"ket" notation, which is a wordplay related to the outline of the integral as a bracket. The conjugated component Ψ_I^{*} is the "bra" while the Ψ_J is the "ket", being affected by the operator. The condition (1.18) is called ortho-normalization, adding the orthogonality of different solutions, aside the normalization of each one. The orthogonality constraint is a way to say that the information contained in the function Ψ_I is distinctly non-redundant from those carried by any other Ψ_J component. Otherwise, a non-null overlap (such integration without any operator is called overlap integral) can be always formulated as the mixing of a Ψ_I part into Ψ_J (or vice versa). The non-orthogonal bases can be brought by a linear transformation into an ortho-normal one. Thus, the condition (1.18) is not restraining the generality. In cases when such an adaptation is not possible there is something wrong with the chosen basis (e.g. incompleteness).

For a given operator the series of wave eigenfunctions may be regarded as a vector space, organized with the help of an ortho-normalization condition. The vector space has to be complete and it may be infinite, the related algebra being called the Hilbert space. Completeness means that the action of considered operators over functions from the known set must retrieve a combination of functions from the same set. In such context, the obtained eigenfunctions are also eigenvectors.

We started with the special case of an operator satisfying the eigenvalue problem. In the most general circumstances, an operator $\hat{a}$ applied to a function that is an eigen-solution of another operator, say the Hamiltonian, results in an expansion into eigenfunctions of its space:

$$\hat{a}\Psi_I = \sum_J a_{JI}\Psi_J. \tag{1.20}$$

Then, in the space of ortho-normal eigenvectors of the Hamiltonian, the action of the $\hat{a}$ operator can be characterized by the matrix built with the following integrals:

$$\langle\Psi_J|\hat{a}|\Psi_I\rangle = a_{JI}. \tag{1.21}$$

The diagonal elements, named expectation values,

$$\langle a\rangle_I = \bar{a}_I = \langle\Psi_I|\hat{a}|\Psi_I\rangle = \int\limits_{\text{all } V \text{ space}} \Psi_I^*\hat{a}\Psi_I \mathrm{d}V, \tag{1.22}$$

bear the meaning of the average of the magnitude described by the operator $\hat{a}$ on the state Ψ_I.

The $\hat{a}$ operator may describe perturbations driving the interaction between states (such as an electromagnetic wave), e.g. triggering a $I \longrightarrow J$ transition that occurs with the quantified $|E_I - E_J|$ energy gap.

In general, two different operators may not have the same eigen-solutions. However, such a regularity happens when the composite operator,

$$[\hat{a}, \hat{b}] = \hat{a}\hat{b} - \hat{b}\hat{a}, \tag{1.23}$$

called a commutator, becomes null. In other words, the operators that commute have common eigenvectors.

Let us go to an important pair of non-commuting operators: impulse and position, namely the couples that are conjugated variables in the analytical mechanics.

For a selected component, say the z Cartesian axis, taking the corresponding commutator applied to an arbitrary function:

$$\begin{aligned}[\hat{p}_z, \hat{z}]\psi &= \left[\frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial z}, \hat{z}\right]\psi \\ &= \frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial z}(z\psi) - z\frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial z}\psi = \left(\frac{\hbar}{i}\frac{\partial}{\partial z}z\right)\psi = \frac{\hbar}{\mathrm{i}}\psi.\end{aligned} \tag{1.24}$$

we end with a non-null operation. Or, in another formulation, expressing the "hungry" operator without a function aside, the non-commutative relation of impulse-space coordinates is written:

$$[\hat{p}_\xi, \widehat{\zeta}] = \frac{\hbar}{\mathrm{i}}\delta_{\xi\zeta}, \tag{1.25}$$

where denoted by $\xi - \zeta$ are various couples of x, y, z coordinates. The non-vanishing impulse-space commutators forbid the concept of trajectory in quantum mechanics and drive the celebrated uncertainty relationships with which Heisenberg puzzled the world. Turning to the operators customized for problems of spherical symmetry, one may check by formulas (1.11)–(1.13) that the momentum operators are implied in the following non-commutative relations:

$$[\hat{l}_\xi, \hat{l}_\zeta] = -\frac{\hbar}{\mathrm{i}}\hat{l}_\tau, \tag{1.26}$$

where the $\xi\zeta - \tau$ series of symbols refer to the cyclic permutation of Cartesian indices: $xy - z$, $yz - x$, and $zx - y$. This means that the rotation moments cannot be simultaneously resolved or measured. However, there is an important commutation relationship between the square of the operator and its z component,

$$[\hat{l}^2, \hat{l}_z] = 0, \tag{1.27}$$

meaning that the squared modulus and the projection on the quantization axis (the convened z vector) can be simultaneously defined with the same set of eigenstates. It is also interesting to verify with Cartesian definition that the kinetic operator (1.10) and the z momentum component obey the following commutation relation:

$$[\nabla^2, \hat{l}_z] = 0. \tag{1.28}$$

For the case of a free particle, with energy based totally on the kinetic operator, this implies also a commutation of the Hamiltonian operator with the kinetic moment. The property (1.28) may occur in problems with certain symmetry, spherical or axial. For the free particle, the commutation of the Hamiltonian goes equally with all the x, y, and z kinetic momentum components, expressing the isotropic nature of the space, aside the translational symmetry. In the spherical and axial cases the z coordinate is conventionally selected as quantization axis, while x and y do not show simultaneously the same properties. The analysis of commutation properties is a way to introduce quantum numbers in a given treatment.

1.2.5 Hamiltonian Matrices, Non-orthogonal Bases, Variational Methods

It is possible to work with non-orthogonal functions. For two general functions, say Φ_p and Φ_q, the integral $\langle \Phi_p | \Phi_q \rangle$ can differ from the Kronecker definition, δ_{pq}. The $\langle \Phi_p | \Phi_q \rangle$ works as the equivalent of scalar product known from geometry or linear algebra. In a simplistic analogy, we can recall the x, y, z Cartesian frame as an example of an orthogonal basis. In certain problems, such as the crystallography of a triclinic system with the (a, b, c) axes and (α, β, γ) angles (between respective $b - c$, $a - c$, and $a - b$ axes pairs), must work in the non-orthogonal frame. After all, it admits a linear transformation to a rectangular one.

Since the wave function space is considered to be complete, meaning that any conceivable function related with the problem at hand (and any operation on it) must be retrieved as linear combinations of the Ψ_I basis set, let us take the general element Φ_p as the following expansion:

$$\Phi_p = \sum_I u_{Ip}\, \Psi_I. \tag{1.29}$$

Even more, consider that a series of Φ_p components forms a new basis of the space, instead of the Ψ_J functions that we convened as exact solutions of a Schrödinger equation. The matrix representation of the Hamiltonian in a general basis will be as follows:

$$H_{pq} = (\mathbf{H})_{pq} = \langle \Phi_p | \widehat{H} | \Phi_q \rangle = \sum_I \sum_J u_{Ip}^* u_{Jq} \langle \Psi_I | \widehat{H} | \Psi_J \rangle = \sum_I u_{Ip}^* u_{Iq} E_I. \tag{1.30}$$

We help ourselves assuming the idealized knowledge of the E_I elements of the energy spectrum. The eigenvalues of the Hamiltonian, as should be the case also for any operator related with a physical observable, are real quantities. We can check now the self-adjoint property of the Hamiltonian matrix, namely that it equals its conjugated transpose. Thus, if take the transpose of the H_{pq} from the above equation, namely H_{qp}, we will have it as a summation of the $u_{Iq}^* u_{Ip} E_I$ terms. If apply the conjugation to these elements, we transmute them into: $u_{Iq} u_{Ip}^* E_I = u_{Ip}^* u_{Iq} E_I$. Rearranging the summation, one finds that the Hamiltonian matrix is self-adjoint, or Hermitical:

$$H_{pq} = H_{qp}^{*}, \tag{1.31}$$

a property obeyed by any operator with real eigenvalues.

We can work in a generally non-orthogonal basis, with the quantities

$$\left\langle \Phi_p | \Phi_q \right\rangle = S_{pq} \neq \delta_{pq}, \tag{1.32}$$

called overlap integrals. In principle, we can regard the Φ_p elements as results of deliberated basis change, starting from the exact functions Ψ_I basis, but it is more reasonable to think that the Φ_p are the primarily known objects, as a sort of available guess, from which the Hamiltonian equations can be started. The aim is then to find the reverse transformation of (1.30), arriving to the solution, as a linear combination of the Φ_p approximations. Besides, the Φ_p can be quite crude estimations, and their set incomplete (as practical compromise), but still can use the principle of linear combination, to advance toward a reasonable interpolation of the Hamiltonian eigenvalues–eigenstates problem. Previously, we noted by capital Greek Psi letter the exact eigenfunctions, Ψ_I. Now let us denote by corresponding lower-case Greek psi letter (ψ_I) the best possible approximations that can be constructed from prefabricated pieces, Ω_p:

$$\psi_I = \sum_{q=1}^{n} c_{qI} \Omega_q. \tag{1.33}$$

To mark the limitations, related to practical tractability, we introduced the finite size of the basis set, to a n-dimensional vector space, while, previously, avoiding the notation of limit on running indices, we suggested any necessary size, even an infinite space. Within the above-defined basis, relationships resembling the (1.18)–(1.19) conditions for energy and ortho-normalization, can be searched in a variational manner. This means finding a null variation under formal differentiation:

$$\mathrm{d}\Big(\langle \psi_J | \widehat{H} | \psi_I \rangle - E_I \Big) = \mathrm{d}\langle \psi_J | \widehat{H} | \psi_I \rangle = 0, \tag{1.34}$$

$$\mathrm{d}(\langle \psi_J | \psi_I \rangle - \delta_{IJ}) = \mathrm{d}\langle \psi_J | \psi_I \rangle = 0. \tag{1.35}$$

The intermediate terms in the above equation are nothing else than the E_I and δ_{IJ}, which, regarded as numbers, are quenched in the differentiation process. Since the two conditions have to be simultaneously accounted, a Lagrange multiplier, ε, linking them is introduced:

$$\mathrm{d}\Big(\langle\psi_J|\widehat{H}|\psi_I\rangle - \varepsilon\langle\psi_J|\psi_I\rangle\Big) = 0. \tag{1.36}$$

Expanding the target functions ψ_I and ψ_J into the Ω-type basis components, the above line is rewritten as follows:

$$\mathrm{d}\sum_{p=1}^{n}\sum_{q=1}^{n} c_{pJ}^{*}c_{qI}\left(\left\langle\Omega_p\middle|\widehat{H}\middle|\Omega_q\right\rangle - \varepsilon\left\langle\Omega_p\middle|\Omega_q\right\rangle\right) = 0, \tag{1.37}$$

and then we develop it to:

$$\begin{aligned}&\sum_{p=1}^{n}\mathrm{d}c_{pJ}^{*}\sum_{q=1}^{n}c_{qI}\left(\left\langle\Omega_p\middle|\widehat{H}\middle|\Omega_q\right\rangle - \varepsilon\left\langle\Omega_p\middle|\Omega_q\right\rangle\right)\\ &\quad+\sum_{q=1}^{n}\mathrm{d}c_{qI}\sum_{p=1}^{n}c_{pJ}^{*}\left(\left\langle\Omega_p\middle|\widehat{H}\middle|\Omega_q\right\rangle - \varepsilon\left\langle\Omega_p\middle|\Omega_q\right\rangle\right) = 0\end{aligned} \tag{1.38}$$

With arbitrary variation of coefficients the condition turns in the separate vanishing each of the inner summations (those factored by dc*), e.g.:

$$\sum_{q=1}^{n}c_{qI}\left(\left\langle\Omega_p\middle|H\middle|\Omega_q\right\rangle - \varepsilon\left\langle\Omega_p\middle|\Omega_q\right\rangle\right) = 0 \tag{1.39}$$

This is picked from the first part of the (1.38) equation. In the second part of (1.38) one can formally swap the p and q indices, obtaining a formula containing the c_{pI}^{*} factors and the transposed matrix elements $\left\langle\Omega_q\middle|\widehat{H}\middle|\Omega_p\right\rangle$ and $\left\langle\Omega_q\middle|\Omega_p\right\rangle$. If apply now the conjugation over the whole factored parenthesis, transform the c_{pI}^{*} into c_{pI} and, grace to self-adjoint nature of the Hamiltonian and overlap matrices, we end with a formula equivalent to (1.39) isolated from the first part of (1.38). The linear equations (1.39) must be accomplished irrespective of the i-index or, in fact, for every i element in the given vector space. Or, in other words, one may form a stack of equations like the above one, with i = 1, n, which can be reformulated in the matrix form:

$$\mathbf{H}\mathbf{c}_I = \varepsilon_I\,\mathbf{S}\mathbf{c}_I, \tag{1.40}$$

where $\mathbf{c}_I$ is a column of c_{pI} coefficients associated with specific ε_I multiplicators, **H** is the Hamiltonian matrix with the $\left\langle\Omega_p\middle|\widehat{H}\middle|\Omega_q\right\rangle$ elements and **S** is the overlap matrix, made from the $\left\langle\Omega_p\middle|\Omega_q\right\rangle$ integrals. Recall that the Hamiltonian and overlap matrices are self-adjoint: $\mathbf{H} = (\mathbf{H}^{\mathrm{T}})^{*} = \mathbf{H}^{\dagger}$, and $\mathbf{S} = (\mathbf{S}^{\mathrm{T}})^{*} = \mathbf{S}^{\dagger}$. This is a linear algebra problem, well known as an eigen-system. For square matrices of dimension n there is a set of n multipliers ε, corresponding to the desired E_I eigenvalues set since, with the appropriate matrix **c** solving the (1.40) equations, a solution similar to (1.19) conditions is achieved. In the used notation, the columns of the matrix **c** are corresponding to the eigenvectors, namely the combination coefficients that define an eigenfunction, in the selected basis.

A slight reformulation of (1.40) is done by putting all the ε values on the diagonal of matrix **E**:

$$\mathbf{Hc} = \mathbf{ScE}. \tag{1.41}$$

Multiplying from the left side with transpose and conjugated coefficient matrix, symbolized with dagger superscript, $\mathbf{c}^{\dagger} = (\mathbf{c}^{\mathrm{T}})^{*}$, the conditions from Eqs. (1.18–1.19) are fulfilled via the variation formulation from (1.39):

$$\mathbf{c}^{\dagger}\mathbf{Hc} = \mathbf{c}^{\dagger}\mathbf{ScE} = \mathbf{E} \tag{1.42}$$

The last multiplication brings the overlap to the identity matrix $\mathbf{c}^{\dagger}\mathbf{Sc} = \mathbf{I}$, while that involving the Hamiltonian to a diagonal matrix **E** containing the eigenvalues E_I. The eigenvalues– eigenvectors problem, in its matrix form, stays at the very core of applied quantum mechanics and computational chemistry.

The Schrödinger equation is soluble for relatively few problems (e.g. harmonic or Morse oscillators, free 2D or 3D rotors, free particle, or particle in a box). Among the chemical species, it is approachable only for the hydrogen atom, H, and hydrogen molecule ion, H_2^+. The wave functions of the one-electron problems of H and H_2^+ are called orbitals (atomic orbitals—AOs—or molecular orbitals—MOs, respectively), a name suggesting the replacement of classical orbits with a new concept (based on probabilistic meaning of wave function squares). In more complex problems, the matrix apparatus, in a basis of guessed components, is the practical way of having approximations for the eigenvalue spectrum. For instance, an approximate solution of the H_2^+ can be conceived as linear combination of atomic orbitals (LCAO) taken from hydrogen. At the same time, for atoms with many electrons one may follow the clue of constructing the wave function from pieces resembling hydrogenic orbitals, or even from simpler functions, thinking pragmatically and making compromises with different costs in the approximation level. This is the way followed in quantum chemistry for several decades. The atomic orbital (AO) bases, which are just materials of construction, not solutions of a rigorous atomic problem, are used for producing, by linear combination of atomic orbitals, the molecular orbitals (MOs), that further serve in approximating the many-electron wave functions, encountered on real scale problems. When one selects from the realm of quantum mechanics the smaller areas of interest (such as calculating the energies of formation of molecules from atoms, retrieving the optimum molecular geometries, computing ionization potentials, and simulating spectra or other quantities of chemical flavor), the domain of quantum chemistry is therefore delineated. It is nevertheless a part of structural chemistry, that includes also experimental approaches, such as the elucidation of molecular structures by diffraction techniques, or by interpreting details of various spectra (magnetic resonance, vibrations, visible and ultraviolet records). The orbitals are produced in implementations based on variational methods, optimizing their form iteratively. The interim orbitals, at a given stage of the iteration process, are used to produce model Hamiltonians (containing effective potentials) that lead subsequently to other orbital sets, until a self-consistent field (SCF) level is achieved. Thus, we anticipate very briefly things that will be detailed in the next chapters, dedicated to the practical methods of calculations for atoms and molecules. In the following, we focus again on the fundamental principles of the atom structure.

1.3 Atomic Shell Structure and the Spherical Harmonics

1.3.1 Atomic Orbitals and Quantum Numbers: The Radial-Angular Factorization of the Atomic Wave Functions

We are going to discuss here the wave functions named atomic orbitals, which are the results for the Schrödinger equation of an atom carrying a single electron (aka hydrogenic atoms, with nuclear charge Z and atomic charge $Z - 1$, having the H neutral species as the first member of the series). For atoms with many electrons, the orbitals are yet useful pieces for constructing approximations of the whole wave functions. As will be immediately detailed, the atomic orbitals form classes of symmetry equivalent functions, this leading to a shell pattern of electronic density.

As shown in many manuals and materials introducing the electronic structure, the orbitals, taken at a given point in the space (function of the x, y, z Cartesian coordinates or the r, θ, φ polar ones) are dichotomized in radial, $R(r)$, and angular, $Y_{l,m}$, parts, altogether with a numerical factor, $N_{n,l}$, ensuring the normalization:

$$\psi_{n,l,m}(x,y,z) \equiv \psi_{n,l,m}(r,\theta,\varphi) = N_{n,l} \cdot R_{n,l}(r) \cdot Y_{l,m}(\theta,\varphi). \tag{1.43}$$

The components carry indices (n, l, m), the quantum numbers, which are integer parameters for which certain equations (not detailed here) get solutions. The main quantum number, with positive integer values, $n = 1, 2, \ldots$, will not be discussed now, mentioning only that it bounds the l secondary quantum number to the $n - 1$ limit, i.e. subtending $l = 0, 1, 2, \ldots, n - 1$ series. The m index, running on the $m = \{-l, -l + 1, \ldots -1, 0, 1, \ldots l - 1, l\}$ set, yields a $2l + 1$ count of equivalent functions. Such collections, called orbital multiplets (or shells, in the specific case of atomic orbitals), contain congeners with the same symmetry pattern, the objects being mutually transformable under certain operations such as rotations. An advanced expression of such an equivalence classification is reached within the mathematical concept of symmetry group (continuous symmetry groups, more exactly). In a physical sense, the symmetry equivalence translates into the fact that the $2l + 1$ functions correspond to states with the same energy (so-called degenerate levels).

One may say that quantum mechanics had to struggle mostly with the radial part, since the angular components, $Y_{l,m}$, were known a long time in advance, since the 1780s, due to French mathematicians Laplace and Legendre. For the hydrogen atom case, the formulation of the radial part also benefited from the prefabricated pieces of Laguerre polynomials, provided also in advance of the quantum era, in the middle of the nineteenth century, by the French mathematician with this family name. The fortunate coincidence of already existing mathematical building blocks, to be fed into the atomic theory, can probably be assigned to the inner beauty of the underlying equations, which was spotted by mathematicians, a priori, irrespective of their potential physical meaning. This demonstrates also the absolute need for pure branches of science, unchained from the pressing demands of immediate practical utility.

The radial-angular separation of the atomic wave functions is made possible by the spherical nature of the potential exerted from the central nucleus. In fact, the spherical harmonic functions, whose components are labeled by $Y_{l,m}$ are irreducible representations of the spherical group. The mathematical notion of symmetry group is not detailed here. The reader unacquainted with such aspects may accept the shortcut explanation that the irreducible representations are ways to classify the types of objects that obey a given symmetry. Molecular symmetries relate with various polyhedra, while the atom symmetry is the sphere itself.

The spherical harmonics $Y_{l,m}$ are factorized as functions of the θ and φ polar coordinates:

$$Y_{l,m} \equiv Y_{l,m}(\theta,\varphi) = \left(\frac{(2l+1)(l-m)!}{4\pi(l+m)!}\right)^{1/2} P_l^m(\cos\theta)\cdot\exp(\mathrm{i}m\varphi), \qquad (1.44)$$

where $P_{l,m}$ is the associated Legendre function, the φ-based factor accounting for the axial symmetry (representations on a circle). The first factor in the above formula ensures the normalization conditions (integration of squared modulus over the polar coordinates yields the unity).

For completion, but without reasoning on its origin, we present the general form of associated Legendre polynomials:

$$P_l^m(z) = \frac{(-1)^m}{2^l l!}\left(1-z^2\right)^{m/2}\frac{\mathrm{d}^{l+m}}{\mathrm{d}z^{l+m}}\left(z^2-1\right)^l. \qquad (1.45)$$

Without showing explicitly the normalization factor, for which there are several conventions, we opt for the version satisfying the ortho-normality as follows:

$$\langle Y_{l,m}|Y_{l',m'}\rangle = \int\limits_{\theta=0}^{\pi}\int\limits_{\varphi=0}^{2\pi} Y_{l,m}^{*}(\theta,\varphi)Y_{l',m'}(\theta,\varphi)\sin(\theta)\mathrm{d}\theta\mathrm{d}\varphi = \delta_{ll'}\delta_{mm'}. \qquad (1.46)$$

Another useful convention is the Condon-Shortley phase:

$$Y_{l,m}^{*}(\theta,\varphi)=(-1)^{m}Y_{l,-m}(\theta,\varphi). \tag{1.47}$$

For common purposes it is convenient to do the conversion to real forms, by summing and subtracting the functions factored by the conjugated exp($\pm \mathrm{i}m\varphi$). This gives two series of real functions: one, $Y_{l,m}^{c}$, having the $P_{l,m}$ factored by cos($m\varphi$) and another, $Y_{l,m}^{s}$, by sin($m\varphi$), except the $m = 0$ case that has no φ dependence (taking therefore only $m > 0$ labels).

1.3.2 Intuitive Primer on the Pattern of Atomic Orbitals

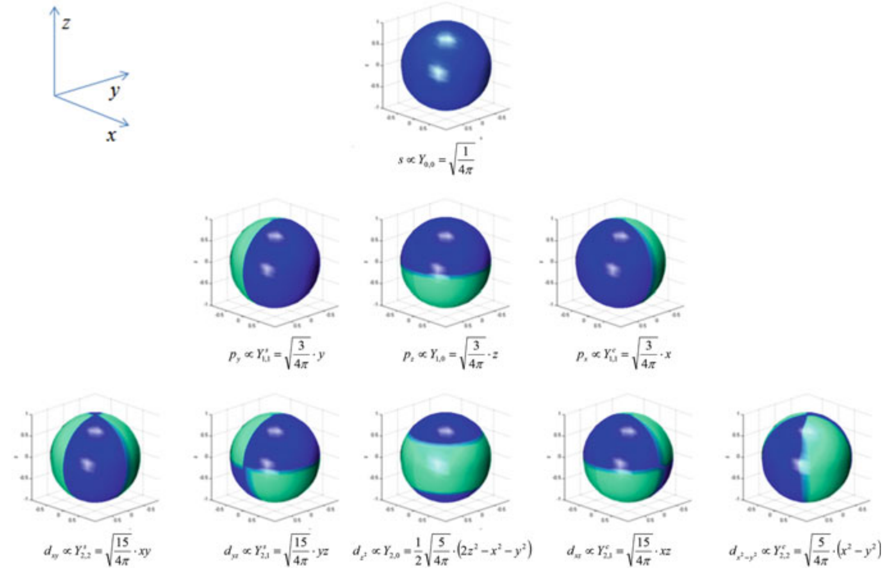
A transparent re-notation of the real spherical harmonics uses the transformation of the trigonometric formula with θ and φ variables into Cartesian coordinates x, y, and z, restricted on the unit sphere, i.e. $x^2 + y^2 + z^2 = 1$. The monomials or polynomials resulting in this way serve for labeling the orbitals, in the most common cases. For instance, the p orbitals are indexed with the well-known p_x, p_y, and p_z subscripts because the $l = 1$ set of spherical harmonics do resemble the respective sin(θ)cos(φ), sin(θ)sin(φ), and cos(θ) polar equivalents of the Cartesian x, y, z elements. For the d-type set, the d_{xy}, d_{xz} d_{yz}, $\mathrm{d}_{x^2-y^2}$, d_{z^2} orbitals are proportional to the xy, xz, yz, $x^2 - y^2$ nominal formulas, while the subscript z^2 stands as shorthand notation for a $2z^2 - x^2 - y^2$ polynomial. Going back to the s orbitals, this is the trivial case of proportionality to the $x^2 + y^2 + z^2$ combination which equals the unity, being equivalent at end with the polynomial zero degree. Alternatively, one may regard the orbitals from the s, p, d, f (and so on) sets as made from combinations of monomials of 0, 1, 2, 3 (etc.) degrees. The s is the trivial zero order case, while the p orbitals are first-order x, y, and z monomials. The p orbitals are mutually orthogonal. This means that the product of two different components, integrated over the all space, e.g. $\int x \cdot y\,\mathrm{d}V$, in a loosely defined notation, is null. It can be figured that the $x{\cdot}y$ product contains equal amounts of positive and negative zones, which are summed to zero. We discard here the question of normalization.

For the second-order case, there are six monomial possible components, xy, xz, yz, x^2, y^2, and z^2. However, since these are linked by the $x^2 + y^2 + z^2 = 1$ condition, we end with five components, rearranging the squared components into the $x^2 - y^2$ and $2z^2 - x^2 - y^2$, which also obey the condition of orthogonality, between them and against the other monomials, namely xy, xz, and yz. If we consider a basis, made from the above-listed six monomials, we can see that the first three are orthogonal between them and against the last three ones. For instance the product of xy with yz, $\int xy \cdot yz\,\mathrm{d}V \equiv \int y^2 \cdot xz\,\mathrm{d}V$, has a null volume integral since the y^2 factor is positive or null over all the range, while the xz part creates equal positive and negative content. For similar reasons, the first three monomials are orthogonal against the squared ones. At the same time, one may note that the squared forms are not mutually orthogonal, since their products, e.g. $\int x^2 \cdot y^2 \, \mathrm{d}V$, are non-negative everywhere and cannot lead to null integration. The orthogonalization by remixing the x^2, y^2, and z^2 components into the independent $x^2 - y^2$ and $2z^2 - x^2 - y^2$ and eliminating the $x^2 + y^2 + z^2$, as spurious part, leads to the well-known set of d orbitals.

Going to the third order, we have in principle ten monomials, xyz, xy^2, x^2y, xz^2, x^2z, yz^2, y^2z, x^3, y^3, z^3. However, only seven are independent, as we know for the $l = 3$, f-type orbitals, since three components, that can be grouped as $x \cdot (x^2 + y^2 + z^2)$, $y \cdot (x^2 + y^2 + z^2)$ and $z \cdot (x^2 + y^2 + z^2)$ are in fact equivalent to the p-type set, x, y, z, and should be removed from the final count. The customary notation of real f orbitals is as follows: f_{z^3}, f_{xz^2}, f_{yz^2}, f_{xyz}, $\mathrm{f}_{z(x^2-y^2)}$, $\mathrm{f}_{x(x^2-3y^2)}$ and $\mathrm{f}_{y(3x^2-y^2)}$, the components being (except the normalization factors) defined by the respective polynomials $z \cdot (2z^2 - 3x^2 - 3y^2)$, $x \cdot (4z^2 - x^2 - y^2)$, $y \cdot (4z^2 - x^2 - y^2)$, xyz, $z \cdot (x^2 - y^2)$, $x \cdot (x^2 - 3y^2)$ and $y \cdot (3x^2 - y^2)$. Such forms are obtained either by transforming to real the $Y_{3,m}$spherical harmonics (with $m = -3$ to 3) or by performing the diagonalization of the overlap integral matrix between the ten monomials of third order.

In some quantum chemical programs, for sake of expediency, the d and f orbitals are introduced in the basis of six or ten monomials of second or third order, bringing together spurious s respective p basis components. The undesired components do not impinge much in the practice, since, in the applied computational approach, the basis sets are regarded as rich baskets of trial functions, without strict link with the atom in a given state. It is the task of iterations, by variational procedures, to pick what is needed from these bases and optimize a result as close as possible to the physical reality. For technical reasons, the quantum chemistry may use atomic shells with larger secondary quantum numbers, $l > 3$, e.g. g and h orbitals, although these upper sets are not among the objects of the customary intuition. On the other hand, the involvement of high quantum numbers is possible in excited states and the atom in the molecule can be regarded as deformed by mechanisms infusing local excitations and mixing with the neighbor wave functions.

As pointed out previously, the spherical harmonics are special functions, the subject of advanced mathematics. However, the mathematical intricacies can partly be avoided by heuristic suggestions. Thus, in a very qualitative fashion, the real spherical harmonics are classified as the possible ways of painting a sphere in two colors, by cutting borders between areas of different type, the so-called nodal planes. The colors will correspond, in fact, to the "+" and "−" signs, while the nodal planes are formed by the collection of points where the function becomes null. The index l from the $Y_{l,m}$ notation, assigned in the atomic theory to the secondary quantum number, corresponds also to the number of nodal planes. As shown in Fig. 1.8, the $l = 0$ case is a uniformly colored sphere, without nodal borders. The $l = 1$ implies one border between hemispheres with different coloring (or opposed sign of the function). Next sets with $l = 2$, 3 etc. imply further partition with 2, 3, nodal planes and so on. We can understand from this perspective too why the x^2, y^2, and z^2 are not "good orbitals", because being overall positive (or null at respective $x = 0$, $y = 0$ and $z = 0$) they do not show the proper nodal structure and sign alternation, assigned to the d orbitals (namely two nodal planes).



$$s \propto Y_{0,0} = \sqrt{\frac{1}{4\pi}}$$

$$p_y \propto Y_{1,1}^s = \sqrt{\frac{3}{4\pi}} \cdot y \qquad p_z \propto Y_{1,0} = \sqrt{\frac{3}{4\pi}} \cdot z \qquad p_x \propto Y_{1,1}^c = \sqrt{\frac{3}{4\pi}} \cdot x$$

$$d_{xy} \propto Y_{2,2}^s = \sqrt{\frac{15}{4\pi}} \cdot xy \qquad d_{yz} \propto Y_{2,1}^s = \sqrt{\frac{15}{4\pi}} \cdot yz \qquad d_{z^2} \propto Y_{2,0} = \frac{1}{2}\sqrt{\frac{5}{4\pi}} \cdot \left(2z^2 - x^2 - y^2\right) \qquad d_{xz} \propto Y_{2,1}^c = \sqrt{\frac{15}{4\pi}} \cdot xz \qquad d_{x^2-y^2} \propto Y_{2,2}^c = \sqrt{\frac{5}{4\pi}} \cdot \left(x^2 - y^2\right)$$

Fig. 1.8 The sign pattern for the first sets of real spherical harmonics, represented by coloring (blue = positive, green = negative). Note that the index l, associated to the quantum number determining the atomic shells equals the number of nodal planes (borders between positive and negative areas): $l = 0$, s-type orbitals, no nodal surface, $l = 1$, p-type orbitals, one nodal plane, $l = 2$, d-type orbitals, two nodal planes, etc.

The $\exp(im\varphi)$ component of the spherical harmonics, or equivalently, the real-type description by $\{\sin(m\varphi), \cos(m\varphi)\}$ couples determines the axial symmetry, or the representation on a circle, suggested in Fig. 1.9, where we see the sign of trigonometric functions. The first member, $m = 0$, is the trivial case with the same sign (conventionally positive) on all the sections. On the left side, we see the sign of $\sin(m\varphi)$ functions which has a nodal plane along the horizontal x axis, where the function vanishes. By contrary, the $\cos(m\varphi)$ has a maximal amplitude at $\varphi = 0$, having lobes along x axis. The m index describes the way in which nodal lines and two-color partitioning may be represented over a circle. The axial symmetry factors are common to different spherical harmonics sets. For instance the $m = 0$ uniformly colored circle is found from an upper view, along the z axis, on all the $Y_{l,0}$ functions represented on a sphere, e.g. s, p_z, d_{z^2}, f_{z^3}, etc. The profile colored in two halves (second line of Fig. 1.9 reading from top to bottom), related with the sign of the $\{\sin(\varphi), \cos(\varphi)\}$ functions is the same for all the $\left\{Y_{l,1}^s, Y_{l,1}^c\right\}$ couples, e.g. $\{\mathrm{p}_y, \mathrm{p}_x\}$, $\{\mathrm{d}_{yz}, \mathrm{d}_{xz}\}$, $\left\{\mathrm{f}_{xz^2}, \mathrm{f}_{yz^2}\right\}$, from Fig. 1.8 in the view along z. The components with two nodal lines and four colored patches, $m = 2$, appear at spherical harmonics with $l \geq 2$, $\left\{\mathrm{d}_{xy}, \mathrm{d}_{x^2-y^2}\right\}$, $\left\{\mathrm{f}_{xyz}, \mathrm{f}_{z(x^2-y^2)}\right\}$, etc. The last line in Fig. 1.9 shows three nodal lines, appearing first in the $\left\{\mathrm{f}_{x(x^2-3y^2)}, \mathrm{f}_{y(3x^2-y^2)}\right\}$ sequence and, of course, at sets with $l > 3$. If the atoms were two-dimensional, then the

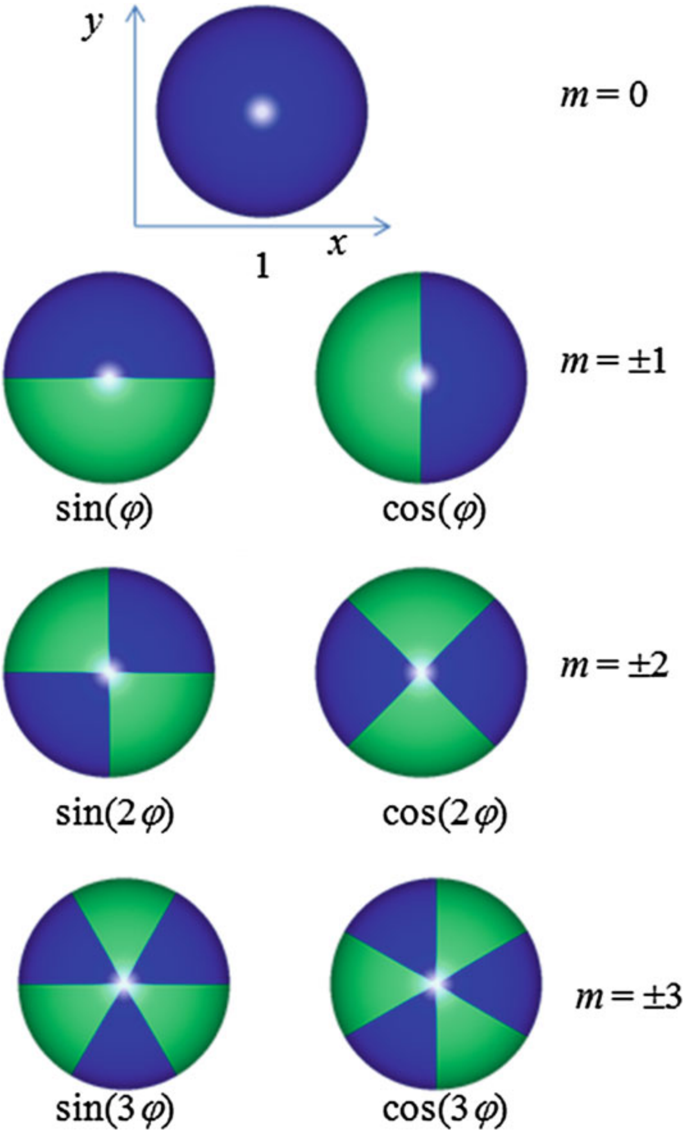


Fig. 1.9 The sign pattern for the axial components of real spherical harmonics, represented by coloring (blue = positive, green = negative). The number of nodal lines is parallel with the m index, driving the sign variation in the $\{\sin(m\varphi), \cos(m\varphi)\}$ couples ($m = 0$, no nodes; $m = 1$, one nodal line; $m = 2$, two nodal lines, etc.).

Schrödinger equation would be factorized in a radial part and a simple $\exp(\mathrm{i}m\varphi)$ angular component. The axial symmetry is applied in the diatomic molecules and is relevant for the general classification of bonding types.

In Fig. 1.8 we suggested only the signs of angular components of the atomic orbitals. The usual representation with lobes can be realized by replacing the colored patches with a lobe of the same color, yet bending their profiles toward the null radius when coming closer the nodal zones. More concretely, the polar maps for the corresponding angular functions represent the qualitative orbital lobes. A polar map of a trigonometric function is obtained scanning the angle (the φ variable in a 2D representation or the θ and φ in the 3D case) and tuning the radius equal to the absolute value of the represented function.

Thus, the representation of a constant value will be a sphere with the radius equal to it. Then, the s orbitals, having no angular dependence, are drawn as spheres, as is well known. Considering the normalization factor, a sphere with radius $\sqrt{1/4\pi}$ is drawn in the left side of Fig. 1.10. The p_z orbital is proportional with the $\cos(\theta)$ function. Its polar representation is obtained scanning a radius pointing toward a grid of the θ and φ coordinates (similar to latitude and longitude on the globe map) and scaling its extension with absolute value of $\cos(\theta)$. The drawing is symmetric around the z axis (because the function does not depend on φ), and reaches maximal extension (equaling the $\sqrt{3/4\pi} \sim 0.49$ normalization factor) at $\theta = 0$ and $\theta = \pi$ directions. The variation of sign is figured by conventional coloring of the lobes, as seen in the middle panel of Fig. 1.10.

The right side of Fig. 1.10 shows the case of d_{z^2}, proportional to $2z^2 - x^2 - y^2$ Cartesian form, or to the $3\cos(\theta)^2 - 1$ polar representation. The normalization factor is $(1/2)\sqrt{5/4\pi} \sim 0.315$. At $\theta = 0$ and $\theta = \pi$, the product of factor and trigonometric function yield the maximal value, ~ 0.63, that decides the elongation

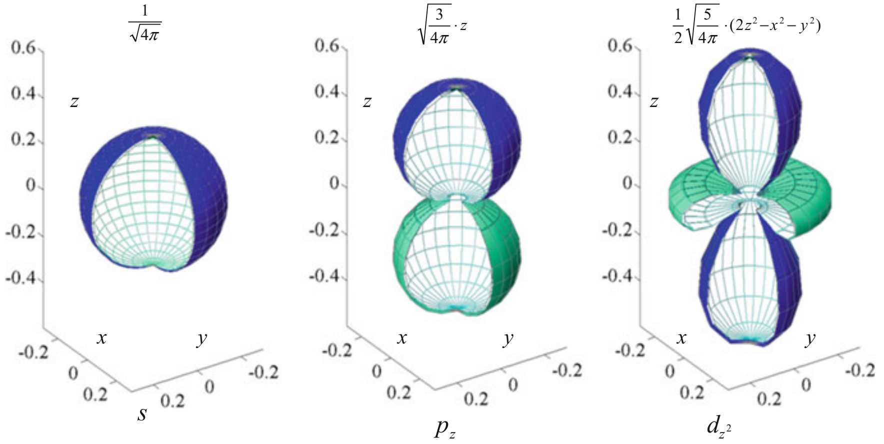


Fig. 1.10 The orbital shapes as polar surfaces of the corresponding trigonometric function related with their angular part. Namely, for a given direction, from the center to outside, determined by the θ, φ, polar coordinate, the distance to the surface is proportional to the amplitude of the wave function. The surface is "squeezed" to touch the center in the nodal zones, where the represented function is null. The sign of function is marked by coloring: positive = blue, green = negative.

of the lobe. At θ values varying slowly from the poles toward the "tropics", the function decreases rapidly, e.g. at $\theta = \pi/6$ the distance between center and distance is about ~ 0.4. The polar shape goes toward a nodal plane that happens when $3\cos(\theta)^2 = 1$, i.e. at a $\theta = \arccos(\sqrt{1/3}) \sim 0.955$ rad ~ 54.7 degrees, where the radius collapses to zero. In between $\theta = \arccos(\sqrt{1/3})$ and $\theta = \pi - \arccos(\sqrt{1/3})$ the module of radius increases again (while the sign turns negative) with a new maximum at equator, $\theta = \pi/2$. The shape is symmetric at the rotation around the z axis, since no φ dependence occurs in the chosen function.

1.3.3 Toward Setting the Schrödinger Equation in Atoms

We will not solve the Schrödinger equation for the hydrogen-like atoms. In turn, we will perform certain transformations that may suggest the structure of the solutions. It is useful to rewrite the kinetic energy operator in spherical coordinates, or its core made of the Delta symbol (alias Nabla square). It is a basic exercise of coordinate changing, for which we present the result:

$$\Delta = \nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\left(\frac{\partial^2}{\partial \theta^2} + \frac{\cos\theta}{\sin\theta}\sin\varphi\frac{\partial}{\partial\varphi} + \frac{1}{(\sin\theta)^2}\frac{\partial^2}{\partial\varphi^2}\right). \tag{1.48}$$

It is interesting to remark that the angular part is proportional (by $-\hbar^2 r^2$) to the square of momentum operator:

$$\hat{l}^2 = \hat{l}_x^2 + \hat{l}_y^2 + \hat{l}_z^2 + \hat{l}_x\hat{l}_y + \hat{l}_y\hat{l}_x + \hat{l}_x\hat{l}_z + \hat{l}_z\hat{l}_x + \hat{l}_z\hat{l}_y + \hat{l}_y\hat{l}_z, \tag{1.49}$$

the Nabla square operator being then tailored as follows:

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} - \frac{1}{\hbar^2}\frac{\hat{l}^2}{r^2}, \tag{1.50}$$

which is a form to remember.

Coming back to the spherical harmonics, one may see that, considering the separation into factors function of θ and φ variables, like in (1.44), applying the z-component of kinetic momentum directly verifies the following relationship:

$$\hat{l}_z Y_{l,m} = \hbar m Y_{l,m}. \tag{1.51}$$

For simplicity, we omit detailing the polar coordinates, keeping in mind the $Y_{lm} \equiv Y_{lm}(\theta, \varphi)$ equivalence. The above equation looks like an eigenvalue equation, with the general format suggested in (1.5). In fact, the spherical harmonics are eigenfunctions of the z-component of kinetic momentum and the m indices are the l_z eigenvalues: $m \equiv l_z$. The kinetic operator obeys another operator equation:

$$\hat{l}^2 Y_{l,m} = \hbar^2 l(l+1) Y_{l,m}, \tag{1.52}$$

which establishes the modulus of kinetic moment operator. In atomic units, one may consider m and $l(l + 1)$ as eigenvalues for the projection and square momentum operators. Later on, we will see this pattern for other quantum operators (the spin S and the J resultant of spin and orbital moments). In evasive manner, one may observe that the $2l + 1$ degeneracy looks like a “density of states” (number of states found in an infinitesimal interval, divided to the interval size) associated with the $\mathrm{d}[l(l + 1)]/\mathrm{d}l = 2l + 1$ derivative. This is a peculiarity, interpreted with reserve, since, of course, we are not allowed to take derivatives with respect of integer quantum numbers.

The spherical harmonics are obeying the Laplace equation, this being their birth certificate:

$$\nabla^2 \left(r^l Y_{l,m} \right) = 0. \tag{1.53}$$

For this reason, the Nabla square operator is also called Laplacian. Expanding the operator with the previously discussed equivalence (1.50), the Laplace equation becomes:

$$\frac{\partial^2}{\partial r^2}\left(r^l Y_{l,m} \right) + \frac{2}{r}\frac{\partial\left(r^l Y_{l,m} \right)}{\partial r} - \frac{1}{\hbar^2} r^{l-2} \hat{l}^2 \left(Y_{l,m} \right) = 0. \tag{1.54}$$

Considering that the radial derivatives do not operate over the Y_{lm} factor and dividing with the r^{l-2} factor, one retrieves the (1.53) eigenvalue of the squared kinetic momentum. The $r^l Y_{lm}$ functions are called solid spherical harmonics. The solid spherical harmonics obey the same eigenvalue relationships pointed out for the genuine functions, since the multiplication with the isotropic radial factors does not alter their properties with respect of polar coordinates.

One may observe that the r^l factor brings a dimensionality that was suggested previously when the spherical harmonics were discussed in terms of the polynomial expressions. If we return to Cartesian coordinates, the solutions of the Laplace equation can be envisaged as linear combinations of monomials of rank l, namely $x^i y^j z^k$, with $i + j + k = l$. The first cases, with $l = 0$ and 1 are trivial. The $r^0 Y_{00}$ function is a constant that will yield immediately null value at derivation by Laplacian operator. The $l = 1$ is also immediate, since any x, y, or z component, or any arbitrary linear combination of them, will yield zero under the second derivative of the considered operator. In this way, the real solutions were tacitly considered. The imaginary forms can be equally conceived too, as corresponding linear combinations of the real harmonics. The $l = 2$ is yet simple. Any mixed monomial xy, xz, or yz, are also becoming null after operated with the

$\partial/\partial x^2, \partial/\partial y^2$, and $\partial/\partial z^2$ operator components. The remaining two $l = 2$ congeners can be put in simple form: $ax^2 + bx^2 + cx^2$ and $a'x^2 + b'x^2 + c'x^2$. The action of the Laplacian on the first combination is straightforward: $(\partial/\partial x^2 + \partial/\partial y^2 + \partial/\partial z^2)(ax^2 + bx^{\ 2} + cx^2) = a + b + c$, the second function yielding, similarly, the $a' + b' + c'$ result. The Laplace equation on these forms reads simply as $a + b + c = 0$ and $a' + b' + c' = 0$. Disregarding other conditions imposed on the function, one may see that possible choices, are $a = -1$, $b = -1$, $c = 2$ and $a' = 1$, $b' = -1$, $c' = 0$. This choice also obeys the orthogonality condition $aa' + bb' + cc' = 0$. Rescaling with $(a^2 + b^2 + c^2)^{-1/2}$ and $(a'^2 + b'^2 + c'^2)^{-1/2}$ respective factors, the normalization is also achieved, the obtained functions being the d_{z^2} and $\mathrm{d}_{x^2-y^2}$ orbitals. This pair of solutions is not unique. For instance the permutation of (a, b, c) and (a', b', c') sets of coefficients are also solutions. This means that, for instance, d_{x^2} and $\mathrm{d}_{y^2-z^2}$ are equally good orbitals, the choice of axis of quantization, usually taken as z, being a conventional step. Higher l solutions can in principle be constructed as combination of products between x, y, z and elements of a previously resolved $l - 1$ harmonics, or reworking from scratch any situation as linear expansion in terms of $x^i y^j z^k$ monomials (with $i + j + k = l$). With the above divagation, we hope that the topic of spherical harmonics has been made a bit more vividly palpable.

1.3.4 The Schrödinger Equation for the One-Electron Atom: The Radial Part

Let us write the Schrödinger equation for one electron and a fixed nucleus with Z charge. This aim can be achieved by replacing in the generic formula (1.15) the kinetic energy for a single electron, ascribed in the polar form (1.50) and the electrostatic term as potential V, imposing also the radial-angular factorization of the wave functions:

$$-\frac{\hbar^2}{2m_\mathrm{e}}\nabla^2\big(R(r)Y_{l,m}(\theta,\varphi)\big) - \frac{Ze^2}{4\pi\varepsilon_0 r}R(r)Y_{l,m}(\theta,\varphi) = E\,R(r)Y_{l,m}(\theta,\varphi). \tag{1.55}$$

In the following we will switch to the convenient scale of atomic units, where the factors $\hbar^2/2m_\mathrm{e}$ and $e^2/4\pi\varepsilon_0$ become both equal to 1 (here m_e and e are mass and charge of the electron, while ε_0 is the permittivity of the vacuum). We also renounce specifying the explicit dependence on r in the radial part, or on θ and φ in the spherical harmonics. Then, the schematized equation for the one-electron atom becomes:

$$-\frac{1}{2}\nabla^2\big(RY_{l,m}\big) - \frac{Z}{r}RY_{l,m} = E\,RY_{l,m}. \tag{1.56}$$

In order to use the previously discussed Lagrange equation (1.53), let us enforce a formal re-factorization, introducing the $r^l Y_{l,m}$ solid spherical harmonics, at the expense of making the R/r^l the new radial part:

$$R \cdot Y_{l,m} \Rightarrow \left(\frac{R}{r^l}\right) \cdot \left(r^l Y_{l,m}\right). \tag{1.57}$$

The Nabla square operator can be written as follows:

$$\nabla^2\left[\left(\frac{R}{r^l}\right)\left(r^l Y_{l,m}\right)\right] = \left[\frac{\partial^2}{\partial r^2}\left(\frac{R}{r^l}\right) + \frac{2(l+1)}{r}\frac{\partial}{\partial r}\left(\frac{R}{r^l}\right)\right] r^l Y_{l,m} + \left(\frac{R}{r^l}\right)\nabla^2\left(r^l Y_{l,m}\right), \tag{1.58}$$

observing that the last term contains the vanishing Laplace equation (1.53) as factor. This leads to a form where the angular part vanished:

$$-\frac{1}{2}\left[\frac{\partial^2}{\partial r^2}\left(\frac{R}{r^l}\right) + \frac{2(l+1)}{r}\frac{\partial}{\partial r}\left(\frac{R}{r^l}\right)\right] - \frac{Z}{r}\left(\frac{R}{r^l}\right) = E\left(\frac{R}{r^l}\right). \tag{1.59}$$

A further handling leads to:

$$-\frac{1}{2}\left[\frac{\partial^2 R}{\partial r^2} + \frac{2}{r}\frac{\partial R}{\partial r} - \frac{l(l+1)}{r^2}R\right] - \frac{Z}{r}R = ER, \tag{1.60}$$

which, otherwise, can be obtained replacing in (1.55) the spherical harmonics property of producing eigenvalues for squared kinetic moment, combining (1.50) and (1.52) equations. Multiplying the (1.60) equation by r^2, the $l(l + 1)R$ term remains the only one not affected by a factor that enforces vanishing at $r = 0$. This probes that, nearby nucleus if $l > 0$, the radial function must trend to zero. The $l = 0$ case is allowed to be finite, since the discussed cancelation is ensured by the $l(l + 1)$ factor.

Consider the $l = 0$ case (which means the discarding of the $1/r^2$ term) and multiply now by r the (1.60) equation. In this case, the parts that are not enforced to vanish at $r = 0$ are the first derivative and the Coulomb terms, which must then cancel each other. In this way, we reached a condition known as Kato's cusp (Kato 1957):

$$\left(\frac{\partial R}{\partial r}\right)_{r\to 0} = -ZR, \tag{1.61}$$

stating the form of wave function and related density at nucleus. The density at nucleus is finite, but discontinuous, with a sharp pattern. Note that the nucleus density comes only from $l = 0$ functions. At infinity, all the terms with r in denominator are going extinct, having then:

$$\left.\frac{\partial^2 R}{\partial r^2}\right|_{r\to\infty} = -2ER = 2|E|R. \tag{1.62}$$

Knowing that bound states must keep $E < 0$ and that a zero energy is already the atom with its electron ionized, we transmuted the minus factor to the module of the energy. Then, in atomic units, the tail of the wave function at large distances would be:

$$R(r)|_{r\to\infty} \sim \exp\left(-\sqrt{2|E|}\,r\right), \tag{1.63}$$

where the negative sign inside the exponential function ensures its proper decay to zero at large r, since we do not want the electron outside the atom orbits.

Several other common functions can satisfy the (1.63) condition, e.g. sine, cosine, or the exponential form for periodic conditions. Not allowing the function to extend at infinity, the periodic solutions are ruled out, choosing then the (1.63) exponential with negative coefficient, quenched at infinity.

Multiplying by r the whole Eq. (1.60), one observes the possibility of a rearrangement implying only the second derivative term; at the expense of reformulating the radial part as the rR function:

$$-\frac{1}{2}\left[\frac{\partial^2(rR)}{\partial r^2} - \frac{l(l+1)}{r^2}(rR)\right] - \frac{Z}{r}(rR) = E\cdot(rR). \tag{1.64}$$

This formulation of radial function is convenient, since its square, $(rR)^2$, renders directly the radial density probability and the normalization condition:

$$\int\limits_{r=0}^{\infty} (rR(r))^2 \mathrm{d}r = 1. \tag{1.65}$$

Playing with variable changes and choosing

$$\rho = (l+1)r, \tag{1.66}$$

Equation (1.64) is brought to

$$\begin{aligned} -\frac{1}{2}\left[(l+1)^{l+2}\frac{\partial^2}{\partial\rho^2}\left(\frac{R}{\rho^l}\right) + \frac{2(l+1)^{l+2}}{\rho}\frac{\partial}{\partial\rho}\left(\frac{R}{\rho^l}\right)\right] - (l+1)^{l+1}\frac{Z}{\rho}\left(\frac{R}{\rho^l}\right) \\ = E\,(l+1)^l\left(\frac{R}{\rho^l}\right), \end{aligned} \tag{1.67}$$

which, simplified by $(l + 1)^2$, becomes:

$$-\frac{1}{2}\left[\frac{\partial^2}{\partial\rho^2}\left(\frac{R}{\rho^l}\right)+\frac{2}{\rho}\frac{\partial}{\partial\rho}\left(\frac{R}{\rho^l}\right)\right]-\frac{Z/(l+1)}{\rho}\left(\frac{R}{\rho^l}\right)=\left(E/(l+1)^2\right)\left(\frac{R}{\rho^l}\right). \quad (1.68)$$

Rescaling the terms, the radial equation becomes:

$$-\frac{1}{2}\left[\frac{\partial^2\widetilde{R}}{\partial\rho^2}+\frac{2}{\rho}\frac{\partial\widetilde{R}}{\partial\rho}\right]-\frac{\widetilde{Z}}{\rho}\widetilde{R}=\widetilde{E}\,\widetilde{R}, \quad (1.69)$$

where $\widetilde{Z}=Z/(l+1)$, $\widetilde{E}=E/(l+1)^2$ and $\widetilde{R}=R/\rho^l$.

In this format, there is no explicit dependence on l (although tacitly incorporated in the performed rescaling), so that one may suggest that different classes of orbitals have isomorphous master equations. For $l = 0$, one may directly suggest a first simple solution:

$$\widetilde{R}=\ \exp(-\widetilde{Z}\rho). \quad (1.70)$$

One may immediately check that the first derivative of this function cancels the electrostatic term and the energy remains identical to:

$$\widetilde{E}=-\widetilde{Z}^2/2 \quad (1.71)$$

In the $l = 0$ case the transformed variables and functions are identical to the genuine ones (R, Z, E), i.e.

$$R_1=\ \exp(-Z\rho)\ \equiv\ \exp(-Zr), \quad (1.72)$$

and

$$E_1=-Z^2/2. \quad (1.73)$$

We will pass on to non-null l quantum numbers, aiming to restore the function by the reverse transformation $R=\rho^l\widetilde{R}$. Actually, the ρ is equivalent to r, without considering its formal back-transformation, since both variables are playing the same variation from 0 to ∞, being mutually replaceable. The $l = 1$ case can be tackled immediately by replacing $Z \rightarrow Z/2$ and $E \rightarrow E/4$, reaching the following solutions:

$$R_2=\rho\ \exp(-Z\rho)\equiv r\ \exp(-Zr/2), \quad (1.74)$$

$$E_2=E_1/4=-(1/2)\ (Z/2)^2. \quad (1.75)$$

Here, the normalization factor was neglected, since it is not changing the structure of the differential equations, while it is explicitly useful in matrix formulation of the problem. In similar manner, the l general case, treated with the $Z \rightarrow Z/(l + 1)$ and $E \rightarrow E/(l + 1)^{2}$ replacements leads to:

$$R_{l+1} = \rho^{l} \exp(-Z\rho) \equiv r^{l} \exp(-Zr/(l+1)), \tag{1.76}$$

$$E_{l+1} = E_{1}/(l+1)^{2} = -(1/2)(Z/(l+1))^{2}. \tag{1.77}$$

The E_1, E_2, …, E_n must be the lowest eigenvalues encountered for the sets of $l = 0, 1, \ldots, n - 1$ quantum numbers. At the same time, the sets may have multiple solutions, with higher energies. However, in (1.69) we formulated a general equation for any possible case. Then, we must find repeated solutions in each l set, based on the formal equivalence of equations, irrespective of this index. Therefore, the E_1, E_2, …, E_n solutions are expected in the $l = 0$ case too. Analogously, the $l = 1$ starts with E_2, but will continue with the same elements in the row E_2, E_3, …, E_n. The $l = 2$ spans the E_3, …, E_n series, etc. Then, one may regroup the solutions in classes of energy equivalence: E_1 appears once, for $l = 0$, E_2 occurs for $l = 0$ and $l = 1$, E_3 for $l = 0$, $l = 1$, and $l = 2$, etc. In general, the E_n level admits n solutions, running in the $l = 0, \ldots, n - 1$ interval. We reached then the suggestion of a regularity managed by an index n that gets the quality of a quantum number.

The above reasoning is not a completed analytical proof, but it seems a suggestive way for guessing the pattern of eigenvalues for the atom with one electron, driven by a central electrostatic field. Interestingly, the energy formulas are the same as in the case of a Bohr atom:

$$E_n = \frac{E_1}{n^2} = -\frac{Z^2}{2n^2}. \tag{1.78}$$

The simplified reasoning does not cover the finding of the full sets of wave functions. The (1.76) formulas are valid only for the $l = n - 1$ elements, while the $l < n - 1$ cases of a given n are getting more complicated (multi-exponential) expressions.

The n index can be identified as the main quantum number, and l as the secondary one ($l = 0, 1, \ldots n - 1$). Recall the magnetic quantum number, m running from $-l$ to $+l$, appearing as index in the $Y_{l,m}$spherical harmonics angular factor, going back from radial problem, to the full format of atomic orbitals.

1.3.5 A Qualitative Analysis of the Radial Nodal Structure of the Atomic Orbitals

Resuming, the atomic structure can described as made of shells with $2l + 1$ orbitals, labeled by merging the n quantum number and the letter customized for the first l values (s, p, d, f for respective $l = 0, 1, 2, 3$). The larger $l = 4, 5$, etc. indices get the letters in the alphabetic order, g, h, etc. skipping however the j letter (reserved for the *j* quantum number met in the quantum relativistic theory of the atom) and also s or p (taken at beginning). Thus, the hydrogen levels are successively (1s) (2s2p)(3s3p3d) etc.

Aside the $2l + 1$ degeneracy determined by the symmetry equivalence of the $Y_{l,m}$ spherical harmonics, we found (strictly for the case of one-electron atom) an energy equality relationship for different l sets bound to the same main quantum number, n, expressed by (1.78). The chemists are inclined to assume different energies for each l, but this is a consequence of using the orbitals as effective approximations for the many-electron atom. If we ignore the relativistic effects (which lead to another split pattern, under the systematics of the j quantum number), in the hydrogen-type (one electron) atoms all l shells originating from the same n are equal in energy.

As discussed previously, the l quantum number induces l nodal contours on the surface of the sphere scanned in θ, φ coordinates. The radial part has, in its series of solutions, also an increasing number of nodes. For instance $l = 0$ starts with no node at $n = 1$, and has 1, 2, … etc. crosses with the zero value axis for $n = 2, 3, \ldots$ and so on. The $l = 1$ starts nodeless at $n = 2$ and acquires one node at each n step. In fact, each first apparition of an l at $n = l + 1$ has no node, these occuring at higher quantum numbers, at energies growing with the number of nodes. Or, in other words, each function characterized by n and l quantum numbers shows $n - l - 1$ radial nodes and l angular ones. Then, each quantum number n is characterized by a total of $n - 1$ nodes, counting both the radial and angular ones. Thus, the $n = 2$ case must be characterized by one node. The angular part of $n = 2$ and $l = 1$ already has one node, so that the radial factor has none. In turn, the $l = 0$ ($n = 2$), being isotropic, must form a node in the radial part. At $n = 3$ nodes are as follows: two angular and none radial for $l = 2$, one angular and one radial for $l = 1$, none angular and two radial for $l = 0$. There is a certain topology equivalence between the angular and radial nodes, that ultimately leads to the somewhat unexpected degeneracy along the $l = 0, 1, \ldots n - 1$ series.

Without dedicating here to mathematical scrupulosity, just allowing ourselves a qualitative evasiveness, we present in Fig. 1.11 a process persuading the idea of radial versus angular equivalency in the nodal pattern. Starting from a plane-wave picture (that admits, by symmetry, solutions of $\exp(ikx)$, $\exp(iky)$, $\exp(ikz)$, or their sine-cosine equivalents) with symmetry equivalent solutions (see left side of Fig. 1.11) the drawn landscape is deformed, by a procedure resembling those called in mathematics conformal mapping (Di Francesco et al. 1997). An intermediate stage of this transformation is suggested in the middle part of Fig. 1.11. After completing the conformal mapping, we arrive (on the right side of Fig. 1.11) at figures similar to the cases of $n = 2$, $l = 0$ (with one radial node) versus $n = 2$, $l = 1$ (with one angular node).

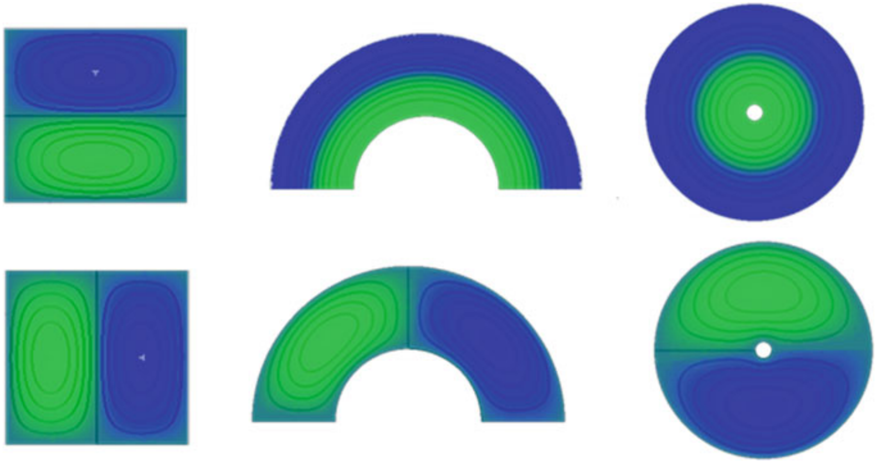


Fig. 1.11 A suggestion of topological equivalence between radial and angular nodes in states with different l quantum numbers belonging to the same n set. A conformal mapping of plane-wave solutions into the spherical ones is qualitatively drawn. The solutions with the same energy for the one-electron atom have the same total in radial plus angular nodes.

1.3.6 The Complete Analytic Formulas of the Atomic Orbitals

One may loosely suggest a certain analogy between the associated Legendre polynomials $P_n^l\ (z)$ that decide the node pattern in the angular part and the associated Laguerre functions contained in the general expression of the radial part for the Schrödinger solutions of the one-electron atom.

The associated Laguerre polynomials are defined as follows:

$$L_n^a(r) = \frac{r^{-a}\exp(r)}{n!}\frac{\mathrm{d}^n}{\mathrm{d}r^n}\left(\exp(-r)r^{n+a}\right), \tag{1.79}$$

this being also a solution ready-made before the age of quantum mechanics, by mathematicians of past centuries, endeavoring to solve equations of different general patterns. Since the second-order equations were the focus of mathematics from the eighteenth and the nineteenth centuries, and the Schrödinger equation belongs to this class, it benefited from the outlining of several prototypic solutions. Aside the already encountered Legendre and Laguerre functions, we point also to the utility of Hermite polynomials (actually, initially due also to Legendre) in the quantum solutions of the harmonic oscillator. All these special functions have also the feature of orthogonality between the congeners of the series (Abramowitz and Stegun 1965), a property of essential importance in conceptual and applied quantum theory. Such polynomials are of great importance in general numerical analysis, able to do exact integration or interpolations of an arbitrary function, working with a finite number of properly selected points along the investigated curve.

Various programming media offer convenient calls of the special functions. For instance, in the current most powerful program for symbolic algebra, named Mathematica$^{\text{TM}}$ (Wolfram Research 2014; Wolfram 2003), the keywords for some of the invoked functions are: LaguerreL, LegendreP, SphericalHarmonicY, and HermiteH.

We complete now the topic of the Schrödinger equation for the hydrogen atom and one-electron congeners by defining the radial function met in the (1.43) formula in terms of Laguerre associate polynomials:

$$R_{n,l}(r) = \left(\frac{2Zr}{na_0}\right)^l \exp\left(-\frac{Zr}{na_0}\right) L_{n-l-1}^{2l+1}\left(\frac{2Zr}{na_0}\right). \tag{1.80}$$

The corresponding normalization factor from (1.43) is:

$$N_{n,l} = \left(\frac{2Z}{na_0}\right)^{3/2} \left(\frac{(n-l-1)!}{2n(n+l)!}\right)^{1/2}. \tag{1.81}$$

In the previous series of equations we worked in atomic units, where the radius of the first Bohr orbit is $a_0 = 1$. If we want to express the radial function in other units, we must introduce the corresponding value, e.g. $a_0 = 0.529177$ Å, if we follow the Ångstrom length unit (1 Å = 10^{-10} m). Introducing the above-defined radial component and its normalization factor in generic formula of orbital functions (1.43) altogether with previously discussed angular functions, one obtains the complete description of the Schrödinger solutions for the atom with one electron and fixed nucleus with Z point charge.

For a touch of concreteness, we present below a Mathematica$^{\text{TM}}$ definition for the general wave functions of the one-electron atom as function of atomic charge (see first square parenthesis), the set of quantum numbers (the second parenthesis), and space variables (the third square parenthesis):

```
psiH[Z_][n_, l_, m_][r_, theta_, phi_] :=
Sqrt[((2 Z/n)^3) (n - l - 1)!/(2 n*(n + l)!)]*
(2 Z*r/n)^l Exp[-Z*r/n] *LaguerreL[n - l - 1, 2 l + 1, 2 Z*r/n]*
SphericalHarmonicY[l, m, theta, phi]
```

This formula, applied in one row (here truncated for editing reasons) can be called with a combination of numeric and symbolic variables, to obtain concrete analytic definitions of the orbitals, or to handle them by plotting, integrating, etc. The above form is assumed in atomic units. For other options, must replace by the corresponding r/a_0 ratio the actual r variable.

For instance, the successive calls:

```
psiH[1][1,0,0][r,θ,φ],psiH[1][2,0,0][r,θ,φ],psiH[1][2,1,-1][r,θ,φ],
psiH[1][2,1,0][r,θ,φ], psiH[1][2,1,1][r,θ,φ]
```

will render the functions belonging to the $n = 1, 2$ orbital sets. Or, the command.

```
Plot[{r*psiH[1][1,0,0][r,0,0],r*psiH[1][2,0,0][r,0,0],
r*psiH[1][2,1,0][r,0,0]},{r,0,10},PlotStyle->{Red, Green, Blue}]
```

is an example for drawing (in respective red, blue, and green colors) the radial dependencies of the $r\psi_{1,0,0}(r, 0, 0)$, $r\psi_{2,0,0}(r,0,0)$, $r\psi_{2,1,0}(r, 0, 0)$ functions, revealing the maxima at a_0 and about $4a_0$ for the $n = 1$ and $n = 2$ cases, respectively. More concretely, these are the maxima for the 1s and 2p curves, since the 2s (with one node) has two extrema at $3 \pm 5^{1/2}$, a fact that can be checked equating in Mathematica^{TM} the vanishing of the first derivative of the $r\psi_{2,1,0}(r, 0, 0)$, by typing

```
Solve[D[r*psiH[1][2,0,0][r,0,0], {r,1}] == 0, {r,1}]
```

It is interesting that for the 1s function, having the maximum of rR radial function at exactly the a_0 value predicted by the Bohr model, the quantum interpretation does not correspond, in fact, to the electron orbiting in the planetary style. In a permissive perspective, we may be tempted to perceive the spherical profile of the wave function with maximum density of probability at the Bohr orbit as the puckering of the trajectory (by positional uncertainty) and tumbling of the 2D Bohr picture into a 3D average. However, the $l = 0$ quantum number tells us that the electron in this state has no freedom to move around the atom, because of the null kinetic momentum. Therefore, the *s*-type orbitals are merely the result of the denied fall of the electron on the nucleus along the radius lines, rather than of equilibration between centrifugal and electrostatic attraction forces, as conceived in the Bohr model.

1.3.7 A Philosophical Divagation

Fantasizing a bit with a sort of counterfactual history (what would have happened if some past events were different from their actual record), we speculate that, in a branch of not materialized history, it was possible to have a quantum description of the atom even in advance of the proper quantum mechanics. Thus, if a genius of multilateral knowledge had seen a connection with the classical image from antiquity (revived by John Dalton in the first decade after 1800), according to which atoms are spheres, it appears that these objects can be described with harmonic functions (available already at the beginning of the nineteenth century). Let us further realize a parallelism between the length of lines (2, 4, 10, 14) from the periodic table (attributed to Mendeleev, in 1869) and the double of the $(2l + 1)$ multiplicities of the Y_{lm} sets. Then, we speculate that an atomic model could have emerged from such a vision. However, the first periodic tables had not yet reached the optimal level of organization of the modern ones (deliberately correlated with the known atomic structure) and maybe the suggested heuristic correlation was not very visible. Actually, Bohr, who headed the quantum theory evolution even beyond the frames of his incipient model, was quite close to such correlative ideas, bringing the clue of spherical symmetry and the possibility of intermediate shells as rationale for poly-electronic atomic spectra (Bohr 1923). It is interesting to contemplate that factors related to spherical symmetry (as the spherical harmonics were described), played a decisive role in the structure of the atom and finally in the properties of the whole series of existing atoms.

We have clarified now the complete wave function structure of the first element, the hydrogen. Even though one cannot exactly solve the quantum equations, we can say that, while accounting for the heavier atoms with many electrons, for the elementary sake of symmetry, the spherical harmonics should be retrieved. It appears that a “song of spheres” is shaping somehow the structure of our material universe.

1.4 Elements of Relativistic Quantum Mechanics

1.4.1 *The Electronic Spin, the Missing Link Between Atomic Shell Scheme and Chemical Systematics from the Periodic Table of Elements*

The relativistic quantum theory appeared in 1928, due to Paul Adrien Maurice Dirac (1902–84), soon after Heisenberg’s matrix mechanics (1925) and Schrödinger’s wave equation (1926). Given the vogue of Einstein’s restricted and generalized relativity theories (in 1905 and 1915), a quantum version was a must (a quest still continuing nowadays). Such a challenge was not just a matter of pride and honor, but a necessary completion in knowing the true nature of the atomic structure. The major advance of the relativistic quantum theory consisted not only in a quantitative correction to the energy scheme, which is quite necessary for heavy atoms (where the expectation values for the electron speed on lower orbits reach significant fractions from the light speed) but in giving the physical fundaments for new quantum numbers.

Wolfgang Pauli (1900–58) pointed out the need for a supplementary quantum number in 1924, by the analysis of complex spectra (Pauli 1924). The atomic levels of hydrogen show, experimentally, a finer structure than predicted by the wave mechanics and undergo further splitting in a magnetic field. The helium atom could be guessed as containing two electrons sharing the same hydrogen-type orbit, but it was not clear why the heavier atoms do not accommodate all the electrons on the same lower state. Such puzzles were solved with Pauli's exclusion principle adding a new double-valued quantum number (Pauli 1925), now known as the spin of the electron (s_z). This postulate says that the atom is not allowed to have electrons with a repeated set of quantum numbers (n, l, m from Schrödinger's equation, and the newly added s_z). If those resulting from the solution of space-coordinate based equations are coincident, the further one acts as seemingly allowing the coupling of electrons in pairs on the same (n, l, m) orbital, by taking two different indices (whose non-coincidence decides different quantum sets).

As he recalls in his Nobel lecture (awarded for the exclusion principle and related merits) (Pauli 1964), there were serious efforts in the frame of what we call now "old quantum mechanics" to figure a relationship between the atom structure and the periodic table. Rydberg observed the correlation between the lengths of periodic table rows, 2, 8, 18, and the $2n^2$ count. Like Lewis from another perspective, Sommerfeld was speculating about the number 8 as "magic configuration", by the electron arrangement in the corners of a cube. Bohr came up with ideas on a 3D atom (Bohr 1923) that implied quantum numbers related with the degeneracy and angular momentum, going conceptually (though not quantitatively and analytically) quite close to the complete picture, as resulted later from Schrödinger's solution.

The idea of electronic spin was proposed initially by a less famous physicist, Ralph Kronig (1904–95), of German origin, who received his academic degrees in the United States. He described his image of a rotating electron generating its own magnetic field, with two orientations, in some short encounters with Pauli (and in subsequent letters). Pauli initially mocked Kronig about such a classical mechanics flavored idea, a fact that hindered him from publishing or disseminating his point. Fortunately, Kronig was not bitter toward Pauli, and they remained friends (Pauli calling Kronig as assistant during his professorship tenure in Zürich, in 1928). Shortly after Kronig's and Pauli's pre-relativistic ideas about the electronic spin, the young Dutch scientists Uhlenbeck and Goudsmit (1925) cemented in 1925 the concept of a quantum number with $s = 1/2$ value and two $s_z = \pm 1/2$ projections, interpreting the experiments of Gerlach and Stern (1922). These were using silver atoms, not free electrons, but it was clear that the behavior was intrinsic to the electron itself. Later tests on electrons confirmed this fact (Batelaan et al. 1997). The idea of the new quantum number, the spin, was spinning around the community of quantum scientists for quite a while, but it received full theoretical support with Dirac's relativistic equation.

Before turning to the relativistic approach, an illustration of the relationship between the periodic table and the scheme of the electrons filling the atomic shells is given in Fig. 1.12. The idea is that the orbitals are used to accommodate

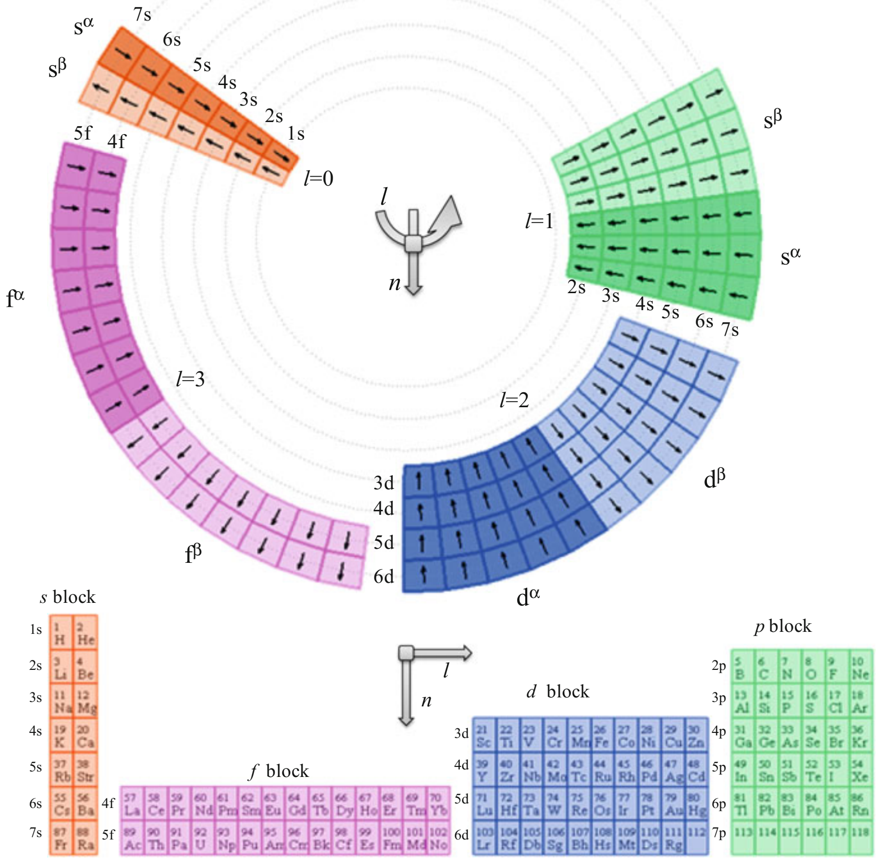


Fig. 1.12 The scheme of the periodic table and its relationship with the ordering of the electron placement in the orbital shells of the atoms. The rows are assimilated to the spin–orbitals sets for given l quantum number. For a certain atom, the position in the periodic table indicates the shells where the "last" electron is placed. The cells with smaller indices (upper and at the left) indicate orbitals already completed. The *aufbau* ordering is obtained reading the cells of the periodic table from left to the right and then from up to down, until the targeted element is reached. Considering Hund's rule of maximal spin multiplicity, the first halves of the rows are conventionally made of α spin–orbitals ($s_z = +1/2$) while the second parts correspond to the β spin–orbitals ($s_z = -1/2$).

electrons. The filling of symmetry-equivalent orbital components belonging to a given quantum number l gives rise to an electronic shell. The spin quantum number, with its two projections, doubles the occupation capacity of a shell, from the $2l + 1$ orbital multiplicity to $4l + 2$. Spin–orbital functions are defined by coupling the orbital denominations with the spin projection. The two orientations of the spin are labeled α and β, corresponding to the +1/2 and −1/2 projections. The spin-up versus spin-down and figurative representation with arrows having such orientations is also used as customary labeling. One may understand the fractional quantum s number as necessary to get the doublet multiplicity when applying the 2s + 1 formula, in analogy to the $2l + 1$ count.

The occupation scheme for most atoms can be obtained with a simple algorithm by reading the periodic table (see Fig. 1.12). Taking the lines from the left to right, and advancing progressively to the next rows, from up to down, exactly like the usual reading of a page, one finds the approximate ordering of orbital energies. The orbitals are occupied in a scheme similar to the successive laying of bricks first along horizontal lines, then from lower to higher potential energy. This algorithm, called "*aufbau*", the German word for building, or, more specifically, for growing a brick wall, is kept in the quantum chemical lexicon in honor of the German pioneers (e.g. Hund) who figured these regularities. In the convention of the periodic table, the energy of orbitals grows from up to down, so that with respect of vertical, the bricks are placed actually in reverse order. A better suggestion is obtained by bending the periodic tables to match the ideas of orbits, the outer ones having smaller absolute values of negative energy (see Fig. 1.12).

With the isomorphism between shell structure and periodic table established, we can find, in a certain approximation, how the spin–orbitals related with the cells in the periodic table are occupied in the ground-state of a given atom. Since in the poly-electronic atom the orbitals do not hold the same properties as in the hydrogen scheme, the ordering is different from those driven by the n quantum index, especially for the orbitals with higher l quantum numbers. Thus, the 3d orbitals are not equal in energy with the 3s and 3p shell, being interlaced between the 4s and 4p ones. A similar shift occurs for the 4d and 5d. The 4f orbitals are more displaced in comparison to a hydrogen-type scheme, being placed above the 5s, 4d, and 5p shells. Thus, the structure of the periodic table is a mnemonic for the effective orbital ordering in the complex atom.

Thus, the "periodic table" of orbitals, starting from first position is read as: $1s^{\alpha}$, $1s^{\beta}$, $2s^{\alpha}$, $2s^{\beta}$, $3 \times (2p^{\alpha})$, $3 \times (2p^{\beta})$, $3s^{\alpha}$, $3s^{\beta}$, $3 \times (3p^{\alpha})$, $3 \times (2p^{\beta})$, $4s^{\alpha}$, $4s^{\beta}$, $5 \times (3d^{\alpha})$, $5 \times (3d^{\beta})$, etc. However, there are several reversions from the simple scheme, due to intrinsic complexities induced by the so-called exchange effects, or by the interference of relativity consequences. For instance, the configuration of the neutral vanadium atom can be read as having the 1s, 2s2p, 3s3p shells completed in the same manner as the previous noble gas, the argon, so that one may ascribe as $[Ar]4s^2 3d^3$ its atomic ground structure, the three electrons in the d shell being understood as spin up: $3d^{3\alpha}$. The structure of the next atom, chromium, is not ending with a $3d^{4\alpha}$ configuration, because the exchange effects are leading to a specific preference for the half-completed shell, $3d^{5\alpha}$, so that the chromium has the particular $[Ar]4s^1 3d^5$ configuration. A similar situation occurs at the end of the 3d series, the copper having $[Ar]4s^1 3d^{10}$ instead of simplistically predicted $[Ar]4s^2 3d^9$. The situation occurs also in the positions preceding half- or full- completion of 4d and 5d shells, even with more inversions from the regular completion, for heavy transition metal elements. Another irregular step occurs at the border with lanthanides and actinides. For instance, according to the periodic table reading algorithm, the lanthanum should have the [Xe]$6s^2 4f^1$ configuration, showing instead [Xe]$6s^2 5d^1$. The next lanthanide element, cerium, shows [Xe]$6s^2 4f^1 5d^1$, while the simple mnemonics gives [Xe]$6s^2 4f^2$. The next elements show a regular configuration [Xe]$6s^2 4f^n$ with $n = 3$–7, 9–14, except the central element, gadolinium, that adopts a [Xe]$6s^2 4f^7 5d^1$ state, for the sake of stabilizing features of the half-filled shell. The lutetium, usually considered as a lanthanide, starts filling the 5d orbitals, having a closed 4f shell [Xe]$6s^2 4f^{14} 5d^1$, so that it is included in a d-block in the actual scheme of the periodic table. In common prints, the lanthanides and actinides are outlined as footnotes, showing only the inset between the s and d blocks at sixth and seventh rows. If both La and Lu are considered lanthanides, their row will count 15 cells, while the capacity of the f shell is limited to 14, being formally necessary to move one of them to the d-block. Otherwise, since the chemistry of lanthanides and actinides is merely based on ionized atoms, where the ns and $(n - 1)$d electrons are stripped, the properties are due to the $(n - 2)$f shells (with specific $n = 6$, 7 quantum numbers).

Thus, the orbitals are used as building blocks for the atom with many electrons. Qualitatively, electrons are housed in different spin–orbitals, which cannot contain more than one electron. Or, in other words, one orbital contains no more than two electrons that are then of opposite spin. In this way, since one spin–orbital is characterized, in atom, by a set of four quantum numbers, n (principal), l (orbital), m (magnetic), and s_z (spin), the Pauli exclusion principle is satisfied, having no repeated set of indices. Quantitatively, for tackling the quantum Hamiltonian of the poly-electronic atom, some more technical details have to be worked. In a following chapter, the trial wave functions will be presented as determinants, that have the property of incorporating the exclusion principle (two identical functions imply equal lines and the quenching of the determinant) fulfilling also the idea of indiscernible electrons (implying all possible permutations in the design). The relativistic treatments bring a full justification for the spin degree of freedom and also a new effect, its coupling with the orbital momentum, giving rise to another quantum number j. The j quantum number is a reorganization of all the combinations of projection indices possible for a given l and s sets, the spin–orbit coupling replacing the use of independent spin and orbital quantization schemes.

1.4.2 First Principles of Relativistic Quantum Mechanics: Klein-Gordon and Dirac Equations

The essence of the relativistic approach is regarding the product of time with light speed, factored with the imaginary unit, ict, as a new space coordinate. The special relativity results as rotation in this four-dimensional space-time frame, similar to Lorentz transformations in electromagnetism. Whether in relativity the space and time are on an equal footing, in Schrödinger's equation the space coordinates are entered as second-order derivatives, and the time as first derivative (in explicit time-dependent formulation). Attempting to bring both space and time derivatives at the same ranking, the Klein-Gordon equation results in settling them in the second order (Klein 1926; Gordon 1926). For a free particle with static mass m_0, this equation results starting from the $p^2c^2 + m_0c^2 = E^2$ identity, introducing the p as the differential operator from Eq. (1.9) and energy as time derivative $E\Psi = \mathrm{i}\hbar \mathrm{d}\ \Psi/\mathrm{d}t$ in analogy with the Schrödinger time-dependent form (1.7). It results:

$$\frac{\hbar^2}{m_0}\nabla^2\Psi - \frac{\hbar^2}{m_0c^2}\frac{\partial^2\Psi}{\partial t^2} = m_0c^2\Psi. \tag{1.82}$$

However, this does not account well for the hydrogen atom, being, in fact, valid for a spinless particle. Dirac showed his brilliant imaginativeness and mathematical prowess, succeeding in bringing both the space and time derivatives to the first order (Dirac 1928). The Pauli equations were presented as follows:

$$\frac{\hbar}{\mathrm{i}}\left(\alpha_x\frac{\partial\Psi}{\partial x} + \alpha_y\frac{\partial\Psi}{\partial y} + \alpha_z\frac{\partial\Psi}{\partial z} + \frac{\partial\Psi}{c\partial t}\right) + \beta m_0c\Psi = 0, \tag{1.83}$$

imposing the α and β factors in such a manner that the product of the left side row with its complex conjugate renders the Klein-Gordon equation. In order to achieve this property, α and β must be at least 4 × 4 matrices, presented as tableaus of 2 × 2 blocks:

$$\alpha_\xi = \begin{pmatrix} 0_{2\times2} & \sigma_\xi \\ \sigma_\xi & 0_{2\times2} \end{pmatrix}, \quad \beta = \begin{pmatrix} 1_{2\times2} & 0_{2\times2} \\ 0_{2\times2} & -1_{2\times2} \end{pmatrix}, \tag{1.84}$$

where the index ξ denotes the x, y, and z coordinates, $0_{2\times2}$ is a null matrix of dimension 2, and $1_{2\times2}$ is the identity matrix of the same size.

The σ_ξ are the so-called Pauli matrices:

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}; \quad \sigma_y = \begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix}; \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}; \quad 1_{2\times2} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \tag{1.85}$$

the $1_{2\times2}$ identity matrix being also made explicit.

The Pauli matrices show anti-commutation relationships similar to those initially remarked for kinetic momentum:

$$\left[\sigma_x, \sigma_y\right] = 2\mathrm{i}\sigma_z; \quad \left[\sigma_y, \sigma_z\right] = 2\mathrm{i}\sigma_x; \quad \left[\sigma_z, \sigma_x\right] = 2\mathrm{i}\sigma_y, \tag{1.86}$$

forming the basis for the components of the spin quantum number:

$$\hat{s}_{\xi} = \frac{\hbar}{2}\sigma_{\xi}, \tag{1.87}$$

with the index ξ representing the x, y, and z. The factor ($\hbar/2$) can be briefly explained as useful to bring the commutation formulas parallel to those shown in Eq. (1.26):

$$\left[\hat{s}_{\xi}, \hat{s}_{\zeta}\right] = -\frac{\hbar}{\mathrm{i}}\hat{s}_{\tau}, \tag{1.88}$$

the subscript indices running cyclic permutations of the xyz triad. Also the

$$\left[\hat{s}^2, \hat{s}_z\right] = 0 \tag{1.89}$$

relationship is held.

Due to the four-fold pattern, the Dirac equation apparently yields more solutions than needed. Two of them are welcomed as the expected new quantum number called the electron spin. Another couple represents the so-called positronic states, proposing mirror solutions for an anti-particle of the electron, not yet discovered at the launch of Dirac's equations. However, the positron was discovered a few years after, in 1930, as a coronation of the absolute power of pure and strong theory. Dirac was not much interested in the metaphysics behind the physics but held a strong belief that the ultimate realities are hidden in equations and that the beauty of mathematical constructs is a strong criterion for validating a model, even prior to the comparison with experiment.

The formula (1.83) may be rearranged such that it connects with the Hamiltonian for the four-component Dirac equation:

$$\widehat{H}\Psi = \frac{\hbar c}{\mathrm{i}}\left(\alpha_x\frac{\partial}{\partial x} + \alpha_y\frac{\partial}{\partial y} + \alpha_z\frac{\partial}{\partial z}\right) + \beta m_0 c^2 = -\frac{\hbar}{\mathrm{i}}\frac{\partial\Psi}{\partial t} = E\Psi, \tag{1.90}$$

the end-notation suggesting the case of time-independence. The summation of the three elements from parenthesis can be condensed as $\alpha \cdot \nabla$ scalar product (with matrices as objects). Recall that the above equation is still for a free particle (since no field term was introduced).

1.4.3 The Quantum Numbers of Dirac Relativistic Equations

Since for the Schrödinger equation case the Hamiltonian commutes with the kinetic momentum components, one may inquire about this property for Dirac formalism. The following check:

$$\left[\widehat{H},\hat{l}_z\right] = -\hbar^2 c\left[\alpha\cdot\nabla,\left(x\frac{\partial}{\partial y}-y\frac{\partial}{\partial x}\right)\right] = -\hbar^2 c\left(\alpha_x\frac{\partial}{\partial y}-\alpha_y\frac{\partial}{\partial x}\right), \tag{1.91}$$

suggests that the kinetic momentum projection has lost the quality of being a quantum number generator. Searching for something else resembling the kinetic moment projection, one may guess that a 4 × 4 matrix with σ_z as diagonal blocks will suggest the pattern of opposite spin projections for electronic and positronic states. Proposing the form from the first equality:

$$\widehat{\Sigma}_z = \frac{\hbar}{2}\begin{pmatrix}\sigma_z & 0\\ 0 & \sigma_z\end{pmatrix} = \frac{\hbar}{2\mathrm{i}}\alpha_x\alpha_y = \frac{\hbar}{4\mathrm{i}}\left[\alpha_x,\alpha_y\right], \tag{1.92}$$

and checking the commutation:

$$\left[\widehat{H},\widehat{\Sigma}_z\right] = -\frac{\hbar^2 c}{2}\left[\alpha\cdot\nabla,\widehat{\Sigma}_z\right] = \hbar^2 c\left(\alpha_x\frac{\partial}{\partial y}-\alpha_y\frac{\partial}{\partial x}\right), \tag{1.93}$$

one observes a result opposite in sign, compared to the (1.91) case.

Therefore, composing the following operator

$$\hat{j}_z = \hat{l}_z + \widehat{\Sigma}_z, \tag{1.94}$$

one reaches the aimed null commutation:

$$\left[\widehat{H},\hat{j}_z\right] = 0. \tag{1.95}$$

This z component identified in (1.94) suggests the full operator:

$$\hat{j} = \hat{l} + \widehat{\Sigma}, \tag{1.96}$$

where:

$$\widehat{\Sigma} = \frac{\hbar}{4}\alpha\times\alpha. \tag{1.97}$$

All the components of the $\hat{j}$ operator are commuting with the Hamiltonian. Another formulation of four-component spin matrices is:

$$\widehat{\Sigma}_{\xi} = \frac{\hbar}{2}\begin{pmatrix} \sigma_{\xi} & 0_{2\times 2} \\ 0_{2\times 2} & \sigma_{\xi} \end{pmatrix}, \tag{1.98}$$

with ξ standing as the x, y, and z coordinates.

The conversion of the Dirac operator to polar coordinates looks like "deformation" of the classical transformation of impulse operator from Cartesians, see Eq. (1.14), into the metrics created by the α matrices:

$$\frac{\hbar}{\mathrm{i}}\alpha\cdot\nabla = \frac{\hbar}{\mathrm{i}}\frac{1}{r^2}(\alpha\cdot\vec{r})(\vec{r}\cdot\nabla) - \frac{1}{r}\alpha\cdot(\vec{r}\times\hat{l}) = \frac{\hbar}{\mathrm{i}}\frac{1}{r}(\alpha\cdot\vec{r})\frac{\partial}{\partial r} - \frac{1}{r}\alpha\cdot(\vec{r}\times\hat{l}). \tag{1.99}$$

One may also algebraically check the following identity (Thaller 2002):

$$-\frac{1}{r}\alpha\cdot(\vec{r}\times\hat{l}) = \frac{2\mathrm{i}}{r}(\alpha\cdot\vec{r})(\hat{l}\cdot\widehat{\Sigma}), \tag{1.100}$$

that introduces a scalar product between spin and orbital moments, which leads the spin–orbit coupling effects:

$$\frac{\hbar}{\mathrm{i}}\alpha\cdot\nabla = \frac{\hbar}{\mathrm{i}}\frac{1}{r}(\alpha\cdot\vec{r})\frac{\partial}{\partial r} + \frac{2\mathrm{i}}{r}(\alpha\cdot\vec{r})(\hat{l}\cdot\widehat{\Sigma})) = \frac{\alpha\cdot\vec{r}}{r}\frac{\hbar}{\mathrm{i}}\left(\frac{\partial}{\partial r} - \frac{2}{\hbar}\hat{l}\cdot\widehat{\Sigma}\right). \tag{1.101}$$

We noted here the spin from the four-dimensional relativistic approach by Σ to distinguish it from the two-component form introduced by Pauli matrices.

1.4.4 The Two Quantum Worlds of Dirac Equations: Small and Large Spinor Components

The β matrix shows two solutions: the "normal" ones are in the range of $+m_0c^2$, while the exotic positronic states are with large negative values, $-m_0c^2$. To explain why the electrons do not stay on the huge negative energy states must postulate that these are already completed, forming a world invisible to us. However, when large energies are invested and one electron is expelled from these hidden levels, the emptied place appears as a positron, the particle with the same features as the electron, except the positive charge. The trend of anti-matter to be annihilated by particles of the common world would in fact reflect the imperious need to de-excite the system, consuming one electron from the "real" world (placed around the $+m_0c^2$ level), to fill back the deep sea from the $-m_0c^2$ range. This releases the $2m_0c^2$ energy, corresponding to the erasing of one electron and one positron, both with m_0

masses. Thus, in the relativistic approach we have a huge positive shift of the scale, due to the energy incorporated in the mass. In the atomic units, where we take the electron mass equal to 1, the speed of light has the value of 137.036. Therefore, the positive mass energy for a system made of a single electron is the square of this number, 18,780 Hartree (energy atomic units), sensibly larger than the −0.5 Hartree found for the first Bohr orbit.

Shifting to zero the electronic part (pushing to $-2m_0c^2$ the positronic branch), the four component time-independent Dirac equations can be rewritten in terms of 2 × 2 block matrices:

$$V\psi + c(\sigma \cdot \hat{p})\eta = E\psi, \tag{1.102}$$

$$c(\sigma \cdot \hat{p})\psi + (V - 2m_0c^2)\eta = E\eta, \tag{1.103}$$

where the two-component (ψ and η) wave functions are called spinors, comprising, each, the two degrees of freedom related to the spin quantum number. Since we are not so much interested in the η spinor of the positronic “underground” world, comfortably spaced by the large $-2m_0c^2$ energy amount, we can formally eliminate its explicit intervention. From the second equation of the above set, the spinor related with large negative energy eigenvalues is obtained:

$$\eta = (E - V + 2m_0c^2)^{-1}c(\sigma \cdot \hat{p})\psi. \tag{1.104}$$

Replacing it in the first equation, the elimination of the small component (η) is achieved:

$$\left(c(\sigma \cdot \hat{p})\frac{1}{E - V + 2m_0c^2}c(\sigma \cdot \hat{p}) + V\right)\psi = E\psi, \tag{1.105}$$

the mass term $2m_0c^2$ predominating over the $E - V$ part. For a particle free of potential, one may roughly assume for E the kinetic energy only, approximating the small spinor as follows:

$$\begin{aligned}\eta &\approx \left(\frac{p^2}{2m_0} + 2m_0c^2\right)^{-1} c(\sigma \cdot \hat{p})\psi = \frac{1}{2m_0c}\left(1 + \frac{p^2}{4m_0^2c^2}\right)^{-1}(\sigma \cdot \hat{p})\psi \\ &\approx \frac{1}{2m_0c}\left(1 - \frac{p^2}{4m_0^2c^2}\right)(\sigma \cdot \hat{p})\psi.\end{aligned} \tag{1.106}$$

This truncation includes the effect of renormalization due to the small spinor component. Solving the effective equation based on the large component, the normalization tacitly regards the $\psi^*\psi \to 1$ goal, while it should concern the full four component wave function, $\psi^*\psi + \eta^*\eta \to 1$. Introducing this correction, the equation becomes:

$$V\psi + \frac{(\sigma \cdot \hat{p})^2}{2m_0}\psi - \frac{(\sigma \cdot \hat{p})p^2(\sigma \cdot \hat{p})}{8m_0^3c^2}\psi = E\psi. \tag{1.107}$$

Treating the factor in p^2/c^2 as having numerical (not operator) nature, because of approximate reasoning about the renormalization factor, the equation of the main spinor is:

$$V\psi + \left(1 - \frac{p^2}{4m_0^2c^2}\right)\frac{(\sigma \cdot \hat{p})^2}{2m_0}\psi = E\psi. \tag{1.108}$$

Using a property that can be simply verified, $(\sigma \cdot a)$ $(\sigma \cdot b) = (a{\cdot}b) + \mathrm{i}\sigma \cdot (a \times b)$, the momentum based operator is transformed as follows:

$$(\sigma \cdot \hat{p})^2 = \hat{p}^2 + \mathrm{i}\sigma \cdot (\hat{p} \times \hat{p}). \tag{1.109}$$

1.4.5 Toward the Relativistic Atom: Electromagnetism Instead of Electrostatics

Working in relativity, the electrostatics cannot be separated from magnetism, the full set of Maxwell equations being, in principle, necessary. Aside the electric potential V, it must include the magnetic field B. Since the magnetic component obeys the $\nabla \cdot B = 0$ Maxwell equation, a mathematical trick is to present it as $B = \nabla \times \mathrm{A}$, where A is the so-called vector potential. In this form, the vanishing of the divergence from B will automatically be accomplished, due to the property $\nabla \cdot \nabla \times \mathrm{A} = 0$, valid for any vector. The vector potential A is non-unique, since any arbitrary vector can be added and the above conditions will be fulfilled. One of the conventions able to eliminate the arbitrariness of the A vector potential is by imposing the $\nabla \cdot \mathrm{A} = 0$ condition (so-called Coulomb gauge). In time-independent circumstances, the Maxwell rules imply $\nabla \times B = 0$, i.e. $\nabla \times \nabla \times \mathrm{A} = 0$, expanded to $\nabla^2\mathrm{A} - \nabla(\nabla{\cdot}\mathrm{A}) = 0$, (according to the general $\mathrm{a} \times \mathrm{b} \times \mathrm{c} = \mathrm{b}(\mathrm{a} \cdot \mathrm{c}) - \mathrm{c}(\mathrm{a} \cdot \mathrm{b})$ vector operation). Once the Coulomb gauge is imposed, it results that $\nabla^2\mathrm{A} = 0$. This means that each component of the vector potential follows a Laplace equation, $\nabla^2\mathrm{A}_x = 0$, $\nabla^2\mathrm{A}_y = 0$, and $\nabla^2\mathrm{A}_z = 0$. As discussed in the atomic orbitals topic, there is a large variety of functions satisfying a Laplace format. The monomials x, y, z are trivial cases of Laplace equation solutions. For instance, to describe a homogenous magnetic field B_0 along the z axis one may take $\mathrm{A}_x = -B_0/2$, $\mathrm{A}_y = B_0/2$, and $\mathrm{A}_z = 0$, the curl operation from this giving $B_x = 0$, $B_y = 0$, and $B_z = B_0$. For an arbitrary orientation of the homogenous field, the following choice

$$\mathrm{A} = \frac{1}{2}\vec{B} \times \vec{r} \tag{1.110}$$

is a conventional solution. This methodology implies a gauge dependence upon the choice of space coordinates, which does not impinge upon the magnetic field, but affects subsequent equations. The advantage of the vector potential formalism is the merging of magnetic components with the impulse vector:

$$\hat{p} = \frac{\hbar}{\mathrm{i}}\nabla + e\mathrm{A}, \tag{1.111}$$

the new momentum describing the speed of the charged particle in a magnetic field. In the following we will expand different terms obtained from entering the vector field in the Dirac equations and subsequent approximations. Introducing the generalized momentum in the first term of the right side member of Eq. (1.109), one obtains:

$$\begin{aligned}(\hat{p}\cdot\hat{p})\psi &= (-\mathrm{i}\hbar\nabla + e\mathrm{A})\cdot(-\mathrm{i}\hbar\nabla + e\mathrm{A})\psi \\ &= -\hbar^2(\nabla^2)\psi - \mathrm{i}e\hbar\nabla\cdot(\mathrm{A}\psi) - \mathrm{i}e\hbar\mathrm{A}\cdot(\nabla\psi) + e^2\mathrm{A}^2\psi.\end{aligned} \tag{1.112}$$

The first element in the last equality is the kinetic energy, in Schrödinger-like form. The term $e^2\mathrm{A}^2$ is a small effect that leads to the diamagnetism of matter. The middle terms are expanded into:

$$-\mathrm{i}e\hbar\nabla\cdot(\mathrm{A}\psi) - \mathrm{i}e\hbar\mathrm{A}\cdot(\nabla\psi) = -\mathrm{i}e\hbar(\nabla\cdot\mathrm{A})\psi - 2\mathrm{i}e\hbar\mathrm{A}\cdot(\nabla\psi). \tag{1.113}$$

The first term after the equality sign disappears by the convened Coulomb gauge. Entering the back transformation of the vector potential to magnetic field,

$$\begin{aligned}-2\mathrm{i}e\hbar\mathrm{A}\cdot(\nabla\psi) &= -\mathrm{i}e\hbar(\vec{B}\times\vec{r})\cdot(\nabla\psi) = -\mathrm{i}e\hbar(\vec{r}\times\nabla\psi)\vec{B} \\ &= -\mathrm{i}e\hbar(\vec{r}\times\nabla)\cdot\vec{B}\psi = e(\hat{l}\cdot\vec{B})\psi,\end{aligned} \tag{1.114}$$

one finds a term describing the interaction of the orbital momentum with the external magnetic field.

The second term in the right side of (1.109) can be expanded in first instance as:

$$\begin{aligned}(\hat{p}\times\hat{p})\psi &= (-\mathrm{i}\hbar\nabla + e\mathrm{A})\times(-\mathrm{i}\hbar\nabla + e\mathrm{A})\psi \\ &= -\hbar^2(\nabla\times\nabla)\psi - \mathrm{i}e\hbar\nabla\times(\mathrm{A}\psi) - \mathrm{i}e\hbar\mathrm{A}\times(\nabla\psi) + e^2\mathrm{A}\times\mathrm{A}\psi.\end{aligned} \tag{1.115}$$

The $\nabla \times \nabla$ and $\mathrm{A} \times \mathrm{A}$ terms are disappearing due to basic vector product properties (visible if we rely on the determinant formulation of the vector product, where two lines become equal), remaining with

$$(\hat{p} \times \hat{p})\psi = -\mathrm{i}e\hbar(\nabla \times \mathrm{A})\psi - \mathrm{i}e\hbar(\nabla\psi) \times \mathrm{A} - \mathrm{i}e\hbar\mathrm{A} \times (\nabla\psi). \tag{1.116}$$

The first two elements of expansion appeared because the derivative Nabla operator acts separately on the elements of the $\mathrm{A}\psi$ product. Because of the $a \times b = -b \times a$ property, the last two terms are mutually cancelling, ending with:

$$\mathrm{i}\sigma(\hat{p} \times \hat{p})\psi = \sigma e\hbar(\nabla \times \mathrm{A})\psi = e\hbar\mathrm{i}\sigma B\psi = 2e\hat{s} \cdot B. \tag{1.117}$$

Here, the conventional definition of magnetic field B as curl from the vector potential was introduced, converting the term to a spin operator in scalar product with the magnetic field.

Returning to the complete equation for the large component (the ψ spinor), we must note that the numerator should be treated as an operator, the derivative contained in the left side impulse factor acting over the potential V:

$$\begin{aligned}(c\sigma \cdot \hat{p})&\frac{1}{E - V + 2m_0c^2}(c\sigma \cdot \hat{p}) \\ &= \frac{c^2}{E - V + 2m_0c^2}(\sigma \cdot \hat{p})^2 + c^2\left(\frac{1}{E - V + 2m_0c^2}\right)^2(-\mathrm{i}\hbar\sigma \cdot \nabla V)(\sigma \cdot \hat{p}).\end{aligned} \tag{1.118}$$

The first term in the right side member corresponds to the trivial operation over the scalar, where both the derivative and vector field potential components of the generalized impulse behave in simple multiplicative manner. The second term catches the action of the derivative part of the impulse over the V from the denominator. The operator of first term is worked as described previously in (1.112). The second operator is detailed as follows:

$$-\mathrm{i}\hbar(\sigma \cdot \nabla V)(\sigma \cdot \hat{p}) = -\mathrm{i}\hbar(\nabla V \cdot \hat{p}) + \hbar\sigma \cdot (\nabla V \times \hat{p}). \tag{1.119}$$

From all the possible terms appearing when the generalized p operator is detailed, we will be interested in the part due to genuine impulse operators, since the main part, due to action of the external magnetic field, was approximated in the previous step. Then, without the A components, we remain with the $-\mathrm{i}\hbar^2\sigma \cdot (\nabla V \times \nabla)$ operator. Assuming an isotropic case, valid for spherical or plane-wave based problems, the gradient is expressed as below:

$$-\mathrm{i}\hbar^2\sigma \cdot (\nabla V \times \nabla) = \hbar\frac{1}{r}\frac{\partial V}{\partial r}\sigma \cdot \left(\vec{r} \times \frac{\hbar}{\mathrm{i}}\nabla\right) = \hbar\frac{1}{r}\frac{\partial V}{\partial r}\sigma \cdot \hat{l} = \frac{2}{r}\frac{\partial V}{\partial r}\hat{s} \cdot \hat{l}. \tag{1.120}$$

The spin operator (see Eq. 1.87) was introduced instead of Pauli matrices. Without a complete algebraic expansion, one may guess that the above term brings the spin–orbit coupling.

1.4.6 Concluding the Types of Relativistic Hamiltonian Terms: Zeeman, Spin–Orbit, Mass-Correction, Darwin, Breit, Breit-Pauli

Picking from the previous discussion the terms selected from the expansion of the operators appearing in the attempt to eliminate the small components of the Dirac equation, the Hamiltonian is given as the following summation:

$$\widehat{H} = \widehat{T} + V + \widehat{H}_{\text{Zeeman}} + \widehat{H}_{\text{SO}} + \widehat{H}_{\text{rmc}} + \widehat{H}_{\text{Darwin}}, \tag{1.121}$$

where the first two terms are the classical kinetic energy and the multiplicative potential. The Zeeman Hamiltonian expresses the interaction of the orbital and spin moments with an external magnetic field:

$$\widehat{H}_{\text{Zeeman}} = \frac{e}{2m_0}\left(\hat{l}\cdot\vec{B} + 2\hat{s}\cdot B\right) = -\frac{\mu_B}{\hbar}\left(g_l\hat{l}\cdot\vec{B} + g_{\text{e}}\hat{s}\cdot B\right), \tag{1.122}$$

while spin–orbit term, the mutual coupling of these moments:

$$\widehat{H}_{\text{SO}} = -\frac{1}{2m_0^2c^2}\left(\frac{1}{r}\frac{\partial V}{\partial r}\right)\left(\hat{s}\cdot\hat{l}\right). \tag{1.123}$$

Note that the negative in the definition of the Zeeman Hamiltonian sign appeared from making explicit the electron charge when the Bohr magneton, μ_{B} (see definition 1.4), is brought as factor. The gyromagnetic factors were introduced. According to the previous derivation, these are $g_l = 1$ for the orbital part and $g_e = 2$ for the electronic spin. The last one, receiving higher order relativistic increments is, more precisely, $g_{\text{e}} = 2.0023$. The relativistic mass correction

$$\widehat{H}_{\text{rmc}} = -\frac{p^2}{8m_0^3c^2}, \tag{1.124}$$

and the Darwin term

$$\widehat{H}_{\text{Darwin}} = \frac{\text{i}\hbar(\nabla V\cdot\hat{p})}{4m_0^2c^2}, \tag{1.125}$$

are important when the total energy of the relativistic system is concerned, while the Zeeman and spin–orbit are needed for the split of the spectral terms, in comparison to the Schrödinger quantization. In spectral or magnetic problems, where the differences between energy terms are concerned, the mass and Darwin increments can be ignored (as common shifts in all the states).

The above dichotomy of the Hamiltonian resulted in perturbation theory manner, assuming the predominance of the $2m_0c^2$ over the $E - V$. To make things more flexible, one includes the potential into the denominator of the expansion factor: $E/(2m_0c^2 - V)$.

Then the operator from (1.105) is expanded into:

$$\frac{1}{E - V + 2m_0c^2} = \frac{1}{2m_0c^2 - V} - \frac{E}{(2m_0c^2 - V)^2} + \cdots. \tag{1.126}$$

Confining to the first (zero order) term, the so-called ZORA (Zero Order Regular Approximation) (see van Lenthe et al. 1993; van Leeuwen et al. 1994) is obtained:

$$E_{\mathrm{ZORA}} = \left\langle \psi_{\mathrm{ZORA}} \middle| T + V + (c\sigma \cdot \hat{p}) \frac{1}{2m_0c^2 - V} (c\sigma \cdot \hat{p}) \middle| \psi_{\mathrm{ZORA}} \right\rangle, \tag{1.127}$$

where the potential V is the subject of a self-consistent approach. Since the right side operators act over the potential part in the manner outlined in previous discussion, the spin–orbit results naturally as output of the ZORA procedures (Faas et al. 2000).

We tacitly referred until now to the one-electron case. The main part of relativistic effects is of one-electron nature, the poly-electronic problems implying a summation of the kinetic Dirac operators for each electron. The potential operator must be amended for reasons of quantum electrodynamics, to be distinguished from the classic Coulomb interaction, which acts as if it were instantaneous in time. Since no information can be propagated faster than the light speed, an adjusting ingredient must be added to the $1/\mathrm{r}_{12}$ Coulomb interaction of two electrons, labeled 1 and 2, taking the so-called Breit Hamiltonian (Breit 1932), without detailing the proof:

$$\widehat{H}_{\mathrm{Breit}}(1,2) = -\frac{1}{2r_{12}} \left(\alpha(1) \cdot \alpha(2) + \frac{(\alpha(1) \cdot r_{12})\,(\alpha(2) \cdot r_{12})}{r_{12}^2} \right). \tag{1.128}$$

Here a represent the sets of Dirac matrices for the two electrons, 1 and 2, the equation being therefore devised for the four-component formalism. The symbol of scalar product should be understood as summation over the three space components, e.g. $\alpha \cdot \alpha = \alpha_x \cdot \alpha_x + \alpha_y \cdot \alpha_y + \alpha_z \cdot \alpha_z$. Introducing this in the approximations related to the elimination of small spinor, it leads to various terms, such as a two-electron contribution to the spin–orbit parameters (sometimes called Breit-Pauli Hamiltonian) and some more exotic ingredients, such as spin–spin relativistic effects, orbit–orbit or spin-other-orbit couplings. However, the main relativistic contributions are still related with the one-electron terms, some effects such as the spin–orbit coupling in complex atoms being ascribed in this effective manner.

According to the discussion of the Dirac equation, it seems that the spin is a relativistic consequence, a fact that also may induce the subjective satisfaction that the other pillar of modern physics, relativity, plays an essential role in quantum mechanics. On the other hand, some interpretations are saying that it may arise in a non-relativistic frame, if we simply replace the p^2 kinetic part by $(\sigma p)^2$ in the Schrödinger equation (Jensen 2007). In this case, the Zeeman interaction can be obtained, but not yet the spin–orbit part. At the same time, the non-relativistic spin was proposed by Pauli by reasons of conceiving the completion with electrons of the atomic shells. Equally, the experimental finding of the Zeeman effect demanded the new quantum number. The split of the spectral lines in the magnetic field was observed much in advance of the old or new quantum mechanics era (Zeeman 1897), a part of it being understandable in term of the electrodynamics governed by Lorentz or Maxwell formulas. The Bohr model allowed conceiving the orbits as coils of electric current, suggesting then the orbital momentum as a source of atomic inner magnetic fields that can interact with the outer ones. However, the spectral details were not understandable in this way. Named initially the anomalous field effect, these were transitions involving the spin of electrons. Although the spin can be introduced in a non-relativistic manner, in the style of the Pauli postulate, it nevertheless results in full algebraic splendor in the more sophisticated paradigm staying at the ground of Dirac derivation. Besides, the full consequences of the spin will be not complete without the spin–orbit part, which definitely comes from the coupling of the large spinor with the small component, so that the spin can be vindicated as a messenger from a deeper world of relativity and anti-particle underground sea. Relativistic quantum chemistry is nowadays a well-established field, in theoretical backgrounds and applications (Reiher and Wolf 2009).

1.4.7 The Spin–Orbit Coupling: A Term to Remember

The most important way in which relativity is reflected in the optic and magnetic properties of atoms and molecules is the spin–orbit coupling, occurring inside a spectral term with non-vanishing orbital and spin quantum numbers. The preponderant one-electron nature of this effect makes possible to regard it as included in the orbital part. Then, if consider that the radial part of an orbital set characterized by the n and l quantum numbers is integrated to the factor $\zeta_{n,l}$:

$$\zeta_{n,l} = -\left\langle R_{n,l}(r) \middle| \frac{1}{2m_0^2c^2}\left(\frac{1}{r}\frac{\partial V}{\partial r}\right) \middle| R_{n,l}(r) \right\rangle, \tag{1.129}$$

one deals, in continuation, with the phenomenological form:

$$\widehat{H}_{\mathrm{SO}} = \zeta_{n,l}\hat{l} \cdot \hat{s}, \tag{1.130}$$

targeted to describe new orbital quantum numbers and energies. Since the gradient of the potential at the nucleus is negative, the integral in (1.129) gets positive. In the general algebra of the moments, with particularization on the l and s couple, the newly composed quantum number, j in our case, takes values between the $|l - s|$ and $l + s$ limits. Actually, we are treating now orbitals, objects of a single electron function, having then $s = 1/2$. Then, the $2l + 1$ degeneracy of the Schrödinger equation, enhanced formally to the $4l + 2$ doubling by the two $s_z = \pm 1/2$ spin projections, goes to description by the new quantum number $j = l + 1/2$ and $j = l - 1/2$, which corresponds to the split in two subsets with $2j + 1$ multiplicities, respectively $2l + 2$ and $2l$. The gap between the relativistic atomic orbitals can be calculated easily by a trick that can transform the above scalar product of operators in numbers, expanding the square of the $\hat{j}$ operator:

$$\hat{j}^2 = (\hat{l} + \hat{s})^2 = \hat{l}^2 + \hat{s}^2 + 2\hat{l} \cdot \hat{s}. \tag{1.131}$$

We know that the square of a momentum operator, e.g. $\hat{j}^2$, must yield an eigenvalue like $j(j + 1)$, a similar regularity acting in the l and s cases. This means that replacing the scalar product extracted from (1.131) into (1.130), one obtains a closed formula for the spin–orbit gap, inside a shell described the l quantum number (and assigned to an n main index):

$$E_{n,j(l)} = E_{n,l} + \frac{1}{2}\zeta_{n,l}(j(j+1) - l(l+1) - 3/4). \tag{1.132}$$

Here it is suggested that the gap occurs on a previously non-relativistic orbital level and, inside the parenthesis the $s(s + 1)$ term, was already particularized for $s = 1/2$. More concretely, given the positive value of the spin–orbit coupling factor $\zeta_{n,l}$, the relativistic orbitals with $j = l - 1/2$ quantum number and $2l$ multiplicity are lower, with the relative energy $(-1/2)\zeta_{n,l}$ $(l + 1)$, while the $j = l + 1/2$ of $2l + 2$ degenerate levels are placed at $(1/2)\zeta_{n,l}l$. The respective orbitals are labeled $[l]_{l\text{-}1/2}$ and $[l]_{l+1/2}$, where $[l]$ stands for the literal label of the shell. Thus, from p shell one obtains the $\mathrm{p}_{1/2}$ and $\mathrm{p}_{3/2}$ relativistic companions, from d the $\mathrm{d}_{3/2}$ and $\mathrm{d}_{5/2}$, and from f the $\mathrm{f}_{5/2}$ and $\mathrm{f}_{7/2}$ couple. Obviously, for s orbitals there is no spin–orbit spacing.

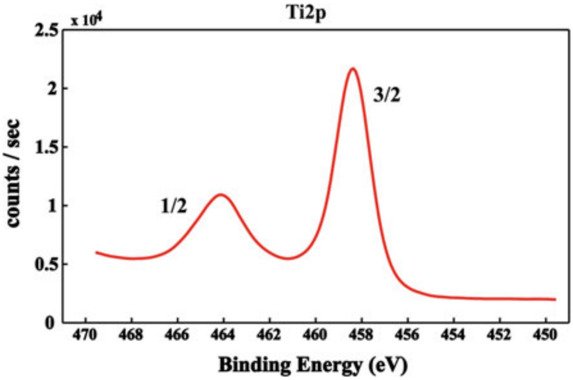


Fig. 1.13 The photoelectron 2p doublet of Ti in TiO_2 XPS spectrum. The spin–orbit parameter, which is assigned as the energy difference between the two split components (2p3/2; 2p1/2) exhibits a value of 5.54 eV. The same parameter for the elemental (metallic) Ti shows a value of 6.17 eV. Data, by courtesy of Petre Osiceanu from the Institute of Physical Chemistry, Bucharest, recorded on PHI-Quantera SXM (ULVAC-PHI Co).

The magnitude of the relativistic orbital gap increases for the heavier atoms and for the orbitals from the core, placed closer to the nucleus, sensible to the gradient expressed in the definition of the coupling parameter as radial integral. Figure 1.13 illustrates X-ray photoelectron spectroscopy (XPS), reflecting the relativistic orbital energies resulting from the spin–orbit spacing of the core 2p orbital of titanium atom in the TiO_2 oxide lattice. The areas of the peaks are proportional with the $2j + 1$ multiplicities of the components (respectively, 2 and 4 for the $2p_{1/2}$ and $2p_{3/2}$ couple). The abscissa represents the energy for extracting one electron from the $2p_{1/2}$ and $2p_{3/2}$ relativistic shells, its negative being assignable to the orbital energies.

The spin–orbit coupling is of major importance in the magnetic properties of the atoms and molecules. It gives the mechanism of a special property, the magnetic anisotropy, which is of large interest for the academic focus of molecular magnetism, as well as in applied current and future material sciences.

We clarified the status of relativistic orbitals, as functions of one electron, but paving the way for many-electron description, we will need to take general matrix elements in a given orbital (non-relativistic) basis from the spin–orbit operator. For such technical respects, we must refer to the Hamiltonian handling of the spin–orbit. It is useful to recall first the orbital momentum operators, $\hat{l}_x$, $\hat{l}_y$ and $\hat{l}_z$, realizing the following combinations:

$$\hat{l}_+ = \hat{l}_x + \mathrm{i}\hat{l}_y, \tag{1.133}$$

$$\hat{l}_- = \hat{l}_x - \mathrm{i}\hat{l}_y, \tag{1.134}$$

called ladder (or shift) operators, because they can provoke the rising and lowering of the l_z projection. Concretely, the orbital operators refer to spherical harmonics bases, but for sake of more general notation we will ascribe $|l, l_z\rangle$ instead of the Y_{l,l_z} functions. Starting from formula (1.26), the commutation rules with the new operators are identified:

$$\left[\hat{l}_z, \hat{l}_\pm\right] = \pm\hbar\hat{l}_\pm, \tag{1.135}$$

$$\left[\hat{l}_+, \hat{l}_-\right] = 2\hbar\hat{l}_z. \tag{1.136}$$

Now, recall how the z component works, rewriting:

$$\hat{l}_z|l, l_z\rangle = \hbar l_z|l, l_z\rangle, \tag{1.137}$$

and apply the left and right members of commutator from (1.135) to a basis component:

$$\hat{l}_z\hat{l}_\pm|l, l_z\rangle - \hat{l}_\pm\hat{l}_z|l, l_z\rangle = \pm\hbar\hat{l}_\pm|l, l_z\rangle. \tag{1.138}$$

Letting the element having the z operator nearby the ket to act as in (1.137) and regrouping, one arrives at:

$$\hat{l}_z\left[\hat{l}_\pm|l, l_z\rangle\right] = \hbar(l_z \pm 1)\left[\hat{l}_\pm|l, l_z\rangle\right]. \tag{1.139}$$

Now, one observes that the z operator from the left side can obtain the $l_z \pm 1$ factors only if the object comprised in square brackets, in both members, would be proportional to the $|l, l_z \pm 1\rangle$ function, namely if the ladder operators indeed shift the projection values by ±1. It remains to know the factors of the ladder operators, which, without continuing the proof, are presented as:

$$\hat{l}_\pm|l, l_z\rangle = \sqrt{(l \mp l_z)(l \pm l_z + 1)}_z|l, l_z \pm 1\rangle. \tag{1.140}$$

The demonstration comes from retrieving the $|l, l_z\rangle$ component by operating it successively, with up and down operations, then by down and up, using the other commutator relationship, from (1.27).

For the orbital momentum, we started with the operators for which we had a concrete expression, with filiations in classical mechanics. But the same formalism can be simply proposed, by extension, to other objects consisting in manifolds with indexed projections, e.g. to the spin:

$$\hat{s}_\pm|s, s_z\rangle = \sqrt{(s \mp s_z)(s \pm s_z + 1)}_z|s, s_z \pm 1\rangle. \tag{1.141}$$

The ladder operators act also on the j and $j_z$quantum numbers:

$$\hat{j}_{\pm}|j,j_z\rangle = \sqrt{(j\mp j_z)(j\pm j_z+1)}_z|j,j_z\pm 1\rangle. \tag{1.142}$$

Up to now we acted tacitly as for one-electron operators (as the orbital momentum can be thought of as attached to one moving particle and the spin meant that of the electron itself). Similar procedures of indenting quantum numbers assignable to projections on the z axis can be conceived for more general states, of poly-electronic nature, usually designated by capital letters $|L, L_z\rangle$, $|S, S_z\rangle$ and $|J, J_z\rangle$ resulting from appropriate build-up from one-electron states (orbitals).

Returning to the spin–orbit operator, a convenient rewriting of the scalar product is realized as follows:

$$\hat{l}\cdot\hat{s} = \hat{l}_x\hat{s}_x+\hat{l}_y\hat{s}_y+\hat{l}_z\hat{s}_s = \frac{1}{2}\left(\hat{l}_+\hat{s}_-+\hat{l}_-\hat{s}_+\right)+\hat{l}_z\hat{s}_s. \tag{1.143}$$

With this form, based on ladder operators, one may easily equate the action of the operator upon an atomic spin–orbital, which is a spherical harmonics decorated with the spin-up α or spin-down β label. The spin operators act on the spin label:

$\hat{s}_+|\beta\rangle = |\alpha\rangle$, $\hat{s}_-|\alpha\rangle = |\beta\rangle$, $\hat{s}_+|\alpha\rangle = 0$, $\hat{s}_-|\beta\rangle = 0$, $\hat{s}_z|\alpha\rangle = (1/2)|\alpha\rangle$ and $\hat{s}_z|\beta\rangle = (-1/2)|\beta\rangle$.

Denoting an atomic spin–orbital with known quantum numbers $\chi = |n,l,m,\sigma\rangle \equiv |n,l,l_z,s_z\rangle$, where σ stands for the α or β spin components (or, equivalently, $s_z = \pm 1/2$ projections), the scalar product of the spin–orbit operator acts as follows:

$$\begin{aligned}(\hat{l}\cdot\hat{s})|n,l,l_z,s_z\rangle = {} & \frac{1}{2}\sqrt{(l-l_z)(l+l_z+1)(s+s_z)(s-s_z+1)}|n,l,l_z+1,s_z-1\rangle \\ & + \frac{1}{2}\sqrt{(l+l_z)(l-l_z+1)(s-s_z)(s+s_z+1)}|n,l,l_z-1,s_z+1\rangle \\ & + l_z s_z|n,l,l_z,s_z\rangle.\end{aligned} \tag{1.144}$$

Put in other notation, we have for α- and β-type spin–orbitals:

$$(\hat{l}\cdot\hat{s})|n,l,m,\alpha\rangle = \frac{1}{2}\sqrt{(l-m)(l+m+1)}|n,l,m+1,\beta\rangle + \frac{1}{2}m|n,l,m,\alpha\rangle, \tag{1.145}$$

$$(\hat{l}\cdot\hat{s})|n,l,m,\beta\rangle = \frac{1}{2}\sqrt{(l+m)(l-m+1)}|n,l,m-1,\alpha\rangle - \frac{1}{2}m|n,l,m,\beta\rangle. \tag{1.146}$$

Multiplying from the left side with different “bra” functions $\langle n,l,m',\sigma'|$ one identifies the non-vanishing elements of the $\hat{l}\cdot\hat{s}$ operator as the numeric factors of components matching in the operated “ket” the same series of indices as on the right side:

$$\langle n,l,m,\alpha|(\hat{l}\cdot\hat{s})|n,l,m,\alpha\rangle = \frac{1}{2}m, \tag{1.147}$$

$$\langle n,l,m,\beta|(\hat{l}\cdot\hat{s})|n,l,m,\beta\rangle = -\frac{1}{2}m, \tag{1.148}$$

$$\langle n,l,m-1,\alpha|(\hat{l}\cdot\hat{s})|n,l,m,\beta\rangle = \frac{1}{2}\sqrt{(l+m)(l-m+1)}, \tag{1.149}$$

$$\langle n,l,m+1,\beta|(\hat{l}\cdot\hat{s})|n,l,m,\alpha\rangle = \frac{1}{2}\sqrt{(l-m)(l+m+1)}. \tag{1.150}$$

The following chapter describes how a matrix in a many-electron basis is constructed, focusing explicitly on the one-electron part, taken as kinetic plus electron–nuclear interaction and inter-electronic terms. Thinking more generally and considering the above defined matrix elements as one-electron part in the expansion recipes described later, one reaches the issue of spin–orbit coupling in many-electron states (spectral terms of atoms and molecules). Basically, the predominant part of the spin–orbit in molecules comes from intra-atom contributions, making the above discussion confined to atomic quantum numbers worth extending in practical respects.

1.5 Perturbation Theory Application: Quantum Polarizability

Since the Schrödinger equation (or its equivalent matrix quantum mechanics) can be exactly solved only in a limited number of cases, the methods of approximation are highly priced, to find practical ways toward significant complex problems. A way of approximation uses iterative (self-consistent) procedures (based on model Hamiltonians depending on the wave functions from a preceding step). The application of this strategy depends specifically on the problem at hand. The perturbation theory unfolds from the series expansion of the Hamiltonian terms and wave functions. Tacitly, we used such a strategy in the previous section, in the separation of the large and small components of the relativistic Dirac equation. The perturbation method starts by defining a zero order Hamiltonian, with known solutions, while the other terms are small contributions with respect of this reference. Therefore, the additional terms are the subject of the series expansion, stopping usually at smaller ranks, first or second order (Putz 2010a, 2016a, b).

Let us consider the non-degenerate non-perturbed discrete (stationary) solved problem (Putz 2016a)

$$\widehat{H}_0|\varepsilon_k\rangle = \varepsilon_k|\varepsilon_k\rangle, \tag{1.151}$$

whose eigen-states made the ortho-normalized basis:

$$\langle\varepsilon_j \mid \varepsilon_k\rangle = \delta_{jk}, \tag{1.152}$$

$$\hat{1}_{\{|\varepsilon_k\rangle\}} = \sum_{\substack{k=1\\ k\in \mathrm{N}}}^{\infty} |\varepsilon_k\rangle\langle\varepsilon_k|. \tag{1.153}$$

Here, we adopted another notation, with standalone "bra" $\langle\, |\text{and}\,''\text{ket}''|\,\rangle$ symbols, representing respectively the complex conjugate and the "direct" wave functions attached to the eigenvalues enclosed inside. The Eq. (1.153) is in fact an operator. When it is integrated (multiplied with a "bra" from the left side and a "ket" from the right), the "ket" of the operator falls in an overlap relationship with the "bra" of the formed integral, while the right side operator "bra" is coupled and integrated with the added "ket". More precisely, (1.153) is an operator for the resolution to identity, whose task is to retrieve the (1.152) ortho-normalization conditions when operated with functions from the same set constituting it. This is another way to state the completeness of the basis set.

In these conditions, the perturbed eigen-states are generically written as a superposition of all non-perturbed eigenstates:

$$|E(\lambda)\rangle = \sum_k c_k(\lambda)|\varepsilon_k\rangle, \tag{1.154}$$

while the perturbation itself is comprised of the expansion coefficients:

$$c_k(\lambda) = c_k^{(0)} + \lambda c_k^{(1)} + \lambda^2 c_k^{(2)} + \cdots \tag{1.155}$$

The perturbed eigen-problem equivalently becomes:

$$\begin{aligned}
\widehat{H}(\lambda)|E(\lambda)\rangle &= E(\lambda)|E(\lambda)\rangle \\
&\Leftrightarrow \left(\widehat{H}_0+\lambda\widehat{H}_1\right)\sum_k c_k(\lambda)|\varepsilon_k\rangle = E(\lambda)\sum_k c_k(\lambda)|\varepsilon_k\rangle \\
&\Leftrightarrow \sum_k c_k(\lambda)\underbrace{\widehat{H}_0|\varepsilon_k\rangle}_{\varepsilon_k|\varepsilon_k\rangle}+\lambda\sum_k c_k\hat{H}_1|\varepsilon_k\rangle = E(\lambda)\sum_k c_k(\lambda)|\varepsilon_k\rangle \\
&\overset{\langle\varepsilon_j|}{\Leftrightarrow} \sum_k c_k(\lambda)\varepsilon_k\underbrace{\langle\varepsilon_j \mid \varepsilon_k\rangle}_{\delta_{ik}}+\lambda\sum_k c_k\langle\varepsilon_j|\widehat{H}_1|\varepsilon_k\rangle = E(\lambda)\sum_k c_k(\lambda)\underbrace{\langle\varepsilon_j \mid \varepsilon_k\rangle}_{\delta_{jk}} \\
&\Leftrightarrow c_j(\lambda)\left[E(\lambda)-\varepsilon_j\right] = \lambda\sum_k\langle\varepsilon_j|\widehat{H}_1|\varepsilon_k\rangle c_k \\
&\Leftrightarrow \left[c_j^{(0)}+\lambda c_j^{(1)}+\lambda^2c_j^{(2)}+\cdots\right]\left[E^{(0)}-\varepsilon_j+\lambda E^{(1)}+\lambda^2E^{(2)}+\cdots\right] \\
&= \lambda\sum_k\langle\varepsilon_j|\widehat{H}_1|\varepsilon_k\rangle\left[c_k^{(0)}+\lambda c_k^{(1)}+\lambda^2c_k^{(2)}+\cdots\right]
\end{aligned} \tag{1.156}$$

from where, by equal power of coefficients one successively gets the cut-offs:

Order (0):

$$c_j^{(0)}\left[E^{(0)}-\varepsilon_j\right]=0 \tag{1.157}$$

Order (I):

$$\left[E^{(0)}-\varepsilon_j\right]c_j^{(1)}+E^{(1)}c_j^{(0)}=\sum_k\langle\varepsilon_j|\widehat{H}_1|\varepsilon_k\rangle c_k^{(0)} \tag{1.158}$$

Order (II):

$$\left[E^{(0)}-\varepsilon_j\right]c_j^{(2)}+E^{(1)}c_j^{(1)}+E^{(2)}c_j^{(0)}=\sum_k\langle\varepsilon_j|\widehat{H}_1|\varepsilon_k\rangle c_k^{(1)} \tag{1.159}$$

…

Order (p):

$$\left[E^{(0)}-\varepsilon_j\right]c_j^{(p)}+E^{(1)}c_j^{(p-1)}+\cdots+E^{(p)}c_j^{(0)}=\sum_k\langle\varepsilon_j|\widehat{H}_1|\varepsilon_k\rangle c_k^{(p)} \tag{1.160}$$

Let us now analyze each order in perturbation, based on the above separate, however somewhat iterative, equations.

Order (0): The solution of this (unperturbed) problem is immediate:

$$E^{(0)} = \varepsilon_n \tag{1.161}$$

recovering the whole isolated energy spectrum, while for the wave function reads as:

$$\left|E^{(0)}\right\rangle = \sum_k c_k^{(0)} |\varepsilon_k\rangle \overset{!}{=} |\varepsilon_n\rangle \tag{1.162}$$

from where there follows the necessary identity:

$$c_k^{(0)} = \delta_{kn} \tag{1.163}$$

so that the 0th order equation is verified as:

$$c_j^{(0)}\left[E^{(0)} - \varepsilon_j\right] = 0 \Leftrightarrow \delta_{jn}\left[\varepsilon_n - \varepsilon_j\right] = 0 \tag{1.164}$$

Order (I): Here, apart from employing the results of the order (0) perturbation analysis, two cases are distinguished, namely one in which the associate equation is specialized for some $j = n$ in the non-perturbed discrete spectrum that gives:

$$\underbrace{[\varepsilon_n - \varepsilon_n]}_{0} c_n^{(1)} + E^{(1)} \underbrace{\delta_{nn}}_{1} = \sum_k \langle\varepsilon_n|\widehat{H}_1|\varepsilon_k\rangle\delta_{kn} \tag{1.165}$$

releasing the first-order energy perturbation

$$E^{(1)} = \langle\varepsilon_n|\widehat{H}_1|\varepsilon_n\rangle \tag{1.166}$$

as the average of the perturbation Hamiltonian over the non-perturbed eigen-states, while emphasizing the impossibility of $c_n^{(1)}$ evaluation since canceling its energy multiplication, but assuming with indeterminate expression:

$$c_n^{(1)} = \delta_{jn} Z^{(1)} \tag{1.167}$$

Instead, for the case in which $j \neq n$ the corrected energy vanishes while allowing the determination of the first-order perturbation coefficient:

$$\left[\varepsilon_n - \varepsilon_j\right] c^{(1)}_{j\neq n} + E^{(1)} \underbrace{\delta_{j\neq n}}_{0} = \sum_k \left\langle \varepsilon_j \middle| \widehat{H}_1 \middle| \varepsilon_k \right\rangle \delta_{kn} \tag{1.168}$$

$$c^{(1)}_{j\neq n} = \frac{\left\langle \varepsilon_j \middle| \widehat{H}_1 \middle| \varepsilon_n \right\rangle}{\varepsilon_n - \varepsilon_j} \tag{1.169}$$

Combining both cases, the first-order perturbation coefficient of the perturbed wave function looks like:

$$c^{(1)}_j = \delta_{jn} Z^{(1)} + \left(1 - \delta_{jn}\right) \frac{\left\langle \varepsilon_j \middle| \widehat{H}_1 \middle| \varepsilon_n \right\rangle}{\varepsilon_n - \varepsilon_j} \tag{1.170}$$

Order (II): The same procedure as for the previous order applies, however with a supplemented degree of complication since we are considering the results and cases raised from lower orders. As such, for the $j = n$ case the original equation of second-order perturbation unfolds as:

$$\begin{aligned} &\underbrace{\left[\varepsilon_n - \varepsilon_n\right]}_{0} c^{(2)}_j + E^{(1)} \underbrace{c^{(1)}_{j=n}}_{Z^{(1)}} + E^{(2)} \underbrace{\delta_{nn}}_{1} = \sum_k \left\langle \varepsilon_n \middle| \widehat{H}_1 \middle| \varepsilon_k \right\rangle \overset{\overset{c^{(1)}_k}{\downarrow}}{\overbrace{k = n \quad k \neq n}} \\ &\Leftrightarrow E^{(2)} = \underbrace{-E^{(1)} \cancel{Z}^{(1)} + \underbrace{\left\langle \varepsilon_n \middle| \hat{H}_1 \middle| \varepsilon_n \right\rangle}_{E^{(1)}} \underbrace{c^{(1)}_{k=n}}_{Z^{(1)}}}_{0} + \sum_k \left\langle \varepsilon_n \middle| \widehat{H}_1 \middle| \varepsilon_k \right\rangle \underbrace{c^{(1)}_{k\neq n}}_{\frac{\left\langle \varepsilon_k \middle| \hat{H}_1 \middle| \varepsilon_n \right\rangle}{\varepsilon_n - \varepsilon_k}} \end{aligned} \tag{1.171}$$

until we give the expression of the second-order energy perturbation:

$$E^{(2)} = \sum_{k\neq n} \frac{\left| \left\langle \varepsilon_k \middle| \widehat{H}_1 \middle| \varepsilon_n \right\rangle \right|^2}{\varepsilon_n - \varepsilon_k} \tag{1.172}$$

while leaving, as before, the $j = n$ second-order coefficient of wave function expansion as undetermined:

$$c^{(2)}_n = \delta_{jn} Z^{(2)}. \tag{1.173}$$

Analogously, the $j \neq n$ case leaves us with the second-order coefficient determination while canceling the associate energy:

$$\begin{aligned}
&\left[\varepsilon_n - \varepsilon_j\right] c^{(2)}_{j\neq n} + \underbrace{E^{(1)}}_{\langle \varepsilon_n|\widehat{H}_1|\varepsilon_n\rangle} \underbrace{c^{(1)}_{j\neq n}}_{\frac{\langle \varepsilon_j|\widehat{H}_1|\varepsilon_n\rangle}{\varepsilon_n-\varepsilon_j}} + E^{(2)} \underbrace{\delta_{n\neq j}}_{0} \\
&= \sum_k \langle \varepsilon_j|\widehat{H}_1|\varepsilon_k\rangle \underset{\overbrace{k = n \quad k \neq n}}{\underset{\downarrow}{c^{(1)}_k}} \\
&\Rightarrow c^{(2)}_{j\neq n} = \frac{1}{\varepsilon_n - \varepsilon_j} \left\{ \begin{array}{l} - \langle \varepsilon_n|\widehat{H}_1|\varepsilon_n\rangle \dfrac{\langle \varepsilon_j|\widehat{H}_1|\varepsilon_n\rangle}{\varepsilon_n - \varepsilon_j} \\ + \langle \varepsilon_j|\widehat{H}_1|\varepsilon_n\rangle \underbrace{c^{(1)}_{k=n}}_{Z^{(1)}} + \sum\limits_{k\neq n} \langle \varepsilon_j|\widehat{H}_1|\varepsilon_k\rangle \underbrace{c^{(1)}_{k\neq n}}_{\frac{\langle \varepsilon_k|\widehat{H}_1|\varepsilon_n\rangle}{\varepsilon_n-\varepsilon_k}} \end{array} \right\} \\
&= Z^{(1)} \frac{\langle \varepsilon_j|\widehat{H}_1|\varepsilon_n\rangle}{\varepsilon_n - \varepsilon_j} - \frac{\langle \varepsilon_j|\widehat{H}_1|\varepsilon_n\rangle \langle \varepsilon_n|\widehat{H}_1|\varepsilon_n\rangle}{\left(\varepsilon_n - \varepsilon_j\right)^2} \\
&\quad + \sum_{k\neq n} \frac{\langle \varepsilon_j|\widehat{H}_1|\varepsilon_k\rangle \langle \varepsilon_k|\widehat{H}_1|\varepsilon_n\rangle}{\left(\varepsilon_n - \varepsilon_j\right)\left(\varepsilon_n - \varepsilon_k\right)}
\end{aligned} \tag{1.174}$$

Combining both cases we can write for the second-order coefficient of perturbed wave function the general expression:

$$\begin{aligned}
c^{(2)}_j &= \delta_{jn} Z^{(2)} + \left(1 - \delta_{jn}\right) Z^{(1)} \frac{\langle \varepsilon_j|\widehat{H}_1|\varepsilon_n\rangle}{\varepsilon_n - \varepsilon_j} \\
&\quad + \left(1 - \delta_{jn}\right) \left[\sum_{k\neq n} \frac{\langle \varepsilon_j|\widehat{H}_1|\varepsilon_k\rangle \langle \varepsilon_k|\widehat{H}_1|\varepsilon_n\rangle}{\left(\varepsilon_n - \varepsilon_j\right)\left(\varepsilon_n - \varepsilon_k\right)} - \frac{\langle \varepsilon_j|\widehat{H}_1|\varepsilon_n\rangle \langle \varepsilon_n|\widehat{H}_1|\varepsilon_n\rangle}{\left(\varepsilon_n - \varepsilon_j\right)^2} \right]
\end{aligned} \tag{1.175}$$

Now, it is worth making the observation according to which the corrections $Z^{(1)}$ and $Z^{(2)}$ are not entering the perturbed energies corrections, thus may be principally set as being equal with zero (0) since they do not affect the perturbed spectra. Moreover, it can be easily proved that such choice is equivalent with the condition that perturbed states are orthogonal on the non-perturbed eigen-states: if one defined the "p" order states as:

$$|p\rangle = \sum_k c^{(p)}_k |\varepsilon_k\rangle \tag{1.176}$$

and the "*p*" undetermined correction coefficient as:

$$Z^{(p)} = c_{k=n}^{(p)} = \sum_k c_k^{(p)} \delta_{nk} = \sum_k c_k^{(p)} \langle \varepsilon_n \mid \varepsilon_k \rangle = \langle \varepsilon_n | \underbrace{\sum_k c_k^{(p)} |\varepsilon_k\rangle}_{|p\rangle} = \langle \varepsilon_n \mid p \rangle \quad (1.177)$$

there is the immediate result that the condition:

$$0 = Z^{(p)} = \langle \varepsilon_n \mid p \rangle, \quad \forall |\varepsilon_n\rangle \in \left\{ \widehat{H}_0 \right\}_{\text{spectra}} \& \, |p\rangle \in \left\{ \widehat{H}_1 \right\}_{\text{spectra}} \quad (1.178)$$

leaves with the physical condition that the Hilbert (sub)spaces of the isolated and perturbation Hamiltonians are orthogonal, $\mathbf{H}_{\left\{\widehat{H}_0\right\}} \perp \mathbf{H}_{\left\{\widehat{H}_1\right\}}$, thus allowing their direct product to reproduce the whole-problem spectra (levels and states) of the perturbed system:

$$\mathbf{H}_{\left\{\widehat{H}_0 + \lambda \widehat{H}_1\right\}} = \mathbf{H}_{\left\{\widehat{H}_0\right\}} \otimes \mathbf{H}_{\left\{\widehat{H}_1\right\}} \quad (1.179)$$

With this remarkable result, the full perturbed $(\lambda = 1)$ energy and wave function may be written as the series:

$$E_n(\lambda = 1) = \varepsilon_n + \langle \varepsilon_n | \widehat{H}_1 | \varepsilon_n \rangle + \sum_{k \neq n} \frac{\left| \langle \varepsilon_k | \widehat{H}_1 | \varepsilon_n \rangle \right|^2}{\varepsilon_n - \varepsilon_k} + \cdots \quad (1.180)$$

$$\begin{aligned} |E_n(\lambda = 1)\rangle &= |\varepsilon_n\rangle + \sum_{k \neq n} |\varepsilon_k\rangle \frac{\langle \varepsilon_k | \widehat{H}_1 | \varepsilon_n \rangle}{\varepsilon_n - \varepsilon_k} \\ &\quad + \sum_{k \neq n} |\varepsilon_k\rangle \left[\sum_{j \neq n} \frac{\langle \varepsilon_k | \widehat{H}_1 | \varepsilon_j \rangle \langle \varepsilon_j | \widehat{H}_1 | \varepsilon_n \rangle}{(\varepsilon_n - \varepsilon_k)(\varepsilon_n - \varepsilon_j)} - \frac{\langle \varepsilon_k | \widehat{H}_1 | \varepsilon_n \rangle \langle \varepsilon_n | \widehat{H}_1 | \varepsilon_n \rangle}{(\varepsilon_n - \varepsilon_k)^2} \right] + \cdots \end{aligned} \quad (1.181)$$

while, usually, in practice, there are retained only the expansion until the second order in energy and the first order in wave function, respectively. Even so, the calculations imply the evaluation of all matrix elements $\langle \varepsilon_k | \widehat{H}_1 | \varepsilon_n \rangle$, this being non-trivial algebra unless some of them are identically null (Putz 2016a).

Other special appearances are next unfolded for the stationary perturbations for some paradigmatic physical situations (Putz 2010a, 2016b). Starting from so-called second-order perturbation energy, see Eq. (1.181):

$$E^{(2)} = \sum_{k \neq n} \frac{\left| \langle n | \widehat{H}_1 | k \rangle \right|^2}{E_k - E_n} \tag{1.182}$$

is specialized for the Stark potential produced by the applied external electric field with the amplitude ε in the $0x$ direction

$$\widehat{H}_1 = V(\hat{x}) = -\hat{x} Z e_0 \varepsilon \tag{1.183}$$

under the form

$$E^{(2)} = -\frac{1}{2} \alpha \varepsilon^2 \tag{1.184}$$

that allows for α-polarizability in (1.184) the general hydrogenoid (Z-dependent) formulation

$$\alpha = 2 e_0^2 Z^2 \sum_{k \neq n} \frac{\left| \langle n | \hat{x} | k \rangle \right|^2}{E_n - E_k} \tag{1.185}$$

where

$$e_0^2 = \frac{e^2}{4 \pi \varepsilon_0} \tag{1.186}$$

is the reduced squared elementary charge.

Now, going on to evaluate the atomic polarizability in terms of the quantum basic information contained within the atomic quantum numbers (e.g. n, k), one starts recognizing the general operatorial identity over the complete set of quantum (eigen) states (Putz 2010a)

$$\begin{aligned} \sum_k \left| \langle n | \widehat{O} | k \rangle \right|^2 &= \sum_k \langle n | \widehat{O} | k \rangle \langle k | \widehat{O} | n \rangle \\ &= \langle n | \widehat{O} \underbrace{\left\{ \sum_k | k \rangle \langle k | \right\}}_{1} \widehat{O} | n \rangle = \langle n | \widehat{O}^2 | n \rangle . \end{aligned} \tag{1.187}$$

Equation (1.187) represents the sum rule of Bethe and Jackiw (1968) and Jackiw (1967), while its simplest dipole matrix element sum rule casts as

$$\sum_k |\langle n|\hat{x}|k\rangle|^2 = \langle n|\hat{x}^2|n\rangle \tag{1.188}$$

On the other hand, recalling the basic quantum commutation rule of momentum with space coordinate

$$[\hat{p}, \hat{x}] = \frac{\hbar}{\mathrm{i}} \tag{1.189}$$

along the companion energy-coordinate commutator

$$\left[\widehat{H}, \hat{x}\right] = \left[\frac{\hat{p}^2}{2m} + V(\hat{x}), \hat{x}\right] = \frac{1}{2m}\left[\hat{p}^2, \hat{x}\right] = \frac{\hbar}{m\mathrm{i}}\hat{p} \tag{1.190}$$

there can be inferred the quantum relationship

$$\frac{\hbar}{\mathrm{i}} = \langle n|(\hat{p}\hat{x} - \hat{x}\hat{p})|n\rangle = \sum_k \left\{ \begin{array}{c} \langle n|\hat{p}|k\rangle\langle k|\hat{x}|n\rangle \\ -\langle n|\hat{x}|k\rangle\langle k|\hat{p}|n\rangle \end{array} \right\} \tag{1.191}$$

upon inserting of the above quantum closure relation over the complete set of eigen-states. The first term in the right-hand side of the last expression may be reformulated as

$$\begin{aligned} \langle n|\hat{p}|k\rangle &= \langle n|\frac{m\mathrm{i}}{\hbar}\left[\widehat{H}, \hat{x}\right]|k\rangle \\ &= \frac{m\mathrm{i}}{\hbar}\langle n|\left(\widehat{H}\hat{x} - \hat{x}\widehat{H}\right)|k\rangle = \frac{m\mathrm{i}}{\hbar}(E_n - E_k)\langle n|\hat{x}|k\rangle \end{aligned} \tag{1.192}$$

and along the similar relation that springs out from the second term in (1.191) one gets the equation (Putz 2010a)

$$\frac{\hbar}{i} = \frac{m\mathrm{i}}{\hbar}\sum_k [(E_n - E_k) - (E_k - E_n)]|\langle n|\hat{x}|k\rangle|^2 \tag{1.193}$$

that can be rearranged under the so-called Thomas-Reiche-Kuhn (TRK) energy-weighted sum rule (Reiche and Thomas 1925; Thomas 1925; Kuhn 1925)

$$\frac{\hbar^2}{2m} = \sum_k (E_k - E_n)|\langle n|\hat{x}|k\rangle|^2. \tag{1.194}$$

Remarkably, the expansion (1.194) may be also obtained by requiring that the Kramers-Heisenberg dispersion relation reduce to the Thomas scattering formula at high energies; indeed, through rewriting Eq. (1.194) in the form

$$\sum_k \frac{2m(E_k - E_n)}{\hbar^2} |\langle n|\hat{x}|k\rangle|^2 = \sum_k f_{n,k} = 1 \tag{1.195}$$

it provides an important theoretical support for the experimental checks of the oscillator strengths ($f_{n.k}$) as a confirmation of early quantum results (Mehra and Rechenberg 1982; Bethe 1997).

Now, returning to the evaluation of polarizability given by (1.185) one can use the recipe (1.194) to facilitate the skipping out of the energy-singularity toward the all-eigen-state summation (1.188) with the successive results (Putz 2010a)

$$\begin{aligned}
\alpha &= 2e_0^2 Z^2 \sum_{k\neq n} \frac{|\langle n|\hat{x}|k\rangle|^2}{E_n - E_k} = 2\frac{2me_0^2}{\hbar^2} Z^2 \frac{\hbar^2}{2m} \sum_{k\neq n} \frac{|\langle n|\hat{x}|k\rangle|^2}{E_n - E_k} \\
&= \frac{4me_0^2}{\hbar^2} Z^2 \left\{ \sum_k (E_k - E_n) |\langle n|\hat{x}|k\rangle|^2 \right\} \sum_{k\neq n} \frac{|\langle n|\hat{x}|k\rangle|^2}{E_n - E_k} \\
&\xrightarrow{\text{all } k} 2\frac{4me_0^2}{\hbar^2} Z^2 \left(\sum_k |\langle n|\hat{x}|k\rangle|^2 \right)^2 \\
&= 8\frac{me_0^2}{\hbar^2} Z^2 \left|\langle n|\hat{x}^2|n\rangle\right|^2 = 8\frac{Z^2}{a_0} \left|\langle n|\hat{x}^2|n\rangle\right|^2
\end{aligned} \tag{1.196}$$

where we recognized the first Bohr radius expression (1.280).

Finally, the obtained expression (1.196) is unfolded through replacing the coordinate observation with the atomic radius as the quantum average displacement respecting its instantaneous value (Putz 2010a) $x \to r - \langle r\rangle_{nl}$. It allows the immediate formation of the squared coordinate expression $x^2 = r^2 - 2r\langle r\rangle_{nl} + \langle r\rangle_{nl}^2$ of which the observed quantum average looks like $\langle n|\hat{x}^2|n\rangle \to \langle x^2\rangle_{nl} = \langle r^2\rangle_{nl} - \langle r\rangle_{nl}^2$ and whose replacement in the polarizability (1.196) produces its radial averages' dependency

$$\alpha = 8\frac{Z^2}{a_0} \left[\langle r^2\rangle_{nl} - \langle r\rangle_{nl}^2 \right]^2 \tag{1.197a}$$

While replacing the first- and second-order quantum averages for the atomic radius of a hydrogenic system in terms of the principal and azimuthal quantum numbers n and l, respectively (Morse and Feshbach 1953)

$\langle r\rangle_{nl}=\frac{1}{2}\left(\frac{a_0}{Z}\right)[3n^2-l(l+1)]$ and $\left\langle r^2\right\rangle_{nl}=\frac{1}{2}\left(\frac{a_0}{Z}\right)^2 n^2[5n^2-3l(l+1)+1]$ the static atomic polarizability (1.197a) takes the analytical form (Putz 2010a)

$$\alpha_{nl}(Z)=\frac{a_0^3}{2Z^2}\left[n^2\left(2+n^2\right)-l^2(1+l)^2\right]^2 \tag{1.197b}$$

remarkably recovering the exact result for the hydrogen limiting case

$$\alpha_{n=1,l=0}(Z=1)=\frac{9}{2}a_0^3. \tag{1.197c}$$

1.6 Atomic Stability: The Proof by Quantum Path Integrals

Despite the quantum arsenal of tools and relationships, above presented, the stability of matter resists explanation in a consistent way. Paradoxically, the proof of matter's stability at quantum level is not direct, i.e. by using the differential equations of quantum mechanics, since the inherent quantum evolution opposite behavior to stability itself. Therefore, the alternative integral approach should be formulated—indeed the integral picture contains the information of all-possible evolutions, averaged and appropriately weighted, so furnishing the stability output; at the same time, such a picture, in order to be accepted, should first provide its firm connection and equivalence with the fashioned Schrodinger formulation; this section aims to achieve this double goal.

1.6.1 Schrodinger Equation by Quantum Path Integral

The starting point is the manifested *equivalence* between the path integral propagator and the Green function, with the role of transforming one wave function registered on one space-time event into another one, either in the future or past quantum evolution (Putz 2009, 2016a). Here we consider only retarded phenomena,

$$(x_2,t_2;x_1,t_1)=\mathrm{i}G^+(x_2,t_2;x_1,t_1) \tag{1.198}$$

in accordance with the very beginning path integral construction and the so-called quantum Huygens principle of wave-packet propagation (Greiner and Reinhardt 1994):

$$\psi(x_2,t_2)=\int(x_2,t_2;x_1,t_1)\psi(x_1,t_1)\mathrm{d}x_1,\quad t_2>t_1 \tag{1.199}$$

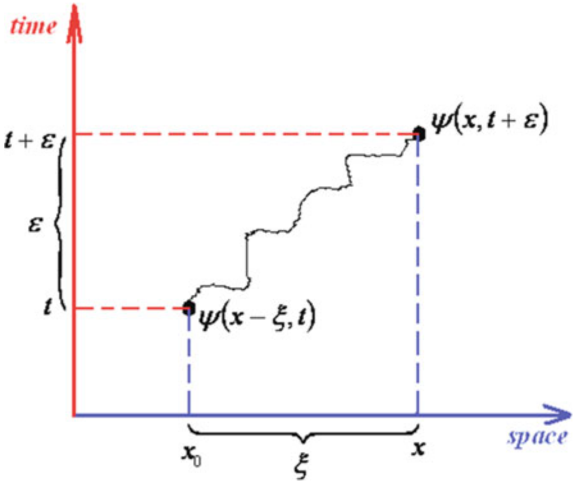


Fig. 1.14 Depiction of the space-time elementary retarded path connecting two events characterized by their dynamic wave functions (Putz 2009, 2016a).

Yet, we will employ Eq. (1.199) for an *elementary* propagator, for a quantum evolution as presented in Fig. 1.14, thus becoming like:

$$\psi(x,t+\varepsilon)=A\int\exp\left[\frac{\mathrm{i}}{\hbar}\varepsilon L\left(\frac{x+x_0}{2},\frac{x-x_0}{2},t+\frac{\varepsilon}{2}\right)\right]\psi(x-\xi,t)\mathrm{d}x_0 \tag{1.200}$$

where A plays the role of the normalization constant in (1.200) to assure the convergence of the wave function result. Equation (1.200) may still be transformed through employing the geometrical relation:

$$x=x_0+\xi \tag{1.201}$$

to compute the space and velocity averages:

$$\frac{x+x_0}{2}=\frac{2x-\xi}{2}=x-\frac{\xi}{2} \tag{1.202}$$

$$\frac{x-x_0}{\varepsilon}=\frac{\xi}{\varepsilon} \tag{1.203}$$

respectively, while changing the variable

$$\mathrm{d}x_0=-\mathrm{d}\xi \tag{1.204}$$

to the actual form:

$$\begin{aligned}\psi(x,t+\varepsilon) &= \widetilde{A}\int \exp\left\{\frac{\mathrm{i}}{\hbar}\varepsilon\left[\frac{m}{2}\frac{\xi^2}{\varepsilon^2} - V\left(x-\frac{\xi}{2},t+\frac{\varepsilon}{2}\right)\right]\right\}\psi(x-\xi,t)\mathrm{d}\xi\\ &= \widetilde{A}\int \exp\left[\frac{im}{2\hbar\varepsilon}\xi^2\right]\ \exp\left[-\frac{\mathrm{i}}{\hbar}\varepsilon V\left(x-\frac{\xi}{2},t+\frac{\varepsilon}{2}\right)\right]\psi(x-\xi,t)\mathrm{d}\xi\end{aligned} \tag{1.205}$$

where Lagrangian was considered with its canonical form, and the new constant factor was considered assimilating the minus sign of (1.205).

Next, since noticing the square dependence of ξ in (1.205) there will be assumed the series expansion in coordinate (ξ) and time (ε) elementary steps restrained to the second and first order, respectively, being the time interval cut-off in accordance with the general $\varepsilon^2 \cong 0$ prescription. Thus we have:

$$\psi(x-\xi,t) \cong \psi(x,t) - \xi\left[\frac{\partial}{\partial x}\psi(x,t)\right]_{\xi\to 0} + \frac{\xi^2}{2}\left[\frac{\partial^2}{\partial x^2}\psi(x,t)\right]_{\xi\to 0} \tag{1.206}$$

$$\psi(x,t+\varepsilon) \cong \psi(x,t) + \varepsilon\left[\frac{\partial}{\partial t}\psi(x,t)\right]_{\varepsilon\to 0} \tag{1.207}$$

$$\exp\left[-\frac{\mathrm{i}}{\hbar}\varepsilon V\left(x-\frac{\xi}{2},t+\frac{\varepsilon}{2}\right)\right] \cong 1 - \frac{\mathrm{i}}{\hbar}\varepsilon V(x,t) \tag{1.208}$$

and the form (1.205) successively rearranges:

$$\begin{aligned}&\psi(x,t) + \varepsilon\left[\frac{\partial}{\partial t}\psi(x,t)\right]\\ &= \widetilde{A}\int \mathrm{e}^{-\frac{m}{2\mathrm{i}\hbar\varepsilon}\xi^2}\left[1-\frac{\mathrm{i}}{\hbar}\varepsilon V(x,t)\right]\left\{\psi(x,t) - \xi\left[\frac{\partial}{\partial x}\psi(x,t)\right] + \frac{\xi^2}{2}\left[\frac{\partial^2}{\partial x^2}\psi(x,t)\right]\right\}\mathrm{d}\xi\\ &= \widetilde{A}\psi(x,t)\int \mathrm{e}^{-\frac{m}{2\mathrm{i}\hbar\varepsilon}\xi^2}\mathrm{d}\xi - \widetilde{A}\left[\frac{\partial}{\partial x}\psi(x,t)\right]\int \xi\mathrm{e}^{-\frac{m}{2\mathrm{i}\hbar\varepsilon}\xi^2}\mathrm{d}\xi + \widetilde{A}\frac{1}{2}\left[\frac{\partial^2}{\partial x^2}\psi(x,t)\right]\\ &\times\int \xi^2\mathrm{e}^{-\frac{m}{2\mathrm{i}\hbar\varepsilon}\xi^2}\mathrm{d}\xi\\ &- \widetilde{A}\frac{\mathrm{i}}{\hbar}\varepsilon V(x,t)\psi(x,t)\int \mathrm{e}^{-\frac{m}{2\mathrm{i}\hbar\varepsilon}\xi^2}\mathrm{d}\xi + \widetilde{A}\frac{\mathrm{i}}{\hbar}\varepsilon V(x,t)\left[\frac{\partial}{\partial x}\psi(x,t)\right]\int \xi\mathrm{e}^{-\frac{m}{2\mathrm{i}\hbar\varepsilon}\xi^2}\mathrm{d}\xi\end{aligned} \tag{1.209}$$

where we have neglected the mixed orders producing a total order beyond the maximum two, e.g. $\varepsilon\xi^2 \cong 0$, and where we arranged the exponentials under integrals of Gaussian type (i.e. employing the identity $-i = 1/i$). Now, the integrals appearing on (1.209) are of Poisson type of various orders, and solves for notation

$$\frac{m}{2\hbar\varepsilon\mathrm{i}} \equiv a \tag{1.210}$$

as:

$$\int \mathrm{e}^{-\frac{m}{2\mathrm{i}\hbar\varepsilon}\xi^2}\mathrm{d}\xi \to \int_{-\infty}^{+\infty} \exp\left(-a\xi^2\right)\mathrm{d}\xi = \sqrt{\frac{\pi}{a}} = \sqrt{\frac{2\pi\hbar\varepsilon\mathrm{i}}{m}} \tag{1.211}$$

$$\int \xi\mathrm{e}^{-\frac{m}{2\mathrm{i}\hbar\varepsilon}\xi^2}\mathrm{d}\xi \to \int_{-\infty}^{+\infty} \xi \exp\left(-a\xi^2\right)\mathrm{d}\xi = 0 \tag{1.212}$$

$$\int \xi^2\mathrm{e}^{-\frac{m}{2\mathrm{i}\hbar\varepsilon}\xi^2}\mathrm{d}\xi \to \int_{-\infty}^{+\infty} \xi^2 \exp\left(-a\xi^2\right)\mathrm{d}\xi = \frac{1}{2a}\sqrt{\frac{\pi}{a}} = \frac{\hbar\varepsilon\mathrm{i}}{m}\sqrt{\frac{2\pi\hbar\varepsilon\mathrm{i}}{m}} \tag{1.213}$$

With these the expression (1.209) simplifies to:

$$\psi(x,t) + \varepsilon\left[\frac{\partial}{\partial t}\psi(x,t)\right] = \widetilde{A}\sqrt{\frac{2\pi\hbar\varepsilon\mathrm{i}}{m}}\left[1 + \frac{1}{2}\frac{\hbar\varepsilon\mathrm{i}}{m}\frac{\partial^2}{\partial x^2} - \frac{\mathrm{i}}{\hbar}\varepsilon V(x,t)\right]\psi(x,t) \tag{1.214}$$

which in the limit $\varepsilon \to 0$, common for path integrals, leaves with identity:

$$\psi(x,t) = \lim_{\varepsilon\to 0}\left(\widetilde{A}\sqrt{\frac{2\pi\hbar\varepsilon\mathrm{i}}{m}}\right)\psi(x,t) \tag{1.215}$$

from where the convergence constant of path integral (1.205) is found

$$\widetilde{A}(\varepsilon) = \sqrt{\frac{m}{2\pi\hbar\varepsilon\mathrm{i}}}. \tag{1.216}$$

Nevertheless, with the constant (1.216) back in (1.214) we get the equivalent forms:

$$\begin{aligned}\psi(x,t)+\varepsilon\left[\frac{\partial}{\partial t}\psi(x,t)\right] &= \psi(x,t)+\frac{1}{2}\frac{\hbar\varepsilon \mathrm{i}}{m}\frac{\partial^2}{\partial x^2}\psi(x,t)-\frac{\mathrm{i}}{\hbar}\varepsilon V(x,t)\psi(x,t)\\ &\Leftrightarrow \frac{\partial}{\partial t}\psi(x,t)=\frac{1}{2}\frac{\hbar \mathrm{i}}{m}\frac{\partial^2}{\partial x^2}\psi(x,t)-\frac{\mathrm{i}}{\hbar}V(x,t)\psi(x,t)\\ &\Leftrightarrow \mathrm{i}\hbar\frac{\partial}{\partial t}\psi(x,t)=\left[-\frac{1}{2}\frac{\hbar^2}{m}\frac{\partial^2}{\partial x^2}+V(x,t)\right]\psi(x,t)\end{aligned}\tag{1.217}$$

this last one identically recovering the Schrödinger wave function equation.

By the present result (1.217) we have thus proved that the Feynman path integral may be reduced to the quantum wave-packet motion while carrying also the information that connects coupled events across the paths' evolution, this being a general approach in quantum mechanics and statistics.

The next section(s) will deal with the practical application/calculation of the path integrals for the fundamental quantum problem, i.e. the stability of Bohr's atom in particular and of general matter especially.

1.6.2 Feynman-Kleinert Effective Density Formalism

The effective electronic density may be analytically unfolded with the aid of path integrals formalism, for which the Feynman and Kleinert (1986) formalism may be considered as a meaningful analytical model; it starts from the quantum statistic representation of the partition function (Feynman and Kleinert 1986; Kleinert 2004; Kleinert et al. 2002; Putz 2009):

$$Z=\oint_{\mathbf{r}(0)=\mathbf{r}(\hbar\beta)} D\mathbf{r}(\tau)\,\exp\left\{-\frac{1}{\hbar}\int_0^{\hbar\beta}\mathrm{d}\tau\left[m_0\frac{\dot{\mathbf{r}}^2(\tau)}{2}+V(\mathbf{r}(\tau))\right]\right\}\tag{1.218}$$

in which the periodicity $\mathbf{r}(0)=\mathbf{r}(\hbar\beta)$ of the paths on the temporal (imaginary) axis is admitted, being the quantum statistical measure of integration in the Wick-rotated quantum mechanical one, i.e. performing the transformations:

$$\begin{cases} t:=-\mathrm{i}\tau\\ \frac{\mathrm{d}}{\mathrm{d}_t}=\frac{\mathrm{d}_\tau}{\mathrm{d}_t}\frac{\mathrm{d}}{\mathrm{d}_\tau}=\mathrm{i}\frac{\mathrm{d}}{\mathrm{d}_\tau}\end{cases}\cdot\tag{1.219}$$

Since the Fourier decomposition of the periodical paths is considered:

$$\mathbf{r}(\tau)=\mathbf{r}_0+\sum_{m=1}^{\infty}\left(\mathbf{r}_m\,\exp[\mathrm{i}\omega_m\tau]+\mathrm{c.c.}\right)\tag{1.220}$$

being $\omega_m = 2\pi m/(\hbar\beta)$ the Matsubara frequencies, with m the integer number of indexation, the quantum statistic partition function (1.218) further becomes:

$$Z = \int_{-\infty}^{+\infty} \frac{\mathrm{d}x_0}{\sqrt{2\pi\hbar\beta/m_0}} \left\{ \prod_{m=1}^{\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \frac{\mathrm{dRe}x_m \mathrm{dIm}x_m}{\pi/(m_0\beta\omega_m^2)} \exp\left[\begin{array}{c} -\beta m_0 \sum\limits_{m=1}^{\infty} \omega_m^2 |x_m|^2 \\ -\frac{1}{\hbar} \int\limits_0^{\hbar\beta} \mathrm{d}\tau V(x(\tau)) \end{array} \right] \right\} \tag{1.221}$$

This form of the partition function has the advantage of including all the periodic paths, the quantum statistical ones, that characterize a given many-electronic ensemble, but having also the disadvantage of requiring the calculus of an infinite product of integrals. This is why the approximations are necessary, to enable the approach of the path integrals to become analytically applicable.

Firstly, we will formally rewrite the partition function (1.221) in a more compact form, which requires a single path integral only, governed by the formal *effective classical potential*, $V_{\mathrm{eff,cl}}(\mathbf{r}_0)$, instead of the entire Hamiltonian:

$$Z = \int_{-\infty}^{+\infty} \frac{\mathrm{d}\mathbf{r}_0}{\sqrt{2\pi\hbar^2\beta/m_0}} \exp[-\beta V_{\mathrm{eff,cl}}(\mathbf{r}_0)]. \tag{1.222}$$

The $\mathbf{r}_0$ variable represents the average position of all the possible quantum statistical paths on the imaginary temporal axis:

$$\mathbf{r}_0 \equiv \bar{\mathbf{r}} = \frac{1}{\hbar\beta} \int_0^{\hbar\beta} \mathrm{d}\tau\, \mathbf{r}(\tau). \tag{1.223}$$

In order to build up a formalism with a sufficient accuracy for the classical effective potential approximation, one has to consider a trial path integral, as a superposition of path integrals with harmonic potentials centered in different $\mathbf{r}_0$ positions, each one of them having its own trial frequency, $\Omega^2(\mathbf{r}_0)$.

Afterwards, the superposition and the respectively associated frequency will be chosen in the optimal way, so that the classical effective potential of the system should correspond to a quantum state as close as possible to that approximated by the effective potential.

Consequently, the trial quantum statistic partition function (Z_1) successively becomes:

$$Z_1 \equiv \int_{-\infty}^{+\infty} \frac{\mathrm{d}\mathbf{r}_0}{\sqrt{2\pi\hbar^2\beta/m_0}} \exp[-\beta W_1(\mathbf{r}_0)] \tag{1.224}$$

and the trial partition function appears now re-expressed in terms of the introduced trial potential W_1:

$$\begin{aligned} W_1(\mathbf{r}_0) = \frac{1}{\beta}\log\left\{\frac{\sinh[\hbar\beta\,\Omega(\mathbf{r}_0)/2]}{\hbar\beta\,\Omega(\mathbf{r}_0)/2}\right\} \\ + V_{a^2(\mathbf{r}_0)}(\mathbf{r}_0) - \frac{m_0}{2}\Omega^2(\mathbf{r}_0)a^2(\mathbf{r}_0) \end{aligned} \tag{1.225}$$

determined such that $W_1(\mathbf{r}_0)$ to correspond to the optimal state, i.e. the closest one to the classical effective potential.

$$V_{\mathrm{eff,cl}}(\mathbf{r}_0) \le W_1(\mathbf{r}_0) \tag{1.226}$$

The new introduced potential:

$$V_{a^2(\mathbf{r}_0)}(\mathbf{r}_0) = \int\limits_{-\infty}^{+\infty} \frac{\mathrm{d}\mathbf{r}_0'}{\sqrt{2\pi a^2(\mathbf{r}_0)}} V(\mathbf{r}_0') \exp\left[-\frac{(\mathbf{r}_0' - \mathbf{r}_0)^2}{2a^2(\mathbf{r}_0)}\right] \tag{1.227}$$

appears from the original potential, the $V(\mathbf{r}_0)$ one, by its expansion in the neighborhood of each effective event-point $\mathbf{r}_0$, as a Gaussian package with the width $a^2(\mathbf{r}_0)$. This modified smeared out potential (1.227) takes into consideration all the quantum statistic fluctuations on the evolution of the considered electronic system.

The introduced $a^2(\mathbf{r}_0)$ and $\Omega^2(\mathbf{r}_0)$ parameters fulfill the relations:

$$a^2(\mathbf{r}_0) = \frac{1}{m_0\beta\,\Omega^2(\mathbf{r}_0)}\left\{\frac{\hbar\beta\,\Omega(\mathbf{r}_0)}{2}\coth\left[\frac{\hbar\beta\Omega(\mathbf{r}_0)}{2}\right] - 1\right\} \tag{1.228}$$

$$\Omega^2(\mathbf{r}_0) = \frac{2}{m_0}\frac{\partial V_{a^2(\mathbf{r}_0)}(\mathbf{r}_0)}{\partial a^2(\mathbf{r}_0)} \tag{1.229}$$

The computation of the electronic density will be carried out within the Feynman-Kleinert-Putz *PI* formalism, by using the following expressions:

$$\rho_1(\mathbf{r}_0) = Z_1^{-1}\frac{1}{\sqrt{2\pi\hbar^2\beta/m_0}}\exp[-\beta\,W_1(\mathbf{r}_0)] \tag{1.230}$$

$$Z_1 = \frac{1}{\sqrt{2\pi\hbar^2\beta/m_0}}\int\limits_{-\infty}^{+\infty}\mathrm{d}\mathbf{r}_0\,\exp[-\beta\,W_1(\mathbf{r}_0)] \tag{1.231}$$

and where the path influence was comprised within the introduced Feynman centroid $\mathbf{r}_0$, see Eq. (1.223). It is worth noting that the electronic density (1.231) fulfills the normalization condition:

$$\int_{-\infty}^{+\infty} \rho_1(\mathbf{r}_0)\mathrm{d}\mathbf{r}_0 = 1 \tag{1.232}$$

as specific to conceptual quantum theory. However, relation (1.232) is also in agreement with the *Density Functional Theory* theorems as far as the evaluation of electronegativity and of the related quantities is under focus; it is worth noticing that electronegativity characterizes the whole system at the frontier limit, i.e. at the valence or to the outer electronic shell. Often, the effective electron can be added or released from the valence shell according with the electronegativity tendency describing the frontier shell. Therefore, the condition (1.232), used to characterize the effective valence electron behavior, is well justified.

However, it is worth noticing that, in general, through the density functional description by means of the path integrals the memory effects can be limited by imposing the so-called Markovian condition

$$\hbar\beta \to 0 \tag{1.233}$$

with the merit of canceling the low temperature quantum fluctuations by such a high temperature limit, which is nevertheless specific to chemical systems in their valence state (Putz 2012). Due to the temporal nature of the quantum statistical quantity $\hbar\beta \propto \Delta t$, the limit (1.233) corresponds also to the ultra-short correlation of the involved electrons with the applied external potential. This means that, since initially the free motion of the electrons in the absence of an external potential ($\Delta t = 0 \Leftrightarrow \beta = 0$) is assumed, as far as the external potential is then applied, an immediate orbit stabilization of the electronic system is reached ($\Delta t \to 0 \Leftrightarrow \beta \to 0$); in other words, the escape (unstable) paths are precluded. Finally, this limit introduces also *correlation effects* with the medium. Therefore, it is worth applying the limit (1.233) also to the *PI* Feynman-Kleinert results, see Eqs. (1.224)–(1.229). The smeared out potential (1.227), by changing the variable in such a way that:

$$z(\mathbf{r}'_0) = \frac{|\mathbf{r}'_0 - \mathbf{r}_0|}{\sqrt{2a^2(\mathbf{r}_0)}}, \quad \mathrm{d}z(\mathbf{r}'_0) = \frac{\mathrm{d}|\mathbf{r}'_0|}{\sqrt{2a^2(\mathbf{r}_0)}} \tag{1.234}$$

can be rewritten in terms of the so-called Wigner (equivalent with high temperature) expansion (Wigner 1932), of a high temperature limit (1.233), successively as:

$$
\begin{aligned}
V_{a^2}(\mathbf{r}_0) &= \frac{1}{\sqrt{2\pi\, a^2(\mathbf{r}_0)}} \int\limits_{-\infty}^{+\infty} V(\mathbf{r}_0') \exp\left[-\frac{(\mathbf{r}_0' - \mathbf{r}_0)^2}{2a^2(\mathbf{r}_0)}\right] \mathrm{d}\mathbf{r}_0' \\
&= \frac{1}{\sqrt{2\pi\, a^2(\mathbf{r}_0)}} \sqrt{2a^2(\mathbf{r}_0)} \int\limits_{-\infty}^{+\infty} V\left(\mathbf{r}_0 + \sqrt{2a^2(\mathbf{r}_0)}z\right) \exp\left(-z^2\right) \mathrm{d}z \\
&= \frac{1}{\sqrt{\pi}} \int\limits_{-\infty}^{+\infty} \left\{ \begin{array}{c} V(\mathbf{r}_0) + \sqrt{2a^2(\mathbf{r}_0)}zV'(\mathbf{r}_0) \\ + \frac{1}{2}(2a^2(\mathbf{r}_0))z^2 V''(\mathbf{r}_0) + \cdots \end{array} \right\} \exp\left(-z^2\right) \mathrm{d}z \\
&\cong \frac{1}{\sqrt{\pi}} \int\limits_{-\infty}^{+\infty} \left\{ \begin{array}{c} V(\mathbf{r}_0) \\ + \frac{1}{2}(2a^2(\mathbf{r}_0))z^2 V''(\mathbf{r}_0) \end{array} \right\} \exp[-z^2]\, \mathrm{d}z \\
&= V(\mathbf{r}_0) + \frac{1}{2} a^2(\mathbf{r}_0) V''(\mathbf{r}_0).
\end{aligned}
\tag{1.235}
$$

Now, within the same (1.233) limit, the parameters (1.227) and (1.229) also respectively become:

$$
a^2(\mathbf{r}_0) \cong \hbar^2 \frac{\beta}{12 m_0} \tag{1.236}
$$

$$
\Omega^2(\mathbf{r}_0) \cong \frac{1}{m_0} V''(\mathbf{r}_0) \tag{1.237}
$$

With Eqs. (1.235)–(1.237) back into the potential (1.225) one gets (Putz 2003):

$$
W_1(\mathbf{r}_0) \cong V(\mathbf{r}_0) + \frac{1}{\beta} \ln \left[\frac{\sinh\left(\frac{\hbar\beta}{2}\sqrt{\frac{V''(\mathbf{r}_0)}{m_0}}\right)}{\frac{\hbar\beta}{2}\sqrt{\frac{V''(\mathbf{r}_0)}{m_0}}} \right] \tag{1.238}
$$

from which it appears that the Feynman-Kleinert *PI* constrained-search algorithm in the Markovian limit provides an efficient recipe to compute electronic densities using only the external potential dependence.

However, the resulting W_1 Markovian potential (1.238) is next plugged into the limit (1.233). This last step agrees with the Parr and Yang approach, which has shown (Parr and Yang 1989) that the integral formulation of the Kohn-Sham (orbital) *DFT* arrives at the electronic density expression by performing the Wigner semi-classical expansion combined with the short time approximation (in β parameter). All the potential components around V can be formally interpreted as the *exchange-correlation PI potential* V_{XC}^{PI} of the medium. Even if this potential (1.238) can be expanded into higher orders, it will be here truncated at the second-order expansion, and yields (Putz 2003, 2009):

$$\begin{aligned} W_1(\mathbf{r}_0)_{\beta\to 0} &\cong V(\mathbf{r}_0)+\hbar^2\frac{\beta}{24m_0}V''(\mathbf{r}_0) \\ &= V_{a^2\to\frac{\beta}{12}}(\mathbf{r}_0) \\ &\equiv V(\mathbf{r}_0)+V_{XC}^{PI}(\mathbf{r}_0) \end{aligned} \tag{1.239}$$

in which the exchange-correlation *PI* potential of the medium,

$$V_{XC}^{PI}(\mathbf{r}_0)=\hbar^2\frac{\beta}{24m_0}V''(\mathbf{r}_0) \tag{1.240}$$

corrects the classical external potential V, this way specializing the Feynman-Kleinert formalism for further use and application in chemistry (see Chap. 4, Sect. 4.7.2).

1.6.3 Quantum Smeared Effects and the Stability of Matter

The intriguing role the smeared potential in special and the smearing effect in general play in optimization of the total energy and partition function of a quantum system opens the possibility of analyzing the “smearing” phenomenon of the quantum fluctuation in a more fundamental way (Putz 2009, 2016b).

I. First, it was noted that the smearing potential (1.227) appears as a Gaussian convolution of the applied potential, although modeling the evolution of a wave-packet under that potential; in other words, there appears the fundamental question whether the Gaussian and wave function “kernels” behave in a similar way throughout the smearing effect of quantum fluctuations; analytically, one would like to see whether there holds the smearing average equality:

$$\langle\exp(-\mathrm{i}kx)\rangle_{a^2(x_0)}\overset{?}{=}\left\langle\exp\left(-k^2x^2\right)\right\rangle_{a^2(x_0)}. \tag{1.241}$$

In order to check (1.241) one separately computes each of its sides separately by the aid of k-form

$$\begin{aligned}
V_{a^2(x_0)}(x_0) &= \int_{-\infty}^{+\infty} \frac{\mathrm{d}k}{2\pi} V(k) \exp\left[\mathrm{i}kx_0 - \frac{1}{2}a^2(x_0)k^2\right] \\
&= \int_{-\infty}^{+\infty} \frac{\mathrm{d}k}{2\pi} \int_{-\infty}^{+\infty} \mathrm{d}x V(x) \exp(-\mathrm{i}kx) \exp\left[\mathrm{i}kx_0 - \frac{1}{2}a^2(x_0)k^2\right] \\
&= \frac{1}{2\pi} \int_{-\infty}^{+\infty} \mathrm{d}x V(x) \exp\left[-\frac{(x-x_0)^2}{2a^2(x_0)}\right] \int_{-\infty}^{+\infty} \mathrm{d}k \exp\left[\left(\frac{x-x_0}{\sqrt{2}a(x_0)} - \mathrm{i}\frac{a(x_0)}{\sqrt{2}}k\right)^2\right] \\
&= \frac{1}{2\pi} \int_{-\infty}^{+\infty} \mathrm{d}x V(x) \exp\left[-\frac{(x-x_0)^2}{2a^2(x_0)}\right] \int_{-\infty}^{+\infty} \mathrm{d}k' \exp\left[-\frac{a^2(x_0)}{2}k'^2\right] \\
&= \frac{1}{\sqrt{2\pi a^2(x_0)}} \int_{-\infty}^{+\infty} \mathrm{d}x V(x) \exp\left[-\frac{(x-x_0)^2}{2a^2(x_0)}\right] \\
&\equiv \langle V(x) \rangle_{a^2(x_0)}
\end{aligned} \tag{1.242}$$

and gets successively the smearing average for wave function:

$$\begin{aligned}
\langle \exp(-\mathrm{i}kx) \rangle_{a^2(x_0)} &= \int_{-\infty}^{+\infty} \frac{\mathrm{d}k}{2\pi} \exp\left[-\mathrm{i}kx + \mathrm{i}kx_0 - \frac{1}{2}a^2(x_0)k^2\right] \\
&= \int_{-\infty}^{+\infty} \frac{\mathrm{d}k}{2\pi} \exp\left[-\mathrm{i}k(x-x_0) - \frac{1}{2}a^2(x_0)k^2\right] \\
&= \exp\left[-\frac{(x-x_0)^2}{2a^2(x_0)}\right] \int_{-\infty}^{+\infty} \frac{\mathrm{d}k}{2\pi} \exp\left\{-\frac{a^2(x_0)}{2}\left[k + \mathrm{i}\frac{x-x_0}{a^2(x_0)}\right]^2\right\} \\
&= \frac{1}{2\pi} \exp\left[-\frac{(x-x_0)^2}{2a^2(x_0)}\right] \int_{-\infty}^{+\infty} \mathrm{d}k' \exp\left\{-\frac{a^2(x_0)}{2}k'^2\right\} \\
&= \frac{1}{\sqrt{2\pi a^2(x_0)}} \exp\left[-\frac{(x-x_0)^2}{2a^2(x_0)}\right]
\end{aligned} \tag{1.243}$$

and respectively for the Gaussian packet:

$$\begin{aligned}
\left\langle \exp\left(-k^2x^2\right)\right\rangle_{a^2(x_0)} &= \int_{-\infty}^{+\infty} \frac{\mathrm{d}k}{2\pi} \exp\left[-k^2x^2 + \mathrm{i}kx_0 - \frac{1}{2}a^2(x_0)k^2\right] \\
&= \int_{-\infty}^{+\infty} \frac{\mathrm{d}k}{2\pi} \exp\left[-k^2\left(x^2 + \frac{a^2(x_0)}{2}\right) + \mathrm{i}kx_0\right] \\
&= \exp\left[-\frac{x_0^2}{4(x^2 + a^2(x_0)/2)}\right] \int_{-\infty}^{+\infty} \frac{\mathrm{d}k}{2\pi} \\
&\quad \times \exp\left\{-\left(x^2 + a^2(x_0)/2\right)\left[k - \mathrm{i}\frac{x_0}{2(x^2 + a^2(x_0)/2)}\right]^2\right\} \\
&= \frac{1}{2\pi} \exp\left[-\frac{x_0^2}{4(x^2 + a^2(x_0)/2)}\right] \int_{-\infty}^{+\infty} \mathrm{d}k' \\
&\quad \times \exp\left\{-\left(x^2 + a^2(x_0)/2\right)k'^2\right\} \\
&= \frac{1}{\sqrt{2\pi[2x^2 + a^2(x_0)]}} \exp\left[-\frac{x_0^2}{2(2x^2 + a^2(x_0))}\right].
\end{aligned} \tag{1.244}$$

Now to closely compare the expressions (1.243) and (1.244) the most elegant way is once more to make recourse to the smearing procedure, this time referring both to the entire paths and the Feynman centroid:

$$x_0 = \frac{1}{\hbar\beta} \int_0^{\hbar\beta} x(\tau)\mathrm{d}\tau. \tag{1.245}$$

To this end, the similar result

$$\begin{aligned}
&\left\langle \frac{m}{2}\Omega^2(x_0)(x - x_0)^2 \right\rangle_{a^2(x_0)} \\
&\quad = \frac{m}{2}\Omega^2(x_0) \frac{1}{\sqrt{2\pi a^2(x_0)}} \int_{-\infty}^{+\infty} \mathrm{d}x(x - x_0)^2 \exp\left[-\frac{(x - x_0)^2}{2a^2(x_0)}\right] \\
&\quad = \frac{m}{2}\Omega^2(x_0)a^2(x_0)
\end{aligned} \tag{1.246}$$

is here used explicitly as:

$$\left\langle (x - x_0)^2 \right\rangle_{a^2} = a^2. \tag{1.247}$$

It allows the additional similar relationships:

$$\langle x^2 \rangle_{a^2} = \langle x_0^2 \rangle_{a^2} = \frac{a^2}{2} \tag{1.248}$$

due to the symmetry of the smearing average formula (1.242) at the interchange $x \leftrightarrow x_0$, while the mixed term of (1.247) expansion vanishes, $\langle x x_0 \rangle_{a^2(x_0)} = 0$, in any path representation. With these, practically we can reconsider Eqs. (1.247) and (1.248) by performing the formal equivalences

$$(x - x_0)^2 \approx a^2, \quad x^2 \approx \frac{a^2}{2}, \quad x_0^2 \approx \frac{a^2}{2} \tag{1.249}$$

yielding:

$$\langle \exp(-\mathrm{i}kx) \rangle_{a^2} \approx \frac{1}{\sqrt{2\pi a^2}} \exp\left[-\frac{1}{2}\right] \tag{1.250}$$

$$\begin{aligned} \left\langle \exp\left(-k^2 x^2\right) \right\rangle_{a^2} &\approx \frac{1}{\sqrt{4\pi a^2}} \exp\left[-\frac{1}{8}\right] \\ &= \langle \exp(-\mathrm{i}kx) \rangle_{a^2} \frac{\exp(3/8)}{\sqrt{2}} \end{aligned} \tag{1.251}$$

Since the difference between these expressions is numerically proportional with the factor

$$\frac{\exp(3/8)}{\sqrt{2}} \cong 1.029 \tag{1.252}$$

they can be considered as identical in quantum smearing effects and Eq. (1.241) as valid.

Yet, the quantum identity between the plane-wave and Gaussian packet has profound quantum implications, revealing for instance the de Broglie–Born identity in Gaussian normalization of the de Broglie moving wave-packet. It may express as well the observational Gaussian character of the wave function evolution in Hilbert space. Finally, and very importantly, it leads to *explanation* of Bohr's first postulate, i.e. it is able to explain the stationary wave on orbits under singular (Coulombic) potential thus explaining the matter stabilization on a rigorous quantum base, rather than admitting it by the power of a postulate. This is next to be proved (Feynman and Kleinert 1986; Kleinert 2004; Putz 2009).

II. Let us consider a quantum system evolving under the influence of the Yukawa potential, as a generalization of the Coulomb interaction, available also in the subnuclear world:

$$V_{Yuk}(r) = \frac{A}{r}\exp(-\alpha r), \quad r = x - x_0 \tag{1.253}$$

which goes to the celebrated hydrogen Coulomb central potential in the limit:

$$\lim_{\substack{\alpha \to 0 \\ A = -e_0^2}} V_{Yuk}(r) = V_H(r) = -\frac{e_0^2}{r}, \quad e_0^2 = -\frac{e^2}{4\pi\varepsilon_0}. \tag{1.254}$$

Now, we would like to investigate the smeared version of the Yukawa potential (1.253). In 3D toward radial formulation the general definition (1.242) specializes as:

$$\begin{aligned} \langle V_{Yuk}(r = x - x_0)\rangle_{a^2} &= A4\pi \int_0^{+\infty} \frac{r^2 \mathrm{d}r}{\left(\sqrt{2\pi a^2}\right)^3} \frac{\mathrm{e}^{-\alpha r}}{r} \exp\left[-\frac{(x - x_0)^2}{2a^2}\right] \\ &= A2\pi \mathrm{e}^{\alpha x_0} \int_0^{+\infty} \frac{\mathrm{d}(r^2)}{\left(\sqrt{2\pi a^2}\right)^3} \mathrm{e}^{-\alpha x} \exp\left[-\frac{r^2}{2a^2}\right] \end{aligned} \tag{1.255}$$

In the last expression one can recognize the squared integration variable, of the same nature as fluctuation width, see Eq. (1.249) with $r = x - x_0$, so that the passage to integration upon the variable a^2 seems natural, yet meaning that the path-dependent terms become smeared respecting the fluctuations, and the integration (lower) limit changes accordingly:

$$\langle V_{Yuk}(r_0)\rangle_{a^2} = A2\pi \langle \mathrm{e}^{\alpha x_0}\rangle_{a^2} \int_{a^2}^{+\infty} \frac{\mathrm{d}(\tilde{a}^2)}{\left(\sqrt{2\pi \tilde{a}^2}\right)^3} \langle \mathrm{e}^{-\alpha x}\rangle_{\tilde{a}^2} \mathrm{e}^{-\frac{r_0^2}{2\tilde{a}^2}}. \tag{1.256}$$

In this new integral form only one smeared term is truly of the compulsory form (1.243), namely

$$\langle \mathrm{e}^{-\alpha x_0}\rangle_{a^2} = \langle \exp[-\mathrm{i}(\mathrm{i}\alpha)x_0]\rangle_{a^2} \cong \left\langle \exp\left[-(\mathrm{i}\alpha)^2 x_0^2\right]\right\rangle_{a^2} \tag{1.257}$$

where also the proved identity (1.241) was considered upon it. Yet, the Eq. (1.257) may transformed by the application of the Jensen-Peierls equality limit

$$\langle \exp[O] \rangle \geq \exp[\langle O \rangle] \tag{1.258}$$

to yield

$$\langle \mathrm{e}^{-\alpha x_0} \rangle_{a^2} \cong \left\langle \exp\left[\alpha^2 x_0^2\right] \right\rangle_{a^2} \approx \exp\left[\alpha^2 \left\langle x_0^2 \right\rangle_{a^2}\right] = \exp\left(\alpha^2 a^2/2\right) \tag{1.259}$$

when the smeared rules (1.248) are counted as well. The other similar term in (1.256) is, however, evaluated by the approximated inverse identity:

$$\langle \mathrm{e}^{\alpha x} \rangle_{\tilde{a}^2} \cong \frac{1}{\langle \mathrm{e}^{-\alpha x} \rangle_{\tilde{a}^2}} \cong \exp\left(-\alpha^2 \tilde{a}^2/2\right). \tag{1.260}$$

However, based on the unconnected version of the second-order Wick cumulant

$$\langle \mathrm{e}^{\alpha x} \rangle_{\tilde{a}^2} \langle \mathrm{e}^{-\alpha x} \rangle_{\tilde{a}^2} \cong \langle \mathrm{e}^{\alpha x} \mathrm{e}^{-\alpha x} \rangle_{\tilde{a}^2} = \langle 1 \rangle_{\tilde{a}^2} = 1 \tag{1.261}$$

with expressions (1.259) and (1.260) back into the smeared Yukawa potential (1.256) it becomes:

$$\langle V_{Yuk}(r_0) \rangle_{a^2} = A 2\pi\, \mathrm{e}^{\frac{\alpha^2 a^2}{2}} \int_{a^2}^{+\infty} \frac{\mathrm{d}(\tilde{a}^2)}{\left(\sqrt{2\pi \tilde{a}^2}\right)^3} \mathrm{e}^{-\frac{\alpha^2 \tilde{a}^2}{2} - \frac{r_0^2}{2\tilde{a}^2}}. \tag{1.262}$$

Now, through considering the variable exchange under the integral:

$$\zeta = \frac{r_0}{\sqrt{2\tilde{a}^2}} \tag{1.263}$$

there result the following transformations:

$$\tilde{a}^2 = \frac{r_0^2}{2\zeta^2}; \quad \frac{\mathrm{d}(\tilde{a}^2)}{\left(\sqrt{\tilde{a}^2}\right)^3} = -\frac{2\sqrt{2}}{r_0} \mathrm{d}\zeta \tag{1.264}$$

so that the smeared potential (1.262) is finally cast as:

$$\langle V_{Yuk}(r_0) \rangle_{a^2} = A \frac{\exp(\alpha^2 a^2/2)}{r_0} \frac{2}{\sqrt{\pi}} \int_0^{r_0/\sqrt{2a^2}} \mathrm{d}\zeta \, \exp\left[-\left(\zeta^2 + \frac{\alpha^2 r_0^2}{4\zeta^2}\right)\right] \tag{1.265}$$

which has no longer singularity at origin, since the integral in (1.265) is behaving like its integration interval for the limit $r_0 \to 0$, which gives:

$$\langle V_{Yuk}(0)\rangle_{a^2} = A\frac{2\,\exp(\alpha^2 a^2/2)}{\sqrt{2\pi a^2}} \tag{1.266}$$

Now, it is clear that under the Coulombic limit (1.254) the resulting atomic (say for the hydrogen case) smeared effect leaves it with the form:

$$\langle V_{\mathrm{H}}(r_0)\rangle_{a^2} = -\frac{e_0^2}{r_0}\frac{2}{\sqrt{\pi}}\int\limits_0^{r_0/\sqrt{2a^2}} \mathrm{d}\zeta\,\exp\left(-\zeta^2\right) = -\frac{e_0^2}{r_0}\mathrm{erf}\left(r_0/\sqrt{2a^2}\right) \tag{1.267}$$

while its value on origin is of finite value:

$$\langle V_{\mathrm{H}}(0)\rangle_{a^2} = -\frac{2e_0^2}{\sqrt{2\pi a^2}} \tag{1.268}$$

thus assuring (and explaining) why the atomic electron(s) do not fall onto the nucleus.

Therefore the smearing procedure plays a kind of renormalization role in transforming singular potential in finite interactions by means of quantum fluctuation effects. Such a picture strongly advocates for powerful path integral formalism in general and for that of Feynman-Kleinert in particular since it explicitly accounts for the fluctuation width in optimizing the quantum equilibrium states. Nevertheless, it is worth particularizing the Feynman-Kleinert formalism to the ground and excited states cases to better capture its realization and limits.

1.6.4 Ground State ($\beta \to \infty$, T $\to$ 0 K) Case

The basic ground state conditions in terms of thermodynamic factor (β) or the temperature (T),

$$\beta \to \infty \Leftrightarrow T \to 0 \tag{1.269}$$

aim to bring the Feynman-Kleinert formalism, through its working potential (Feynman and Kleinert 1986):

$$W_{\mathrm{FK}}(x_0) = \frac{1}{\beta}\ln\left[\frac{\sinh(\hbar\beta\Omega(x_0)/2)}{\hbar\beta\Omega(x_0)/2}\right] + V_{a^2(x_0)}(x_0) - \frac{m}{2}\Omega^2(x_0)a^2(x_0) \tag{1.270}$$

to the variational ground state as usually provided by the quantum variational principle. For this purpose it will be first specialized within the general limit (1.269) and then tested for the paradigmatic hydrogen ground state case for investigating the accuracy of the formalism itself (Putz 2009, 2016a).

As such, the components of the Feynman-Kleinert potential (1.270) have the ground state limits:

$$\begin{aligned}&\lim_{\beta\to\infty}\left\{\frac{1}{\beta}\ln\left[\frac{\sinh(\hbar\beta\Omega(x_0)/2)}{\hbar\beta\Omega(x_0)/2}\right]\right\}\\&=\frac{\hbar\Omega}{2}\lim_{\beta\to\infty}\frac{\cosh(\hbar\beta\Omega(x_0)/2)}{\sinh(\hbar\beta\Omega(x_0)/2)}-\lim_{\beta\to\infty}\frac{1}{\beta}\\&=\frac{\hbar\Omega}{2}\end{aligned}\tag{1.271}$$

which recognizes the ground state of harmonic motion of trial fluctuations, while the ground state of the fluctuation width (1.228) reads as

$$\begin{aligned}\lim_{\beta\to\infty}a^2(x_0)&=\lim_{\beta\to\infty}\left\{\frac{1}{m\beta\Omega^2}\left[\frac{\hbar\beta\Omega}{2}\coth\left(\frac{\hbar\beta\Omega}{2}\right)-1\right]\right\}\\&=\frac{\hbar}{2m\Omega}\lim_{\beta\to\infty}\frac{\cosh(\hbar\beta\Omega(x_0)/2)}{\sinh(\hbar\beta\Omega(x_0)/2)}-\lim_{\beta\to\infty}\frac{1}{m\beta\Omega^2}\\&=\frac{\hbar}{2m\Omega}\end{aligned}\tag{1.272}$$

from where also the trial fluctuations frequency springs as:

$$\lim_{\beta\to\infty}\Omega=\frac{\hbar}{2ma^2(x_0)}.\tag{1.273}$$

Considering the relations (1.272) and (1.273) yields for the working general effective-classical approximation potential (1.270) the general ground state limit:

$$\begin{aligned}W_{\mathrm{FK}}^{T\to0}(x_0)&=\lim_{\beta\to\infty}\left\{\begin{array}{c}\frac{1}{\beta}\ln\left[\frac{\sinh(\hbar\beta\Omega(x_0)/2)}{\hbar\beta\Omega(x_0)/2}\right]\\-\frac{m}{2}\Omega^2(x_0)a^2(x_0)\end{array}\right\}+V_{a^2(x_0)}^{T\to0}(x_0)\\&=\frac{\hbar\Omega}{4}+V_{a^2(x_0)}^{T\to0}(x_0)\\&=\frac{\hbar^2}{8ma^2}+V_{a^2(x_0)}^{T\to0}(x_0)\end{aligned}\tag{1.274}$$

with the ground state smeared out potential remaining for individuation for a given problem. Very interestingly, the expression (1.274) entirely corresponds to the smeared out effect applied on the ordinary quantum Hamiltonian:

$$\widehat{H} = -\frac{\hbar^2}{2m}\partial_x^2 + V(x) \tag{1.275}$$

which one can immediately check out by applying the general smearing averaging definition (1.242) on it:

$$\begin{aligned}
\left\langle \widehat{H} \right\rangle_{a^2(x_0)} &= \frac{1}{\sqrt{2\pi a^2(x_0)}} \int_{-\infty}^{+\infty} \mathrm{d}x \left[-\frac{\hbar^2}{2m}\partial_x^2 + V(x)\right] \exp\left[-\frac{(x-x_0)^2}{2a^2(x_0)}\right] \\
&= -\frac{\hbar^2}{2m}\frac{1}{\sqrt{2\pi a^2(x_0)}} \int_{-\infty}^{+\infty} \mathrm{d}x \left\{\frac{\partial^2}{\partial x^2}\exp\left[-\frac{(x-x_0)^2}{2a^2(x_0)}\right]\right\} + V_{a^2(x_0)}^{T\to 0}(x_0) \\
&= -\frac{\hbar^2}{2m}\frac{1}{\sqrt{2\pi a^2(x_0)}} \int_{-\infty}^{+\infty} \mathrm{d}x \left\{\left[\frac{(x-x_0)^2}{2a^2(x_0)} - 1\right] \exp\left[-\frac{(x-x_0)^2}{2a^2(x_0)}\right]\right\} \\
&\quad + V_{a^2(x_0)}^{T\to 0}(x_0) \\
&= \frac{\hbar^2}{8ma^2} + V_{a^2(x_0)}^{T\to 0}(x_0).
\end{aligned} \tag{1.276}$$

The identity between expressions (1.274) and (1.276) presents the important idea that the smearing operation produces in fact the average of quantum fluctuation for the ground state equilibrium. For the Coulomb interaction, say on the hydrogen, either expression produces the working form

$$W_{\mathrm{FK-H}}^{T\to 0}(x_0) = \left\langle \widehat{H}_{\mathrm{H}} \right\rangle_{a^2(x_0)} = \frac{3\hbar^2}{8ma^2} - \frac{2e_0^2}{\sqrt{2\pi a^2}} \tag{1.277}$$

where the 3D version of the kinetic term of (1.276) was here considered aside the smearing out potential in the origin (1.268) to produce the form ready for ordinary minimization respecting the fluctuation width:

$$\frac{\partial}{\partial a^2(x_0)}\left\langle \widehat{H}_{\mathrm{H}} \right\rangle_{a^2(x_0)} = 0. \tag{1.278}$$

The solution of Eq. (1.278) with the form (1.277) produces the optimum width for quantum fluctuations:

$$a_{\mathrm{FK}}^{\mathrm{opt}} = \frac{3\hbar^2\sqrt{2\pi}}{8me_0^2} \tag{1.279}$$

which, in terms of the standard first Bohr radius

$$a_0 = \frac{\hbar^2}{me_0^2} \tag{1.280}$$

reads as

$$a_{\mathrm{FK}}^{\mathrm{opt}} = \sqrt{\frac{9\pi}{32}}a_0 \cong 0.94a_0 \tag{1.281}$$

thus producing only a 6% error in predicting the localization for the stabilization of electronic ground state orbit closer to the nucleus respecting the exact Bohr-Schrödinger solution. However, the predicted approximated ground state energy error is a bit higher due to the energy dependency

$$\begin{aligned} E_{\mathrm{FK-H}}^{\min} &= \left\langle \widehat{H}_{\mathrm{H}} \right\rangle_{a^2(x_0)} \left(a_{\mathrm{FK}}^{\mathrm{opt}}\right) \\ &= -\frac{e_0^2}{\sqrt{2\pi}a_{\mathrm{FK}}^{\mathrm{opt}}} = -\frac{8}{3\pi}\left(\frac{e_0^2}{2a_0}\right) = \frac{8}{3\pi}E_0^{\mathrm{H}} \cong 0.84E_0^{\mathrm{H}} \end{aligned} \tag{1.282}$$

this way lying about 16% higher than the exact ground state of the hydrogen atom.

Such a "universal" quantum statistical picture of equilibrium is hard to find in quantum theory, at the same level of elegance, analyticity, and complexity (Dirac 1944; Duru and Kleinert 1979, 1982; Blinder 1993; Kleinert 1996).

1.7 Free and Observed Quantum Evolution: Extended Heisenberg Uncertainly Relationship (HUR) by Path Integrals

Beside the stability of matter, the duality versus complementarity of matter's nature, either as wave or particle, and their uncertainty, remains another "big challenge" of quantum mechanics in general, and of matter structure in particular. Path integral formalism offers, nevertheless, a unique opportunity to treat the Heisenberg uncertainty relationship, and even allowing its extension so that both free and observed quantum evolutions can be described in quantum terms (Putz 2010b, 2016a, b).

1.7.1 HUR by Periodic Paths

Since its inception, the Heisenberg Uncertainty Relationship (HUR) (Heisenberg 1927) has been one of the most fascinating and controversial issues of quantum mechanics. Under its customary presentation

$$\Delta x \Delta p \geq \frac{\hbar}{2} \tag{1.283}$$

as independently proved by Robertson and Schrodinger (Robertson 1929; Schrödinger 1930) working out the standard deviation of coordinate (x) and momentum (p)

$$\Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2}, \quad \Delta p = \sqrt{\langle p^2 \rangle - \langle p \rangle^2} \tag{1.284}$$

it was eventually criticized as being no more than the experimental realization of the operatorial (non-)commutation relation $[x, p] = \mathrm{i}\hbar$ that implicitly contains the incompatibility between the coordinate and momentum spaces (Ozawa 2002, 2003a, b).

Here, the philosophy is to introduce appropriately the quantum fluctuation information $a = a(x_{0)}$ respecting the average of the observed coordinate (x_0), by the Feynman integration rule founded in the ordinary quantum average [Eq. (1.285)]

$$\langle f \rangle_{a^2(x_0)} = \int_{-\infty}^{+\infty} \mathrm{d}x \psi^*\left(x, a^2(x_0)\right) f \psi\left(x, a^2(x_0)\right) \tag{1.285}$$

for the normalized Gaussian wave function [Eq. (1.286)]

$$\psi\left(x, a^2(x_0)\right) = \frac{1}{\left[2\pi a^2(x_0)\right]^{1/4}} \exp\left[-\frac{(x - x_0)^2}{4a^2(x_0)}\right] \tag{1.286}$$

recovering the *de Broglie wave-packet* (Feynman and Kleinert 1986; de Broglie 1987) upon which a quantum property may be estimated.

It is obvious that Eqs. (1.285) and (1.286) fulfill the necessary (natural) condition according which the average of the coordinate over the quantum fluctuations recovers the observed quantity of the Feynman centroid, based on simple Poisson integration rules

$$
\begin{aligned}
\langle x\rangle_{a^2(x_0)} &= \frac{1}{\sqrt{2\pi a^2(x_0)}}\int_{-\infty}^{+\infty} \mathrm{d}x[x-x_0+x_0]\ \exp\left[-\frac{(x-x_0)^2}{2a^2(x_0)}\right]\\
&= \underbrace{\frac{1}{\sqrt{2\pi a^2(x_0)}}\int_{-\infty}^{+\infty} \mathrm{d}x[x-x_0]\ \exp\left[-\frac{(x-x_0)^2}{2a^2(x_0)}\right]}_{0}\\
&\quad+\underbrace{\frac{1}{\sqrt{2\pi a^2(x_0)}}\int_{-\infty}^{+\infty} \mathrm{d}x[x_0]\ \exp\left[-\frac{(x-x_0)^2}{2a^2(x_0)}\right]}_{\langle x_0\rangle_{a^2(x_0)}} \qquad (1.287)\\
&= x_0\underbrace{\frac{1}{\sqrt{2\pi a^2(x_0)}}\int_{-\infty}^{+\infty} \mathrm{d}x\ \exp\left[-\frac{(x-x_0)^2}{2a^2(x_0)}\right]}_{1} = x_0;\\
\langle x\rangle_{a^2(x_0)} &= \langle x_0\rangle_{a^2(x_0)} = x_0.
\end{aligned}
$$

The next test is about the validity of Eq. (1.283)—the HUR itself. To this end with the aid of the Feynman-de Broglie rule (1.286) the quantities of Eq. (1.284) are computed:

$$\left\langle (x-x_0)^2\right\rangle_{a^2(x_0)} = \frac{1}{\sqrt{2\pi a^2(x_0)}}\int_{-\infty}^{+\infty} \mathrm{d}x(x-x_0)^2 \exp\left[-\frac{(x-x_0)^2}{2a^2(x_0)}\right] = a^2. \qquad (1.288)$$

Then, through combining the expression

$$a^2 = \left\langle (x-x_0)^2\right\rangle_{a^2(x_0)} = \left\langle x^2\right\rangle_{a^2(x_0)} - 2\langle x\rangle_{a^2(x_0)}\langle x_0\rangle_{a^2(x_0)} + \left\langle x_0^2\right\rangle_{a^2(x_0)} \qquad (1.289)$$

with the prescription (1.287) we are left with the actual result

$$\left\langle x^2\right\rangle_{a^2(x_0)} = a^2 + x_0^2 \qquad (1.290)$$

which, when plugged into the basic Eq. (1.284) alongside the information of Eq. (1.287), yields the coordinate dispersion

$$\Delta x = a \qquad (1.291)$$

featuring it in a direct relationship with the quantum fluctuation width.

In the same manner, the evaluations for the integrals of the first and second orders of kinetic moment unfold as

$$\begin{aligned}\langle p\rangle_{a^2(x_0)} &= \frac{1}{\sqrt{2\pi a^2(x_0)}}\int_{-\infty}^{+\infty} \mathrm{d}x\, \exp\left[-\frac{(x-x_0)^2}{4a^2(x_0)}\right](-\mathrm{i}\hbar\partial_x)\exp\left[-\frac{(x-x_0)^2}{4a^2(x_0)}\right]\\ &= \frac{\mathrm{i}\hbar}{2a^2(x_0)}\frac{1}{\sqrt{2\pi a^2(x_0)}}\int_{-\infty}^{+\infty} \mathrm{d}x(x-x_0)\, \exp\left[-\frac{(x-x_0)^2}{2a^2(x_0)}\right] = 0\end{aligned} \tag{1.292}$$

$$\begin{aligned}\langle p^2\rangle_{a^2(x_0)} &= \frac{1}{\sqrt{2\pi a^2(x_0)}}\int_{-\infty}^{+\infty} \mathrm{d}x\, \exp\left[-\frac{(x-x_0)^2}{4a^2(x_0)}\right]\left(-\hbar^2\partial_x^2\right)\exp\left[-\frac{(x-x_0)^2}{4a^2(x_0)}\right]\\ &= -\frac{\hbar^2}{a^2(x_0)\sqrt{2\pi a^2(x_0)}}\int_{-\infty}^{+\infty} \mathrm{d}x\left[\frac{(x-x_0)^2}{4a^2(x_0)}-\frac{1}{2}\right]\exp\left[-\frac{(x-x_0)^2}{2a^2(x_0)}\right] = \frac{\hbar^2}{4a^2}\end{aligned} \tag{1.293}$$

while when plugging them into Eq. (1.284) produce the momentum dispersion expression

$$\Delta p = \frac{\hbar}{2a}. \tag{1.294}$$

It is worth noting that from the coordinate and momentum dispersions, Eqs. (1.291) and (1.294), it appears that the dependency of the Planck constant is restricted only to the latter, whereas the quantum fluctuations are present in both, in a direct and inverse manner, respectively.

However, Heisenberg uncertainty as the exact specialization of Eq. (1.283) is re-obtained when multiplying the expressions (1.291) and (1.294), i.e.

$$\Delta x\Delta p = \frac{\hbar}{2} \tag{1.295}$$

this way resembling in an elegant manner the previous result of statistical complementary observables of position and momentum (Hall 2001).

1.7.2 *Wave-Particle Ratio Function*

The present algorithm may be specialized to the analysis of the wave-particle duality. This is accomplished by means of considering further averages over the quantum fluctuations for the mathematical objects $\exp(-\mathrm{i}kx)$ and $\exp(-k^2x^2)$ that are most suited to represent the waves and *particles*, due to their obvious shapes, respectively. By employing the Fourier k-transformation as resulted from the de Broglie packet (1.286), we have successively (Putz 2010b, 2016b):

$$\begin{aligned}
\langle f(x,k)\rangle_{a^2(x_0)} &= \frac{1}{\sqrt{2\pi a^2(x_0)}}\int\limits_{-\infty}^{+\infty} \mathrm{d}x f(x,k)\ \exp\left[-\frac{(x-x_0)^2}{2a^2(x_0)}\right]\\
&= \frac{1}{2\pi}\int\limits_{-\infty}^{+\infty} \mathrm{d}x f(x,k)\ \exp\left[-\frac{(x-x_0)^2}{2a^2(x_0)}\right]\int\limits_{-\infty}^{+\infty} \mathrm{d}k'\ \exp\left[-\frac{a^2(x_0)}{2}k'^2\right]\\
&= \frac{1}{2\pi}\int\limits_{-\infty}^{+\infty} \mathrm{d}x f(x,k)\ \exp\left[-\frac{(x-x_0)^2}{2a^2(x_0)}\right]\int\limits_{-\infty}^{+\infty} \mathrm{d}k\\
&\quad\times\ \exp\left[\left(\frac{x-x_0}{\sqrt{2}a(x_0)}-\mathrm{i}\frac{a(x_0)}{\sqrt{2}}k\right)^2\right]\\
&= \int\limits_{-\infty}^{+\infty}\frac{\mathrm{d}k}{2\pi}\int\limits_{-\infty}^{+\infty} \mathrm{d}x f(x,k)\ \exp(-\mathrm{i}kx)\ \exp\left[\mathrm{i}kx_0-\frac{1}{2}a^2(x_0)k^2\right]\\
&= \int\limits_{-\infty}^{+\infty}\frac{\mathrm{d}k}{2\pi}f(k)\ \exp\left[\mathrm{i}kx_0-\frac{1}{2}a^2(x_0)k^2\right].
\end{aligned} \tag{1.296}$$

With the rule (1.296) one may describe the average behavior of the wave and particle, respectively, as

$$
\begin{aligned}
\langle \exp(-\mathrm{i}kx)\rangle_{a^2(x_0)} &= \int\limits_{-\infty}^{+\infty} \frac{\mathrm{d}k}{2\pi} \exp\left[-\mathrm{i}kx + \mathrm{i}kx_0 - \frac{1}{2}a^2(x_0)k^2\right] \\
&= \int\limits_{-\infty}^{+\infty} \frac{\mathrm{d}k}{2\pi} \exp\left[-\mathrm{i}k(x - x_0) - \frac{1}{2}a^2(x_0)k^2\right] \\
&= \exp\left[-\frac{(x-x_0)^2}{2a^2(x_0)}\right] \int\limits_{-\infty}^{+\infty} \frac{\mathrm{d}k}{2\pi} \exp\left\{-\frac{a^2(x_0)}{2}\left[k + \mathrm{i}\frac{x-x_0}{a^2(x_0)}\right]^2\right\} \\
&= \frac{1}{2\pi} \exp\left[-\frac{(x-x_0)^2}{2a^2(x_0)}\right] \int\limits_{-\infty}^{+\infty} \mathrm{d}k' \exp\left\{-\frac{a^2(x_0)}{2}k'^2\right\} \\
&= \frac{1}{\sqrt{2\pi a^2(x_0)}} \exp\left[-\frac{(x-x_0)^2}{2a^2(x_0)}\right]
\end{aligned}
\tag{1.297}
$$

and

$$
\begin{aligned}
\left\langle \exp\left(-k^2x^2\right)\right\rangle_{a^2(x_0)} &= \int\limits_{-\infty}^{+\infty} \frac{\mathrm{d}k}{2\pi} \exp\left[-k^2x^2 + \mathrm{i}kx_0 - \frac{1}{2}a^2(x_0)k^2\right] \\
&= \int\limits_{-\infty}^{+\infty} \frac{\mathrm{d}k}{2\pi} \exp\left[-k^2\left(x^2 + \frac{a^2(x_0)}{2}\right) + \mathrm{i}kx_0\right] \\
&= \exp\left[-\frac{x_0^2}{4(x^2 + a^2(x_0)/2)}\right] \int\limits_{-\infty}^{+\infty} \frac{\mathrm{d}k}{2\pi} \\
&\quad \times \exp\left\{-\left(x^2 + \frac{a^2(x_0)}{2}\right)\left[k - \mathrm{i}\frac{x_0}{2(x^2 + a^2(x_0)/2)}\right]^2\right\} \\
&= \frac{1}{2\pi} \exp\left[-\frac{x_0^2}{4(x^2 + a^2(x_0)/2)}\right] \int\limits_{-\infty}^{+\infty} \mathrm{d}k' \\
&\quad \times \exp\left\{-\left(x^2 + \frac{a^2(x_0)}{2}\right)k'^2\right\} \\
&= \frac{1}{\sqrt{2\pi[2x^2 + a^2(x_0)]}} \exp\left[-\frac{x_0^2}{2(2x^2 + a^2(x_0))}\right].
\end{aligned}
\tag{1.298}
$$

It is worth observing that the practical rule (1.296) is indeed consistent since recovering in (1.297) the kernel of the Gaussian de Broglie wave-packet—for the *wave* behavior of a quantum object—as expected. Consequently, the result (1.298) is a viable analytical expression for characterizing the complementary *particle* nature of the quantum manifestation of an object.

Next, the ratio of Eqs. (1.297) and (1.298) is formed:

$$\begin{aligned}\frac{\text{Particle}}{\text{Wave}} &\equiv \frac{\left\langle \exp(-k^2x^2)\right\rangle_{a^2(x_0)}}{\left\langle \exp(-\mathrm{i}kx)\right\rangle_{a^2(x_0)}}\\ &= \sqrt{\frac{a^2(x_0)}{2x^2+a^2(x_0)}}\exp\left[-\frac{x_0^2}{2(2x^2+a^2(x_0))}+\frac{x^2-2xx_0+x_0^2}{2a^2(x_0)}\right]\end{aligned} \tag{1.299}$$

giving the working tool in estimating the particle-to-wave content for a quantum object by considering various coordinate average information.

1.7.3 Extended HUR

We would like to identify the general quantum fluctuation conditions, i.e. whether the HUR is valid and when it is eventually extended. We already noted that, whereas relations (1.292)–(1.294) fix the momentum dispersion computation, the evaluation of the coordinate dispersion has more freedom in its internal working machinery, namely:

(i) considering the condition (1.287) as an invariant of the measurement theory since it assures the connection between the average over quantum fluctuation of the coordinate and the observed averaged coordinate;
(ii) specializing the quantum (average) relationship (1.289) for the condition given by Eq. (1.287);
(iii) obtaining the average of the second-order coordinate (1.290);
(iv) combining steps (i) and (ii) by computing the coordinate dispersion Δx as given by Eq. (1.284);
(v) and making the *formal* identity of the coordinate quantities in Eq. (1.299) with the respective values as furnished by steps (i)–(iii) of the above coordinate averages' algorithm

$$x_0 \leftrightarrow \langle x_0\rangle_{a^2(x_0)},\quad x \leftrightarrow \langle x\rangle_{a^2(x_0)},\quad x_0^2 \leftrightarrow \left\langle x_0^2\right\rangle_{a^2(x_0)},\quad x^2 \leftrightarrow \left\langle x^2\right\rangle_{a^2(x_0)} \tag{1.300}$$

since they nevertheless emerge from quantum average operations (measurements).

Now we are ready to present the two possible scenarios for quantum evolutions along the associate HUR realization and the wave-particle behavior.

For the case of observed quantum evolution, the averaged observed position is considered in relation with the quantum fluctuation by the general relationship

$$\langle x \rangle_{a^2(x_0)} = \langle x_0 \rangle_{a^2(x_0)} = x_0 = na, \quad n \in \Re \tag{1.301}$$

implying that the average of the second-order of the Feynman centroid looks like

$$\left\langle x_0^2 \right\rangle_{a^2(x_0)} = n^2 a^2. \tag{1.302}$$

When (1.301) and (1.302) are introduced into the identity (1.290), according with step (iii) above, the actual average of the second-order coordinate is obtained:

$$\left\langle x^2 \right\rangle_{a^2(x_0)} = a^2\left(1 + n^2\right). \tag{1.303}$$

Not surprisingly, when further combining relations (1.301) and (1.303) in computing the coordinate dispersion of Eq. (1.284), i.e. fulfilling step (iv) above, one regains the value of Eq. (1.291) that recovers in its turn the standard HUR no matter how much the quantum fluctuation is modulated by the factor *n*. However, the P(article)/W(ave) ratio of Eq. (1.299) takes the form

$$\left(\frac{\text{Particle}}{\text{Wave}}\right)_{\substack{\text{Observed}\\ \text{Evolution}}} = \frac{1}{\sqrt{3 + 2n^2}} \exp\left(\frac{3 + n^2}{6 + 4n^2}\right) = \begin{cases} 0.952 & \ldots \quad n = 0 \\ 0.667 & \ldots \quad n = 1 \\ 0 & \ldots \quad n \to \infty \end{cases} \tag{1.304}$$

showing that the wave-particle duality is indeed a reality that can be manifested in various particle-wave (complementary) proportions—yet never reaching perfect equivalence (the ratio approaching unity). Moreover, because $(\mathrm{P/W})_{\mathrm{Obs}} < 1$, it appears that the general behavior of a quantum object is merely manifested as a wave when observed, from which arises the efficacy of spectroscopic methods in assessing the quantum properties of matter.

Moving to the treatment of the *free quantum evolution*, the average of the first-order coordinate is vanishing

$$\langle x \rangle_{a^2(x_0)} = \langle x_0 \rangle_{a^2(x_0)} = x_0 = 0 \tag{1.305}$$

since the quantum object, although existing, is not observed (see the spontaneous broken symmetry mechanism in Chap. 4).

The relation with quantum fluctuation is apparent by the average of the second order of the Feynman centroid—considered under the form

$$\left\langle x_0^2 \right\rangle_{a^2(x_0)} = n^2 a^2. \tag{1.306}$$

Note that Eqs. (1.305) and (1.306) parallel the statistical behavior of error in measurements that being vanishing in the first case as mean deviation results in the second as squared deviation (dispersion), respectively.

Next, through recalling the referential Eq. (1.289)—step (ii) in the above algorithm—the average of the second-order coordinate provides now the expression

$$\left\langle x^2 \right\rangle_{a^2(x_0)} = a^2\left(1 - n^2\right). \tag{1.307}$$

The result (1.307) restrains the domain of the free evolution quantum fluctuation factor n to the realm $n \in [0, 1]$. With Eqs. (1.305) and (1.307), step (iii) in the above algorithm, one finds the coordinate dispersion

$$\Delta x = a\sqrt{1 - n^2} \tag{1.308}$$

with the immediate consequence in adjusting the basic HUR as

$$\Delta x \Delta p \geq \frac{\hbar}{2}\sqrt{1 - n^2} \tag{1.309}$$

On the other hand, within conditions fixed by Eqs. (1.305)–(1.307) the P(article)/W(ave) index of Eq. (1.299) becomes

$$\left(\frac{\text{Particle}}{\text{Wave}}\right)_{\substack{\text{Free}\\ \text{Evolution}}} = \frac{1}{\sqrt{3 - 2n^2}} \exp\left(\frac{3 - 3n^2}{6 - 4n^2}\right) = \begin{cases} 0.952 & \ldots \quad n = 0 \\ 1 & \ldots \quad n_\Omega = 0.54909 \\ 1.048 & \ldots \quad n = 0.87 \\ 1 & \ldots \quad n_\alpha = 1 \end{cases}. \tag{1.310}$$

Through characterizing the numerical results of Eq. (1.310), one first observes that they practically start from where the P/W function of Eq. (1.304) approaches its highest output. In other words, this furnishes remarkable information according to which the *observed and free quantum evolutions are continuous realities*, *being smoothly accorded in the point of precise measurement* ($n = 0$). Another very interesting observation is that the P/W ratio symmetrically spans in (1.310) the

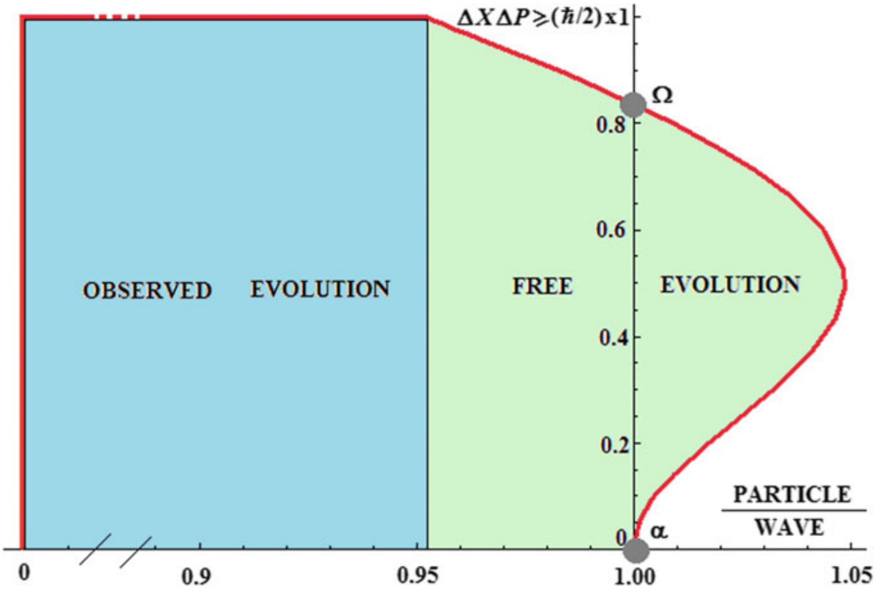


Fig. 1.15 The Heisenberg Uncertainty Relationship (HUR) appearance for observed and free quantum evolutions covering the complete scale of the particle to wave ratios as computed from Eqs. (1.304) and (1.310), respectively; the points Ω and α correspond to wave-particle precise equivalence and to the special extended HURs of Eqs. (1.311) and (1.312), respectively (Putz 2010b, 2016b).

existence domain either for wave P/W∈[0.952, 1) or particle P/W∈(1, 1.048] manifestations around their exact equivalence P/W = 1 (Fig. 1.15). However, the precise wave-particle equivalence is twofold, namely in the so-called *omega* (Ω) and *alpha* (α) points of Eq. (1.310) characterized by the extended HUR versions of Eq. (1.309); written, respectively:

$$(\Delta x \Delta p)_{\Omega} \geq 0.418\hbar \tag{1.311}$$

$$(\Delta x \Delta p)_{\alpha} \geq 0. \tag{1.312}$$

Note that the possibility that a quantum object is manifested *only* under particle behavior (i.e. for P/W→∞) is forbidden. This is an important consequence of the present analytical discourse that is in agreement with the Copenhagen interpretation according to which the quantum phenomena are merely manifested as undulatory (viz. Schrödinger equation) although some particle information may be contained but *never* in an exclusive manner (naturally, otherwise the Newtonian object would exist with no Planck constant and HUR relevance upon it).

1.8 Conclusions

The main items learned in the present chapter for the further theoretical and applicative investigation of atomic and matter's quantification pertain to the following:

- Highlighting the role of quantum mechanics in the panoply of knowledge.
- Tracing the facts and reasons leading to various levels of atomic theory.
- Contouring the further relations between atomic and molecular structure and determinative lines to properties and applications of materials.
- Defining the quantum paradigm: wave functions, wave equations (Schrödinger, Klein-Gordon, Dirac), operators (impulse, momenta, Hamiltonian), matrix representation (Heisenberg), path integrals (Feynman).
- Assimilating the modes and limits of interpretation (indetermination relationships, commutators).
- Employing approximation methods: variation and perturbation theory.
- Characterizing the shell atomic structure with the help of spherical symmetry reasons (spherical harmonics). New hints and heuristic keys.
- Solving the Schrödinger equation for a one-electron atom (hydrogenoid) with change variable strategies. New transformation methods, corroborated with inductive reasoning.
- Writing the hydrogenoid atomic orbitals with the support of computer algebra codes.
- Understanding the principles and manifestations of relativistic quantum effects.
- Concluding a conceptual synopsis and extrapolating a methodological *organon*.
- Regaining the Schrodinger equation by the alternative path integral method.
- Formulating the effective density formalism within quantum statistics specialized as Feynman-Kleinert formalism.
- Explaining atomic stability by path integrals in ground state asymptotic limit of quantum statistical description of central potential.
- Discovering that while the observed reality is fully covered by the standard HUR albeit with an undulatory predominant manifestation of the quantum objects, P/W $\in$ [0, 0.952], the free evolution corresponds with isolated (not measured) quantum systems/states with a symmetrical appearance between the particle and wave dominant manifestations around their perfect equivalency, P/W $\in$ [0.952, 1.048]—however, with the price of altering HUR realization with the factor $\sqrt{1-n^2}$ in terms of the quantum fluctuation magnitude $n \in [0, 1]$.

References

Abramowitz M, Stegun IA (1965) Handbook of mathematical functions: with formulas, graphs, and mathematical tables. Dover, New York

Batelaan H, Gay TJ, Schwendiman JJ (1997) Stern-Gerlach effect for electron beams. Phys Rev Lett 79:4517–4521

Bethe H (1997) Theory of the passage of fast corpuscular rays through matter (translated). In: Bethe H (ed) Selected works of Hans A. Bethe with commentary. World Scientific series in 20th century physics. World Scientific, Singapore, pp 77–154

Bethe H, Jackiw R (1968) Intermediate quantum mechanics, 2nd edn. Benjamin, New York

Blaga L (1943) Trilogia cunoasterii. The trilogy of knowledge. Reprinted (2013), Humanitas, Bucharest

Blinder SM (1993) Analytic form for the nonrelativistic Coulomb propagator. Phys Rev A 43:13–16

Bohr N (1923) Linienspektren und atombau. Ann Phys 71:228–288

Breit G (1932) Dirac's equation and the spin–spin interactions of two electrons. Phys Rev 39:616–624

de Broglie L (1987) Interpretation of quantum mechanics by the double solution theory. In: Annales de la Fondation Louis de Broglie, vol 12. Fondation Louis de Broglie. Paris, France, pp 399–421

Di Francesco P, Mathieu P, Sénéchal D (1997) Conformal field theory. In: Graduate texts in contemporary physics. Springer, Berlin

Dirac PAM (1928) The quantum theory of the electron. Proc R Soc Lond A 117:610–624

Dirac PAM (1944) The principles of quantum mechanics. Oxford University Press, Oxford

Duru IH, Kleinert H (1979) Solution of the path integral for the H-atom. Phys Lett B 84:185–188

Duru IH, Kleinert H (1982) Quantum mechanics of H-atom from path integrals. Fortschr Physik 30:401–435

Faas S, van Lenthe JH, Hennum AC, Snijders JG (2000) An ab initio two-component relativistic method including spin–orbit coupling using the regular approximation. J Chem Phys 113:4052–4059

Feynman RP, Kleinert H (1986) Effective classical partition function. Phys Rev A 34:5080–5084

Gerlach W, Stern O (1922) Das magnetische moment des silberatoms. Z Physik 9:353–355

Gordon W (1926) Der comptoneffekt nach der schrödingerschen. Z Physik 40:117–133

Greiner W, Reinhardt J (1994) Quantum electrodynamics. Springer, Berlin

Hall MJW (2001) Exact uncertainty relations. Phys Rev A 64:052103

Heisenberg W (1927) Über den anschulichen Inhalt der quantentheoretischen Kinematik und Mechanik. Z Phys 43:172–198

Jackiw R (1967) Quantum mechanical sum rules. Phys Rev 157:1220–1225

Jensen F (2007) Introduction to computational chemistry. Wiley, Chichester

Joas C, Lehner C (2009) The classical roots of wave mechanics: Schrödinger's transformations of the optical-mechanical analogy. Stud Hist Philos M P 40:338–351

Kato T (1957) On the eigenfunctions of many-particle systems in quantum mechanics. Comm Pure and Appl Math 10:151–177

Klein O (1926) Quantentheorie und fünfdimensionale relativitätstheorie. Z Physik 37:895–906

Kleinert H (1996) Path integral for a relativistic spinless coulomb system. Phys Lett A 212:15–21

Kleinert H (2004) Path integrals in quantum mechanics: statistics and polymer physics, 3rd edn. World Scientific, Singapore

Kleinert H, Pelster A, Putz MV (2002) Variational perturbation theory for Markov processes. Phys Rev E 65:066128/1-7

Kuhn W (1925) Regarding the total strength of a condition from outgoing absorption lines. Z Phys 33:408–412

Mehra J, Rechenberg H (1982) The historical development of quantum theory: the formulation of matrix mechanics and its modifications 1925–1926. Springer, New York

Morse PM, Feshbach H (1953) Methods of theoretical physics. McGraw-Hill, New York

Noether E (1918) Invariante variations probleme. In: Weidmannsche Buchhandlung, Berlin, vol 18, pp 235–257

Ozawa M (2002) Position measuring interactions and the Heisenberg uncertainty principle. Phys Lett A 299:1–7

Ozawa M (2003a) Physical content of the Heisenberg uncertainty relation: limitation and reformulation. Phys Lett A 318:21–29

Ozawa M (2003b) Universally valid reformulation of the Heisenberg uncertainty principle on noise and disturbance in measurement. Phys Rev A 67:042105/1-6

Parr RG, Yang W (1989) Density functional theory of atoms and molecules. Oxford University Press, New York

Pauli W (1924) Zur frage der theoretischen deutung der satelliten einiger spektrallinien und ihrer beeinflussung durhc magnetische Felder. Naturwissenschaften 12:741–743

Pauli W (1925) On the connexion between the completion of electron groups in an atom with the complex structure of spectra. Z Physik 31:765–785

Pauli W (1964) Nobel lecture, December 13, 1946: exclusion principle and quantum mechanics. Nobel lectures, physics. Elsevier Publishing, Amsterdam, pp 1942–1962

Putz MV (2003) Contributions within density functional theory with applications in chemical reactivity theory and electronegativity. Parkland, Florida. Dissertation.com

Putz MV (2009) Path integrals for electronic densities, reactivity indices, and localization functions in quantum systems. Int J Mol Sci 10:4816–4940

Putz MV (2010a) Compactness aromaticity of atoms in molecules. Int J Mol Sci 11:1269–1310

Putz MV (2010b) On Heisenberg uncertainty relationship, its extension, and the quantum issue of wave-particle duality. Int J Mol Sci 11:4124–4139

Putz MV (2012) Valence atom with Bohmian quantum potential: the golden ratio approach. Chem Central J 6:1–16. doi:10.1186/1752-153X-6-135

Putz MV (2016a) Quantum nanochemistry: a fully integrated approach. Vol I: quantum theory and observability. Apple Academic Press, CRC Press, Toronto

Putz MV (2016b) Quantum nanochemistry: a fully integrated approach. Vol II: quantum atoms and periodicity. Apple Academic Press, CRC Press, Toronto

Putz MV (2017) Chemical field theory: the inverse density problem of electronegativity and chemical hardness for chemical bond. Curr Phys Chem 7(2):133−146. doi:10.2174/1877946806666160627101209

Reiche F, Thomas W (1925) Uber die Zahl der dispersionselektronen, die einem stationären Zustand zugeordnet sind. Z Phys 34:510–525

Reiher M, Wolf A (2009) Relativistic quantum chemistry: the fundamental theory of molecular science. Wiley-VCH, Weinheim

Robertson HP (1929) The uncertainty principle. Phys Rev 34:163–164

Schrödinger E (1926) An undulatory theory of the mechanics of atoms in molecules. Phys Rev Lett 28:1049–1070

Schrödinger E (1930) About Heisenberg uncertainty relation. Proc Pruss Acad Sci Phys Math 19:296–303

Sundermeyer K (2014) Symmetries in fundamental physics. Springer, Heidelberg

Thaller B (2002) The Dirac operator. In: Schwerdtfeger P (ed) Relativistic electronic structure theory: fundamentals. Elsevier Science, Amsterdam

Thomas W (1925) Uber die zahl der dispersionselectronen, die einem starionären zustande zugeordnet sind. Naturwissenschaftern 13:510–525

Uhlenbeck GE, Goudsmit S (1925) Ersetzung der hypothese vom unmechanischen zwang durch eine forderung bezüglich des inneren verhaltens jedes einzelnen elektrons. Naturwissenschaften 47:953–954

van Leeuwen R, van Lenthe E, Baerends EJ, Snijder JG (1994) Exact solutions of regular approximate relativistic wave equations for hydrogen-like atoms. J Chem Phys 101:1272–1281

van Lenthe E, Baerends EJ, Snijder JG (1993) Relativistic regular two-component Hamiltonians. J Chem Phys 99:4597–4610 von Meyenn K (1994) Quantenmechanik und Weimarer Republik. Friedr. Vieweg Sohn Verlagsgesellshaft, Braunschweig, Wiesbaden

Wigner E (1932) On the quantum correction for thermodynamic equilibrium. Phys Rev 40:749–759

Wolfram S (2003) The mathematica book, 5th edn. Wolfram-Media, Champaign, Illinois

Wolfram Research, Inc. (2014) Mathematica. Champaign, Illinois

Zeeman P (1897) On the influence of magnetism on the nature of the light emitted by a substance. Phil Mag 43:226–239