

STATIONARY STATES IN A POTENTIAL WELL

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Summary

In the early days of the 20th century a set of important observations in atomic and molecular physics could not be explained on the basis of the laws of classical physics. One of the main findings was the emission of light by excited atoms with very particular frequencies. To explain those findings a new development in physics was necessary, now known as quantum mechanics. In particular, the concept of stationary states was introduced by Niels Bohr, in 1913, in order to explain those observations and the stability of atoms. According to E.C. Kemble (1929), the existence of discrete atomic and molecular energy levels brought into mechanics a new kind of atomicity superposed on the atomicity of electrons and protons. We review here in a historical context the topic of stationary states in the quantum world, including the generalization to the primary ideas. We also discuss the stationary states in one dimensional parabolic wells and the three dimensional Coulomb and parabolic cases.

1. Introduction

At the beginning of the 20th century, some experimental observations in atomic and molecular physics were impossible to explain on the basis of classical physics. It was necessary to introduce revolutionary concepts that led to the foundation of quantum mechanics. In this context the concept of stationary states played an essential role in the development of new ideas that started to explain the atomic world.

In 1908 J.R. Rydberg and W. Ritz studied in detail the spectra of the light emitted by excited atoms. They found that the spectra consisted of a set of defined lines of particular wavelengths. Furthermore, the set of spectroscopic lines were dependent only on the atom under study. Through the so-called combination principle they put the data in a most systematic form. Their principle states that the frequency of a particular spectral line can be expressed as a difference between some members of the set of frequency lines.

These findings could not be explained by the accepted atomic model at that time, proposed by J.J. Thomson, claiming that the electrons were embedded in a positively charged cloud, whose extent was determined by the atomic radius. That model could not explain also the data obtained by H.W. Geiger and E. Mardsen, who under the supervision of Rutherford, were studying the interaction of charged α -particles with gold foils [1]. They observed that a considerable fraction of the α -particles was deflected by large angles. This effect could not be attributed to the electrons since they are much less massive. Thus, they concluded that the source of deflection must be the positive charge concentrated in a much smaller volume than the one generated by the atomic radius. In 1911 Rutherford proposed a new atomic model which assumed that all the positive charge is located at the center of the atom with a very dense distribution with a radius much smaller than the atomic one. The electrons then would circulate around the nucleus in a way similar to the planets moving around the sun.

Although Rutherford's planetary atomic model explained qualitatively well the deflection of α -particles, it had two major deficiencies. First it could not account for the spectra of radiation from atoms, which was not continuous but discrete. The other major problem was that, according to electrodynamics, an electron moving around the nucleus is under a constant acceleration, must radiate energy. This fact would lead to a

situation in which the electron would lose energy continuously and would collapse on the nucleus.

2. Stationary Orbits in Old Quantum Mechanics

2.1. Quantized Planetary Atomic Model

In 1911, the two-and-a-half-thousand-year-old philosophical concept of atom turned into a scientific matter when Rutherford's planetary atomic model emerged from the interpretation of the experimental data on the scattering of α particles [1]. The curious fact that has been noticed while these particles were shot at gold foils was that some of them bounced as if they were colliding with very massive objects. To explain these findings Rutherford proposed that the atom was composed of a positive central massive nucleus and the electrons were revolving around it, i.e. very similar to a miniature solar system. However, this famous model was not electrostatically viable. Atomic stability was simply not assured for Rutherford's semiempirical model, since accelerated charges radiate energy and the electrons moving around the nucleus would lose energy and eventually collapse on to the nucleus.

Another important set of empirical data, is that obtained from the emission of light by excited atoms. It was observed that the light emitted had very characteristic frequencies and was a footprint for each atom. These observations were put in a systematic form in 1908 through the so-called combination principle formulated by J.R. Rydberg and W. Ritz. Their principle says that the frequency of a spectral emission or absorption line can be expressed as a difference between the members of a set of well defined frequency terms. Rutherford's model was completely silent on the dynamical origin of the spectral lines. It was the great merit of Bohr to formulate in 1913 the hypotheses, or postulates, that could allow the explanation of the atomic spectral lines based on the planetary atomic structure.

2.2. Bohr's Hypotheses and Quantized Circular Orbits

The hypotheses that Bohr added to the Rutherford model in order to explain the spectroscopic information are the following [2]:

1. An atom can exist only in special states with discrete values of energy. In other words, the electrons moving around an atom can be found only in certain special orbits that Bohr called *stationary states*.
2. When an atom makes a *transition* from one stationary state to another, it emits or absorbs radiation whose frequency ν is given by the frequency condition

$$h\nu = E_1 - E_2, \quad (1)$$

where E_1 and E_2 are the energies of two stationary states and h is Planck's constant.

The value of Planck's constant is

$h = 6.6260693(11) \times 10^{-34} \text{ J}\cdot\text{s} = 4.13566743(35) \times 10^{-15} \text{ eV}\cdot\text{s}$. This is according to CODATA of 31 December 2002. CODATA is published every four years. The two digits between the parentheses denote the uncertainty (standard deviation) in the last two digits of the value

3. In the stationary states, the electrons move according to the laws of classical theory. However, only those motions are performed for which the following *quantum condition* is fulfilled

$$\oint p dq = nh, \quad (n = 1, 2, 3, \dots), \quad (2)$$

where p is the momentum of the electron and q is its coordinate along the stationary orbit. The integration should be taken along the orbit over one period of the cyclic motion.

Bohr's theory claimed that those frequency terms, when multiplied by h , give distinct energy levels in which the electrons move around the nucleus. This meant that these were the only possible states in which the electrons in the atom could exist.

Let us assume that an electron in a Hydrogen atom is revolving around the nucleus on a circular orbit according to the Newtonian equations of motion. For a circular orbit, the absolute value of the momentum p is constant and then the quantum hypothesis (3) leads to

$$p \cdot 2\pi a = nh, \quad (n = 1, 2, 3, \dots) \quad (3)$$

where a is the radius of the orbit. Thus, a is given by the value of the momentum that can be obtained from the balance between the centrifugal force and the Coulomb force, i.e.,

$$\frac{p^2}{ma} = \frac{e^2}{4\pi\epsilon_0 a^2}. \quad (4)$$

Combining the two equations, one obtains

$$a_n = \frac{\epsilon_0 h^2 n^2}{\pi m e^2} \quad (n = 1, 2, 3, \dots). \quad (5)$$

The latter formula gives the radii of the quantized electron circles in the hydrogen atom.

In particular, $a_1 \equiv a_B = \frac{\epsilon_0 h^2}{\pi m e^2}$, is known as the Bohr radius and is taken as an atomic length unit.

2.3. From Quantized Circles to Elliptical Orbits

Wilson [3] and Sommerfeld [4] extended Bohr's ideas to a large variety of atomic systems between 1915 and 1916.

The main idea is that the only classical orbits that are allowed as stationary states are those for which the condition

$$\oint p_k dq_k = n_k h \quad k = 1, \dots, n, \quad (6)$$

with n_k a positive integer, is fulfilled. The weak theoretical point is that in general these integrals can be calculated only for *conditionally periodic systems*, because only in such cases a set of coordinates can be found, each of which goes through a cycle as a function of the time, independently of the others. Sometimes the coordinates can be chosen in different ways, in which case the shapes of the quantized orbits depend on the choice of the coordinate system, but the energy values do not.

In particular, when the 3D polar coordinates are employed, Eq. (6) gives the Sommerfeld ellipses characterized by

$$\oint p_r dr = n_r h, \quad \oint p_\theta d\theta = n_\theta h, \quad \oint p_\phi d\phi = n_\phi h. \quad (7)$$

Now, since p_ϕ is a constant, one gets immediately the 'quantization' of the angular momentum of the ellipse along the z axis

$$p_\phi = \frac{mh}{2\pi}, \quad m = \pm 1, \pm 2, \dots \quad (8)$$

The quantum number m was called the magnetic quantum number by Sommerfeld who used it as a measure of the direction of the orbit with respect to the magnetic field and thus explaining the Zeeman effect, i.e., the splitting of the spectroscopic lines in a magnetic field. Unless for the value $m = 0$ which is considered as unphysical, this 'old' m is practically equivalent with Schrödinger's m , which mathematically is the azimuthal separation constant but has a similar interpretation.

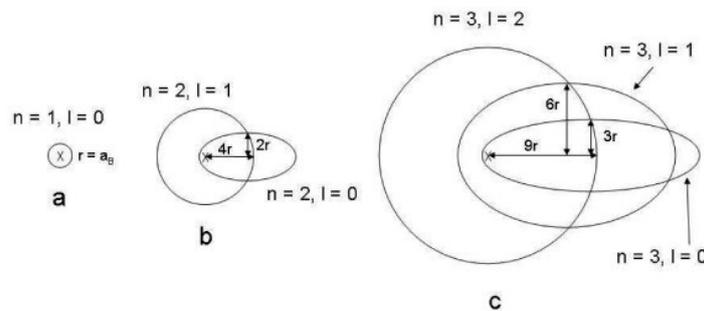


Figure 1. Bohr-Sommerfeld electron orbits for $n = 1, 2, \text{ and } 3$, and the allowed values

for l .

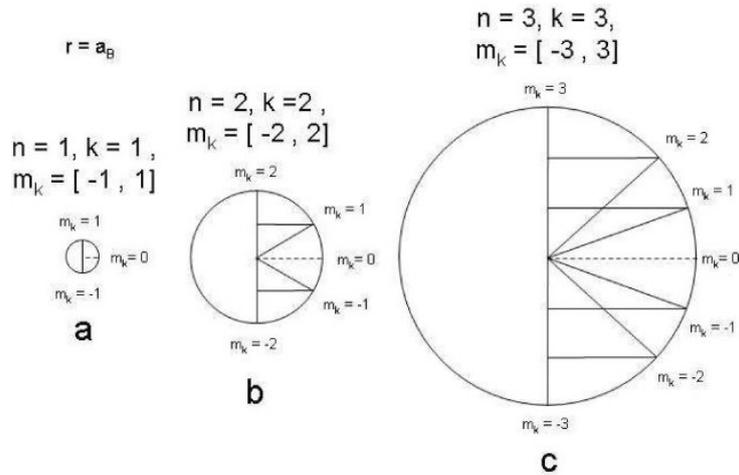


Figure 2. Spatial quantization of Bohr-Sommerfeld orbits for azimuthal numbers $k = 1, 2,$ and 3 .

Interestingly, and this is sometimes a source of confusion, the ‘old’ azimuthal quantum number is denoted by k and is the sum of n_θ and m . It gives the shape of the elliptic orbit according to the relationship $\frac{a}{b} = \frac{n}{k}$, where $n = n_r + k$, established by Sommerfeld. Actually, this k is equivalent to Schrödinger’s orbital number l plus 1, but again their mathematical origin is quite different.

2.4. Experimental Proof of the Existence of Atomic Stationary States

The existence of discrete atomic energy levels was evidenced for the first time by J. Franck and G. Hertz in 1914 [5]. They observed that when an electron collides with an atom (mercury in their case), a transfer of a particular amount of energy occurred. This energy transfer was recorded spectroscopically and confirmed Bohr’s hypotheses that atoms can absorb energy only in quantum portions. Even today, the experiment is preferentially done either with mercury or neon tubes. From the spectroscopic evidence, it is known that the excited mercury vapor emits ultraviolet radiation whose wavelength is 2536 \AA , corresponding to a photon energy $h\nu$ equal to 4.89 eV .

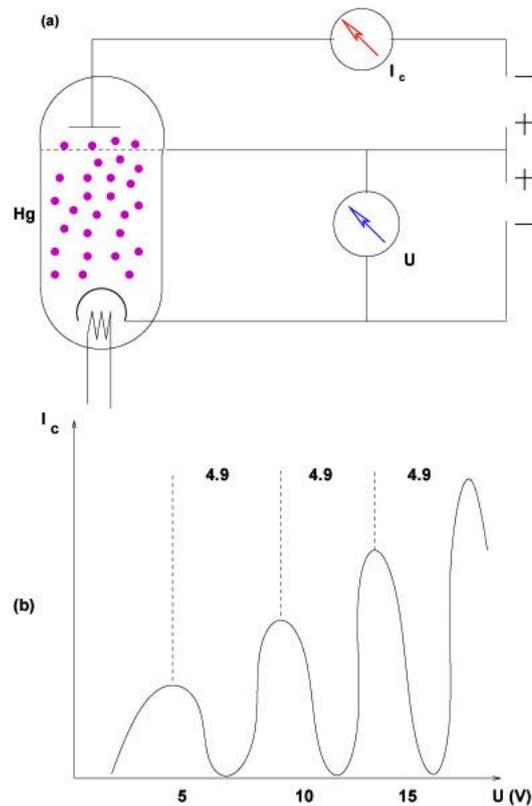


Figure 3. (a) Schematic diagram of the Franck-Hertz experiment, where the tube is filled with a gas of Mercury; (b) typical plot recorded in a Franck-Hertz experiment with mercury, showing the periodic maxima.

The famous Franck-Hertz curves represent the electron current versus the accelerating potential, shown in Fig. 3. The current shows a series of equally spaced maxima (and minima) at a distance of ~ 4.9 V. The first dip corresponds to electrons that lose all their kinetic energy after one inelastic collision with a mercury atom, which is then promoted to its first excited state. The second dip corresponds to those electrons that have the double amount of kinetic energy and loses it through two inelastic collisions with two mercury atoms, and so on. All these excited atoms emit the same radiation at ~ 2536 Å. But which is the 'first' excited state of mercury? It is spectroscopically denoted by 3P_1 in Fig. (4). Notice that the other two P states cannot decay to the ground state 1S_0 because the dipole emission is forbidden for them and therefore they are termed metastable. More details, such that the observed peak separation depends on the geometry of the tube and the Hg vapor pressure, are explained in the readable paper of Hanne [6].

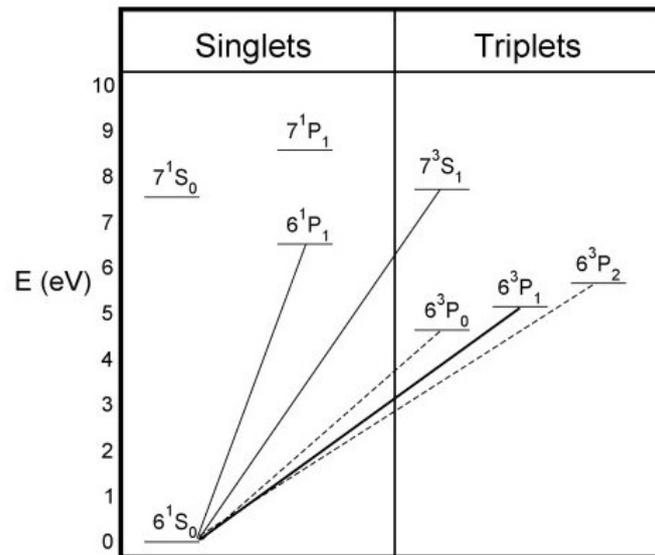


Figure 4. Simplified Mercury's level diagram in the low-energy region in which the so-called hyperfine structure is neglected. The numbers 6 and 7 are Bohr's 'whole numbers' or Schrödinger's principal quantum numbers.

3. Stationary States in Wave Mechanics

3.1. The Schrödinger Equation

According to L. Pauling and E. Bright Wilson Jr. [7], already in the years 1920-1925 a decline of the 'old quantum theory' as the Bohr-Sommerfeld atomic theory is historically known and which is based on the 'whole number' quantization of cyclic orbits was patent; only very recently there is some revival, especially in the molecular context [8]. But in 1925, a quantum mechanics based on the matrix calculus was developed by W. Heisenberg, M. Born, and P. Jordan and the best was to come in 1926 when Schrödinger in a series of four papers developed the most employed form of quantum mechanics, known as *wave mechanics*. The advantage of his theory of atomic motion is that it is based on standard (partial) differential equations, more exactly on the Sturm-Liouville theory of self-adjoint linear differential operators. Schrödinger starts the first paper in the 1926 series with the following sentence [9]:

"In this paper I wish to consider, first the simplest case of the hydrogen atom, and show that the customary quantum conditions can be replaced by another postulate, in which the notion of 'whole numbers', merely as such, is not introduced."

Indeed, he could obtain the basic equation of motion in nonrelativistic quantum mechanics, the so called Schrödinger equation for the wavefunctions $\Psi(x,t)$, and provided several analytical applications, among which was the hydrogen atom. The original derivation is based on variational calculus within the Sturm-Liouville approach and was given eighty years ago. In his first paper of 1926, Schrödinger states that the wavefunctions Ψ should be such as to make the 'Hamilton integral'

$$\mathcal{J}_S[\Psi] = \int \left(\hbar^2 T(q, \partial \psi / \partial q) + \Psi^2 V \right) d\tau, \quad (9)$$

stationary subject to the normalizing condition $\int \Psi^2 d\tau = 1$ which can be incorporated through the Lagrange multipliers method. The Euler-Lagrange equation of the functional $\mathcal{J}_S[\Psi]$ is the time-dependent Schrödinger equation

$$i\hbar \frac{\partial \Psi}{\partial t} = H\Psi. \quad (10)$$

When the wave function of the time-dependent Schrödinger equation is written in the multiplicative form $\Psi(x, t) = \psi(x)\mathcal{F}(t)$ one obtains a complete separation of the space and time behaviors of Ψ : on one side, one gets the stationary Schrödinger equation for $\psi(x)$,

$$-\frac{\hbar^2}{2m} \frac{d^2 \psi}{dx^2} + V(x)\psi = E\psi, \quad (11)$$

and on the other side, the simple time-dependent equation for the logderivative of \mathcal{F}

$$i\hbar \frac{d \ln \mathcal{F}}{dt} = E \quad (12)$$

where the Dirac's constant $\hbar \triangleq h / 2\pi$. This decoupling of space and time components is possible whenever the potential energy is independent of time.

The space component has the form of a standing-wave equation. Thus, it is correct to regard the time-independent Schrödinger equation as a wave equation from the point of view of the spatial phenomenology.

3.2. The Dynamical Phase

Furthermore, the time-dependence is multiplicative and reduces to a modulation of the phase of the spatial wave given by

$$\mathcal{F} = e^{-iEt/\hbar} = \cos(Et/\hbar) - i \sin(Et/\hbar). \quad (13)$$

The phase factor $\mathcal{F} = e^{-iEt/\hbar}$ is known as the *dynamical phase*. In recent times, other parametric phases have been recognized to occur, e.g., the Berry phase. The dynamical phase is a harmonic oscillation with angular frequency $\omega = E/\hbar$ and period $T = \hbar/E$. In other words, a Schrödinger wavefunction is flickering from positive through imaginary to negative amplitudes with a frequency proportional to the energy. Although it is a wave of constant energy it is not stationary because its phase is time dependent (periodic). However, a remarkable fact is that the product $\Psi^* \Psi$, i.e., the modulus $|\Psi|^2$ of the Schrödinger constant-energy waves remains constant in time

$$\Psi^* \Psi = \psi^* \psi \quad (14)$$

It is in the sense of their constant modulus that Schrödinger constant-energy waves are called stationary states.

3.3. The Schrödinger Wave Stationarity

Thus, non-relativistic quantum stationarity refers to waves of constant energy and constant modulus, but not of constant phase, which can occur as solutions of Schrödinger equation for time-independent potentials. In the Schrödinger framework, the dynamical systems are usually assumed to exist in stationary states (or waves of this type). It is worth noting that the preferred terminology is that of states and not of waves. This is due to the fact that being of constant energy the Schrödinger stationary waves describe physical systems in configurations (or states) of constant energy which can therefore be naturally associated to the traditional conservative Hamiltonian systems. Moreover, the localization of these waves can be achieved by imposing appropriate boundary conditions.

3.4. Stationary Schrödinger States and Classical Orbits

In the Schrödinger theory, a single stationary state does not correspond to a classical orbit. This is where the Schrödinger energy waves differ most from Bohr's theory which is based on quantized classical cyclic trajectories. To build a wave entity closer to the concept of a classical orbit, one should use superpositions of many stationary states, including their time dependence, i.e., what is known as wave packets. Only monochromatic plane waves of angular frequency ω correspond through the basic formula $E = \hbar\omega$ to a well-defined energy E of the 'classical' particle but unfortunately there is no relationship between the wavevector k and the momentum p of the corresponding particle since a plane wave means only the propagation at constant (phase) velocity of infinite planes of equal phase. In other words, a criterium for localization is required in order to define a classical particle by means of a wave approach.

In the one-dimensional case, a wave packet is constructed as follows

$$\psi(x, t) = \int_{-\infty}^{+\infty} f(k') e^{i(k'x - \omega t)} dk', \quad (15)$$

with obvious generalization to more dimensions. If $f(k')$ is written in the polar form $F(k')e^{i\alpha}$ and F is chosen with a pronounced peak in a wavenumber region of extension Δk around the point $k' = k$, then the wave packet is localized in a spatial region of extension $\Delta x \approx \frac{1}{\Delta k}$ surrounding the "center of the wavepacket". The latter is equivalent to the concept of material point in classical mechanics and travels uniformly

with the group velocity $v_g = \frac{d\omega}{dk}$. This is the velocity that can be identified with the particle velocity $v = \frac{dE}{dp}$ in classical mechanics and which leads to the de Broglie formula $p = \hbar k = \frac{h}{\lambda}$, relating the momentum p and the wavelength λ of the quantum particle.

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Biographical Sketches

Haret C. Rosu, was born in Bucharest, Romania, in 1952. He studied physics at the University of Bucharest and obtained the PhD degree in nuclear physics in 1987 during his period as researcher in the campus Magurele-Bucharest (1980-1990). Between 1990-1993 he was visiting professor at the Abdus Salam International Centre for Theoretical Physics in Italy. Starting March 1993 he worked for eight years as Associate Professor at the Institute of Physics of the University of Guanajuato (IFUG), in Leon, Mexico, and since January 2002 he is a Full Professor in the Institute for Scientific and Technological Research in San Luis Potosí, Mexico (IPICyT). Dr. Rosu published 110 research papers and is known as an expert in supersymmetric quantum mechanics as well as other areas of theoretical physics. He also published 2 book chapters and has many contributed papers in proceedings of workshops. Some of his graduate courses on quantum and classical mechanics are freely available in the Internet at the arXiv and other sites.

José L. Morán-López, was born in Charcas, San Luis Potosí, Mexico in 1950. He got his M.Sc. from the Center for Research and Advanced Studies, Mexico City (1974) and the Doctor Rerum Naturalium Degree from the Freie Universitaet Berlin, Germany (1977). Later, he spent two years as a Posdoc at University of California, Berkeley, USA. He was the Founder General Director of the Institute for Scientific and Technological Research in San Luis Potosí, Mexico, 2000-2005. Now he is Professor at the Division of Advanced Materials of the Institute for Scientific and Technological Research in San Luis Potosí, Mexico, and is the Academic Coordinator of the National Supercomputing Centre. He was John Simon Guggenheim Fellow (USA) 1984-1985. Then he got a fellowship at the International Centre for Theoretical Physics, Trieste, Italy, 1985-1991, and Senior Associate for the period 1992-1997. He received the C. V. Raman Award, given by the International Centre for Theoretical Physics, Trieste, Italy, 1990. He was Alexander von Humboldt Fellow (Germany) in 1992-1993. In 1993 he was distinguished as a Fellow by the American Physical Society. He is member of the Academy of Sciences for the Developing World (TWAS) since 1991. His contributions for science were recognized by the Mexican Government by awarding him the National Prize on Sciences and Arts in the area of Exact and Natural Sciences in 1995. He acted as Editor of the Mexican Journal of Physics during the period 1996-2000. In 1999 he was elected as Vice-president of the Union of Pure and Applied Physics for the period 1999-2002. The last academic recognition to his scientific achievements was the TWAS Medal Lecture in 2004. His main scientific interests are the physicochemical properties of nanostructures materials. Other interests are phase transitions in low dimensional and confined systems