

ATOMS AND MOLECULES

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Keywords: Atoms, spectroscopy, atomic collisions, exotic atoms, Rydberg atoms, atom optics, molecules, relative molecular mass, binding energies, electronic energy, vibrational energy, rotational energy, molecular geometry, chemical reactions, photosynthesis.

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Summary

Basic general properties of atoms are pointed out. Some selected current research topics are briefly described. In the second part of this contribution, molecules, and some of its physical and chemical properties are discussed.

1. Introduction

An atom is a system formed by a pack of electrically charged particles Q called nucleus and N identical particles of charge $-q$. Molecules are systems with several nuclei which may not necessarily be identical. In almost all matter, the nuclei are conglomerates of neutrons and protons and the N remaining particles are electrons. Other atomic systems will be described in the exotic atoms section.

In order to understand the properties of atoms it is necessary to take into account some general properties of their constituents. Electrons and protons have opposite charge of

magnitude $e = 1.60217653(14) \times 10^{-19}$ C; neutrons do not have net electric charge. While electrons can be regarded as point particles, protons and neutrons classical sizes are $\sim 1.2 \cdot 10^{-15}$ m. The mass of the neutron $m_n = 1.67492729(28) \cdot 10^{-27}$ kg is also similar to that of the proton $m_p = 1.67262171(29) \cdot 10^{-27}$ kg, both being much bigger than that of the electron $m_e = 9.1093826(16) \cdot 10^{-31}$ kg. Neutrons and protons interact among themselves through an attractive force stronger than the electromagnetic one and of a much shorter range. This force does not act directly on the electrons so that the atomic nucleus can be regarded as a compact charged particle while the electrons move around it in a larger region that involves typical distances of about one Bohr radius, $a_0 = 5.291772108(18) \cdot 10^{-11}$ m.

Another important property of electrons, protons and neutrons is that they respond to a magnetic field \vec{B} as having an *intrinsic* magnetic dipole moment of magnitude $\mu_e = -928.476362(37) \cdot 10^{-26}$ J/T, $\mu_p = 1.410606633(58) \cdot 10^{-26}$ J/T and $\mu_n = -0.96623640(23) \cdot 10^{-26}$ J/T. Experiments indicate that, for all these particles, the magnetic interaction energy $-\vec{\mu} \cdot \vec{B}$ cannot take any value within the continuous interval $[-|\mu B|, |\mu B|]$ expected from classical electromagnetism. In fact, just two discrete or quantized possibilities are observed. For electrons the values of these interaction energies are $\pm 1/2(e\hbar/2m_e)B$ with $\hbar = 1.05457168(18) \cdot 10^{-34}$ J·s Planck's constant that has units of angular momentum. It is then natural that, given an intrinsic magnetic moment $\vec{\mu}$, an intrinsic angular momentum \vec{s} be assigned to the electron, proton and neutron. This angular momentum is called the spin. Notice that as a consequence of this relation the observed projections of the angular momentum along a magnetic field $\vec{B} = B\hat{z}$ are just $s_z = \pm 1/2\hbar$. Besides, the natural unit to measure the magnetic moment of the electron is the so called Bohr magneton $\mu_B = e\hbar/2m_e = 927.400949(80) \cdot 10^{-26}$ J/T.

The translational motion of charged particles can also generate an additional magnetic moment. The magnetic field produced by all these magnetic dipole moments gives rise to internal energies within atomic systems. In general, these energies are much smaller than those associated to electric interactions among nuclei and electrons.

Finally an electron-nucleus weak interaction has quantitatively negligible consequences in the atom structure. Nevertheless, this interaction is particularly interesting since it gives rise to phenomena that breaks the spatial inversion symmetry (parity nonconservation).

The mechanical description of the structure of atoms must be done within the quantum physics formalism. Thus, the state of an atomic system is specified by a wave function $\Psi(x_i; X_k; t)$ that depends on the position and spin of its constituent electrons and nuclei, denoted by x_i and X_k respectively. This state is not unique and depends on time.

Quantum particles can be classified according to whether the projection of their intrinsic

angular momentum in any given direction takes values that are integer or semi-integer multiples of \hbar . The former are called bosons the latter fermions. Thus electrons, neutrons and protons are fermions. All fermions satisfy the Pauli exclusion principle according to which the wave function changes its sign under the interchange of any two identical particles.

In spite of the fact that the equations that describe an atom or a molecule cannot be solved analytically, a very good description can be done, in general, by using the so called mean field approximation. In it, a series of quantum levels are assigned to each of the particles within the atom. The most usual levels in atoms are a natural number followed by one of the letters s , p , d , f ... This notation has a direct physical interpretation, the letter corresponds to particular values of the square of the magnitude of the translational (orbital) angular momentum of each electron: $s \rightarrow 0\hbar$, $p \rightarrow 1(1+1)\hbar^2$, $d \rightarrow 2(2+1)\hbar^2$, ... It also gives rise to specific probabilistic clouds for the angular locations of an electron within an atom. The orientations of these clouds are not unique in general, i.e., there are three orientations for p states, five for d states, etcetera. Finally the number beside these letters, e. g. $1s$, $2s$, labels the radial behavior; for a given ℓ greater values of n lead to greater mean radii for the electron probability cloud. Each set nl together with the orientation of the orbital and spin angular momentum denotes a spinorbital.

In the mean field approach, the Pauli exclusion principle precludes the possibility that two electrons occupy the same spinorbital. This fact gives an extra relevance to the electron spin. As mentioned before, internal magnetic interactions in atoms are much smaller than electric ones. Nevertheless, since the spin orientations are just two, at most two electrons may occupy the same translational state within an atom.

In general, different configurations give rise to different internal energies. These energies include the magnetic interactions. For light atoms, magnetic interactions are such that one can assign both a total intrinsic \vec{S} and orbital \vec{L} angular momenta to the electronic part of the atom. Magnetic interactions lead also to a total electronic angular momentum \vec{J} that magnetically couples to the angular momentum \vec{I} of the nuclei giving rise to the **global** angular momentum \vec{F} of the atom.

The ground state of an atomic system is that with a minimum internal energy. It is a remarkable fact that the scheme described above allows the understanding of many ground state atomic characteristics including the general features of elements as summarized in Mendeleev periodic table.

However, atomic physics goes beyond the identification of the atomic ground state. Atoms in a state with higher energy than the ground state energy are said to be in an excited state. Under proper conditions the internal configuration of the atom can change by dramatic processes like collisions with other atomic systems or by the more gentle but not less interesting interaction with electromagnetic waves. The latter process is responsible for the atomic spectra. An atom in an excited state E_b makes a transition to a state with lower energy E_a with the simultaneous emission of a photon with a

frequency $\omega = (E_a - E_b)/\hbar$. This process can occur spontaneously or may be induced by light incident on the atom with this frequency. In the process the elementary mechanical properties of the atom-light system are conserved. These properties are energy, momentum and angular momentum. Thus, there is a slight recoil movement of an atom when it emits a photon. Besides, not all transitions are allowed but just those that take into account that a photon has an angular momentum with square magnitude $1(1+1)\hbar^2$. In fact circularly polarized photons carry an angular momentum with $\pm\hbar$ projection along its direction of propagation. Selection rules reflect the conservation laws and describe which transitions are allowed. The frequencies related to all allowed transitions in a given atom form its atomic spectrum. This spectrum is different for different atomic elements; precise measurements show that these spectra have a gross, fine and hyperfine structure that reflect the subtle relevance of magnetic interactions and many body effects within an atom.

This introduction summarizes some general features of atoms. Nevertheless, the evaluation and measurement of the characteristics of specific atoms with increasing accuracy and level of predictability has been the subject of study of thousands of researchers since the 1920s. The relevance of these studies lies in their multiple consequences in many areas. For instance, historically the first scenario for testing the ability of quantum mechanics to describe physical systems was provided by atoms. Many of the numerical and analytical tools developed for dealing with quantum many body systems were conceived by having atoms in mind. The knowledge of atomic properties like their spectra allows the identification of elements in laboratory samples or in astronomical objects. The understanding of the chemical behavior of elements is in general preceded by a study of the atoms that will form molecules. A similar argument concerns solid state physics.

In recent years atomic physics research has been focused on several fascinating topics. Some of them will be briefly described in the following sections.

In the last section, the structure of molecules is described and discussed. Their richness in structure and possible technological implications are indicated.

2. High Precision Atomic Spectroscopy

High precision spectroscopy refers to the measurement and/or calculation of transition probabilities and frequencies at the border of current capabilities.

There are several sources of uncertainty in the measurement of spectral lines. One of them refers to the dependence of the frequency of emitted light on the state of movement of its source (Doppler effect). Another is associated to statistical errors arising from the fact that these measurements are performed with a sample that has many atoms which are not necessarily in the same initial state. The latter errors have classical and quantum aspects. Besides, measurements always refer to comparison with scales that in fact are known to within a finite number of significant figures. High precision spectroscopy is linked to the development of new technologies that allow the maximum available control of these and other factors. In the search of better precision measurements, atom cooling techniques have diminished the uncertainty due to Doppler

effects; mechanism for controlling the quantum state of atoms should soon lead to lower statistical errors; translating optical measurements to much easily measurable microwave frequencies allows high precision measurements in a broader spectral range (optical combs).

From a theoretical point of view, high precision calculations involve two essential aspects. One corresponds to the physical model that establishes the equations to be solved. The second corresponds to the computational techniques necessary to solve these equations to a given degree of accuracy. The latter are roughly classified as perturbative, variational and variational-perturbative. At the present time, high precision calculations require the incorporation of relativistic effects in the physical model. The basic theory behind these is quantum electrodynamics which was first developed for an electron interacting with its own electromagnetic field. The extension of this formalism for a set of electrons bound to a nucleus is a challenge so far giving only partial but nevertheless useful answers. In general, relativistic effects are especially relevant for electrons in orbitals closer to a heavy nucleus. Loosely speaking the velocity of those electrons is typically $Z\alpha c$ where Z is the number of protons in the nucleus, $\alpha = e^2/\hbar c = 1/137.03599911(46)$ is a fundamental non-dimensional constant that determines the natural strength of electromagnetic interactions and $c = 299,792,458$ m/s is the velocity of light.

Applications of high precision spectroscopy are both practical and fundamental. Among the latter, in recent years there has been an increasing interest in using spectroscopic theoretical and experimental knowledge to study variation of fundamental constants over cosmological time or testing special and general relativity theories.

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Biographical Sketches

Rocio Jáuregui Renaud, born in Mexico City in 1958, she got her Ph. D. (Physics) in 1983 from the Science Faculty of the Universidad Nacional Autónoma de México (UNAM). After a postdoctoral fellowship at the Science Faculty in the Universidad de Barcelona, España, she incorporated to the Physics Institute in UNAM where she has developed most of her scientific and teaching activities receiving the award Distinción Universidad Nacional para Jóvenes Académicos, Investigación en Ciencias Exactas, UNAM in 1997.Her first scientific contributions were on high precision atomic structure calculations of multiple excited atoms and the prediction of negative ions. Later, she worked on the relativistic many body problem in classical and quantum scenarios, and the search of relativistic variational schemes for atomic calculations. The Casimir effect, the description of trapped atoms in quantum interesting states, and the generation and the effects of non-conventional laser beams on atomic systems are the subject of her latest research works.

Carlos Federico Bunge, born March 27, 1941, in Buenos Aires, Argentina. Lic. in Chemical Sciences by Universidad Nacional de Buenos Aires (1962). Ph.D. in Physical Chemistry by University of Florida (1966). Int. Assist. Professor at University of Florida (1966-67).Post-doctoral fellow at Indiana University (1967-68). Asst. Professor at Escuela de Química, Universidad Central de Venezuela (1968-70). Profesor at Instituto de Física e Química de Sao Carlos of Universidade de Sao Paulo (1971-76). Researcher at Instituto de Física and Professor at the Facultad de Ciencias, and Facultad de Química, Universidad Nacional Autónoma de México (1976-present).Specialized in rigorous application of quantum mechanics to electronic structure of atoms and molecules. Developed computational strategies to predict atomic spectra to within 0.1 percent of error, later applied to the study of core-excited states. Predicted first radiative transition between levels of a negative ion verified later experimentally, also predicted existence of metastable negative ions in several experiments and advanced one of earliest proposals to construct a soft X-ray laser.Between 1982 and present developed a modular library for atomic and molecular electronic structure calculations, in both non-relativistic and relativistic realms. His most recent contributions are a variational theorem for atomic relativistic states based on an exact decoupling between (+) and (-) energy states, an accurate method (of spectroscopic accuracy) to evaluate correlation energies of small electronic systems including all atoms, and use of strictly variational wave functions incorporating (+) and (-)-energy orbitals in calculations of all kinds of radiative transition probabilities.