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## **Topics in Atomic Physics – from Spectroscopy to Current Problems**

We know for a long time that the world is made up of small entities called “atoms”. Many important properties of atoms were discovered after the beginning of spectroscopy in the mid-19th century. But a more detailed understanding of atomic structure was only possible with the help of quantum mechanics, which originated about 60 years ago. This article from the working group for theoretical physics aims to review the historical development of atomic theory in order to shed some light onto the continuous improvement of our understanding of atomic structure but also onto some of the revolutionary advances that have happened over the years.

Atomic and molecular physics is as old as the concepts of Dalton and Faraday. Their laws of mass conservation, multiple proportions and also Faraday’s laws formed the foundation for our knowledge about the existence of atoms. Atomic and molecular physics were virtually synonymous with optical spectroscopy in the second half of the last century. Spectral analysis was discovered by Bunsen and Kirchhoff in 1859. Scientist realised at that time that a characteristic spectrum corresponds to each chemical element in a particular state of ionisation. But the intense efforts to find a systematic scheme in the arrangements of spectral lines were unsuccessful for a long time, with the exception of Balmer’s rule for the

spectral lines of the hydrogen atom. Vast amounts of unexplained high precision results had been accumulated in the archives of the spectroscopists at the turn of the century. We will quote from an article by H. Kayser and C. Runge in "Spectren Der Elemente" (1888) to shed some light on the historical situation of atomic physics at that time:

"The aims of spectroscopy have changed considerably since its introduction by Bunsen and Kirchhoff in 1859. Spectral features are not commonly used as a replacement or support of chemical analysis, the spectroscopic identification of various rare earth elements being an exception. An approximate determination of their spectra suffices for the discrimination of most other elements. The presence of a chemical element can be decided on the basis of the occurrence of a few known major lines in the spectrum.

A more detailed investigation has replaced the initial cursory examination of the major lines of the elements. The interest has focused on the changes that are associated with changing conditions of the elemental vapours. The advances of gas kinetics and theoretical chemistry have led to the recent shift in emphasis. We have accepted the notion of a molecule as an entity endowed with particular forces and properties and formed by the association of atoms under well-defined rules. In addition to the thermal motion of the molecule as a whole, its constituent atoms move against each other, the energy of the intra-molecular motion being proportional to the thermal energy of the molecules. The thermal motion (with the exception of their velocity and mean free path) of the molecules is independent of the species of gas or vapour; this, however, is not the case for their internal motions. The movements of the constituent atoms of any molecule depend on their relative position, their numbers and masses as well as on their binding forces and the kind of collisions that happen between molecules. The atomic motion within molecules, which had been neglected before the scientific acceptance of kinetic theory, turns out to be an interesting and important aspect which enables us, together with other chemical and physical properties, to obtain more detailed knowledge of the real nature of molecules. In studying the changes of atomic motions brought about by minute changes in atomic positions together with their binding forces we have a better opportunity to gain insight into the nature and properties of molecules than by almost any other means. Many different investigations with methods ranging from electrolysis to studies with polarised light have been successfully undertaken, but none are as promising as spectral analysis, although admittedly its success up until now has not been too great."

This last sentence is characteristic of the situation of atomic and molecular physics until the mid 1920s.

### *Paradigm Shift – Quantum Mechanics*

The formulation of quantum mechanics in the 1920s brought the solution. Erwin Schrödinger solved the structure of the hydrogen atom and obtained its spectrum already in his first paper in 1926 where he introduced his famous equation for the description of quantum mechanical phenomena.

It became evident that the Schrödinger Equation is the key to the description of atomic spectra, but its solution for complex systems was impossible at the time because of computational difficulties. Most of the accumulated problems in atomic physics were solved in principle within a few years after the introduction of the Schrödinger Equation: in 1927 the formulation of the Thomas and Fermi statistical atom model, in 1928 the formulation of the many body problem by Hartree and its extension to a general formulation with exchange terms by Fock. Dirac proposed his equation in 1928 and thus enabled the relativistic description of atomic quantum problems. Spectral fine structure could also be explained and the agreement of the theoretically predicted hydrogen spectrum to the experimentally obtained ones was so extraordinary that all the principal problems seemed to have been solved. The discovery of the positron as the electron's anti-particle was further conclusive evidence for the value of the concepts embodied in the Dirac equation. In their famous book Condon and Shortley covered the intricacies of multiplet structure and the different coupling modes of valence electrons. Another advance was made by Breit in 1929 with his concept of the Breit operator for the description of magnetic interactions.

A thorough description of atomic systems was thus achieved in a matter of a few years. But no methods existed for explicit calculations of real problems. Hartree's work was an exception: in 1930 he managed to calculate the complicated multi-particle wave functions of multi-electron atomic systems in a arduous effort with the aid of only a mechanical calculator.

The incredible advance of atomic physics proved to be fruitful for other areas too. Molecular physics expanded with new concepts of similar principal importance. Two other branches of physics, however, became the main focus of attention: solid state physics and nuclear physics, which gained rapidly in importance. Theoretical advances in atomic

physics were matched by a growing trend towards UV and VUV spectroscopy in the twenties. New techniques developed in Sweden enabled spectroscopy down to a few Ångströms. Their precision remained a standard for thirty to forty years. The Swedish researcher Edlen discovered a minute discrepancy to the Dirac theory in the spectrum of lithium at the beginning of the thirties. It took ten years to recognise and explain this discrepancy as a Lamb shift. The discovery of the Lamb shift ushered in a period of extremely rapid theoretical advances. Quantum electrodynamics (QED) was formulated around 1950 and turned out to be the most accurate of all physical theories. The verification of its accuracy motivates a considerable amount of research in atomic physics even today.

But the predicted values for the binding energy of inner electrons agree only within about 1% with the experimental facts. Theoretical interest has focused on this difference in the last ten years. Four additional effects are considered for its explanation: magnetic interaction between electrons, retarded potentials, vacuum polarisation and self energy, – the last two being the QED corrections that account for the Lamb shift. Electron correlation is negligible for the inner shells but we will discuss it in connection with outer electron shells. The calculation of these four effects formed a significant advance in theoretical physics in the last fifteen years. A more accurate calculation of the Breit operator was necessary in order to deal with the first two effects. Terms in addition to the Uehlig potential were found for the vacuum polarisation and a totally new method of calculating the self energy for heavy atoms was conceived.

The Hartree and Fock theory for the structure of atomic shells was one of the first highlights in atomic theory in the twenties. Its application to real cases was, however, impossible because of the afore-mentioned computational difficulties. Only the development of more and more powerful computers enabled the explicit calculation of increasingly complex atomic structures from the fifties onwards. But the quality of these models is still under review after more than twenty years of intensive research. Their success is also related to questions of the accuracy of QED models in atomic physics.

In order to show the scale of the different effects we will briefly discuss some of the theoretical concepts involved. For each of the atom's electrons one has to solve the (relativistic) Dirac equation where the potential is formed by the nuclear charge and the effect of all other electrons. Mathematically it involves the solution of  $2N$  coupled first order differential equations ( $N$  being the number of electrons in the system). In practice one usually solves the Dirac equation for a simpler relativistic

potential like the Thomas-Fermi potential to calculate the wave functions of all  $N$  electrons and their resulting potential. Its computed value is usually different from the initial potential, so that iterations are necessary until the differences are small enough and a self-consistent solution is found. The wave functions of the individual electrons, their effective charge distribution and the energy eigenvalues and total energy of the atomic system are thus obtained.

But the energy eigenvalues cannot be directly measured in experiments as binding energies; all that is measurable is the energy difference between the atom in its ground state and the ion where a single electron has been liberated from the atomic system. Hence two independent calculations are required to obtain the difference between the two total energies of the different atomic systems.

These ab initio calculations without any free parameters are fairly accurate, which reflects on the accuracy of the Hartree-Fock model which yields 99% of the result and the calculation of the four correction terms. The surprising accuracy of the Hartree-Fock model combined with QED corrections is still not quite understood by theoreticians.

The remaining difference of a few eV however is of continued interest because it constitutes the only test of QED corrections for atoms with high nuclear charge  $Z$ . Muonic atoms are a useful test for the values of vacuum polarisation, which contributes four terms in this case. One electron systems with high  $Z$  are of great interest as they enable the study of QED effects in hydrogen-like atoms.

Atomic systems also constitute an ideal field to obtain evidence of the neutral currents which are a concept of increasing importance in high energy physics. But atomic levels are mainly determined by electromagnetic forces; the weak interaction contributes only  $10^{-6}$  to their energy. Such precision is currently very difficult to obtain for theory and experiments. But this example shows how modern physics is re-integrating its atomic and molecular branches.

Atoms for which the electromagnetic coupling constant is greater than unity are of particular interest for atomic physicists. This coupling constant is the product of the Sommerfeld fine structure constant  $\alpha \approx 1/137$  and the nuclear charge  $Z$ . The Dirac equation for a point like nucleus has no real valued solution for  $Z = 137!$  There are nevertheless solutions if the extension of the nucleus is taken into account. But the effect mentioned above become large. The lowest (1s) level dips into the sea of negative continuum levels that are also solutions of the Dirac equation. The resulting new effects like spontaneous positron emission and vacuum charges are hot topics of current research. Unfortunately such heavy atoms do

not exist in nature. They can only be briefly created in nuclear collisions of two heavy atoms. But the combined system thus created evolves through a quasi-molecular state, which implies that the experimental results are a combination of molecular and quasi-atomic effects. This has generated new research topics for molecular physics too.

Last but not least one needs to address the question of electronic correlations. The view that multi-electron systems are described by a superposition of infinitely many configurations is well established today. Many practical computational problems which cannot be discussed here are the result. One attempt at their solution is the (as yet unproven) Hohenberg-Kohn theorem stating the existence of a single-density functional which is sufficient for the description of any quantum mechanical system. The correlation problem would be solved if such a density functional could be found for complex atoms. Opinions differ as to whether such a functional is possible and a solution is not in sight but some rather simple local density functionals already allow quite good descriptions of solids and molecules.

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The authors of this article are members of the working group for theoretical physics.