A Fragmentary Tale of the Atom

Bicentennial Tribute
to
John Dalton’s ‘A New System of Chemical Philosophy’ (1808)

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I. Introduction:

Richard Feynman chose the “atomic hypothesis” to be the most important single statement to be passed on to posterity if only one sentence would outlive a catastrophe in which all else would perish. This well-known hypothesis, is that “All things are made of atoms – little particles that move around in perpetual motion, attracting each other when they are a little distance apart, but repelling upon being squeezed into one another”. The beginnings of this idea are traced to John Dalton’s hypothesis made in 1808 that all matter consists of tiny, indivisible particles, called atoms. Two hundred years have elapsed since Dalton’s publication of ‘A New System of Chemical Philosophy’. It is interesting at this point to reflect on how the atomistic model has grown, providing insights in fundamental laws of nature, and producing modern gadgets that have pushed the frontiers of technology at an incredible pace. Man’s exploration in the physics of the atom continues to provide new insights in the fundamental laws of physics. A synopsis of the developments of atomic science over two hundred years is both an exciting and a challenging task, even if only a very few of its select fragments can scarcely be touched upon. This tale will attempt just that.

Analysis of the physical world in terms of the tiniest of the material particles is in fact very old, an ancient one. In fact, it precedes Dalton’s revolutionary system of chemical philosophy [1]. The first known conception of the atomistic approach to the material world is perhaps found in the works of Maharshi Kanad (600 BC) who developed the Vaisesika philosophy. In this philosophy, the atomistic model of the material world is propounded. However the Vaisesika philosophy goes well beyond the material world and it seeks to explore the cognizable material universe in terms of nine elements: air, earth, fire, mind, self, sky, space, time and water. Maharshi Kanad’s contributions to scientific analysis of the universe are extensive. The Brahma Vaivart Puran in fact narrates that Maharshi Kanad was a reincarnation of Sage Gautama, who was ordained by Lord Shiva himself to reappear in the role of Kanad.

In the post Galileo-Newton period, the atomistic model was propounded along a modern analytical scientific approach by John Dalton, born on the 6th of September 1766 at Eaglesfield, Cumberland, in England. Dalton’s early work included maintaining meteorological records and he even published a book on English grammar, which earned him membership of the Manchester Literary and Philosophical Society. He reported extensively on color blindness, which afflicted both him and his
brother, and often referred now as ‘Daltonism’. Dalton investigated several principles in chemistry and thermodynamics and went on to formulate his ‘atomic model’ of condensed matter which was recognized and included by Dr. Thomas Thomson, Professor of Chemistry at the University of Glasgow, in the III Edition of his book ‘A System of Chemistry’, published in 1807. This work came in the exciting period hailed as one in which chemistry achieved “maturity as a science” [2]. An excellent review of Dalton’s contributions and his personality can be found in the review by Bolton [3]. John Dalton is amongst the most celebrated chemists. This can be seen from the fact that the Royal Society of Chemistry, which came into being through an amalgamation of four very prestigious academic bodies [(i) ‘The Chemical Society’ (founded in 1841), (ii) ‘The Society for Analytical Chemistry’ (founded in 1874), (iii) ‘The Royal Institute of Chemistry’ (founded in 1877) and (iv) ‘The Faraday Society’ (founded in 1903)] publishes a journal named ‘Dalton Transactions’. This is the most prestigious publication of the RSC and has the highest impact factor amongst the European journals in the field of inorganic, bioinorganic and organometallic chemistry.

Essential elements of John Dalton’s atomistic view are contained in the following postulates he made about the atom namely:

- Matter consists of tiny, indivisible particles, called atoms, which are unchangeable.
- Atoms of one particular element are all exactly alike, but atoms of different elements are different.
- Atoms of elements combine to form molecules of a ‘compound’ formed through chemical reactions in which atoms are neither created nor destroyed, but are only rearranged.

Dalton’s monograph ‘A New System of Chemical Philosophy’ was published in 1808 [1]. Soon after, atomic science progressed in a very big way when Fraunhoffer (1817), while carrying out some tests on the new prisms he had made, reported ‘dark lines’ in the spectra of stars [4]. He systematically catalogued his observations accurately. These ‘dark’ or ‘missing’ lines are called the Fraunhoffer lines. Fraunhoffer reported 574 missing lines in the solar spectrum and this raised a fascinating question: why wouldn’t the sun emit just these colors? Fraunhoffer’s expertise was on making lenses and prisms and optical devices rather than spectroscopy [5, 6], and he did not really explain the origins of the ‘missing’ or ‘dark’ lines. In fact, it was the work of John Herschel and David Brewster which provided an interpretation of the Fraunhoffer lines which they explained could either be caused by absorption in a cool gas in the earth’s upper atmosphere or in the star’s outer atmosphere. Finally, the reversibility of the absorption and the emission spectrum was demonstrated and explained by Kirchoff and Bunsen in 1860 [7].

The nineteenth century witnessed observations such as the Dobereiner’s law of triads and Newland’s octaves which were the precursors of the tabular arrangement of the periodic properties of atoms, developed independently by Lothar Meyer and Dmitri Ivanovich Mendeleev. Dalton’s atom now had a firm place at the very base of the science of materials; the periodic properties of elements were connected to atomic weights by Mendeleev [8].
II. Development of Atomic Physics as an Empirical Science:

In the meanwhile, the Swedish spectroscopist Anders Jonas Angstrom (1814-1874) built high precision spectrometers and carried out accurate measurements [9] of wavelengths in the solar spectrum and reported over a hundred spectral lines. He was able to deduce from his spectra that hydrogen was present in the solar atmosphere. Angstrom’s pioneering work in precision spectroscopy is one of the most important developments in our story of the atom.

Ångström, Anders Jöns
1814–74,

Swedish Physicist

Ångström’s spectrometer

4101.2, 4340.1, 4860.74 and 6562.10 Å

Angstrom’s measurements on the spectrum of the hydrogen atom (1853)

Angstrom measured with great precision the wavelengths of the visible lines in the emission spectrum of the hydrogen atom. The four visible lines had wavelengths of 4101.2, 4340.1, 4860.74 and 6562.10 Å, in units of length named after this skillful Swedish experimentalist. Even on the second look, very few, if any, would recognize a pattern in these four numbers, but Johan Jacob Balmer, who was a teacher of Mathematics in a secondary school for girls figured out in 1884 that each of these four wavelengths conform to the following mathematical relation:

\[ \lambda = b \left( \frac{n^2}{n^2 - 4} \right), \]

with \( b = 3645.6 \) Angstroms and \( n = 3, 4, 5, 6. \)
Balmer’s ingenious mind went on to predict that there would be other lines in the spectrum, as were indeed found later in the infrared part of the spectrum corresponding to \( n = 7, 8, \) etc., and he predicted also that the number 4 in the above formula could be replaced by squares of other integers, 9, 16, 25,…, etc.

Six years later, in 1890, Johannes Robert Rydberg (1854 – 1919) deduced independently, without making any reference to Balmer’s formula that he was unaware of, that the four spectral lines in the visible part of the hydrogen atom conformed to the following relation:

\[
\frac{1}{\lambda} = R_H \left[ \frac{1}{n^2} - \frac{1}{m^2} \right],
\]

wherein \( n \) and \( m \) are integers, and \( R_H \) is a constant, now known as the Rydberg’s constant, having a value of 109,737 cm\(^{-1}\). Balmer and Rydberg’s work epitomizes the grand success of pre-quantum-mechanics empirical science.

II. Development of Quantum Mechanics:

Progress in the development of the empirical science of the atom overlapped with three major developments in Physics:

[i] - the struggles in the understanding of the spectral intensity distribution of radiation from a ‘black body’, in the works of Gustav Kirchhoff (1859, 1860), Josef Stefan (1879), Ludwig Boltzmann (1884), Wilhelm Wien (1896) and Max Planck (1899) [10].

[ii] - the discovery (1887) of the photoelectric effect in the works of Heinrich Hertz and Philipp Lennard, and its interpretation by Albert Einstein (1905) [11].

[iii] - the discovery of radioactivity and eventual recognition of the \( \beta \) particle as the electron [10].

Each of the above three developments were to have a huge impact on the development of quantum mechanics and atomic physics which in fact took place hand in hand. The first of these arguably contained the genesis of quantum theory in the ‘corpuscular’ hypothesis made by Planck. However, notwithstanding the success of his hypothesis, Planck was himself very weary of the corpuscular hypothesis he had made as an “act of desperation” to explain the black body radiation spectral intensity distribution. Thomas Kuhn therefore argues that it is not to Planck in 1899 but to Einstein in 1905, in his explanation of the Hertz-Lennard experiment, that we owe the origins of quantum theory, for it was Einstein rather than Planck who placed the quantization of the electromagnetic radiation on firm logical footing [12]. The discovery of the electron, on the other hand, laid the foundation for the Rutherford model of the atom. Working in the laboratory of J. J. Thomson, Ernest Rutherford, the First Baron of Nelson and Cambridge, carried out some of the most fascinating experiments that showed that the atom is mostly hollow, with a positive charge packed in a rather dense and very tiny region while much of the empty space was occupied by the electrons that made the atom neutral. Rutherford’s model [13] of the atom was deduced from his experiments on the scattering of alpha particles from gold. It was a great improvement over Thomson’s ‘jelly’ model, and the immediate precursor [14] to the atom of Niels Bohr (1913).
The stability of the atom, considering the fact that electrons revolving around Rutherford’s nucleus would radiate and lose energy, was explained away soon by the bold hypothesis made by Niels Bohr [15] which envisaged ‘stationary’ orbits traced periodically by electrons along trajectories which would ‘quantize’ their angular momenta. The Bohr model found quick verifiability [16] in the experiment on electron-atom collisions conducted by James Frank and Gustav Ludwig Hertz (nephew of Heinrich Hertz).

The Rutherford-Bohr model gave credibility to the Balmer-Rydberg expression for atomic spectral lines, but depended on intangible trajectories which required for their being the simultaneous knowledge of both position and momentum of the electrons. This was one the most exciting periods in the development of quantum theory whose story interlaces intimately with the understanding of the atom. The inaccessibility of the dynamically conjugate observables position and momentum for simultaneous accurate measurements placed a lower limit on the accuracy with which the two could be measured simultaneously, and this recognition laid the foundation of quantum theory enunciated in the celebrated ‘uncertainty principle’ of Heisenberg. This principle negates the existence of orbits/trajectories.

Banesh Hoffman describes in her book [17] Rutherford-Bohr orbits in a chapter titled the ‘atom of Niels Bohr’, but in the very next chapter in which she dispenses with the very notion of orbits/trajectories. Aptly, she has titled this chapter as ‘the atom of Bohr kneels’.

Subsequent developments in quantum theory have no easy classical analogues. The formalism required reconciliation between tangible observations and mathematical abstractions and the growth of the subject was entirely due to the passionate pursuits of intricate ideas by intellectual giants of that era. Intellectual giants debated consistencies and compatibilities [18], and quantum theory emerged triumphant in its ability to explain and predict physical observation. Throughout the development of the quantum theory, atomic physics remained at the focus. In fact, it was the systematic organization of the atomic spectral line intensities and the frequencies predicted by the Rayleigh-Ritz combination rules which led Heisenberg to dispense with the intangible orbits of Niels Bohr and develop a scheme that would address observables alone. The mathematical relationships that emerged from this consideration led Heisenberg to the now famous commutation rules for the position and momentum operators [19].

At his point, rather than getting drawn deeply into the development of quantum theory, we return to developments directly in atomic physics. We consider the similarities between optical transitions giving rise to the alkali atom spectra which are very similar to the spectrum of the hydrogen atom. Consider the sodium atom for example with its 3s electron outside the neon-core making it very analogous to the two-body proton-electron problem of the hydrogen atom. An interesting variance is the fact that while the H-atom energy eigenstates are degenerate with respect to the orbital angular momentum quantum number l, such is not the case for the Na-atom. The classic illustration of this fact is the appearance of the famous yellow line(s) of the sodium vapor lamp which result from electronic transitions between the 3p and 3s levels. In the H-atom, these states would be degenerate, and there would be no spectral transition between them. Now, there is a close connection between symmetry and degeneracy; when the symmetry of a Hamiltonian is lowered by a perturbation (as in the Zeeman/Stark effect), the degeneracy is lifted (partially/wholly). This raises an interesting question: just what is the symmetry responsible for the degeneracy with respect to the l quantum number in the case of the H-atom that is broken in the case of the Na-atom? Later work by Vladimir Fock [20] provided the subtle answer to this by explaining that hydrogen wavefunctions possess the O(4) symmetry. The ‘Fock Symmetry’ of the hydrogen atom explains the degeneracy of hydrogen...
wavefunctions, and this explanation is easily one of the most important milestones in the fascinating saga of atomic physics. These issues continue [21] to move the frontiers of science.

In some sense, the symmetry responsible for the degeneracy with respect to the $l$ quantum number is due to the ‘dynamical symmetry’ linked to the constancy of the so-called Laplace-Runge-Lenz vector. The potential seen by an electron in the 3s state of the sodium atom would not be strictly given by inverse-length causing the Bohr-Kepler orbit to precess and require an energy correction associated with the precessional motion. On the other hand, the notion of ‘orbits’ being abandoned in formal quantum theory, the energy corrections are explained by analyzing analytical properties of the electron eigenfunctions when the electron’s wave mechanics is determined by the electric field of a positive ion. This formalism is known as the ‘quantum defect theory’ and it provides a common framework to deal with atomic bound states, series perturbations, autoionization states and also electron-ion scattering [22].

**III. The ‘Fourth’ Quantum Number of Atomic Electrons:**

We now return to a further detail of the sodium yellow spectrum, the most prominent feature of which is the appearance of not one, but two lines, respectively of wavelengths 5896 Å and 5890 Å. These two spectral lines are respectively called the D1 and the D2 lines which originate due to splitting of the 3p levels by a tiny 0.0021 eV. We know now that this splitting is due to what is called as the ‘spin-orbit’ interaction, but the understanding of the electron’s spin was a huge challenge in development of physics, not just atomic.

Wolfgang Pauli had proposed in order to explain the filling of the atomic shells according to the aufbau principle that there had to be an additional *double-valued* quantum number. Pauli conjectured that inclusive of this new quantum number, no two electrons in an atom could have the same set of four quantum numbers. This inference is at the heart of what is called as the ‘Pauli exclusion principle’, but it did not, at this point of time [23], invoke the idea of ‘spin’. Even as Pauli’s ‘exclusion principle’ for the ‘four quantum numbers’ was formulated in 1924, the idea of half-integer spin quantum number itself would need to wait … for George Uhlenbeck and Samuel Goudsmit!

Uhlenbeck and Goudsmit were students of Ehrenfest and were struggling to understand the additional structure that was observed in the spectral lines of helium in the laboratory of Louis Paschen. By playing with the numbers, Uhlenbeck and Goudsmit arrived [24] at the correct numerical estimate of an additional angular momentum that an electron would have, but this would require ‘half-integral’ quantum numbers which was a very repugnant idea in the context of its time when physicists had, after all, reconciled with ‘integral’ quantum numbers! Amongst those who violently opposed the idea of half-integer quantum numbers were some of the very founders of quantum mechanics, including Heisenberg and Sommerfeld, and even Pauli himself!

The relationship between spin and statistics can be stated very simply: particles with integer spins are described by Bose-Einstein statistics, and those with half-integer spins by Fermi-Dirac statistics. This connection is nevertheless very subtle, and the complexities are best described by Feynman [25]: “It appears to be one of the few places in physics where there is a rule which can be stated very simply, but for which no one has found a simple and easy explanation. The explanation is down deep in relativistic quantum mechanics. This probably means that we do not have a complete understanding of the fundamental principles involved”.

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The electron ‘spin’ would subsequently find its formal place in quantum mechanics only in the relativistic formalism of Dirac [26, 27]. One of the very best sources to learn about ‘spin’ is Tomonaga’s book [28]. Experimental correctness of the electron spin is best illustrated by the Stern-Gerlach experiment.

A memorial plaque honoring Otto Stern and Walther Gerlach, mounted in February 2002 near the entrance to the building in Frankfurt, Germany [29].

Inscription translation: "In February 1922 . . . was made the fundamental discovery of space quantization of the magnetic moments of atoms. The Stern-Gerlach experiment is the basis of important scientific and technological developments in the 20th century, such as nuclear magnetic resonance, atomic clocks, or lasers. . . .”

Before we proceed to discuss further details, we remind, even at the cost of possible redundancy, that the spin quantum number has nothing to do with ‘spin’ in the sense of a ‘spinning earth’, in as much as the orbital angular momentum has nothing to do with ‘orbit’ in the classical sense of an ‘orbit/trajectory’ which would require simultaneous knowledge of both position and momentum. The hallmark of quantum mechanics is the principle of uncertainty, which limits the number and nature of observables that are measurable simultaneously and accurately. A complete set of such quantities is the most a physicist explores in order to get the maximum information about the quantum system. When the atom is placed in a magnetic field, the relative strengths of the spin-orbit interaction and the coupling of the electron’s magnetic moment with the external magnetic field determine which set of four compatible measurements constitute the best set of ‘good quantum labels’. Exploration of atomic properties by using external magnetic fields constitutes the rich field of Zeeman-Paschen-Back spectroscopy. Likewise, Stark spectroscopy has become a rich probe in which external electric fields are employed to reduce the symmetry of the atomic Hamiltonian and lift degeneracy.

IV. The ‘Many-Electron’ Atom:

The many-electron problem poses a completely new kind of difficulty: the problem can be posed formally, but the conceptualization of the N-electron problem leads to immediate difficulties, as the
solution to the N-electron Schrodinger equation requires the corresponding Hamiltonian, which itself requires for its construction the very same solutions! This can be readily seen from the following two relations:

\[ H^{(N)} \psi^{(N)} = E^{(N)} \psi^{(N)} \]

\[ H^{(N)} = \sum_{i=1}^{N} \left( -\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} \right) + \sum_{i<j=1}^{N} \frac{1}{r_{ij}} \]

One can come out of the dilemma, following a technique introduced by D.R.Hartree (1897-1958), by starting out with trial wavefunctions, generate the Hamiltonian in terms of these trial functions, and then solve the problem numerically and iteratively till self-consistency is reached. The N-electron wavefunctions \( \psi^{(N)} \) are expressed as an antisymmetrized product written often in a determinantal form, known as the Slater determinant. The process of getting such ‘self consistent field’ (SCF) solutions is completely equivalent to a variational procedure that would seek to minimize the average value \( < \psi^{(N)} | H^{(N)} | \psi^{(N)} > \) while maintaining the individual electron wavefunctions in the antisymmetrized product orthogonal and normalized. The resulting SCF procedure is often called as the Hartree-Fock (HF) method [30], when two-component electron spin wavefunctions are employed in the single-particle states, or the Dirac-Fock (DF) method [31] when four-component relativistic bispinors are employed. D.R. Hartree’s work was numerically intensive, and he was invited to the USA to advise on the development of the world’s first computer, the ENIAC, by John Eckert. However, Hartree’s original numerical work was in the pre-computer era, using mechanical differential analyzers he built, supported by his enthusiastic father William Hartree.

The variational approach employed in the HF/DF method however makes use what is known as the ‘frozen orbital approximation’. Essentially, it does not take into account the fact that if one were to remove one of the N-electrons from the system, the wavefunctions of the remaining N-1 electrons...
would, in some sense, relax. Within the framework of the frozen orbital approximation, the HF/DF equations connect the variational parameters of the SCF methodology to the binding energy of the atomic/molecular system. This result is known as the celebrated Koopmans’ theorem, after the solitary paper [32] Koopmans wrote in atomic physics before he switched over his attention to mathematical problems in Economics. He was even awarded in 1975 the ‘Sveriges Riksbank Prize in Economic Sciences’ in memory of Alfred Nobel.

For accurate estimates of atomic properties, it should now be clear to the reader that one must employ a relativistic model (such as the Dirac-Fock) and also go beyond the ‘frozen orbital approximation’. The latter would give many-electron wavefunctions that are superpositions of various Slater determinants, one for each possible configuration that is worthy of consideration. One is thus led to the MCHF (Multi-Configurational Hartree-Fock) or MCDF (Multi-Configurational Dirac-Fock) schemes that represent this broad approach. If one were to look for exact analytical solutions of the N-electron atomic/molecular system, as G.E.Brown put it, “having no body at all is already too many” [33]. One must therefore make approximations, and the challenge in many-body theory is to make the best and the most consistent approximation that one can. Powerful approximation methods such as the method of configuration interaction, MBPT (many-body perturbation theory) [34], diagrammatic perturbation theory [35], the relativistic random phase approximation (RRPA) [36], etc. are developed for this purpose, details of which go beyond the scope of this overview.

V. ‘Atomic Physics’ at the Forefront of Fundamental Physics:

The presence of electron spin, we have seen above, gives rise to the ‘fine structure’ of the atomic energy levels. This ‘constant’ is denoted by $\alpha = e^2/\hbar c$ and gets its name from the kind of splitting of atomic energy levels due to spin-orbit interaction which give rise, for example, to the D1 and D2 lines of the sodium atomic spectrum as noted in Section III. Nevertheless, $\alpha$ impacts physics in a multitude of ways and has fascinated physicists ever since its discovery. Said Feynman: “It has been a mystery ever since it was discovered ….. and all good theoretical physicists put this number up on their wall and worry about it” [37]. The fine-structure constant scales the strength of the interaction between a charged particle and the EM field. In the ‘renormalization’ formalism of quantum field theory, the coupling strength is allowed to depend on the energy-scale. This is often referred to as ‘running of the coupling constant’. Thus the ‘constant’ perhaps changes. Laboratory high precision measurements can be performed that may not yield an accurate determination of $\alpha$ itself, but would reveal if the value determined could in fact vary with time. By studying how light was absorbed by metallic atoms in gas clouds about 12 billion light-years away, the atomic astrophysical spectroscopy research group of John Webb at University of New South Wales claimed that the structure of the atoms from distant quasars would have been just slightly different, due to a different value of $\alpha$ [38]. On the other hand, more recent measurements [39] suggest that the value of the fine-structure constant is not changing by more than 1.6 quadrillionths of 1 percent per year, with an uncertainty of 2.3 quadrillionths of 1 percent per year. The fine-structure constant can be measured by carrying out different kinds of experiments which are just as challenging as much as the value of $\alpha$ defies any simple theoretical prediction. There may be new physics that would throw up new questions if theoretical predictions and accurate measurements of the fine structure constant fail to converge to the same value. Advances in ‘atom interferometry’ have enabled the measurement of $\alpha$ with a relative uncertainty of $4.5 \times 10^{-9}$ [40].
Atomic physics is today contributing significantly to the relationships between symmetry and conservation laws, pushing the frontiers of physics to test the ‘standard’ model of physics and/or to explore physics beyond the standard model. As is well known, parity violating processes were admitted in Physics in the early work due to Lee and Yang (1956) on weak interactions ($\beta$ decay) and detected by Wu (1957). Following the electroweak unification in the Glashow-Weinberg-Salam model, search for parity nonconservation (PNC) in atomic processes began in the 1970s [41]. The gauge Boson $Z^0$ of the standard model, unlike the $W^\pm$ gauge Bosons, is neutral and would mediate an interaction between atomic electrons and the nucleus. The so-called ‘nuclear weak charge’ $Q_W$ is to $Z^0$, what the electric charge is to the Coulomb interaction. The usual radiative transitions in atomic processes are governed by parity conserving selection rules imposed by the ‘electromagnetic’ Hamiltonain. The ‘electroweak’ Hamiltonian, however, does not commute with the parity operator and enables detection of parity-violating atomic transitions. In fact, there are two sources of parity nonconservation (PNC) in atoms: (1) the electron-nucleus weak interaction and (2) the interaction (sometimes called as PNC hyperfine interaction) of electrons with the nuclear anapole moment. PNC effect in atomic cesium yields the value of $Q_W^{(133\text{Cs})}\approx -72.90$, not in unreasonable disagreement with the value of $Q_W^{(133\text{Cs})}\approx -73.09$ obtained from high-energy experiments extrapolated to atomic scale [42]. A significantly large value of the anapole moment of the nucleon has been estimated in the case of cesium, augmented by collective nuclear effects. The discovery of CP violation in the decay of $K$ mesons prompted the search for violation of the time-reversal symmetry. Violation of T symmetry would require an elementary particle, atom or molecule to possess a permanent electric dipole moment (EDM), which is expected to be enhanced in heavy atom/molecule. The ‘standard model’ of particle physics predicts dipole moments that would be too tiny to be observable at all. EDM measurements therefore provide fascinating tests to explore ‘new’ physics beyond the standard model. Reliable accurate measurements in agreement with predictions of a robust theoretical formulation has the potential of telling us if and what physics is there beyond the ‘standard’ model, since limits on EDMs would put conditions on supersymmetric gauge theories [43,44].

This ‘fragmentary’ tale has had to not only skip some very exciting developments, but also has to hop back and forth in time to pick up pieces crucial to this variegated theme.
One of the very important consequences of Dirac’s relativistic solution to the quantum hydrogen atom problem is that the energy levels depend on the \((n,j)\) quantum number; it gives degenerate solutions for different values of \(l\). This turns out to be only approximately correct, for it ignores, as explained by Bethe, the quantization of the electromagnetic field and the correction to this was observed in the beautiful experiment carried out by W.E.Lamb and R.C.Retherford in 1947. The inclusion of this effect manifests as an energy shift, called the ‘Lamb Shift’ between the \(2S_{1/2}(n=2,l=0,j=1/2)\) and \(2P_{1/2}(n=2,l=1,j=1/2)\) levels. Corrections that result in the Lamb shift are about 10% of the fine-structure for the \(l=0\) states (and much smaller for larger \(l\)). These terms are best expressed using Feynman diagrams for vacuum polarization, electron mass renormalization, etc. of ‘quantum electrodynamics’ (QED). The contributors to QED, Dyson, Feynman, Schwinger and Tomonaga, were men of exceptional brilliance [45]. The magnetic moment of protons and neutrons comes from the quarks and the gluons and all this adds up to provide a net spin magnetic moment to the nucleus which interacts with the electron’s magnetic moment to generate what is called as the ‘hyperfine structure’. High precision hyperfine structure studies provides an extremely valuable tool in providing stringent tests on the quality of atomic wavefunctions, since it can usually be measured very accurately, and the nuclear magnetic moment can be determined independently.

VI. ‘Atomic Physics’ at the Frontier of Technology:

The radiation pressure that turns a comet’s tail away from the sun has extremely fascinating applications in laboratory atomic physics and is at the very root of the entire discipline of laser cooling and trapping. Atoms and/or molecules at room temperature move at about 300 m/s, which is close to the speed of sound. To do precision spectroscopy of atoms and to develop atomic clocks, atoms must be slowed down. What one exploits to achieve this is the electromagnetic radiation pressure exerted on the atoms. The resulting interactions are broadly, in this context, classified as ‘scattering force’ and a ‘dipole force’. The former results in scattering of the incident radiation in random directions and the latter induce a dipole moment in the atom which interacts with the
gradient of the incident electromagnetic field. The cooling and trapping of atoms is an extra-ordinary phenomenon which is achieved by these processes and investigated further by techniques such as the high precision magneto-optical trap recoil-ion momentum spectroscopy. Further ‘evaporative cooling’ techniques are employed to achieve temperatures that are cold enough to attain Bose-Einstein condensation. This is an unusual state of matter since all the atoms of the system coalesce into a quantum state in which their individual identity is overtaken by a condensed state of the many-atom system in which each has the same state and the same phase. Such a state was predicted by Bose and Einstein in their joint publication of 1922, and achieved for the first time in a laboratory in 1995 by E.A. Cornell and C.E. Wieman. Developments in laser techniques and associated quantum optics have led to the following Nobel prizes in the field of atomic physics in recent years:

1) For the development of methods to cool and trap atoms with laser light [Steven Chu,; Claude N. Cohen- Tannoudji ; William D. Phillips, 1997],
2) For achieving the Bose-Einstein condensation in alkali atoms [E.A.Cornell, C.E. Wieman, Wolfgang Ketterle, 2002] and
3) For precision laser spectroscopic measurements and quantum optics [John L. Hall,; Theodor W. Hänsch, ; Roy Glauber, 2005].

Laser cooling and trapping of atoms has led to many fascinating applications, since when an object bends light, the momentum of light changes, and to conserve momentum, the momentum of the object itself must undergo an opposite change (conservation of momentum) - effectively, it is like a force acting on the object. One can thus use light to manipulate microscopic objects as small as single atoms [46].

Using laser cooling techniques, one can not only tweeze and manipulate tiny objects of atomic dimensions, but also achieves tremendous enhancement in the accuracy of atomic clocks.

A modern atomic mercury ion clock [48] which measures optical frequency of a single ion in an ultra-cold electromagnetic trap is now developed that provides extremely accurate determination of time standard. This clock would not gain or lose even one second in 400 million years!

Measurements of optical frequencies with such amazing accuracy is enabled by advances leading to the femtosecond laser frequency comb and very narrow linewidth lasers. The atomic mercury clock is about five times more accurate than the cesium fountain clock. Improved accuracy in time measurement is continuously sought since it is of tremendous consequence navigation, global positioning systems, deep-space communication, etc. Besides, highly accurate measurement of time is required to investigate if the ‘fundamental constants’ of nature vary over long periods through which the universe evolves.
Other quantum controls on positioning single atoms have led to extraordinary advances in nanotechnology. These are inspired by the question Richard Feynman asked in his famous talk 'There is Plenty of Room at the Bottom' given at Caltech in 1959: "What would happen," Feynman asked, "if we could arrange the atoms one by one the way we want them?"

A 3sp³ state points towards the surface normal on the Si (111) surface, and the image of this atom should be symmetric with respect to the z-axis.

Because images in AFM are a convolution of tip and sample states, and the sample state is well known in this case, the tip state is most likely to be two 3sp³ states originating in a single Si tip atom [50].

A team of scientists at Osaka, for example, used the tip of an atomic force microscope to lift a single atom from a surface and then replace it [49]. This approach brings within reach assembling nanogadgets by bringing together atoms one by one!

One can excite an electron in an atom selectively by using UV laser pulses and lower frequency electromagnetic waves to a highly excited ‘Rydberg’ state and scoop out the electron density distribution so as to leave a desired pattern, such as would generate the word ‘OPTICS’ [50]. The amount of information that can thus be stored in a single atom is incredible! Besides, Rydberg atoms are potential candidates for making a quantum computer [52]. Furthermore, it has been found very recently [53] that highly excited (n = 72) can be produced by linearly polarized light at microwave frequency shone on Li atom to first lock the electron motion into an approximate semi-classical orbit. By subsequent control of the polarization state of the applied microwave field, specifically by changing it to circular polarization somewhat slowly compared to orbital frequency, the motion of the electron is then describable in terms of a non-dispersive Bohr wave packet. This has been hailed as a superb demonstration of Bohr’s correspondence principle [54] and described as an atomic analogue of the motion of the classical five ‘Lagrange’ points of the sun-earth system, with the earth’s effect replaced by that of the circularly polarized microwave field.

We conclude by highlighting the fact that Dalton’s atomistic model laid seminal foundation for the scientific, analytical approach to investigate condensed matter. In fact, even as we know now that the atom has cognizable parts in conflict with Dalton’s first postulate, it is the very atomistic approach which continues to provide insight into deep-seated fundamental laws of nature which reveal themselves through the discovery and predictions of elementary particles inclusive of those which mediate interactions between them. It is not surprising then to understand why Richard Feynman [55] said: “If, in some cataclysm, all of scientific knowledge were to be destroyed, and only one sentence passed on to the next generations of creatures, what statement would contain the most information in the fewest words? I
believe it is the atomic hypothesis (or the atomic fact or whatever you wish to call it) that all things are made of atoms—little particles that move around in perpetual motion, attracting each other when they are a little distance apart, but repelling upon being squeezed into one another.”

This tale is, as the title confesses, an essentially fragmentary one. Very many important developments are omitted. The field is vast, but even a narrow view of it seems to be an exciting one! There would be many alternative views of the developments in the field, even non-overlapping, that must be integrated to get a complete picture which is dismally beyond the scope of the present attempt.

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