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The evolution of the atom

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Abstract. An informal history of the concept of the atom is described from its earliest inception to the current quantum mechanical model.

1. The early days

The birth of the concept of 'atom' is conventionally traced to the early Greek philosophers, particularly Leucippus (c. 500 BCE), Democritus (c. 400 BCE) and Epicurus (c. 300 BCE) with elaboration inevitably by Aristotle (384−322 BCE), who doubted their existence. But do not let us get carried away by a combination of awe and admiration. It is right to admire them for ploughing furrows in the virgin intellectual landscape and opening the eyes of humanity to the power of thought. It is wrong to admire them for identifying the atom as the ultimate particle of matter. For one thing, it is not. For another, theirs were only philosophical musings perhaps better characterised as guesses. That their guesses were largely right has secured them a place in intellectual history, whereas those who guessed the opposite have fallen foul of modern respect. Guessing is not science. Guessing without an iota of evidence is not science. It might be the precursor to the gathering of evidence and scientific discovery, but it is not science nor more broadly is it a contribution to knowledge. Good for them that they thought about things at a deep and then novel way, but it is inappropriate to ascribe to them the discovery of atoms.

Even their guessing, unbounded as it was by any evidence whatsoever, led to what would now be regarded as error. Thus, not only did they consider an atom to be the final uncrossable frontier of slicing matter into bits, they ascribed atoms to bitterness (atoms with spikes), sweetness (atoms with a soft aspect) and to the soul (whatever that means). They were simply carried away by the allure of the concept and being unconstrained by experiment were able to fly off into fantasy. Good for them that they pointed the way to the exercise of thought, but one should not admire them for guessing partly correctly. Or were they even partly right? This point will be returned to in the coda to this paper with a reflection on whether they were totally wrong and that one should really admire their contemporary non-atomist guessers, even Aristotle himself.

Mankind then slept for two thousand years as it grappled with the properties of leprechauns, angels, the Trinity and the afterlife and applied the sword, the flame and the bomb to argue its position on what was no more than opinion and being only opinion, it could not be argued rationally or by experiment. Only death of the opponent was a way of vanquishing opponents in such discussions. The first awakening of rational argument concerning the indivisibility of matter can be ascribed to the application of one of the most powerful scientific instruments ever created: the chemical balance.

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2. The modern emergence

The balance initially in the hands of the still un-beheaded Antoine Lavoisier (1743−1794; his beheading by the revolutionary mob, like the murder of Archimedes by a sword's stroke of a Roman soldier representing everything academics have to fear, the retarding of intellectual progress by the wanton hooliganism of the mindless mob) and his wife enabled numbers to be attached to matter. Think how extraordinary it was that as matter underwent change it adhered to constraints represented by the characteristics of arithmetic.

The intellectually cautious John Dalton (1766−1844) built upon the realisation that numbers could be attached to matter and thus by proposing that there are entities that are preserved when matter undergoes a chemical reaction and one substance is transformed into another, he brought the first glimmerings of evidence into the discussion. Did he really believe that his units of accounting were real? Some suspect not and the thought lingered even into the early 20th century that Dalton's hypothetical atoms were but beads on his abacus. If one is generous, one can allow Dalton to think of his immutable entities as perhaps he did, as little eternal, immutable, hard spheres, all for a given element of exactly the same mass and thus acting as a quantum of calculation,

There must have been a wondering among the emerging legion of scientists as that name became adopted whether there were experimental ways of demonstrating the actual existence of atoms. For reality to bite, these wonderers would need to know not merely the relative masses of the notional entities (which Dalton had got right a lot of the time but not in every case) but their actual masses and some indication of their physical size. How otherwise could they be brought into the theatre of everyday contemplation? How can the unseeable be rendered as if seen? Philosophers might continue to wonder whether capturing such parameters as mass and size amounted to the confirmation of reality, but scientists prefer to pin down properties in the hope of reaching the bedrock of reality rather than wondering whether it is all merely a mutually satisfying social construct and therefore at its heart a waste of time (which when the Sun burns out might be the correct if disheartening conclusion).

There are many such glimmerings. Pierre Gassendi (1592−1655) promoted Epicurean ideas but muddled his thought like so many then and since with theological nonsense and Walter Charlton (1619−1707) likewise reflected on Epicurean ideas and managed to infer with reasonable accuracy the number of atoms in a typical sample of matter. It is hard to believe that such estimates were stimulated by anything other than a sense of the physical reality of atoms.

3. The modern view

Centuries passed. The glimmerings ignited into light when Jean-Baptiste Perrin (1870−1942) reviewed a range of different determinations of Avogadro's constant (a quantity used to evaluate the number of atoms in a sample) by a wide variety of techniques, saw their convergence and inferred that only if atoms were real could that convergence be explained. Philosophers predictably and perhaps rightly dismiss such convergences as nothing more than the matching of empirical data to preferred hypotheses. The existence of atoms is perhaps clinched now that we can see them (figure 1). Of course it is always arguable that an apparatus has been assembled to generate images that one can pretend are visualisations of atoms even though they are nothing of the sort. Thus, in the case illustrated the image was constructed by monitoring the flow of current through a needle-like probe as it tracks over a surface and then depicts that flow in what philosophers might regard as a deceptively contrived visualisation. Scientists will probably argue that cynicism should stop somewhere; philosophers probably not.

There comes a point though where empirical data guides the elaboration of models rather than merely replacing them with something better preferred. Science progresses even when revolutions overthrow the established, which is then to be seen in the light of a different illumination, not as crass stupidity. Quantum theory replacing classical mechanics is a particularly appropriate example in this context with the former not merely replacing the latter but illuminating it too and explaining its adequacy for accounting for certain phenomena such as the motion of macroscopic bodies. On the whole science progresses by enhancing understanding, not overthrowing it.

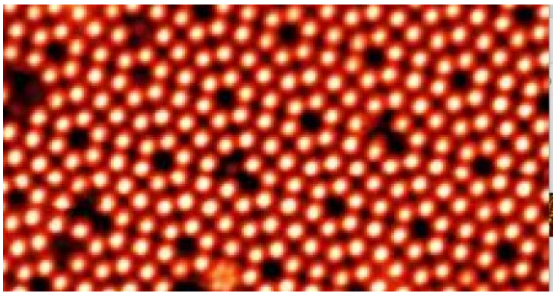

Figure 1. A surface tunnelling microscopy (STM) image of a surface, leaving little room for doubt that atoms exist.

This progressive elaboration and perhaps realisation of the concept of atom began in 1897 with the discovery by J.J. Thomson (1856−1920) that they had stuff inside them, namely electrons, which could be extracted and characterised. Electrons, it appeared, are a universal component of matter. There was some inkling of the mass of an electron inferred from the heat that a beam of them deposited when it impacted on a target even though its precise value was not determined for some years. The immediate problem once their mass and charge had been discovered was to determine how many electrons were in each atom and how they were arranged. Rather alarmingly the known mass of a hydrogen atom and the recently estimated mass of an electron suggested that even for hydrogen there were around a thousand electrons in each atom. Thomson proposed the 'plum pudding' model of an atom, so named despite it bearing little resemblance to an actual plum pudding, in which this swarm of mobile, orbiting electrons are embedded in a positively charged, imponderable jelly-like substance which cancelled the negative charge of the electrons and left the atom electrically neutral. No one had a clue about how the swarm might be distributed within the jelly and the elaborate and nearly theological interpretations of their motion in terms of vortices led nowhere.

The plum pudding model was almost literally shot down by the Geiger−Marsden experiment, carried out under the direction of Ernest Rutherford (1871−1937), a student of Thomson. (Moral: beware especially of one's own students.) That now famous experiment in which α particles were directed at an initially platinum and later a gold foil target led to the identification of the nucleus. As Rutherford remarked, the observation of an α particle scattering through a large angle '*was like an artillery shell fired at tissue paper and coming back to hit you*'. Thus, it appeared that the positive electric charge and the mass of an atom were accumulated in a relatively tiny body, in due course called the atomic nucleus, with electrons swarming around it.

Rutherford was able to make an estimate on the charge of the nucleus, but it was really Henry Moseley (1887−1915) through his analysis of the frequencies of X-rays emitted by atoms, who was able to identify the charge of the nucleus of each atom, to ascribe to them an ordinal number now known as the atomic number and by implication to identify the number of electrons in the extranuclear swarm, which for hydrogen of course was merely 1 and for the then heaviest known element, uranium, was 92.

Hydrogen became the centre of attention for its spectrum was known in detail and all that was necessary to be done was to identify the trajectory of the single electron presumably in orbit around the central, relatively massive nucleus under the influence of its Coulombic field. The Coulomb field though is a seductive beauty. In this case it lured Niels Bohr (1885−1962) into the belief that he had cracked atomic structure by allowing him to deduce almost exact agreement with the orbital energies of hydrogen and spectroscopic data on it on the basis of a wholly incorrect physical model. It is easy to imagine the thrill that Bohr must have felt when his calculation turned up numbers that agreed so well with observation and his model is an important step in the history of science, being the first attempt at bringing quantum ideas to bear on a mechanical system. Unfortunately the image he conjured based on Rutherford's vision of an electron in orbit around a central nucleus was so compelling that it has embedded itself into the cultural awareness of just about everyone and has become the icon of the representation of atoms almost universally despite being almost entirely wrong (figure 2). The planetary Bohr model is now an ineluctable image of an atom in the public gallery of ideas. The model also inspires the thought that an atom is almost entirely empty space, a miniscule nucleus surrounded by pointlike electrons orbiting in in a void.

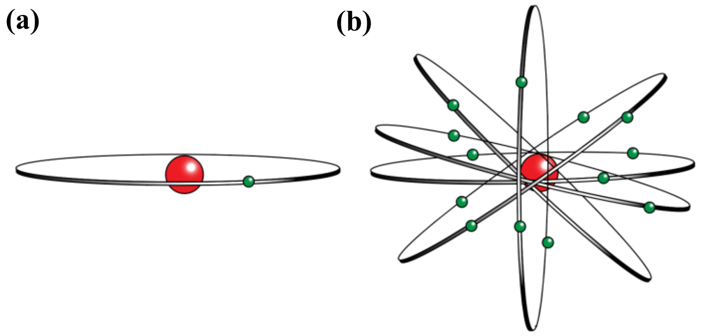

Figure 2. (a) The ground state of the hydrogen atom according to Bohr and **(b)** one of the galaxy of representations it has inspired and embedded in the popular perception of atoms.

Erwin Schrödinger (1887−1961), up a mountain with a mistress, must have had a similar moment of intellectual bliss when for relaxation from his pleasures he solved his own equation for the hydrogen atom and ended up with almost exact agreement with observation but on a fully quantum mechanical basis, not one in which classical and quantum concepts had been, however imaginatively, cobbled together. The Schrödinger model of the hydrogen atom with subsequent important tidying up to bring it into line with special relativity by Paul Dirac (1902−1984) is where things remain today.

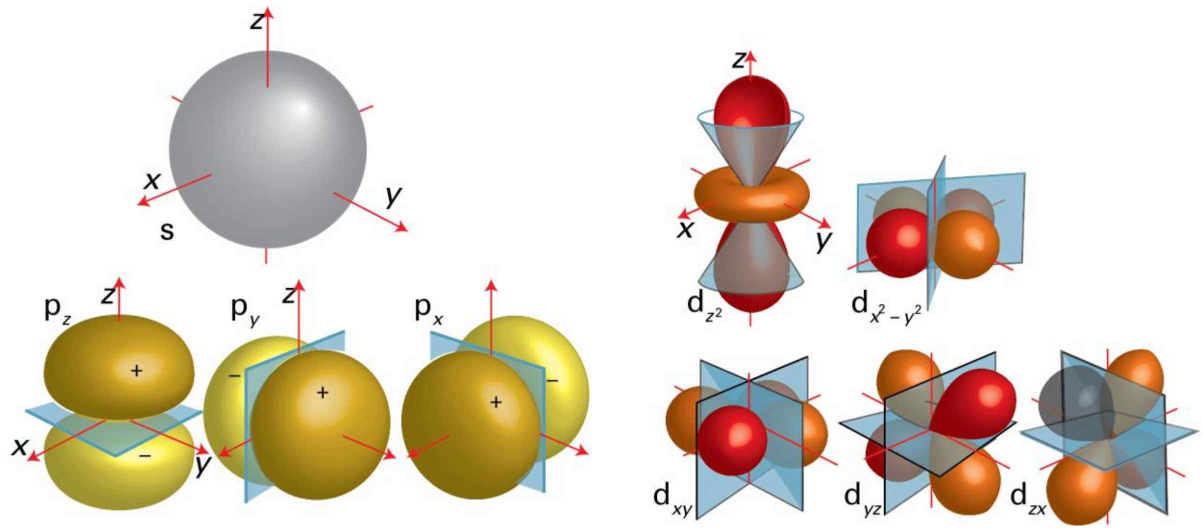

Figure 3. Three kinds of orbitals encountered in the hydrogen atom depicted as surfaces that bound most of the electron density. The notation is s for $l = 0$, p for $l = 1$ and d for $l = 2$. The planes indicate surfaces on which the electron will not be found: they are the 'nodal planes' of the orbitals.

Now the atom is envisaged as having a single massive positively charged nucleus with the electron distributed in one of an infinite number of one-electron wavefunctions referred to as orbitals and specified by the principal quantum number $n = 1, 2, \ldots$, the orbital angular momentum quantum number $l = 0, 1, 2, \ldots, n - 1$ and the magnetic quantum number $m_l = 0, \pm 1, \ldots, \pm l$, each one being confined to a range of values as indicated (figure 3). In its ground state, its lowest energy state ($n = 1$, $l = 0$, $m_l = 0$), the electron is distributed spherically symmetrically in a cloud around the nucleus with that cloud densest at the nucleus and its density falling away exponentially with distance (figure 4). There is no orbital angular momentum to withstand the Coulomb attraction of the nucleus: the stability of this state comes from a balance of the kinetic energy of the electron (which is related to the curvature of that exponential decay) and the potential energy of the electron in the field of the nucleus. There is no void: the electron may be found anywhere but with different probabilities at different distances from the nucleus. In that sense an atom has no empty space; it is not a scarcely populated void like an actual solar system. Nor is an atom a sharply defined sphere: although the overall electron density in a many-electron atom is spherical, its edge is a rapidly exponentially declining fuzz.

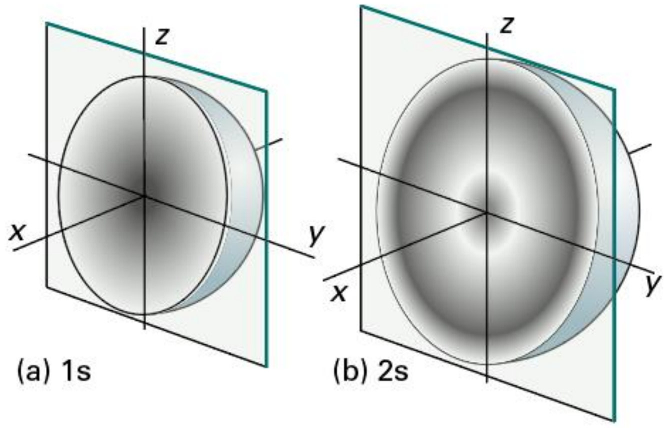

Figure 4. The internal structure as indicted by the distribution of electron density of the 1s and 2s orbitals of a hydrogen atom.

4. The beauty beneath the surface

The Coulomb potential's hidden beauty is apparent in Schrödinger's model just as it was in Bohr's and probably stems from the same source. In the former case, there is a peculiar degeneracy: all states of the same principal quantum number *n,* and there are n^2 of them, have the same energy regardless of the value of the orbital angular momentum. Degeneracy (the existence of different states of the same energy) can always be traced to symmetry, but in this case although wavefunctions of different values of m_l (and the same values of *n* and *l*) can be rotated into each other, accounting for their degeneracy, the wavefunctions of different values of *l* (such as orbitals with $n = 2$ and $l = 0$ and 1, the 2s and 2p orbitals) cannot be rotated into each other.

The resolution of this issue is that the symmetry group of the Coulomb potential is SO4, the special orthogonal group of rotations in four dimensions with SO3 simply a subgroup. This hidden symmetry can be visualised by stepping down a dimension and representing 2s and 2p orbitals in two dimensions and considering how they can be interrelated in three dimensions. To do so, regard the orbitals as projections onto a plane of a three-dimensional patterned sphere (figure 5). It should be easy to see that rotation of the pattern in three dimensions results in a rotation of the projected patterns. Thus, the degeneracy of the hydrogen atom is a result of the hidden SO4 symmetry of the Coulomb potential.

Although fascinating, the hydrogen atom is only the starting point for understanding the atoms of all the currently known one hundred and eighteen elements, each, other than hydrogen, with more than one electron. The presence of a second electron in helium and by extension of many electrons in other elements results in the breaking of the SO4 symmetry of the potential they experience, and states of the same value of *n* but different values of *l* are no longer degenerate. This symmetry breaking is commonly interpreted in terms of the penetration of the electrons through inner shells of electron density and shielding, the consequent modification of the Coulomb potential due to the nucleus. It can of course be calculated by the armoury of numerical techniques that have for decades now been able to compute atomic energies and electron distributions to high precision.

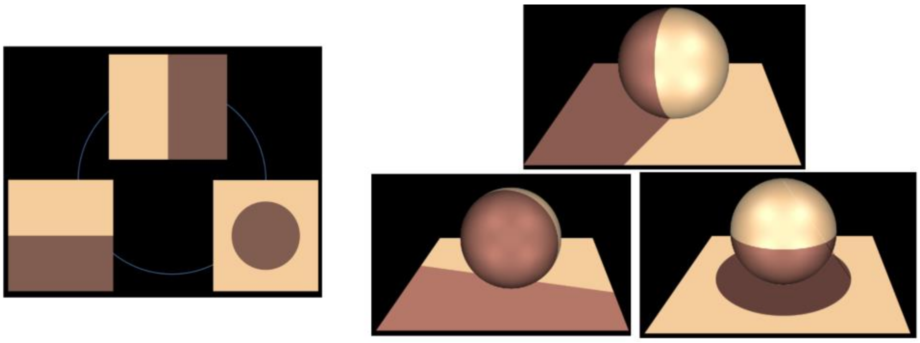

Figure 5. Of the three patterns on the left, only two can be interrelated by rotations in two dimensions, but can be interrelated by three dimensions if as on the right they are regarded as the projections of a pattern in a higher dimension.

The symmetry of the Coulomb potential (in its hidden form as well as its overt form) and the symmetry breaking that removes degeneracy are not the only aspects of symmetry needed to account for the electronic structures of many-electron atoms. That atoms have bulk stems from the symmetry expressed by the Principle proposed by Wolfgang Pauli (1900−1958): the Pauli Principle requires a wavefunction to change sign when any pair of fermions is transposed. The implication is the Pauli Exclusion Principle for electrons: that no two may have the same set of four quantum numbers (n, l, m_l and m_s, the last quantum number denoting the orientation of an electron's spin in the case of the orbital model of atoms). Thus, for atoms with more than two electrons (lithium onwards) the electrons cannot all be in the 1s orbital. The pattern of occupation of the orbitals that ensues, in which their various orbitals are occupied in accord with the Pauli Exclusion Principle, is then found to correspond to the pattern of the Periodic Table and the periodicity of the properties of the elements that are then observed and which it summarises. Such atoms have overall fuzzy-edged spherical symmetry with radially varying electron density showing maxima that suggest the existence of concentric shells of electrons (figure 6).

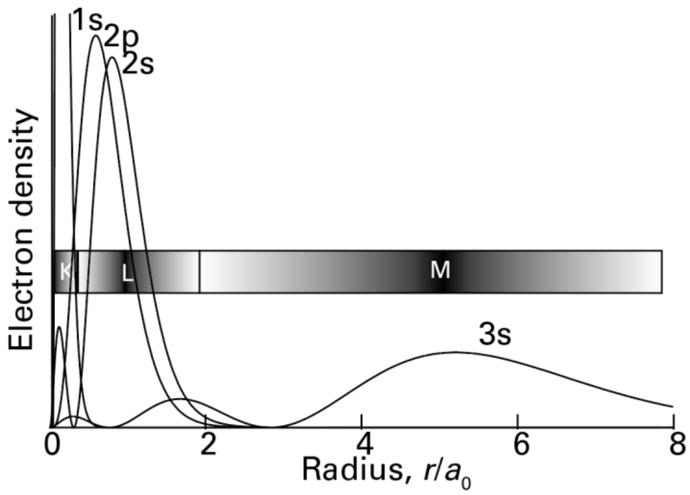

Figure 6. The radial distribution of electron density in a sodium atom suggesting the presence of shells of electrons (the shells are labelled K, L and M).

5. A coda

There have been two thousand years since an atom was first conceived, two hundred years since evidence rendered its existence plausible and about twenty years since its visual depiction rendered its

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reality irrefutable. But could it all be wrong? Merely for the sake of a satisfying sequence of numbers, could it be that in the past two years doubts have arisen, not the doubts of ever-doubting philosophers but actual scientifically principled doubts? One is reminded of Beethoven's Diabelli variations when after spinning thirty two of them from the original seed of a waltz, Beethoven concluded teasingly with the thought that it might work better as the equivalent of a quickstep.

Think of the following. The essence of an atom is localisation: it is a localised body and in some sense, a sense that preserves its character, indivisible. But quantum theory reveals another way of regarding localisation, as the superposition of waves with constructive interference in a small region and destructive interference elsewhere. In that sense, our perception of an atom is a delusion. It is in fact (whatever that means) a superposition of infinitely extended waves. In that sense, matter is a continuum and atoms are a deception.