From Pauli’s birthday to ‘Confinement Resonances’ – a potted history of Quantum Confinement.

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Abstract. Quantum Confinement is in some sense a new subject. International meetings dedicated to Quantum Confinement have occurred only recently in Mexico City (the first in 2010 and the second, in September 2011). However, at least in principle, the subject has existed since a very long time. Surprisingly perhaps, it lay dormant for many years, for want of suitable experimental examples. However, when one looks carefully at its origin, it turns out to have a long and distinguished history. In fact, the problem of quantum confinement raises a number of very interesting issues concerning boundary conditions in elementary quantum mechanics and how they should be applied to real problems. Some of these issues were missed in the earliest papers, but are implicit in the structure of quantum mechanics, and lead to the notion of Confinement Resonances, the existence of which was predicted theoretically more than ten years ago. Although, for several reasons, these resonances remained elusive for a very long time, they have now been observed experimentally, which puts the whole subject in much better shape and, together with the advent of metallofullerenes, has contributed to its revival.

1. Introduction
Until the development of quantum confinement and the discovery of metallofullerenes, the best ways of investigating atomic structure were via the excitation and/or ionisation of one or more electrons or else via electron attachment.

However, excitation and/or ionisation, by reducing electronic screening, actually increase the influence of the nuclear charge as compared with electron-electron interactions.

Most of the unsolved problems of atomic physics concern electronic correlations (the many-body problem). Increasing the influence of the nuclear charge means moving towards the part of the problem which is mostly considered as solved. In this respect, excitation and/or ionisation act against correlation forces. Electronic attachment, from this perspective, is better, but results in a more fragile system with very few quantum states available for study. Until fairly recently, there seemed to be no other viable approach

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Quantum confinement provides a much richer alternative. It consists in trapping the atom within a cavity (endohedrally, from the Greek ‘endo’ meaning inside’ and ‘hedron’ which denotes the geometrical face of the cavity) whose dimensions are small enough to alter its fundamental properties quite significantly. Ideally, one should also be able to control the geometry of the cavity and to ‘tune’ the strength of the confining force, which of course is difficult experimentally.

As regards probing the system experimentally, the aim is still to use the traditional methods of optical spectroscopy in the first place to probe the resulting system, but the observer now has an extra tool in hand: compressing the atom under study and watching how its properties are changed.

2. Defining the ‘Ideal Problem’
As just explained, the aim is to trap a many-electron atom inside and preferably at the centre of a spherical cavity, so we can easily calculate its properties just by altering either the boundary conditions or the radial potential in the Schroedinger equation of the test atom. In principle, one aims for a many-electron atom if the purpose is to probe correlations, although it is advisable (as all atomic physicists know) to start by understanding hydrogen. Of course, such an ideal situation does not exist (as usual in physics). Even if the ‘confining cavity’ is C60, one must remember that it is not a sphere (a perfect sphere, in quantum mechanics, would not even be able to rotate). Also, in ‘real’ experiments, one can only tune the confining force rather clumsily (by ionising the fullerene, or adding other shells around it) and one can only alter the size of the confining cavity in rather large steps (by using another fullerene, for example). Then, we have no guarantee that the confined atom will simply sit at the centre of the confining cavity. Usually, it does no such thing, but will rattle around off-centre. Last but not least, the cavity also has quantum properties, i.e. its own intrinsic excitation spectrum.

Nonetheless, there are well-established virtues in Physics of studying ideal problems, whose basic property is that the equations describing them can be solved exactly even if the systems cannot actually be made or observed. As examples, one need only think of the perfect black-body or of Einstein’s two-level atom. Similarly, one cannot actually observe a hydrogen atom in the absence of any radiation field. The exact solution for hydrogen is nonetheless a fundamental example in Quantum Mechanics. Indeed, idealised systems with exact solutions usually turn out to be of extreme importance. The solutions themselves can often be adapted to match ‘real’ problems, and their properties define what regions of parameter space should be explored. Thus, the whole basis of quantum defect theory in Atomic Physics comes from phase shifting regular and irregular solutions of the hydrogen atom problem with respect to each other to match other spherical boundary conditions.

3. The Founding Paper of the Physics of Confined Atoms
It happens that the problem of Hydrogen confined in a sphere with infinite non-penetrable walls can be solved exactly. This property was first noticed by Sommerfeld and Welker [1]. Of course, the whole problem was treated in absence of any radiation field, and indeed the sphere, being impenetrable, renders the whole system unobservable. There were no fullerenes in the literature at that time, and quantum confinement did not even exist. The only reason for considering this problem in the first instance was that it is tractable, i.e. it can be solved. That was reason enough to work it out theoretically, and it was fortunate for the authors that Wolfgang Pauli’s sixtieth birthday occurred around this time, so they were able to bring the solution along as a birthday present and have it published in a special issue of the Annals of Physics. Unfortunately, the date of publication was not a very favourable one, and there are comparatively few copies remaining of this original paper, written in German. It is, however, the seminal paper for the whole subject of Quantum Confinement.

By using this simple example, Sommerfeld and Welker [1] established a few important facts. For instance, they showed that the optical electron, when a confining cavity is small enough, becomes delocalised, i.e. no longer bound to the atom, but only confined by the cavity. They compared this
mechanism with the formation of the conduction band in a solid, in which an atom is confined within a
cage defined by its neighbours and they also related their study to the properties of atoms under very
high pressure, reported by Michels et al [2] at an earlier birthday party, in honour of van der Waals.

Interestingly, what prevents electrons from penetr ating a real conducting shell is the Pauli force,
and the van der Waals correction to the ideal gas law involves the volume occupied by atoms.
Sommerfeld and Welker’s [1] paper implied that atomic volume itself would be dependent on the
confining pressure, a quantum effect which would rather spoils the van der Waals correction at very
high pressures, but nobody (not even the authors) noticed that, so all was well. Much more detailed
and realistic parametric models for the conduction band in solids soon became available. While
Sommerfeld and Welker [1] had uncovered a good picture of the mechanism involved in delocalising
the conduction band without any adjustable parameters, their model could not readily be adapted to
the representation of an infinite solid, so this application was discarded.

Eventually, however, the subject of quantum confinement was to surface again, but many years
after this somewhat neglected (and soon forgotten) first step. Indeed, it seems likely that the problem
was reinvented independently many years later by the other researchers, since the work of Sommerfeld
and Welker [1] was rarely cited.

4. The Rebirth of Quantum Confinement
The main difficulty with the new subject invented by Sommerfeld and Welker [1] was the lack of real
applications. Because the impenetrable sphere is rather like a piston compressing the atom from
outside, they had discussed atoms under extreme pressure, which was as close as they could come to a
real application. A first step was naturally to extend such ideas to molecules as done by Ley Koo and
Cruz in Mexico in 1981 [3], but this still did not provide a real experimental system to probe.

There is also a situation where applying pressure is relevant: when one considers the reversible
insertion of an ion into a solid. In a lithium ion battery, Li insertion is necessary to make useable
electrodes. In fact, this is a very topical problem today, connected with the need for better high power
batteries to power electric motor cars, and the study of reversible insertion is a key technological issue.

So perhaps, the first application of confined atoms to a problem of practical importance was the
suggestion of modelling reversible insertion via a chemical pressure, using quantum confinement as
the driving ‘piston’ [4,5]. This is an important problem, which raises many interesting questions about
the confinement of many-electron atoms (as opposed to hydrogen). I will return later in the present
paper to considering the special properties of confined many-electron atoms

Exploring the theory of confined atoms also led to a revival, in which the problem studied was the
same as originally set up, except that more values of angular momentum were considered
(Sommerfeld and Welker [1] had only included s-states), and the possibility that the confined atom
might lie away from the centre of the confining sphere was also raised [6,7].

The reason for the renewed interest so long after the work of Sommerfeld and Welker [1] had been
put aside as a mere curiosity was of course the discovery of the fullerene molecule and the realisation
that, because it is hollow, it would be possible to trap an atom (A) inside it. A distinction was drawn
between a molecule consisting of a fullerene with an atom stuck to it on the outside and a fullerene
with the atom encapsulated within it. The latter (endoehedral trapping) was denoted as A@C_{60}. The
gometry of the fullerene was of close course enough to that of a confining sphere, although it soon
turned out that the nature of the confinement in an endohedral fullerene is rather different from the
problem considered by Sommerfeld and Welker [1].
Figure 1. Structure of some of the closed shell fullerenes, which are hollow and can contain endohedral atoms or molecules (from ref [18]).

Experimentally, making endohedral systems and in particular the metallofullerenes in quantity proved difficult. Initially, they could readily be produced for detection of their presence only by very sensitive techniques such as mass spectroscopy, using methods of synthesis which range from collection in discharges to ionic bombardment [8], but producing them in large enough quantity for probing their physical properties, for example by using spectroscopy, was a more challenging task. The development of new chemical pathways holds much promise. Another option for the future will be trapping them. Then, even a single one will become accessible by spectroscopy.

The delay involved in resolving this experimental issue has provided an opportunity for theoretical work on endohedral systems with the challenge of predicting their properties ahead of observation.

5. The nature of the confining sphere

Although endohedral systems were elusive, much progress was made in understanding the properties of C_{60} itself, and experiments led to a better knowledge of the properties of the confining sphere.

In photoionisation studies, interference effects were observed, resulting in oscillations of the cross section [9]. From the frequency of these oscillations, it proved possible to deduce a lot of useful information about the geometry of the average potential experienced by electrons escaping from the C_{60} sphere. Of course, such information is relevant for metallofullerenes only, insofar as one assumes that this sphere remains relatively unchanged by the inclusion of any particular endohedral atom. One may anticipate that such an approximation must work best for smaller sizes of endohedral atoms.

Furthermore, in scattering experiments (collisions of C_{60} with Rydberg atoms), the formation of the C_{60} negative ion was observed [10]. This observation implies that the potential due to the sphere is not repulsive (as in the work of Sommerfeld and Welker [1]) but attractive. Endohedral confinement by an attractive shell may seem surprising at first sight if one thinks purely classically. It is in fact a quantum
effect, which is best understood by reference to the well known problem of reflection at an attractive potential barrier in textbook scattering problems.

An exact result immediately followed, but only for repulsive confinement, within penetrable or impenetrable walls. It is in some sense quite an obvious result for confinement by a repulsive cube or sphere that the endohedral atom must live at the geometrical centre in its ground state [11].

6. Quantum states of the confining sphere

One aspect of the problem does not usually intrude much in confinement by a repulsive well and was actually missed by Sommerfeld and Welker in their treatment of the problem. It is the influence of quantum states of the confining well. These began to emerge as ‘glitches’ in numerical work by Baltenkov and also by Connerade and Dolmatov, performed in Tashkent, but their physical origin remained mysterious until systematic studies by Connerade, Dolmatov, Lakshmi and Manson [12].

Originally, these ‘glitches’ were suspected to be artifacts of the numerical method used, but Connerade, et al [12] varied the strength of the confining potential (which of course one is free to do theoretically), thereby tuning the quantum states of the confining shell and controlling the energy degeneracy between them and the excited states of the confined atom. This revealed Wigner repulsion or avoided crossings, and thus demonstrated that they are, in fact, genuine quantum states of the combined system, originating from those of the confining spherical attractive shell. In Fig. 2 some of these avoided crossings are shown.

![Figure 2. Avoided crossings in H@C6o from reference [12]. Note that labelling of the states by principal quantum number is somewhat arbitrary, depending on whether one follows a curve according to node structure or according to the binding energy.](image)

A further aspect was confirmed in calculations by Kengkan Seehamart and Connerade [13] performed in Khon Kaen: these authors used one dimensional modelling of the same system and demonstrated that the avoided crossings are actually independent of geometry. They originate solely from the energy spectrum due to the double-well potential of the combined system. Figure 3 shows...
how this was established: the points are from \textit{ab initio} one-dimensional calculations and the curves are from the three-dimensional calculations by Connerade, Dolmatov and Manson [12]. Quite clearly, there is no discernible difference between the two. This is precisely what one expects for avoided crossings because their properties are controlled by energy degeneracy and the range of the interactions.

![Figure 5. Comparison between one- and three-dimensional calculations of the avoided crossings in H@C_{60} after ref [13].](image)

7. The classification of resonances

It thus became apparent that several kinds of resonance were present simultaneously in the spectrum of the confined atom system (which of course must include the cavity). Fullerene is not an ideal sphere (as the approximation made in the theory omits), but is a proper molecule, which can rotate and which possesses excited states of its own. Taking this into account, the issue of how to classify all the resonances was addressed by Connerade, Dolmatov and Manson [14] on the basis of their origin, which gives rise to the following distinct types for the A@C_{60} system.

(a) atomic resonances modified by confinement;
(b) confinement resonances due to the cavity, modified by the inclusion of the atom and
(c) molecular resonances due to the fullerene, modified by the presence of the endohedral atom.

8. The Quest for Confinement Resonances

Theoreticians at large accepted these ideas, and calculations of endohedrally confined atoms thenceforth allowed for the occurrence of confinement resonances. There was, however, a problem which gradually became a worry. Although calculations often revealed many such resonances, they never seemed to be observable experimentally, and this remained a mystery for some time.
Eventually, in a paper entitled *Confinement resonances in photoionization or endohedral atoms: a myth or reality?* Korol and Solov’yov [15] found that the structure of confinement resonances in the photoionisation cross section is extremely sensitive to the mean displacement of the atom from the cage centre. This at least provided some hint as to why confinement resonances might, in practice, never be observed. If one likens the confined atom system to a ‘quantum mechanical rattle’, the endohedral atom might be always on the move, and confinement resonances would be washed out by phase cancellation effects. This hypothesis provided a nice way out, but had the unfortunate consequence of leaving in the literature the theoretical prediction of unobservable quantum effects, which seemingly could never be verified. Quite apart from the need to check theory against experiment, this would have left the question open whether or not their presence should be included in calculations and then averaged out or whether confinement resonances should be left out completely.

9. The First Observation of Confinement Resonances
So matters remained until 2010, when Kilkoyne *et al* [16] announced the first observation of Confinement Resonances in the photoionization spectrum of Xe@Cl₆₀⁺. The experiment was performed by using a mass and charge selected ion beam of the endohedral atomic ion and merging it with a beam of synchrotron radiation. The phenomenon was detected in the Xe@Cl₅₈³⁺ product ion channel. Figure 6 shows the resulting spectrum.

![Figure 6](image)

**Figure 6.** Confinement resonances in the spectrum of endohedral Xe in C₆₀ after ref [16]. The experimental points (large dots) carry statistical error bars of one standard deviation. A many-body calculation for the giant resonance of the free atom is shown for comparison (black curve with a single broad maximum) and the dashed curve shows many-body calculations.

The Confinement Resonances are observed in the giant 4d resonance of Xe, a very broad and strong feature as its name indicates, which facilitates the observation, as it is predicted by theory to fragment into four components. The structure is not exactly as predicted by theory, but the
fragmentation is indeed convincingly revealed. It is interesting that giant resonances were initially believed by some to be a property of condensed matter, because of their resemblance to band structure and their persistence in the spectra of solids. The Russian physicist Zimkina from St Petersburg, who studied them in the soft X-Ray spectra of solids, argued strongly that they are of atomic origin [17] and the experiment which established this fact [18] in 1974 was also performed by using synchrotron radiation. When first reported, they were described in [18] as an ‘atomic plasmon’ because they are dominated by many-body effects. Giant resonances, because they persist in many different atomic environments ranging from the free atom to condensed matter, provide an excellent tool for comparative studies of atoms in different environments (see [19]).

Returning to the issue of why Confinement Resonances become conspicuous in this case, it is clearly relevant that the size of a Xe Atom is large enough that it only just fits inside the confining fullerene sphere. Thus, it has much less freedom to rattle around, to use the descriptive analogy made above.

The fact that Xe@C_{60} is more favourable for the observation of Confinement Resonances than other comparable systems has led to many new calculations being performed. Thus, in Figure 7, we show some recent theoretical data for generalised oscillator strengths [20] by both independent particle (Hartree-Fock) and many body theories (RPAE). It is interesting that the structure due to Confinement Resonances is much more prominent in many-body calculations. Again, as mentioned in the introduction to the present paper, endohedral trapping provides a new tool to probe correlations in atoms and other small quantum systems.

Figure 7. Comparisons between many-body calculations and independent particle model calculations for structure due to confinement Resonances in the generalised oscillator strength of XeC_{60} (see text and also reference [20]).
The prediction of ‘confinement resonances’ by Connerade, Dolmatov and Manson [14] was published in the year 2000. For 10 years, the reality of such resonances remained in doubt and their observability was called into question. Because they were so elusive, they became a real test of Quantum Confinement as a subject: the issue was whether the approximations made in describing confinement by using spherical shells and neglecting many molecular and inter-molecular forces were too crude to represent reality, or whether the model was indeed well-adapted to the situation and could capture the basic physics involved. The observation of Confinement Resonances puts paid to such doubts by validating the approximations involved.

10. The plasmon of the Fullerene
Plasmons, when they appear, are not just a property of a specific system, but a general property of any system when its dynamics are dominated by a collective oscillation. The atomic giant resonance is simply an overdamped version of the Mie resonance in classical physics, which is a collective motion of all the electrons of a shell. This is not only a property of the atom, but also of any quantum sphere or shell. The fullerene shell has 240 electrons available, and therefore can be considered as a highly conducting shell of electrons. The fullerene plasmon is observed experimentally to occur around 20eV excitation energy.

The dynamical polarisability of the charge shell is responsible for the optical giant resonances or plasmons, which arise simply from the collective motion of delocalised electron. So, when one observes a Mie resonance, it is a signature of a good conductor, for example a metallic sphere or shell. Of course, a highly conducting sphere should obey the laws of electrodynamics, and so one would expect it to act like a Faraday cage, screening the atom placed inside it from any external fields.

The fact that the fullerene can be considered as a highly conducting cage led Harneit [21] to suggest a very neat solution to a problem which occurs in quantum computing, namely how to make a compact and simple register without using atomic traps, by exploiting the screening due to this conducting cage to isolate the spins of individual atoms and thus to enable both the construction and the preservation of q-bits.

11. The quantum Faraday cage
For full screening, it is considered important to use endohedrals with the atom close to the centre of the confining fullerene. Nitrogen has been proposed as the best case. One problem of course is to avoid distortions of the sphere when placed close to a surface. Other questions which arise are: how good is the screening provided by the Faraday cage? How would such a quantum Faraday cage really work? Is it true that full screening occurs at the quantum level?

One senses that that, if full screening were really to occur at the quantum level, electromagnetic radiation could never penetrate the confining shell, and endohedral atoms would become unobservable. In fact, in atomic physics more generally, there would be a strong attenuation which could inhibit the excitation of inner shell spectra in atoms completely. Clearly, this is not the case. But why not?
This issue was addressed by Connerade and Solov'yov [22], who investigated the dynamical screening of a confined atom by a fullerene, and who included in their model the effects of the fullerene Plasmon on the dynamical polarisability of the system.

They found that the photoabsorption of the endohedral atom screened by the cage can be expressed as the product of two factors, namely the response of the atom itself and a dynamical enhancement factor $F(\omega)$ which appears as a pure number, due entirely to the polarizability of the metallic sphere. This enhancement factor is frequency dependent and, not surprisingly, maps out the profile of the fullerene giant resonance, as shown in Figure 9.

![Figure 9. General form of the dynamical enhancement factor [22].](image)

From this result, we see that:

(i) at very low frequencies, we have full screening (classical Faraday situation);

(ii) at the plasmon frequency, the confining cage acts like an antenna, *amplifying* the electromagnetic field around the confined atom;

(iii) at very high frequencies, the shell has no effect, i.e. the atom sees undisturbed radiation, which is how atomic inner shells can be excited.

This behaviour can broadly be described as a quantum ‘skin effect’ because of its frequency dependence. Clearly, should the shell actually amplifies the effect of external radiation rather than screen the atom inside, this would become a concern for making stable $q$-bits, which depend on screening for their survival. One can show that these results apply for the whole space within the confining sphere, which is in some sense a generalisation of the usual theorems applying to the Faraday cage in electromagnetism.
It is of course not obvious that the spherical cage will not be distorted by the presence of a surface, and this may also spoil the quality of screening. Creating a viable register for a quantum computer is thus no easy task.

12. Confinement by Oblate and Prolate Fullerenes
The fullerenes are not all spherical, of course, and even the near-spherical ones may become distorted by (for example) interactions with a nearby surface, so it is interesting to consider how the system behaves when this happens. The case of an elongated or squashed surrounding cage can be handled on the same principles as for a sphere by applying a geometrical distortion to the problem [23] which turns the sphere into a prolate or oblate spheroid. When one applies this method to hydrogen confined at the centre, states which were energy-degenerate in spherical symmetry of course become split and the degeneracy is resolved. In consequence, the spectrum begins to resemble that of a diatomic molecule. One can deduce that the spectrum of such a system carries all the necessary information to measure the extent of the deformation.

13. Atomic Size Effects
As the reader will have noticed, Confinement Resonances were discovered experimentally for Xe, a rather large atom, whereas most of the description of effects due to quantum confinement above has been based on the example of confined hydrogen.

In fact, size effects must clearly play an important role once the confining cavity becomes small enough to be comparable to the endohedral atom itself. As pointed out in ref. [15], it is very unlikely that small atoms will remain at the centre of an attractive confining sphere (even less so if it is distorted, of course) and the quest for the elusive Confinement Resonances indeed illustrates this point. If one approaches quantum confinement from the angle of probing correlations, the heavier atoms are the most interesting. Furthermore, from the angle of applications, it turns out that heavier atoms are more relevant.

Once the size of the atom approaches that of the confining cage, there is the question: what effect does confinement have on the size of the atom, as well as the related question: what effect does confining an atom have on the size of the cage? The second question is difficult to answer theoretically but, for endohedral fullerenes, it can probably be addressed by analysing the properties of Confinement Resonances, since they carry information about the geometry of the confining shell.

As regards the first question (What happens to many-electron atoms under confinement?) Hydrogen is a very uninteresting atom in its response: all one can do is to reduce the number of quantum states or to detach the electron by confinement. It is much more worthwhile is to study atoms whose properties (chemistry) can be significantly altered under compression.
Such atoms belong to the sequences known as the transition elements, rare-earths, lanthanides and actinides, which were arranged into a quasi-periodic table describing their localisation-delocalisation properties (the first order Mott transitions in solids) by Smith and Kmetko [24]. For fundamental reasons [18], these also turn out to be atoms which exhibit giant resonances, which frequently possess valence instabilities and which violate the simple\textit{aufbau} principle of Bohr and Stoner.

An atom in a key position from this point of view is of course La, and it is interesting to consider theoretically what happens to La under confinement by a fullerene cage. This problem becomes rather more complex than the cases treated above. The behaviour of the lanthanides is extremely sensitive, because of the development of a double-well radial potential, due to centrifugal barrier effects which have been discussed extensively in the literature (see ref [19] for details). In this situation, the behaviour of the atom becomes strongly influenced by relativistic effects, and a proper treatment is correspondingly more difficult.

This case has been addressed by using fully relativistic Dirac-Fock theory [25], and the outcome indeed demonstrates that the atom is ‘soft’ under confinement, i.e. that the outermost electron depends very sensitively for its mean radius on the properties of the confining sphere. The treatment is rendered even more difficult by the fact that boundary conditions must be applied with some caution to the fully relativistic problem. The reason one must be cautious is best understood by reference to the confinement problem first studied by Sommerfeld and Welker [1], in a cavity with infinitely high repulsive walls. If one applies the same Dirichlet boundary conditions for this case to the Dirac equation, they turn out to violate relativity by forcing both the large and the small component of the relativistic wavefunction to zero at a point other than the origin (which would artificially lead to spontaneous electron-positron pair creation as in Klein’s paradox). To avoid this unphysical situation, one has to apply the boundary condition in a different way. Fortunately, one may either (a) apply one of the other boundary conditions suggested by ref [26] or (b) deal only with problems in which the step height at the boundary remains very small compared to the rest mass of the electron, and make the approximation that the boundary condition applies only to the large component, which turns out to be sufficient for a number of situations.

\textbf{Figure 11.} (after ref. [25]) Variation of atomic size with applied pressure (a) experimental (b) relativistic and (c) non-relativistic limit of the relativistic calculation. The large discontinuity is due to 6s-5d orbital rearrangement. The small discontinuity in the experimental curve is due to recrystallisation.
By using the latter approach, Connerade and Semaoune [27] have studied Cs in a cavity with repulsive walls, and shown that the \textit{ab initio} Dirac-Fock method correctly reproduces the switch between 6s and 5d orbitals under pressure which is observed experimentally as a discontinuity in the atomic size of Cs compressed by a diamond anvil.

Connerade and Semaoune [25] applied the same method to study the case of La in an attractive spherical shell with the geometrical parameters of C\textsubscript{60}, and found that the 5d wavefunction is indeed extremely sensitive to confinement. Figure 12 shows how the mean radius of the 5d wavefunction varies between the free atom and the atom confined in an attractive shell. Note the very large change of radius of the main maximum.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure12.png}
\caption{Change in the radial 5d wavefunction of La between the free atom and the atom confined by an attractive shell of depth 8.22 eV according to relativistic Dirac-Fock calculations [25].}
\end{figure}

14. The Periodic Table Under Pressure
The examples just given show that many-electron atoms can be profoundly affects by confinement, to the extent that the filling of their outer shells is modified. The shell structure of course controls their valence and thus their chemistry. It is well known in compounds (for example SmS) that the appearance and physical properties of compounds can, under high pressure, undergo discontinuous changes and localisation / delocalisation transitions (termed first order Mott transitions) in solids. These fluctuations of valence or changes in physical properties occur for atoms located along the diagonal of Smith and Kmetko’s [24] Quasi-Periodic Table for transition elements and rare-earths, and the underlying physics is discussed in ref [19]. It is clearly of atomic origin.

For confined atoms, the same or similar behaviour occurs, and for the same reasons: the immediate environment of the atom is capable of tipping the balance between the inner and outer reaches of the
atomic potential for the $d$ and $f$ electrons. Broadly speaking, elements which do not follow the order of filling predicted by the Bohr-Stoner aufbau or ‘building-up’ principle can be made to follow it by placing them under high pressure. Thus, as explained in ref [28], the Periodic Table of certain atoms under high pressure is not the same as the Periodic Table of free atoms. This has a variety of interesting implications, including the fact that their chemistry is altered.

15. Confinement and reversible storage
The subject of reversible Li$^{+}$ ion storage [4,5] is a vast one, with huge industrial and commercial implications, and it is therefore rather difficult to review it. Much of the research is unpublished. It would anyway be beyond the scope of the present article to attempt such a review, but some connections deserve mention here.

As is well-known, the rechargeable battery is the Achilles’ heel of many commercial products, including in particular the electric vehicle. From the power to weight ratio of batteries, it turns out that Lithium rather than lead provides the ideal ion for a rechargeable cell. It is also a non-polluting element. However, for reasons of safety, one cannot make a lithium battery by using just the metal as the electrode as such a cell would readily catch fire and explode. Therefore, it is necessary to insert the lithium ion inside the electrode material, where it is no longer possible that it comes into direct contact with air. Obviously, if this process fails after a number of cycles and metallic lithium is deposited on the surface of the electrode, this would be a safety hazard.

The insertion process must be reversible, which means that the electrode must not undergo any phase transition such as recrystallisation during the charging / discharging cycle. It is also necessary that the Li$^{+}$ ions should be able to migrate freely within the electrode material and find spaces within which to be encapsulated and from which they can readily be recovered during the cycle. Nor should these ions form permanent chemical bonds which would have to be broken to recover them. It is in practice very difficult to achieve a high level of reversible storage, and finding an appropriate electrode material for a high power Li$^{+}$ reversible or ‘rocking chair’ battery remains a challenging problem. Much of the progress in this area is shrouded in commercial secrecy.

It is clear, however, that the mechanism involved in quantum confinement is of central interest: if the host material which temporarily holds the Li$^{+}$ ions in place is made from ‘flexible’ atoms of the type just described and if there are spaces within it of sufficient size to pack ions inside, one has a basis for a good electrode material. It has also been found that the materials which have a sheet structure and which expand only in one dimension when lithiated (for example, some of the transition metal oxides) tend to weaken on repetitive cycling and become fragile. Thus, it is desirable to pick materials which expand in 3D on lithiation as well as being porous to the ions.

Figure 13. The Li-coated $C_{60}$ molecule whose structure is shown alongside has been proposed as a medium for hydrogen storage in fuel cells. Similar molecules are also under investigation in connection with reversible lithium storage. Molecules suitable for this purpose must be readily penetrable by the ions and also provide cavities in which the ion can temporarily be stored. (see text)
Physically, the problems of storing Li$^+$ reversibly and the problem of storing hydrogen reversibly are quite closely related, and both of them provide options in the general quest for non-polluting and reversible energy storage. Quite often, similar host materials are involved in both cases. One seeks materials which can adapt to contain Li$^+$ ions by what is called *polaronic distortion* (no change of structural symmetry) so that the process remains reversible.

Much research today is devoted to Li$^+$ storage for future electric cars. In principle, the properties required and the processes by which higher current densities can be achieved for Li storage are well understood, but finding the best materials for the purpose is the main difficulty. Many different molecules have been suggested. They all seem to involve some at least of the principles described in the present article. For example, the role of LiFePO$_4$ as a suitable electrode material has been investigated. This again is a molecule which, under packing to form a material, creates a fairly open structure to enhance Li$^+$ mobility and which also contains the atom Fe, which is one of the ‘soft’ atoms near the diagonal of Smith and Kmetko’s Quasi-Periodic Table. It thus possesses properties very suitable to enhance lithium ion storage (see Fig. 14). Readers interested in the application of Li batteries to electric vehicle propulsion can refer to some general papers on the subject e.g. ref. [29]

![Figure 14. Structure of the LiFePO$_4$ molecules, proposed as the building block of a reversible lithium ion battery electrode material for high current applications. The molecule has an open structure favourable to lithium ion mobility and also contains the ‘soft’ atom Fe which facilitates polaronic distortion for storage. (see text).](image)

Carbon is by no means the only atom from which to make hollow microspheres. Indeed, there are many alternatives. In 2008, Li$_4$Ti$_5$O$_{12}$ microspheres were made in Dalian (China) and also turned out to possess excellent properties as anode materials [30]. Over 500 charge/discharge cycles, their capacity is very stable, with a loss of only 0.01% per cycle. Besides ordinary hollow spheres of this anode material, 3D hierarchical hollow microspheres assembled in thin nano-sheets have since been created. Hollow structured nanomaterials of other insertion-type oxide materials have equally been reported. The deposition of microspheres on graphene surfaces seems very promising.

16. Confinement versus ionisation

At the outset of the present paper, it was observed that, in the quest to control and probe atomic properties by external means, compression by a cavity provides a very useful and in some ways more
subtle alternative to the rather more violent process of ionisation. So, it is perhaps interesting to conclude by comparing the levels of atomic compression achievable by both methods.

In order to do this, the best approach is to start with a rather compressible or soft ion, which displays the effects more clearly. The lightest one available is Ca+, which possesses a highly compressible $3d$ wavefunction analogous to the $5d$ wavefunction of La or of Cs discussed above. It experiences a strong centrifugal barrier which results in fairly flat external reaches of the effective atomic potential. Figure 15 illustrates the consequences of this (a) for confinement by an external barrier and (b) for incremental changes in the atomic number, which simulates progressive excitation / ionization.

![Figure 15](image)

Of course, increasing the charge state in this way is not achievable for free ions, although it may resemble what occurs for ions in certain solids. On the other hand, confining ions in spherical shells of different depths is in principle possible, for example by exciting or ionizing the outer electrons of a fullerene shell. Thus, confinement could be used as a tool to probe electron-electron interactions in a confined atom by exercising direct control on the compression. This would provide a new and very interesting technique for the study of correlations in multi-electron systems.

17. Conclusions

In the present review, I have not discussed a number of other interesting issues which concern quantum confinement and which may prove important for the future.
One of these is to explore effects similar to those which occur in thermodynamics when the compressibility of gases is discussed. It will not have escaped the reader that atomic volume and a quantum (or Hellman Feynman) pressure were both introduced in the context of quantum confinement, and that the effect of confinement compressing the atom was likened to an ‘atomic piston’. This of course is a language similar to that of thermodynamics, except that the atom, considered here as the compressed medium, obeys the Schroedinger equation rather than the usual equation of state. In principle, it is possible to consider and set up an ideal compression cycle (involving, for example, the compression of a two-level atom (as done by Einstein to study radiation field effects) and thus to introduce a pseudo-temperature into the problem. One then has all the thermodynamic ingredients and one can set up some kind of idealised theory.

Amongst the problems of potential interest using this approach is the possibility to set up an ideal reversible Li ion storage cycle analogous in some sense to the Carnot cycle of thermodynamics, which could serve as a useful measure for an ‘ideal battery’ against which the performance of real batteries could be assessed.

Among experimental developments for the future is the fact that, as mentioned in the present paper, metallofullerenes can be transported in beams and, most probably, will soon be trapped. It is likely therefore that the laser spectroscopy of metallofullerenes will be developed to enable much more detailed studies than have been achieved so far. In this connection, it will become important to compute, not only the single-photon cross section, but also three-photon and eventually multiphoton properties.

Obviously, what I have described represents work by many collaborators over a long period, and I take this opportunity to thank them all. There are plenty of other important subjects I did not touch on which also involve quantum confinement, such as, e.g., high pressure bubbles in solids (in the walls of nuclear reactors, for example), zeolites, quantum dots, etc, etc. It would be difficult to cover all of these in a single review, which demonstrates that atomic confinement really is a growing field, and presents many new opportunities for research.

18. References

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