

Quasi-atoms, super-atoms and quantum confinement

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Abstract . The terms 'quasiatom' and 'superatom' are introduced. A quasi-atom, for example contains two ions of opposite charge, which behave like an atom, forming Rydberg states. A superatom also contains many atoms, but behaves in a simple way, and can be modelled within the central field approximation. Both are examples of many-body systems which emulate quasi-particle properties. Their behaviour is the opposite of quasi-particle breakdown in isolated atoms. However, it also probes the boundary between simple and complex behaviour, for species larger than atoms. Examples are given, ranging from shallow donor impurities in semiconductors, through ion-pair molecules, confined and endohedral atoms, to metallic clusters.

Keywords . Endohedral atoms; clusters, semiconductors

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1. Introduction

Since the late 70's, there has been interest in the non-Rydberg spectroscopy of atoms [1], in which the approximate regularities of the independent particle model are replaced by very complex manifestations of many-body forces, (complex spectra of 'simple' atoms [2]) or even by coherent, collective oscillations (the 'giant resonances'[3]). Rydberg series in many-electron atoms can occasionally suffer explosions of complexity ('quantum chaos' [4]) or, conversely, disappear completely from view, giving up all of their available oscillator strength to but a few isolated resonances. Both aspects of non-Rydberg behaviour are regarded as manifestations of many-body forces [5]. However, non-Rydberg behaviour in isolated atoms is comparatively unusual. Mostly, even complex atoms choose to follow the predictions of the independent electron, central field approximation. In this light, we can interpret Rydberg behaviour as the self-organisation of many-electron atoms, or as a manifestation of quasi-particle behaviour in a many-body system.

Indeed, there is a remarkable tendency of complex systems to conceal their many-body nature, by forming quasi-particles (vacancies, or holes) whose behaviour is quite close to that of the real particles [6]. For example, in X-ray spectra, a nearly-

complete shell with one electron missing appears as a vacancy, whose properties are analogous to those of a single particle. This tendency poses an intriguing question of scale size : how large can a quantum system be and still continue to exhibit this property?

Recently, a variety of systems have been uncovered which are not atoms, being composed of several, or of many atoms, but which nonetheless self-organise in a manner similar to complex atoms, and possess properties not normally associated with multi-atomic objects. We shall refer to them as *quasi-atoms* and *super-atoms*, depending on their size and complexity. A *quasi-atom* is a system larger than an atom (for example : a metallic cluster) which can be modeled theoretically as a single quasi-atomic object, within a theoretical scheme which is adapted from atomic physics. A *super-atom*, on the other hand, is a group of particles (for example : a pair of ions of opposite charge), which together form bound states analogous to (but different from) the Rydberg states of a free atom.

The properties of interest in both cases are precisely those which tend to persist in many complex atoms as their size increases, and which underpin atomic physics, in particular the central field approximation.

The approach in studying quasi-atoms and super-atoms is exactly the opposite of the search for many-body effects in atomic spectra. In non-Rydberg spectroscopy, one seeks to uncover many-body effects due to the breakdown of the independent particle approximation for complex atoms. When dealing with quasi-atoms or super-atoms, on the other hand, one is looking for the persistence of regular atomic or quasi-atomic behaviour in systems much larger still than many-electron atoms.

Both approaches are ways of probing a frontier, where the fundamental simplicity characteristic of small multiparticle quantum systems eventually gives way to the complexity characteristic of large systems. The fact that this happens differently in different situations, and the role of symmetry in determining such behaviour are the subject of the present Comment. Many of the systems involved possess an enhanced degree of spherical symmetry, which combines with the Pauli principle to simplify the many-body problem. In the classical limit, a many-body system can become chaotic, and so the fundamental role of both spherical symmetry and the Pauli principle as inhibitors of chaos stands out rather clearly in the quantum case. These emerge as the two main features which help to make the many-body problem tractable in quantum mechanics.

2. Rydberg states in a solid : shallow donor impurities

When an impurity atom is inserted into a solid, it is possible for new bound states to appear. At first sight, it might seem that Rydberg excitations would arise, involving only very few low members, small enough to fit within the interstices of the lattice. Indeed it might appear impossible to associate any genuine Rydberg character with condensed matter, because so few states would appear.

There are, however, Rydberg excitations in solids of quite a different kind, for which the value of the Rydberg constant (and of the effective mass of the electron) are totally different from those of free atoms.

If an electron is ejected from the valence band directly into the conduction band of a solid, it leaves behind it a hole, which behaves exactly like a particle except that its charge and momentum are both equal and opposite to that of the electron. Thus, overall neutrality is preserved and the total momentum is zero. Electron and hole then move apart from one another, usually rather rapidly.

If the process takes place in excited states near the band edge (see Figure 1), then the momentum of the particle and of the hole are almost zero, and they experience a mutual Coulomb attraction. The problem is essentially the same as the H atom, or the energy levels of positronium : the electron and hole possess discrete energy levels with binding energies given by the Rydberg formula $E_n = -(m_r/m) R/n^2$, where n is

the principal quantum number, m is the mass of a free electron, and m_r is the reduced mass, obtained from the equation : $m_r = m_e m_h / (m_e + m_h)$, where m_e and m_h are the effective masses of the electron and the hole in the solid. In practice, these are rather different from those for free particles and so the *apparent* Rydberg constant $(m_r/m) R$ is very different from that for atoms (instead of an energy scale in eV as for atoms, one finds energy scales in tens of meV)

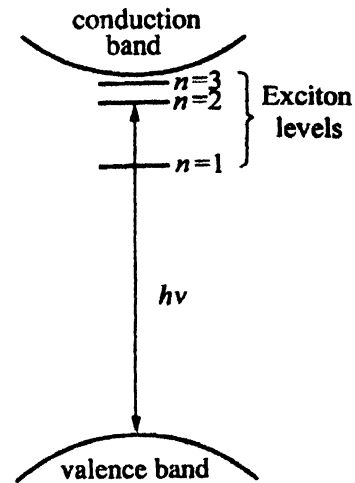


Figure 1. Schematic representation, showing the energy level structure for the excitation of a shallow donor impurity in a semiconductor material

Such aggregates, involving two or more charged particles, which are effective mass particles (*e.g.* electrons in the conduction band or holes in the valence band) are referred to generically as 'effective-mass-particle complexes'. The bound electron-hole system is of course an *exciton*. It can be thought of as a 'quasi-atom', formed from the particle and the hole, with the two objects rotating about a common centre of mass, the angular momentum being quantised. Just as, in atomic physics, one generalises by considering the electron in a many-electron atom as a quasiparticle, we can now replace the positive centre of charge by a hole. This system is often regarded as the solid state analogue of positronium. In general, there are two kinds of exciton : when the electron and hole are fully delocalised from any specific atomic site and form bound states, one has a Wannier-Mott exciton. When both the electron and hole are localised on or near a specific atomic site in the solid, so that the exciton is formed from atomic or molecular states perturbed by the crystalline environment, one has a Frenkel-Peierls exciton.

This electron-hole 'pseudoatom' or 'pseudohydrogen' corresponds to such a large spatial separation that the Coulomb attraction is almost negligible, which is consistent with excitation to the base of the conduction band, as shown in the energy-level diagram of Figure 1. Such states are created when an impurity atom acts as a donor, *i.e.* when an atom with a low ionisation potential is substituted for one of the atoms in

a semiconductor host. The ionisation energy of an electron bound to the donor impurity can be much smaller than the energy gap of the semiconductor. One then refers to a *shallow donor impurity* [7].

An example of the 'Rydberg' series arising by excitation of these shallow excitonic bound states is shown in Figure 2,

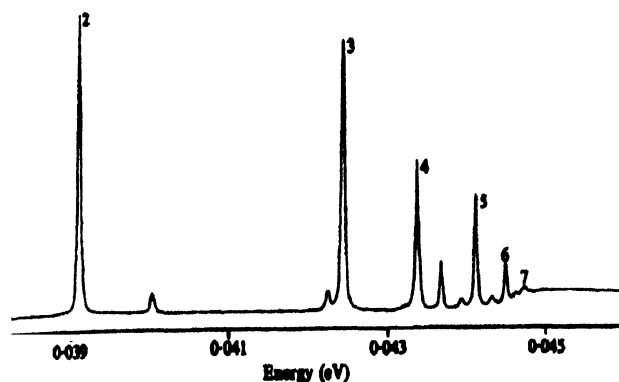


Figure 2. Example of a Rydberg series whose energy splittings are determined by solid state effects: the absorption spectrum of P as a donor impurity in silicon (see reference [7] for further details).

which corresponds to the situation of Figure 1. In fact, the excitonic states are identified by the presence of a Rydberg-like spectrum in some semiconductors with large enough energy gaps. Because of the much smaller value of the effective Rydberg constant in the solid, the highest n states are actually much larger than atomic Rydberg states of the same n . They can possess radii of 100 nm or more. Such giant Rydberg states allow one to explore an otherwise inaccessible regime of atomic physics, as will be explained below. Another interesting point is the presence of displaced lines in the spectrum, which do not fit the main Rydberg series. These can be attributed to a departure from sphericity: in the solid: the effective mass is not a scalar but a tensor quantity, and the symmetry is ellipsoidal. Thus, the resonances are split into two modes along the axes of symmetry. A similar kind of splitting arises for plasmon resonances in metallic clusters [8].

There even exist problems of atomic physics which cannot be explored in the laboratory by using atoms, but only by using 'pseudoatoms'. One such is that of the atom in such a strong magnetic field that it exceeds the internal fields of the atom (superstrong magnetic fields). This requires field strengths in excess of the atomic unit of magnetic field, *i.e.* greater than 2.35×10^5 T, which is unattainable, except in the atmospheres of white dwarf or neutron stars [9, 10]. However, if one replaces a normal atom by a pseudoatom, consisting of a shallow donor impurity in a semiconductor such as InP, GaAs or InP, then giant quasihydrogenic orbits are produced, and even the ground state is very wide. Taking GaAs as our

example, the effective mass m_e of the electron is $0.065 m$, so the orbits are some 200 times wider than for the atom.

As a result, with an external magnetic field of about 6.5 T (readily achieved in the laboratory), the superstrong magnetic field condition can be reached [11]. This system has been investigated experimentally in fields as high as 14 T [12], and can be accounted for within a simple theoretical model. In this unique situation (known as the Landau limit) the term quadratic in the magnetic field strength B dominates the Hamiltonian, while the Coulomb field becomes a small perturbation.

Under these conditions, the spectrum becomes a series of equally spaced Landau levels, to each one of which a Rydberg series converges. Above the lowest Landau limit, a continuum occurs, and therefore, even in hydrogen, excited states above this limit experience autoionisation in the superstrong field condition [13]. While the autoionisation rate for hydrogen has been calculated theoretically, there is no way of performing controlled experiments in the laboratory to test the theory for a real atom. The test has been carried out by making use of pseudohydrogenic states in GaAs, and scaling the results [14]. This provides a beautiful example of the unity of physics in the study of very unusual highly-excited atomic states.

3. Rydberg states of ion pairs

Another good example of quasi-atomic behaviour involving quasi-particles rather than particles is the formation of Rydberg states of ion pairs [15]. Consider the dissociation of a diatomic molecule. If the fragments are neutral, then the potential at large radius r describing the attraction between the fragments has the form of an inverse power law $1/r^k$, where k is a positive non-zero integer, equal to 4 for ion-neutral interactions, 6 for van der Waals forces, *etc.* However, if the fragments are charged, then the force between them at large r will be Coulombic $1/r$. A long range Coulombic potential supports an infinite number of bound states, whereas forces which vary as $1/r^k$ do not. Thus, one finds, for this particular kind of dissociation, vibrational states which obey the Rydberg formula, except that the Rydberg constant is scaled by the effective masses of the ionic fragments. However, since the energy density of such states is very high, ordinary spectroscopic means are not appropriate to detect these 'new kinds of Rydberg atom' [16].

Instead, what has been developed is a new kind of zero kinetic energy threshold spectroscopy. The method known as ZEKE is well established for the observation of very high Rydberg states of both atoms and molecules [17]. It consists in applying a pulsed electric field with a time delay after the

initial photoexcitation. During this time, all the electrons with kinetic energy have time to escape from the interaction region. When the weak ionisation pulse is applied, only the 'zero' kinetic energy states are detected, *i.e.* the highly-excited Rydberg states. For molecules, a similar principle can be exploited, *i.e.* a pulsed field can be applied to dissociate highly vibrationally-excited ion pair states, after a time delay which allows the prompt ion-pair fragments to escape detection. In practice, this is a little more difficult than discriminating against prompt electrons [18]. A DC field has to be applied during the waiting period, and so the technique also allows a mass analysis of the ion fragments to be performed. For this reason, it is called MATI (Mass Analysed Threshold Ionisation Spectroscopy). The difficulty with MATI, as opposed to the ZEKE technique for electrons, is that the DC electric field applied during the waiting period does not allow very high Rydberg levels to be reached. However, the principle that Rydberg states are formed by such complex objects as ion pairs is now well established [19].

4. Confined atoms, and atoms under pressure

Whenever atoms are confined, which happens in a variety of situations, the atomic model must be altered in some way. An obvious example is the construction of a solid from individual identical atoms, in which case an atomic model is appropriate close to the nucleus, but the asymptotic behaviour of the potential must be modified, to take account of confinement within the Wigner-Seitz cell. Of course, a quasi-atomic model alone does not describe most of the properties of the solid, but there are some specific ones for which it provides the most appropriate starting point, and examples of that will be given.

Recently, many other situations (some of them, quite unexpected) have also been uncovered to which simple 'quasi-atomic' models can be applied, and turn out to contain the essentially relevant physics. Some examples are : atoms confined in high-pressure bubbles, atoms confined in zeolite traps, atoms under pressure, super-dense matter, atoms in clusters, atoms trapped endohedrally in fullerene cages, *etc.* Of all these examples, perhaps the last one is receiving most attention, as it seems likely that metallofullerenes will soon be available in large enough quantity [20] for spectral studies of their electronic excitations in the ultraviolet and vacuum ultraviolet ranges to be undertaken.

5. Confined hydrogen

The simplest theoretical example of a confined atom was introduced by Sommerfeld and Welker [21], in a very remarkable birthday offering to Wolfgang Pauli. This was not actually the first paper on the subject. Michels *et al* [22] had already presented some arguments on this theme in another paper, similarly dedicated to van der Waals. Indeed,

it is quite remarkable how early the study of confined atoms began, and how soon after the birth of quantum mechanics. It is also very inspiring that Sommerfeld, one of the great masters of the subject, was one of the originators of the subject.

Indeed, Sommerfeld provided a most elegant solution to the simplest problem : it is the case of hydrogen confined at the centre of an impenetrable sphere. Unfortunately, although this problem can be solved exactly, an atom placed inside an impenetrable sphere is unobservable. It is not the only situation of this kind in Quantum Mechanics. We all happily solve for particles in infinitely deep potential wells, and we regard the solutions as teaching us something about the subject, although such systems are similarly impossible to observe and thus (in the sense of Dirac's famous remark) pertain to philosophy rather than physics. Another example is the perfect black body, which can be solved exactly, but does not truly 'exist' for precisely the same reason. So, we should not be too worried by this aspect of the impenetrable sphere.

The approach used by Sommerfeld was the most direct one. Since, for free hydrogen, the wavefunctions have nodes at well-known radii, one can place an infinitely high wall at any one of these nodes, and the solutions for excited states of the free atom then provide suitable ground state solutions for confined hydrogen at certain cavity radii. By considering the properties of such solutions, Sommerfeld and Welker [21] worked out a general formula for the energy of hydrogen confined inside a sphere of any radius. They showed that the energy rises (binding energy decreases) as the atom is squeezed inwards by the sphere.

6. Delocalisation

By using this approach, Sommerfeld and Welker [21] established a few very useful facts. For example, they showed that the electron, when the cavity is made small enough, can *delocalise*. This means that it no longer remains bound to the atom, but is only confined by the walls of the cavity. They concluded that this is similar to the formation of the conduction band in a solid, since, in the latter case, the electron is only confined by the lattice, and is free to transfer from one atom to another.

The energy at which this occurs is quite simply the energy at which the ground state of the confined atom rises above the ionisation potential of free hydrogen. This occurs for small confinement radii, just a little larger than the size of the atoms, which is exactly the situation in a solid. We may note that there are certain atoms for which a localisation-delocalisation (first order Mott) transition occurs in the solid, namely the transition metals and rare-earths as a result of an effect known as orbital collapse, and this already suggests that confinement of such atoms might provide a route to alter their chemical properties [22].

1. Where is the atom ?

It is of course not obvious (and in general not true) that the atom will stay in the centre of a sphere. This depends on the nature of the confining potential. An obvious case, as pointed out by Pupyshev [23], is that repulsive spherical walls tend to push the atom to the centre. However, walls are not necessarily repulsive, and, indeed, in some of the important examples we will discuss, the walls are attractive. It is then not true that the atom will stay at the centre of the sphere, which is one of the limitations of the simplest theoretical model. Within a similar approach, departures from sphericity may easily be tackled, not only for confined atoms which are not at the centre of the sphere, but also for confining surfaces which become distorted from sphericity. Of course, the spherical solution is the starting point, even for thinking about the more complex situations.

The revival

Many years after the early papers [20,21], interest in confined atoms has suddenly revived. We will not trace all the stages of the revival, beyond noting that there is currently a rush of recent papers about confined hydrogen (for example Varshni [5], Connerade *et al* [26], Huang *et al* [27], Shi *et al* [28]). This comes after a long period of comparative neglect, during which this problem was not at all in the limelight. Now, suddenly, even as abstruse a situation as hydrogen inside a sphere has become a relevant and topical subject. This, as I will argue, is because confined atoms are now about to become readily available in the laboratory. Many experiments are just around the corner, and so there is a great chance for theorists to get in quickly and make some relevant predictions for these new systems.

Other atoms

Hydrogen is far from the most interesting example of confinement. In fact, it is a rather poor atom to consider. With only one wave function present, there is not much chance for varied and interesting behaviour. For example, the 'atomic ring' mechanism, in which the self-consistent field organises the atom in response to external forces [22] requires many electrons to be present. Once this happens, there is potentially a choice between quite different configurations having the same energy, because some of this energy can be stored as angular momentum, and some as electrostatic potential energy. Thus, the angular momenta of the electrons can be different from each other in different configurations having nearly the same energy.

Not only may we find different combinations of electronic states for a given energy, but they will respond differently to confinement, leading to avoided crossings and interactions of all kinds. The question whether electron-electron

correlations are enhanced or inhibited by confinement arises, and standard tools of atomic theory for free atoms (such as the RPAE) are available, which can be adapted and applied to the problem [29]. In fact, the most interesting features of confined species relate to a rather unusual new concept: *atomic compressibility*. Of course, hydrogen has only one option to reorganise itself under compression because the one electron can only become unbound. With several electrons present, the options are much more varied, and one finds that atoms are more or less readily deformable when confined, owing to differences in their electronic shell structure.

A rather nice example of this is the reorganisation of the Cs atom, which leads to a discontinuity in its compressibility at high pressures. Atoms confined within more or less penetrable spheres or shells (both attractive and repulsive) are similarly a new kind of quantum object. Their properties can be computed from first principles by solving the Schrödinger equation with confining boundary conditions. One can treat several problems in this way, from metallofullerenes to atoms under pressure.

10. Fullerenes

A simple way of approaching confinement within the C_{60} fullerene is to first model it as a spherical shell. A shell is appropriate, because it is known that the fullerene is hollow (for example, it exhibits a surface, but no volume plasmon). Of course no fullerene is strictly spherical, even if all the atoms lie on a sphere as in the case of C_{60} , since, in quantum mechanics, a perfect sphere is unable to rotate. Thus, in principle, one would need to model the full Platonic solid to represent the system properly. Very fortunately, however, there are different energy ranges corresponding to different phenomena in metallofullerene spectra. For some parts of the spectrum, the spherical approximation is not only satisfactory, but actually gives the clearest indication of what is happening. Indeed, it allows the results of much more complex computer modelling (multicentre expansions) to be understood.

An indication of how to proceed comes from electron scattering experiments on fullerenes [35], which have been interpreted by using a very simple model, involving an attractive 'square well' shell. Thus, characteristic quantum scattering resonances can be attributed to standing waves in the shell. It may seem surprising at first sight that the well should be attractive. However, experiment tells us that the fullerenes form negative ions, and their electron affinities are even determined experimentally [36]. It is therefore possible to adjust the binding strength of the attractive shell in a spherical model until the experimental value for the affinity of the negative ion is recovered.

11. Modelling metallofullerenes

By using this spherical shell, it also becomes possible to model the properties of metallofullerenes, if we make the simple approximation of placing a confined intruder atom at the centre of the shell. Such a system is called 'endohedral', to emphasise that the atom is inside the fullerene cage. We write, for example, $\text{Ca}@C_{60}$, for calcium inside a buckyball. Within the centred spherical approximation, several interesting features have emerged from theory so far. For example, the resonances of metallofullerenes have been classified [37] as belonging to one of three general types, namely :

1. Atomic resonances : these are already present in the atom before confinement, and are merely modified by the presence of the confining cage.
2. Confinement resonances : these are characteristic of the cage, although they appear in the spectrum of the confined atom (usually, they lie in the photoionisation continuum [38], and appear as a result of interferences involving the wavefunction of the escaping electron).
3. Molecular resonances : these are due to breakdown of the angular momentum characterisation of the electrons, as a result of which new channels open which are not allowed in the free atom.

Resonances of types 1 and 2 are realistically modelled in the spherical shell approximation, within which the angular momentum about the centre of the system is conserved. On the other hand, molecular resonances will not appear in the spherical models, and this is actually a useful way of distinguishing them from the others. To represent molecular resonances requires the fullerene shell to be represented in a much more complex way, as a multicentre expansion [38]. Fortunately, they turn out to occur at lower energies than 1 and 2.

There has been a great deal of theoretical work on the properties of metallofullerenes, and on the basic principles of the simple models we have described. What may be concluded from these zero-order models is that the atomic spectrum, in general, becomes 'dressed' by the spectral response of the confining cage [34]. In some cases, enhancements of spectral features [29] and avoided crossings [26] can occur. It is also possible for atomic orbital collapse effects to be modified by the presence of the cage, leading to a redistribution of oscillator strengths [29], which can be dramatic in critical cases.

Apart from the molecular effects alluded to above, the main effects which are neglected in the model calculations are (a) exchange between the electrons of the metal and of the fullerene, (b) departures from central symmetry .

An interesting advantage of the spherical shell model is that it does allow electron correlations to be handled. Thus, the RPAE method has been implemented for a confined atom

[39], and has revealed interactions between atomic and cavity resonances which are not present otherwise. Interesting questions arise concerning the behaviour of correlations for confined systems. One may ask whether they should increase or decrease with increasing confinement. The answer seems to be that this depends on their nature. Some correlations grow, when different configurations become degenerate as the atom is confined, while others diminish, when the configurations become separated in energy. It thus appears that there is no simple general rule.

12. Atoms under pressure

The metallofullerenes are an example of confinement within an attractive shell. However, it is also possible to confine atoms within a cavity with repulsive walls. This is closer to the original idea of Sommerfeld and Welker [20], and is the situation encountered when an atom is put under extremely high pressure. In fact, as long as the cavity is external to the atom, confinement within an attractive shell leads to dilation, while the repulsive step leads to compression.

The idea that atoms are compressible may seem strange. Normally, one thinks of atoms as incompressible. For example, in the kinetic theory of gases, atoms are treated as point masses. Even when this idea is extended by allowing them to occupy a finite volume, as in the corrections to the ideal gas law introduced by van der Waals, their compressibility is still not envisaged in Thermodynamics.

Despite this, however, atoms are compressible at the quantum level, and the atomic compressibility is a true quantum-mechanical observable. Because a many-electron atom is capable of reorganising itself under pressure, its shell structure can change, and the Periodic Table for atoms under pressure is not the same as for free atoms [39]. This has many implications for the chemistry of atoms under pressure

12.1. Introducing the pressure :

To introduce the pressure [40], just consider the standard relation :

$$dE = TdS + PdV \quad (1)$$

For individual atoms, there can be no change in entropy, so $dS = 0$, and the temperature disappears from the problem. However, one still has :

$$p = dE/dV, \quad (2)$$

which we can regard as defining the Hellmann-Feynman pressure for Hartree-Fock atoms. Since both E and V are observables, whose expectation values are fully defined, changes in both of these quantities are measurable, and the pressure P is a meaningful quantity. Both stress and strain can be defined, so the compressibility of the atom is observable. However, it turns out to be strongly non-linear, as we will emphasise below.

12.2. Building solids :

If a cluster or solid is built up from atoms, then there are two possibilities. Either the lattice is open, with wide spacing between the atoms, in which case atomic compressibility plays no role, or else the lattice is very closely packed, in which case external pressure translates into a microscopic pressure applied to each one of the individual atoms. In the latter instance, quantum compressibility becomes important.

12.3 Practical motivation: an ideal battery :

The Li ion battery is the ideal 'rocking chair' or rechargeable battery. It has the best electro-chemical properties and power-to-weight ratio, and its manufacture is non-polluting, in contrast to that of lead-acid accumulators. However, the problem of making large and efficient, reasonably inexpensive electrodes must be solved before it can be used for heavy-duty applications, such as to power town cars of the future.

Thus, an example of a practical application is the insertion of lithium ions into solids. This is a very important process in the design of electrodes for lithium ion batteries : lithium metal makes a poor electrode, as batteries using Li metal could eventually explode. Safely rechargeable Li ion batteries are based on ion insertion in solids, which avoids deposition of the metal.

A simple approach to model reversible insertion is to describe it by introducing a pseudo-pressure exerted by the ions on the lattice. This works because reversibility implies the absence of phase transitions. *i.e.* that there should be no recrystallisation on insertion and the effects are then due to the radial part of the Schrödinger equation. Atomic compressibility is thus an ideal driving mechanism. Experience confirms that host materials involving compressible atoms actually do work best. This key observation is a strong pointer towards the importance of quasi-atomic effects. It leads to the notion of a new kind of 'soft chemistry' involving only radial atomic changes [22], an approach which helps to explain a number of features of reversible lithiation [41].

Experience also shows that the softest atoms are those whose wave-functions are subject to the 'orbital collapse' phenomenon [42–44]. This provides a powerful motivation to study confined atoms of the transition periods and rare-sequences. It is known experimentally that atomic orbital collapse can be driven by ionisation [45]. Since we now know that ionisation produces effects similar to compression, this also suggests that orbital collapse can be controlled by compression, and thus studied theoretically by using the confined-atom model. For example, it has been demonstrated in this way that lanthanum is a particularly 'soft' atom [46].

13. Relativistic confinement

There are several reasons for which the relativistic problem is especially important :

1. Without it, one cannot treat the confinement of heavy atoms;
2. One cannot tackle orbital collapse properly without it;
3. The boundary conditions for confinement are not the same as for the non-relativistic case [47] (in part, because of Klein's Paradox [48]).

The question of relativistic confinement has also been raised in a quite different context from the one considered here. Because spin is intrinsically quantum-mechanical, with no obvious classical analogue, the classical correspondence of the Dirac equation is not fully resolved. One approach to this problem is to confine Dirac particles in cavities whose dimensions and geometry can then be varied [49]. Such studies, of course, concern large cavities, whereas our interest here is in the opposite situation, *viz.* the quantum limit.

A great deal of effort is now devoted to the relativistic extension of confined atom modelling. Because of the need for a single consistent approach, within which the properties of all atoms can be systematically intercompared.

14. Generalisation of the quantum pressure

As we have seen, when the atom is allowed to change its volume, the existence of an external pressure is implied. An increasing number of papers ([39] and refs therein) have either introduced explicitly an atomic pressure [22,40,50,51] or implied the existence of the quantum compressibility as a quantity enabling some rather special properties of matter to be described [25,52,53]. In our work, we consider the concepts of pressure and compressibility at the atomic level, and the manner in which their variation can be described for many-electron atoms. In particular, we consider the 'hardest' and 'softest' atoms, and the criteria which allow them to be recognised as such. We now show that atomic compressibility consists of two factors : a static scaling term, which depends only on the properties of the free atom, and a dynamical factor, which is strongly nonlinear and can, for some atoms, exhibit discontinuities analogous to a phase transition.

We introduce a dimensionless representation which allows the compressibilities of atoms to be systematically intercompared. There are two factors. One is a scaling, which depends on free-atom properties and varies from atom to atom by a factor of up to 2000, and the other is a dimensionless, nonlinear ratio, which can be plotted for all atoms onto a single graph.

Our discussion refers to the most fundamental atomic model, *viz.* the self-consistent field atom. Single configuration

calculations demonstrate the basic principles involved. However, the scaling rules can readily be used in conjunction with *any* atomic model as required. In order to extend our discussion to heavy atoms, which can exhibit exceptionally interesting variations of compressibility, we adopt a fully relativistic Dirac-Fock approach. However, all the effects we describe have also been investigated and found to occur in a qualitatively similar way for a non-relativistic Hartree-Fock model.

Atomic pressure, as an explicit observable, deduced by solving the Schrödinger equation, was introduced above. Let the free atom binding energy $E_B^f = E_A^f - E_I^f$ where E_I^f is the total energy of the free ion ground state, and E_A^f is the total energy of the free atom ground state. The analogous quantities for the atom under pressure are $E_B^p = E_A^p - E_I^p$ and we can define a dimensionless or reduced binding energy ε where

$$\varepsilon = E_B^p / E_B^f. \quad (3)$$

The dimensionless quantity ε can then be calculated under any kind of external perturbation of the atom. For example, it can be computed under progressive increase of the effective nuclear charge Z through non-integral values, or indeed under any other kind of spherical perturbation, such as confinement in a cavity of arbitrary radius and spherical potential. In practice, when using *ab initio* theory to determine ε , it is simpler and gives more consistent results to replace the E_B^f and E_B^p by the Koopmans removal energies of the appropriate Dirac-Fock orbitals, which is convenient for our discussion.

A confined atom is subjected to a quantum pressure which differs in nature from the kinetic pressure alluded to above. As noted in the Introduction, Numerous examples of quantum confinement exist, for instance endohedral atoms in metalofullerenes [54–56], atoms confined in zeolites [57], atoms in solids treated through the Watson sphere [58,59], atoms in bubbles [60], in quantum dots [61], in clusters [62], in superdense or compressed matter [63], in the reversible lithiation of solids [64], *etc. etc.* From a purely formal point of view, we can also consider a fictitious atom of non-integral nuclear charge as an example of spherical compression [65].

Indeed, for the purposes of our argument, we regard confinement of the atom within an impenetrable sphere and the introduction of a fictitious non-integral nuclear charge as the two hypothetical limiting cases which represent, respectively, totally external and totally internal spherical perturbations.

Let the mean volume occupied by the free atom $V^f = 4\pi \langle r^3 \rangle / 3$, where $\langle r^3 \rangle$ is the expectation value of r^3 , calculated from the outermost wavefunction of the atom. Then, the corresponding quantity V^p can again be defined for the atom under a pressure P , arising from any kind of spherical

potential, as explained above. We introduce the dimensionless shrinkage parameter :

$$\xi = V^p / V^f. \quad (4)$$

From the definitions, we can deduce that the quantum pressure :

$$\begin{aligned} P &= \Delta E / \Delta V = (E_B^f / V^f) \{(\varepsilon - 1) / (\xi - 1)\} \\ &= (E_B^f / V^f) p \\ &= \eta P, \end{aligned} \quad (5)$$

where p is a *reduced pressure*. What our definitions of ε and ξ achieve is to scale all the variables systematically by the appropriate factor for each atom, yielding a *reduced compressibility*. The important point, as we now show, is that most of the variation of compressibility from atom to atom is removed by this method of scaling. For all atoms, the actual variation in ε as a function of ξ turns out to be almost the same. Some indication of how this occurs comes from magnitudes obtained for free atoms. From multi-configurational Dirac-Fock calculations, we find, for caesium

$$\eta_{Cs} = 3/4 E_{6s} / \langle r_{6s} \rangle^3 = 1.3591 \times 10^{-4} \text{ a.u.}^{-2}, \quad (6)$$

while, for helium :

$$\eta_{He} = 3/4 E_{1s} / \langle r_{1s} \rangle^3 = 0.27491 \text{ a.u.}^{-2}, \quad (7)$$

which implies that Cs (one of the largest atoms in the Periodic Table) is roughly 2000 times more compressible than He (the smallest atom), provided ε and ξ exhibit variations similar to each other for both cases.

Since both ε and ξ are dimensionless, we can now plot the reduced compressibility, or (ε, ξ) curves for all atoms onto a single graph, as shown in Figure 2, obtained by fully relativistic Dirac-Fock calculations for the extreme cases of Cs (the typical soft atom) and He (the typical hard atom). Again, a relativistic approach is necessary, to make the comparison, because we are treating very light and rather heavy atoms within the same theoretical scheme. We therefore used the GRASP code [66] with modifications [6] to treat spherical confinement, as previously described.

From the data used to plot the confined atom curves, we can also deduce the reduced quantum pressure p by using equation (5). This can be plotted against the volume ratio. The interesting feature of such a plot is that, again, there is marked similarity between the curves, despite an enormous difference of hardness between the two atoms. With appropriate scaling, even the functional variations turn out to be nearly the same over a wide range.

We now enumerate some general features of (ε, ξ) curves

- (i) As the spherical perturbation tends to zero (for example the height of the confining step V tends to 0, or nuclear charge tends to that of the neutral atom) both $\varepsilon = 1$ and $\xi = 1$, so that all the (ε, ξ) curves

through a universal point (1,1), which has the practical advantage that it lies near the centre of the graph. This point is common to all the (ϵ, ξ) -curves, despite the fact that they are in principle different from each other, not only from atom to atom, but also according to the nature of the spherical perturbation.

- (ii) Since a free neutral atom exists only at zero pressure and, since zero pressure corresponds to $d\epsilon/d\xi = 0$, it follows that the slope of the (ϵ, ξ) curve for the neutral atom confined by a sphere tends to zero as (ϵ, ξ) tend to (1,1). Interestingly, this rule does not apply to the curve obtained by variation of the nuclear charge because, if nuclear charge were allowed to vary freely, there could be no equilibrium or zero-pressure energy.
- (iii) For atoms compressed by an impenetrable repulsive sphere, there is a confining radius within which E_B^P , and therefore also ϵ , changes sign, *i.e.* the (ϵ, ξ) -curve crosses the $\epsilon = 0$ abscissa. Formally, this resembles ionisation, but actually it corresponds to delocalisation, *i.e.* the outermost electron is no longer confined by the atomic potential, but only by the impenetrable sphere.
- (iv) For atoms compressed by an increase in nuclear charge, the ionisation potential increases with charge, *i.e.* as the atom becomes smaller, its binding energy also increases, so the (ϵ, ξ) curves veer upwards rather than downwards, and can never cross the $\epsilon = 0$ abscissa, *i.e.*, in this case, delocalisation cannot occur as it does when the confining sphere becomes smaller. This distinguishes between the two mechanisms of compression (external and internal).
- (v) Atoms can be dilated as well as compressed by a spherical perturbation, either by a reduction of nuclear charge, or by an attractive spherical shell or step. In this case, the binding energy is always reduced, until eventually ionisation occurs. Since, whatever the mechanism, an increase in ionisation potential never occurs on dilation, there is a forbidden region for $\xi > 1, \epsilon > 1$ in the (ϵ, ξ) plane. Within the Dirac-Fock method as implemented in the GRASP code, we were unable to obtain convergence for an attractive outer sphere. Thus, the dilation branches of the curves corresponding to confinement by a spherical cavity are absent from our calculations and from Figure 2. However, it is easy to deduce what their properties should be. First, they must be continuous with the corresponding compression branch, which means that $d\epsilon/d\xi$ tends to 0 as the point (1,1) is approached from right to left in the figure. Second, electron detachment or ionisation must occur in a sufficiently attractive external well, so the curves must veer down again as ξ increases, eventually crossing the abscissa at an ionisation point. This also implies that there must be a

second crossing point between the curves for dilation by a spherical cavity and the curves for decreasing nuclear charge.

- (vi) The real physical pressure is given by :

$$P = \eta'(\epsilon - 1)/(\xi - 1). \tag{8}$$

As noted above, the first factor undergoes a very large variation from atom to atom, from the smallest atom in the Periodic Table with the highest binding energy, which is He, to the largest atom with the smallest binding energy, *i.e.* a heavy alkali (Cs or Fr), which thus define the hardest and softest atoms respectively.

- (vii) The difference between the scaled (ϵ, ξ) -curves for different atoms can be represented by a slight rotation about the (1,1) point as a pivot. This slight rotation is sufficient to encompass the behaviour of nearly all the elements in the Periodic Table, whose hardness is generally intermediate between that of He and that of Cs. The rotation is anticlockwise for increasing hardness.
- (viii) The nonlinear variation of compressibility is entirely contained in the (ϵ, ξ) -curves, and even its functional form is not grossly different for different atoms. A discontinuity in the curve for confined caesium has already been noted and explained in an earlier paper [51]. It corresponds to an observed effect in the solid, namely orbital collapse induced by external compression. It might be thought that atomic physics could do little to model such phenomena in solids. However, it is becoming clear that, once an orbital collapses into the inner reaches of the atom, it is screened from the fields of the solid, and its atomicity is dramatically enhanced, which is why essentially atomic calculations are successful in describing a wide range of orbital collapse phenomena in solids and compounds [22,40,50,52,68].

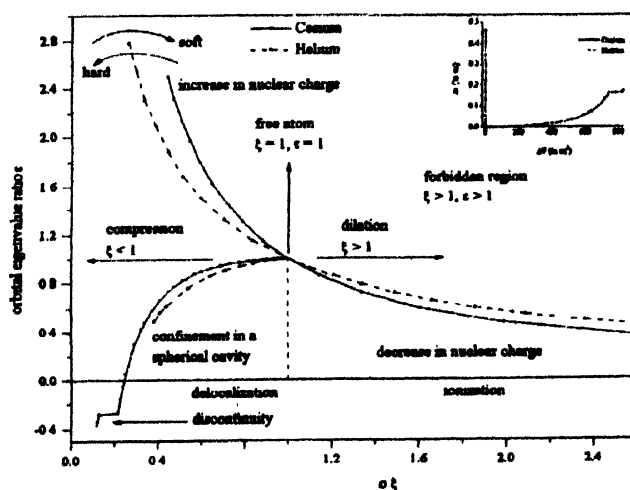


Figure 3. Showing the generalised coordinates or reduced pressure plot described in the text.

15. Conclusion

We have presented a general introduction to the subject of confined atoms, quasi-atoms and superatoms, which together constitute a new strand of atomic physics extending its applicability to larger systems. In addition, we have introduced a new parametrisation based on quantum confinement, which allows the compressibilities of different atoms to be inter-compared and a general description of quantum compressibility to be attempted for all the atoms in the Periodic Table. It is hoped that our method will find application to a wide range of phenomena, extending into solid state physics, clusters physics, reversible lithiation, and matter under very high pressures.

An additional problem which is very interesting to consider is the nature of the confinement conditions for the fully relativistic situation. When the Dirac equation is solved, a two-component wavefunction is introduced. The large component is normally regarded as the more 'physical' simply because it turns into the ordinary wavefunction in the non-relativistic limit, whereas the small component then tends to zero. However, in a relativistic situation, both must be treated as equally important. It then becomes difficult to decide what the correct confinement condition is. Ultimately, there is a problem due to Klein's paradox if the conditions are inconsistent with relativity or are wrongly applied.

We have investigated how this problem can be addressed along the same lines as in the M.I.T. bag model of Nuclear Physics. Relativistic confinement turns out to be a specific and different problem from the nonrelativistic case, because the appropriate boundary condition depends on the conditions imposed on the Dirac current by charge conservation.

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On the reversible insertion of Li^+ ions in battery electrodes: The investigation is carried out in collaboration with researchers from the University of Montpellier (France), Dr. Jean-Claude Jumas, Dr. Josette Olivier-Fourcade, Dr. Pierre Lippens, and, from the Institut d'Electronique du Nord in Lille (France), Dr. Lefebvre-Devos. The involvement of the battery manufacturer SAFT (a division of the Alkate group) is also gratefully acknowledged.

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