atoms

Opinion

The Atom at the Heart of Physics

Jean-Patrick Connerade [1,2]

[1] Quantum Optics and Spectroscopy Group, Physics Department, Imperial College London, London SW7 2BZ, UK; jean-patrick@connerade.com
[2] European Academy of Sciences Arts and Letters (EASAL), 75006 Paris, France

Abstract: A number of reasons are advanced for which atoms stand at the heart of research in the physical sciences. There are issues in physics which are both fundamental and only partly resolved or, at least, imperfectly understood. Rather than chase them towards higher and higher energies, which mainly results in greater complexity, it makes sense to restrict oneself to the simplest systems known, held together by the best understood force in nature, viz. those governed by the inverse square law. Our line of argument complements the adage of Richard Feynman, who asked: should Armageddon occur, is there a simple, most important idea to preserve as a testament to human knowledge? The answer he suggested is: the atomic hypothesis.

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1. Introduction

Scientists, although it may not always be apparent, do follow trends, and scientific fashions, like others, come and go. We see the birth of new journals, covering areas nobody had named before and there is always a temptation to consider that a subject must appear strikingly new to be of interest. However, novelty is more elusive than it seems. Some areas use new words, but the key point is whether they involve new principles. In reverse, when considering the importance of a field of research, it is just as relevant to enquire how long it has been pursued fruitfully rather than always insisting on evident novelty. Thus, Richard Feynman [1], in his celebrated series of lectures, once asked a fundamental question. In the event of Armageddon, were all human knowledge to be threatened with extinction, is there one single idea which should be preserved for future inhabitants of our planet? The answer he suggested is *The atomic hypothesis*, namely that all matter is made of atoms. When one considers how ancient this idea is, stretching back at least as far as Democritos, issues of fashion may well appear secondary. There is, however, another aspect to consider. Once a problem is fully resolved, a subject previously regarded as very relevant may suddenly cease to be attractive. So, a periodic re-appraisal of central themes is a necessity in scientific research to make sure they remain relevant.

2. Concerning Unsolved Problems

Unanswered questions and unsolved problems are the true stimulus of scientific investigation. The discussion presented here is an attempt to consider why atomic physics is useful from the standpoint: how does it help us deal with so far incompletely resolved issues in science?

This form of discussion is more difficult than presenting results. Conventionally, through the corpus of research papers, scientists must present solutions, i.e., answers which advance our understanding. Discussing unsolved problems means approaching research from the opposite point of view. The importance of an area of work then stems from the difficulty of discovering answers or, to put it another way, 'so far unsolved' problems are regarded as very significant. If an area of investigation does not call for new methods or principles, it then implements nothing fundamentally 'new'. As a simple example, biochemistry is an important subject, because, despite great strides in contemporary research, nobody can claim to understand how a particular molecular structure comes to life while another, little different and of equivalent complexity, remains inert. (e.g., Salam [2]).

Model problems which can be solved exactly in physics are all very interesting, but turn out to have limited scope. Inevitably, they involve some kind of compromise with reality. Thus, an allegedly simple situation, such as the two-body problem (hydrogen) in quantum mechanics is closely related to Newton's exact solution of the two-body problem in celestial mechanics, but neither of them really exists in nature. Taking hydrogen first [3], there are different degrees of approximation. The Schrödinger equation possesses many wonderful properties, but there are also difficulties associated with its use. Its leading term is the nonrelativistic kinetic energy, which obeys the Galilean transformation law. The next term is a scalar electric potential, i.e., an incomplete electromagnetic term. One can insert the vector potential of electromagnetism into the first term, but the result is no substitute for a proper covariant equation.

In addition, there is the difficulty that time, in quantum mechanics, possesses no associated operator and is not 'quantised'. It appears in the Schrödinger equation as a classical parameter (see, e.g., [4] for discussion) and is therefore different from space in this respect. The next improvement is to replace the Schrödinger equation by the Dirac equation [5] which, at least formally, satisfies the Lorentz transformation, but this does not dispel the qualitative difference between space and time just noted. Furthermore, this is still not enough, because neither of these equations allow for the quantisation of radiation. Further progress takes us into quantum electrodynamics and quantum field theory, for which we must accept that no exact solution is known. One usually resorts to the so called Furry picture [6], which introduces radiation via a perturbative scheme, with a complexity increasing order by order as the calculations are improved and further extended. At present, this is seemingly the best one can do to compute the two-body problem in quantum mechanics.

3. Is There a 'Pure' Two-Body Problem?

One might at first suspect that the problem just described occurs only due to the radiation field. However, even in celestial mechanics, it turns out, first, that there is no such thing as an isolated two-body system in nature and, second, that the gravitational field is not the only force between two particles. The first of these problems was addressed by Poincaré in 1891 [7]. He considered the three-body problem and proved that the orbits do not close. They give rise to chaos (non-integrable solutions of the equations of motion), even allowing only for a pure gravitational field. The best one can do is to obtain very local solutions, such as the one discovered by Lagrange [8] in connection with the system known as 'the Greeks and the Trojans' in astronomy.

The second issue (i.e., the existence of further fields of force) emerges in high energy physics. Accelerators of ever greater sophistication allow all of the forces between a pair of particles to be explored by increasing their relative energies to extremely high values. Entirely novel systems of particles then appear. This has opened up a magnificent and inspiring intellectual adventure in modern physics, culminating in the unification of all the fundamental forces (with the sole exception of gravitation [9]. Its crowning achievement is the Weinberg–Salam theory. The next unification point (to include gravitation) would require an energy of 10^{17} GeV, way beyond what can be reached experimentally, except perhaps through astronomical observation of early (remote) stages of the universe. These are all wonderfully impressive developments, but they do not bring us closer to resolving the issue raised at the outset of the present comment.

Chasing the two-body problem towards higher and higher energies does not preserve the simplicity of the original two-body system. In fact, one of the main consequences is the production of many new particles, which of course can be classified through a novel form of spectroscopy. However, their presence complexifies the system. I will argue that, in quantum mechanics, even at low energies, the pure two-body problem is something of an illusion, despite the impression that 'exact solutions' exist. In reality, the closest we can get to it, and to extending it to a few bodies, occurs in atomic physics.

4. The Challenge of the 'Few-Body' Problem

So far, the problem uncovered by Poincaré in classical mechanics remains unsolved, even at low energies, and this transposes into quantum mechanics when the latter is set up following the path of Landau and Lifshitz [10,11]. One can well argue that, in addition to discovering new particles or unifying the fundamental forces, one should continue to study an energy range within which interactions remain limited to the best-documented interactions in physics (i.e., those governed by the inverse square law) and to investigate the effect of slowly increasing the number of interacting particles (essentially electrons, protons and neutrons) within a system. This brings us straight back to atomic physics and to the periodic table of elements as the set of basic situations to study. Atoms thus appear as the ideal testing ground for the many-body problem.

Although one refers to 'many-body' effects in atomic and molecular physics, this terminology is not really the most accurate. The word 'many' creates the impression that the difficulties involved necessarily increase with number. In fact this is not the case. For example, an infinite 'sea' of occupied states (as considered originally by Dirac to handle the negative energy states in his equation) minus only one particle behaves as just a single 'antiparticle', viz: the positron. Likewise, the fundamental antisymmetry of many-electron states lead to the discovery of 'closed electronic shells' and a single 'hole' in a closed shell is, again, similar in behaviour to a single 'antiparticle'. Thus, in some situations, quantum mechanics allows a more promising description of the many-body problem than classical mechanics. In a sense, this is a surprising consequence of a more sophisticated theory. 'Few-body problem' might be a better description.

Perhaps one should even restrict the definition of the most suitable energy range by excluding excitation energies high enough to produce electron–positron pairs. This would avoid not only single excitations of very high energy, but also multiphoton excitation by very intense laser fields and would stay more closely within the first order of the Furry picture [6].

5. The Awkward Connection between Classical and Quantum Mechanics

Even if we do restrict ourselves carefully, as just described, there are deeper issues to consider. As already noted, the three-body problem in classical mechanics cannot be solved exactly. This may seem semantic, since pretty accurate perturbative methods, well known to astronomers, can handle most practical problems when computing orbits. However, the issue looms again in the formulation of elementary quantum mechanics.

For this purpose, we need to specify the correct Hermitian operator to associate with each and every observable while avoiding an extensive and clumsy table as a separate postulate. A first approach, suggested by Bohr and Sommerfeld and refined by Landau and Lifshitz [10,11], was to study the so-called 'semiclassical limit' of quantum theory via the 'correspondence principle' through which the quantum and classical theories are supposed to merge. To be useful, the process would need to be applied 'backwards' i.e., from classical to quantum physics, since the classical problem is the one regarded as 'well-understood'. The procedure, however, involves integration around closed orbits of the underlying classical systems.

The difficulty, as Einstein famously objected, is: what should one do if the orbit never closes? Unfortunately, this is precisely the case for the few-body problem, as Poincaré [7] had discovered. So, the Bohr–Sommerfeld 'principle' actually fails in most situations except for a few ideal, integrable problems, such as the harmonic oscillator, Newton's two-body problem, etc. There are some complicated orbits (the Landau orbits) which resemble Lissajoux figures in phase space because they 'eventually' close, but these are not sufficient in number to account for all possible orbits of a non-integrable system.

Thus, 'difficult' situations, such as three-body problem, a pendulum with a magnet, etc., cannot strictly be handled in this way. In classical physics, a pen attached to a pendulum with a magnet underneath will write all over a piece of paper within the constraint imposed by its total energy and will never follow the same path twice, i.e., the orbit will never close. This leaves us with the complication that, despite the intuitively rather obvious correspondence principle, classical mechanics contains information which simply cannot be transferred to quantum mechanics. Why this happens remains a matter of opinion.

We end up with two physical theories connected by an imperfect correspondence. On the one hand, classical mechanics contains systems with both integrable and non-integrable solutions, while, on the other, quantum mechanics seemingly allows only one kind of solution. A legitimate question becomes: does the semi-classical limit of quantum mechanics recover *all* or can it recover *only a part* of classical mechanics?

To this one can add, starting out from the Dirac equation, that no semi-classical limit is known for this case, since the solutions involve spinors, and spin does not exist in classical physics. Hence, in the relativistic theory, the whole concept of the correspondence principle as the basis of a systematic method to set up quantum mechanics breaks down, which is why, in response to the question 'why is there no book by Landau and Lifshitz on relativistic quantum mechanics?', Lev Landau is said to have replied; "Because there is no such theory!"

6. The Structure of Empty Space

Another way of looking at the question is to ask what one would mean by orbits which do or do not 'close' in quantum mechanics. Would asking this very question imply a violation of the uncertainty principle? In quantum mechanics, should one consider phase-space itself as exhibiting a granular structure, with dimensions of individual grains determined by the magnitude of Planck's constant? Would it then suffice for the electron to return to within one such grain for an orbit to be regarded as 'closed'? This of course suggests a different definition of dynamical 'chaos' for classical and for quantum systems. There has been much discussion of the issue since the earliest experiments, by Garton and Tomkins [12], revealed the problem.

The refinement would be all well and good were it not that the theory of relativity requires space-time to be continuous and freely differentiable in the sense of classical mechanics. Hence, no doubt, Einstein's insistence that the Bohr–Sommerfeld quantisation was unsatisfactory. The nature of space (continuous or granular) becomes an awkward issue. It is even more so when we consider the difference between space (a true observable) and time (a classical parameter) in quantum mechanics, already noted above. There is perhaps no other situation in which the incompatibility of the two conceptions of empty space is so apparent as in atomic physics.

The problem of infinite divisibility, first raised by Pascal [13] in connection with the structure of atoms and of matter itself, re-emerges when one attempts to extend the equipartition theorem to microscopic systems. As commented by Dirac [5], it would ultimately imply infinite specific heats. Granularity is therefore also an essential ingredient in thermodynamics and this remark provided one of the earliest 'proofs' of the necessity of quantum mechanics.

7. Compressed Atoms

In the kinetic theory of gases, atoms and molecules also play an essential role without which the concept of pressure would remain undefined. It is assumed that they behave as point-like masses, bombarding one side of the walls of the container. The average force they exert is given as the origin of pressure, which becomes a macroscopic thermodynamic variable. Unfortunately, this picture, as so often happens in physics, becomes less straightforward as corrections to the ideal gas law are introduced. The first, due to van der Waals, involves attributing intrinsic volume to the atoms or molecules, but this volume is considered as 'fixed'. The reason for imposing this restriction is to preserve the consistency of the formalism, but it is obvious that a physical volume cannot remain fixed as the pressure increases. The real situation must of necessity be more complex.

Within the Thomas–Fermi model of the atom [14,15], the effect of externally applied pressure is readily understood as the compression of an electron 'gas'. One can simulate it by changing the external boundary condition and studying how the total energy and occupied volume are related. Within the Schrödinger picture also, the electron cloud is a kind of 'fluid' with the Schrödinger equation as an equation of state. Changes in the external boundary conditions then act like the external piston. The model just described was developed by Hellman [16], Feynman [17] and Feynman et al. [18]. Within it, there are difficult issues relating to the different definitions of probability in thermodynamics and in quantum physics which have to be reconciled.

This takes us to the area of microscopic thermodynamics and confined atomic systems ([19] and refs. therein). The natural starting point is still the Thomas–Fermi model of the atom because it provides the atom with a well-defined volume to start with. However, there is nothing to prevent extending the idea to the Hartree–Fock and Dirac–Fock equations (see [20] and earlier refs. therein). One readily establishes that the periodic table for atoms under compression is not the same as for free atoms because the order of filling is modified and actually approaches the ideal and complete *aufbau* principle (see [21]) more and more closely as the pressure is increased. A whole new chemistry opens up for study, for underlying reasons which stem from atomic physics, but it remains necessary to perform extensive ab initio calculations to account for them in detail (see e.g., [22]). One can think of many experimental applications (bubbles in solids, clusters, polaronic insertion of ions, atoms under extreme pressure, etc.).

8. Endohedral Confinement

Closely related to the atom under pressure is another novel area of research, namely the atom endohedrally confined within a hollow molecule, the most typical example being the metallofullerene. There are basically two conceptual approaches for such systems. The first is to attempt full molecular calculations, from which geometrical structures and symmetries can in principle be deduced (e.g., [23]). The second is to approximate the confining molecule semi-empirically as a hollow, spherical potential shell whose properties can be deduced experimentally from electron scattering experiments [24]. Apart from greater simplicity, the latter approach allows one to include some important quantum effects, such as the occurrence of confinement resonances [25].

9. Many-Body Theories of the Atom

Returning to the (unsolved) many-body problem, three general remarks can be made. The first, as noted above, is that many-electron states in quantum mechanics obey the Pauli principle. There is no such principle in classical physics, so we have good reason to hope for a better understanding of the many-body problem. The periodic table informs us about the properties of closed shells. They imply that atoms return regularly to nearly spherical shapes at each period as the number of electrons is increased, which is the crucial simplifying feature.

A first step towards the many-body theory of the atom is of course to solve the coupled system of 'independent electron' Schrödinger equations by the Hartree–Fock method [26], refined by the introduction of mixing between configurations. This method has been successfully extended to the Dirac equation [27] despite a complication originally pointed out by Brown and Ravenhall [28] for the multiconfigurational Dirac–Fock method: namely that configuration mixing, in this case, might involve negative energy states which cannot all be 'filled' simultaneously, in which case the variational principle upon which the Hartree–Fock method rests for convergence would collapse. This is somewhat controversial because properly converged multiconfigurational Dirac–Fock solutions have been obtained [27] and correspond very well with experimental data. It would be desirable for practitioners of the method to dispel any residual uncertainty surrounding this alleged 'dissolution into the negative energy continuum' if it is indeed a real effect.

Plasmon excitations (i.e., oscillations of closed shells) in free atoms can be computed either by the many-body perturbation theory (MBPT Kelly [29]) or by the random phase approximation with exchange (RPAE Amus'ya et al. [30]). These two theories are not equivalent, even when the perturbative expansions are performed on the same independent electron atomic basis. In the MBPT, all of the terms identified by their Feynman graphs are summed up to a given order, but the summation cannot be extended to the high order, as the computations become progressively more and more extensive. In the RPAE, only two classes of diagrams are treated (the forward bubble diagrams and their exchange equivalents) but they are summed to the infinite order. Obviously, the two approaches cannot be equivalent. These are the two theories we have at our disposal, neither of which is 'complete'. Both are useful, generally in different situations, the MBPT being more appropriate for open-shell systems and the RPAE for closed shell or half-closed shell atoms.

This ambivalence, again, can be taken to express the fact that we have no general solution of the many-body problem in quantum mechanics. The study of plasmon effects (giant resonances) in free atoms and in atoms trapped in different environments is one of the more promising areas for developing and improving theoretical tools to handle many-body systems.

The formation of negative ions by addition of an electron to a neutral atom also goes beyond the convergence capabilities of the Hartree–Fock basis. The polarisation of atomic shells by the extra electron is the mechanism involved. In this situation, a new model has been developed based on the many-body Dyson equation [31] which holds great promise for systematic computations of different negative ion species.

10. Wigner Scattering Theory and the Wigner Time delay

Atoms, of course, involve no new forces as compared to other physical systems and, in line with the economy of principles which should ultimately underpin a general understanding of nature, would be best described within the same, single, conceptual framework as all the other physical systems. The theory which best accomplishes this is the Wigner scattering theory [32,33], because it is extremely general in its formulation. It applies to all branches of physics where quantum scattering occurs and does not even require an explicit solution of the Schrödinger equation, but only postulates the existence of a differential equation of the Schrödinger type, together with the boundary conditions usual in quantum mechanics.

Even in this general context, however, atoms still have a very special role to play, by virtue of the asymptotic inverse square law of force, which allows the external K-matrix to be inverted analytically [21,34,35]. This situation is unique, on a par with Kepler's laws of planetary motion in a central inverse square field of force.

Scattering is, of course, not an instantaneous process because it involves the propagation of a scattered wave. This implies a time delay which, as shown originally by Wigner, is given by the derivative of the phase shift of the scattered wave with respect to energy. In the context of condensed matter or of large molecules or clusters, Wigner time delays are readily measurable by short pulse laser techniques. For individual atoms, this can also be true. A pioneering example is the work of Bourgain et al. [36] on the resonance line of a single trapped Rb atom, for which a time resolution of 256 ps proves adequate. The really interesting situation, however, is for interacting autoionizing resonances [35], where the time scales generally become much shorter (in the attosecond range) so that experimentation has only become feasible recently by ultrashort pulse technology.

11. Atomic Clusters

Traditionally, the transition from the free atom to the solid state has always been imagined by 'piling up' atoms or attempting to model infinite sequences similar to crystals. More recently, it has been shown [37] that this description gives an incomplete picture of the transition from the free atom to the solid. In reality, when atoms are piled together one by one, they first form clusters and several different transition points occur, depending on which physical variable is under study. Thus, the emergence of solid state properties occurs in different ranges as the size of a cluster is increased (e.g., [37–41]) etc.

Again, via the physics of clusters, the properties of atoms are central to a good understanding of condensed matter, achieved by adding them together one by one. Experimentally, the evolution of clusters as a function of size is now accessible by the study of mass-selected clusters. This is particularly interesting in the context of the present article for metallic clusters, because they possess delocalised electrons (precursors of the conduction bands in solids) and form closed electronic shells similar in principle to those of noble gas atoms.

12. Mie and Shape Resonances—Wigner Time Delays

The dynamics of such shells turn into the Mie resonances of classical electrodynamics [42]. In quantum systems with closed shells, they become shape or giant resonances. As such, they involve the collective pulsation of several electrons, i.e., an intrinsic 'many-body' effect which, however, is very short-lived as it is strongly damped. It can be calculated by the many-body perturbation theory (RPAE or MBPT) in non-relativistic or in relativistic versions and can also be modelled by using an effective atomic potential, which must include the influence of the centrifugal barrier, i.e., the angular momentum term in the radial Schrödinger equation. They are due to the shape of this effective potential, hence the name.

The physics of atoms with d and f subshells and the study of metallic clusters with delocalised electrons forming closed shells have revealed for both atoms and metallic clusters, the importance of the collective many-body phenomena or plasmon excitations [43]. By analogy with nuclear physics and in connection with the sum rule for a given atomic shell, they are termed 'giant resonances' when they exhaust most of the available oscillator strength available within a single feature. A peculiar property of these excitations for atoms is that they occur deep inside the system and are able to survive in different phases, from the free atom to clusters, molecules and solids [44], in contrast with other atomic states which are destroyed. This opens up new possibilities for extending and adapting many-body theories within different environments.

Giant resonances, or rather their Fourier transforms, yielding observable Wigner time delays, are also relevant in attosecond spectroscopy. As noted above, this new range of time intervals has recently become accessible to ultrafast laser experiments. A fine example is by Biswas et al. [45]. The observation of photoionization and the corresponding time-resolved atomic spectra provide complementary information which may eventually help to discriminate between the predictions of different models, such as the RPAE, RRPAE and MBPT theories and pseudopotential models.

13. Cooling, etc.

Last but by no means least, an area not covered in the present Comment, because it is a huge subject in its own right and would require a good deal more space, is the theme of atomic cooling and trapping, the Bose–Einstein condensation and all of the effects described by the Gross–Pitaevsky theory of ground-state bosonic fluids [46,47]. A Bose–Einstein condensate is a gas of bosons which are all in the same quantum state, described by a single wavefunction. The Gross–Pitaevsky equation is essentially a transposition of the Hartree–Fock theory to the ground state of a quantum system of identical bosons using a pseudopotential interaction. Both in terms of the general principles involved and the fluids to which they are applied, atomic physics is central also to this extensive area of study.

14. Conclusions

In summary, atomic physics remains a privileged testing ground for the fundamental problems of physics which are so far incompletely resolved, extending from the many-body theory to relativistic mechanics, the nature of ‘empty’ space and the principles of quantum field theory, as well as the full connection between quantum mechanics and classical physics, also including thermodynamics. Thus, the atom, as a system, remains very much at the heart of contemporary research in physics and chemistry.

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References

1. Feynman, R.P. *The Feynman Lectures on Physics*; Feynman, R., Robert, B., Eds.; Leighton and Matthew Sands; Addison Wesley: New York, NY, USA, 1964; Volume 3.
2. Salam, A. The role of Chirality in the Origin of Life. *J. Mod. Evol.* **1991**, *33*, 105. [CrossRef]
3. Series, G.W. *The Spectrum of Atomic Hydrogen*; World Scientific Publishing Co.: Singapore, 1988.
4. Briggs, J.S.; Rost, J. Time dependence in quantum mechanics. *Eur. Phys. J. D* **2000**, *10*, 311. [CrossRef]
5. Dirac, P.A.M. *The Principles of Quantum Mechanics*; Oxford University Press: Oxford, UK, 1930.
6. Furry, W.H. Bound States and Scattering in Positron Theory. *Phys. Rev.* **1951**, *81*, 115. [CrossRef]
7. Poincaré. *Sur le Problème des Trois Corps*; Bulletin astronomique, Observatoire de Paris Année; Paris Observatory Bulletin: Paris, France, 1891; pp. 12–24.
8. Lagrange, J.-L. Oeuvres de Lagrange sur GDZ (Göttingen). 1772. Available online: http://gdz.sub.uni-goettingen.de/dms/load/toc/?PID=PPN308899466 (accessed on 30 January 2023).
9. Salam, A. Gauge Unification of Fundamental Forces. *Rev. Mod. Phys.* **1980**, *52*, 525. [CrossRef]
10. Landau and Lifshitz. *Physics Textbooks Series: Classical Mechanics*, 3rd ed.; Vol. 3—Landau, Lifshitz—Identifier landau-and-lifshitz-physics-textbooks-series; Identifier-ark ark:/13960/t7sn92122; Pergammon Press: Oxford, UK, 1976.
11. Landau and Lifshitz. *Physics Textbooks Series: Quantum Mechanics—Non-Relativistic Theory*, 3rd ed.; Vol 4—Landau, Lifshitz Identifier landau-and-lifshitz-physics-textbooks-series; Identifier-ark ark:/13960/t7sn92122; Pergammon Press: Oxford, UK, 1991.
12. Garton, W.R.S.; Tomkins, F.S. Diamagnetic Zeeman effect and magnetic configuration mixing in long spectral series of Ba I. *Astrophys. J.* **1969**, *158*, 839. [CrossRef]
13. Pascal, B. *Les Pensées de M. Pascal sur la Religion et Sur Quelques Autres Sujets, Qui ont été Trouvées Après sa Mort parmy Ses Papiers*; Port-Royal des Champs: Paris, France, 1670.
14. Thomas, L.H. The Calculation of Atomic Fields. *Math. Proc. Camb. Philos. Soc.* **1927**, *23*, 542–548. [CrossRef]
15. Fermi, E. Eine statistische Methode zur Bestimmung einiger Eigenschaften des Atoms und ihre Anwendung auf die Theorie des periodischen Systems der Elemente. *Z. Phys.* **1928**, *48*, 73–79. [CrossRef]
16. Hellmann, H. *Einführung in die Quantenchemie*; Franz Deuticke: Leipzig, Germany, 1937; p. 285.
17. Feynman, R.P. Forces in Molecules. *Phys. Rev.* **1939**, *56*, 340–343. [CrossRef]
18. Feynman, R.P.; Metropolis, N.; Teller, E. Equations of State of Elements Based on the Generalized Fermi-Thomas. *Theory Phys. Rev.* **1949**, *75*, 1561.
19. Jaskólski, W. Confined many-electron systems. *Phys. Rep.* **1996**, *27*, 1–56. [CrossRef]
20. Connerade, J.-P. Confining and compressing the atom. *Eur. Phys. J. D* **2020**, *74*, 211. [CrossRef]
21. Connerade, J.-P. *Highly Excited Atoms*; Cambridge University Press: Cambridge, UK, 1998; ISBN 9780511524.
22. Rahm, M.; Cammi, R.; Ashcroft, N.W.; Hoffmann, R. Squeezing All Elements in the Periodic Table: Electron Configuration and Electronegativity of the Atoms under Compression. *J. Am. Chem. Soc.* **2019**, *141*, 10253. [CrossRef] [PubMed]
23. Madjet, M.E.A.; Ali, E.; Carignano, M.; Vendrell, O.; Chakraborty, H.S. Ultrafast Transfer and Transient Entrapment of Photoexcited Mg Electron in Mg@C_{60}. *Phys. Rev. Lett.* **2021**, *126*, 183002. [CrossRef]
24. Dolmatov, V.K.; Baltenkov, A.S.; Connerade, J.-P.; Manson, S.T. Structure and photoionization of confined atoms. *Radiat. Phys. Chem.* **2004**, *70*, 417–433. [CrossRef]
25. Connerade, J.-P.; Dolmatov, V.K.; Manson, S.T. On the nature and origin of confinement resonances. *J. Phys. B At. Mol. Opt. Phys.* **2000**, *33*, 2279. [CrossRef]
26. Froese–Fischer, C. *The Hartree–Fock Method for Atoms, a Numerical Approach*; Wiley: New York, NY, USA, 1977.
27. Grant, I.P.; Quiney, H.M. Application of relativistic theories and quantum electrodynamics to chemical problems. *Int. J. Quantum. Chem.* **2000**, *80*, 283–297. [CrossRef]
28. Brown, G.E.; Ravenhall, D.G. On the Interaction of Two Electrons. *Proc. R. Soc. London* **1951**, *A208*, 552.
29. Kelly, H.P. Many-Body Perturbation Theory Applied to Atoms. *Phys. Rev.* **1964**, *136*, B896. [CrossRef]
30. Amus’ya, M.Y.; Amus’ya, N.A.; Cherepkov, L.V. Chernysheva. *Zh. Eksp. Teor. Phys.* **1961**, *60*, 160.
31. Chernysheva, L.V.; Gribakin, G.F.; Ivanov, V.K.; Kuchiev, M.I. Many-body calculation of negative ions using the Dyson equation. *J. Phys. B At. Mol. Opt. Phys.* **1988**, *21*, L419–L425. [CrossRef]
32. Wigner, E.P.; Eisenbud, L. Higher Angular Momenta and Long Range Interaction in Resonance Reactions. *Phys. Rev.* **1947**, *72*, 29. [CrossRef]

33. Wigner, E.P. Lower Limit for the Energy Derivative of the Scattering Phase Shift. *Phys. Rev.* **1955**, *98*, 145. [CrossRef]
34. Lane, A.M. The application of Wigner's R-matrix theory to atomic physics. *J. Phys. B At. Mol. Phys.* **1986**, *19*, 253. [CrossRef]
35. Connerade, J.-P. Wigner scattering theory for systems held together by Coulombic forces. *Eur. Phys. J. D* **2020**, *74*, 107. [CrossRef]
36. Bourgain, R.; Pellegrino, J.; Jennewein, S.; Sortais, Y.R.P.; Browaeys, A. Direct measurement of the Wigner time-delay for the scattering of light by a single atom. *Opt. Lett.* **2013**, *38*, 1963–1965. [CrossRef]
37. Cohen Marvin, L.; Knight Walter, D. The Physics of Metal Clusters. *Phys. Today* **1990**, *43*, 42. [CrossRef]
38. Bréchignac, C.; Broyer, M.; Cahuzac, P.; Delacretaz, G.; Labastie, P.; Wolf, J.P.; Wöste, L. Probing the transition from van der Waals to metallic mercury clusters. *Phys. Rev. Lett.* **1988**, *60*, 275. [CrossRef]
39. Lyalin, A.; Solov'yov, I.A.; Solov'yov, A.V.; Greiner, W. Strontium clusters: Electronic and geometry shell effects. In *Latest Advances in Atomic Cluster Collisions: Structure and Dynamics from the Nuclear to the Biological Scale*; Solov'yov, A.V., Ed.; Imperial College Press: London, UK, 2008; pp. 105–127.
40. March, N.H.; Angiella, G.G.N. *Exactly Solvable Models in Many-Body Theory*; World Scientific Press: London, UK; Singapore, 2016.
41. Forte, G.; Grassi, A.; Lombardo, G.M.; Pucci, R.; Angilella, G.G.N. From Molecules and Clusters of Atoms to Solid State Properties. In *Many-Body Approaches at Different Scales*; Angilella, G., Amovilli, C., Eds.; Springer: Cham, Switzerland, 2018. [CrossRef]
42. Mie, G. Beiträge zur Optik trüber Medien speziell kolloidaler Goldlösungen (contributions to the optics of diffuse media, especially colloid metal solutions). *Ann. Phys.* **1908**, *25*, 377. [CrossRef]
43. de Heer, W.A.; Selby, K.; Kresin, V.; Masui, J.; Vollmer, M.; Chatelain, A.; Knight, W.D. Collective dipole oscillations in small sodium clusters. *Phys. Rev. Lett.* **1987**, *59*, 1805. [CrossRef]
44. Connerade, J.-P.; Esteva, J.-M.; Karnatak, R.C. (Eds.) *Giant Resonances in Atoms, Molecules, and Solids*; NATO Advanced Study Institute Plenum Press: New York, NY, USA, 1987.
45. Biswas, S.; Trabattoni, A.; Rupp, P.; Magrakvelidze, M.; Madjet ME, A.; De Giovannini, U.; Castrovilli, M.C.; Galli, M.; Liu, Q.; Månsson, E.P.; et al. Attosecond correlated electron dynamics at C_{60} giant plasmon resonance. *At. Phys.* **2022**, arXiv:2111.14464.
46. Gross, E.P. Structure of a quantized vortex in boson systems. *Il Nuovo Cimento* **1961**, *20*, 454–457. [CrossRef]
47. Pitaevskii, L.P. Vortex lines in an imperfect Bose gas. *Sov. Phys. JETP* **1961**, *13*, 451–454.