Electronic Shells and Supershells in Metal Clusters.

S. BJØRNHOLM, J. BORGGREEN, K. HANSEN and J. PEDERSEN

The Niels Bohr Institute, University of Copenhagen
Blegdamsvej 17, DK-2100, Copenhagen Ø, Denmark

As constituents of all matter, nuclei are fundamental to physics in general; and the strong force assuring nuclear cohesion is also fundamental. The next level in the description of matter is, on the other hand, completely dominated by electrons interacting with each other and with the inert nuclei through electromagnetic forces. It is, therefore, no wonder that nuclear physics and condensed-matter physics have established themselves as separate disciplines within physics. But separation is not equivalent to isolation. The various fields of physics are after all resting on a common base, with numerous methods and concepts being shared by them all. One theme common to several subfields concerns the many-body properties of fermion systems. In this lecture we describe an example where there is a strong conceptual overlap in the physics of seemingly quite different systems.

1. – Metal clusters.

Conduction electrons move freely and independently inside a metal, but they are confined by the surface. Their freedom is also restricted by the well-known phenomenon of ohmic resistance. At ambient temperatures this limits their mean free path to some hundred ångstrøm. For metallic droplets that are smaller than this it should be possible to describe the electrons to a rather good approximation as a system of independent fermions moving in a common mean field, in close analogy to the mean-field description of nucleonic motion in the nucleus. The dimensions and the energy scale in metal drops are, of course, quite different, and the cohesive forces have a completely different origin. Thus the analogue to the strong nuclear spin-orbit force is negligible, for example. Nevertheless it seems obvious that there ought to be many and interesting analogies between nuclei and small drops of metal, or clusters as they are

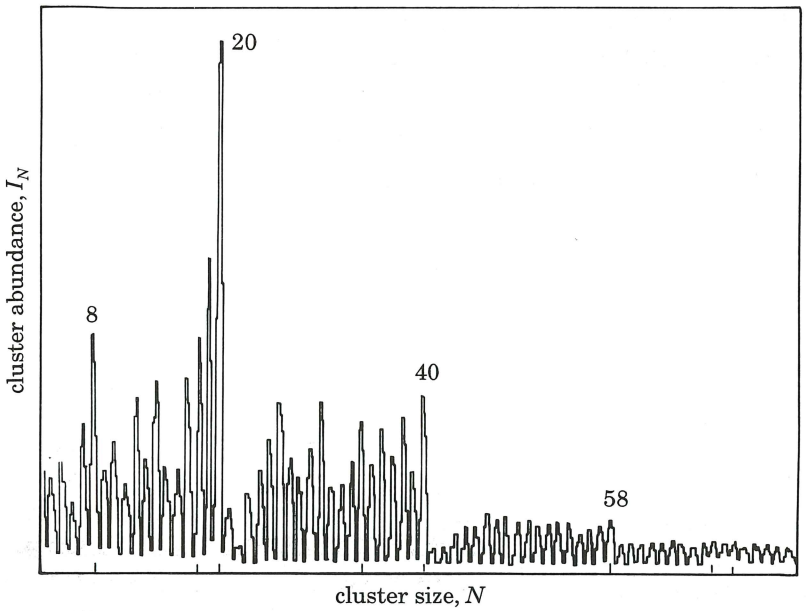

Fig. 1. – Distribution of sodium droplets according to numbers of sodium atoms per droplet, produced by expanding hot sodium vapour through a fine nozzle [1].

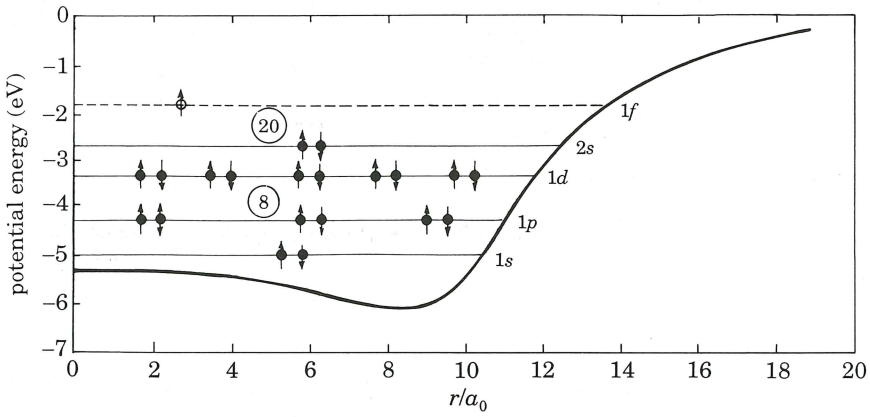

Fig. 2. – Ekardt's self-consistent electron potential [2], calculated for a spherical sodium cluster with twenty atoms. The calculated single-electron energy levels are also shown. Filled circles indicate electrons occupying the lowest levels; the open circle shows where the 21st electron would have to go.

called. Strangely enough, it was not until 1984 that this analogy became apparent, through the experimental discovery of shell structure and magic numbers in abundance spectra of sodium clusters by W. D. KNIGHT and his group at U.C. Berkeley [1], and through parallel theoretical work by W. EKARDT [2] at the

Fritz Haber Institute in Berlin (see fig. 1 and 2). Since then nuclear physics has been providing input to the understanding of metal clusters. The nuclear shell model and the Nilsson model of independent-particle motion in spherical and nonspherical potentials, the dichotomy between single-particle and collective motion, odd-even effects, fission ... all find their counterparts in the measured properties of clusters of simple metals [3].

2. – The Balian-Bloch effect.

Recently a group of nuclear physicists at the Niels Bohr Institute established a small laboratory for the study of metal clusters. The first problem engaged by the group relates to the nuclear physicists' quest for superheavy elements. One of the motivations for this quest is to demonstrate that nuclear shell structure has been understood well enough to make reliable predictions for systems with very large mass numbers. The most far-reaching extrapolation of that kind is due to BALIAN and BLOCH [4]. While inspired by the nuclear shell model, they formulate a theory that goes far beyond realistically reachable nuclear sizes. Instead, they illuminate what may happen in the correspondence limit when shell model quantum numbers become very large. BALIAN and BLOCH show that the eigenvalue spectrum of independent fermions, moving in a spherical potential with infinite walls, will exhibit shell structure with magic numbers proportional to the cube root of the number of constituents, N. Moreover, they predict that about ten consecutive shells will group together into a supershell, which is separated from adjacent supershells by a minimum in the amplitude of the shell effect—like a beat mode. The theory [4] relates the quantum shell structure to the system of closed orbits available to a classical particle moving in the same potential. It describes the density of quantum energy eigenvalues of independent fermions in terms of an infinite series of contributions from the classical orbits with characteristic phases and amplitudes. Since the potential is flat inside, the orbits will be polygons. The line of arguments represents a generalization of Bohr's original model of the hydrogen atom and its eigenvalue spectrum. In the hydrogen problem, all bound orbits are Kepler ellipses, and it is possible to establish a one-to-one correspondence between classical ellipses and the quantum eigenstates. The situation in a spherical cavity is more complex. There are many classical orbits. Some never close in themselves; and those that do will have different shapes, *i.e.* pendulating orbits, triangles, squares, pentagons, ... starlike figures, etc. From the semi-classical description it is possible to see that the quantum beat mode comes about as a result of interference between classical triangular and square orbits, since these emerge as the dominant and at the same time equally important contributors to the quantum shell structure [4, 5] for large systems.

In a recent theoretical study [5], the theory of Balian and Bloch was extend-

ed and applied to idealized spherical sodium droplets with the somewhat diffuse potential walls of a Woods-Saxon potential. Again a quantum beat is found in the shell structure with a pronounced minimum predicted around size $N = 1000$. Also, the semi-classical results are compared to and found to agree quite closely with the eigenvalue spectrum obtained by solving the stationary Schrödinger equation for independent electrons in the same Woods-Saxon potential.

In the following we shall show how sodium droplets prove to be realistic model systems for the study of these so far hypothetical quantum effects.

3. – Experiments with sodium droplets.

In preliminary experiments it was shown that the spherical-mean-field assumption used in the shell structure calculations is valid for sodium clusters extending in size beyond 600 [6, 7]. Magic numbers are seen as steps in the measured abundances of sodium droplets of various sizes in analogy to the results shown in fig. 1.

Our more recent experiments are also based on measurements of the size distribution of metal droplets produced in our machine by expansion of metal vapour through a fine nozzle. The sodium vapour is generated in a stainless-steel vessel held at (700 ÷ 800) °C and the expansion is assisted by pressurizing

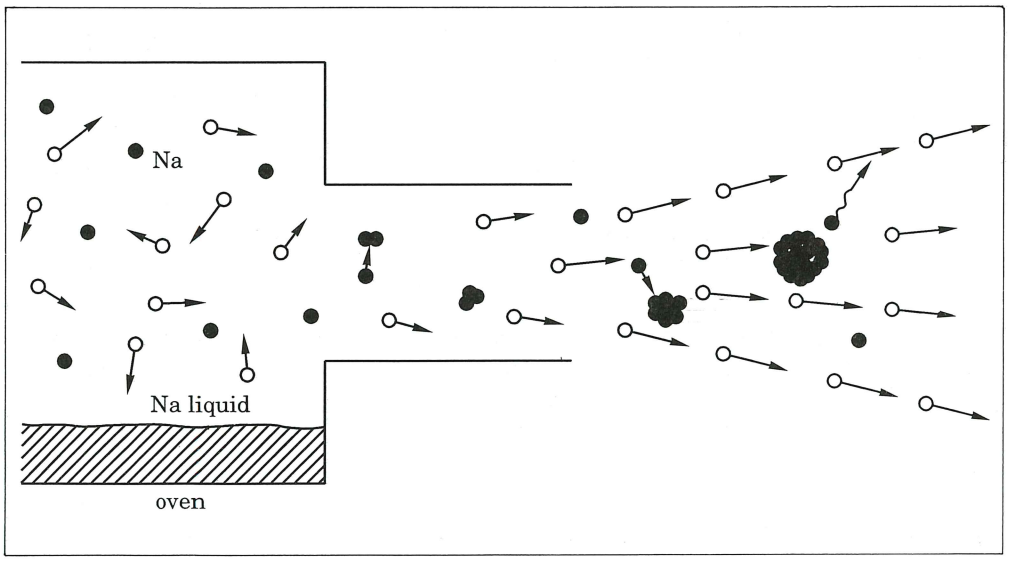

Fig. 3. – Production of sodium clusters. In the expansion of an inert gas through a small nozzle, random thermal motion is converted to uniform translational motion, resulting in strong cooling of the inert gas. Introducing atomic sodium vapour into this medium, the sodium atoms aggregate into clusters with a broad, uniform size distribution.

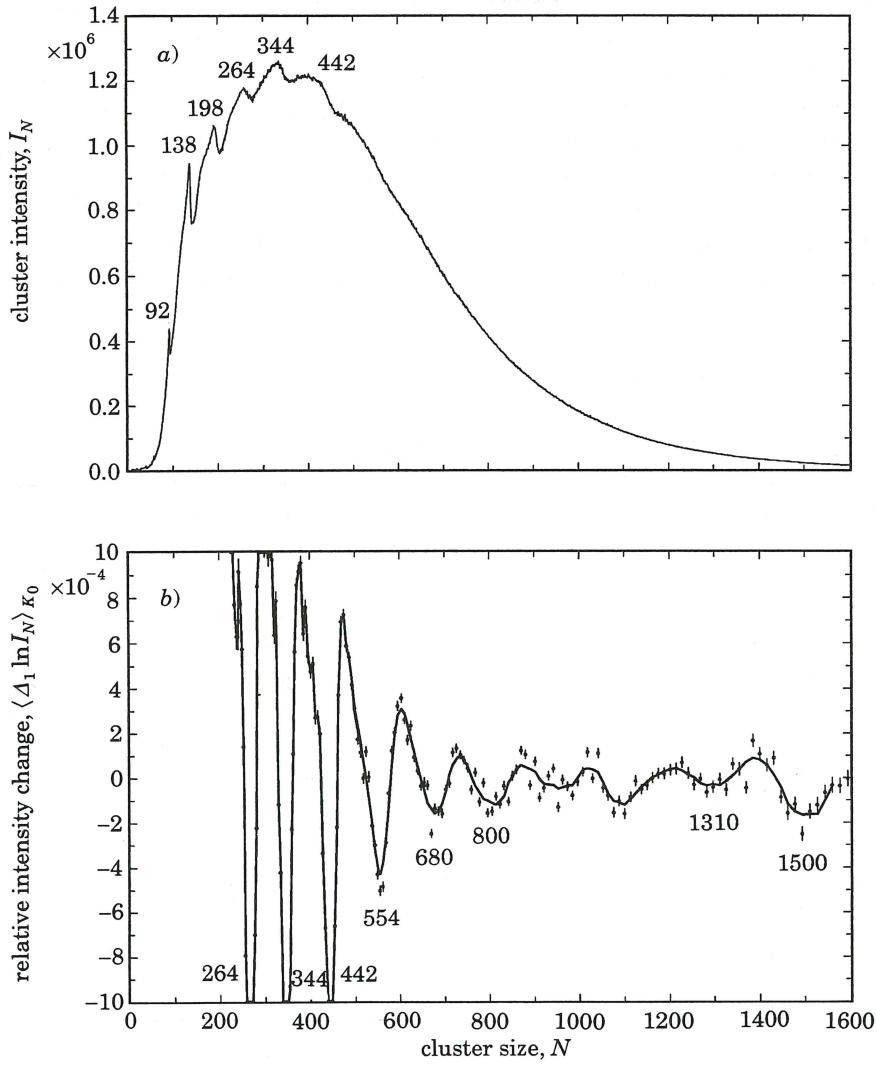

Fig. 4. – Mass spectrum and its logarithmic derivative [8]. Top panel: Example of an abundance distribution for sodium clusters produced by adiabatic expansion with xenon gas and measured after a one-metre free flight by time-of-flight mass spectrometry. Bottom panel: Logarithmic derivative $\langle \Delta_1 \ln I_N \rangle_{K_0}$ of the results in top panel, averaged over size intervals $K_0 = \pm 0.03 N$.

the vessel with a large surplus of argon or xenon gas (see fig. 3). The mixture is expanded into a three-metre long, differentially pumped flight tube, resulting in a narrow beam of free-flying metal clusters [6]. In the expansion and clustering process, lasting about 100 ns, the noble-gas medium cools to a few tens of kelvin [9]. In the sodium clusters, on the other hand, there will be a competition

between heating, due to condensation, and cooling, due to collisions. We believe that the resulting internal temperature in the freshly formed clusters is just some (100 ÷ 200) °C below the oven temperature, *i.e.* (500 ÷ 600) °C. In the ensuing free flight for about one millisecond the droplets will loose sodium atoms by stepwise evaporation, cooling to about (100 ÷ 200) °C. The evaporation process is sensitive to shell-like variations in the atomic separation energies, which in turn reflect variations in the electronic separation energies (cf. fig. 2), because the removal of an atom involves removal of the least bound electron. These variations are thought to be responsible for the steplike modifications of the experimentally observed size distributions [10].

One metre downstream the size distribution is sampled by time-of-flight mass spectrometry [6]. Figure 4, upper part, shows an example of an abundance distribution I_N *vs.* N obtained in this way. For sizes up to $N = 300$ the global bell-shaped abundance distribution is clearly scarred with saw-tooth or s-shaped irregularities at certain «magic» sizes. Since the interest focusses on these, it is convenient to display the experimental result in terms of relative intensity changes, *i.e.*

$$\Delta_1 \ln I_N = \ln (I_{N+1}/I_N) \approx 2 \frac{I_{N+1} - I_N}{I_{N+1} + I_N} . \tag{1}$$

This makes the magic numbers stand out very clearly as dips [6]. These become smaller and broader with increasing magic number, N_0. As one sees from fig. 4*a*), the steps signalling shell closures become very small. They will tend to drown in noise due to finite counting statistics for the higher N-values. In this situation we have found it useful to generalize eq. (1). This is achieved by computing a weighted logarithmic derivative $\langle \Delta_1 \ln I_N \rangle_{K_0}$ for suitably chosen size intervals $2K_0 + 1$ and properly spaced mass points N. In this way it becomes realistic to scale up the measured derivatives in order to display very small irregularities in the intensity pattern. Figure 4*b*) shows the result.

As one sees from this figure, there are indeed shell oscillations all the way up to droplets with 1500 atoms (and 1500 conduction electrons). On the other hand, there is not much indication of a beat mode as expected from theory [5]. Instead one notices a general and quite strong decrease in the shell amplitude.

This decrease is partly due to a reduction in the magnitude of the shell spacings $\hbar\omega_{\text{shell}}$ with increasing size. Another, more important, reason is temperature [10-12]. It tends to wash out the observable shell structure exponentially [11] as a function of the effective temperature parameter τ,

$$\tau = k_B T \frac{2\pi^2}{\hbar\omega_{\text{shell}}} , \tag{2}$$

with

$$\hbar\omega_{\text{shell}} \approx 2\varepsilon_F/n \sim N^{-1/3} . \tag{3}$$

Here k_B is Boltzmann's constant, T is the real temperature at the time of sampling the abundance distributions, estimated [13] to be $(400 \div 500)$ K, n is the shell number, while $\varepsilon_F = 3.24$ eV is the Fermi energy for electrons in sodium metal.

4. – The quantum beat.

In order to compensate for these effects, we scale the logarithmic derivatives, $\langle \Delta_1 \ln I_N \rangle_{K_0}$, with the factor $N^{1/2} \exp[cN^{1/3}]$, setting $c = 0.65$. The results are presented in fig. 5, where they are plotted as a function of the linear dimensions of the clusters, $\sim N^{1/3}$. One sees first of all that the shell dips are equidistantly spaced. In addition, the amplitudes of the dips vary systematically. Since the scaling function is monotonously increasing, it is unlikely to be responsible for the large-scale modulations seen in fig. 5. They indeed have the character of a beat mode with a minimum near $N = 1000$ as predicted by semi-classical theory [4, 5].

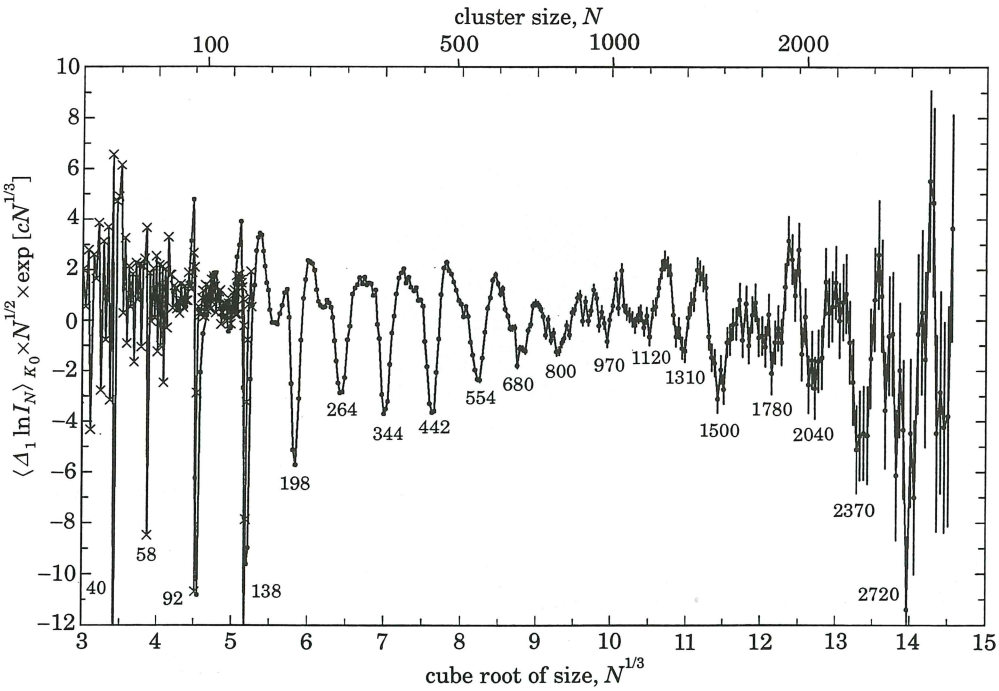

Fig. 5. – The quantum beat. Relative changes $\langle \Delta_1 \ln I_N \rangle_{K_0}$ in experimental cluster abundance I_N, corrected for the effect of temperature and size [8].

The length of the shell periods, $(0.61 \pm 0.01)\ \Delta N^{1/3}$, invites an interpretation in terms of triangular and square orbits [6]. Electrons moving classically in triangular and square orbits will have integer action values, $pL = nh$ for sizes N_s spaced at intervals $\Delta N_s^{1/3} = 0.61$, provided they have a momentum p equal to the Fermi momentum in sodium metal, *i.e.* to the momentum of the least bound particles. This follows from the expression for the Fermi momentum in terms of the Wigner-Seitz radius [14] (*i.e.* density parameter relating the radius to the

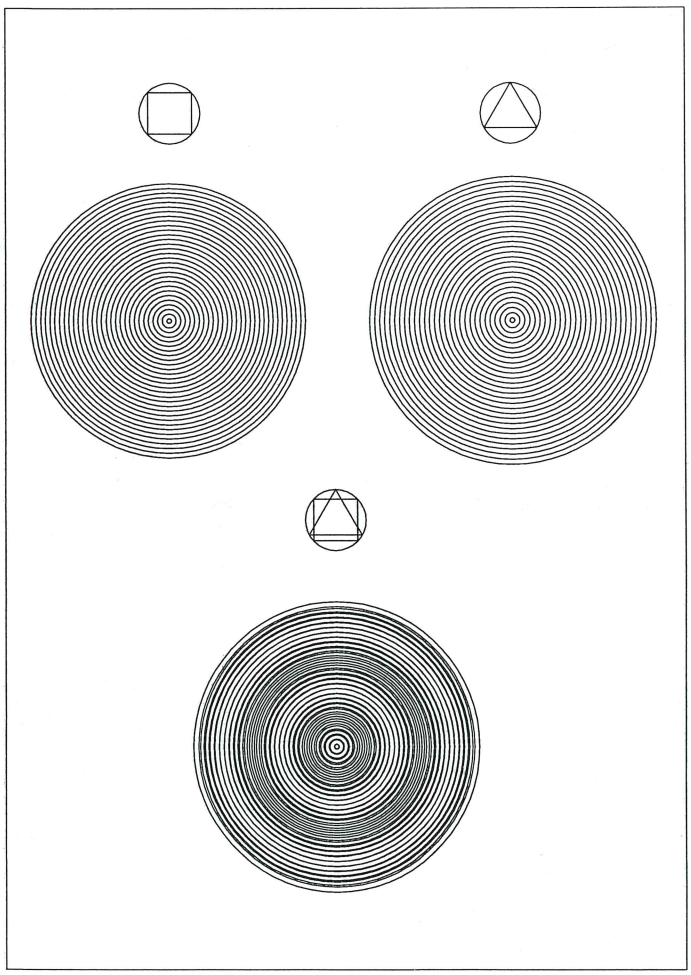

Fig. 6. – Beating between competing radii (Balian-Bloch effect). An electron moving classically and with constant momentum inside a spherical droplet in a triangular orbit will have integer action values, $pL = nh$, for definite discrete values of the radius R, upper right-hand figure. For square orbits there will be another set of radii, where the electron fulfils Bohr's quantization condition, upper left-hand figure. Drop sizes where both conditions are fulfilled simultaneously will exhibit constructive interference as shown below.

size, *viz.* $R = r_{WS} N^{1/3}$) and the expression for the length of the two orbits, $3\sqrt{3}R$ and $4\sqrt{4}R$, respectively. For other sizes, the momentum and energy of the least bound particles will have to be somewhat larger or a bit smaller in order to fulfil Bohr's quantization condition above. This is one way of picturing the shell oscillations. (In order to arrive at a consistent picture one will have to show, in addition, that the shell degeneracies are proportional to $N^{2/3}$.) The beat mode comes about because the lengths L of triangular and square orbits differ slightly. Figure 6 illustrates how.

Summarizing, our simple and quite crude experiment [8] shows that small sodium droplets grow in a steplike fashion. Whenever the linear size increases by a definite amount, there is a recurrence of a particularly stable (closed-shell) configuration. The beat pattern tells us that there are actually two preferred sets of radii (fig. 6). One of these can be brought into correspondence with classical integer-action orbits of triangular shape and Fermi momentum, the other with square orbits. Although this has some similarity to the way BOHR arrived at a discrete hydrogen spectrum in 1913 by quantizing individual Kepler ellipses, it really represents a much more advanced case. None of the individual eigenstates in the sodium droplets can be associated with a triangle, nor with a square. The role of these two classical orbits is to exert a dominating influence on the function describing the density of the numerous individual eigenstates—as a function of energy—, or alternatively the density of eigenstates at the Fermi energy as a function of size N. In this sense, sodium clusters are definitely more interesting than the hydrogen atom.

The experiments were performed with clusters having finite temperatures, while the theories quoted [4, 5] apply to zero temperature. As a result, the observable effects are attenuated hundreds of times compared to the zero-temperature predictions. The survival of measurable effects connected with the interference between triangular and square orbits in the presence of overwhelming thermal noise is not the least surprising insight emerging from our study.

5. – Other examples.

In the discussion above we have introduced the effective temperature τ, eq. (2), in order to arrive at the particular form of the scaling function used in the preparation of fig. 5. This is again a loan from nuclear physics [11], where the problem of attenuation of shell effects with increasing excitation energy is a familiar issue. In nuclei, the heat bath allowing one to speak of a temperature is the nucleonic fermion system itself. In a metal cluster, the positive ions in the molten droplet absorb all but a tiny fraction of the excitation energy, forming a classical heat bath with a well-defined temperature in which the electrons move. This offers very favourable conditions for studying the effect of temperature on shell structure. The exploitation of the opportunities offered by this

new situation is in progress, in particular based on the theoretical work of Brack *et al.* [12, 15].

In its simplest form, shell structure is described in terms of the motion of perfectly independent particles in a common potential. Every nuclear spectroscopist knows that for nuclei this is an idealization that holds at best for the first few single-particle excitations around the Fermi energy. In atomic spectroscopy the approximation is more nearly valid, allowing for the observation of relatively sharp K X-rays for all Z-values. The situation in metal clusters can be studied by photoelectron spectroscopy, using lasers [16, 17]. It appears to be intermerdiate between the nuclear and the atomic case, but much work remains to be done.

Light will also excite collective excitations of the electron system in metal clusters. So far, considerable work has been done with the so-called surface plasmon excitation, which is analogous to the giant-dipole mode in nuclei. In sodium clusters it is excited by visible light as a rather broad resonance. There are indications of a splitting of the resonance into two or even three peaks for nonmagic clusters, reflecting a deviation from spherical symmetry analogous to nuclear deformations [18-20]. On the other hand, the resonance frequency is virtually independent of cluster size, whereas in nuclei it decreases as one divided by R, the radius. This reflects a fundamental difference between the two media. The nucleus is a quantum liquid, whereas the metallic medium is more like a plasma with quantized negative charges and classical positive charges [21].

At practically occurring temperatures no pair correlations are expected in simple metal clusters. Nevertheless one observes clear odd-even effects in the abundance spectra and in threshold photoionization experiments. These effects may be important clues for characterizing the effective electron-electron interactions in the medium [22].

6. – Clusters, a bridge to condensed-matter physics.

The view taken so far in this lecture is that metal clusters represent an interesting new playfield for nuclear physicists, where they can extend the application of their ideas and probe the validity of nuclear many-body theory in a wider context. Nuclear physicists are always very interested in the evolution of nuclear properties as a function of the number of nuclear constituents. However, this is just one way of looking at the situation. At the other extreme, the nucleus can be seen as just one particular example of an aggregate of like constituents. Aggregates of electrons and positive ions (as in simple metals), or of carbon atoms, or helium atoms, or positive and negative ions (as in rock salt) are other examples. Any macroscopic substance can be viewed as the end product from a condensation process, where the elementary constituents are added one by one. In this sense, clusters in general represent condensed matter in embry-

onic form [21]. One studies them [23] for the same reason biologists study the embryonic development of different species.

Embryology is an old and well-established discipline, which forms an effective bridge from the biology of the individual cell to the description of the highly differentiated multicellular organisms. Cluster physics and chemistry are, on the other hand, very new disciplines. At present there is quite a gap between the rather simple problems of cluster physics and chemistry presented in this volume and the highly sophisticated discussions of fine-tuned many-body correlations, which is also presented in this volume by those who study specially selected macroscopic samples. But cluster studies are advancing rapidly. It will be interesting to see how and when an effective bridge between these two worlds, the microscopic and the macroscopic world, will take concrete form.

REFERENCES

[1] W. D. KNIGHT, K. CLEMENGER, W. A. DE HEER, W. A. SAUNDERS, M. Y. CHOU and M. L. COHEN: *Phys. Rev. Lett.*, **52**, 2141 (1984).
[2] W. EKARDT: *Phys. Rev. B*, **29**, 1558 (1984).
[3] T. P. MARTIN: this volume, p. 139.
[4] R. BALIAN and C. BLOCH: *Ann. Phys. (N.Y.)*, **69**, 76 (1972).
[5] H. NISHIOKA, K. HANSEN and B. R. MOTTELSON: *Phys. Rev. B*, **42**, 9377 (1990).
[6] S. BJØRNHOLM, J. BORGGREEN, O. ECHT, K. HANSEN, J. PEDERSEN and H. D. RASMUSSEN: *Phys. Rev. Lett.*, **65**, 1627 (1990).
[7] T. P. MARTIN, S. BJØRNHOLM, J. BORGGREEN, C. BRÉCHIGNAC, P. CAHUZAC, K. HANSEN and J. PEDERSEN: *Chem. Phys. Lett.*, **186**, 53 (1991).
[8] J. PEDERSEN, S. BJØRNHOLM, J. BORGGREEN, K. HANSEN, T. P. MARTIN and H. D. RASMUSSEN: *Nature (London)*, **353**, 733 (1991).
[9] W. A. DE HEER, W. D. KNIGHT, M. Y. CHOU and M. L. COHEN: *Solid State Phys.*, **40**, 93 (1987).
[10] S. BJØRNHOLM, J. BORGGREEN, O. ECHT, K. HANSEN, J. PEDERSEN and H. D. RASMUSSEN: *Z. Phys. D*, **19**, 47 (1991).
[11] A. BOHR and B. R. MOTTELSON: *Nuclear Structure*, Vol. II (Benjamin, London, 1975), p. 607.
[12] M. BRACK, O. GENZKEN and K. HANSEN: *Z. Phys. D*, **19**, 51 (1991).
[13] C. BRÉCHIGNAC, PH. CAHUZAC, J. LEYGNIER and J. WEINER: *J. Chem. Phys.*, **90**, 1492 (1989).
[14] N. W. ASHCROFT and N. D. MERMIN: *Solid State Physics* (Saunders College, Philadelphia, Penn., 1976).
[15] M. BRACK, O. GENZKEN and K. HANSEN: *Z. Phys. D*, **21**, 65 (1991).
[16] T. BERGMANN and T. P. MARTIN: *J. Chem. Phys.*, **90**, 2848 (1989).
[17] K. J. TAYLOR, C. L. PETTIETTE, M. J. CRAYCRAFT, O. CHESHNOVSKY and R. E. SMALLEY: *Chem. Phys. Lett.*, **152**, 347 (1988).
[18] K. SELBY, V. KRESIN, J. MASUI, M. VOLLMER, W. A. DE HEER, A. SCHEIDMANN and W. D. KNIGHT: *Phys. Rev. B*, **43**, 4565 (1991).

[19] C. YANNOULEAS, J. M. PACHECO and R. A. BROGLIA: *Phys. Rev. B*, **41**, 6088 (1990).
[20] J. PEDERSEN, J. BORGGREEN, P. CHOWDHURY, N. KEBAILI, L. LUNDSBERG-NIELSEN, M. B. NIELSEN and H. D. RASMUSSEN: in *Proceedings of the Sixth International Meeting on Small Particles and Inorganic Clusters* (*Chicago, Ill., 1992*), edited by R. S. BERRY, J. BURDETT and A. W. CASTLEMAN: *Z. Phys. D*, **26**, 281 (1993).
[21] S. BJØRNHOLM: *Contemp. Phys.*, **31**, 309 (1990).
[22] B. R. MOTTELSON: private communication.
[23] *Proceedings of the Fifth International Meeting on Small Particles and Inorganic Clusters* (*Konstanz 1990*), edited by O. ECHT and E. RECHNAGEL, *Z. Phys. D*, **19** and **20** (1991); and the volume ref. [20] with its supplement.