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To the Memory of Vilen M. Strutinsky

SHELLS, SHAPES AND CLASSICAL ORBITS IN METALLIC CLUSTERS

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Abstract

We give a short overview of the physics of metallic clusters and the role of electronic shell effects which lead to properties that are similar in many respects as those observed in atomic nuclei. We emphasize in particular those aspects which can be described using methods introduced and developed by the late Vilen M. Strutinsky.

Almost 26 years ago I had the chance to go to Copenhagen where I joined the research group of V. M. Strutinsky at the Niels Bohr Institute. There I met for the first time this remarkable man with his dark eyeglasses and eyebrows, but with warm and humorous eyes underneath, speaking fast and at a low voice, always ready for a good joke. He introduced me to the rich and fascinating world of nuclear shapes and shell structure. There is no need here to present Strutinsky's shell-correction method [1] and its application to nuclear fission. But it is always good to recall the excitement we had in those years 1968 – 1970, when the double-humped fission barriers were constantly being measured [2], calculated [3] and discussed during the weekly Monday morning group meetings at Blegdamsvej. Let me take the occasion here to express my deep gratitude to Vilen Mitrafanovich Strutinsky for having educated and trained me in this interesting field of physics.

Today I shall also speak of shells and shapes and of their relations to classical orbits – a subject to which Strutinsky and his collaborators in Kiev have made important contributions [4, 5] – but in a different and relatively new domain of physics: that of metallic clusters. Ten years ago, Knight, de Heer and collaborators at Berkeley discovered the enhanced stability of alkali metal clusters with the 'magic numbers' of valence electrons N=2,8,20,40,58,... [6]. Since then, a lot of experimental evidence has been gained for the decisive role of electronic shell effects in determining the shapes and the stability of alkali

(and some other simple metal) clusters. (For a recent experimental review, see de Heer [7].) The valence electrons in these systems are strongly delocalized, and it appears that for many observables in metal clusters, they are the most important degrees of freedom and can be treated, to a very good lowest-order approximation, in a selfconsistent mean field theory (see Ref. [8] for a recent theoretical review on simple metal clusters).

For a quantitative description, in particular of small microclusters at low temperatures up to sizes with ~ 20 atoms, the geometric structure of the atoms (or ions) does play a role and can be treated with quantum-chemical *ab initio* methods (see Bonačić-Koutecký *et al.* [9] for a recent review) or by molecular dynamics simulations [10]. But for not too small clusters at room temperature and above, the electronic shell effects dominate and can explain the observed magic numbers. These do not only appear in the mass yields which are determined by the overall binding energy, but also in the ionization potentials and electron affinities which exhibit a saw-tooth behaviour similar to the neutron and proton separation energies in nuclei. Another feature which reminds of nuclear physics is the appearance of a strong resonance in the photoabsorption cross section of metal clusters (see Refs. [7, 11, 12] and the literature quoted therein). It is dominated by a strongly collective dipole oscillation of the valence electrons against the ions, analogous to the nuclear giant dipole resonance between neutrons and protons, and known in the limit of a macroscopic metal sphere as the 'Mie plasmon' [13].

Thus, the simple but surprisingly relevant picture of a metal cluster we have in mind is that of the quasi-free valence electrons moving in a mean field which is constituted by balance between the attractive potentials of the ionic cores and the mutual Coulomb repulsion between the electrons themselves. Due to the finiteness of the clusters, the electronic orbits have quantized energy levels which are typically grouped into bunches or shells, and the Pauli principle plays its usual role of giving the electrons only a limited access to each shell. In other words: metal clusters provide a new and interesting periodic system [14]. In contrast to the atomic and nuclear periodic systems, there is no limit to the size of metal clusters: they are bound and stable for any number of atoms.

In the so-called 'jellium model' (see Ref. [8] for details), the structure of the ions is neglected and replaced by a uniformly charged background of flexible shape. This model works astonishingly well, in particular for the lighter alkalis like sodium and potassium and, if an effective mass of the electrons is included, also for lithium clusters. This can be partially explained by the softness of the effective potentials (i.e., the pseudopotentials [15]) felt by the valence electrons, the de Broglie wave length of the valence electrons at the Fermi surface which is larger than the interionic distance, and the temperature motion of the ions which tends to smear out their structure. The jellium model was used by Lang and Kohn in 1970 [16] to evaluate the electronic properties of metallic surfaces within the framework of density functional theory, using the local density approximation. For finite clusters, it was first used by Cini [17] and later by others [18, 19] in semiclassical extended Thomas-Fermi (ETF) density variational calculations. Selfconsistent quantum-mechanical Kohn-Sham calculations were first performed in the spherical jellium model

independently by Hintermann and Manninen [20], by Beck [21], and by Ekardt [22] who was the first to predict correctly the magic numbers of spherical metal clusters.

The selfconsistent potential and the density of the valence electrons resemble very much those of the neutrons in a nucleus: they are approximately constant in the inner part (i.e., the bulk region) of the cluster due to the cancellation of the classical Coulomb (i.e., the electronic Hartree, the ionic and the electron-ion) potentials: the bulk metal is neutral and bound mainly due to electronic exchange and correlation effects. The spherical cluster has a radius that grows like $R=r_s N^{1/3}$ with the number N of atoms, where r_s is the Wigner-Seitz radius characterizing the metal. The surface is rather steep – the diffusivity parameter a is typically one atomic length unit (a.u.), compared to the radius with ten to hundreds of a.u. – so that the potential can well be parametrized by a Woods-Saxon shape [23], or, in very large metal clusters, even by a steep reflecting wall (as we shall see further below). Thus, the valence electrons in a metal cluster form a 'leptodermous' system and, like for nuclei [24, 25], a liquid-drop or droplet model can be developed systematically from semiclassical density variational calculations [26] by expanding the total energy (and other observables) in powers of $a/R \sim N^{-1/3}$. Unlike in nuclei, all important volume and surface parameters appearing in the mass formula are known from experiment: the binding energy per electron (or the cohesive energy), the density and the compression modulus of the bulk metal, and the the surface tension and work function for an infinite metal plane (i.e., the semi-infinite system).

The results obtained with the jellium model for the properties of metal clusters until early 1993 are extensively documented in Ref. [8]. I refer to this review for formal details as well as illustrative figures and references. In the following, I shall briefly discuss some very recent successful applications of the methods introduced and developed by V. M. Strutinsky in the context of nuclear physics.

In the mass yields observed by the Berkeley group [6], it was evident that between the most prominent magic numbers, corresponding to spherical shapes of the clusters, there are also enhanced stabilities observable which correspond to deformed shapes. These 'deformed-magic numbers' were successfully interpreted by Clemenger [27] who introduced a modified version of the Nilsson model to cluster physics (without spin-orbit term, since no corresponding splittings of the valence electron levels occur in metal clusters). Soon, the selfconsistent jellium model was also extended to describe clusters with spheroidal [28, 29], triaxial quadrupole [30] and higher-order axial multipole deformations [31]. Solving the Kohn-Sham equations for these systems requires a numerical effort that is very similar to that of Hartree-Fock calculations for nuclei using effective interactions of the Skyrme type [32, 33]. Such calculations for deformed clusters have so far been performed for sizes up to $N \sim 60$ atoms and will, also in the age of supercomputers, probably be limited to N of the order of one to two hundreds.

Therefore, the shell-correction method is the ideal tool for an approximately selfconsistent description of large clusters, especially when triaxial and parity violating shapes

are investigated. Shell-correction calculations for spheroidal metal clusters up to $N \sim 800$ were performed in a Nilsson model whose parameters were chosen to fit the the Kohn-Sham levels of selfconsistent jellium model results for spherical clusters [34], and several deformed-magic numbers corresponding to prolate ground-state deformations could be found to be in good agreement with finer structures in the experimental mass yields [35]. Similar calculations were done for a Woods-Saxon potential [23] including axial quadrupole and higher multipole deformations [36]. Triaxial quadrupole shapes have also been included in the Nilsson model for metal clusters [37]; the shell-correction method yields very similar results as the corresponding self-consistent Kohn-Sham calculations [30] up to $N = 20$, but can be pushed to much larger sizes. In all these calculations, one exploits the fact that the average cluster energy can be taken from the liquid drop(let) model with experimentally known empirical parameters, thus using Strutinsky's original idea of renormalizing the wrong average part of the energy obtained in the phenomenological shell-models (or, for that matter, in the jellium model).

Thus, a lively discussion of shells and shapes in metal clusters is taking place, and much of the experience and the technology from nuclear physics can be used. There are many resemblances between clusters and nuclei concerning the kind of deformations encountered and the systematics of transitions between spherical, prolate, oblate and triaxial shapes – but also differences. Metal clusters turn out to be more soft towards octupole and hexadecapole deformations than nuclei. Indeed, the cluster Na_{40} and its next neighbours with $N > 40$ are predicted to have a static octupole moment in their ground state [31, 36]. The combined effects of hexadecapole and octupole deformations in the selfconsistent jellium model [31] explain correctly the experimental evidence [12] for an oblate shape of the clusters with 42 – 46 valence electrons. That clusters just above the spherically-magic ones, starting with $N = 40$, turn oblate is, in fact, different from the nuclear case and explains itself by the steepness of the confining potential (see also the discussion further below). So far, the only experimental information on cluster shapes comes from splittings of the dipole resonance in the photoabsorption data [12], which yield mainly the quadrupole deformations. The interpretation of these data is made difficult by the large widths of the resonances and a relatively important fragmentation of the collective strength (cf. Ref. [8] for a discussion) in many clusters. No clear triple splitting indicating a triaxial shape could yet be observed. Triaxial octupole deformations are also expected to play an important role in larger clusters [38].

An exciting subject which is being studied intensively and attracts the attention of nuclear physicists is the fission of multiply charged metal clusters [39]. For small and hot clusters, where the fission process is in strong competition with the evaporation of neutral atoms, the fissility parameter x is of order ~ 0.3, so that even in the liquid drop model the asymmetric fission is preferred. Indeed, the emission of charged trimers is the most abundant decay channel, which receives an extra contribution to its Q-value from the enhanced binding energy of the two-electron system and resembles the α decay of nuclei. Symmetric (or nearly symmetric) fission with the strongly necked-in deformed

shapes known from nuclei [3] has not been observed so far and is expected for very large, highly ionized clusters. One of the main differences between charged metal clusters and nuclei is that in the clusters, the charges sit mainly on the surface. But they are freely movable, so that the mass and charge ratios of the fission fragments are two independent degrees of freedom, whereas in nuclei, they are bound to be very close due to the strong attraction between neutrons and protons.

Perhaps the most exciting and spectacular manifestation of the electronic shell effects in metal clusters is the so-called 'supershell' structure. Since there is no limit to the size of a metal cluster, the old dream of nuclear physicists to produce 'superheavy' elements (cf. Ref. [40]) can easily be realized in this new periodic system. The regularity of the main spherical electronic shells manifests itself by a constant increase $\Delta N^{1/3}$ of the cube roots of the corresponding magic numbers. Up to date, such shell structure has been observed in metal clusters of various kinds, containing up to several thousand valence electrons [41, 42, 43, 44, 45]. The amplitude of the oscillating part of the level density or that of the shell-correction energy does, however, not grow monotonously with $N^{1/3}$ as known for the region of existing nuclei, but it slowly oscillates with a half-period of about 9 – 10 in units of $N^{1/3}$, thus grouping the shells into supershells. These cannot be observed for nuclei, since more than $\sim$ 800 – 1000 particles are needed to reach the first supershell minimum.

This effect was found already in 1972 by Balian and Bloch [46] who studied the density of eigenmodes in a spherical cavity with reflecting walls. The gross-shell behaviour of the level density can be explained semiclassically as an interference between the two dominating classical periodic orbits of a particle enclosed in a spherical box, namely the triangular and the squared orbits, leading to a beating amplitude of the shell oscillations. The average length of these two orbits determines the rapid oscillations, giving the main spherical shells with a spacing $\Delta N^{1/3}$=0.603, whereas the difference of their lengths determines the amplitude modulation, i.e. the period of the supershells.

The theory of Balian and Bloch is a special case of the semiclassical periodic orbit theory which was developed for the most general case of non-integrable systems by Gutzwiller [47]. Its main outcome is the so-called trace formula which states that the oscillating part of the level density of a given quantum system is (approximately) given by a spectral sum over all periodic orbits of the corresponding classical system. The orbits with the shortest periods (or actions) determine the gross-shell behaviour, whereas contributions of longer orbits give finer details. (Mathematically, the 'trivial' orbits with zero length give the average or extended Thomas-Fermi part of the level density, which can also be obtained by Strutinsky-smoothing the exact level density [1].)

The Gutzwiller theory [47] was formulated for systems without continuous symmetries, i.e. with only isolated periodic orbits, and does therefore not apply directly to most integrable systems. Strutinsky and his collaborators in Kiev [4, 5] generalized it to take into account also degenerate orbits occurring in integrable systems and applied it to

Woods-Saxon and harmonic oscillator potentials. A major success of their work was the semiclassical explanation of the main systematics of nuclear ground-state deformations [5].

A similar theory, starting from the Einstein-Brillouin-Keller (EBK) quantization for integrable systems [48], has been developed by Berry and Tabor [49]. They surmised that the Gutzwiller theory (where it applies) should be equivalent to EBK quantization. Indeed, it has been shown numerically for the spherical square-well potentials in three and two dimensions that both the Balian-Bloch and the extended Gutzwiller theory, which yield the same analytical trace formula, give the EBK quantum spectrum when one sums over sufficiently many and sufficiently long periodic orbits [50].

Only in exceptional cases does the trace formula yield a full and exact quantization [47]. The main interest of the periodic orbit theory is therefore to interpret (or predict) the gross-shell behaviour of a quantum system in terms of the shortest classical orbits. When two (or a few) orbits have similar actions and similar amplitudes, they interfere and yield beats in the quantum spectrum. One example is the supershell beat under discussion here. Another example is being studied in connection with octupole deformations of superdeformed nuclei with high spin [51]. Quantum beats were recently also found in the two-dimensional Hénon-Heiles potential which classically exhibits chaos [52].

Turning back to metal clusters: Nishioka *et al.* [23] applied the method of Berry and Tabor to a Woods-Saxon potential fitted to selfconsistent jellium model results for spherical sodium clusters. They found that the beat structure of the level density in this potential is very similar to that of the Balian-Bloch sphere, and they predicted that supershells should exist in metal clusters. Indeed, the experimentally observed shell structure does have the right characteristics: the main shells have a spacing with $\Delta N^{1/3}=0.61\pm0.01$ (where N is the number of valence electrons), which is in excellent agreement with the Balian-Bloch result 0.603. This spacing is the same for all metals (Na, Li, Ga, Al). Indeed, using a simple Bohr-Sommerfeld quantization argument, one can show that the value 0.603 does not depend on the Wigner-Seitz radius of the metal (see Sect. V.A.2 of Ref. [8]). The Woods-Saxon potential of Ref. [23] and selfconsistent jellium Kohn-Sham calculations of the supershells [53] both give the same value $\Delta N^{1/3}=0.61$, showing that the mean field of large spherical metal clusters is, in fact, very close to a spherical cavity with reflecting walls.

It is not easy to exhibit directly the supershell beat experimentally, due to the finite temperature which tends to smear out the shell effects. In fact, finite-temperature Kohn-Sham calculations [53, 54] showed that the first and second differences of the total free energy, which determine the mass yields [35, 54], depend very sensitively on the temperature. As a result, the expected beating amplitude of the oscillating mass yields disappears exponentially for clusters larger than $N\sim 600$, where kT becomes comparable with the spacing of the electronic single-particle levels. One therefore faces a dilemma: in order to exhibit the electronic shell structure, the clusters must be produced sufficiently hot so that the evaporation process enhances the stable magic species. But if they are too hot, the

temperature suppresses the shell effects. In the experiment with sodium clusters [42], this dilemma was solved by explicitly compensating the exponential temperature suppression factor in the analysis of the experimental mass yields and, indeed, the beating supershell amplitude was put into evidence. For gallium clusters, the beat could recently be shown directly [44] without such a manipulation.

An indirect evidence for the supershell beat comes from the phase shift which the rapid main-shell oscillations undergo when passing from one supershell to the next. When plotting the cube-roots $N^{1/3}$ of the electronic magic numbers versus main-shell number, one obtains a straight line with slope $\Delta N^{1/3} \simeq 0.61$. But around the supershell minima (where the interference between triangular and squared orbits is destructive), that straight line is interrupted and displaced; the data pass smoothly from one line to the parallel line over some 3 – 6 shell numbers. This feature could, indeed, be observed experimentally for sodium [41, 42], lithium [43] and gallium clusters [44]. The beat minimum, where this transition occurs, depends on the surface diffuseness of the potential and on the type of metal used; it is an important bench mark for testing the theory. There is no time and place here to discuss the ionic structure effects which also become important and, in fact, competing for colder and larger clusters. Here, too, a lot has to be done and learned in order to improve our detailed understanding of cluster physics.

Metal clusters have thus turned out to be an ideal system for studying the semiclassical theory of shell structure, since they can be made sufficiently large. They show many analogies and resemblances to atomic nuclei; several concepts and techniques developed in nuclear physics have been applied successfully to metal clusters. But we should not be tempted to apply the nuclear experience too blindly: although the resemblances and parallels inspire and motivate us, it is from the differences that we learn most.

I would like to conclude my talk with a personal note again. In June 1993, we applied the semiclassical analysis of nuclear deformations by Strutinsky and his coworkers [5] to large deformed sodium clusters. We found that the main contributions from the triangular and rhombic classical orbits in a spheroidal cavity give a perfect fit to the spheroidal ground-state deformations obtained in the Nilsson model for sodium clusters [34] with $N \geq 50$, see Figure 6 of Ref. [55]. Very excitedly, we sent that figure to Strutinsky and wrote him that his theory could be successfully applied to metal clusters. A few days later, Vilen Mitrafanovich called me from Catania. He liked that result. He was otherwise depressed, because he had not been invited to a major conference on nuclear physics that month, where also nuclear shapes and shells were discussed – a topic to which he certainly has contributed more than anyone else. But he was about to leave for a conference in Santorini on nuclear and atomic cluster phenomena, and he told me that he was going to show our figure in his talk about the semiclassical theory of shell structure. In the following week, on his trip to Santorini, Vilen M. Strutinsky suddenly deceased. With him, we have lost an outstanding scientist and a great human being.

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