ОБЪЕДИНЕННЫЙ
ИНСТИТУТ
ЯДЕРНЫХ
ИССЛЕДОВАНИЙ

Дубна

E4-99-50

V.O.Nesterenko[1], W.Kleinig[2], F.F. de Souza Cruz[3]

A VARIETY OF GIANT RESONANCES IN METAL CLUSTERS

To be published in Proceedings of the International Workshop «Collective Excitations in Fermi and Bose Systems», September 14–17, 1998, Serra Negra, Brazil

[1]E-mail: nester@fsc.ufsc.br
[2]On leave of absence: Institut für Analysis, Technische Universität Dresden, D-01062 Dresden, Germany; E-mail: kleinig@thsun1.jinr.ru
[3]Departamento de Fisica, Universidade Federal de Santa Catarina, Florianópolis, SC, 840000-900, Brasil
E-mail: fred@fsc.ufsc.br

1999

Нестеренко В.О., Клайниг В., де Соуза Круз Ф.Ф. E4-99-50
Многообразие гигантских резонансов в металлических кластерах

Дается обзор мультипольных электрических и магнитных гигантских резонансов в металлических кластерах и проводится сравнение с соответствующими резонансами в атомных ядрах. Основное внимание уделяется $E1$-резонансу (дипольный плазмон).

Работа выполнена в Лаборатории теоретической физики им. Н.Н.Боголюбова ОИЯИ.

Препринт Объединенного института ядерных исследований. Дубна, 1999

Nesterenko V.O., Kleinig W., de Souza Cruz F.F. E4-99-50
A Variety of Giant Resonances in Metal Clusters

Multipole electric and magnetic giant resonances in metal clusters are reviewed and compared with their counterparts in atomic nuclei. The main attention is paid to $E1$-resonance (dipole plasmon).

The investigation has been performed at the Bogoliubov Laboratory of Theoretical Physics, JINR.

Preprint of the Joint Institute for Nuclear Research. Dubna, 1999

1 Introduction

Metal cluster (MC) is a bound system consisting of atoms of some metal. The amount of atoms can vary from a few to many thousands. Some MC, mainly of alkali (Li, K, Na, ...) and noble (Ag, Au, ...) metals, demonstrate a striking similarity to atomic nuclei (see reviews [1-5]). In these clusters the valence electrons are *weakly* coupled to the ions and, like nucleons in nuclei, are not strongly localized. The mean free path of valence electrons is of the same order of magnitude as the size of the cluster. This favors the valence electrons to form a mean field of the same kind as in nuclei (with the similar shell structure and magic numbers). In addition to the mean field, MC demonstrate other similarities with atomic nuclei: deformation in the case of open shells, variety of giant resonances (GR), fission, etc.. As a result, many theoretical ideas and methods of nuclear physics can, after a certain modification, be applied to MC [1, 3, 5].

This review is devoted to collective oscillations of valence electrons in MC. Valence electrons can be considered as the counterparts of nucleons in nuclei, and their oscillations as the counterparts of nuclear GR. Investigation of GR in MC is interesting in two aspects: it allows to understand deeper general properties of collective modes in finite Fermi systems and, simultaneously, allows to study peculiarities of MC. GR in clusters and atomic nuclei are well overlapped. However, some specific properties of MC cause considerable differences in the behavior of GR in these two systems. For example: the Coulomb interaction and the "spill-out" effect provide a specific dependence of GR properties on the mass number; the negligible character of the spin-orbital interaction leads to the decoupling of spin and

orbital magnetic modes; clusters can have much more particles (atoms) than nuclei, which favors very strong orbital magnetic resonances; for most of the clusters the role of the ionic subsystem is important; at different temperatures MC can be in solid, liquid and even "boiling" phases, which greatly influences GR properties; characteristics of GR considerably vary whether the clusters are charged or neutral, free or embedded to a substrate, pure or with impurities atoms, etc..

Our consideration will be limited by certain physical conditions.

– i) The modern techniques allow to fabricate atomic clusters from atoms of about any element of the periodic table. However, the conception of the mean field for valence electrons is realized only for a minority, – mainly for clusters of alkali and noble metals and, in a less extent, for neighboring elements. So, we should limit ourselves by this MC region.

– ii) In some alkali metals (Na and K) the ionic lattice can, to good accuracy, be replaced by a uniform distribution of the positive charge over cluster's volume. This is so-called jellium approximation which greatly simplifies the analysis and calculations. This approximation is enough for the description of many properties of alkali MC and will widely be used in the review. However, it often fails beyond Na and K and then a more explicit treatment of the ionic structure is necessary [3, 4].

– iii) The ionic subsystem is supposed to be "frozen", i.e. we will not consider any ionic phonon excitations.

– iv) The validity of the jellium approximation is supported by temperature fluctuations of ions, which smooth ion positions. It fails in the low temperature region (approximately at $T < 100$ K) where the explicit treatment of the ionic structure is important. At too high temperatures ($T > 1000$ K) the quantum shells of the mean field are washed out, what establishes an upper limit for our considerations. We will consider GR in a temperature interval between these extreme cases.

2 Theoretical Grounds

Due to the similarity between MC and nuclei, many models of nuclear theory have been applied to study MC [1, 3]. In due time, some of them have been introduced to nuclear physics from solid-body field and then subsequently modified to describe *finite* Fermi systems. Now they turn out to be useful for clusters. In particular, a large variety of the RPA methods have been adopted , scaling from simple versions, like the sum rule approach [6-9] and the local RPA [10, 11], to sophisticated full RPA models, like time-dependent Hartree-Fock [12] and time-dependent local density approximation (TD-LDA) [13-26] (for a more complete list of citation see Refs. [1, 3, 26]). The simple models can describe the gross structure of GR but not the fragmentation of the collective strength. The full RPA models can describe the fragmentation but are very time consuming. The last shortcoming becomes crucial for deformed and large spherical clusters where the number of particles, and thus the size of the configuration space, is very large. In this connection, the intermediate class of the models, the RPA with *separable* residual forces (SRPA), seems to be very promising [7,27-35]. The separable ansatz allows one to turn the RPA matrix into a simple dispersion relation. This drastically simplifies the eigenvalue problem preserving, at the same time, the main advantage

of the full RPA to describe the fragmentation of the collective strength. The SRPA version derived in Refs. [27-33] provides the accuracy of full RPA calculations [33], can be applied to systems of any shape [28, 29, 31, 32], and allows to treat GR in MC and atomic nuclei on the same microscopic footing [27, 29, 32]. The results obtained within this SRPA version will be widely used in the review as illustrative examples.

For the description of collective oscillations, the SRPA and most of the other models exploit, as a starting point, the Kohn-Sham energy functional [36, 37] for a system of N_e valence electrons:

$$E\{n(\mathbf{r},t), m(\mathbf{r},t), \tau(\mathbf{r},t)\} = \\ 1/2 \int \tau(\mathbf{r},t) d\mathbf{r} + \int v_{xc}(n(\mathbf{r},t), m(\mathbf{r},t)) d\mathbf{r} \\ +1/2 \int\int \frac{(n(\mathbf{r},t) - n_i(\mathbf{r}))(n(\mathbf{r_1},t) - n_i(\mathbf{r_1}))}{|\mathbf{r} - \mathbf{r_1}|} d\mathbf{r} d\mathbf{r_1}, \quad (1)$$

which includes the kinetic energy, the exchange-correlation term in the local density approximation (LDA) [37, 38] and the Coulomb interaction, respectively. Here, $n(\mathbf{r},t) = n(\mathbf{r},t)_\uparrow + n(\mathbf{r},t)_\downarrow = \Sigma_l |\phi_l(\mathbf{r},t)|^2$, $m(\mathbf{r},t) = n(\mathbf{r},t)_\uparrow - n(\mathbf{r},t)_\downarrow$ and $\tau(\mathbf{r},t) = \Sigma_l | \bigtriangledown \phi_l(\mathbf{r},t)|^2$ are the density, magnetization density (z-component) and kinetic energy density of valence electrons, respectively; $n_i(\mathbf{r})$ is the ionic density in the jellium approximation; $\phi_l(\mathbf{r},t)$ is a single-particle wave function. The convention $e = m_e = \hbar = 1$ is used. The functional (1) can have additional terms if the ionic structure is treated beyond the jellium approximation.

The time-dependent single-particle Hamiltonian is obtained

as

$$H(\mathbf{r},t)\phi_l(\mathbf{r},t) = \frac{\delta E}{\delta \phi_l^*(\mathbf{r},t)}. \quad (2)$$

In the small-amplitude limit of a collective motion, the densities can be written as $n(\mathbf{r},t) = n_0(\mathbf{r}) + \delta n(\mathbf{r},t)$ and $m(\mathbf{r},t) = m_0(\mathbf{r}) + \delta m(\mathbf{r},t)$ where $n_0(\mathbf{r})$ and $m_0(\mathbf{r})$ are the static ground state densities (in spherical clusters with unpolarized ground state $m_0(\mathbf{r}) = 0$) and the values $\delta n(\mathbf{r},t)$ and $\delta m(\mathbf{r},t)$ are small time-dependent density variations (transition densities). Then, in the linear approximation to the density variations, the Hamiltonian (2) is a sum of the static and dynamical parts. The static part

$$H_0(\mathbf{r}) = T + V_0(\mathbf{r}) = -\frac{\Delta}{2} + (\frac{dv_{xc}}{dn})_{n=n_0, m=m_0} + \int \frac{n_0(\mathbf{r_1}) - n_i(\mathbf{r_1})}{|\mathbf{r} - \mathbf{r_1}|} d\mathbf{r_1} \quad (3)$$

constitutes the Kohn-Sham single-particle potential (Eq. 3 is written for the case of spin-saturated clusters). It can be approximated with a good accuracy by phenomenological potentials, such as the harmonic oscillator [7] (for small spherical MC), Nillson-Clemenger [39, 40] (for deformed MC) or Woods-Saxon [30, 41, 42] (for spherical and deformed MC).

In the electric channel (spin degrees of fredom are neglected), the dynamic part of the Hamiltonian (residual interaction) has the form

$$\delta H(\mathbf{r},t) = (\frac{d^2 v_{xc}}{dn^2})_{n=n_0, m=m_0} \delta n(\mathbf{r},t) + \int \frac{\delta n(\mathbf{r_1},t)}{|\mathbf{r} - \mathbf{r_1}|} d\mathbf{r_1}. \quad (4)$$

The dominant term here is the Coulomb interaction. The residual interaction in this channel is always positive (repulsive) and shifts the unperturbed electrical multipole strength from the

typical particle-hole (ph) values $\omega_{ph} = 0.9 - 1.5$ eV to higher energies 2.6-3.2 eV.

In the spin channel, the dynamical part of the Hamiltonian, initiated by the variation $\delta m(\mathbf{r}, t)$. is expressed only through the exchange-correlation term as the single one depending on the magnetization density. The residual interaction here is negative (attractive) and shifts the unperturbed magnetic multipole strength from $\omega_{ph} = 0.9 - 1.5$ eV to lower energies 0.2-0.8 eV.

In what follows we will mainly consider clusters constituted from monovalent atoms, like alkali metals, for which the numbers of valence electrons and atoms coincide, $N_e = N$.

3 Electric Dipole Giant Resonance (E1 GR)

Unlike nuclei, where different kinds of GR are well investigated both experimentally and theoretically, our knowledge in clusters is mainly limited by the electric dipole resonance (dipole plasmon). Experimentally the E1 GR has been observed in a variety of clusters: small and large, spherical and deformed, neutral and charged, hot and cooled (see, for example, Refs. [43-49]). As a rule, the photoabsorption cross section was measured by methods of the depletion spectroscopy. For other GR ($EL(L \neq 1)$, ML) there are only theoretical predictions [6-9,28,30,32,50,51].

Physical interpretations of E1 GR in clusters and nuclei are very similar: while in nuclei it is caused by translations of neutrons against and protons, then in clusters it is a result of translations of the valence electron against ions [16]. In spite of this similarity, the dipole resonance in clusters exhibits many interesting peculiarities which will be discussed below.

3.1 Energy of E1 GR: Step by Step

In general, the description of the E1 energy in clusters is a rather complicated task. For example, while in nuclei the E1-energy depends on the mass number as $A^{-1/3}$, in clusters it can both decrease (Ag clusters) and increase (alkali MC) with the number of atoms. Let us consider this important characteristic step by step.

Step one: Mie frequency and spill-out effect. In the simplest approximation, MC can be considered as a *classical* metallic drop. Then, the E1-energy is described by Mie expression [52]: $\omega_{Mie} = \omega_p/\sqrt{3}$ where ω_p is the plasma frequency. For Na clusters $\omega_{Mie} = 3.41eV$. This value is much higher than the experimental E1-energy which is 2.5-2.8 eV for spherical Na clusters with $N < 100$.

The agreement with the experiment is considerably improved if we take into account the *quantum* spill-out effect. This effect means that, since the valence electrons are quantum entities, they are not well localized and so, unlike the classical ionic jellium, can be partly *spilled out* beyond the jellium boundary. In principle, the spill-out takes place in any two-component quantum system including atomic nuclei and atoms (a "neutron skin" in small nuclei is a relevant example). With the spill-out, the E1 energy in MC is described as [7]

$$\omega_{E1} = \omega_{Mie}(1 - \frac{1}{2}\frac{\delta N_e}{N_e}) \qquad (5)$$

where δN_e is the number of spilled out valence electrons. As a result, the discrepancy with the experiment reduces to 0.2-0.3 eV. The spill-out effect allows to explain the increase of the E1-energy with N, observed in alkali MC. The value δN_e decreases

with the size (for example, $\delta N_e = 1.5(19\%)$ and $9.5(7\%)$in Na_8 and Na_{138}, respectively [53]) leading to the corresponding increase in the E1-energy.

Step two: ionic structure, local and nonlocal effects. The remaining discrepancy can be removed in a large extent by the explicit treatment of the ionic subsystem. First of all, we should take into account that ions are not the points but have a size. Inside this size, ion core electrons (ICE) (do not confuse them with the valence electrons) screen the pure Coulomb interaction of ions and valence electrons. To take into account this screening, the atomic pseudopotentials (PP) are used (see, for instance, [22, 23, 25, 54]). They allow to describe correctly the spectrum of valence electrons in isolated atoms *without* the solution of the complicated many-body atomic task. Being a sum of contributions of ICE with different orbital momenta, PP have *local* (s-electrons) and *nonlocal* (p and d electrons) parts [54]. To avoid dealing with nonlocal functions, the Pseudo-Hamiltonians (PH) were introduced as the next simplifying step [55, 56]. The PH, being derived from PP, lead to less involved (but with the same accuracy) calculations since, unlike the PP, they treat the nonlocality only through the differential operators. Folding the atomic PH with the jellium, one gets the PH for *atomic clusters* [19-21]. The PH have the additional advantage to be easily incorporated to common calculation schemes.

As compared to the conventional Kohn-Sham Hamiltonian, PH include the additional local and non-local (the orbital contribution and the effective mass) terms. As is seen from Figure 1, in K clusters (the same for Na) the nonlocal contributions are negligible and the local term is enough to get good description of the E1-energy [33]. This is not the case for Li clusters,

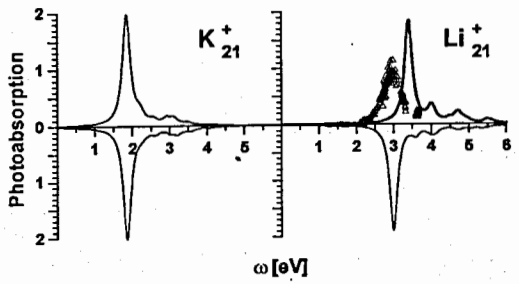

Figure 1: E1 GR (dipole plasmon) in K^+_{21} and Li^+_{21} calculated in the framework of the SRPA with (down) and without (up) the nonlocal ICE contribution [33]. For Li^+_{21} the photoabsorption experimental data [57] ($\triangle$) in $Å^2/N_e$ are compared.

where only both, local and nonlocal, contributions provide the agreement with the experiment [33]. In some studies (see, e.g., Ref. [22]) the ICE effects are taken into account together with some averaged treatment of the ionic arrays in a cluster. The latter leads to an additional, but rather moderate, redshift of the E1-energy.

Step three: direct dynamical ICE contribution. The ICE effects discussed above are realized through the change of the single-particle characteristics with the subsequent renormalization of the residual interaction. Besides this *indirect* way, the ICE can *directly* influence the dynamics and thus lead to new peculiarities of the E1 GR. This can be well demonstrated for Ag clusters where, like atomic nuclei and *unlike* alkali MC, the E1-energy *decreases* with a size [48]. The physics behind is that in these clusters the energy of ICE excitations is comparable to the E1-energy. The coupling of these two modes additionally screens

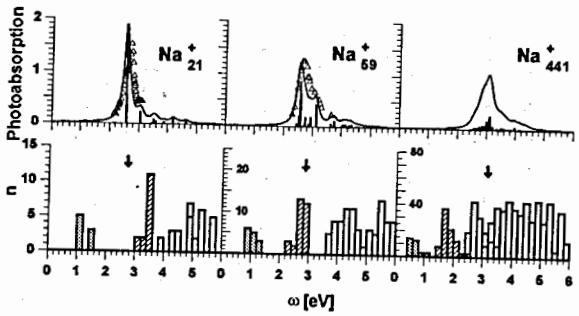

Figure 2: *Top:* E1 GR in spherical Na clusters from different size regions. The SRPA results [33] are shown as bars for every RPA state to demonstrate the Landau damping and as smoothed by a Lorentz function (of the width 0.25 eV) to simulate the typical thermal broadening of the plasmon. The length of the bars is rescaled by the factor 1/2.55 to fit the scale of the smoothed strength. The photoabsorption experimental data are taken from Ref. [43]. *Bottom:* The number of dipole particle-hole configurations, as a function of the energy, corresponding to $\Delta\mathcal{N}$=1 (dotted bricks), $\Delta\mathcal{N}$=3 (dashed bricks) and $\Delta\mathcal{N} \geq$5 (unfilled bricks) dipole transitions in Na clusters presented in the top of the figure. $\mathcal{N}$ is the principal shell quantum number. The arrows mark centroid energies of the plasmon.

the interaction of valence electrons with ions (direct dynamical ICE contribution) and finally causes the redshift (decrease) of the E1-energy [58]. This effect is mainly of a volume character and so intensifies with a cluster size. As a result, the E1 energy in Ag clusters decreases with N. This tendency overpowers the opposite one caused by the spill-out effect.

In alkali MC, where the ICE excitations have much higher energies than the E1 GR, the direct dynamical ICE contribution is negligible and the evolution of the E1-energy with N is determined mainly by the spill-out effect.

4 Landau Damping and Width of E1 GR

The main physical mechanisms forming the plasmon width are the thermal fluctuations of a cluster shape and the Landau damping (RPA fragmentation of the collective strength) [3, 18, 33, 34, 35, 61, 60]. The relative contributions of these two mechanisms change with a cluster size. As is seen from Figure 2, in small clusters, like Na_{21}^{+}, where the Landau damping is weak, the thermal fluctuations determine about all the width. In clusters of a moderate size, like Na_{59}^{+}, the Landau damping is strongest and greatly contributes to the width. This is especially the case for deformed clusters. In large clusters, like Na_{441}^{+}, the Landau damping is weaker though its contribution to the width remains to be considerable.

Figure 2 (bottom) shows that the Landau damping is closely related with the shell structure [33]. In Na_{21}^{+} the dipole plasmon lies in the wide gap between the bunches of $\Delta\mathcal{N}$=1 and $\Delta\mathcal{N}$=3 particle-hole (ph) states and remains almost unperturbed as a collective peak. With increasing the cluster size, the resonance approaches the bunch $\Delta\mathcal{N}$=3 and, in Na_{59}^{+}, already interferes with ph states of this bunch, which leads to the considerable Landau damping. For larger clusters, the plasmon runs to the swamp of ph states. This leads to a general trend of increasing the width which is, however, overlaid by sizeable fluctuations [33, 34]. But here a further mechanism comes into play: the coupling between the resonance and ph states fades away due to increasing mismatch of $\Delta\mathcal{N}$=1 ph configurations (which mainly generate the plasmon) and surrounding ph states with much larger values of $\Delta\mathcal{N}$. This finally leads to the decrease of the plasmon width $\propto N_e^{-1/3}$ estimated analytically in the wall

formula [35] and tested in the RPA calculations [34].

The Landau damping in MC with $N < 40$ is rather sensitive to cluster charge: being strongest in negatively charged MC (anions), the Landau damping is considerably reduced while passing to neutral and then to positively charged clusters (cations) [17]. This effect is caused by the strong dependence of the single-particle potential depth V_0 on the cluster charge. In anions the potential is shallow ($V_0 \simeq -2$ eV), the energy gaps between $\Delta\mathcal{N}$ bunches are very smooth and, so, there are good conditions for a sizeable Landau damping (see discussion above). In neutral clusters and more in cations, the potential depth is increased to about -7 eV, the gaps between $\Delta\mathcal{N}$ bunches in the ph spectrum become more distinctive, which weakens the Landau damping.

5 Temperature Effects

In most of experiments with GR in MC, the typical cluster temperature is estimated to be in the interval 300-900 K which corresponds to the thermal energy $kT = 0.03 - 0.09$ eV. At these temperatures, ions behave as classical particles and quantum properties of the cluster are mainly determined by valence electrons. This can be easily proved [59] by using the uncertainty relation $\Delta x \Delta p \geq \hbar$. This relation gives lower bounds for the momentum and energy of a particle in a system: $\Delta p = \hbar/\Delta x$ and $\Delta E = (\Delta p)^2/2m$, respectively. Taking $\Delta x \geq 1.5\mathring{A}$ (the diameter of Na_{20}) for both ions and valence electrons, one gets

$$\Delta E_e \geq 0.16eV \qquad \text{for electrons,}$$

$$\Delta E_i \geq 10^{-4}eV \quad \text{for ions.}$$

The energy of a quantum motion of valence electrons considerably exceeds the thermal energy, which favors their quantum behavior. Due to much larger ionic mass, the situation with ions is opposite. Ions should exhibit the classical behavior.

The difference in ionic and electron masses leads to other interesting consequence. Namely, almost all the thermal energy is contained in the ionic subsystem. Valence electrons are embedded to the thermal ionic bath. So, unlike atomic nuclei, MC represent the case of the canonical ensemble.

The bulk melting points for K, Na and Li are $T_b = 336$, 371 and 452 K, respectively. This means that most of the measurements for GR in MC have been done for clusters in a liquid-like phase.

As was mentioned above, in small clusters, thermal shape fluctuations provide the dominate contribution to the plasmon width. While in nuclei these fluctuations are mainly of a quadrupole form, in MC they are mainly octupole [60]. The reason is that MC with closed shells and neighboring ones are rather soft to the octupole deformation.

Photoexcitation is a rapid process in the ionic time scale. So, every response of a cluster represents its instantaneous shape and the experimental cross section gives a properly weighted response of all allowed shapes [61].

The higher the temperature, the larger the plasmon width and the smaller the plasmon energy. The temperature shift is estimated as about 1% of the plasmon energy per 100 K [44, 62]. It can be explained by the effectively increase of the cluster size with a temperature. The larger the size, the bigger the static dipole polarizability which is expressed through the cluster radius as $\alpha_{E1} = R^3$. The polarizability is connected with the

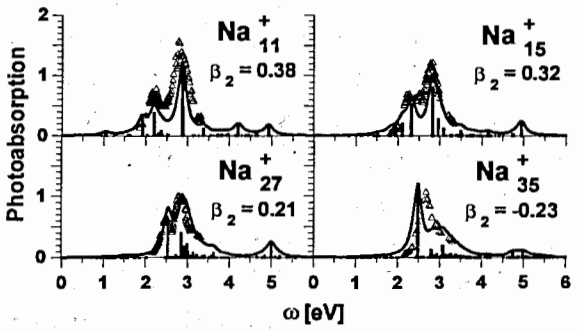

Figure 3: E1 GR in deformed Na clusters. The SRPA results [31] (curves and bars) are given by the same way as in Figure 2. The experimental data are taken from Ref. [69]. The deformation parameter β_2 is extracted from the experiment [69] following the prescription[7].

plasmon energy through the inverse sum rule, $\alpha_{E1} = 2m_{-1} \simeq B(E1)/\omega_{E1}$. So, the higher a temperature, the larger α_{E1} and, consequently, the smaller ω_{E1}.

Recent experiments show that at sufficiently low temperatures the gross-structure of the E1 GR drastically changes [47]. For example, the axially deformed cluster Na_{11}^{+} at 380 K demonstrates the typical two-peak spectrum determined by the deformation splitting of E1 GR. At 35 K the same resonance exhibits much more complicated structure including at least 6 well-distinguished peaks. This structure reflects the ionic arrangement which, at so low temperature, is not washed out by variations of ions. In this case, the jellium approximation is not valid and models based on this approximation cannot be applied. The E1 GR in small clusters at low temperature seems to be best described by *ab initio* quantum-chemical calculations [63].

6 E1 GR in Deformed Clusters

Like nuclei, MC with open shells have quadrupole deformation [45-49,64-68]. There are experimental indications of both prolate and oblate axial quadrupole shapes, as well as of γ-deformation [45-49]. In the framework of different methods (Strutinski's shell correction method, ultimate jellium model, etc.) hexadecapole and octupole deformations as well as high isomerism have been predicted [64-68]. Rather strong quadrupole, hexadecapole and octupole deformations should take place at least up to MC with $N \sim 700$ [65]. Like in nuclei, E1 GR in axially deformed MC exhibits the deformation splitting in two peaks (see Figure 3). The right peak is about twice larger than the left one in prolate clusters (see Na_{11}^{+}, Na_{15}^{+}, Na_{27}^{+}) and, vice versa, in oblate clusters (see Na_{35}^{+}).

Most of MC are deformed. But getting an experimental information on a cluster shape, even in the simplest case of a quadrupole deformation, is rather nontrivial problem. In nuclei rotational bands serve as a source of such information. In principle, deformed clusters can rotate. But, due to a large value of the moment of inertia, rotational energies are very small and, being of the same order of magnitude as the thermal energy, fail to be observed. In this connection, the splitting of E1 GR in deformed clusters is now a *single direct* manifestation of quadrupole deformation and the valuable source of the information about it.

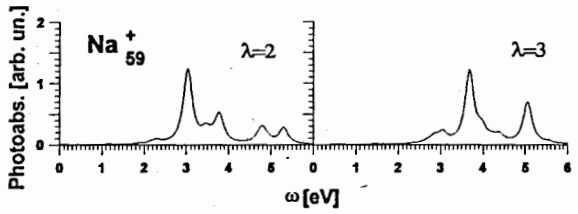

Figure 4: E2 and E3 GR in Na_{59}^{+} calculated within the SRPA.

7 Multipole GR, Asymptotic Trends, Restoring Forces

So far, the depletion spectroscopy methods (photoabsorption and photofragmentation) were mainly exploited for observation of E1 GR in MC [2]. The other reactions $((e,e'),(\gamma,\gamma')$ and etc.) are not yet sufficiently developed, which impedes the observation of other GR. The similar situation took place in nuclear physics in early seventies. For this reason investigation of EL GR with $L \neq 1$ is yet limited to theoretical predictions [6-9,28,30,32,50,51]. In Figure 4, E2 and E3 GR in spherical Na_{59}^{+}, calculated within the SRPA, are presented as typical examples.

It is instructive to consider the main trends of EL GR with the size (N) and multipolarity (L), and also the origin of the GR restoring forces. Such analysis has been done within the sum rule approach (SRA) in Ref. [6]. In the jellium approximation for valence electrons, $n_0(r) = n_i(r) = n^+\theta(r-R)$ (the spill-out effect is neglected), the energy of $EL(L \neq 0)$ GR can be written

as [6]

$$\omega_{EL} = \sqrt{\frac{m_3}{m_1}} = \hbar\sqrt{\frac{2}{3}(2L+1)(L-1)\frac{\beta_F^2}{R^2} + \omega_p^2\frac{L}{2L+1}} \qquad (6)$$

where $m_1 = \sum_i B(EL, gr \to i)\omega_i$ and $m_3 = \sum_i B(EL, gr \to i)\omega_i^3$ are the sum rules, $\beta_F = (3/5)^{1/2}(3\pi^2)^{1/3}n_0^{1/3}/m$ and $R = r_0N^{1/3}$ is the radius of a cluster. The first and second terms in Eq. 6 are the contributions of the kinetic energy (the similar expression have been obtained earlier in Ref. [70]) and the Coulomb interaction, respectively. Eq. 6 shows that E1 GR is determined only by the Coulomb interaction. In the limit of large R, one has

$$\omega_{EL} \to \hbar\omega_p\sqrt{\frac{L}{2L+1}}. \qquad (7)$$

The larger L, the higher the excitation energy of the GR. In general, due to the first term in Eq. 6, the energy of $EL(L \neq 0,1)$ GR is decreased with N. For low L in small clusters this tendency is changed by the spill-out effect.

The separate analysis for E0 GR predicts the increase of the E0 energy with N to the limit $\omega_{E0} \to \hbar\omega_p$.

It is seen from Eq. 6 that the value m_3 has the meaning of a restoring force [10]. In Table 1 the contributions to m_3 from different terms of the Kohn-Sham functional (1) are presented. It is seen that the restoring force for E1 GR is determined by the electron-ion interaction only. With increasing L, the electron-electron contribution (ee) raises and starts to compensate the (ei) Coulomb part. Simultaneously, the kinetic energy term grows. For high L, the contribution of the total Coulomb interaction goes to zero and all the restoring force is determined by

Table 1: Relative contributions to m_3 for Na_{92}: kinetic energy ($m_3(T)$), exchange and correlations ($m_3(xc)$), electron-electron interaction ($m_3(ee)$, electron-ion interaction ($m_3(ei)$) and total Coulomb interaction ($m_3(C) = m_3(ee) + m_3(ei)$) [6].

L	$m_3(T)$	$m_3(xc)$	$m_3(ee)$	$m_3(ei)$	$m_3(C)$
1	0	0	0	1	1
2	0.08	0	-0.77	1.69	0.92
5	0.51	0	-2.29	2.78	0.49

the kinetic energy. Within the LDA, the exchange-correlation term (xc) is of purely volume character (depends only on the electron density) and so does not contribute to m_3.

The restoring force should not be confused with the residual interaction. As is seen from Eq. 4, the residual interaction, unlike the restoring force, has for any L only the (ee)- and (xc)-terms (where the (ee)-term dominates).

8 Anharmonicity and Multiphonon GR

How much harmonic are GR in metal clusters? For one phonon GR (phonons here are superpositions of 1p-1h *electron* excitations, do not confuse them with ionic phonons) the theoretical investigations [71-73] give contradictory answers. The shell-model calculations [71] found for E1 GR in Na_{20} some signals of anharmonicity. The other studies [72, 73] predict for EL and spin-dipole GR the harmonic behavior. It should be noted that all these studies have been performed for rather small clusters with $N \leq 20$. In this size region the GR energy lies safely below the lowest 2p-2h configurations, what does not favor anharmonic

effects. This picture can change in larger clusters where GR approach the region of 2p-2h configurations.

The calculations [72] predict a noticeable anharmonicity for most of *double* (two-phonon) GR placed at 8-15 eV. These GR exhibit a weak mixing with one-phonon states. At the same time, they are well fragmented between two-phonon configurations. Most strong effect is expected for some 0^+ double GR, for example, for $(1^- \otimes 1^-)_{0^+}$ in Na_{21}^+. These predictions are important in connection with the appearance of the new experimental techniques allowing investigation of multiple GR. These techniques use non-intense femtosecond lasers [74] or exploit collisions of a cluster with highly charged ions [75]. Quite recently the multiple GR constructed from 3-4 dipole plasmons has been observed in Na_{93}^+ [74].

9 Magnetic GR

Like in atoms, the spin-orbital interaction in metal clusters is negligible and thus spin and orbital collective magnetic modes are well decoupled. The separation of these two modes in MC is easier than in nuclei.

9.1 Spin-Multipole GR

Magnetic multipole resonances (ML) of spin character caused by the external field $Q_L = \sum_{j=1}^{N} r_j^L Y_{L0} \sigma_j^z$ were studied within the SRA and RPA [8, 9, 50, 51]. For $L = 1$ the operator $Q_1 \sim \sum_{j=1}^{N} z_j \sigma_j^z$ provides the opposite shifts of spin-up and spin-down electrons in z-direction. Unlike EL GR, the residual interaction for ML GR is defined only by the exchange and cor-

relations ((xc)-term) since only the (xc)-term depends on the magnetization density. In this connection, the study of ML resonances can provide a valuable information about (xc)-effects in clusters.

Approximating the electron density by the expression $n_0 = n_{00}/(1 + exp((r - R)/a)$ (the spill-out is effectively taken into account), one gets for the energy of the spin ML GR [9]

$$\omega_{ML} = \sqrt{\frac{m_3}{m_1}} = \hbar[\frac{2}{5}(2L+1)(L-1)\frac{\beta_F^2}{R^2} + \frac{e^2}{m}4\pi aL\frac{n_0}{R^{2L-1}} + \frac{1}{m}L(v_{xc}^{(02)}(n_0,m_0) - v_{xc}^{(20)}(n_0,m_0))\frac{n_0}{6aR}]^{1/2} \quad (8)$$

where $v_{xc}^{(pq)}(n_0,m_0) = \frac{d^p}{dn^p}\frac{d^q}{dm^q}v_{xc}^{(pq)}(n,m)\mid_{(n=n_0,m=m_0)}$. For other notation see Eq. 6. Due to the presence of the spin in the operator Q_L, the (xc)-term contributes to m_3, unlike the case of EL GR. However, the exchange contributions (Pauli principle) to v_{xc}^{20} and v_{xc}^{02} are the same and then, only correlations enter Eq. 8. The energies of spin ML resonances decrease with N and run to zero for large sizes. The larger L, the higher the GR energy. The behavior of spin ML GR much depends on the diffuseness parameter a.

Table 2 demonstrates that the restoring force for spin-multipole GR differs from the one for EL GR. Namely, the contribution of correlations [38] dominates for $L = 1$ and 2 and remains to be considerable for larger L. The correlation term includes long-range RPA correlations [76-78], short-range correlations [79] and others. The correlations greatly influence both static and dynamical characteristics of MC [37,38,76-78] and their investigation is very important.

Table 2: Relative contributions to m_3 for Na_{92} and Na_{912} : kinetic energy ($m_3(T)$), correlation ($m_3(c)$) and total Coulomb interaction ($m_3(C)$). The data are extracted from the Fig. 1 of Ref. [9].

	Na_{92}			Na_{912}		
L	$m_3(T)$	$m_3(c)$	$m_3(C)$	$m_3(T)$	$m_3(c)$	$m_3(C)$
1	0	0.77	0.23	0	0.30	0.70
2	0.50	0.49	0.01	0.31	0.68	0.01
5	0.76	0.20	0.04	0.59	0.38	0.03

9.2 Orbital GR

Since the number of atoms in MC can be much more than the number of nucleons in nuclei, much larger values of the single-particle orbital moment can be achieved. This can give the origin to very strong *orbital* ML GR. Clusters can exhibit the same orbital ML GR as in nuclei ("scissors", twist mode, etc.) but these GR can be much stronger [7, 80].

Investigations of the specific low-energy orbital M1 GR, which can exist only in *deformed* clusters, have shown that this GR can serve as a good indicator of the cluster quadrupole deformation [7,81-83]. Indeed, in some cases the deformation splitting of E1 GR is washed out by other effects and is not enough distinctive to get a reliable information on cluster deformation. Then the orbital M1 GR can be used for this aim. Macroscopically, this resonance is treated as small-angle rigid rotations of the ellipsoid of valence electrons against the ionic ellipsoid. Such collective mode was shown to be coupled with the quadrupole component, $\nabla(yz)$, of the displacement field [7, 81]. The orbital

Table 3: The excitation energy and strength (within the interval 0-1 eV) of orbital M1 GR, calculated within the SRPA [82, 83]. See the text for notation.

	Na_{15}^+	Na_{27}^+	Na_{35}^+	Na_{119}^+	Na_{295}^+
β_2	0.32	0.23	-0.23	0.25	0.24
ω_{M1}, eV	0.63	0.29	0.35	0.26	0.21
$B(M1), \mu_b^2$	27	56	41	229	757

M1 GR has the counterpart in deformed nuclei, well known as the "scissors" mode [84]. The latter describes the rotations of the neutron ellipsoid against the proton one. The orbital M1 GR is represented by $K^\pi = 1^+$ states (K is the angular-momentum projection) with a low excitation energy and strong M1 transitions to the ground state. For Na clusters these characteristics are estimated as [7, 81] $\omega_{M1} = 4.6\beta_2 N_e^{-1/3}(1 + 5\frac{\omega_0}{\omega_p})^{-1/2}$ eV and $B(M1) = 1.1\beta_2 N_e^{4/3}\mu_b^2$ where β_2 is the deformation parameter, $B(M1)$ is the reduced transition probability and ω_0 is the harmonic oscillator frequency. Both ω_{M1} and $B(M1)$ are proportional to the deformation parameter and so the orbital M1 GR survives only in deformed clusters.

The results of the realistic RPA calculations for orbital M1 GR [82, 83] are given in Table 3. It is seen that this resonance has low excitation energies. The most remarkable result is that already in clusters with about 300 atoms, the orbital M1 GR strength reaches very high values, 700-800 μ_b^2. This GR is described in detail in Ref. [83] of the present Proceedings.

10 Other GR in Atomic Clusters

As compared to nuclei, atomic clusters provide many specific manifestations of E1 GR. For example, clusters embedded in a dielectric matrix demonstrate a strong screening effect: the matrix screens the residual interaction between valence electrons in a cluster, which results in the considerable decrease of E1-energy [85]. In mixed and coated clusters the impurity (or coated) atoms much influence both the ground state and properties of E1 GR (see, e.g. Refs. [86-88]). In the fullerene C_{60}, two E1 GR are known as determined by weakly bonded π electrons and strongly bonded σ electrons (see, e.g. Ref. [89]).

^3He and ^4He clusters representing collections of fermions (^3He atoms) and bosons (^4He atoms), respectively, should be mentioned. In ^3He clusters just ^3He atoms (not valence electrons) form a mean field with quantum shells [59, 90, 91]. These clusters are characterized by strong surface effects. Unlike nuclei and MC, ^3He clusters represent the case of *one-component* Fermi-system and, so, have no E1 GR. At the same time, the study of other EL GR reveals new possibilities, for instance, the comparison of the GR properties in Fermi (^3He clusters) [92, 93] and Bose (^4He clusters) [94] systems.

Summary

Giant resonances in atomic clusters have been observed. Being much similar to their counterparts in atomic nuclei, GR in MC demonstrate, at the same time, numerous exciting peculiarities. The unique situation takes place now in many-body physics where, in addition to atoms and atomic nuclei, a new

family of small Fermi systems (MC, fullerenes, He^3 clusters, quantum dots) appears. This greatly enlarges our possibilities in many-body studies. All mentioned systems possess, in a different extent, a mean field with quantum shells.

It should be noted that atomic clusters are attractive both for fundamental studies and practical applications [95]. Last achievements (creation of new materials, machinning superhard surfaces, creation of extremely large energy densities in a matter, catalysis, microelectronics, microcomputering, etc.) show that, due to atomic clusters, one may expect in a recent future a remarkable progress in many high-tech fields.

Acknowledgments

We are grateful to M. Schmidt and H. Haberland for communication the experimental results. The work was also partly supported by CAPES (V.O.N.) and FINEP Brasil (V.O.N. and F.F.S.C.).

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Received by Publishing Department
on March 2, 1999.