Orbital magnetism in axially deformed sodium clusters: From scissors mode to dia-para magnetic anisotropy

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Abstract

Low-energy orbital magnetic dipole excitations, known as scissors mode (SM), are studied in alkali metal clusters. Subsequent dynamic and static effects are explored. The treatment is based on a self-consistent microscopic approach using the jellium approximation for the ionic background and the Kohn-Sham mean field for the electrons. The microscopic origin of SM and its main features (structure of the mode in light and medium clusters, separation into low- and high-energy plasmons, coupling high-energy M1 scissors and E2 quadrupole plasmons, contributions of shape isomers, etc) are discussed. The scissors M1 strength acquires large values with increasing cluster size. The mode is responsible for the van Vleck paramagnetism of spin-saturated clusters. Quantum shell effects induce a fragile interplay between Langevin diamagnetism and van Vleck paramagnetism and lead to a remarkable dia-para anisotropy in magnetic susceptibility of particular light clusters. Finally, several routes for observing the SM experimentally are discussed.
I. INTRODUCTION

This paper deals with orbital magnetism in metal clusters. Because of a possibly large number of atoms, the valence electrons may accede single-particle orbitals with very high angular momenta. The occupation of these orbitals has a large impact in cluster static magnetism [1, 2, 3] or in collective magnetic modes of orbital nature [1, 4, 5, 6]. Two remarkable examples are the scissors [1, 4, 5] and twist [6] modes. The scissors mode is strictly correlated with cluster deformation. It can be viewed as a small-amplitude rotational oscillation of a spheroid of valence electrons against a spheroid of the ionic background (hence the name SM).

The SM is a general dynamical phenomenon already found or predicted in different quantum finite systems. It was first proposed [7] and observed [8] in atomic nuclei where it still remains a hot topic for both experimental and theoretical studies (for a review see [9]). It was later predicted in a variety of different systems, like metal clusters [1, 4], quantum dots [10] and ultra-cold superfluid gas of fermionic atoms [11]. More remarkably, it was predicted [12] and observed [13] in a Bose-Einstein condensate. All these different systems have two features in common: The broken spherical symmetry and the two-component nature (neutrons and protons in nuclei, valence electrons and ions in atomic clusters, electrons and surrounding media in quantum dots, atoms and the trap in dilute Fermi gas and Bose condensate).

The SM strongly affects orbital magnetism in alkali metal clusters. It can be described in terms of Larmor diamagnetism and temperature-independent van Vleck paramagnetism [1, 2]. They are both weak and, therefore, need to be studied in systems, like alkali metal clusters, where strong forms of magnetism, like ferromagnetism, are absent. Being a low-energy mode, the SM determines the van Vleck paramagnetism and causes a strong anisotropy in the magnetic susceptibility [1, 14]. Moreover, some particular light clusters can exhibit dia-para anisotropy, being diamagnetic along the z symmetry axis and paramagnetic in x-, y-directions [14].

The SM has already been studied in schematic [1] and microscopic [4, 14, 15] approaches. The microscopic calculations, though accounting for quantum shells effects, were not fully self-consistent. A deformed Woods-Saxon [16], rather than a self-consistent Kohn-Sham, one-body potential was adopted. The quadrupole deformation was deduced from other
models or experimental estimates. Certainly, we need to perform fully self-consistent calculations based on density-functional theory in order to settle the subtle issues, like the fragile dia-para anisotropy, the role of the ionic structure, triaxiality, shape isomers, etc..

Self-consistent calculations, accounting for the ionic structure, were performed for spin-saturated ground and spin-polarized isomeric states of light sodium clusters Na\textsubscript{12} and Na\textsubscript{16}[5]. It was found that the scissors response remains determined basically by the global deformation, in spite of the fact that triaxiality and ionic structure induce a strong fragmentation in the strength. It was also shown that the detailed ionic structure destroys locally spherical symmetry thereby causing a finite, though very weak, M1 response (transverse optical mode) even in clusters with zero global deformation.

Calculations of the same level of completeness become prohibitive as one moves to heavier clusters. For this reason, we are forced to use in the present paper the Kohn-Sham approach with a soft jellium model for the ionic background [17]. This simplifies greatly the calculations and allows to proceed to heavier clusters. At the same time, the jellium approach is accurate enough for the principle problems considered here. The treatment of the electrons is fully self-consistent. We adopt a deformed Kohn-Sham mean field using the energy functional of [18]. The cluster shape (in terms of axial quadrupole and hexadecapole deformations) is determined by varying the jellium deformation and minimizing the total energy of the system. The optical response in the linear regime is calculated within the separable random-phase-approximation (SRPA) method [19, 20] self-consistently derived from the Kohn-Sham functional. The SRPA has been already successfully employed for the description of the dipole plasmon in spherical [21] and deformed [20, 22] alkali metal clusters.

In the present paper, we will consider both the optical M1 response and static magnetic orbital effects. In Section 2, macroscopic and microscopic treatments of the SM are briefly outlined. In Section 3 the calculation scheme is presented. The optical response is discussed in Sections 4 and 5. It will be shown that, in analogy with the electric dipole plasmon in deformed clusters [20, 22], the M1 response in light clusters has a distinctive profile determined by the deformation. Instead, due to a strong Landau damping and contributions of shape isomers, the response in medium clusters becomes vague and the SM can be viewed as a statistical mix of contributions from different cluster shapes. Besides, we discuss structure of the residual interaction and explain a small collective shift in SM excitations. The coupling between the high-energy SM branch and the electric quadrupole plasmon is demonstrated.
In Section 6, the dia-para anisotropy is discussed. In Section 7, we estimate perspectives to observe the SM in photo-absorption, Raman scattering and inelastic electron scattering. The conclusions are given in Section 8.

II. THE SCISSORS MODE: BRIEF OUTLINE

The macroscopic and microscopic treatment of the SM in clusters is discussed in detail in Refs. [1,4,5]. Thus, we give here only a brief outline for a better understanding of the results presented in the next sections.

In the geometrical model of [7], the SM arises from a rotational oscillations of valence electrons versus the ions, both assumed to form distinct spheroids (see left part of Fig. 1). Following the alternative view of [1] (right part of Fig. 1, the displacement field of the mode is a sum of the rigid rotation and a quadrupole term (the latter provides vanishing velocity of electrons at the surface):

$$u(r) = \Omega \times r + \delta_2 (1 + \delta_2/3)^{-1} \nabla(yz)$$

(1)

where \(\delta_2\) is the quadrupole deformation parameter (to be defined in the next section). In axially symmetric systems, the SM is generated by the orbital momentum fields \(L_x\) and \(L_y\) perpendicular to the symmetry axis \(z\), and it is characterized by the quantum numbers \(|\Lambda^\pi = 1^+ >\) where \(\Lambda\) is the eigenvalue of \(L_z\) and \(\pi\) is the space parity. Energy and magnetic strength of the mode can be estimated macroscopically [1,4]:

$$\omega = \frac{20.7}{r_s^2} N_e^{-1/3} \delta_2 \ eV,$$

(2)

$$B(M1) = \frac{4}{3} \langle 1^+ | \mathbf{\hat{L}}_x | 0 \rangle^2 \mu_b^2$$

$$= \frac{2}{3} N_e < r^2 > \omega \mu_b^2$$

$$\simeq N_e^{1/3} \delta_2 \mu_b^2$$

(3)

where \(N_e\) is the number of valence electrons and \(r_s\) the Wigner-Seitz radius. We use here natural units \(m_e = \hbar = c = 1\). The value \(B(M1)\) stands for summed strength of the degenerated x- and y-branches. The z-branch vanishes for symmetry reasons. It is worth noting that \(B(M1)\) does not depend on \(r_s\) and so is the same for different metals.
The microscopic treatment of the SM yields the shell structure of an axially deformed mean field. One can characterize the emerging single-electron states in terms of the quantum numbers of the axially deformed harmonic oscillator (Clemenger-Nilsson basis). These are the triplets \( \nu = [N_nz_\Lambda] \) where \( n_z \) labels the number of nodes in \( z \)-direction (=symmetry axis) and \( N \) is the principle shell number \( N = n_z + 2n_r + \Lambda \) (from which one can derive the number \( n_r \) of radial nodes). The angular momenta orthogonal to the symmetry axis, \( \hat{L}_x \) and \( \hat{L}_y \), promote low-energy \( \Delta N = 0 \) transitions inside the valence shell and high-energy \( \Delta N = 2 \) transitions across two shells. Moreover, one may expand wave functions in terms of the spherical basis \( (nL\Lambda) \)

\[
\Psi_{\nu=[N_nz_\Lambda]} = \sum_{nL} a_{nL}^\nu R_{nL}(r) Y_{L\Lambda}(\Omega).
\]

This allows to evaluate the single-particle orbital M1 transition amplitude between hole \((\nu = h)\) and particle \((\nu = p)\) states

\[
\langle \Psi_p | \hat{L}_x | \Psi_h \rangle \propto \delta_{\pi_p,\pi_h} \delta_{\Lambda_p,\Lambda_h \pm 1} \sum_{nL} a_{nL}^p a_{nL}^h \sqrt{L(L+1) - \Lambda_h (\Lambda_h \pm 1)}. \tag{5}
\]

Eq. (5) shows that the scissors mode is generated by \( \Lambda_p = \Lambda_h \pm 1 \) transitions between the components of one and the same spherical \((nL)\)-level. In spherical systems, \((nL\Lambda)\)-states belonging to the level \((nL)\) are degenerate while in deformed systems they exhibit the deformation splitting and so may be connected by M1 transitions with non-zero excitation energies. This is the origin of the scissors mode. The energy scale of the scissors mode is determined by the deformation energy splitting and so is rather small. This explains the predominantly low-energy \((\Delta N=0)\) character of the scissors mode. Just the low-energy branch carries most of the scissors \(B(M1)\) strength (see also discussion in Section [V]). The high-energy \((\Delta N=2)\) branch of the mode is much weaker since the particle states involved into \((\Delta N=2)\) transitions include only small \((nL)\)-components from the valence shell.

III. CALCULATION SCHEME

Our approach [20] employs the Kohn-Sham equations for the electronic mean field using actually the energy-density functional of [18]. The positive ionic background is modeled by
TABLE I: Ground state deformation parameters $\delta_2$ and $\delta_4$ and moments $\beta_2$ and $\beta_4$. For $\text{Na}_{55}^+$ and $\text{Na}_{119}^+$ the deformation parameters for the isomeric states together with their energy deficits $\Delta E$ are also given.

| Cluster  | $\delta_2$ | $\delta_4$ | $\beta_2$ | $\beta_4$ | $\Delta E$, eV |
|----------|------------|------------|-----------|-----------|----------------|
| $\text{Na}_{11}^+$ | 0.355 | 0.25 | 0.44 | 0.41 | - |
| $\text{Na}_{15}^+$ | 0.59 | -0.19 | 0.47 | -0.02 | - |
| $\text{Na}_{19}^+$ | -0.285 | -0.09 | -0.21 | -0.02 | - |
| $\text{Na}_{27}^+$ | 0.33 | 0.08 | 0.36 | 0.17 | - |
| $\text{Na}_{35}^+$ | -0.21 | 0.02 | -0.18 | 0.04 | - |
| $\text{Na}_{55}^+$ | 0.18 | -0.07 | 0.17 | -0.05 | - |
| $\text{Na}_{119}^+$ | -0.11 | -0.07 | -0.09 | -0.05 | 0.020 |
| $\text{Na}_{119}^+$ | -0.27 | -0.14 | -0.20 | -0.06 | - |
| $\text{Na}_{119}^+$ | 0.24 | -0.04 | 0.24 | ~ | 0.004 |
| $\text{Na}_{119}^+$ | -0.04 | -0.22 | -0.02 | -0.18 | 0.024 |

a soft jellium density

$$\rho_I(r) = \frac{\rho_{I0}}{1 + \exp((r - R(\theta))/\alpha)}$$ (6)

where quadrupole and hexadecapole axial deformations are introduced through the jellium radius as

$$R(\theta) = R_0 [1 + \delta_2 Y_{20}(\theta) + \delta_4 Y_{40}(\theta)].$$ (7)

The optimal deformation parameters $\delta_2$ and $\delta_4$ are determined by minimizing the total energy.

We consider the clusters $\text{Na}_{11}^+$, $\text{Na}_{15}^+$, $\text{Na}_{19}^+$, $\text{Na}_{27}^+$, $\text{Na}_{35}^+$, $\text{Na}_{55}^+$, and $\text{Na}_{119}^+$, which, according to jellium estimates [20, 22, 23, 24, 25, 26], exhibit axial deformations. These clusters represent a wide size region and, as shown in Table I, cover prolate ($\text{Na}_{11}^+$, $\text{Na}_{15}^+$, $\text{Na}_{27}^+$, $\text{Na}_{55}^+$) and oblate ($\text{Na}_{19}^+$, $\text{Na}_{35}^+$, $\text{Na}_{119}^+$) shapes in ground states. Moreover, few of them ($\text{Na}_{55}^+$ and $\text{Na}_{119}^+$) have shape isomers with a tiny energy deficit $\Delta E \sim 0.02$ eV [20, 22] and with quadrupole deformation of opposite sign with respect to the ground state. The largest sample $\text{Na}_{119}^+$ has also a hexadecapole isomer.
Table I also shows the multipole moments

$$\beta_\lambda = \frac{4\pi}{3} \int dr \rho_0(r) r^\lambda Y_\lambda^0, \quad \tilde{R} = \sqrt{\frac{5}{3} \int dr \rho_0(r) r^2}$$

where $\lambda = 2, 4$ and $\rho_0(r)$ is the ground state density of valence electrons. The dimensionless multipole moments $\beta_\lambda$ are less model dependent because they are computed from expectation values. Thus they can serve for robust characterization of the deformation and for comparison between different models. The quantities $\delta_\lambda$ in the jellium model [3] coincide with the $\beta_\lambda$ for small deformation.

The optical response is calculated in the framework of the random phase approximation (RPA). Full RPA for deformed systems is extremely involved. We employ a separable approximation of RPA where the residual interaction is expanded into a sum of separable terms [20]. The expansion employs local one-body operators $Q_{\lambda p}(r)$. Their structure is constructed as to map the response mean-field in RPA and the generating operators (to which response is explored) are chosen to cover the leading multipole operators. The expansion coefficients are computed self-consistently. It was shown that this procedure provides a sufficiently precise reproduction of the exact residual interaction [20]. In particular, for the description of the SM, we use the basis of generating operators

$$f_{21p} = r^{2+p}(Y_{21}(\theta) + Y_{21}^\dagger(\theta)), \quad p = 0, 2, 4,$$

$$f_{41p} = r^{4+p}(Y_{41}(\theta) + Y_{41}^\dagger(\theta)), \quad p = 0, 2.$$  

(9)

The same set of operators was used for the description of $\lambda \mu = 21$ branch of the quadrupole plasmon [20]. The close similarity between scissors and quadrupole fields was discussed in [4]. The $p = 0$ component of the input field $f_{210}$ has a form of the external quadrupole field in the long-wave approximation. It generates the main piece of the separable interaction, peaked at the surface of the system. The next two quadrupole fields ($p = 2$ and $4$) result in the separable operators $Q_{21p}(r)$ peaked in more interior of the cluster. We include also hexadecapole fields $f_{41p}$ in order to account for coupling between quadrupole and hexadecapole modes, arising with the onset of deformation, especially in systems having both quadrupole and hexadecapole deformations. The set of the fields [9] ensures good convergence of the separable expansion to exact results. Explicit expressions for $Q_{\lambda p}(r)$ are given in [20].

We study the SM response in terms of photo-absorption. In axially deformed systems, the photo-absorption cross-section from the ground state to the excited state $j = \Lambda^\pi$ of
excitation energy $\omega_j$ is

$$\sigma(X\lambda\mu, gs \to j) = \frac{8\pi^3\lambda+1}{\lambda[(2\lambda+1)!!]^2} \frac{(\omega_j)^{2\lambda-1}}{\hbar c} |< j|\hat{O}_{\lambda\mu}^X|gs >|^2$$

where $< j|\hat{O}_{\lambda\mu}^X|gs >$ is the reduced transition matrix element and $\hat{O}_{\lambda\mu}^X$ is the operator of electric ($X = E$) or magnetic ($X = M$) transition. For the scissors mode, we have $\hat{O}_{11}^M = \hat{l}_x$ (in Bohr magnetons $\mu_B$). The selections rules are $\mu = \Lambda$ and $(-1)^{\lambda} = \pi$ for ($X = E$) or $(-1)^{\lambda+1} = \pi$ for ($X = M$). The electric photo-absorption strength ([10] will be used in Section VII for estimation of the competition between the scissors and low-energy electric excitations.

Useful measures for the SM are provided by the sum rules

$$S_m(M1) = \sum_j \omega_j^m B(M1)_j$$

for $m = -1, 0, 1$. The ratios $\omega = \sqrt{S_1/S_{-1}}$ or $\omega = S_1/S_0$ provide a rough energy centroid of the low-energy mode. The $S_{-1}$ is proportional to the paramagnetic susceptibility and $S_1$ to the integral photo-absorption cross section. The detailed values for the $S_m$ are obtained from explicit RPA results. A simple estimate for $S_1$ can be obtained using Eqs. (2) and (4):

$$S_1(M1) = \sum_j \omega_j B(M1)_j = \frac{20.7}{r^2} N_e \delta^2_2 \mu^2_b.$$

Sum rules do exist also for electric excitations where they can be reduced to the simple expressions [19]

$$S_1(E\lambda) = \sum_j \omega_j |< j|e^{r\lambda}Y_{\lambda\mu}|gs >|^2$$

$$= \frac{\hbar^2 e^2}{8\pi m_e} \lambda(2\lambda + 1)^2 N_e < r^{2\lambda-2} > .$$

### IV. SCISSORS RESPONSE

The M1 optical responses in light clusters are shown in Fig. 2. The present Kohn-Sham calculations yield results close to the ones obtained by using a deformed Woods Saxon potential [4]. Only the excitation energies in prolate clusters are ~ 0.2 eV higher, because of the larger quadrupole deformations obtained in the self-consistent approach. The main characteristic of the M1 response is the occurrence of one or two prominent peaks below 1
TABLE II: Sum rules $S_m$ (in eV$^m \mu_\lambda^2$) calculated in the energy region 0-6 eV. The fractions for the region 0-1 eV are given in parenthesis.

| Cluster | $S_{-1}$ | $S_0$ | $S_1$ |
|---------|----------|------|------|
| Na$^{+}_{11}$ | 16.5 (92%) | 14.7 (72%) | 21.5 (34%) |
| Na$^{+}_{15}$ | 18.7 (84%) | 19.2 (69%) | 25.9 (43%) |
| Na$^{+}_{19}$ | 11.3 (98%) | 8.2 (90%) | 7.4 (67%) |
| Na$^{+}_{27}$ | 80.6 (96%) | 35.6 (74%) | 37.7 (25%) |
| Na$^{+}_{35}$ | 38.9 (97%) | 17.2 (84%) | 13.3 (43%) |
| Na$^{+}_{55}$ | 94.9 (97%) | 32.6 (78%) | 30.2 (26%) |
| Na$^{+}_{119}$ | 544 (97%) | 138 (80%) | 103 (36%) |

eV. They are only slightly shifted from their unperturbed 1ph (particle-hole) spectrum. In the low-energy region, the 1ph $|\Lambda^\pi = 1^+ >$ spectrum is very dilute and, therefore, does not meet the conditions for Landau fragmentation or for pronounced coherent superpositions. Because of these features, the low-energy scissors strength can be associated to well defined 1ph transitions. In the Nilsson-Clemenger notation $[Nn,\Lambda]$, they are $[110] \rightarrow [101]$ in Na$^{+}_{11}$, $[211] \rightarrow [202]$ and $[211] \rightarrow [200]$ in Na$^{+}_{15}$, $[211] \rightarrow [220]$ in Na$^{+}_{19}$, $[321] \rightarrow [310]$ and $[321] \rightarrow [312]$ in Na$^{+}_{27}$, $[310] \rightarrow [321]$ and $[312] \rightarrow [321]$ in Na$^{+}_{35}$.

As shown in Fig. 2 (compare full and dashed lines), the residual interaction induces a rather moderate blue-shift that is much smaller than e.g. the shift for the electric dipole plasmon. The underlying physics is explained in Fig. 3 where the exchange-correlations and Coulomb contributions to the leading part of the separable operator $Q_{211}(\mathbf{r})$ are presented for the case of Na$^{+}_{19}$ (the repulsive Coulomb is negative in this representation). It is seen that both contributions compensate each other to a large extent. The final outcome is a slight repulsive interaction responsible for the blueshift. It is worth noting that the balance between these two contributions is rather fragile and can be affected by different factors, e.g. triaxiality and detailed ionic structure, making even the sign of the net interaction uncertain [5].

Table II collects summed scissors strengths in wide- (0-6 eV) and low-energy (0-1 eV) regions, calculated within the SRPA. It is seen that the $\Delta N = 0$ low-energy scissors mode, being mainly concentrated below 1 eV, contributes strongly to $S_{-1}$ and $S_0$. This justifies
using $S_{-1}$ and $S_0$ for a rough estimation of the energy of the mode as $\omega = \sqrt{S_1/S_{-1}}$ (or $\omega = S_1/S_0$). Besides, since $S_{-1}$ is proportional to the paramagnetic susceptibility, this means that just the low-energy SM determines the van Vleck paramagnetism (see discussion in Section VI). The high-energy part of the scissors strength (associated with $\Delta N = 2$ transitions) contributes appreciably to the $S_1$ sum rule, i.e. to the total photo-absorption cross section. Table II also shows that the increase of the $S_m$ with cluster size is not monotonous. The fluctuations are caused by the predominantly 1ph character of the low-energy SM and by the difference in cluster deformations. Na$_{27}^+$ demonstrates especially strong M1 strength, while in oblate clusters Na$_{19}^+$ and Na$_{35}^+$ the strength is relatively weak.

Fig. 4 illustrates the coupling of the high-energy scissors branch to the quadrupole plasmon in Na$_{55}^+$. The correlation between M1 and E2 peaks at $\sim 3$ eV is clearly seen. The coupling of electric and magnetic modes with the same quantum numbers $\Lambda^\pi$ is a general feature of deformed finite quantum systems. It is well known, for example, in atomic nuclei (see, e.g. [9, 27]).

The coupling of the SM with dipole and spin-dipole oscillations in clusters was discussed in detail in Ref. [5]. In particular, it was shown that breaking the symmetry by the ionic lattice results in a weak coupling between these oscillations of opposite space parity. This feature may change for clusters deposited on a surface since symmetry breaking is much stronger there.

V. EFFECTS OF SHAPE ISOMERS AND IONIC STRUCTURE

The calculations [20, 22] show that light axially deformed clusters ($N_e < 40$) have at the deformation-energy surface one distinct minimum corresponding to the ground-state deformation. The heavier clusters ($40 < N_e < 100$) have usually two minima with opposite quadrupole deformations (prolate and oblate) and very close energies. The energy difference between the ground and the shape isomeric states is often less than 0.02 eV = 200 K. The number of shape isomers with a tiny energy deficit increases with cluster size. These isomers may have a variety of very different shapes. And significant amounts of isomers can be found in a thermal ensemble and thus contribute to the SM, e.g., at room temperature.

Fig. 5 compares the scissors modes built on the ground and isomeric states in Na$_{55}^+$. Both of them show a rich spectrum of low lying M1 states. But the spectra and typical...
strengths of the two states differ substantially. Indeed, the M1 spectra are generated by several 1ph M1 transitions between the levels lying in the vicinity of the Fermi surface. Prolate and oblate shapes yield different sequences of the single-particle levels just at the Fermi surface. As a result, some of the 1ph M1 transitions which are significant in the prolate case are transformed to 1pp or 1hh transitions in the oblate case, thus strongly decreasing the strength.

Fig. 5 compares also the SRPA results obtained with soft jellium model \((3)\) and detailed ionic structure \([5]\). In the case of the ionic structure, the global cluster deformations slightly deviate from those in the jellium case. It is seen that calculations with the ionic structure give somewhat different positions of the SM peaks with respect to the jellium case. Such a redistribution of the peaks is due to different energies of the single-particle levels in the ionic calculations. The photo-absorption response in the ionic case is stronger, which is also explained by the redistribution of the levels in the mean field. The level sequence in this case favors a few more 1ph transitions of M1 type.

Altogether, the calculations demonstrate some important points concerning the SM in medium clusters:

i) The mode is distributed over several 1ph transitions.

ii) The single particle spectrum near the Fermi level is rather dense and so even small changes in the calculation scheme can redistribute visibly the spectrum and open (or close) some relevant 1ph transitions.

iii) As was mentioned above, the ground and first isomeric states in medium clusters can be very close in energy. So, the scissors mode in free medium clusters should be considered as a statistical mixture of contributions from different shapes (predominantly of the ground state and first isomer). Such kind of the analysis (involving the deformation splitting, Landau fragmentation and contributions of shape isomers) was recently applied to explain experimental E1 optical response in deformed sodium clusters with \(50 < N_e < 60 \) \([22]\). Less ambiguous deformations will be provided by the SM in metal clusters deposited on insulating substrates \([28]\). These clusters are oblate and their mean size and magnitude of the deformation can be well controlled. Such clusters seem to be the most promising systems for experimental search of the SM.
VI. MAGNETIC ANISOTROPY

RPA calculations show that the SM energies and B(M1) strengths scale with the deformation $\delta_2$ and the electron number $N_e$ basically according to the trends (3) and (4). Strong fluctuations, however, take place in small clusters [4]. They reflect the $1p\hbar$ nature of the transitions and may affect the magnetic susceptibility.

The total orbital magnetic susceptibility in clusters is the sum of Langevin diamagnetic and van Vleck paramagnetic terms [1, 2]:

$$\chi_k = \chi_k^{dia} + \chi_k^{para},$$

where

$$\chi_k^{dia} = -\mu_b^2 N_e < \rho^2_k > = -\mu_b^2 \Theta^R_k,$$

$$\chi_k^{para} = 2\mu_b^2 \sum_j \frac{|< j|\hat{L}_k|0 >|^2}{\omega_j} = \mu_b^2 \Theta_k,$$

having denoted by

$$\Theta_k = 2 \sum_j \frac{|< j|\hat{L}_k|0 >|^2}{\omega_j}$$

the moment of inertia and by

$$\Theta^R_k = N_e < \rho^2_k >$$

its rigid-body value. The sum in (14) and (17) runs over excited states. Further, $k = x, y, z$ is the coordinate index. In axial systems, one has $\rho^2_z = 2 < x^2 >$ and $\rho^2_{x,y} = < x^2 > + < z^2 >$.

Note that for $k = x, y$ the operator entering in the matrix element in (14) is exactly the scissors generator. This makes evident that just the low-energy SM mainly contributes to $\chi_{x,y}^{para}$. Indeed Table II shows that contribution of the low-energy scissors mode to the value $S_{-1} \sim \chi_{x,y}^{para}$ achieves 85 – 100%. So, just the SM determines the van Vleck paramagnetism.

In the schematic model [1], the moment of inertia comes out as the rigid-body value, so that $\theta_{x,y} = \theta^R_{x,y}$ and, therefore, $\chi_{x,y}^{para} = -\chi_{x,y}^{dia}$, i.e. a complete compensation of dia- and para-magnetic terms in $\chi_{x,y}$ takes place. Due to axial symmetry, one also has $\chi_{x,y}^{para} = 0$.

The total susceptibility becomes, therefore, strictly anisotropic [1]

$$\chi_x = \chi_y = 0, \quad \chi_z = \chi_z^{dia},$$

going from zero to diamagnetic values.
On the other hand, strong shell effects in some peculiar light clusters may alter appreciably the above result. This is illustrated for $\text{Na}_{27}^+$ in Fig. 6. Because of very low excitation energy of the SM in this cluster (see an exceptionally large value of $S_{-1}$ for $\text{Na}_{27}^+$ in Fig. 2 and, also, in Table II, the paramagnetic susceptibility is enhanced considerably and is no longer balanced by the diamagnetic term. So, $\text{Na}_{27}^+$ should be paramagnetic in x,y-directions and diamagnetic in z-direction. The cluster $\text{Na}_{11}^+$ also hints this property. The magnetic moments in $\text{Na}_{27}^+$ are sufficiently large to allow for a measurement of the dia-para anisotropy. The observation of this effect would provide a strong (though indirect) evidence of the SM in clusters.

VII. EXPERIMENTAL PERSPECTIVES

A. General analysis

As was mentioned in the Introduction, the SM is not yet observed experimentally in metal clusters. The search of the SM is hindered by several factors:

1) The mode has very low photo-absorption cross section. Following our results, in sodium clusters with $N_e \simeq 10 - 10^2$, $\sigma(M1)/N_e \simeq 10^{-5} - 10^{-7} \AA^2$ as compared to $\sigma(E1)/N_e \simeq 2 \AA^2$ for the dipole plasmon. Such a weak M1 signal is at the edge of the sensitivity of modern detectors.

2) Eqs. (10)-(13) allow to estimate the ratios for maximal optical responses as

$$\frac{\sigma(E1)}{\sigma(M1)} = 0.35 \cdot 10^5 \AA^{-2} \left( \frac{r_s}{\delta_2} \right)^2 (20)$$

and (for $\omega_{E2} \simeq 3$ eV [19, 20])

$$\frac{\sigma(E2)}{\sigma(M1)} = 0.82 \cdot 10^{-2} \AA^{-4} \left( \frac{r_s^2}{\delta_2} \right)^2 N_e^{2/3} . (21)$$

This gives for deformed ($\delta_2 = 0.2$) sodium ($r_s = 2.1 \AA$) clusters $\sigma(E1)/\sigma(M1) \simeq 4 \cdot 10^6$ and $\sigma(E2)/\sigma(M1) \simeq 10^2$ (the latter for $N_e = 125$). So, the SM suffers from the competition with E1 and E2 strengths. Besides, the competition with E2 increases with cluster size. The above estimates compare the SM optical response with the maximal responses of E1 and E2 plasmons. As is shown in the next subsection, the competition is much weaker in the low-energy region where the SM has its stronghold, but one has still to be aware of large amounts of E1 strength.
3) The low-energy scissors mode lies in the infrared region where commonly used detectors for a visible light are not efficient enough.

4) The SM energy decreases with cluster size and reaches the region of phonon excitations, \( \sim 0.1 \text{eV} \), in very big clusters.

In spite of these hindrances, clusters offer enough opportunities to look for the optimal conditions for observing the SM: one may change cluster size and (or) deformation, use different metals, choose between free and supported clusters, etc. The macroscopic estimates (2)-(4) and the present jellium RPA calculations may serve as a guide. Such analysis is briefly given below. To this purpose, we consider, as a typical case, sodium clusters with a moderate deformation \( \delta_2 = 0.2 \).

Larger clusters help because the M1 photo-absorption cross section grows linearly with the size. Already in deformed clusters with \( N_e = 10^4 - 10^6 \) the scissors signal should be detectable. Unfortunately, the corresponding energy \( \omega \simeq 0.1 - 0.01 \text{eV} \) approaches or even covers the region of phonon excitations. Thus the best compromise for free sodium clusters is achieved at \( N_e \sim 10^3 \). Besides that, these clusters are large enough to ensure the dominance of the orbital scissors mode over spin M1 excitations.

We may also look for clusters of larger density and deformation to increase the energy and the strength of the mode. For example, Li clusters \( (r_s = 1.7 \text{ Å}) \) allow to increase both the energy and optical response by a factor of \( \sim 1.5 \) with respect to Na \( (r_s = 2.1 \text{ Å}) \). Further improvement may be achieved with Ag \( (r_s = 1.6 \text{ Å}) \), Mg \( (r_s = 1.4 \text{ Å}) \), or Al \( (r_s = 1.1 \text{ Å}) \). In any case, highly deformed clusters are welcome because \( \sigma(M1) \sim \delta_2^2 \) and \( \omega \sim \delta_2 \).

In general, free clusters seem not suitable for observing the SM. They are well mass-separated only up to sizes of hundred atoms. However, these systems have a weak M1 signal. As for heavier clusters, they suffer from a poor mass separation and are expected to be weakly deformed \[26\]. Moreover, as was discussed in Section \[VI\], their M1 signal is a statistical mix of contributions of different shapes given by the ground state and isomers.

Deposited clusters look more promising. One can adopt techniques that allow to get oblate clusters (Na and Ag) on dielectric surfaces \[28\] and, more remarkably, to monitor their size and deformation. Clusters with \( 10^2 - 10^6 \) atoms can be used for this aim. In this way, one can obtain supported clusters of a desired size and shape. High density of clusters on the surface gives good statistics in the measurements. Last but not least, monitoring the shape of clusters gives the chance to use the trends \( \sigma(M1) \sim \delta_2^2 \) and \( \omega_{M1} \sim \delta_2 \) to
distinguish the SM from the E1 and E2 signals. To this end, one has to irradiate clusters of
the same size but of different deformations. Then the low-energy E1 and E2 cross sections
are also affected but, hopefully, in an irregular fashion (thus averaging out) or, at least, in
a way different from the trends mentioned above. The cross sections measured at different
deformations can be mutually subtracted to extract a small useful signal. For the analysis of
such experiments, we need accurate theoretical estimates accounting for all the main factors
and, in particular, the influence of the surface on the electric and scissors plasmons. Such
work is in progress.

The competition with E1 and E2 modes may be bypassed partly by resorting to specific
reactions and techniques capable of hindering if not suppressing the E1 and E2 channels.
We will discuss this issue for three relevant reactions: photo-absorption, resonance Raman
scattering, and inelastic electron scattering.

B. Photo-absorption

The SM lies much lower than the dipole and quadrupole plasmon modes (0.2-1.0 eV
against 2.5-3.0 eV for the dipole and 2-4 eV for the quadrupole [19, 20]). In principle, one
could exploit this energy separation to focus on the SM. However, its M1 photo-absorption
cross section is still very small as compared to the E1 strength and can be masked by the
tail of close E1 modes. This is illustrated in Fig. 7 which compares E1, E2 and M1 photo-
absorption strengths calculated within SRPA approach[20] in axially deformed Na$^{+}_{119}$ (ground
state). The E1 strength, though extremely small compared to the dipole plasmon peak, is
still strong enough to mask the SM. The competition with the quadrupole E2 strength in
Na$^{+}_{119}$ is negligible (though it can be stronger in heavier clusters).

The competition with the E1 channel can be decreased by using deformed (oblate) clusters
with $N \simeq 10^3 - 10^4$ atoms, supported on dielectric surfaces, and adopting infrared techniques
with polarized light. For the SM, the magnetic field of the incoming light should be parallel
to the surface. This can be done with both s- and p-polarizations (with the electrical field
to be perpendicular and parallel to the incident plane, respectively). The s-polarized light
under an angle $\sim 0^\circ$ with the surface normal suppresses the $\mu = 0$ E1 branch without
weakening the SM. The p-polarized light at angle $\sim 90^\circ$ suppresses the $\mu = 1$ E1 branch,
again without weakening the SM. The second variant seems to be preferable since the $\mu = 1$
branch is generally stronger (see, e.g., Fig. 7.

C. Resonant Raman scattering

In resonance Raman scattering (inelastic scattering of polarized photons), the SM may be populated through the de-excitation of the dipole plasmon excited by the incoming photon. The difference between energies of incoming and outgoing photons gives the energy of the mode. One must look at E1 decays, which represent the leading channel and may populate in deformed systems M1 as well as E2 states. With respect to photo-absorption, resonance Raman scattering has the advantage of excluding the competition with the strong E1 mode and to work in the visible light region. An experiment of this kind was carried out in supported Ag clusters [29]. The analysis of the data suggested, however, that the E2 rather than the SM was populated through the E1 decay. On the other hand, it is not simple to separate clearly the E2 from the M1 modes which are mixed in deformed systems.

D. Inelastic electron scattering

Inelastic electron scattering is also a promising technique. At backward scattering angles, the M1 signal should prevail over the electric ones. This property enabled the discovery of the scissors mode in deformed atomic nuclei [8]. Polarization of the electrons provides additional possibilities to extract the magnetic response. In nuclear physics, electrons with very high energies (tens and hundreds MeV) are used, which favors creation of well collimated, intense and monochromatic electron beams. Moreover, at so high energies, it is easier to enhance the relative contribution of the transverse form factor.

The low-energy, intense and monochromatic electron beams, suitable for our purpose, as well as the angular resolved techniques are now available [30]. To our knowledge, however, inelastic electron scattering was used so far only to observe the dipole plasmon. Theoretical estimates [31] show that at certain scattering angles the dipole contribution can be well suppressed in favor of the quadrupole plasmon, which, therefore, can be observed. From the latter analysis, we may infer that also the SM may be extracted. Indeed, in the low-energy region the SM can be stronger excite in the photo-absorption than the E2 mode. The analogy with atomic nuclei suggests that it should be favored even more in electron
VIII. CONCLUSIONS

The scissors mode (SM) in axially deformed sodium clusters has been studied within a self-consistent RPA approach based on the soft jellium model for the ionic background and density-functional theory for the electrons. The calculations show that the distribution of the low-energy scissors strength is dominated by $1ph$ states with only small shifts by the residual interaction. The SM thus reflects almost directly the density of $1ph$ M1 transitions near the Fermi surface and exhibits an extreme sensitivity to the actual deformation. The SM is rather unambiguous in light clusters ($N_e < 40$) while it should be a statistical mix of contributions from different shapes in heavier clusters. Furthermore, the high-energy branch of the SM in deformed systems is coupled with the quadrupole plasmon.

The calculations show that the SM determines the Van Vleck paramagnetism and results in a strong anisotropy of the magnetic susceptibility. Moreover, due to quantum shell effects, some clusters (Na$_{27}^+$) demonstrate dia-para anisotropy when the axial cluster is diamagnetic along the symmetry axis and paramagnetic along other two axes. The magnetic moments are large enough to be measured. The experimental observation of the dia-para anisotropy, being interesting itself, could also serve as an indirect evidence of the SM in clusters.

A general analysis of possible routes for experimental observation of the scissors mode was done. The photo-absorption with a polarized light, inelastic electron scattering and Raman scattering were considered. The former two reactions seem to be more promising. Moreover, deposited clusters favor the detection of the SM. Its features need yet to be worked out in detail. Work along that direction is in progress.

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FIGURE CAPTIONS

Figure 1: Macroscopic view of scissors mode: rigid rotation $\mathbb{R}$ (left), and rotation within a rigid surface $\mathbb{R}$ (right).

Figure 2: Photo-absorption cross-section for the scissors mode, weighted by the Lorentz function with the averaging parameter 0.25 eV. The responses with (solid curve) and without (dashed curve) the residual interaction are presented.

Figure 3: Radial profile of the residual interaction in Na$_{19}^+$. Exchange-correlation (long-dashed curve) and Coulomb (shot-dashed curve) contributions are given together with their sum (solid curve).

Figure 4: Coupling between the high-energy scissors branch and E2 quadrupole plasmon in prolate Na$_{55}^+$. M1 and E2 photo-absorptions are weighted by the Lorentz function with the averaging parameter 0.25 eV.

Figure 5: The strength distribution of the scissors modes in Na$_{55}^+$, built on the prolate ground state (upper panel) and oblate first isomer (lower panel). Jellium (solid curve) and ionic (dashed curve) SRPA results are compared.

Figure 6: Normalized diamagnetic, paramagnetic and summed moments $\mu = \chi B \ (B = 4T)$ in axial deformed clusters Na$_{11}^+$, Na$_{15}^+$, Na$_{19}^+$, Na$_{27}^+$, Na$_{35}^+$, Na$_{55}^+$ and Na$_{119}^+$. 

Figure 7: Photo-absorption E1, E2 and scissors cross sections in Na$_{119}^+$ weighted by the Lorentz function with the averaging parameter 0.25 eV. The E1 $\mu = 0$ and 1 branches are given separately to show their relative contributions to the competition with the scissors mode.
\[ Q_{21} \text{ [arb. un.]} \]

\[ r \text{ [Å]} \]

- **Coulomb Part**
- **Exchange-Corr. Part**
- **Total**

\[ \text{Na}_{19}^+ \]
