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Optical response of metal microclusters: Atomic analog of the giant dipole resonance in nuclei

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From the analogy between the collective vibrations of delocalized electrons against the positive charged background provided by the ions in small metal clusters and the vibrations of protons against neutrons (giant dipole resonance) in nuclei, it is possible to formulate a model for the damping mechanism of plasma oscillations that exhibits an interesting correspondence between atomic and nuclear statistical processes.

A fundamental question of solid-state physics may be stated as follows: How do the properties of a solid gradually evolve as atoms are brought together to form increasingly larger units? In particular, how many metal atoms are required to form a cluster that has metallic properties?[1]

To address this question, we note that a characteristic property of a metal is its optical response, i.e., its interaction with light. A single Li atom has a very simple absorption spectrum: It consists essentially of one line in the visible. This line can be well described as a one-electron transition from the $2s$ state to a $2p$ state. A lithium crystal, on the other hand, has a completely different absorption spectrum. The absorption is strong in the far-infrared, goes through a minimum in the visible, and then rises again in the ultraviolet. The reason for this behavior is that very-low-energy photons can excite electrons from the continuum of states just below the Fermi energy to states just above it. The strong ultraviolet absorption is caused by interband transitions.

Suppose one chips off a small corner of the crystal, producing a microcrystal (metal cluster) that contains 50 atoms only. Again, the absorption spectrum is fundamentally altered: A relatively broad absorption region appears in the visible. This absorption is due to a collective excitation of delocalized valence electrons, namely, a plasma excitation. The Li bulk crystal also exhibits plasma excitations. However, in the bulk crystal, these modes have a purely longitudinal character and thus do not couple to transverse light waves. In the microcrystal, one can consider the plasmon as a collective sloshing motion of the electrons from one side of the microcrystal to the other side. Such a motion has a strong dipole moment, thus giving rise to the strong absorption band in the visible.

The absorption of light by a Li atom is well described within the one-electron picture. However, even qualitatively, this picture cannot account for the plasma excitations that dominate the optical response of a 50-atom cluster. Between the case of a few atoms (≤ 5) to the case of 50 atoms, there is a qualitative change in the physics of the optical response. The study of metal clusters offers a laboratory for the understanding of this change.

In this quest, the analogies pioneered by Knight and collaborators[3–6] that can be drawn between a metal cluster and an atomic nucleus can be used with profit (cf. Table I). In particular, in the study of the properties of the surface plasmon[7–11] which in nuclei has its counterpart in the giant dipole resonance known now for over forty years (cf., e.g., Ref. 12).

When one shines nuclei or metal microclusters with a source of photons of variable frequency, one observes for a given range of energies, typically around 15 MeV and 2 eV, respectively, that the amount of energy absorbed by the system grows markedly. Since the associated wavelengths of the electric fields acting on the systems under consideration are much larger than the size of these systems, the charged particles see a nearly uniform field. Consequently, the observed resonances are of a dipole character having negative parity.

In the nuclear case, the electric field exerts a force on the positively charged protons, moving them away from the neutrons. Since the center of mass of the nucleus remains at rest, neutrons, although electrically neutral, are forced to move in the opposite direction. Thus, nuclear photoresonances are isovector excitations, that is, excitations in which protons and neutrons move with opposite phases. A similar situation is found in the dipole vibration of small metallic clusters, where the electrons move out of phase with respect to the positive inert ionic background.

TABLE I. Schematic dictionary bridging some aspects of the physics associated with atomic nuclei with corresponding aspects of the physics of metal microclusters (the case of Na_8 which is reasonably well described by the one-pole, surface-plasmon approximation is displayed). Both systems display a marked resonance to a beam of photons of variable energy, as shown at the top of the table. From the wavelength of the radiation and from the radius of the systems—which depends on the mass number A in the nuclear case and on the number N_e of delocalized electrons in the cluster—one can conclude that the electric field associated with the absorbed photons is uniform over the entire volume. Thus only the dipole modes are excited; they are known as giant pole resonances in the nuclear case, and as surface plasmons in the cluster case. Making use of the Thomas-Reiche-Kuhn (S_1) and of the static polarizability (S_{-1}) sum rules, it is possible to approximately calculate the energy centroid $\hbar\omega_D$ of the dipole vibration. The coupling of the vibration to quadrupole deformations of the surface leads to a spread in frequencies that is controlled by the deformation parameter $\delta = \Delta R/R$, where ΔR is the difference between the major and minor radii of the spheroid. Such a spread in frequency is also operative in spherical systems, due to the fluctuations of the surface around the equilibrium position. The small quadrupole fluctuations around the local Hartree-Fock configuration are present both at zero as well as at finite temperature, since they are quantal in character. At finite temperature, the surface also displays large amplitude thermal fluctuations.

GIANT DIPOLE RESONANCE

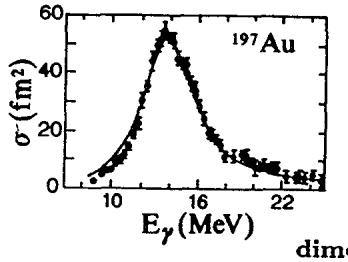
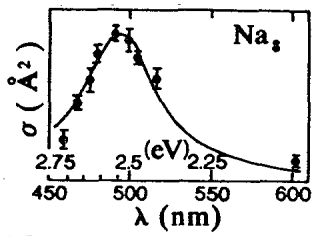
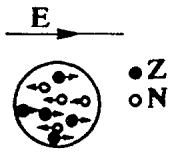
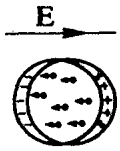
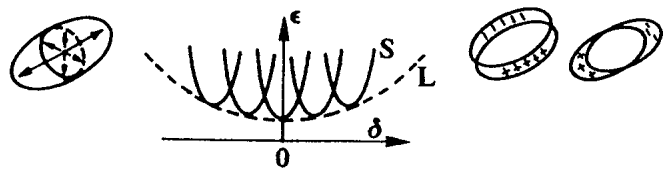
NUCLEI	CLUSTERS
	
dimensions	
$R = r_0 A^{1/3};\ A = N + Z$	$R = r_s N_e^{1/3}$
$(r_0 \approx 1.2\, fm)$	$(r_s = 4a_0 \approx 2\text{Å})\ (Na)$
wavelength	
$\frac{\lambda}{R} = \frac{2\pi c}{R\omega_D}$	
$10\ (\hbar\omega_D \sim 15\, MeV)$	$500\ (\hbar\omega_D \sim 2.5\, eV)$
γ-ray	visible
uniform electric field (dipole)	
	
centroid	
$\hbar\omega_D = (S_1/S_{-1})^{1/2}$	
$\frac{100}{R}\ MeV$	$\left(\frac{\hbar^2 e^2}{m_e r_s^3}\right)^{1/2} \left(1 - \frac{3}{2}\frac{t}{R}\right)$
relaxation (beyond mean field)	
coupling to surface quadrupole ($(2^+ \otimes 1^-)1^-$)	
$\omega_\kappa \approx \frac{100}{\hbar R_\kappa}$	$\omega_\kappa \approx \left(\frac{N_e e^2}{m_e \alpha_\kappa}\right)^{1/2}$
$\approx \omega_D \times \begin{cases} (1 - \frac{2}{3}\delta)\ (\kappa = 3) \\ (1 + \frac{1}{3}\delta)\ (\kappa = 1, 2) \end{cases}$	$\approx \omega_D \times \begin{cases} (1 - \frac{2}{5}\delta)\ (\kappa = 3) \\ (1 + \frac{1}{5}\delta)\ (\kappa = 1, 2) \end{cases}$

TABLE I. (*Continued*).



$$\frac{\Delta\omega}{\omega_D} = -b\,\frac{\Delta R}{R} = b\delta$$

$b = 1$ $\qquad$ $b = 0.6$

small amplitude fluctuations

$$\frac{\Gamma_Q}{\hbar\omega_D} \sim 1.7\left(\frac{\hbar\omega_2}{2C_2^S}\right)^{1/2} b$$

0.25 $\qquad$ 0.004

large amplitude fluctuations

$$\frac{\Gamma_T}{\hbar\omega_D} \sim 1.7\left(\frac{T}{C_2^f}\right)^{1/2} b$$

0.3 $\qquad$ 0.1

$$\Gamma_{tot}/\hbar\omega_D$$

0.4 $\qquad$ 0.1

The integrated photoabsorption cross section in both nuclei and metal clusters is found to be proportional to the total number of relevant charged particles in the system (protons and delocalized electrons, respectively), implying the collective response of the system. For this reason, it is natural that these modes are known, in the nuclear case, as (isovector) giant dipole resonances (GDR).

The centroid of these resonances can be calculated making use of the Thomas-Reiche-Kuhn and of the polarizability sum rules. In the nuclear case, the resulting frequencies are inversely proportional to the different lengths of the principal axes of the nuclear droplet, whose most general shape can be triaxial, namely ellipsoidal (the most common nuclear case of axially symmetric, spheroidal average shape, as well as the fully spherical one, result as special cases of the ellipsoidal). This result, which is borne out in detail by the experimental findings, has also important consequences for the damping width of the GDR.[13,14] As befitted a finite system, the nuclear surface fluctuates. The coupling of these fluctuations to the GDR leads to a spread in frequency, as they change the principal dimensions of the system (while maintaining a constant volume) and thus explore the variety of deformations around the average shape. Decomposing the surface fluctuations into multipoles, it is easy to see that quadrupole fluctuations play a central role in the coupling. In fact, states with spin and parity 2^+ are the only ones that can directly couple with the GDR to total spin and parity 1^-. Such couplings account for a large fraction of the observed damping widths, which are typically a factor of 2–3 times smaller than the centroid energies, implying that the nucleus, once excited into a GDR, goes through two to three periods of oscillation before its energy and angular momentum are shared among all nucleons.

Making use of the analogies that can be drawn between the collective motion of the delocalized electrons in metal clusters and of the nucleons in nuclei, as well as of the shape fluctuations of the nucleus and of the clusters, the damping mechanism discussed above has been proposed[15–18] to describe the damping of the plasmons in small metal clusters. This conjecture might seem surprising at first, since the plasma frequency in metal microclusters is independent of the size of the system, but for a correction term arising from the spill-out of the delocalized electrons. One has, however, to remember that the back and forth sloshing of the electrons in a quadrupole, deformed cluster gives rise to electric fields that differ appreciably depending on whether the dipole vibration takes place along the major or minor principal axis. This effect makes itself explicit in the directional polarizabilities, quantities which depend on the length of the different principal axes of the ellipsoid.

The frequency with which the cluster surface fluctuates is determined by the ratio of the restoring force for quadrupole deformations, which is provided by the variation in the electronic energy, over the corresponding inertial mass, which is provided by the much heavier ions. The resulting values are of the order of 50–150 K. Conse-

quently, at room temperature the plasmon experiences the ensemble of shapes associated with the quadrupole fluctuations of the cluster droplet in an essentially static way. The average photoabsorption cross section can then be calculated by taking into account the surface fluctuations in the adiabatic approximation. One gets[19]

$$\langle \sigma(\omega) \rangle = \sum_{\kappa} \int d\tau \, \sigma_{\kappa}(\omega;\beta,\gamma) P(\beta,\gamma) \ , \tag{1}$$

where $\kappa = 1,2,3$ labels the oscillations along the principal axes of the ellipsoid and σ_{κ} the associated photoabsorption cross section. The quantity

$$P(\beta,\gamma) = \mathcal{Z}^{-1} \exp[-\Phi(\beta,\gamma)/T] \tag{2}$$

is the probability that the system has a shape specified by the intrinsic deformation parameters β and γ, which measure the quadrupole deformation and thus the departure from spherical or axial symmetry, respectively. The quantity $\mathcal{Z}$ is the partition function, $\Phi(\beta,\gamma)$ being the free energy and T is the temperature.

In what follows, we will assume that all the oscillator strength is concentrated in a single peak. In general, this surface-plasmon-pole approximation is insufficient as far as the small clusters are concerned. Detailed time-dependent local-density calculations,[20–22] as well as random-phase-approximation studies,[23] have shown that substantial fragmentation of the photoabsorption strength does occur even for spherical clusters, e.g., in the case of Na_{20} and Na_{40} (cf. also Ref. 7). However, the one-pole approximation describes sufficiently well several cases, e.g., Na_8, K_9^+, and K_{21}^+.[9,17] In the case of multiple fragmentation, the broadening described by Eqs. (3)–(5) below will have to be repeated for each line, taking, however, into consideration its partial strength.

In keeping with the assumption of a single peak, the photoabsorption cross section

$$\sigma_{\kappa}(\omega;\beta,\gamma) = S_0 S_{\kappa}(\omega;\beta,\gamma) \tag{3}$$

is written in terms of the Thomas-Reiche-Kuhn sum rule

$$S_0 = \frac{2\pi^2 N_e e^2}{3 m_e c} \tag{4}$$

and of the line shape

$$S_{\kappa}(\omega;\beta,\gamma) = \frac{2}{\pi} \frac{\omega^2 \Delta}{[\omega^2 - \omega_{\kappa}^2(\beta,\gamma)]^2 + \omega^2 \Delta^2} \ , \tag{5}$$

which for simplicity is chosen to be a Lorentzian function. The number and mass of the electrons are denoted by N_e and m_e, respectively, while $\omega_{\kappa}(\beta,\gamma)$ are the frequencies of the surface plasmon associated with the three principal directions of the ellipsoid. The intrinsic width Δ takes into account, in some average way, the coupling to all other degrees of freedom, but the surface fluctuations.[24]

Quantitative estimates of the coefficients appearing in the above expressions lead to estimates[14–16] of the damping factor—that is, of the ratio of the full width at half maximum (FWHM) to the centroid ω_D of the photoabsorption excitation function (5)— of the order of 0.1 at room temperature, consistent with the experimental evidence.[8,9,11]

From the above discussion, one can conclude that the motion of nucleons inside the nucleus is a valid analog for the motion of delocalized valence electrons in a metal cluster. From this analogy, a simple, yet realistic, model for the damping of the plasma resonance in small metal clusters can be extracted.

[1]This question has been put forward in a very lucid way by T. P. Martin in Ref. 2, from which we quote almost verbatim.

[2]T. P. Martin, in *Elemental and Molecular Clusters,* edited by G. Benedek, T. P. Martin, and G. Pacchioni, Springer Series in Material Sciences Vol. 6 (Springer-Verlag, Heidelberg, 1988), p. 2.

[3]W. A. de Heer and W. D. Knight, in *Elemental and Molecular Clusters* (Ref. 2), p. 45.

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[24]At low temperatures, the intrinsic width is found to be much smaller than the width of the photoabsorption cross section, and thus not to contribute significantly to the FWHM or to the plasmon line shape. At higher temperatures, however, its contribution is expected to be moderate (cf. Ref. 17).