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Multiple plasmons and anharmonic effects in small metallic clusters

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Processes leading to possible anharmonic dipole-plasmon oscillations in alkali-metal clusters are investigated. The electronic excitation spectrum of sodium clusters including highly excited states with more than one plasmon is calculated with an approach based on the separation of center of mass and intrinsic motion of delocalized electrons. The spectrum is analyzed in terms of collective plasmon oscillations, intrinsic electron motion, and their interaction. The latter is of primary importance. It is responsible for the anharmonicity of giant dipole oscillations. The predicted nonlinear blueshift of the dipole resonance is comparable with its spreading width, and therefore ought to be observed in photoabsorption experiments.

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I. INTRODUCTION

The giant dipole resonance is one of the most important collective excitations in finite fermionic systems [1,2]. In the case of alkali-metal clusters [3,4], for which valence electrons are delocalized throughout the whole volume, this collective mode, usually named surface plasmon, corresponds to a coherent oscillation of the electron cloud against the positively charged ionic background. This means a vibration of the electronic center of mass (c.m.). As a dipole external electromagnetic field couples directly with the electronic c.m., the dipole surface plasmon dominates the cluster response to a laser field, as reported in numerous experimental works on cluster spectroscopy [3–9].

For relatively low laser intensities the optical response is adequately described within the linear response (LR) theory using either the time-dependent local-density approximation (TDLDA) [10–12] or the random-phase approximation with exchange (RPAE) [13–15]. However the LR theory can describe only weakly excited electronic systems and the question whether the dipole surface plasmon in metallic clusters is harmonic enough to allow multiple-plasmon excitations still remains open. Note that a similar question is of current interest in nuclear physics [16–19]. In cluster physics several approaches to the problem have been considered. In TDLDA numerical simulations (see, e.g., Refs. [20,21]) the oscillations of the electron cloud after an initial displacement have been analyzed, giving evidence for plasmon resonances. Moreover, it was found that the dipole power spectrum at large displacements differs from that in the linear regime [21]. In particular a blueshift of the resonance frequency has been observed. These numerical results indicate anharmonic effects.

Other theoretical methods to build the excitation energy spectrum of jellium clusters and to search for anharmonic plasmon oscillations have also been put forward [22,23] and contradictory results have been obtained. On one hand Catara *et al.* [22] reported a large anharmonic effect. They did not observe any two-plasmon state in the excitation spectrum of the sodium cluster Na_{20} calculated within the boson expansion method. On the other hand Hagino reported a negligibly small anharmonicity of plasmon oscillations [23]. His calculations for Na_{92} based on the time-dependent variational principle [16] gave a frequency shift for the two-plasmon state of about 1 meV. Note that the nonlinear frequency shift predicted by Hagino is negative, at variance with the results of numerical simulations [21].

The aim of the present study is to clarify the nature of anharmonicity of dipole plasmon oscillations in metallic clusters. Similarly to Refs. [22,23] we analyze the dipole excitation spectrum and investigate whether multiple plasmon states can be excited. Our interest to this problem is stimulated by recent experimental [24] and theoretical [25] works devoted to the interaction of small metallic clusters with strong femtosecond laser pulses. Being irradiated by an intense laser field, the electronic system of a metallic cluster is no longer in a regime of small oscillations, and collective electronic excitations can exhibit anharmonic features. From the standpoint of theory, the linear-response theory cannot be applied any more, and we need to go beyond it.

In the present paper we develop a method of description of highly excited states including multiple-plasmon excitations. Our method is based on the separation of c.m. and intrinsic motions of delocalized electrons. The zeroth approximation where the intrinsic electron motion does not couple with the c.m. motion, is equivalent to the model of collective oscillations employed by Hagino [23]. Within this zeroth approximation the anharmonic effects are negligible as long as the cluster is not too small. Indeed the anharmonicity arises from the coupling of the c.m. and intrinsic electron motions. The latter is also important in the linear regime of plasmon oscillations, where, in addition to the spill out effect [2,4], it shifts the plasmon resonance frequency.

For the sake of simplicity we describe the cluster background within the standard spherical jellium model [26,10], which neglects the internal ionic structure. This allows one to use standard methods of many-body theory to describe the electronic motion, such as RPAE [13,14,27,15]. Thus we restrict our calculations to alkali-metal clusters with closed electronic subshells, for which the jellium model has proven successful [7,12].

The paper is organized as follows. In Sec. II we outline the basic expressions for the separation of the c.m. and in-

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trinsic electronic motions. In this section we also formulate our zeroth approximation that reproduces Hagino's results [23]. In Sec. III we analyze the effect of coupling between the c.m. and intrinsic motions on the collective dipole excitation both in linear- (single-plasmon) and multiple-plasmon regimes. In this section we outline our procedure for numerical calculations. In Sec. IV we discuss the energy spectrum of dipole excitations calculated for spherical sodium ions and we estimate the amplitude of nonlinear effects in the process of photoabsorption in a strong laser field. An atomic system of units ($\hbar = e = m_e = 1$) is used throughout the paper.

II. SEPARATION OF CENTER OF MASS AND INTRINSIC ELECTRON MOTION

To distinguish the dipole plasmon mode from other electron excitations, it is convenient to separate the intrinsic and the c.m. electron coordinates. We start with the total electron Hamiltonian of the cluster, which includes the electron kinetic energy, energy of interelectronic Coulomb interaction, and interaction with ionic background,

$$H = \sum_a \frac{p_a^2}{2} + \frac{1}{2} \sum_{a \neq b} \frac{1}{|\mathbf{r}_a - \mathbf{r}_b|} + \sum_a V_{ion}(\mathbf{r}_a), \tag{1}$$

where $V_{ion}(\mathbf{r}_a)$ is the ionic background potential; the sum is performed over all valence electrons, one per atom. Let us denote the c.m. vector by $\mathbf{R}$ and the intrinsic electron coordinates by $\mathbf{r}'_a$:

$$\mathbf{R} = \frac{1}{N} \sum_a \mathbf{r}_a, \quad \mathbf{r}'_a = \mathbf{r}_a - \mathbf{R}, \tag{2}$$

where N is the number of electrons. Similarly, the momentum of the center of mass motion is equal to $\mathbf{P} = \Sigma_a \mathbf{p}_a$ and the intrinsic momenta are $\mathbf{p}'_a = \mathbf{p}_a - \mathbf{P}/N$, respectively. We separate the intrinsic and c.m. coordinates in Eq. (1) assuming that the amplitude of the displacement of $\mathbf{R}$ is much smaller than the cluster radius R_0, $R_0 = r_s N^{1/3}$, where r_s is the Wigner-Seitz radius of the bulk material ($r_s = 4$ a.u. for sodium) [28]. Expanding the ionic background potential $V_{ion}(\mathbf{r}'_a + \mathbf{R})$ in Eq. (1) in power series with respect to $\mathbf{R}$, the total Hamiltonian can be written as

$$H = H' + \frac{P^2}{2N} + U(\mathbf{r}', \mathbf{R}), \tag{3}$$

where $U(\mathbf{r}', \mathbf{R})$ is

$$\begin{aligned} U(\mathbf{r}', \mathbf{R}) &\equiv \sum_a U(\mathbf{r}'_a, \mathbf{R}) = \sum_a [V_{ion}(\mathbf{r}_a) - V_{ion}(\mathbf{r}'_a)] \\ &= \sum_{n=1} \sum_a \frac{1}{n!} (\mathbf{R} \cdot \boldsymbol{\nabla})^n V_{ion}(\mathbf{r}'_a), \end{aligned} \tag{4}$$

and H' is the Hamiltonian of intrinsic motion. It has the form of the total Hamiltonian with natural replacement of all electronic coordinates and momenta by corresponding values in the c.m. system.

We set a zeroth approximation such that the c.m. and intrinsic electron motions are independent. This choice is based on the following simple fact. Within the standard jellium model [26,10,12], the ionic background is described by a homogeneously distributed positive charge density $\rho_i = 3/4\pi r_s^3$. For sufficiently large clusters, neglecting the electrons that spill out the surface, the potential V_{ion} is purely parabolic. Using the condition $\Sigma_a \mathbf{r}'_a = \mathbf{0}$, one immediately finds that $U(\mathbf{r}', \mathbf{R}) = NR^2/2r_s^3$ does not depend upon the intrinsic electron coordinates. The harmonic frequency at which the c.m. oscillates is the well-known Mie frequency $\omega_{Mie} = \sqrt{1/r_s^3}$. Now, as we consider finite-size clusters having some electronic spill out, we write the Hamiltonian of Eq. (3) as the sum of a model Hamiltonian H_0 and a residual interaction V_{res}:

$$H = H_0 + V_{res}, \tag{5}$$

with

$$H_0 = H' + \frac{P^2}{2N} + U_{eff}(\mathbf{R}) \tag{6}$$

and

$$V_{res}(\mathbf{r}', \mathbf{R}) = U(\mathbf{r}', \mathbf{R}) - U_{eff}(\mathbf{R}). \tag{7}$$

The model Hamiltonian H_0 being separable, one writes its total-electron eigenfunction as a product of wave functions,

$$\Psi^0_{n,\nu}(\mathbf{r}_a) = \Psi_n(\mathbf{R}) \Phi_\nu(\mathbf{r}'_a). \tag{8}$$

The wave function $\Phi_\nu(\mathbf{r}'_a)$ is an eigenfunction of the intrinsic Hamiltonian H' with corresponding eigenenergy ε_ν, ($\nu = 0$ denotes the ground state of intrinsic motion), and $\Psi_n(\mathbf{R})$ is one of the effective plasmon Hamiltonian,

$$\mathcal{H} = \frac{P^2}{2N} + U_{eff}(\mathbf{R}). \tag{9}$$

The effective potential for c.m. motion, $U_{eff}(\mathbf{R})$, is obtained by averaging the exact potential $U(\mathbf{r}', \mathbf{R})$ over the ground-state electron density $\rho_e(\mathbf{r})$:

$$\begin{aligned} U_{eff}(\mathbf{R}) &= \sum_{n=1} U_{eff}^{(n)}(\mathbf{R}) \\ &= \sum_{n=1} \frac{1}{n!} \int \rho_e(\mathbf{r}) (\mathbf{R} \cdot \boldsymbol{\nabla})^n V_{ion}(\mathbf{r}) d^3 r. \end{aligned} \tag{10}$$

All odd terms vanish after averaging whenever the ground-state density is spherically symmetric. The first nonvanishing term corresponds to the pure oscillator potential

$$U_{eff}^{(2)}(\mathbf{R}) = N \frac{\omega_{sp}^2 \mathbf{R}^2}{2}, \quad \omega_{sp}^2 = \frac{4\pi}{3N} \int \rho_e \rho_i d^3 r, \tag{11}$$

where ρ_e and ρ_i are the electronic and ionic densities, respectively. Thus within this approximation the electron energy spectrum is given by the sum of intrinsic energy ε_ν and energy of harmonic c.m. oscillation:

$$E_{n,\nu}=\varepsilon_\nu+\omega_{sp}(n+\tfrac{1}{2}), \tag{12}$$

where n is the quantum number of the oscillator state $\Psi_n(\mathbf{R})$, i.e., the number of excited plasmons.

Within the dipole approximation, an external laser field interacts directly with the c.m. coordinate and does not excite the intrinsic motion, i.e., $\nu\equiv 0$. Therefore in the present approximation the dipole excitation spectrum is purely harmonic, $E_{n,0}-E_{0,0}=n\omega_{sp}$.

In the special case of spherical clusters with a homogeneous sharp edged ionic background distribution

$$\rho_i=\frac{3}{4\pi r_s^3}\,\theta(r-R_0), \tag{13}$$

Eq. (11) gives

$$\omega_{sp}=\omega_{Mie}\sqrt{1-\frac{\delta N}{N}}, \tag{14}$$

where δN is the number of spill-out electrons.

In our zeroth approximation the anharmonic corrections to the plasmon excitations originate from the higher terms of the expansion given by Eq. (10). The first anharmonic term in the effective potential $U_{eff}(\mathbf{R})$ is of the fourth power of R,

$$U_{eff}^{(4)}(\mathbf{R})=\beta R^4, \quad \beta=\frac{1}{4!R^4}\int \rho_e(\mathbf{r})(\mathbf{R}\cdot\boldsymbol{\nabla})^4 V_{ion}(\mathbf{r})d^3r. \tag{15}$$

The integral on the right-hand side can be easily evaluated in the case of spherical clusters. The averaging over the spherical ground-state density distribution is equivalent to the averaging over all orientations of vector $\mathbf{R}$. Using the relation $\overline{R_iR_jR_kR_l}=R^4(\delta_{ij}\delta_{kl}+\delta_{ik}\delta_{jl}+\delta_{il}\delta_{jk})/15$, one finds that

$$\beta=\frac{4\pi}{5!}\int \rho_e\Delta\rho_i d^3r=\frac{\pi N^{2/3}}{10r_s}\left.\frac{d\rho_e}{dr}\right|_{r=R_0}. \tag{16}$$

Note that our result for β differs by a numerical factor 9/5 from that given by Eq. (21) in Ref. [23]. We follow the prescription of Refs. [23,16] to obtain the multiple-plasmon frequencies. This requires using the Bohr-Sommerfeld quantization condition for orbits in the anharmonic potential, $U_{eff}(\mathbf{R})=N\omega_{sp}^2\mathbf{R}^2/2+\beta R^4$. We obtain

$$E_{n,0}-E_{0,0}=n\omega_{sp}+n^2\frac{3\beta}{2N^2\omega_{sp}^2}. \tag{17}$$

The anharmonic shift of the nth plasmon defines the anharmonic parameter ζ_0 in terms of the second difference:

$$\zeta_0=E_{n+1,0}-2E_{n,0}+E_{n-1,0}=\frac{3\beta}{(N\omega_{sp})^2}, \tag{18}$$

which is independent of n. One observes that the coefficient β and therefore the frequency shift of the double-plasmon ζ_0 are negative. Quantitative estimates of anharmonic shifts in sodium clusters at the present zeroth approximation will be given in the following section.

III. COUPLING BETWEEN CENTER OF MASS AND INTRINSIC ELECTRON MOTIONS

Let us go beyond the uncoupled approximation and consider intrinsic excitations caused by the plasmon oscillations. Formally the coupling between the c.m. and intrinsic electron motions originates from the nondiagonal matrix elements of $V_{res}(\mathbf{r}',\mathbf{R})$. We recall that

$$\begin{aligned}V_{res}(\mathbf{r}',\mathbf{R})&=\sum_{n=1} V_{res}^{(n)}(\mathbf{r}',\mathbf{R})\\&=\sum_{n=1}\left(\frac{1}{n!}(\mathbf{R}\cdot\boldsymbol{\nabla})^n\sum_a V_{ion}(\mathbf{r}_a')-U_{eff}^{(n)}(\mathbf{R})\right).\end{aligned} \tag{19}$$

In a first step we shall consider the coupling terms as a small perturbation and get a rough estimate of the anharmonic effect; this qualitative approach will help us to discuss *ab initio* calculations presented in a second step.

The first term of the expansion of $V_{res}(\mathbf{r}',\mathbf{R})$ yields the leading contribution to the coupling. We keep only this term for the perturbation,

$$W(\mathbf{r}_a',\mathbf{R})=V_{res}^{(1)}(\mathbf{r}',\mathbf{R})=\sum_a (\mathbf{R}\cdot\boldsymbol{\nabla})V_{ion}(\mathbf{r}_a'). \tag{20}$$

This potential $W(\mathbf{r}',\mathbf{R})$, which is associated with the additional time-dependent electromagnetic field arising in the c.m. system due to the plasmon oscillations, has the form of a separable interaction between dipole plasmon and single-particle excitations. The total Hamiltonian H of Eq. (3) can then be written as

$$H=H'(\mathbf{r}')+\mathcal{H}(\mathbf{R})+W(\mathbf{r}',\mathbf{R}), \tag{21}$$

where the operator $W(\mathbf{r}',\mathbf{R})$ couples unperturbed states $\Psi_{n,0}$ and $\Psi_{n\pm 1,\nu}$. Let us evaluate the corresponding corrections to the energy spectrum given by Eq. (12). In the second order of perturbation theory the energy shift is

$$\Delta E_{n,0}^{(2)}=\sum_{n'\neq n,\nu\neq 0}\frac{|\langle n',\nu|W|n,0\rangle|^2}{E_{n,0}-E_{n',\nu}}, \tag{22}$$

where $|n,\nu\rangle$ denotes the unperturbed state $|\Psi_n(\mathbf{R})\Phi_\nu(\mathbf{r}_a')\rangle$. The oscillator part of the matrix element is equal to $\langle n\pm 1|R|n\rangle=\sqrt{(n+1/2\pm 1/2)/2N\omega_{sp}}$. Thus $\Delta E_{n,0}^{(2)}$ contains terms proportional to n and leads to a shift of the harmonic frequency:

TABLE I. Spill-out parameter $\delta N/N$, plasmon frequency ω_{sp} accounting only for spill-out effect Eq. (14), plasmon resonance energy in the RPAE spectrum, and anharmonicity parameters ζ and ζ_0 calculated for spherical sodium cluster ions of different sizes.

	Na_9^+	Na_{21}^+	Na_{41}^+	Na_{59}^+	Na_{93}^+
$\delta N/N$	0.14	0.13	0.12	0.096	0.084
ω_{sp} (eV)	3.15	3.17	3.20	3.24	3.26
ω_{RPAE} (eV)	2.98	2.88	2.76	2.88	2.84
ζ (eV)	0.055	0.12	0.27	0.22	0.27
ζ_0 (eV)	-0.023	-0.0072	-0.0029	-0.0017	-0.0009

$$\Delta\omega_{sp}^{(2)} \equiv \frac{d\Delta E_{n,0}^{(2)}}{dn} = \frac{1}{2N\omega_{sp}} \sum_{\nu\neq 0} \frac{2\omega_\nu \left| \left\langle \nu \left| \sum_a v(\mathbf{r}'_a) \right| 0 \right\rangle \right|^2}{\omega_{sp}^2 - \omega_\nu^2}, \tag{23}$$

where $\omega_\nu = \varepsilon_\nu - \varepsilon_0$ is the intrinsic excitation energy, and $v(\mathbf{r})$ is the derivative of the background potential along the direction of plasmon oscillation (let it be the z axis) $v(\mathbf{r}) = dV_{ion}(\mathbf{r})/dz$.

The angular momentum of the operator $v(\mathbf{r})$ coincides with that of the dipole plasmon, $L=1$, as expected from conservation of angular momentum. So the creation or the annihilation of one dipole plasmon generates a dipole excitation of the intrinsic motion. In small sodium clusters, especially in positive ions, almost all dipole excitations have energies ω_v larger than ω_{sp}. Thus the energy shift (23) is negative. This fact correlates with the experimental data for sodium cluster ions Na_n^+ [3,4,8,9].

According to the existing experimental data for photoabsorption spectra of closed-shell sodium clusters and also in agreement with the results of LR calculations [12,11,13–15], the position of the giant dipole resonance is about 2.8 eV, which is essentially lower than the Mie frequency for sodium $\omega_{Mie} = 3.4$ eV. The spill-out effect that we discussed in the preceding section cannot alone explain such a significant redshift of the plasmon energy. In Table I, we compare the plasmon frequencies calculated within the RPAE with those from Eq. (14). The spill-out correction $\omega_{Mie} - \omega_{sp} \simeq \omega_{Mie}\delta N/2N$ provides only a small fraction of the total redshift for all clusters but the very small ones such as Na_9^+. One concludes that the main contribution to the observed redshift is due to the repulsion interaction between the dipole plasmon and the intrinsic excitations of higher energies, a process that is properly accounted for in RPAE. Nevertheless there is a close connection between these two contributions since both effects arise from the spill-out electrons. Indeed the jellium background potential does not contribute to the coupling in the interior of the cluster since there it is purely parabolic, $V_{ion}(r) = \omega_{Mie}^2 (r^2 - 3R_0^2)/2$. Adding to $v(\mathbf{r})$ in Eq. (23) the linear term $-z/r_s^3$, which inside the cluster is identical to $-dV_{ion}(\mathbf{r})/dz$, does not change the matrix elements, since $\Sigma_{a'} z_{a'} = 0$. Thus $v(\mathbf{r})$ is nonzero only outside the cluster:

$$v(\mathbf{r}) = N\left(\frac{z}{r^3} - \frac{z}{R_0^3}\right)\theta(r - R_0). \tag{24}$$

The relation between both contributions to the redshift can be illustrated by the following simple consideration. Let us put all intrinsic excitation energies equal to some average value $\omega_\nu = \omega'$. Then the sum of the matrix elements in Eq. (23) can be calculated using the sum rule

$$\sum_{\nu\neq 0} 2\omega_\nu \left| \left\langle \nu \left| \sum_a v(\mathbf{r}'_a) \right| 0 \right\rangle \right|^2 = \left\langle 0 \left| \sum_a [\nabla v(\mathbf{r}'_a)]^2 \right| 0 \right\rangle. \tag{25}$$

Since $v(\mathbf{r})$ is nonzero only outside the cluster background, the matrix element on the right-hand side of Eq. (25) is actually formed in the thin layer of spill-out electrons. Using the explicit expression [Eq. (24)] for $v(\mathbf{r})$ we obtain a redshift,

$$\Delta\omega_{sp}^{(2)} = \frac{3}{2r_s^6 \omega_{sp}(\omega_{sp}^2 - \omega'^2)} \frac{\delta N}{N}, \tag{26}$$

which is also proportional to the number of spill-out electrons.

The next order of perturbation theory gives the nonlinear correction to the energy spectrum corresponding to the anharmonic frequency shift

$$\begin{aligned}\Delta E_{n,0}^{(4)} = & -\Delta E_{n,0}^{(2)} \sum_{n'\neq n, \nu\neq 0} \frac{|\langle n',\nu|W|n,0\rangle|^2}{(E_{n,0} - E_{n',\nu})^2} \\ & + \sum_{n_1, n_2, n'\neq n, \nu_1, \nu_2 \neq 0} \frac{\langle n,0|W|n_1,\nu_1\rangle\langle n_1,\nu_1|W|n',0\rangle\langle n',0|W|n_2,\nu_2\rangle\langle n_2,\nu_2|W|n,0\rangle}{(E_{n,0} - E_{n_1,\nu_1})(E_{n,0} - E_{n',0})(E_{n,0} - E_{n_2,\nu_2})}.\end{aligned} \tag{27}$$

Assuming that all excitation energies have the same value $\omega_\nu = \omega'$, the parameter of anharmonicity $\zeta = d^2 E_{n,0}/dn^2$ can be written as

$$\zeta = \frac{(\Delta\omega_{sp}^{(2)})^2 (\omega_{sp}^2 + 3\omega'^2)}{\omega'(\omega'^2 - \omega_{sp}^2)}. \tag{28}$$

Since $\omega_{sp} < \omega'$ the nonlinear frequency shift is positive, $\zeta > 0$ in contrast to the uncoupled contribution $\zeta_0 < 0$, [see Eq. (18)].

Let us estimate the anharmonic parameter ζ. From RPAE calculations we find the parameter ω' in Eq. (26) to be $\omega' \approx 5$ eV for sodium cluster ions Na_n^+, $41 \leqslant n \leqslant 93$. This leads to an anharmonic parameter $\zeta \approx 0.15$–0.2 eV for these clusters. Such an estimation of ζ is larger by two orders of magnitude than the uncoupled anharmonicity parameter ζ_0.

In order to be more quantitative one should take into account the exact positions of the excitation levels. However the simple perturbation theory is no longer valid because some intrinsic levels $E_{n-1,\nu}$ are localized quite close to the unperturbed plasmon excitation $E_{n,0}$. The strong interaction between these states should be taken into account exactly. Another group of intrinsic levels $E_{n+1,\nu}$ is separated from the plasmon excitation level $E_{n,0}$ by a large energy gap of about $2\omega_{sp}$. Therefore the interaction between these states is much weaker and can be neglected. Thus we write the eigen-wave-function of the total cluster Hamiltonian [Eq. (21)] as a superposition of unperturbed states $|n,0\rangle$ and $|n-1,\nu \neq 0\rangle$ coupled by the perturbation $W(\mathbf{r}',\mathbf{R})$:

$$\Psi_k = C_0^k \Psi_n(\mathbf{R}) \Phi_0(\mathbf{r}'_a) + \sum_{\nu \neq 0} C_\nu^k \Psi_{n-1}(\mathbf{R}) \Phi_\nu(\mathbf{r}'_a), \quad (29)$$

where the coefficients C_ν satisfy the following matrix equation:

$$[\varepsilon_\nu + \omega_{sp}(n + \delta_{0\nu} - \tfrac{1}{2}) - E_k] C_\nu^k + \sum_{\nu'} \langle n + \delta_{0\nu} - 1, \nu | W | n + \delta_{0\nu'} - 1, \nu' \rangle C_{\nu'}^k = 0, \quad (30)$$

with E_k being the total energy of the excited state k. The matrix equation [Eq. (30)] follows from the Schrödinger equation $\hat{H}\,\Psi_k = E_k \Psi_k$, where H is given by Eq. (21).

The wave functions of intrinsic excitations will be given by the RPAE [13,15] as a linear combination of electron-hole excitations $\psi_e(\mathbf{r})\psi_h^*(\mathbf{r})$. The basis single-particle functions $\psi_{e,h}(\mathbf{r})$ are obtained as solutions of the Hartree-Fock (HF) equations. However, for our present purpose, the standard RPAE scheme should be modified. Indeed the basis of electron-hole excitations $\psi_e(\mathbf{r})\psi_h^*(\mathbf{r})$ contain both the plasmon and the intrinsic excitations since the dipole matrix element, $z_{eh} = \langle \psi_h | z | \psi_e \rangle \neq 0$. In order to extract the intrinsic components from the electron-hole excitations we use the projector P defined as

$$P\psi_e(\mathbf{r})\psi_h^*(\mathbf{r}) = \sum_{e'h'} \left(\delta_{ee'}\delta_{hh'} - \frac{z_{eh} z_{h'e'}}{\sum_{eh} |z_{eh}|^2} \right) \psi_{e'}(\mathbf{r})\psi_{h'}^*(\mathbf{r}). \quad (31)$$

The dipole matrix element for the resulting intrinsic excitation $P\psi_e(\mathbf{r})\psi_h^*(\mathbf{r})$ identically equals to zero, as desired. The set of intrinsic electron-hole excitations is now used as a basis to construct the stationary intrinsic RPAE excited states:

$$|\Phi_\nu\rangle = \sum_{eh} (X_{eh}^\nu P a_e^\dagger a_h + Y_{eh}^\nu P a_h^\dagger a_e) |\Phi_0\rangle, \quad (32)$$

where $|\Phi_0\rangle$ denotes the HF ground state, $a_e^\dagger$ and a_h are creation and annihilation operators of single-particle HF states, X_{eh}^ν and Y_{eh}^ν are the forward-going and backward-going RPAE amplitudes that measure the contribution of a particular single-particle electron-hole excitation to the collective electron state $|\Phi_\nu\rangle$. Index h spreads over all occupied (hole) HF states while index e spreads over all vacant (electron) HF states. The X_{eh}^ν and Y_{eh}^ν amplitudes satisfy the matrix equation

$$\begin{pmatrix} P & 0 \\ 0 & P \end{pmatrix} \begin{pmatrix} A & B \\ B^* & A^* \end{pmatrix} \begin{pmatrix} P & 0 \\ 0 & P \end{pmatrix} \begin{pmatrix} X^\nu \\ Y^\nu \end{pmatrix} = \omega_\nu \begin{pmatrix} X^\nu \\ -Y^\nu \end{pmatrix}, \quad (33)$$

which differs from the standard RPAE equation only by projection operators P. Matrices A and B are defined as follows:

$$A_{e'h',eh} = (\varepsilon_{e'} - \varepsilon_{h'}) \delta_{h'h} \delta_{e'e} + \langle e'h | \hat{V} | h'e \rangle, \quad (34)$$

$$B_{e'h',eh} = \langle e'e | \hat{V} | h'h \rangle,$$

and the matrix element of residual interelectronic interaction V is equal to

$$\langle \psi_{e'} \psi_h | \hat{V} | \psi_e \psi_{h'} \rangle = \int \frac{\psi_{e'}^*(\mathbf{r}) \psi_e(\mathbf{r}') \psi_h^*(\mathbf{r}') \psi_{h'}(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' - \int \frac{\psi_{e'}^*(\mathbf{r}) \psi_e(\mathbf{r}) \psi_h^*(\mathbf{r}') \psi_{h'}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'. \quad (35)$$

IV. RESULTS AND DISCUSSION

We consider spherical sodium cluster ions Na_n^+ of sizes $n = 9,21,41,59,93$. In a first step we calculate the energies ω_ν and wave functions Φ_ν of intrinsic excitations [Eq. (33)]. For all these jellium clusters the energy spectra exhibit similar features. In Table II (for Na_9^+ and Na_{93}^+) we compare these intrinsic excitation energies with the standard RPAE dipole excitation energies ω_i [13,15]. In the RPAE spectrum one can distinguish a main line with maximum strength just below 3 eV. As this line is absent in the spectrum of intrinsic excitations ω_ν it is associated with the dipole-plasmon excitation, indeed. All other lines of the RPAE spectrum lie close to the corresponding lines of intrinsic excitations, being slightly shifted due to the repulsion interaction with the plasmon.

In a next step, according to Eqs. (29)–(35), we calculate the spectrum of excitations formed by one dipole plasmon state $|1,0\rangle$, and a group of intrinsic excitations $|0,\nu \neq 0\rangle$. In Table II we present the corresponding excitation energies

TABLE II. Excitation energies ω_i and oscillation strengths f_i (in % of the dipole sum rule) calculated within the RPAE for Na_9^+ and Na_{93}^+ clusters. Energies ω_ν of intrinsic excitations are calculated according to Eq. (33). Excitation energies ω_k and oscillation strengths f_k are calculated according to Eq. (30).

	ω_i (eV)	f_I	ω_ν (eV)	ω_k (eV)	f_k
			Na_9^+		
1	2.438	3.3	2.482	2.453	5.2
2	2.978	89.4		2.963	84.4
3	4.536	3.4	4.485	4.567	3.6
4	4.771	2.3	4.743	4.802	4.0
5	5.515	0.6	5.503	5.526	0.9
			Na_{93}^+		
1	1.020	4×10^{-2}	1.038	1.036	8×10^{-2}
2	1.193	4×10^{-3}	1.194	1.194	8×10^{-3}
3	1.876	8×10^{-3}	1.877	1.877	1×10^{-2}
4	1.964	1×10^{-3}	1.964	1.964	2×10^{-3}
5	2.841	40.6		2.798	44.6
6	3.036	11.8	2.972	3.033	8.5
7	3.175	20.1	3.021	3.178	15.3
8	3.390	7.1	3.105	3.397	6.1
9	3.439	0.5	3.353	3.440	0.6
10	3.553	1.6	3.525	3.549	2.6

$\omega_k \equiv E_k$, together with oscillator strengths f_k. Since the initial plasmon excitation $|1,0\rangle$ alone collects the whole strength, the oscillator strength of the resulting excited state $|\Psi_k\rangle$ is determined by the fraction of plasmon state $|1,0\rangle$ in $|\Psi_k\rangle$, $f_k = |C_0^k|^2$. For the sake of illustration, the positions of these excitation levels with a small fraction of pure plasmon excitation are shown in Fig. 1 together with plasmon excitations. Table II and Fig. 1 demonstrate a good agreement between the RPAE spectrum and the spectrum calculated by the method developed here. Thus with reasonable accuracy, we can describe the photoabsorption spectrum in terms of dipole-plasmon oscillations, intrinsic excitations, and their interaction. This interaction leads to the redshift of the plasmon line and a redistribution of the oscillator strength from the plasmon mode to intrinsic excitations.

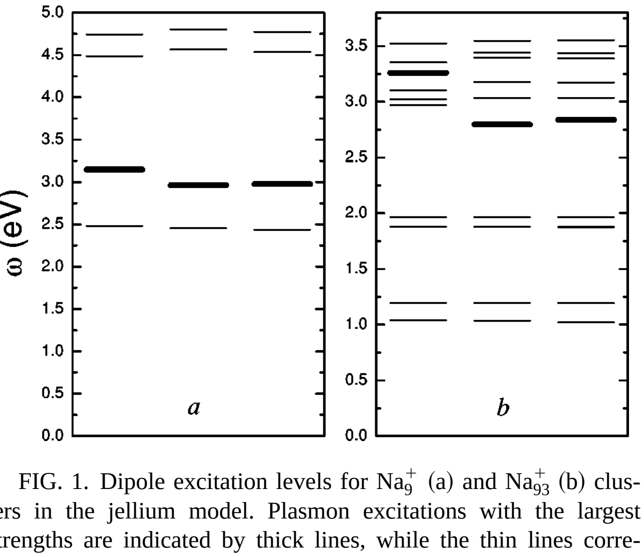

FIG. 1. Dipole excitation levels for Na_9^+ (a) and Na_{93}^+ (b) clusters in the jellium model. Plasmon excitations with the largest strengths are indicated by thick lines, while the thin lines correspond to the levels with a small fraction of pure plasmon excitation. Left column: lowest unperturbed excitation levels, Eq. (12). Middle column: excited levels calculated according to Eq. (30). Right column: RPAE levels.

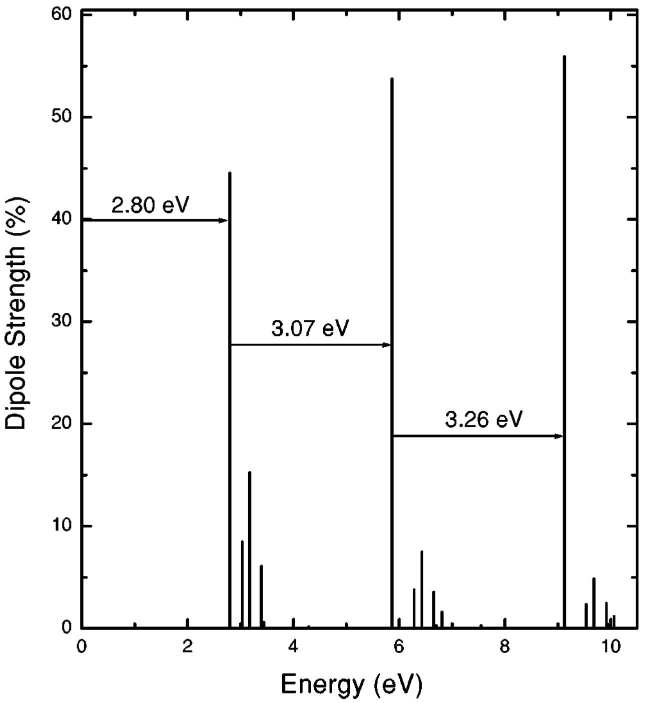

FIG. 2. Excitation energy spectrum including one- $(n=1)$, two- $(n=2)$, and three- $(n=3)$ plasmon states for Na_{93}^+ cluster. The height of any line measures its strength as the fraction of pure plasmon excitation, $|C_0^k|^2$.

The RPAE spectra correspond to the linear regime of photoabsorption where only one electron-hole pair can be excited at a time. Whereas RPAE is restricted to linear regimes, our proposed method allows us to go beyond the linear response. Indeed, Eqs. (29) and (30) describe a possible simultaneous excitation of n plasmons. As an example, in Fig. 2 we present the excitation spectrum, E_k, of Na_{93}^+ calculated using Eq. (30). The strength of the lines corresponds to the fraction of pure plasmon excitation $|n,0\rangle$ in the considered state, $|C_0^k|^2$. As shown by Fig. 2 the excited states are grouped according to the maximum number of plasmons n in the excitation. Each group of excited states with a given value of n is formed by the superposition of basis states $|n,0\rangle$ and $|n-1,\nu\neq 0\rangle$. In each group we can distinguish the state with the largest fraction of pure plasmon excitation. The behavior of these collective states differs from the behavior of other excited levels. Excited states with a small contribution of pure plasmon excitation lie close to the initial uncoupled basis levels $|n,\nu\rangle$. On the contrary, in the case of the excited state with the largest value of $|C_0^k|^2$ the coupling interaction is much stronger. The energy shift between the position of this level and that of the corresponding unperturbed plasmon $\omega_{sp} n$ is larger than 0.4 eV. The wave function of this state is a superposition of pure plasmon oscillations with a large number of intrinsic excitations.

The most important optical dipole transitions that occur within the sequence of multi-plasmon states are shown in Fig. 2 by arrows. The corresponding transition energies, $\Delta E_n = E_p(n) - E_p(n-1)$, i.e., the plasmon frequencies, are also indicated. Anharmonic effects are readily evidenced by the discrepancies we observe, $\Delta E_n = 2.798$ eV, 3.067 eV, $3.256 eV, \ldots$ for $n = 1, 2, 3, \ldots$ plasmons, respectively. The plasmon frequency increases with the number of plasmons, in agreement with the blueshift predicted in the qualitative analysis of the preceding section [see Eq. (28)]. This anharmonic behavior is connected with the dependence of the coupling term W upon the number of plasmons, $W \propto \sqrt{n}$.

The anharmonic shift of the second plasmon defined as $\zeta = E_p(2) + E_p(0) - 2E_p(1)$ is given in Table I for our series of sodium clusters. The numerical values are in agreement with the rough estimate of ζ given in the preceding section by Eq. (28). We also show in Table I the uncoupled contribution ζ_0 to the anharmonicity parameter, Eq. (18). HF calculations yield a derivative of the electron density on the jellium edge, $d\rho_e/dr|_{r=R_0} \simeq -8 \times 10^{-4}$ a.u. for all clusters considered here. One sees that ζ exceeds ζ_0 for all cases. Note that ζ_0 decreases rapidly with increasing cluster size as $N^{-4/3}$. However it turns out to be only two times smaller than ζ in the case of the small Na_9^+ cluster. In contrast, the coupled anharmonicity ζ decreases with size in the case of very small clusters, as the coupling between the collective state and particle-hole excitations is weak. Already for Na_{21}^+, the parameter ζ_0 is smaller than ζ by an order of magnitude and the ratio ζ_0/ζ rapidly decreases with cluster size. In the case of a very large cluster, ζ should go to zero as $N^{-1/3}$ according to Eq. (28), but this takes place for clusters containing more than hundred atoms.

Though the anharmonicity parameter ζ is smaller by an order of magnitude than the plasmon frequency ω_{sp}, one can expect the nonlinear effects in photoabsorption to be sizeable. The anharmonic signal would appear both as an increasing blueshift and a decreasing strength of the giant dipole resonance with increasing electric-field intensity, whereas the double-plasmon state gets more and more excited. The blueshift is of the order of ζ when the probability of exciting the double-plasmon state is large. Thus a possible anharmonicity would be detectable for laser intensities large enough, and for clusters having a plasmon width smaller or comparable with ζ. The last requirement is actually fulfilled for the sodium clusters considered here, for which experimental plasmon widths are about $\Gamma \sim 0.2$–0.3 eV [9].

Let us estimate the intensity I of the laser field for which the probability of exciting the second plasmon is large. At low intensity clusters initially in their ground state undergo only one excitation if any. With increasing intensity a substantial set of these clusters having already experienced a single-plasmon excitation can undergo a further optical transition to the excited state with plasmon number $n = 2$. We can estimate the probability of excitation, i.e., the average number of excited plasmons $\overline{n}$, by assuming the equality of plasmon excitation and relaxation rates [$\sigma(\omega) I/\omega$ and $\Gamma \overline{n}$, respectively], where $\sigma(\omega)$ is the photoabsorption cross section which is given in Ref. [9]. The resulting intensities I necessary for observation of nonlinear effects vary from about 2×10^{10} W/cm^2 for Na_{93}^+ to about 3×10^{10} W/cm^2 for Na_{41}^+. Note that since the photoabsorption cross section is roughly proportional to the number of valence electrons, the threshold intensity decreases with increasing size. In the case of the Na_9^+ cluster we have $\overline{n} \sim 1$ when $I \sim 6 \times 10^{10}$ W/cm^2.

The present theoretical scheme can be easily extended in order to calculate the decay width of the collective motion arising from its coupling to intrinsic excitations. This will not be done in the present paper. However a qualitative estimate can be done. As the coupling matrix W scales with $\sqrt{n}$, one expects the width to increase with the number n of plasmons if taking account only the first term of the expansion [Eq. (4)]. A minimal value for the width of the n-plasmon state will thus be $\Gamma_n = n\Gamma$. For states with a large number of plasmons, contributions of higher-order terms in the expansion [Eq. (4)] will be significant since they scale as $n^2, n^3, \ldots$. Thus the observation of multiple plasmons would be limited to just a few of them.

V. CONCLUSION

In the present paper we investigated the excitation spectrum of sodium clusters and analyze the anharmonicity of dipole-plasmon excitations. A description of the excitation spectrum based on the separation of center of mass and intrinsic electronic motion has been developed. Within the proposed method, highly excited states containing more than one-plasmon excitation can be considered. The formation of the excitation spectrum is analyzed in terms of collective plasmon oscillations, intrinsic electron excitations, and their interaction. The latter is of the primary importance for the photoabsorption spectrum since together with the spill-out effect it determines the position of the plasmon resonance. We demonstrate that this coupling provides the main contribution to the anharmonicity of plasmon oscillations. Though the predicted nonlinear blueshift of the plasmon resonance is much smaller than the plasmon frequency, it can be observed in a photoabsorption study since the shift is comparable with the plasmon resonance width.

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[28] For harmonic oscillations, the average displacement of the electronic c.m. associated with the first plasmon state is $\sqrt{\overline{R^2}}=\sqrt{3\hbar/(2Nm_e\omega_p)}$. The ratio $\sqrt{\overline{R^2}}/R_0$ varies with size N as $N^{-5/6}$. For Na_{93}^{+} and Na_{41}^{+}, $\sqrt{\overline{R^2}}/R_0=0.06$ and 0.12 a.u, respectively. Note however that $\sqrt{\overline{R^2}}$ is only two times smaller than R_0 for Na_9^{+} .