Electric multipole plasmons in deformed sodium clusters

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ABSTRACT

The random-phase-approximation (RPA) method with separable residual forces (SRPA) is proposed for the description of multipole electric oscillations of valence electrons in deformed alkali metal clusters. Both the deformed mean field and residual interaction are derived self-consistently from the Kohn-Sham functional. SRPA drastically simplifies the computational effort which is urgent if not decisive for deformed systems. The method is applied to the description of dipole, quadrupole and octupole plasmons in deformed sodium clusters of a moderate size. We demonstrate that, in clusters with the size $N > 50$, Landau damping successfully competes with deformation splitting and even becomes decisive in forming the width and gross structure of the dipole plasmon. Besides, the plasmon is generated by excitations from both ground state and shape isomers. In such clusters familiar experimental estimates for deformation splitting of dipole plasmon are useless.

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1 Introduction

Most of free atomic clusters are known to exhibit quadrupole, hexadecapole, octupole, etc. deformations (see, e.g., [1]-[11] and references therein). The deformations persist from lightest [5, 11] to heavy [7] clusters and considerably influence cluster’s static and dynamical properties. For example, the axial (triaxial) quadrupole deformation leads to the splitting of the dipole plasmon into two (three) peaks [2, 9, 10] and to specific low-energy orbital magnetic dipole resonance [12]-[14].

Investigation of deformation effects in the dynamics of clusters is a topic of current interest, for reviews and monographs see [15]-[21]. At the same time, the handling of excitations in deformed clusters is much more tedious because there are less selection rules and thus larger irreducible particle-hole spaces. In particular, random-phase-approximation (RPA) calculations for multipole oscillations of the valence electrons (plasmons) require diagonalization of matrices with a very high rank (up to $10^5$ and more).

For this reason, the calculations are mainly limited either to light clusters (with number of atoms $N < 20$) where the computational effort is still acceptable [14], or to very heavy clusters where one may neglect effects of quantum shells and use macroscopic models, thus avoiding a deal with a huge configuration space. The main computational troubles are concentrated in the intermediate size region, $10 < N < 10^3$, where sizable effects of quantum shells take place. Here there exits only few calculations with RPA or fully fledged Time-Dependent Local Density Approximation (TDLDA) (see, for example, [22]-[24]). Thus one often chooses simplified methods, like Sum-Rule Approach (SRA) (see, e.g., [25]) or local RPA (LRPA) [26, 27]. They allow to reproduce the energy and gross structure of the plasmon, but cannot properly describe such important feature of cluster dynamics as Landau damping. At the same time, it is just Landau damping which greatly influences the shape of the plasmon and provides the dominant contribution to its width in medium and heavy clusters [27]-[29]. So, there is the need in RPA approach for deformed clusters, which, on the one hand, gives comprehensive and accurate description of multipole plasmons, including Landau damping effects, and, on the other hand, accomplishes this in economical way.

To this end, a new kind of RPA method has been recently proposed [28, 30]. It invokes a self-consistent expansion of the residual two-body interaction $V_{\text{res}}$ into a sum of separable terms:

$$\langle p_1, p_2 | V_{\text{res}} | h_1, h_2 \rangle \Rightarrow \sum_{k, k'} \kappa_{kk'} \langle p_1 | \hat{Q}_k | h_1 \rangle \langle p_2 | \hat{Q}_{k'} | h_2 \rangle . \quad (1)$$

Here, $\kappa_{kk'}$ is the matrix of strength constants, $\langle p | \hat{Q}_k | h \rangle$ is the particle-hole matrix element of the local one-body operator $\hat{Q}_k(r)$. The expansion index $k$ labels various angular momentum channels $\lambda \mu$ as well as a series of different radial functions within each channel. The method proposed is called as a separable RPA or SRPA. Due to the separable ansatz, SRPA has the advantage to transform the
high-rank RPA matrix to a simple dispersion equation, which drastically reduces the computational effort. This is crucial for studies of the linear response in deformed or large spherical systems, when one has to deal with a huge particle-hole configuration space.

It should be emphasized that SRPA has important distinctions as compared with trivial separable RPA schemes widely used in many-body studies, especially in nuclear theory [31, 32]. Such schemes exploit only one separable term with an intuitive guess for the separable one-body operator \( \hat{Q}(r) \), and the strength constant \( \kappa \) is fitted as to reproduce available experimental data. The present SRPA constitutes a systematic expansion of the self-consistent residual interaction. The analytical expressions for both strength matrix \( \kappa_{kk'} \) and operators \( \hat{Q}_k(r) \) are uniquely prescribed by the given \( \hat{V}_{\text{res}} \). There are thus no adjustable parameters. One can easily control the convergence of the expansion by comparing calculations with different cutoffs \( K \). In fact, already a single SRPA separable term provides a fair description of the gross structures, and a good handful of terms allows to reproduce exact RPA calculations [28, 29]. The SRPA scheme was also proven to cooperate with the more involved Hamiltonians containing non-local pseudo-potentials [23].

The separable expansions [28] and [30] use different self-consistent prescriptions. The method [28] deals with simple \( \hat{Q}_k(r) \) operators but for the price of more separable terms. Vice versa, the operators in [30] are more involved but the method needs less number of separable terms. In the present paper, we will deal with the method [30] where the form of the separable operators \( \hat{Q}_k(r) \) and strength matrix \( \kappa_{kk'} \) are determined from the Vibrating Potential Model (VPM) [33]-[35]. The number of separable terms \( K \) is usually limited by 2-3 and 4-6 in light and heavy clusters, respectively.

First SRPA results for the dipole plasmon and scissors mode in deformed clusters were presented in refs. [13]-[15], [35]-[37]. But these calculations were based on a simple shell-model ground state using a deformed Woods-Saxon potential where the deformations were not obtained within the same calculation scheme but taken from other sources, both experimental and theoretical. In the present paper, we present fully self-consistent SRPA scheme for deformed clusters. Both, the deformed mean field and residual interaction, are derived from the same Kohn-Sham functional. Ground state deformations are optimized by minimization of the total energy. SRPA is applied to detailed description of the dipole, quadrupole and octupole plasmons in axially-deformed singly-charged \( Na \) clusters of a different size. Both quadrupole and hexadecapole deformations are taken into account.

We will show that in light clusters the dipole plasmon exhibits distinctive two-peak structure caused by the deformation splitting and just this splitting is mainly responsible for the plasmon width. The ratio between the peaks allows to conclude on either prolate or oblate shape takes place. The situation changes for medium and heavy deformed clusters where Landau damping becomes the main mechanism defining the width and gross structure of the plasmon. Moreover, such clusters exhibit a complicated energy surface with shape isomers which, in
spite of a tiny energy deficit relative to the ground state, possess quite different deformation. Obviously, such isomers can contribute to the plasmon. Due to both the factors, Landau damping and contributions of shape isomers, gross structure of the dipole plasmon in medium and heavy deformed clusters cannot already serve as a direct fingerprint of the deformation and familiar experimental prescriptions for getting magnitude and kind (prolate or oblate) of cluster’s quadrupole deformation become useless.

In Section 2, the deformed Kohn-Sham mean field is described. The existence of shape isomers in heavy clusters is demonstrated. SRPA equations are derived and specified for deformed clusters. In Sec. 3, SRPA results for the dipole plasmon are discussed. The same is done for quadrupole and octupole plasmons. The summary is given in Sec. 4. Appendixes A-C contain details of the formalism.

2 Deformed Kohn-Sham mean field

2.1 Basic constituents of description

We start with the Kohn-Sham functional for a cluster including \( N_e \) valence electrons and \( N \) atoms

\[
E_{\text{tot}}(t) = E_{\text{kin}}(t) + E_{\text{xc}}(t) + E_{\text{C}}(t)
\]

where

\[
E_{\text{kin}}(t) = \frac{\hbar^2}{2m_e} \int dr \, \tau(r, t)
\]

\[
E_{\text{xc}}(t) = \int dr \, \rho(r, t) \epsilon_{\text{xc}}(\rho(r, t))
\]

\[
E_{\text{C}}(t) = \frac{e^2}{2} \int \int d\mathbf{r} d\mathbf{r}_1 \frac{(\rho(\mathbf{r}, t) - \rho_1(\mathbf{r}_1))(\rho(\mathbf{r}_1, t) - \rho_1(\mathbf{r})))}{|\mathbf{r} - \mathbf{r}_1|}
\]

are the kinetic energy, exchange-correlation (in the local density approximation [38], see Appendix A for details), and Coulomb terms, respectively. Here, \( \rho_1(\mathbf{r}) \) is the ionic density in the jellium approximation, \( \rho(\mathbf{r}, t) \) and \( \tau(\mathbf{r}, t) \) are, respectively, the density and kinetic energy density of valence electrons, expressed through the single-particle wave functions \( \psi_q(\mathbf{r}, t) \) as

\[
\rho(\mathbf{r}, t) = \sum_{q} w_q |\psi_q(\mathbf{r}, t)|^2, \quad \tau(\mathbf{r}, t) = \sum_{q} w_q |\nabla \psi_q(\mathbf{r}, t)|^2
\]

with a temperature \( T \) introduced through thermal occupation weights

\[
w_q = \frac{1}{1 + \exp(\frac{\epsilon_q - \lambda_F}{k_B T})}
\]

Here, \( \epsilon_q \) is the energy of the single-particle state \( q \). The chemical potential \( \lambda_F \) serves to ensure the correct number of valence electrons in the static ground
state, i.e. \( \int dr \rho_0(r) = N_c \). The temperature regulates the occupation numbers of the single-particle states, which becomes important for clusters with partially occupied subshells. In medium and heavy clusters where the energy surface is very complicated the introduction of a temperature softens numerical fluctuations and thus improves the convergence of numerical results.

The Kohn-Sham single-particle Hamiltonian is obtained by variation

\[
\hat{h}(r,t)\psi_q(r,t) = \frac{\delta E_{tot}(t)}{\delta \psi^*_q(r,t)}.
\]

This yields

\[
\hat{h}(r,t) = -\frac{\hbar^2}{2m} \nabla^2 + U_{xc}(r,t) + U_C(r,t), \quad (9)
\]

\[
U_{xc}(r,t) = \epsilon_{xc}(\rho(r,t)) + \rho(r,t) \frac{\delta \epsilon_{xc}(\rho(r,t))}{\delta \rho}, \quad (10)
\]

\[
U_C(r,t) = e \int dr_1 \frac{\rho(r_1,t) - \rho_i(r_1)}{|r-r_1|}, \quad (11)
\]

see Appendix A for more details.

The ionic background is described in the soft jellium approximation. The density of the deformed jellium is

\[
\rho_i(r) = \rho_{i0} \frac{1 + \exp((-r - R(\Theta))/\alpha)}{1 + \exp((-r - R(\Theta))/\alpha)}, \quad (12)
\]

where quadrupole and hexadecapole deformations, \( \delta_2 \) and \( \delta_4 \), are introduced through cluster’s radius as

\[
R(\Theta) = R_0 (1 + \sum_{\lambda=2,4} \delta_\lambda Y_\lambda(\Theta)). \quad (13)
\]

Here \( R_0 = C r_s N^{1/3} \); \( r_s \) is the Wigner-Zeitz radius (\( r_s = 3.96 \) a.u. for Na clusters); the coefficient \( C \) is adjusted to ensure volume conservation \( \int d\mathbf{r} \rho_i(\mathbf{r}) = N \); \( \rho_{i0} = \frac{3}{4\pi r_s^3} \) is the bulk density. The diffuseness values \( \alpha = 1 \) and 0.8 a.u. are chosen for calculations with high \( (T = 400 - 800 \) K) and low \( (T = 105 \) K) temperature, respectively. These values allow to describe the energy of the dipole plasmon in a wide size region (see Ref. [29] and present results). Decrease of the diffuseness parameter results in a redshift of the dipole plasmon which should follow lowering the temperature. The recent experimental data for the dipole plasmon in light and medium clusters [39] were obtained at \( T = 105 \) K. So, just this temperature and the value \( \alpha = 0.8 \) a.u. are used in the paper for all clusters except of the heaviest one \( Na_{119}^+ \). For the latter cluster the experimental data are absent and so the common value \( \alpha = 1.0 \) a.u. is used.
2.2 Representation of wave functions for stationary deformed states

Stationary states of the cluster are obtained as solution of the stationary Kohn-Sham equations \( \hat{h}_0(\mathbf{r}) \psi_q(\mathbf{r}) = \varepsilon_q \psi_q(\mathbf{r}) \) where \( \hat{h}_0(\mathbf{r}) \) is the single-particle Hamiltonian \( \hat{h}_0 \) in the static limit. We expand single-particle wave functions of the deformed Kohn-Sham potential in the complete basis of eigenfunctions \( \phi_s(\mathbf{r}) \equiv \phi_{nl\Lambda}(\mathbf{r}) \) of the same but spherical Kohn-Sham potential:

\[
\psi_q = \sum_{nl} a_{nl}^q \phi_{nl\Lambda}(\mathbf{r}). \tag{14}
\]

The spherical states \( \phi_s(\mathbf{r}) \equiv \phi_{nl\Lambda}(\mathbf{r}) = R_{nl}(r)Y_{l\Lambda}(\Omega) \) are characterized by quantum numbers \( s = nl\Lambda \) (the node number, orbital moment and its projection to the symmetry axis, respectively), where the orbital moment is connected with the space parity as \( \pi = (-1)^l \). For the sake of simplicity, spin functions are omitted though, of course, their contribution is taken into account in all relevant values. Deformed states are specified by asymptotic Nilsson-Clemenger quantum numbers \( q = N_{n_z\Lambda} \) where \( N \) is the principle shell quantum number (the total number of quants, \( N = n_x + n_y + n_z \)) and \( \pi = (-1)^N \). The levels in axially-deformed clusters are twofold (for \( \Lambda = 0 \)) or fourfold (for \( \Lambda \neq 0 \)) degenerated.

The electronic density reads in this representation

\[
\rho_0(\mathbf{r}) = 2 \sum_{q=N_{n_z\Lambda}}^{\infty} (2 - \delta_{\Lambda,0}) w_q |\psi_q(\mathbf{r})|^2. \tag{15}
\]

Making use the multipole expansion for static potentials \( (10)-(11) \) and densities \( (12)-(15) \), the equations to determine single-particle energies \( E_q \) and wave functions \( \psi_q \) are derived. As a first step, the Kohn-Sham problem is solved in the spherical limit and then the basis obtained is used for deformed Kohn-Sham potential. At each iteration, the conservation of \( N_e \) and \( N \) is controlled by fitting the parameters \( \lambda_F \) and \( C \). The procedure is performed for every point in the deformation map \( \{\delta_2, \delta_4\} \). The equilibrium deformation parameters \( \delta_2 \) and \( \delta_4 \) are determined by minimization of the total energy \( (2) \). Details of the calculation scheme are given in the Appendix A.

2.3 Results for stationary states of deformed clusters

We consider axially deformed clusters \( Na_{15}^+, Na_{27}^+, Na_{35}^+, Na_{53}^+, \) and \( Na_{119}^+ \). These clusters cover different size regions and represent both prolate and oblate shapes. Following calculations \( [2]-[8] \), they do not exhibit neither triaxiality, nor octupole deformation and, so, we may safely deal only with axial quadrupole and hexadecapole deformations. The equilibrium values of \( \delta_2 \) and \( \delta_4 \) and the corresponding moments are presented in Table I. The moments are defined as

\[
\beta_\lambda = \frac{4\pi}{3} \int d\mathbf{r} \rho_0(\mathbf{r}) r^\lambda \frac{Y_{\lambda 0}}{N_e \tilde{R}}, \quad \tilde{R} = \sqrt{\frac{5 \int d\mathbf{r} \rho_0(\mathbf{r}) r^2}{3 \int d\mathbf{r} \rho_0(\mathbf{r})}}, \quad \lambda = 2, 4.
\]
As we checked, the calculated moments are close to those obtained within the Structure Averaged Jellium Model (SAJM) \[3\]. Table I shows that some clusters exhibit considerable hexadecapole deformation. Further, in particular clusters the values $\delta_4$ and $\beta_4$ seem to be disentangled. For example, large $\delta_4$ corresponds to small $\beta_4$ in $Na_{15}^+$ and vice versa in $Na_{27}^+$. This reflects the fact that hexadecapole moments are determined by both quadrupole and hexadecapole terms in (13) and, moreover, the role of the quadrupole term is leading.

The calculations show that in light clusters $Na_{15}^+$, $Na_{27}^+$ and $Na_{35}^+$ the ground state deformations are characterized by a deep and distinctive minimum with considerable energy gain as compared with shape isomers. The number of isomers increases and their energy difference shrinks with increasing system size. The first isomers in $Na_{53}^+$ and $Na_{119}^+$ are given in the Table I. They exhibit an opposite sign of quadrupole deformations as compared to the ground state. Fig.1 shows, as an example, the energy surface of $Na_{119}^+$, which has three distinct minima. The second isomer demonstrates a dominant hexadecapole deformation.

In Figs. 2 and 3, the single-particle spectra of prolate $Na_{27}^+$ and oblate $Na_{35}^+$ are shown and compared with the corresponding spectra in the spherical limit. It is well visible how the deformation removes degeneracies. Note that prolate and oblate clusters exhibit the opposite assignment of quantum numbers inside subshells.

3 Separable approach to dynamics

3.1 Small amplitude dynamics

Up to now, we have determined stationary states with a mean field $\hat{h}_0(\mathbf{r})$, density $\rho_0(\mathbf{r})$ and single-particle wave functions $\psi_q(\mathbf{r})$. We are now proceeding the dynamical Kohn-Sham equations

$$\hat{h}(\mathbf{r},t)\psi_q(\mathbf{r},t) = i\frac{\partial}{\partial t}\psi_q(\mathbf{r},t).$$

(16)

The many-body wave functions are composed from the single-particle wave functions $\psi_q(\mathbf{r},t)$ as Slater determinants $\Psi(\mathbf{r}_1, ..., \mathbf{r}_N, t)$. In the linear regime, when only small oscillations about the stationary state are considered, one gets in first order perturbation

$$\Psi(t) \simeq \Psi_0 + \delta\Psi(t),$$

$$\rho(\mathbf{r}, t) \simeq \rho_0(\mathbf{r}) + \delta\rho(\mathbf{r}, t),$$

$$\hat{h}(\mathbf{r}, t) \simeq \hat{h}_0(\mathbf{r}) + \delta\hat{h}(\mathbf{r}, t)$$

where the response mean-field reads in detail

$$\delta\hat{h}(\mathbf{r}, t) = \left(\frac{\delta U_{xc}}{\delta \rho}\right)_{\rho_0}\delta\rho(\mathbf{r}, t) + \int d\mathbf{r}_1 \frac{\delta\rho(\mathbf{r}_1, t)}{|\mathbf{r} - \mathbf{r}_1|} \equiv \text{Tr}_2 \left\{ \hat{V}_{\text{res},12} \delta\rho_2 \right\}.$$  

(17)
The $\hat{\delta}h(\mathbf{r}, t)$ is a purely instantaneous and local operator by virtue of the local-density approximation inherent in the Kohn-Sham scheme used here. For harmonic oscillations it can be written as

$$\hat{\delta}h(\mathbf{r}, t) = \hat{\delta}h^+(\mathbf{r})e^{i\omega t} + \hat{\delta}h^-(\mathbf{r})e^{-i\omega t}. \quad (18)$$

Further, for small-amplitude harmonic oscillations in the vicinity of the static ground state $\Psi_0$, the pertinent ansatz for a perturbation of the wave function reads

$$\delta \Psi(t) = \sum_{ph} \left( c^+_{ph} e^{i\omega t} + c^-_{ph} e^{-i\omega t} \right) \hat{a}^+_p \hat{a}^-_h \Psi_0 \quad (19)$$

where $\hat{a}^+_p$ and $\hat{a}^-_h$ are creation and annihilation operators of particle and hole states, respectively. Insertion of (18) and (19) into the time-dependent Kohn-Sham equation (16) with subsequent linearization and selection of the part $\propto e^{-i\omega t}$ yields finally a standard RPA problem for frequencies $\omega$ and corresponding amplitudes $c^\sigma_{ph}$:

$$\left( \varepsilon_{ph} + \sigma \omega \right) c^\sigma_{ph} + \langle p | \hat{\delta}h^\sigma | h \rangle = 0 \quad (20)$$

where $\sigma = \pm$ and

$$\langle p | \hat{\delta}h^\sigma | h \rangle = \sum_{p'h'} \left( \langle p'h' | \hat{V}_{\text{res}} | h \rangle c^\sigma_{p'h'} + \langle h' | \hat{V}_{\text{res}} | p \rangle c^{-\sigma}_{ph} \right). \quad (21)$$

### 3.2 Separable RPA

The full RPA, although straightforward, can become very expensive because the dimension of the matrix of $\hat{V}_{\text{res}}$ grows huge in demanding applications. The separable approach is designed to reduce the expense of such calculations. Inserting (11) into the full response (21) yields

$$\langle p | \hat{\delta}h^\sigma | h \rangle = \sum_k \alpha^\sigma_k \langle p | \hat{Q}_k | h \rangle, \quad (22)$$

$$\alpha^\sigma_k = \sum_{kk'} \kappa_{kk'} \int d\mathbf{r} Q^\sigma_k(\mathbf{r}) \delta \rho^\sigma(\mathbf{r})$$

$$= \sum_{kk'} \kappa_{kk'} \sum_{ph} \left( \langle p | \hat{Q}_k^\sigma | h \rangle c^\sigma_{ph} + \langle h | \hat{Q}_k^\sigma | p \rangle c^{-\sigma}_{ph} \right). \quad (23)$$

Note that the values $\hat{\delta}h^\sigma(\mathbf{r})$, $\alpha^\sigma_k$ and $\delta \rho^\sigma(\mathbf{r})$ become independent of $\sigma$ for purely local separable operators $\hat{Q}_k(\mathbf{r})$. Such situation takes place when the motion is driven only by variations of time-even densities. This is just the case for clusters where the dynamics is determined by oscillation of time-even density of valence electrons. Then,

$$\alpha_k = \sum_{k'} \kappa_{kk'} \sum_{ph} \langle p | \hat{Q}_{k'} | h \rangle \left( c^+_{ph} + c^-_{ph} \right). \quad (24)$$

Using (22), the RPA equations (20) can be reshuffled into

$$c^\pm_{ph} = -\frac{1}{2} \sum_k \alpha_k \langle p | \hat{Q}_k | h \rangle \left( \varepsilon_{ph} \pm \omega \right). \quad (25)$$
Inserting (25) into (24) yields finally a system of linear homogenous equation for weights $\bar{\alpha}_k$:

$$\sum_{k'=1}^{K} s_{kk'}(\omega) \bar{\alpha}_{k'} = 0 \quad (26)$$

where

$$s_{kk'}(\omega) = \sum_{ph} \frac{<p|\hat{Q}_k|h> <p|\hat{Q}_{k'}|h> \varepsilon_{ph}}{\varepsilon_{ph}^2 - \omega^2} - \frac{1}{2\kappa_{kk'}}. \quad (27)$$

In Eq. (27) the sum runs over all particle-hole states of a given multipolarity. The condition

$$\det | s(\omega) | = 0 \quad (28)$$

gives SRPA dispersion equation for eigenvalues $\omega_j$.

The rank of the SRPA matrix (24) is equal to the number $K$ of the separable operators, which, as is shown below, is typically 3-6. So the rank is dramatically less than in the case of involved RPA methods. This results in drastic simplification of RPA calculations. At the same time, the total number of SRPA roots equals to the number of particle-hole configurations and every SRPA state is a superposition of these configurations. The SRPA keeps the important RPA feature to describe the Landau damping but gets this with much less computational effort.

It's straightforward to show that Eqs. (26)-(28) can be also obtained with a generalized schematic RPA Hamiltonian

$$\hat{H} = \hat{H}_0 - \frac{1}{2} \sum_{kk'} \tilde{\kappa}_{kk'} \hat{Q}_k^\dagger \hat{Q}_{k'} \quad (29)$$

This can be done by substituting the Hamiltonian (29) to the standard RPA equations

$$[\hat{H}, \hat{O}_j^\dagger] = \omega_j \hat{O}_j^\dagger, \quad [\hat{H}, \hat{Q}_j] = -\omega_j \hat{Q}_j, \quad [\hat{O}_j, \hat{O}_j^\dagger] = \delta_{jj'} \quad (30)$$

for the creation phonon operator $\hat{O}_j^\dagger = \sum_{ph} \left( c_{ph}^j \hat{a}_p^+ \hat{a}_h^+ + c_{ph}^{j+} \hat{a}_h^+ \hat{a}_p^+ \right)$ and its hermitian conjugate. The matrix $[\tilde{\kappa}_{kk'}]$ in (29) is inverse to the matrix $[\kappa_{kk'}^{-1}]$ in (27).

Note that relative contributions of operators $\hat{Q}_k(r)$ to RPA states are not fitted but regulated self-consistently by the weights $\bar{\alpha}_k^j$. Every RPA state $j$ has its own set of the weights. The normalization condition for the particle-hole amplitudes $c^{j\sigma}_{ph}$ and weights $\bar{\alpha}_k^j$ can be written through derivatives of $s_{kk'}(\omega_j)$:

$$\sum_{ph} (c^{j-}_{ph})^2 - (c^{j+}_{ph})^2 = \sum_{kk'} \bar{\alpha}_k^j \bar{\alpha}_{k'}^j \sum_{ph} \frac{<p|\hat{Q}_k|h> <p|\hat{Q}_{k'}|h> \varepsilon_{ph}}{\varepsilon_{ph}^2 - \omega_j^2} = \frac{1}{2} \sum_{kk'} \bar{\alpha}_k^j \bar{\alpha}_{k'}^j \frac{\partial}{\partial \omega_j} s_{kk'}(\omega_j) = 2. \quad (31)$$
3.3 Self-consistent prescription for separable operators

Up to now, the operators $\hat{Q}_k(r)$ and strength matrix $\kappa_{kk'}$ were not still chosen. Obviously, the success of SRPA depends on the choice. The better it is, the smaller number of the separable operators we need to reproduce $\hat{V}_{\text{res}}$. We are considering systems with pronounced collective modes (the various plasmons in case of clusters) and so just collective deformations should motivate the form of $\hat{Q}_k(r)$. Here we will follow the VPM prescription [34] which was very effective in the SRPA calculations for spherical clusters [29]. In the VPM, the operators $\hat{Q}_k(r)$ are self-consistently generated by collective variations of the density which in turn is determined by the scaling transformation [34, 41]. Being thus constructed, only few operators are enough to cover successfully the dynamics. Specifically, the collective deformation is achieved by the scaling transformation

$$\Psi(t) = \prod_{k=1}^{K} e^{\alpha_k(t) \sum_{i=1}^{N} [\hat{h}_0(r_i), f_k(r_i)]} \Psi_0.$$ (32)

Here, the local operators $f_k(r)$ determine the intended time-even shape of the deformation. For example, $f = z$ leads to a translation along $z$-direction, $f = r^2 Y_{20}$ results in an ellipsoidal deformation. The collective amplitudes $\alpha_k(t) = \tilde{\alpha}_k \cos \omega t$ determine the relative weights of different deformation modes. For small deformations $\tilde{\alpha}_k$, the density variation becomes

$$\delta \rho(r, t) = (\Psi(t)|\hat{\rho}|\Psi(t)) - (\Psi_0|\hat{\rho}|\Psi_0) \simeq \sum_{k=1}^{K} \alpha_k(t) (\nabla \rho_0(r) \cdot \nabla f_k(r) + \rho_0(r) \Delta f_k(r))$$ (33)

which, after submission into (17), results in the response Hamiltonian

$$\delta \hat{h}(r) = \sum_{k=1}^{K} \alpha_k \hat{Q}_k(r)$$ (34)

composed from the operators

$$\hat{Q}_k(r) = \int dr_1 V_{\text{res}}(r - r_1) (\nabla \rho_0(r_1) \cdot \nabla f_k(r_1) + \rho_0(r_1) \Delta f_k(r_1))$$ (35)

with

$$V_{\text{res}}(r - r_1) = \left( \frac{\partial U_{xc}}{\partial \rho} \right)_{\rho = \rho_0} \delta(r - r_1) + \frac{e^2}{|r - r_1|}.$$ (36)

Operators (35) take, by construction, into account all deformation distortions of the ground state (this point is discussed in the Appendix B where the explicit expression for $\hat{Q}_k(r)$ in deformed clusters is given.) It is now self-suggesting that these operators are identical with the basis operators to be used in the separable ansatz (1). This amounts to identify the collective response (34) of operators (35) with that from the separable ansatz (22), which finally yields the strengths coefficients as

$$\kappa_{kk'}^{-1} = - \int dr Q_k(r)(\nabla \rho_0(r) \cdot \nabla f_{k'}(r) + \rho_0(r) \Delta f_{k'}(r)).$$ (37)
Eqs. (25)-(29), (31), and (35)-(37) constitute the complete set of self-consistent SRPA equations. One has to point out that, like involved RPA, SRPA maintains full details of \(l_{ph}\) structure in the spectra. The only point is that the residual interaction is parametrized in terms of collective picture.

It is easy to see from (32) that just input local operators \(f_k(r)\) determine the character of the perturbation. The choice of the operators is the most delicate point of the approach and devotes a special attention (see discussion in Appendix C). We use the set of hermitian operators:

\[
f_{\lambda_k p_k \mu_k}(r) = r^{\lambda_k + p_k}(Y_{\lambda_k \mu_k}(\Omega) + Y_{\lambda_k \mu_k}^\dagger(\Omega))
\]

with

\[
\lambda_k p_k = 10, 12, 14, 30, 32 \text{ for } (\mu = 0, 1),
\]
\[
\lambda_k p_k = 20, 22, 24, 40, 42 \text{ for } (\mu = 0, 1, 2),
\]
\[
\lambda_k p_k = 30, 32, 34, 50, 52 \text{ for } (\mu = 0, 1, 2, 3)
\]

for dipole, quadrupole and octupole excitations, respectively. It is seen that in all the sets the first operator has the form of the applied electric external field in the long-wave approximation, the others two represent a variety of the radial dependencies to cover different slices of the system and the last ones take into account the coupling of different \(\lambda\)-modes with equal \(\mu\) and parity, which takes place in deformed systems. Relative contributions of different input operators \(f_{\lambda_k p_k \mu_k}(r)\) to the residual interaction are self-consistently regulated by the strict computation of the strengths according to Eq. (37).

### 3.4 Response to electric fields

The photoabsorption cross section for excitation of the state \(j = \Lambda^\pi\) in axially deformed cluster has the form

\[
\sigma(E\lambda\mu; gr \rightarrow j) = 8\pi^3 \frac{\lambda + 1}{\lambda[(2\lambda + 1)!!]^2} \left(\frac{\omega_j}{\hbar c}\right)^{2\lambda-1} \delta_{\Lambda,\mu,\Lambda} M_{\lambda j}^2
\]

where

\[
M_{\lambda j} = \langle j|r^{\lambda}Y_{\lambda\mu}|0\rangle
\]

\[
= \frac{1}{\sqrt{2}} \sum_{p_{ph}} <p|r^{\lambda}Y_{\lambda\mu}|h> (c_{p_{ph}}^+ + c_{p_{ph}}^-) = -\frac{1}{\sqrt{2}} \sum_k \alpha_k^j A_k(\omega_j)
\]

is the reduced matrix element of \(E\lambda\mu\) transition from the ground state to the RPA state \(j\) and

\[
A_k(\omega_j) = \sum_{p_{ph}} \frac{\varepsilon_{p_{ph}} <p|r^{\lambda}Y_{\lambda\mu}|h> <p|\hat{Q}_k|h>}{\varepsilon_{p_{ph}}^2 - \omega_j^2}.
\]

Plasmons in deformed clusters involve a lot of RPA states which in any case cannot be well resolved. So, it worth to consider not every RPA state but an averaged response. Strength function formalism allows to get the averaging response
without dealing with RPA problem for every state, which gives a huge gain in the computational effort. The factorized residual interaction used in SRPA makes derivation of the strength function especially simple \[12\]. Following this line, the strength function is defined as

\[
\sigma(E\lambda\mu, \omega) = \sum_j \sigma(E\lambda\mu; gr \mapsto j) \eta(\omega - \omega_j) 
\]  

(43)

where

\[
\eta(\omega - \omega_j) = \frac{1}{2\pi} \frac{\Delta}{(\omega - \omega_j)^2 + (\Delta/2)^2} 
\]  

(44)

is Lorentz weight with an averaging parameter \(\Delta\). Using Cauchy residue theorem, one may rewrite (43) in the form independent of \(j\) (when the response is directly computed for given \(\omega\)). The derivation starts with the squared matrix element of \(E\lambda\mu\) transition which, provided that SRPA matrix \(s_{kk'}\) (Eq. (27)) is symmetric, can be written as

\[
M^2_{\lambda j} = \frac{G(\omega_j)}{\partial/\partial\omega_j \text{det} |s(\omega_j)|} 
\]  

(45)

where

\[
G(\omega_j) = \sum_{kk'} S_{kk'}(\omega_j) A_k(\omega_j) A_{k'}(\omega_j), 
\]  

(46)

and \(S_{kk'}(\omega_j)\) is the algebraic supplement of the matrix element \(s_{kk'}(\omega_j)\). Then, provided that the function \(1/\text{det} |s|\) has only one-multiple poles \(\omega = \pm \omega_j\), the strength function \([13]\) is expressed through the corresponding residues on the complex plain \(z\):

\[
\sigma(E\lambda\mu, \omega) = 8\pi^3 \frac{\lambda + 1}{\lambda[(2\lambda + 1)!!]^2} \frac{1}{(hc)^{2\lambda-1}} \sum_j \text{Res}[F(\omega, z)]_{z=\pm \omega_j} 
\]  

(47)

where

\[
F(\omega, z) = \frac{z^{2\lambda-1}\eta(\omega - z)G(z)}{\text{det} |s(z)|}. 
\]  

(48)

Following Cauchy theorem, sum of all the residues (covering all possible poles of the function \([18]\)) is zero and so we can express the residues with \(z = \omega_j\) through the rest of the others:

\[
\text{Res}[F]_{z=\omega_j} = - (\text{Res}[F]_{z=-\omega_j} + \text{Res}[F]_{z=\infty}) + \text{Res}[F]_{z=\omega\pm i(\Delta/2)} + \text{Res}[F]_{z=\varepsilon_{ph}}. 
\]  

(49)

It’s easy to prove that \(\lim_{|z| \to \infty} F(\omega, z) = 0\) for \(\lambda = 1, 2\). Also, \(\text{Res}[F]_{z=-\omega_j}\) and \(\text{Res}[F]_{z=\varepsilon_{ph}}\) can be neglected for large positive \(z\)-values in the plasmon energy region and for relevant values of the averaging parameter \(\Delta\). Remaining residues over the poles \(z = \omega \pm i(\Delta/2)\) and \(z = \varepsilon_{ph}\) give the final outcome

\[
\sigma(E\lambda\mu, \omega) = 8\pi^3 \frac{\lambda + 1}{\lambda[(2\lambda + 1)!!]^2} \frac{1}{(hc)^{2\lambda-1}} 
\]  

(50)
Unlike expression for the standard strength function \( [31, 16] \), Eq. (50) consists from two terms. The first one is contribution from the residual interaction and the second one is unperturbed strength function. This form is convenient for the analysis. The standard strength function can be reduced to the form (50) if the width \( \Delta \) is introduced to \( \delta(\omega \pm \omega_j) \)-distribution. This gives the Lorentz shape. Eq. (50) can be used for calculation of E1 and E2 photoabsorption.

Model-independent energy-weighted sum rules (EWSR)

\[
S(E\lambda) = \sum_\mu \sum_{\varepsilon_{ph}} \varepsilon_{ph} < p | r^{\lambda} Y_{\lambda\mu} | h >^2 = \sum_\mu \sum_j \omega_j M_{\lambda\mu j}^2
\]

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

is used to control the completeness of the 1ph configuration space.

4 Results and discussion

4.1 Dipole plasmon

Results of SRPA calculations for the dipole plasmon are exhibited in Figs. 4-6. Two different presentations are used. First, to demonstrate the complex structure of the plasmon and Landau damping, the photoabsorption strength (40) is given for every RPA state by a vertical bar (in eV Å). Second, for the convenience of the comparison with experimental data, the strength function (43) averaged with the Lorentz weight is used. The value of the averaging parameter is \( \Delta = 0.25 \text{ eV} \) to simulate the typical thermal broadening of the plasmon.

In Fig. 4, the photoabsorption is presented for three light deformed clusters, prolate \( Na_{15}^{+} \) and \( Na_{27}^{+} \) and oblate \( Na_{35}^{+} \). The SRPA calculations are compared with recent experimental data [39] obtained at rather low temperature \( T = 105K \). The agreement with experiment is very satisfying. It should be mentioned that the average energy of the plasmon was slightly corrected by decrease of the diffuseness parameter \( \alpha \) in (12) from 1.0 to 0.8 \( a_0 \). The value 1.0 \( a_0 \) chosen to simulate ionic effects at high temperatures (\( T = 400 - 800K \)) [27] is not suitable for \( T = 105K \). The decrease of the surface diffuseness \( \alpha \) leads to a blueshift of the plasmon, which is indeed seen when lowering the temperature. Beside the good description of the average energy, the deformation splitting of the plasmon into two peaks is well reproduced. The peaks correspond to \( \mu = 0 \) and 1 dipole modes. The latter involves contributions from both \( \mu = \pm 1 \) projections and so is about twice as large. This mode forms the upper part of the plasmon spectrum in prolate clusters and the lower part in oblate ones (see also Fig. 9 c). The splitting is well developed in the prolate clusters and less strong in the oblate \( Na_{35}^{+} \). Though first evidence of the Landau damping is already seen, the plas-
mon gross-structure and width are still mainly determined by the deformation splitting.

Following such a splitting analysis, one is tempted to associate with $Na_{53}^+$ (see Fig. 5) an oblate deformation. Its plasmon shape is rather similar to the one for oblate $Na_{35}^+$ and the broad peak with a small right shoulder at 3.1 eV can, in principle, be approximated by two Lorentz curves “justifying” an oblate shape, as done e.g. in [39]. However, our calculations show that this interpretation is misleading. Unlike lighter clusters, $Na_{53}^+$ shows considerable Landau damping (see bars in Fig. 5, top panel). This broadens the plasmon and modifies its gross-structure. In particular, the structure at 3.1 eV is caused not by $\mu = 0$ mode but by the group of $\mu = 1$-states. Our calculations predict for this cluster the prolate shape, which results in very satisfactory agreement with the experimental data. Good description is also obtained for other clusters in this size region (see the comprehensive SRPA analysis of the data [39] in [43]). Our conclusion on prolate shape of clusters in this size region agrees with calculations of other groups [44]. Altogether this means, that generally accepted experimental practice to treat plasmon shape within simple deformation models and thus to conclude on cluster deformation is not appropriate for medium-size clusters. This way does not take into account important role of Landau damping in forming plasmon gross-structure and width and so can be misleading.

For medium and large clusters, the disentangling of the dipole spectrum becomes even more complicated because of possible incoherent contributions from isomers. Table I shows that $Na_{53}^+$ has oblate isomeric state with a tiny energy deficit as compared with the ground state. This isomer can also contribute to the observed spectrum. The bottom panel of Fig. 5 demonstrates that the isomeric state yields similar pattern, in spite of reverse ordering of $\mu = 0$ and 1 modes. In $Na_{53}^+$ both the modes are broad and have two-peak structure. In some important details the isomer plasmon deviates from the experimental data.

The picture is complicated with further growing cluster size. As was shown in Fig.1, the energy surface in $Na_{119}^+$ has already three distinctive minima: oblate ground state, first prolate isomer and second hexadecapole isomer. The corresponding plasmons are exhibited in Fig. 6. Contributions of $\mu = 0$ and 1 modes are also given to show the role of the deformation. All the plasmons demonstrate strong Landau damping which determines, in a large extent, their width. Just because of Landau damping, the plasmons, in spite of different cluster deformations, show very similar broad shapes. Obviously, all three deformation configurations of $Na_{119}^+$ can contribute to the measured spectrum. Indeed, clusters exhibit thermal shape fluctuations which are incoherently added in experiment. The shapes of the ground state and first isomers have to provide the dominant contribution. The observed plasmon reflects a statistical mix of many shapes with a few dominants.

To summarize, the calculations demonstrate increasing importance of Landau damping and isomer mixing for the dipole spectrum. Already at medium cluster sizes these factors cannot be neglected. As a result, the often used prescription to conclude on cluster shape on the grounds of approximation of plasmon shape...
by 1-3 Lorentz curves is insufficient for these system sizes.

The strong fragmentation of the spectra through Landau damping may raise doubts on the collectivity of the plasmon oscillation. The strength is distributed over many sub-states and calculations show that even the strongest RPA states do not exceed more than 2-4 times the strength of particle-hole configurations, in heavy clusters even less. Nevertheless, the entity of RPA states near the plasmon frequency can still be called collective. One may view this as a two step process. The dipole excitation first generates a collective surface plasmon state which is then quickly distributed over the nearby particle-hole states through Landau damping. The lifetime of the collective dipole excitation can be estimated to be about 10 fs in large Na clusters \[21\]. The collectivity is also testified by reach particle-hole structure of RPA states.

### 4.2 Quadrupole and octupole plasmons

In Figs. 7-8 the photoabsorption cross sections for quadrupole and octupole plasmons in prolate \(Na_{27}^+\) and oblate \(Na_{35}^+\) are presented. Contributions from all the projections \(\mu\) are given to demonstrate the role of the deformation broadening.

The figures show strong Landau damping. Its contribution to the width and gross structure of plasmons is of the same scale or even larger than from deformation splitting. The prolate \(Na_{27}^+\) has a strong deformation and we see a distinctive blueshift of \(\mu\)-branches of the plasmon with increasing \(\mu\). This makes the deformation splitting comparable with Landau damping. The deformation is weaker in the oblate \(Na_{35}^+\), which makes the deformation splitting less pronounced than Landau damping.

Both, quadrupole and octupole plasmons, are well concentrated (especially in the less deformed \(Na_{35}^+\)), which helps their experimental observation. The plasmons have a high-energy tail. Analysis of structure of main RPA states from the plasmon region shows that they have about the same character as in the dipole case. There is initially a collective multipole plasmon which is then quickly Landau damped and fragmented over the many nearby particle-hole states.

As is seen from the figures, photoabsorption cross sections for quadrupole and octupole plasmons are \(10^5\) and \(10^{10}\) times weaker than in the dipole case. Both plasmons share the energy region with the all dominating dipole plasmon and so should be completely masked by the latter. Strong Landau damping of the plasmons additionally decreases their chance to be observed in photoabsorption. However, following the estimates \[45\], inelastic electron scattering could resolve these states. At certain angles of outcoming electron, contributions of \(\lambda = 2\) and 3 plasmons to the cross section can successfully compete with the dipole contribution. The reaction is very demanding as it requires an intense, monochromatic and well collimated low-energy electron beam. However, progress of experimental techniques gives us some hope. SRPA results can be used in such experiments as a first guide for plasmon energies and strength distributions.
5 Conclusions

The separable RPA (SRPA), a self-consistent approach to RPA, is presented in connection with investigation of multipole plasmons in deformed clusters. Both ground state properties and RPA response are calculated using the same Kohn-Sham functional for axial shapes. Due to self-consistent factorization of the residual interaction, SRPA dramatically simplifies RPA calculations. At the same time, the method ensures high accuracy of the calculations. As compared with other RPA methods, SRPA provides a comprehensive treatment of Landau damping with a minimal computational effort. This is crucial for deformed systems where one deals with an impressive particle-hole configuration space.

SRPA has been applied to dipole, quadrupole and octupole plasmons in a variety of axial clusters. The main attention was paid to the dipole plasmon. Light, medium and heavy clusters of both prolate and oblate shapes were covered. Both quadrupole and hexadecapole deformations were taken into account. Contributions to the plasmon from both ground and isomeric states were analyzed. Good agreement with available experimental data was achieved.

Unlike light axial clusters, where dipole plasmon has a typical two-peak structure reflecting the deformation splitting, the dipole spectra in medium and heavy deformed clusters show usually a broad bump with relatively small variations of the shape. The deformation splitting is masked by strong Landau damping which inhibits a direct determination of ground state deformations from the spectra. Moreover, such clusters have shape isomers which further overlay the spectra. As a result, a correct treatment of plasmon properties is possible only on the grounds of fully microscopic calculations taking into account all these effects. SRPA is a promising method for such investigations.

Quadrupole and octupole spectra were shown to stay well concentrated in spite of the deformation splitting and Landau damping. Both spectra have a considerable high-energy tail. The quadrupole and octupole spectra cannot be observed directly in photoabsorption experiments but there is some hope to disentangle them in inelastic electron scattering.
Appendix A

The problem (9) for the deformed Kohn-Sham potential

$$(-\frac{\hbar^2}{2m} \nabla^2 + U_C(r) + U_{xc}(r))\psi_q = \varepsilon_q \psi_q$$  \hspace{1cm} (52)$$
can be rewritten as a system of equations for amplitudes $a^q_s$ of the expansion (14):

$$(E_s - \varepsilon_q)a^q_s + \sum_{q'} a'^{q'}_s <\phi_s | \tilde{U}_C(r) + \tilde{U}_{xc}(r)| \phi_{s'}> = 0$$  \hspace{1cm} (53)$$

where

$$\tilde{U}_C(r) = U_C(r) - U^0_C(r),$$  \hspace{1cm} (54)$$
$$\tilde{U}_{xc}(r) = U_{xc}(r) - U^0_{xc}(r),$$  \hspace{1cm} (55)$$

and values $U^0_C(r)$ and $U^0_{xc}(r)$ enter the problem for spherical Kohn-Sham potential

$$(-\frac{\hbar^2}{2m} \nabla^2 + U^0_C(r) + U^0_{xc}(r))\phi_s = E_s \phi_s.$$  \hspace{1cm} (56)$$

For the quantities (12), (15), (54), and (55) the multipole expansion is used. In particular, the electron ground state density (15) is written as (see notations in Sec. 2)

$$\rho_0(r) = \sum_{\lambda} Y_{\lambda 0}(\Omega) \tilde{\rho}_\lambda(r),$$  \hspace{1cm} (57)$$

with

$$\tilde{\rho}_\lambda(r) = \frac{1}{\sqrt{\pi(2\lambda + 1)}} \sum_{q=NNz}^{occ} (-1)^\lambda (2 - \delta_{\lambda,0}) w_q \times \sum_{n_2,l_2,n_1,l_1} \sqrt{(2l_2 + 1)(2l_1 + 1)} C^\lambda_{l_2,0,l_1,0} C^{\lambda,0}_{l_2,-\lambda,l_1,0} a^q_{n_2l_2} a^q_{n_1l_1} R_{n_2l_2}(r) R_{n_1l_1}(r).$$  \hspace{1cm} (58)$$

In all the multipole expansions, including Eq. (57) we take $\lambda = 0, 2, 4, 6, 8$, which provides sufficient numerical accuracy.

Kohn-Sham equations (53) together with the density equation (57) are solved by an iteration method. Eigenvalues $\varepsilon_s$ and eigenfunctions $\phi_s$ for the spherical Kohn-Sham potential are used as the input.

The equilibrium deformations $\delta_2$ and $\delta_4$ are determined by minimization of the total energy (2). It is convenient to use for the kinetic energy the expression

$$E_T = \frac{\hbar^2}{m_e} \sum_{q=NNz}^{occ} (2 - \delta_{\lambda,0}) \sum_{n_1,n_2}^{nnz} \sum_{l} a^q_{n_2l} a^q_{n_1l} \times (\int dr r^2 \frac{dR_{n_1l}(r)}{dr} \frac{dR_{n_2l}(r)}{dr} + l(l + 1) \int dr R_{n_1l}(r) R_{n_2l}(r)).$$  \hspace{1cm} (59)$$
where \((-1)^l = \pi, \Lambda \geq 0\). Further [38],

\[
E_{xc} = \int d\mathbf{r}(\epsilon_{xc}(\rho_0(\mathbf{r})))\rho_0(\mathbf{r})
\]

(60)

with

\[
\epsilon_{xc} = \epsilon_x + \epsilon_c ,
\]

(61)

\[
\epsilon_x = \frac{0.916}{r_s} \text{Ry} a_0, \quad r_s(\rho_0) = \left(\frac{3}{4\pi\rho_0}\right)^{1/3},
\]

\[
\epsilon_c = -0.066 \text{Ry} \{(1 + x^3)\log(1 + x^{-1}) + \frac{1}{2}x - x^2 - 1/3\},
\]

\[
x = \frac{r_s}{11.4 a_0} .
\]

The Coulomb term can be written as

\[
E_C = \frac{e^2}{2} \int d\mathbf{r}(\rho_0(\mathbf{r}) - \rho_i(\mathbf{r}))U_C(\mathbf{r}) .
\]

(62)
Appendix B

Here we present explicit expression for the operator of residual interaction \( \langle 35 \rangle \) in deformed clusters. Making use a multipole expansions for densities \( \langle 12 \rangle \) and \( \langle 13 \rangle \) and potentials \( \langle 34 \rangle \) and \( \langle 35 \rangle \), one gets

\[
Q_k(r) = \sum_{\lambda} \sum_{L} (Y_{L\mu}(\Omega) + Y_{L\mu}^+(\Omega))
\]

\[
\times [C_{\lambda \lambda_0 \lambda_k \mu}^{L \mu} Q_{kLL}^{(C)}(r) + \sum_{\lambda'} \sum_{L'} (Y_{L'\mu}(\Omega) + Y_{L'\mu}^+(\Omega)) C_{\lambda \lambda_0 L \mu}^{L' \mu} Q_{kLL'\lambda' \lambda}^{(xc)}(r)]
\]

where

\[
Q_{kLL'\lambda' \lambda}^{(C)}(r) = -\frac{2}{\sqrt{4\pi(2L+1)} 2L+1}
\]

\[
\times \left[ r^{-(L+1)} \int dr R_{L \lambda}(r_1)r_1^{L+2} + r^L \int dr R_{L \lambda}(r_1)r_1^{-(L-1)} \right],
\]

\[
Q_{kLL'\lambda' \lambda}^{(xc)}(r) = -\frac{1}{2\pi} \left[ \frac{2\lambda' + 1}{2L' + 1} C_{\lambda_0 \lambda \lambda}^{L' 0} R_{L \lambda}(r) U_{xc}(r) \right],
\]

\[
R_{L \lambda}(r) = \frac{1}{2} r^{p_k - 1} \left\{ \frac{d\rho_\lambda(r)}{dr} N_{L \lambda}^{(k)} + \frac{\rho_\lambda(r)}{r} M_{L \lambda}^{(k)} \right\}.
\]

Here, \( \rho_\lambda(r) \) and \( \tilde{U}_{xc}(r) \) are expansion coefficients in \( \langle 38 \rangle \) and \( U_{xc}(r) = \sum_{\lambda} U_{xc}^\lambda(r) Y_\lambda(\Omega) \), respectively, and

\[
N_{L \lambda}^{(k)} = (p_k + \lambda_k + 1) \sqrt{\lambda_k(2\lambda_k - 1)(B_{L \lambda \lambda}^{(1)} - A_{L \lambda \lambda}^{(1)})}
\]

\[
- (\lambda_k - p_k) \sqrt{(\lambda_k + 1)(2\lambda_k + 3)(B_{L \lambda \lambda}^{(2)} - A_{L \lambda \lambda}^{(2)})}.
\]

\[
M_{L \lambda}^{(k)} = (p_k + \lambda_k + 1) \sqrt{\lambda_k(2\lambda_k - 1)((\tilde{\lambda} + 1)B_{L \lambda \lambda}^{(1)} + IA_{L \lambda \lambda}^{(1)})}
\]

\[
+ (\lambda_k - p_k) \sqrt{(\lambda_k + 1)(2\lambda_k + 3)((\tilde{\lambda} + 1)B_{L \lambda \lambda}^{(2)} + IA_{L \lambda \lambda}^{(2)})},
\]

\[
+ (\lambda_k - p_k)(p_k + \lambda_k + 1) \sqrt{(2\lambda_k + 1)(2\lambda + 1)C_{\lambda \lambda_0 \lambda_k 0}^{L 0}}.
\]

where

\[
A_{L \lambda \lambda}^{(1)} = \sqrt{(\tilde{\lambda} + 1)(2\tilde{\lambda} + 3)} \left( \begin{array}{ccc} \tilde{\lambda} + 1 & \lambda_k - 1 & L \\ \lambda_k & \tilde{\lambda} & 1 \end{array} \right) C_{\lambda \lambda_0 \lambda \lambda_k 0}^{L 0}.
\]

\[
A_{L \lambda \lambda}^{(2)} = \sqrt{(\tilde{\lambda} + 1)(2\tilde{\lambda} + 3)} \left( \begin{array}{ccc} \tilde{\lambda} + 1 & \lambda_k + 1 & L \\ \lambda_k & \tilde{\lambda} & 1 \end{array} \right) C_{\lambda \lambda_0 \lambda \lambda_k 0}^{L 0}.
\]

\[
B_{L \lambda \lambda}^{(1)} = \sqrt{\lambda(2\lambda - 1)} \left( \begin{array}{ccc} \lambda - 1 & \lambda_k - 1 & L \\ \lambda_k & \lambda & 1 \end{array} \right) C_{\lambda \lambda_0 \lambda \lambda_k 0}^{L 0}.
\]

\[
B_{L \lambda \lambda}^{(2)} = \sqrt{\lambda(2\lambda - 1)} \left( \begin{array}{ccc} \lambda - 1 & \lambda_k + 1 & L \\ \lambda_k & \lambda & 1 \end{array} \right) C_{\lambda \lambda_0 \lambda \lambda_k 0}^{L 0}.
\]
The values $C^{L\Lambda}_{\tilde{\lambda}\phi\lambda_k A}$ and those in big parentheses are Clebsch-Gordan coefficients and $6j$-symbols, respectively.

Expression (63) shows that coupling of oscillations of given multipolarity $(\lambda_k \mu)$ with the spherical ($\tilde{\lambda} = 0$) and deformed ($\tilde{\lambda} = 2, 4, ..$) parts of the density leads to a family of terms with $|\tilde{\lambda} - \lambda_k| \leq L \leq \tilde{\lambda} + \lambda_k$. Thus the residual interaction driven by the operator (63) takes into account not only the deformation distortions of the ground state density but also the coupling of $\mu^\pi$ modes with different $\lambda$. This coupling is pertinent only to deformed systems (see, e.g. discussion in [13]).
Appendix C

Here we will comment some essential points concerning the scaling (32), choice of input operators $f_{\lambda k \mu}(r)$, and convergence of the SRPA results.

Time-odd hermitian generators $\hat{P}_{\lambda k \mu}(r) = -i[\hat{h}_0(r), f_{\lambda k \mu}(r)]$ entering the scaling result in time-even paths $\alpha_k(t)$. The generators can be considered as momenta conjugate to time-even hermitian coordinate-like operators $f_{\lambda k \mu}(r)$. Since in our case all the dynamics is provided by the time-even electron density, there is no any need in time-even generators. This explains why the scaling includes not full but single-particle Hamiltonian. Indeed, if separable residual interaction in a schematic full Hamiltonian involves only time-even hermitian $\hat{Q}_k(r)$-operators, then

$$[\hat{H}, f]_{ph} \approx [\hat{h}_0, f] - \sum_{kk'} \kappa_{kk'}(\hat{Q}_k < \Psi_0|\hat{Q}_{k'}, f||\Psi_0 >) + < \Psi_0|\hat{Q}_k, f||\Psi_0 > \hat{Q}_{k'} = [\hat{h}_0, f],$$

since averaged commutators between hermitian operators of the same time-parity is zero.

It is easy to see from (32) that collective motion is determined by input operators $f_{\lambda k \mu}(r)$. The choice of the operators is motivated by physical reasons. The number of the operators should be as small as possible to minimize the computational effort and, at the same time, should be sufficient to ensure the convergence of the results. Specifically, if we study response of the system to an external field, then one of the operators must take the form of such field. One input operator is usually not enough to reproduce the true residual interaction, even if the separable interaction is constructed self-consistently. To overcome this trouble, we exploit the idea of the local RPA [26, 27] to use not one but several input operators. In the local RPA the cluster is treated as a system of several coupled oscillators, which allows to describe the gross structure of the resonance. Instead, SRPA can be viewed as a system of coupled schematic RPAs. The operators $f_{\lambda k \mu}(r)$ are chosen so that the corresponding operators of the residual interaction, $\hat{Q}_k$, have maxima at different slices of the system, including both surface and interior. Such input operators can be intuitively associated with different external probes causing the response of different parts of the system. Besides, several operators allow the system to relax additionally, which finally leads to high accuracy of the method [29]. The number of input operators is dictated by convergence of the results and usually 3-6 operators are enough.

Fig. 9 demonstrates the relative role of different input operators in forming the dipole plasmon. Prolate $Na_{27}^-$ and oblate $Na_{35}^-$ are considered as typical examples. It is seen that the residual interaction posed by the leading input operator $rY_{1\mu}$ shifts the unperturbed dipole strength from 1-1.5 eV to the energy $\sim 2.5$ eV. This operator is enough to get the correct excitation energy. However, there still exists an artificial high energy strength at 3.5-5 eV, which is confirmed neither by experimental data nor by the TDLDA results. In fact it is a consequence of a poor separable approximation. Involving additional dipole input operators (panel
c)) weakens the artificial strength. At the same time, the first operator is still leading. Its contribution remains to be overwhelming in most of the RPA states. The panel d) demonstrates the minor role of octupole operators responsible for the deformation coupling of the dipole and octupole modes with $\mu = 0, 1$. Our calculations performed for dipole, quadrupole and octupole plasmons in a variety of deformed clusters show that the deformation coupling of different multipole modes with a given $\mu$ is usually negligible. However, the deformation leads to a strong splitting of the plasmons to branches with different $\mu$ (see panel e) and Figs. 3-6). The comparison with experimental data for the dipole plasmon, given in Figs. 4-5, shows that SRPA correctly describes the deformation splitting.

Fig. 10 compares the dipole strength calculated within exact RPA and SRPA. Cluster $Na_{53}^+$, being in focus of the discussion above, is chosen as a typical example for the comparison. For the simplicity, only $\mu = 0$ dipole mode is considered. The figure demonstrates good agreement which justifies high accuracy of SRPA.

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Figure 1: Energy surface (in Ry) of Na$_{119}^{+}$ as a function of quadrupole and hexadecapole deformations. The iso-energy contours are separated by intervals 0.01 Ry. Three distinct minima are marked by crosses (the energies at the minima are given in Table I).

Figure 2: Single-particle spectrum in cluster Na$_{27}^{+}$ at zero and equilibrium (prolate) deformations. In the latter case the Fermi level is $\mathcal{N} n_{z} \Lambda = 321$. The evolution of the spectrum with deformation is marked by dashed lines.

Figure 3: The same as in Fig. 2 for oblate cluster Na$_{27}^{+}$. The Fermi level is $\mathcal{N} n_{z} \Lambda = 310$.

Figure 4: Photoabsorption cross section for dipole plasmon in small deformed sodium clusters. The deformation parameters are given in boxes. The experimental data [39] (triangles) are compared with SRPA results given as bars for RPA states [10] and as the strength function [43] smoothed by the Lorentz weight. The bars are given in eV$\alpha_{0}$.

Figure 5: Photoabsorption cross section for dipole plasmon in Na$_{53}^{+}$. The experimental data [39] (triangles) are compared with SRPA results for excitations from the prolate ground state (top) and oblate isomer (bottom). Contributions to the strength function from $\mu = 0$ and 1 projections (the latter has twice larger strength) are given by dashed curves. See Fig. 4 for notations.

Figure 6: Calculated photoabsorption cross section for dipole plasmon in Na$_{119}^{+}$. The excitations from the oblate ground state (top), first prolate isomer (middle) and second hexadecapole isomer (bottom) are considered. See Figs. 4 and 5 for notations.

Figure 7: Calculated photoabsorption cross section for quadrupole plasmon in prolate Na$_{27}^{+}$ and oblate Na$_{35}^{+}$. Contributions of projections with $\mu = 0, 1, 2$ and their sum (bottom panel) are given as bars [10] for RPA states and as strength function [43]. The bars are given in eV$\alpha_{0}$.

Figure 8: The same as in Fig. 7 for octupole plasmon.

Figure 9: Calculated photoabsorption cross section for dipole plasmon in prolate Na$_{27}^{+}$ and oblate Na$_{35}^{+}$ (see notations in Fig. 4.). The cases include: a) unperturbed (without the residual interaction) plasmon; b) with residual interaction generating by leading input operator $\lambda_{1} p_{1} = 10$ : $f_{10\mu}(r) = r(Y_{1\mu}(\Omega) + Y_{1\mu}^{\dagger}(\Omega))$; c) with operators $\lambda_{k} p_{k} = 10, 12, 14$; d) with operators $\lambda_{k} p_{k} = 10, 12, 14, 30, 32$, where two last ones provide the coupling with octupole modes; e) contributions of $\mu = 0$ (dashed curve) and $\mu = 1$ (solid curve) projections to the cross section.

Figure 10: Comparison of the dipole strength with $\mu = 0$ (as a squared transition matrix element [41]) calculated within exact RPA (solid curve) and SRPA (dashed curve) in prolate Na$_{53}^{+}$.
Table 1: Deformation parameters $\delta_2$ and $\delta_4$ (as defined in Eq. (13)) and quadrupole and hexadecapole moments $\beta_2$ and $\beta_4$ (16), calculated for the ground and isomeric (in $Na_{53}^+$ and $Na_{119}^+$) states. For isomers the energy deficits $\Delta E$ are given.

| Cluster  | $\delta_2$ | $\delta_4$ | $\beta_2$ | $\beta_4$ | $\Delta E$, eV |
|----------|------------|------------|-----------|-----------|----------------|
| $Na_{15}^+$ | 0.59       | -0.19      | 0.47      | -0.02     | -              |
| $Na_{27}^+$ | 0.33       | 0.08       | 0.36      | 0.17      | -              |
| $Na_{35}^+$ | -0.21      | 0.02       | -0.18     | 0.04      | -              |
| $Na_{53}^+$ | 0.20       | -0.03      | 0.20      | $\sim$ 0  | -              |
|           | -0.14      | -0.09      | -0.11     | -0.06     | 0.016          |
| $Na_{119}^+$ | -0.27      | -0.14      | -0.20     | -0.06     | -              |
|           | 0.24       | -0.04      | 0.24      | $\sim$ 0  | 0.004          |
|           | -0.04      | -0.22      | -0.02     | -0.18     | 0.024          |
\[ \delta_2 = \delta_4 = 0 \quad \delta_2 = -0.27 \quad \delta_4 = 0.02 \]

Diagram showing energy levels for \( \text{Na}^+_{35} \). The energy levels are labeled with their corresponding electron shells and subshells.
$\omega \ [eV]$

$\sigma(E1)/N_e \ [\AA^2]$

$Na_{15}^+$

$\delta_2 = 0.59$

$\delta_4 = -0.19$

$Na_{27}^+$

$\delta_2 = 0.33$

$\delta_4 = 0.08$

$Na_{35}^+$

$\delta_2 = -0.21$

$\delta_4 = 0.02$
$\omega$ [eV] [Å$^2$]

$\sigma(E1)/N_e$

$\delta_2 = 0.20$
$\delta_4 = -0.03$

$\delta_2 = -0.14$
$\delta_4 = -0.09$

$\text{Na}_53^+$
\( \omega [eV] \)

\( \sigma(E1)/N_e [Å^2] \)

\( \text{Na}^{+}_{119} \)

\( \delta_2 = -0.27 \)
\( \delta_4 = -0.14 \)

\( \delta_2 = 0.24 \)
\( \delta_4 = -0.04 \)

\( \delta_2 = -0.04 \)
\( \delta_4 = -0.22 \)
\[
\begin{align*}
\text{Na}_{27}^+ & \quad \mu = 0 \\
\text{Na}_{35}^+ & \quad \mu = 0 \\
\mu = 1 & \\
\mu = 1 & \\
\mu = 2 & \\
\mu = 2 & \\
\text{total} & \\
\text{total} & \\
\end{align*}
\]

\[\sigma (E^2)/N_e \text{ [Å}^2 \times 10^{-5}]\]
\[ \sigma(E_1)/N_e [\text{Å}^2] \]

\[ \omega [\text{eV}] \]

\[ \text{Na}_{27}^+ \quad \text{Na}_{35}^+ \]

(a) 

(b) 

(c) 

(d) 

(e)
\[ \text{Strength} \, \text{[e}^2 \cdot \text{Å}^2 / \text{eV]} \]

\[ \omega \, [\text{eV}] \]

\[ \text{Na}^+_{53} \]