Two-plasmon excitations in metallic clusters

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A boson-expansion method is used to study one- and two-boson states in metallic clusters. A jellium model and local-density-approximation energy-density-functional theory are the starting point for obtaining the basic bosons describing electron excitations. A boson mapping allows one to diagonalize the residual interaction between bosons. For the example of the $Na_{21}{}^{+}$ cluster, it is found that strong anharmonic effects appear in the electronic excitation spectrum.

I. INTRODUCTION

In recent years, photoabsorption experiments have shown the existence of strong dipole modes in alkali metal clusters.[1–3] These plasmon modes are collective excitations of electron-hole configurations[4–6] which are reminiscent of the well-known giant resonances (GR's) in atomic nuclei.[7,8] There are, of course, many analogies between atomic clusters and nuclear systems, but also important differences such as, for instance, the short-ranged character of the nuclear interaction as opposed to the long-range Coulomb force and the presence of a fixed ionic potential inside the metalic cluster. Furthermore, GR's of various multipolarities (L=0,1,2,3,...) are known in nuclei while our present experience in atomic clusters is restricted to dipole plasmons. Nevertheless, it is important to exploit further the analogies and take advantage of what is known in nuclei to gain better knowledge of cluster properties.

A very interesting recent development in nuclear GR studies is the experimental evidence of high-lying excitations which can be interpreted as double GR excitations, i.e., two independent bosons built on top of each other.[9–11] This interpretation is supported by theoretical models which predict the existence of harmonic multiple boson vibrations.[12,13] The spectrum of double GR states in nuclei was studied in Ref. 12 using a boson expansion scheme[14,15] and an effective Skyrme interaction. It was found that the shift of the eigenstates with respect to the unperturbed two-boson energies was small and essentially equal to the diagonal matrix elements of the residual interaction between bosons. The admixture between different two-boson states turned out to be small so that the harmonic picture was not destroyed by the boson-boson interaction. In a subsequent paper[13] the direct electromagnetic decay of two-boson states to the ground state was also studied and it was shown to be appreciable.

The Skyrme-Hartree-Fock approach in nuclei is very similar to the energy-density-functional approach based on the local density approximation (LDA), which is used in atomic clusters. Likewise, the random phase approximation (RPA) with Skyrme interaction has its counterpart in the time-dependent LDA (TDLDA). The TDLDA can be used, in conjunction with the jellium model, to describe the dipole plasmons in clusters.[4–6] Thus, it seems interesting to generalize the TDLDA to study to what extent the two-plasmon states can be harmonic by using the same methods as in Ref. 12. To our knowledge, the excitation spectrum of alkali-metal clusters in the energy range around twice the photoabsorption peak has not been explored experimentally yet and therefore one of the goals of the present work is to make some predictions based on a model which is admittedly phenomenological but which is otherwise relatively successful in explaining the photo-absorption peak and which does not necessitate formidable computations.

In Sec. II we shortly recall the TDLDA, mainly to define the notation and introduce the boson mapping we use to build interacting two-boson states. In Sec. III we present and comment on the results obtained in the $Na_{21}{}^{+}$ system. Finally, in Sec. IV some conclusions are drawn.

II. OUTLINE OF THE METHOD

We shall use in all equations atomic units ($e = m_e = \hbar = c = 1$) for which energies are in units of $2R_y$=27.2 eV and lengths in units of the Bohr radius a_0=0.53 Å, but results will be expressed in eV and Å. The starting point is to write the energy $E[\rho]$ of the system as a functional of the electron local density $\rho(\mathbf{r})$ and kinetic energy density $\tau(\mathbf{r})$:

$$E[\rho] \equiv \int \mathcal{E}(\rho) d^3r$$

$$= \int \left\{ \tau(\mathbf{r}) + \frac{1}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3r' + \rho(\mathbf{r})\mathcal{E}_{\rm xc}(\rho) + \rho(\mathbf{r})V_J(\mathbf{r}) \right\} d^3r + E_{JJ}, \quad (1)$$

where

$$\rho(\mathbf{r}) = \sum_{i=1}^{Z_e} |\phi_i(\mathbf{r})|^2,$$

$$\tau(\mathbf{r}) = \frac{1}{2} \sum_{i=1}^{Z_e} |\nabla\phi_i(\mathbf{r})|^2 . \quad (2)$$

In Eq. (2) the ϕ_i's are the single-particle (SP) wave functions of the Z_e occupied electron orbitals. The first four terms of $E[\rho]$ are, respectively, the electron kinetic energy, the electrostatic electron energy, the exchange-correlation energy, and the electron-ion energy. In the framework of LDA, we adopt the Gunnarsson-Lundqvist parametrization[16] for the exchange-correlation energy density $\mathcal{E}_{\rm xc}(\rho)$. The ionic component of the system is described by the jellium model of a uniformly charged sphere of radius $R = r_s Z^{\frac{1}{3}}$ ($Z = Z_e$ for neutral clusters, $Z > Z_e$ for ionized ones), where r_s is the Wigner-Seitz cell radius corresponding to the studied atoms. The last term E_{JJ} of Eq. (1) is just the Coulomb energy of the jellium sphere. Furthermore, the electron-jellium potential $V_J(\mathbf{r})$ is calculated simply by smearing the Coulomb interaction over the jellium sphere.

The variational procedure applied to $E[\rho]$ leads to the Kohn-Sham equations

$$\left(-\frac{1}{2}\nabla^2 + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3r' + V_J(\mathbf{r}) + \frac{\delta\mathcal{E}_{\rm xc}(\rho)}{\delta\rho} \right) \phi_i(\mathbf{r})$$

$$= \epsilon_i \phi_i(\mathbf{r}), \quad (3)$$

whose self-consistent solution gives the complete set (occupied and unoccupied) of SP states. This determines the ground state static properties in LDA. Furthermore, dynamical properties such as excitation spectra and transition probabilities can be calculated in TDLDA using the quasiparticle effective interaction derived from $E[\rho]$:

$$\hat{V}(\mathbf{r},\mathbf{r}') \equiv \frac{\delta^2\mathcal{E}(\rho)}{\delta\rho\delta\rho}$$

$$= \frac{1}{|\mathbf{r}-\mathbf{r}'|} + \frac{\delta^2\mathcal{E}_{\rm xc}(\rho)}{\delta\rho\delta\rho}\delta(\mathbf{r}-\mathbf{r}'). \quad (4)$$

The solutions of the TDLDA equations, using the above inputs, lead to the usual jellium model description of plasmon modes in clusters.[4–6] These solutions (called RPA states in nuclei) behave like quasibosons.[14] In order to go beyond this single-boson picture, we shall now reformulate the problem in a second quantization form which allows one to introduce easily multiple boson states. Let us write down an effective Hamiltonian for electrons in the form

$$H \equiv H_0 + \hat{V}$$

$$= \sum_i \epsilon_i : a_i^\dagger a_i : + \frac{1}{2} \sum_{ijk\ell} \hat{V}_{ij,k\ell} : a_i^\dagger a_j^\dagger a_\ell a_k : , \quad (5)$$

where $a_i^\dagger$ (a_i) is the creation (annihilation) operator for an electron in the SP state ϕ_i. The normal products are defined with respect to the Slater determinant $|\phi\rangle$ representing the LDA ground state. The (direct) two-body matrix elements are defined as

$$\hat{V}_{ij,k\ell} = \int \phi_i^*(\mathbf{r})\phi_j^*(\mathbf{r}')\hat{V}(\mathbf{r},\mathbf{r}')\phi_k(\mathbf{r})\phi_\ell(\mathbf{r}')d^3r d^3r'. \quad (6)$$

An elementary excitation will be described as the promotion of one particle from a SP state occupied in the ground state (denoted in the following as h) to an unoccupied one (denoted by p). Let us denote by $B_{ph}^\dagger(\lambda\mu)$ the creation operator of a particle-hole (p-h) pair coupled to total angular momentum λ and z component μ:

$$B_{ph}^\dagger(\lambda\mu) \equiv [a_p^\dagger a_h]_{\lambda\mu}. \quad (7)$$

At this point, it must be noted that the operators (7) belong to the set of more general operators $B_{ij}^\dagger(\lambda\mu)$, where i and j can be either occupied or unoccupied states, and that the Hamiltonian (5) can be expressed in terms of $B_{ij}^\dagger(\lambda\mu)$ and $B_{ij}(\lambda\mu)$ operators.

The p-h states are obviously eigenstates of H_0, but the residual interaction $\hat{V}$ will admix them. The TDLDA, or RPA, consists in considering that eigenstates of the system are linear superpositions of p-h configurations built on top of a correlated ground state $|0\rangle$:

$$|\psi_\nu\rangle = O_\nu^\dagger|0\rangle, \quad (8)$$

where $\nu \equiv (N,\lambda,\mu)$ denotes the quantum numbers of the corresponding eigenstate and

$$O_\nu^\dagger \equiv \sum_{ph} [X_{ph}^{(\nu)} B_{ph}^\dagger(\lambda\mu) + (-1)^\mu Y_{ph}^{(\nu)} B_{ph}(\lambda\mu)]. \quad (9)$$

The correlated and uncorrelated ground states $|0\rangle$ and $|\phi\rangle$ are, respectively, the vacuum for the operators O_ν and $B_{ph}(\lambda\mu)$:

$$O_\nu|0\rangle = 0,$$

$$B_{ph}(\lambda\mu)|\phi\rangle = 0. \quad (10)$$

The amplitudes X and Y, as well as the energy $\hbar\omega_\nu$ of the state $|\psi_\nu\rangle$, can be determined by solving the set of equations[14]

$$\begin{pmatrix} A & B \\ B^* & A^* \end{pmatrix} \begin{pmatrix} X^\nu \\ Y^\nu \end{pmatrix} = \hbar\omega_\nu \begin{pmatrix} X^\nu \\ -Y^\nu \end{pmatrix} , \tag{11}$$

where A and B are matrices whose elements are

$$A_{ph,p'h'} = (\epsilon_p - \epsilon_h)\delta_{pp'}\delta_{hh'} + \hat{V}_{ph';hp'},$$

$$B_{ph,p'h'} = \hat{V}_{pp';hh'}. \tag{12}$$

The solutions of Eq. (11) can be called one-boson states since the operators $O^\dagger_\nu$ and O_ν satisfy approximately boson commutation relations. A two-boson state is defined as

$$|\psi^{\lambda\mu}_{\nu_1,\nu_2}\rangle = \frac{1}{\sqrt{1+\delta_{\nu_1,\nu_2}}}[O^\dagger_{\nu_1}O^\dagger_{\nu_2}]_{\lambda\mu}\,|\,0\rangle, \tag{13}$$

and within RPA it will have an energy just equal to the sum $\omega_{\nu_1}+\omega_{\nu_2}$, independently of λ and μ. The inclusion of the parts of the residual interaction which are neglected in RPA, namely the $\hat{V}_{p_1p_2;p_3p_4}$, $\hat{V}_{h_1h_2;h_3h_4}$, $\hat{V}_{p_1p_2;p_3h}$, and $\hat{V}_{h_1h_2;h_3p}$ terms, introduces some mixing of the two-boson states of Eq. (13) among themselves and with the one-boson states of Eq. (8). Thus, an eigenstate of the total Hamiltonian will be of the form

$$|\psi^{\lambda\mu}\rangle = \sum_\nu a_\nu\,|\,\psi^{\lambda\mu}_\nu\rangle + \sum_{\nu_1\nu_2} b^{\lambda\mu}_{\nu_1\nu_2}\,|\,\psi^{\lambda\mu}_{\nu_1,\nu_2}\rangle. \tag{14}$$

Solving the equations of motion in the space spanned by the one- and two-boson states is a formidable task. A way to simplify the problem is to replace the fermionic operators O and B by other operators $\hat{O}$ and $\hat{B}$ satisfying exactly boson commutation relations. In principle, there exist several ways of mapping exactly the space of fermionic operators to that of bosonic operators.[14] All mappings imply representing fermionic operators by infinite series of bosonic ones. In practice, it is necessary to truncate the series at some order. Here, we shall use the following mapping:[17,12]

$$B^\dagger_{ph}(\lambda\mu) \longrightarrow \hat{B}^\dagger_{ph}(\lambda\mu), \tag{15}$$

$$B^\dagger_{pp'}(\lambda\mu) \longrightarrow \sum_{h''}\sum_{\lambda'\mu'\lambda''\mu''} \hat{\lambda}'\hat{\lambda}''(-1)^{j'-j''+\lambda+\lambda'}W(\lambda' j\lambda'' j';j''\lambda)(-1)^{\lambda''-\mu''}(\lambda'\mu'\lambda''-\mu''\,|\,\lambda\mu)\hat{B}^\dagger_{ph''}(\lambda'\mu')\hat{B}_{p'h''}(\lambda''\mu''), \tag{16}$$

$$B^\dagger_{hh'}(\lambda\mu) \longrightarrow \delta_{hh'}\delta_{\lambda 0}\delta_{\mu 0}\hat{j} - \sum_{p''}\sum_{\lambda'\mu'\lambda''\mu''} \hat{\lambda}'\hat{\lambda}''(-1)^{j-j''+\lambda''}W(\lambda'' j\lambda' j';j''\lambda)(-1)^{\lambda''-\mu''}(\lambda'\mu'\lambda''-\mu''\,|\,\lambda\mu)\hat{B}^\dagger_{p''h'}(\lambda'\mu')\hat{B}_{p''h}(\lambda''\mu''), \tag{17}$$

where $\hat{\lambda} \equiv \sqrt{2\lambda+1}$ and W is a Racah coefficient. The operators $\hat{O}^\dagger$ are then defined exactly as in Eq. (9) using the X and Y amplitudes of RPA, but with $\hat{B}$ and $\hat{B}^\dagger$ replacing B and $B^\dagger$. The fermionic ground state $|0\rangle$ is also mapped onto the vacuum of the boson operators: $\hat{O}_\nu|\hat{0}\rangle = 0$.

By the mapping (15)–(17) the Hamiltonian (5) is transformed into a boson Hamiltonian $\hat{H}$, which is expressed in terms of $\hat{B}$ and $\hat{B}^\dagger$. The matrix elements between multiple boson states can be easily computed because the Bogoliubov transformation (9) preserves Wick's theorem. Therefore, the Hamiltonian $\hat{H}$ including the residual interaction can be diagonalized in the one- and two-boson subspace leading to the energies and wave functions of the excited states. It is then possible to calculate the electromagnetic transition probabilities from the ground state to the excited ones. The relevant expressions are given in the Appendix.

III. RESULTS AND DISCUSSION

Starting from the energy functional (1) we have applied the formalism sketched in the preceding section to the $Na_{21}{}^+$ system, which is known to exhibit a giant dipole resonance around 2.7 eV.[3] The value of r_s used in this calculation is 3.93 a.u. The Kohn-Sham equations (3) are solved self-consistently with a box boundary condition at a radius $R = 14$ Å and assuming spherical symmetry. Then, the RPA-type equations (11) are solved for different multipolarities ($0 \le \lambda \le 4$) in order to obtain the basis of one-boson states. In practice, the configuration space must be truncated since its dimension determines the size of the matrix equation (11). For each multipolarity we have checked that the solution of Eq. (11) in the truncated space fulfills within 0.1% the theoretical energy-weighted sum rule (EWSR) of the corresponding multipole operators, the EWSR being calculated exactly

in terms of moments of the electron static density (the well-known f sum rule is just the EWSR in the special case of dipole operator).

We find that for $\lambda > 2$ the one-boson excitation spectrum is almost identical to the p-h spectrum, thus showing little collectivity. In Table I we report the energy and percentage of EWSR of the most collective states (i.e., those exhausting the largest fractions of EWSR) with $\lambda = 0, 1, 2$. For $\lambda = 1$ the excitation spectrum is largely dominated by a single peak at 3.03 eV, in reasonable agreement with the experimental findings. The $\lambda = 2$ spectrum shows three peaks, very close to each other, exhausting in total 86.4% of the corresponding EWSR. The monopole strength is more fragmented with seven states whose fractions of EWSR lie between 6% and 27%. For convenience we have grouped neighboring states into a single one at an energy equal to their centroid energy (see the last column of Table I) and with a strength such that this single state exhausts the same fraction of EWSR as the sum of the original states.

Next, the boson-boson residual interaction is diagonalized in the space spanned by the one- and two-boson states. The results, shown in Table II, are completely different from the corresponding ones in the nuclear case.[12] Indeed, looking at the 0^+ states, we see that the double giant dipole (GD) is completely spread over five states whose energies range from 9.6 to 16.9 eV. Also the double giant quadrupole (GQ) is quite fragmented, but it has a large component in the state at 9.6 eV. Both states are also quite mixed with the double monopole states, while the mixing with the single monopole states is small. In the case of 1^- and 2^+ states, the single GD and GQ bosons, respectively, are mixed very little with the two-boson states whereas the latter states are quite admixed among themselves. However, each 1^- or 2^+ state is dominated by a single component, at variance with the 0^+ case. Looking in more detail into the various terms contributing to the matrix elements of the Hamiltonian, it turns out that the $v_{h_1 h_2; h_3 h_4}$ terms are dominating over all the other ones in this $Na_{21}{}^+$ case, contrarily to what happens in nuclei.

TABLE I. Monopole, dipole, and quadrupole one-boson states in $Na_{21}{}^+$. Only states with the largest fractions of EWSR are shown. The last column shows the centroid energies of groups of states.

N	J^π	EWSR%	E (eV)	E (eV)
1	0^+	15.5	4.13	4.38
2	0^+	27.3	4.54	
3	0^+	12.8	5.20	
4	0^+	8.8	5.49	5.51
6	0^+	12.7	5.87	
5	0^+	6.0	6.47	6.72
7	0^+	11.2	6.87	
8	1^-	83.1	3.03	3.03
9	2^+	5.0	3.27	
10	2^+	20.1	3.33	3.56
11	2^+	60.9	3.67	

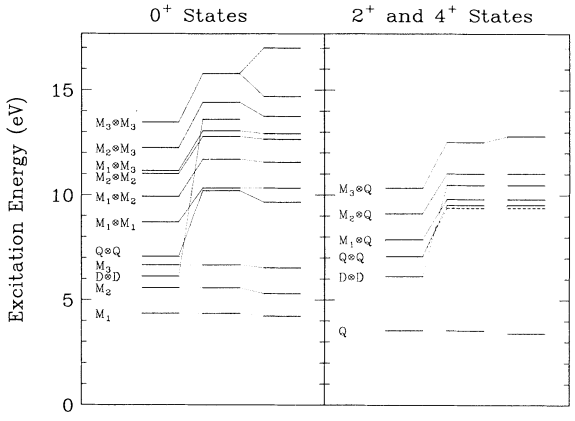

FIG. 1. Positive parity states in one-boson plus two-boson space. The boson labeling corresponds to Table II. The left columns show the spectra of noninteracting bosons, the middle columns show the displacements caused by diagonal matrix elements, and the right columns correspond to the results of diagonalizing the Hamiltonian.

In Figs. 1 and 2 represented are the unperturbed energies, diagonal matrix elements of the Hamiltonian, and eigenvalues obtained after diagonalization for positive and negative parity states, respectively. The most striking result is the huge upward shift of the two-boson states due to the diagonal matrix elements of the residual interaction. This is at variance with our previous results for the ^{40}Ca nucleus[12] obtained by starting from an energy density functional built from an effective Skyrme interaction and using the same procedure as in the present work. In Ref. 18 the same problem of the two-boson spectrum in the $Na_{21}{}^+$ cluster has been studied within the same jellium model by using a method based on a perturbative construction of periodic orbits of the time-dependent mean field equations. The result is a very

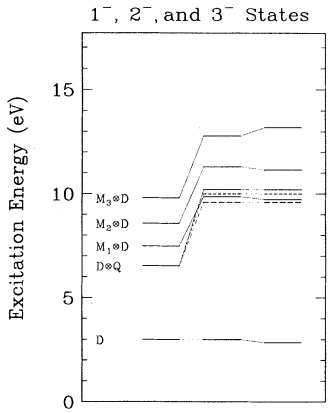

FIG. 2. Same as Fig. 1, but for negative parity states.

small shift, in line with the findings of the same authors[19] in the nuclear case. This may be an indication that their approach, which is expected to be more suited for states of larger angular momenta because of its semiclassical nature, is less appropriate in the present case especially when the effects of the residual interaction are very important, as we find in metal clusters.

We have investigated the possibility that the large shifts found in metal clusters could be due to the long range of the interaction, in contrast with the nuclear case where the interaction is short ranged. Replacing in $\hat{V}$ the Coulomb interaction by a Yukawa form and adjusting the range and strength parameters so that the volume integral inside the box of radius R is conserved, we have calculated a few typical matrix elements contributing importantly to the boson-boson residual interaction. The conclusion of this analysis is that the interaction range is not the origin of the different behavior in nuclei and clusters. On the other hand, examination of the X and Y amplitudes of the bosons show that in the cluster case, the Y amplitudes of the collective bosons are somewhat larger than in the nuclear case where X amplitudes generally dominate. Since boson-boson matrix elements are combinations of fermion-fermion matrix elements weighted by products of four X and Y amplitudes, it is possible that contributions containing products of Y amplitudes remain important in clusters while they vanish in nuclei. It is interesting to note that the occurrence of large Y amplitudes indicates that the cluster ground state $|\,0\rangle$ is strongly correlated. This can be related to

TABLE II. Energies and amplitudes [as defined in Eq. (14)] of eigenstates in the one-boson plus two-boson space.

(a) O^+ states

E (eV)	M_1	M_2	M_3
4.22	−0.981	−0.118	−0.042
5.36	−0.141	0.976	−0.091
6.57	0.044	0.115	−0.983
9.60	−0.019	−0.028	−0.025
10.33	0.054	0.034	0.025
11.57	−0.053	−0.068	−0.044
12.65	−0.016	−0.035	0.005
12.94	0.053	0.077	0.101
13.79	−0.070	−0.83	−0.092
14.70	0.030	0.017	−0.005
16.93	0.030	0.007	−0.050

E (eV)	$M_1 \otimes M_1$	$M_1 \otimes M_2$	$M_1 \otimes M_3$	$M_2 \otimes M_2$	$M_2 \otimes M_3$	$M_3 \otimes M_3$	$D \otimes D$	$Q \otimes Q$
4.22	−0.070	−0.055	−0.014	−0.020	−0.005	0.002	−0.098	0.063
5.36	0.045	0.073	0.032	0.043	0.020	0.004	0.077	−0.059
6.57	−0.036	−0.055	−0.082	−0.031	−0.053	−0.022	−0.048	0.040
9.60	0.026	0.0003	0.006	−0.004	0.001	0.002	−0.374	−0.926
10.33	−0.976	0.188	0.077	0.019	0.005	0.0003	−0.033	−0.017
11.57	0.149	0.928	−0.214	−0.227	−0.064	0.004	0.072	−0.021
12.65	−0.006	0.091	−0.463	0.869	−0.130	0.031	0.041	−0.022
12.94	−0.090	−0.194	−0.796	−0.341	0.321	0.054	−0.264	−0.094
13.79	−0.025	−0.062	−0.011	0.059	0.699	−0.041	0.648	−0.256
14.70	0.060	0.144	0.162	0.185	0.413	−0.728	−0.428	0.173
16.93	0.068	0.158	0.254	0.189	0.462	0.681	−0.401	0.167

(b) 1^- states

E (eV)	$M_1 \otimes D$	$M_2 \otimes D$	$M_3 \otimes D$	$D \otimes Q$	D
2.88	0.122	0.051	−0.009	0.046	0.990
9.81	−0.903	0.268	0.053	−0.218	0.111
10.17	0.172	−0.194	−0.046	−0.964	0.033
11.15	−0.246	−0.872	0.402	0.115	0.073
13.14	−0.173	−0.359	−0.913	0.086	0.027

(c) 2^- states

E (eV)	$M_1 \otimes Q$	$M_2 \otimes Q$	$M_3 \otimes Q$	$D \otimes D$	$Q \otimes Q$	Q
3.43	0.098	0.044	−0.007	−0.066	0.033	0.991
9.46	0.029	−0.003	0.003	0.234	0.972	−0.019
9.72	−0.963	0.239	0.056	0.061	0.016	0.088
10.51	−0.004	0.231	0.026	−0.943	0.226	−0.080
11.02	0.209	0.893	−0.339	0.200	−0.051	−0.048
12.73	0.134	0.302	0.939	0.094	−0.029	−0.012

the fact that matrix elements of the residual interaction between electrons are relatively large in comparison with the typical level spacing of single-particle states, in contrast to the nuclear case. The level spacing depends on the spatial size of the system, and this size is mainly determined by the extension of the ionic background in atomic clusters whereas in nuclei it is governed by the self-consistent mean field.

Coming back to the figures, one can see that the energy splitting of the different total angular momentum components of the two-boson states is quite large. For example, the $D \otimes D$ unperturbed state at 6 eV is split into the $[D \otimes D]_0$ at 13.6 eV and the $[D \otimes D]_2$ at 10.5 eV. Similarly, the $Q \otimes Q$ state at 7 eV is split into $[Q \otimes Q]_0$ at 10 eV, $[Q \otimes Q]_2$ at 9.5 eV and $[Q \otimes Q]_4$ at almost the same energy. For the negative parity states the shift is again quite large while the splitting is less pronounced than in the previous case. Due to the large shift of some two-boson states, just including the diagonal matrix elements of the boson-boson interaction (middle columns of Figs. 1 and 2) results in a quite compressed spectrum in the high energy region as compared with the unperturbed spectrum. It is then an easier job for the nondiagonal parts of the residual interaction to give rise to the large mixing we pointed out before, in the discussion of the tables. The global picture thus emerging from our results is highly anharmonic, in contrast with the nuclear case where an almost perfectly harmonic two-boson spectrum was obtained.

We have also calculated the transition rate for the direct electromagnetic excitation of the 1^- states of Table II(b). The results are collected in Table III, where in the last column we report the contribution from the one-boson component. One sees that, for the highest levels, there is an important constructive interference between the one- and two-boson components. The lowest state, which is essentially a pure one-boson, has the largest rate as expected due to its collectivity. However, the electromagnetic dipole transition rate to the high-lying states is also quite large and the contribution from the two-boson component is very important. In Table III we show also the rate for some 1^- one-boson states, namely those exhausting at least 1% of the dipole EWSR. Comparing with the rate for exciting the two-boson state at 11.1 eV, one can see that it should be possible to detect and isolate such a state from the background.

TABLE III. Electromagnetic excitation rate for the dipole states of Table II(b). In the last column the rate associated with the one-plasmon component of each state is reported. For comparison we also report the rate for the single GD collective state and for some noncollective 1^- states.

	E (eV)	Rate (sec^{-1})	(one-plasmon component)
GD	3.03	0.8142×10^{-8}	
	2.88	0.6894×10^{-8}	0.6882×10^{-8}
1^- two-	9.81	0.2228×10^{-8}	0.3408×10^{-8}
plasmon	10.2	0.1379×10^{-8}	0.3363×10^{-9}
states	11.1	0.4380×10^{-8}	0.2162×10^{-8}
	13.1	0.2802×10^{-7}	0.4848×10^{-9}
	5.10	0.7065×10^{-9}	
non-	5.55	0.5070×10^{-10}	
collective	5.75	0.2261×10^{-9}	
1^-	5.98	0.3936×10^{-10}	
plasmon	6.13	0.4419×10^{-10}	

IV. CONCLUSION

In this work, we have investigated the possibility of finding in atomic clusters harmonic excitations built out of elementary modes such as the giant dipole mode. Starting from an energy density functional and within the jellium model, the elementary modes, or one-boson states, are constructed using the TDLDA approach. Some of these one-boson states can be quite collective in the sense that they account for a large part of the EWSR, which is also a reflection of the fact that their wave function spreads over many PH components. This is in particular the case of the giant dipole state which is known experimentally. Using the one-boson states as building blocks and applying a boson mapping method, it is then possible to calculate the eigenstates of the system in a subspace of interacting one- and two-boson states. The merit of this method is that one can account for correlations which are beyond the RPA picture without having to perform heavy numerical computations.

The main result of the present study is that the harmonic picture does not apply to the excitation spectrum of electrons in alkali-metal clusters. Unlike the situation in atomic nuclei where the giant resonance modes do not experience strong correlations among themselves, the quasibosons in clusters have large mutual interactions. As a consequence, one does not find in the excitation spectrum around twice the energy of the photoabsorption peak states which could be identified as twice the dipole plasmon. On the contrary, one finds that two-boson states are generally shifted strongly upwards from their unperturbed positions and they are largely admixed among themselves. Looking more particularly at dipole states, it is found that some of the states at rather high excitation energy (3 to 4 times the photoabsorption peak energy) have a sizeable electromagnetic transition rate.

The present results have been obtained in the framework of the jellium model and an LDA energy density functional. These calculations could also be done in a Hartree-Fock-RPA approach based on the jellium model.[21] At the level of single-boson states, TDLDA and Hartree-Fock-RPA predictions are rather similar and therefore we do not expect that the large anharmonicities would be much different if one starts from the Hartree-Fock approach. Another point which would deserve further study is the fact that in this work, the exact boson mapping was truncated at second order and it would be interesting to investigate the effects of the next orders. Again, it seems unlikely that the anharmonic behavior would be much reduced by these effects.

APPENDIX

Here we derive the necessary expressions for calculating the electromagnetic transition rates from ground to excited states. First, we decompose the electromagnetic transition operator into multipoles

$$T_{\lambda\mu} = \hat{\lambda}^{-1} \sum_{\alpha\beta} \langle \alpha \parallel T_\lambda \parallel \beta \rangle B^\dagger_{\alpha\beta}(\lambda\mu),$$

where $\langle \alpha \| T \| \beta \rangle$ is the reduced matrix element of the 2^λ-pole operator and the indices α and β can run over both particle and hole states. In order to disentangle the different excitation mechanisms, we separate the multipole operators into a sum of three parts:

$$T^{(p\text{-}h)}_{\lambda\mu} = \hat{\lambda}^{-1} \sum_{ph} \langle p \parallel T_\lambda \parallel h \rangle B^\dagger_{ph}(\lambda\mu) + \langle h \parallel T_\lambda \parallel p \rangle B^\dagger_{hp}(\lambda\mu),$$

$$T^{(p\text{-}p)}_{\lambda\mu} = \hat{\lambda}^{-1} \sum_{pp'} \langle p \parallel T_\lambda \parallel p' \rangle B^\dagger_{pp'}(\lambda\mu),$$

$$T^{(h\text{-}h)}_{\lambda\mu} = \hat{\lambda}^{-1} \sum_{hh'} \langle h \parallel T_\lambda \parallel h' \rangle B^\dagger_{hh'}(\lambda\mu)$$

and use Eqs. (15)–(17) to express the $B^\dagger_{pp}$ and $B^\dagger_{hh}$ operators in terms of $\hat{B}^\dagger_{ph}$ and $\hat{B}_{ph}$. The latter operators can then be expressed in terms of $\hat{O}^\dagger$ and $\hat{O}$. The transition amplitude M can be easily evaluated by using the boson commutation relations of the $\hat{O}^\dagger$ and $\hat{O}$. Starting from the ground state, the $T^{(p\text{-}h)}$ term can only excite a one-boson state while $T^{(p\text{-}p)}$ and $T^{(h\text{-}h)}$ give rise to a direct excitation of the two-boson states. The transition rate for the excitation of a state i from the ground state in the long wavelength limit $j_\lambda(Kr) \simeq (Kr)^\lambda/(2\lambda+1)!!$ is[20]

$$R(i \to 0) = \frac{8\pi(\lambda+1)}{\lambda[(2\lambda+1)!!]^2} \frac{K^{2\lambda+1}}{\hbar} \mid M_i \mid^2,$$

where $K = \omega_\nu/\hbar c$. For the one-boson components of the states of Eq. (14) we have $i = \nu$ and

$$M_\nu = \frac{1}{\pi\hat{\lambda}\sqrt{2}} \sum_{ph} \langle p \parallel r^\lambda Y_\lambda \parallel h \rangle (X^\nu_{ph} - Y^\nu_{ph}),$$

while for two-boson components $i = [\nu_1 \otimes \nu_2]_\lambda$ and

$$M^\lambda_{\nu_1\nu_2} = \frac{1}{\pi\sqrt{2}} \frac{\hat{\lambda_1}\hat{\lambda_2}}{\hat{\lambda}} \frac{1}{\sqrt{1+\delta_{\nu_1\nu_2}}} \Bigg(- \sum_{pp'h''} (-1)^{j'-j''} \langle p \parallel r^\lambda Y_\lambda \parallel p' \rangle \times \left[W(\lambda_2 j \lambda_1 j'; j'' \lambda) Y^{\nu_2}_{ph''} X^{\nu_1}_{p'h''} + (-1)^{\lambda_1+\lambda_2+\lambda} W(\lambda_1 j \lambda_2 j'; j'' \lambda) Y^{\nu_1}_{ph''} X^{\nu_2}_{p'h''} \right] + \sum_{hh'p''} (-1)^{j-j''} \langle h \parallel r^\lambda Y_\lambda \parallel h' \rangle \left[W(\lambda_1 j \lambda_2 j'; j'' \lambda) Y^{\nu_2}_{p''h'} X^{\nu_1}_{p''h} + (-1)^{\lambda_1+\lambda_2+\lambda} W(\lambda_2 j \lambda_1 j'; j'' \lambda) Y^{\nu_1}_{p''h'} X^{\nu_2}_{p''h} \right] \Bigg).$$

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