Configuration interaction study of single and double dipole plasmon excitations in Na$_8$

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Abstract

We carry out a microscopic analysis of the ground and excited states of the Na$_8$ metal cluster within the jellium model. We perform a series of configuration interaction calculations on a Hartree-Fock basis and construct eigenstates of the Hamiltonian which carry up to 4-particle 4-hole components. Based on the analysis of the dipole transition strengths, we single out those states which can be interpreted as the collective dipole plasmon and its double excitations. These modes are found to possess a high degree of harmonicity, deviations from the harmonic limit remaining, however, of the order of 10%.

Key words: Metal clusters, Multiphonon states

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Collective vibrational states are known both in metal clusters [1,2] and in nuclei [3]. They are interpreted as the excitations of vibrational quanta, the so-called plasmons or phonons. In particular, the dipole plasmon excitation in clusters, corresponding to an oscillation of the centre of mass of the valence
electrons against that of the positive ions, is a very collective mode and dominates the response to a laser field. Microscopically, its frequency and strong collectivity are quite well reproduced by the random phase approximation (RPA) within the jellium model. This model [4,5] considers a uniform positive charge distribution generated by the ions (the jellium) which interacts with a cloud of delocalized valence electrons (also interacting among themselves) via the Coulomb interaction. RPA predicts that the plasmon oscillation is perfectly harmonic [6], i.e. that states corresponding to a n-fold excitation of the plasmon exist and their energy is equal to n times that of the single plasmon. If the jellium-electron interaction can be approximated by a harmonic oscillator potential, as it is reasonably true for a highly positively ionized cluster, this is what one expects on general grounds [7]. Indeed, in that case the total electron eigenfunctions are simply products of the type

$$\Psi(r_1, r_2, \ldots r_N) = \psi_{nl}(R) \phi_{\nu \lambda}(r'_1, r'_2, \ldots r'_N),$$  \hspace{1cm} (1)$$

where $R$ is the coordinate of the centre of mass of the electrons with the harmonic oscillator quantum numbers ($nl$) describing its motion, while $r'_i$ are the intrinsic coordinates of the electrons with $\nu$ and $\lambda$ classifying the harmonic oscillator states of their relative motion. A dipole external field acting on the ground state of the system, $\psi_{00}\phi_{00}$, causes the transition to $\psi_{01}\phi_{00}$, acting on the latter excites the states $\psi_{10}\phi_{00}$ and $\psi_{02}\phi_{00}$, and so on, generating a perfectly harmonic band. Of course, other bands exist, based on different intrinsic motion states $\phi_{\nu \lambda}$, with no electromagnetic transitions among them. This was checked numerically in Ref. [8] for the very simple case of two interacting electrons moving in a harmonic oscillator potential. When this potential is replaced by the Coulomb potential generated by the jellium charge distribution the above level scheme is modified and it was found in Ref. [8] that
different bands still exist, deviating from the harmonic limit and with non zero multipole transition probabilities among them. These results show that the anharmonicities in the dipole plasmon excitation are due to the coupling between the intrinsic and centre of mass motions of the electrons.

This has been recently discussed quite in general in Ref. [9]. In this work, the authors make explicit in a very clear way the coupling between intrinsic and centre of mass motions by considering an expansion of the ionic background potential $V_{\text{ion}}(r_i) = V_{\text{ion}}(r'_i + R)$ in power series with respect to $R$. Appreciable deviations from the harmonic scheme are found within this approach [9]. For example, for a Na$_{93}^+$ cluster it is found that the most important optical dipole transitions are separated by a $\Delta E_n$ equal to 2.8 eV, 3.07 eV and 3.26 eV for the single ($n = 1$), double ($n = 2$) and triple ($n = 3$) plasmon excitations, respectively. These results should be compared with the contradictory ones found in Refs. [10] and [11], namely essentially zero and huge anharmonicities, respectively. This is due to the fact that the coupling between intrinsic and centre of mass motions is almost completely neglected in Ref. [10]. On the other hand, the boson expansion used in Ref. [11] was truncated at the same order as previously done for the study of the double excitation of Giant Resonances in atomic nuclei [12]. In the latter case, anharmonicities of the order of a few hundred keV as compared with the harmonic limit energy of $20 \div 30 MeV$ were found. The huge anharmonicities found in metallic clusters are probably an indication that the convergence of the boson expansion is much slower in that case and this can be related to the long range of the Coulomb interaction [7].

To our knowledge, there is no experimental clear evidence on the existence of states corresponding to the double excitation of the dipole plasmon [13,14].
been known for many years [3] and the anharmonicities in their excitation spectra have been found to play a role in several physical processes [15].

This and the very interesting results found in Ref. [9] encouraged us to attempt a configuration interaction (CI) calculation for small metal clusters. Indeed, this is a priori the best method to obtain the energy spectrum. On the other hand, since the states we want to study are quite high in energy, namely at about twice or more that of the plasmon, the configuration space required to get reliable solutions becomes very rapidly prohibitively large when the size of the cluster increases. We have thus limited our analysis to Na$_8$. Similar calculations for several light Na clusters have been reported in Ref. [16] where, however, only the ground state and the singly excited dipole state were studied.

Let us then shortly describe our calculations and discuss the results. Within the jellium model the motion of the valence electrons is determined by the hamiltonian

$$ H = \sum_i h_i + \sum_{i<j} v_{ij}, \quad \text{(2)} $$

with

$$ h_i = -\frac{\hbar^2}{2m} \nabla_i^2 + V(r_i); \quad v_{ij} = \frac{e^2}{4\pi\epsilon_0} \frac{1}{|r_i - r_j|}, \quad \text{(3)} $$

and

$$ V(r) = \begin{cases} 
(1/2r_c)(r^2/r_c^2 - 3) & \text{for } r \leq r_c \\
-1/r & \text{for } r \geq r_c 
\end{cases} \quad \text{(4)} $$

where $r_c$ is the radius of the jellium sphere, i.e. $r_c = r_s N_e^{1/3}$ with $r_s$ the Wigner-Seitz radius which is 4 a.u. for Na and $N_e$ is the number of electrons. We are aware of the fact that, for a small metal cluster, the jellium approximation may
be not completely adequate for a quantitative comparison with experimental data. However, it already contains many important physical features while allowing not too heavy calculations as compared with more elaborated models.

As a first step we make a Hartree-Fock (HF) calculation in order to fix single particle ($sp$) energies and wavefunctions. This is done by allowing the wavefunctions to be superpositions of harmonic oscillator wavefunctions (h.o.w.f.’s). The number of h.o.w.f.’s has to be chosen large enough to get a HF ground state energy satisfactorily stable for small variations of the h.o. parameter around the value giving the minimum. Next, we construct all Slater determinants with fixed values of the projection $M_L$ of the total angular momentum, of the projection $M_S$ of the total spin and of the parity $\pi$. This set is truncated by i) truncating the $sp$ basis; ii) putting a maximum value $n$ for the number of particle-hole excitations ($np-nh$) with respect to the HF ground state and/or for the unperturbed excitation energy. We have considered several truncations corresponding to i) up to 10 HF orbitals above the Fermi level; ii) all Slater determinants having up to 3$p$-3$h$ configurations and containing those 4$p$-4$h$ configurations whose unperturbed energy with respect to the HF ground state is less than a given cutoff energy $E_c$. The use of the HF basis should optimize the convergence of the results because part of the correlations are already taken into account in the reference state.

The largest basis we have been able to manage has dimension $\sim 700000$; it is to be noted, however, that many matrix elements of the hamiltonian in such a basis are zero: the hamiltonian matrix is sparse. We have then used a NAG library routine especially intended for such a case. The routine finds the $N$ eigenvalues of largest absolute value and the corresponding eigenvectors. This method is very suitable for our case since we are interested in the lowest
negative eigenvalues which are the largest ones in absolute value. The time
required by the routine to find the solutions increases very rapidly with \( N \).
Therefore, \( N \) has to be taken as low as possible. From RPA we know that the
excitation energy of the dipole plasmon is located around \( 3 \ eV \). Since we are
interested in single and double dipole plasmon excitations, we have to choose \( N \)
such that all eigenvalues up to \( \sim 7 \ eV \) are determined, and this would mean
a quite large \( N \) since the states of the basis we use do not have a definite
value of the total angular momentum and spin. On the other hand, since the
hamiltonian commutes with \( \hat{L} \) and \( \hat{S} \), its eigenvectors are also eigenvectors of
\( \hat{L}^2 \) and \( \hat{S}^2 \) in addition to \( \hat{L}_z \), \( \hat{S}_z \) and parity. We take advantage of this and
use the following procedure to select the eigenstates of \( H \) belonging to some
definite value of the angular momentum \( \bar{L} \). By running the calculation with
\( M_L = \bar{L} \), the eigenstates with \( L < \bar{L} \) are trivially eliminated. By adding to the
hamiltonian a term \( \alpha[\hat{L}^2 - \bar{L}(\bar{L}+1)] \) with \( \alpha > 0 \) the eigenvalues corresponding
to \( L > \bar{L} \) are shifted up. Therefore, if \( \alpha \) is chosen large enough, only those with
\( L = \bar{L} \) are selected as the lowest ones (i.e. with the largest absolute values).
In reality one must be careful since, if \( \alpha \) is chosen very large, the eigenvalues
corresponding to \( L \gg \bar{L} \) are so much shifted up that they become positive
and the largest ones. Therefore, \( \alpha \) has to be kept not too large and then
a few eigenvalues not corresponding to \( \bar{L} \) may be mixed in the region of the
spectrum we look at. However, this problem is easily eliminated by calculating
after the diagonalization the angular momentum of each eigenstate. The same
reasoning applies also for the spin and we add to the hamiltonian another term
\( \beta[\hat{S}^2 - \bar{S}(\bar{S}+1)] \) with \( \beta > 0 \). The above sketched procedure is very effective
and it has allowed us to limit the number of eigenvalues we are interested in
within a maximum value of 50, for each of the three cases relevant for our
scopes, namely \( L^\pi S = 1^-0, 0^+0 \) and \( 2^+0 \), and an excitation energy less than
The energies of the lowest 12 HF $sp$ states are reported in Table 1. Each $sp$ state has been expressed as superposition of h.o.w.f.’s, with principal quantum number running from 0 to 8. The HF states are labeled by the principal quantum number $n$ of the predominant component and the angular quantum number $l$.

For a start, we have performed two series of calculations by considering those $sp$ states and including all Slater determinants with up to $2p$-$2h$ and $3p$-$3h$ configurations. By comparing the two series of results we have observed that the $2p$-$2h$ space is far from being sufficient for a good description of the states we are interested in. Indeed, the inclusion of the $3p$-$3h$ configurations strongly modifies the energies of the excited states and, to a less extent, of the ground state (see Table II). In order to go further one has to include $4p$-$4h$ configurations. However, in this case the number of configurations is too large and it is necessary to introduce an energy cutoff $E_c$, i.e. to include only those $4p$-$4h$ Slater determinants whose unperturbed energies are not higher than $E_c$ above the $HF$ ground state. By repeating the calculations with $E_c$ increasing from $E_c = 19\, eV$ to $E_c = 25\, eV$ we get a lower and lower ground state energy as shown in Table 2. Looking at the third column of the table, where we show the difference between the ground state energies relative to two successive calculations, one can conclude that a very good numerical convergence has been reached for the ground state energy. Indeed, the values obtained with $E_c = 24$ and $25\, eV$ differ only by $2\, meV$. However, we are also interested in excited states having a quite high energy and convergence must be checked also for them. In order to do that we have calculated the root mean square value $\sigma = \sqrt{1/N \sum_{i=1}^{N} \Delta_i^2}$ of the shifts $\Delta_i$ obtained in two calculations with $E_c$ differing by $1\, eV$. By considering all states having excitation energy less than
7 eV, for the case $L^\pi S = 0^+0$, we have got $\sigma = 0.064\, eV$ when going from $E_c = 20\, eV$ to $E_c = 21\, eV$ while $\sigma = 0.039\, eV$ in going from $E_c = 24\, eV$ to $E_c = 25\, eV$. It is also to be noted that, in the latter case, the largest shift is $\Delta = 0.046\, eV$ corresponding to 0.7 %. Similar results have been obtained for the $2^+ S = 0$ and $1^- S = 0$ spectra.

A further comment has to be added. In order to be able to increase so much the energy cutoff for $4p-4h$ configurations we have followed a suggestion of Ref. [16]. Namely, the high angular momentum $0g$ and $0h$ single particle states have been suppressed from the basis. We have checked that, for $E_c = 20\, eV$, the calculations with and without those states give almost indistinguishable results, more precisely a maximum shift of 0.2 % in the considered energy region. The next two $sp$ states above the twelve ones we have considered in the basis have $l=6$ and $l=7$. Therefore, their inclusion should not modify the spectra. Still above there is a $2d$ orbital, but its $HF$ energy is $2.19\, eV$ and we can reasonably neglect its contribution. From the above considerations we conclude that a satisfactory convergence has been reached and the so obtained energies and wavefunctions can be reliably used in the analysis of anharmonicities.

In order to single out the states which can be interpreted as the collective dipole plasmon and its double excitations we have calculated the electric dipole transition strengths from the initial states $|\psi_i\rangle$, $0^+ S = 0$ and $2^+ S = 0$, to the final states $|\psi_f\rangle$, $1^- S = 0$. More precisely, we have calculated the following quantity:

$$ |T_{fi}(E1)|^2 = |\sum_{\alpha\alpha'} t^{(E1)}_{\alpha\alpha'} < \psi_f | a_{\alpha'}^\dagger a_\alpha | \psi_i > |^2 ,$$  

(5)
with $\alpha = (n_\alpha, l_\alpha, \sigma_\alpha)$ and

$$i_{aa'}^{(E1)} = (\alpha \parallel Y_1 \parallel \alpha') = R_{n_\alpha l_\alpha n_\alpha' l_\alpha'}(l_\alpha \parallel l_{\alpha'})\delta_{\sigma_\alpha \sigma_{\alpha'}} , \quad (6)$$

$$R_{nl,n'l'} = \int r^3 \varphi_{nl}(r)\varphi_{n'l'}(r)dr . \quad (7)$$

The $(l \parallel Y_\lambda \parallel l')$ in eq. (6) are the reduced matrix elements defined as in Ref. [15] and $\varphi_{nl}$ in eq. (7) are the Hartree - Fock sp wave functions. In Fig. (1) we report the largest $|T_{fi}(E1)|^2$ values (greater than 0.8 $\text{Å}^2$) obtained in the calculation performed with 12 HF states and within the 4p-4h space with $E_c = 25$ eV. As we are interested in the study of the collective dipole plasmon and its double excitations, we show only the transitions involving the $1^-_1$ states located around the single plasmon excitation energy.

The selected levels can be grouped in two “bands” based on the ground state and on the lowest $1^-_0$ state $(1^-_1)$, respectively. The two bands are essentially not connected by dipole transitions. The second $1^-_1$ state at 3.07 eV excitation energy is strongly coupled to the ground state and can be identified with the dipole plasmon excitation. The only three excited states having a large dipole transition strength to this $(1^-_1)$ state are two $2^+_1$ states, at 6.41 and 6.42 eV, and one $0^+_1$ state at 6.60 eV, corresponding to an energy jump of 3.34, 3.35 eV and 3.53 eV respectively, to be compared with the 3.07 eV excitation energy of the $(1^-_1)$ state. They might be identified as corresponding to double excitations of the dipole plasmon. Indeed, they are very close to each other and their energy is not far from twice that of the single plasmon. The deviations from the harmonic limit are of the order of 10%. As can be seen from the figure, the strength of the transition connecting the $(1^-_1)$ state to the two-plasmon states is 12.12 $\text{Å}^2$ to be compared with the
harmonic value of 12.36 Å² corresponding to the double of the one-plasmon strength. We also note that this strength is fragmented between the $2^+ S = 0$ and $0^+ S = 0$ states in a proportion close to the harmonic limit, i.e. 4/3 and 2/3 respectively.

The $2^+ S = 0$ and $0^+ S = 0$ having a strong transition to the $(1\bar{1})$ state (see the “lateral band” in the figure) lie at 3.40 eV and 3.65 eV above it. This makes plausible their interpretation as collective dipole excitations built on top of the $(1\bar{1})$ state, all these states being characterized by an intrinsic motion wave function $\phi_{01}$ (see eq. (1)). This also justifies the extremely small value (0.002 Å²) of the transition strength between the ground state and the $(1\bar{1})$ state.

The quality of the results obtained in the present calculations can be judged by looking at sum rules. It is well known [6] that, if $|0\rangle$ and $|\nu\rangle$ are the exact ground and excited states of a system, then the following equality holds

$$\sum_{\nu} (E_{\nu} - E_0)|\langle \nu | T_{\lambda} | 0 \rangle|^2 = \frac{1}{2} |\langle \nu | [T_{\lambda}, [H, T_{\lambda}]] | 0 \rangle |^2 , (8)$$

where $H$ is the total hamiltonian and $T_{\lambda}$ the transition operator of multipolarity $\lambda$. The r.h.s. of the above equation can be evaluated exactly and is (see eq. (2.47) of Ref. [15])

$$EWSR = \frac{\hbar^2 \lambda(2\lambda + 1)^2}{8\pi m} N_e \langle r^{2\lambda-2} \rangle , (9)$$

where $m$ is the mass of the electron and $\langle r^{2\lambda-2} \rangle$ is the expectation value of the indicated quantity in the ground state. Since we are looking at $\lambda = 1$ transitions, the EWSR is completely independent of the ground state and is equal to 21.83 Å²·eV. The l.h.s. of eq. (8) turns out to be 21.62 Å²·eV which is 99.04% of EWSR. Therefore, we can conclude that our calculated energies
and wavefunctions satisfy up to an extremely good level this very stringent condition. In order to further check the numerical convergence we have compared the results obtained with 12 HF orbitals and cutoff energies equal to $E_c = 22, 23, 24, 25 \text{ eV}$, finding a smaller and smaller variation at each step, the last one being 0.06 $\AA^2 \cdot \text{eV}$, i.e. 0.2 %. It is also worth mentioning that the contribution of the second $1^- \text{ state to the sum is } 19.01 \AA^2 \cdot \text{eV}$, which means 87% of the total. Therefore, its identification with the collective dipole plasmon state is very well justified.

By summarizing, in this work we have carried out a microscopic analysis of the ground and excited states of the Na$_8$ metal cluster within the jellium model. We have performed a series of configuration interaction calculations in a Hartree-Fock basis and constructed eigenstates of the Hamiltonian which carry up to 4-particle 4-hole components. Based on the analysis of the dipole transition strengths, we have singled out those states which can be interpreted as the collective dipole plasmon and its double excitations. These modes have been found to possess a high degree of harmonicity, deviations from the harmonic limit remaining, however, of the order of 10%. These values are consistent with the anharmonicities found by Gerchicov et al. [9], using a different technique, in heavier clusters. We want to stress that in principle a configuration interaction calculation is the most accurate approach to reproduce the spectrum of the system and then to evaluate its anharmonicities. On the other side, a limitation of this kind of calculations is that they are very heavy numerically and this is the reason why we limited our analysis to the small cluster Na$_8$. 

11
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Fig. 1. The largest $|T_{f1}(E1)|^2$ from the $0^+ S = 0$ and $2^+ S = 0$ states to the $1^- S = 0$ ones. The values, in Å$^2$, are indicated in brackets. The calculation is done within the to $4p-4h$ space with an energy cutoff equal to 25 eV and 12 HF orbitals. The states are grouped in two bands based on the ground state and on the lowest $1^- S = 0$ state. For the excited states we report the energies corresponding to the transitions indicated by the arrows. The two arrows in correspondence with the highest $2^+$ state refer to two almost degenerate states which are not distinguishable in the figure (see the text).

| $n$ $l$ | 0 0 | 0 1 | 0 2 | 1 0 | 1 1 | 1 2 |
|---------|-----|-----|-----|-----|-----|-----|
| E (eV)  | -6.85 | -4.38 | 0.15 | 0.25 | 0.50 | 0.83 |

| $n$ $l$ | 0 3 | 2 0 | 0 4 | 0 5 | 2 1 | 1 3 |
|---------|-----|-----|-----|-----|-----|-----|
| E (eV)  | 0.86 | 1.12 | 1.16 | 1.46 | 1.62 | 1.76 |

Table 1

Energies (eV) of the lowest 12 HF $sp$ states; $n$ is the principal quantum number of the predominant component and $l$ is the angular quantum number.
|                        | $E_0$ (eV) | $\Delta_0$ (eV) |
|------------------------|------------|-----------------|
| 2p-2h                  | -142.095   | -               |
| 3p-3h                  | -142.176   | -0.081          |
| 4p-4h, $E_c = 19$ eV   | -142.235   | -0.059          |
| 4p-4h, $E_c = 20$ eV   | -142.248   | -0.013          |
| 4p-4h, $E_c = 21$ eV   | -142.252   | -0.004          |
| 4p-4h, $E_c = 22$ eV   | -142.258   | -0.006          |
| 4p-4h, $E_c = 23$ eV   | -142.275   | -0.017          |
| 4p-4h, $E_c = 24$ eV   | -142.283   | -0.008          |
| 4p-4h, $E_c = 25$ eV   | -142.285   | -0.002          |

Table 2

In the second column the ground state energies are reported for each calculation.

In the third column $\Delta_0$ represents the difference between the corresponding ground state energy and that reported in the previous line.