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## Two-phonon states in alkali-metal clusters.

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### Abstract

Two phonon-states of alkali-metal clusters (treated as jellium spheres) are calculated by using a method based on a perturbative construction of periodic orbits of the time-dependent mean-field equations. Collective vibrations with various multipolarities in charged  $Na_2^+$  are considered.

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## INTRODUCTION

For metallic clusters, it appears reasonable to approximate the valence electrons as a system of independent fermions enclosed in a box, in close analogy with the mean-field description of nucleonic motion in nuclei. The many body methods developed for collective modes in nuclei are thus a natural tool to investigate, in a first stage, collective motion in metallic clusters. The length and the energy scales in metallic clusters and nuclei are of course widely different. The interactions also have a different nature. The strong force mediated by pion exchanges ensures nuclear binding while electrons interact with each other and with the nuclei through electromagnetic forces.

The analogies between nuclei and metallic clusters became apparent in 1984 with the experimental discovery of shell structure and magic numbers in sodium clusters by W. D. Knight *et al* [1] and parallel theoretical efforts by W. Ekardt [2]. Since then, the physics of metallic clusters has been of continuing interest [3]. The valence electrons in these clusters can be described as delocalized particles moving in a mean-field due to their mutual interaction and to a uniform positive background. This approximation is known as the jellium model. As a result, the ionic background contributes only an electrostatic attraction to the mean-field, whereas the valence electrons are treated as quantum particles exhibiting exchange and correlation effects in addition to their electrostatic repulsion. This treatment is usually carried out in the framework of the density-functional formalism [4, 5].

The experimental discovery of a giant dipole resonance in metallic clusters interpreted as a collective electronic excitation (surface plasmon) [6, 7, 8] induced a substantial theoretical effort. To understand the presence of collective motion, the usual random-phase approximation approach (RPA) and the time-dependent local-density approximation (TDLDA) have been applied [9-14]. Our aim in this article is to describe collective motion of large amplitude in metallic clusters with a method which is more general than RPA. It is based on secular perturbation theory. More precisely we start from a perturbative method to construct finite-amplitude periodic orbits of the nonlinear time-dependent mean-field equations. This method

was developed recently to describe giant collective resonances in nuclear physics [15, 16] and the Skyrmion breathing mode in hadronic physics [17]. Although this method is not always applicable due to the possible presence of branches and bifurcations [18] we found it well adapted to investigate giant collective oscillations in the case of nuclei. From the knowledge of periodic orbits we were able to calculate collective energy spectra by a semiclassical quantization or by a construction of the collective Bohr-type Hamiltonian.

The present article is organized as follows. Sec. I presents a summary of the self-consistent spherical jellium-background model and defines our notation. In Sec. II we review briefly the expansion method of Refs. [15, 16, 17] and we specialize to the alkali-metal clusters case. In Sec. III we present our results concerning monopole, dipole, quadrupole and octupole modes in charged  $Na_{21}^+$  (closed-shell spherical cluster with 20 electrons), and perform a comparison with available data [19, 20] and other theoretical results [9, 11, 21]. In Sec. IV we discuss the applicability of the method to metallic clusters and summarize our main conclusions.

## 1 The jellium model

In the jellium model, the  $N$  ions are replaced by a uniform background of positive charge having radius  $R = r_s N^{1/3}$  where  $r_s = 3.93$  a.u. for sodium. In the density functional approach the electrons gas energy  $E[\rho]$  is assumed to be a function of the one-body electron density matrix  $\rho(t)$

$$\langle \mathbf{r} | \rho(t) | \mathbf{r}' \rangle = \sum_{i=1}^A \phi_i(\mathbf{r}, t) \phi_i^*(\mathbf{r}', t), \quad (1.1)$$

where the  $\phi_i$ 's are the single particle wave functions of the  $A$  occupied single electrons orbitals. In this work, we use the density functional (see Ref. [4] for a general discussion )

$$E[\rho] = \int d^3r \left\{ \frac{1}{2} \tau(\mathbf{r}, t) - \frac{3}{4} \left( \frac{3}{\pi} \right)^{1/3} \rho^{4/3}(\mathbf{r}, t) + \rho(\mathbf{r}, t) \mathcal{E}_{xc}(\rho) + \frac{1}{2} \int d^3r' \frac{\rho(\mathbf{r}, t) \rho(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} + V_J(\mathbf{r}) \rho(\mathbf{r}, t) \right\} + E_{JJ} . \quad (1.2)$$

We use atomic units ( $e = m_e = \hbar = c = 1$ ) for which energies are expressed in units of  $2R_y = 27.2$  eV ( $R_y$  being the Rydberg constant) and lengths in units of the Bohr radius  $a_0 = 0.53\text{\AA}$ . In Eq. (1.2) the first term is the kinetic energy density  $\tau(\mathbf{r}, t) = \sum_{i=1}^A |\nabla\phi_i(\mathbf{r}, t)|^2$ , the second term is the Coulomb exchange in the local density approximation. The third one simulates correlations, while the fourth one is the direct Coulomb term. The fifth term is the Coulomb interaction of the electrons with the jellium. For an uniform density distribution for the  $N$  ions, the jellium coulomb energy  $E_{JJ}$  is  $\frac{3}{5}N^2/R$  and  $V_J$  is given by

$$V_J(r) = \begin{cases} -N/r & r > R \\ -\frac{3}{2} \frac{N}{R^3} (R^2 - \frac{r^2}{3}) & r < R. \end{cases} \quad (1.3)$$

For the correlation term, we follow the Gunnarsson-Lundqvist parametrization [5]:

$$\mathcal{E}_{xc} = -0.0333 G\left[\frac{1}{11.4} \left(\frac{3}{4\pi\rho}\right)^{1/3}\right] \quad (1.4)$$

where the function  $G$  is defined by

$$G(x) = (1 + x^3) \text{Ln}[1 + 1/x] - x^2 + x/2 - 1/3.$$

The time-dependent mean-field equation reads [22]

$$i\dot{\rho} = [W(t), \rho(t)], \quad (1.5)$$

where  $W(t)$  is the mean-field Hamiltonian  $\delta E/\delta\rho$ . It reads  $-\frac{1}{2}\Delta + U(\mathbf{r}, t)$  with

$$U(\mathbf{r}, t) = -\left(\frac{3}{\pi}\right)^{1/3} \rho^{1/3}(\mathbf{r}, t) - 0.0333 \text{Ln}\left[1 + 11.4 \left(\frac{4\pi}{3} \rho(\mathbf{r}, t)\right)^{1/3}\right] + \int d^3r' \frac{\rho(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} + V_J(r) \quad (1.6)$$

Finally, we recall that the one-body density matrix defined in Eq. (1.1) must satisfy at all times the conditions  $\text{Tr}\rho(t) = A$  ( $A$  being the number of electrons) and  $\rho^2(t) = \rho(t)$  [22].

At this stage a word of caution about the application of the variational procedure should be given. The energy functional should be minimized with respect to the electron density only. In contrast it should not be minimized with respect to the jellium parameters. Indeed, such a procedure would lead to the prediction that potassium and sodium clusters have the same radius, which is in conflict with observations. This difference also suggests that it is not legitimate to perform a minimization with respect to the shape of the jellium.

## 2 The method

The method we use to construct periodic orbits of the mean-field equation (1.5) with a given period  $T$  consists in expanding the one-body density matrix  $\rho(t)$  as a power series in the amplitude of the vibration  $\epsilon$  [16]. In order to take into account the dependence of the frequency  $\omega = 2\pi/T$  on the amplitude [23], we expand  $\rho(t)$  as

$$\rho(t) = \rho_0 + \epsilon \rho_1\left(\frac{\omega}{\omega_0}t\right) + \epsilon^2 \rho_2\left(\frac{\omega}{\omega_0}t\right) + \epsilon^3 \rho_3\left(\frac{\omega}{\omega_0}t\right) + \dots \quad (2.1)$$

with

$$\omega = \omega_0 + \epsilon \omega_1 + \epsilon^2 \omega_2 + \dots \quad (2.2)$$

The first order equation is solved by the usual ansatz [22]

$$\rho_1(t) = \eta \exp(-i\omega_0 t) + \eta^+ \exp(+i\omega_0 t). \quad (2.3)$$

After inserting the expression of  $\rho(t)$  given above in Eq. (1.5), we obtain the evolution equations of the successive terms  $\rho_k$  ( $k = 0, 1, 2, \dots$ ) by identifying the various powers of  $\epsilon$  :

$$i\dot{\rho}_k = \sum_{j+m=k} \{ [W_j, \rho_m] - i\Omega_j \rho_m \}. \quad (2.4)$$

In Eq. (2.4), the operator  $W_j$  corresponds to the  $j$ -th order contribution to the mean-field Hamiltonian  $W(\rho) = \sum_k \epsilon^k W_k$  while  $\Omega_j$  is the  $j$ -th order contribution to the following expression

$$1 - \frac{\omega_0}{\omega} = \sum_{l=1}^{\infty} \frac{\epsilon^l \omega_l}{\omega_0} - \sum_{l,l'} \frac{\epsilon^{l+l'} \omega_l \omega_{l'}}{\omega_0^2} + \sum_{l,l',l''} \frac{\epsilon^{l+l'+l''} \omega_l \omega_{l'} \omega_{l''}}{\omega_0^3} - \dots$$

The static mean-field solution  $\rho_0$  of Eq. (1.5) corresponds to  $k = 0$  in the notations of Eq. (2.4). It satisfies the static equation  $[W_0, \rho_0] = 0$  where  $W_0$  is the static mean-field Hamiltonian. We define hole ( $h$ ) and particle ( $p$ ) states (normalized to one) by

$$\rho_0|\phi_h\rangle = |\phi_h\rangle, \quad \rho_0|\phi_p\rangle = 0, \quad W_0|\phi_h\rangle = e_h|\phi_h\rangle, \quad W_0|\phi_p\rangle = e_p|\phi_p\rangle.$$

In first order one recovers the well known linearized mean-field (RPA) equation  $i\dot{\rho}_1 = \mathcal{M}\rho_1$  which is solved by the ansatz (2.3). The RPA matrix  $\mathcal{M}$  is defined by

$$\mathcal{M}\rho_1 = [W_0, \rho_1] + [W_1, \rho_0].$$

Since  $\rho(t)$  must correspond to a Slater determinant, it must satisfy the condition  $\rho^2(t) = \rho(t)$  to each order in  $\epsilon$ . In  $k$ -th order ( $k = 0, 1, 2, \dots$ ), this condition reads

$$\rho_k = \sum_{j+m=k} \rho_j \rho_m. \quad (2.5)$$

An immediate consequence of this last equation is that it provides at once the particle-particle and hole-hole matrix elements of the operator  $\rho_k$  from the knowledge of the lower order terms  $\rho_{k-1}, \rho_{k-2}, \dots$ . After checking that the matrix elements  $\langle p | \rho_k | p' \rangle$  and  $\langle h | \rho_k | h' \rangle$  given by Eq. (2.5) are consistent with the corresponding evolution equations (2.4), one sees that the information contained in Eq. (2.4) concerns only the particle-hole and hole-particle matrix elements of  $\rho_k$ .

The corrections  $\omega_l$  ( $l = 1, 2, \dots$ ) to the harmonic frequency  $\omega_0$  are determined by requiring that there is no resonant term with frequency  $\omega_0$  in the evolution equation of the particle-hole matrix elements of  $\rho_{l+1}$ . We wish to emphasize that this procedure is sometimes inapplicable. Indeed, resonant terms with frequencies equal to  $2\omega_0, 3\omega_0, \dots$  may appear in the construction of higher-order terms when these frequencies already belong to the continuous spectrum of the RPA matrix. However, one can circumvent this difficulty by generalizing the ansatz (2.3). The treatment of resonant terms is developed in Refs. [16, 24].

Once the periodic orbits are obtained, they can be used to construct energy spectra of  $N$ -body systems. The standard procedure is to perform a semiclassical quantization of these orbits [25]. This prescription consists in selecting those solutions for which the mean-field action  $I$  along a periodic orbit  $\rho(t)$ ,

$$I = \sum_h \int_0^T dt \langle \phi_h(t) | i\partial_t - \frac{\theta_h}{T} | \phi_h(t) \rangle \quad (2.6)$$

is equal to an integer multiple of Planck's constant (or in atomic units,  $I = 2\pi n$ ). The summation runs over the quasi-periodic single-particle occupied states and  $\theta_h$  is the so-called Floquet-Lyapounov phase [16].

We now apply the method discussed above to the case of collective oscillations of metallic clusters (see Eqs. (1.2) and (1.6)). In order to be able to discuss the two-phonon states, we perform the calculations up to the third order in the amplitude of the orbits. The explicit

expressions of the contributions  $W_k (k = 0, 1, 2, 3)$  to the mean-field Hamiltonian  $W$  appearing in Eq. (2.4) are

$$\begin{aligned}
 W_0(\mathbf{r}) &= -\frac{1}{2}\Delta + F_0(\mathbf{r}) + \int d^3\mathbf{r}' \frac{1}{|\mathbf{r} - \mathbf{r}'|} \rho_0(\mathbf{r}') + V_J(\mathbf{r}) \\
 W_1(\mathbf{r}, t) &= \frac{dF_0}{d\rho_0} \rho_1(\mathbf{r}, t) + \int d^3\mathbf{r}' \frac{1}{|\mathbf{r} - \mathbf{r}'|} \rho_1(\mathbf{r}', t) \\
 W_2(\mathbf{r}, t) &= \frac{dF_0}{d\rho_0} \rho_2(\mathbf{r}, t) + \int d^3\mathbf{r}' \frac{1}{|\mathbf{r} - \mathbf{r}'|} \rho_2(\mathbf{r}', t) + \frac{1}{2} \frac{d^2 F_0}{d\rho_0^2} \rho_1^2(\mathbf{r}, t) \\
 W_3(\mathbf{r}, t) &= \frac{dF_0}{d\rho_0} \rho_3(\mathbf{r}, t) + \int d^3\mathbf{r}' \frac{1}{|\mathbf{r} - \mathbf{r}'|} \rho_3(\mathbf{r}', t) + \frac{d^2 F_0}{d\rho_0^2} \rho_1(\mathbf{r}, t) \rho_2(\mathbf{r}, t) + \frac{1}{6} \frac{d^3 F_0}{d\rho_0^3} \rho_1^3(\mathbf{r}, t)
 \end{aligned} \tag{2.7}$$

The quantity  $F_0(\mathbf{r})$  in this last equations is

$$F_0(\mathbf{r}) = -\left(\frac{3}{\pi}\right)^{1/3} \rho_0^{1/3}(\mathbf{r}) - 0.0333 \text{ Ln}[1 + 11.4 \left(\frac{4\pi}{3} \rho_0(\mathbf{r})\right)^{1/3}] \tag{2.8}$$

and the notation  $\rho_k(\mathbf{r}, t) (k = 0, 1, 2, 3)$  means  $\langle \mathbf{r} | \rho_k(t) | \mathbf{r} \rangle$ .

The RPA matrix  $\mathcal{M}^{(\lambda)}$  corresponding to the angular-momentum  $\lambda$  can be written as (see, e.g., Ref. [22]) :

$$\mathcal{M}^{(\lambda)} = \begin{pmatrix} A^{(\lambda)} & B^{(\lambda)} \\ -B^{*(\lambda)} & -A^{*(\lambda)} \end{pmatrix} \tag{2.9}$$

where the matrix  $A^{(\lambda)}$  and  $B^{(\lambda)}$  are

$$\begin{aligned}
 A_{\alpha_p \alpha_h \alpha_p' \alpha_h'}^{(\lambda)} &= \delta_{\alpha_p \alpha_p'} \delta_{\alpha_h \alpha_h'} (e_p - e_h) + B_{\alpha_p \alpha_h \alpha_p' \alpha_h'}^{(\lambda)} \\
 B_{\alpha_p \alpha_h \alpha_p' \alpha_h'}^{(\lambda)} &= \frac{1}{2\pi} f_{\alpha_p \alpha_h}^{(\lambda)} f_{\alpha_p' \alpha_h'}^{(\lambda)} \int_0^\infty dr r^2 R_{\alpha_p}(r) R_{\alpha_h}(r) \times \\
 &\quad \left( \frac{dF_0}{d\rho_0} R_{\alpha_p'}(r) R_{\alpha_h'}(r) + \frac{4\pi}{2\lambda + 1} G_{\alpha_p' \alpha_h'}^{(\lambda)}(r) \right)
 \end{aligned} \tag{2.10}$$

In equations (2.10) we have introduced the notation  $\alpha_a \equiv n_a, l_a$  where  $n_a$  is the principal quantum number and  $l_a$  the orbital angular momentum of the single particle static wave function  $\langle \mathbf{r} | \phi_a \rangle$ . The quantities  $e_a$  and  $R_{\alpha_a}(r)$  are respectively the single particle energies and the radial

part of  $\langle r|\phi_a\rangle$ . The coefficient  $f$  is given by

$$f_{\alpha_p\alpha_h}^{(\lambda)} = \sqrt{(2l_p+1)(2l_h+1)} \begin{pmatrix} l_p & l_h & \lambda \\ 0 & 0 & 0 \end{pmatrix}$$

while  $F_0(r)$  is already defined in Eq. (2.8). The function  $\mathcal{G}$  appearing in these equations is :

$$\mathcal{G}_{\alpha_p\alpha_h}^{(\lambda)}(r) = \int_0^\infty dr' r'^2 \frac{r'_<^\lambda}{r'_>^{\lambda+1}} R_{\alpha_p}(r') R_{\alpha_h}(r')$$

where  $r_<$  stands for  $\text{Min}(r, r')$  while  $r_> = \text{Max}(r, r')$ .

### 3 Results

In this section we present some results obtained with the above formalism for monopole, dipole, quadrupole and octupole modes in charged  $Na_{21}^+$ . Calculations were performed on a lattice including 100 mesh points whose total size is 30 a.u., i.e., 15.9Å. In a first step we have solved the static equations. The values we have found for the binding energy, radius and single particle energies of  $Na_{21}^+$  are given in Table I. These values are in excellent agreement with those obtained by Catara, Chomaz and Van Giai [21] who use the same energy functional but a different numerical method. In a second step we have performed RPA calculations. The results for the energies of collective states of multipolarities  $L = 0, 1, 2, 3$  and the corresponding percentages of the sum rule and energy weighted sum rule are collected in Table II. These values also agree well with those of reference [21] for collective modes. It can be noted from Table II that dipole and quadrupole modes exhibit a strong collective character while such is not the case for octupole and especially monopole modes. For the monopole mode one observes two neighbouring states with similar sum rule fractions. The monopole mode is a nearly unbound RPA state while other modes are bound. However, two-phonon states would belong to the continuum in the harmonic approximation. Transition densities of dipole and quadrupole states are displayed on Figs. 1 and 2. The fact that these modes are bound is reflected by the rapid decrease of these densities at large distance. For reference the static electron density is shown on the same scale (solid line).



The observation of the dipole resonance in alkali-metal clusters including the charged  $Na_{21}^+$  has been reported by several experimental groups, e.g., Bréchnac *et al* [19] and J. Pedersen *et al* [20] (see also Ref. [26] for a review). A pronounced peak in the photoabsorption cross section is seen at  $\approx 2.7$  eV. This observation agrees with the RPA calculations of Refs. [9, 11]. These authors predict the dipole mode in  $Na_{21}^+$  at  $\approx 3.0$  eV with  $\approx 80\%$  of the sum rule and  $\approx 83\%$  of the energy weighted sum rule. These results also agree well with ours.

In a third step we have determined the location of the not yet observed two-phonon states by performing a semiclassical quantization of our second order periodic orbits as prescribed by Eq. (2.6). This prescription has been supplemented by an approximate angular momentum projection which generates a splitting of two-phonon states with different  $J$ 's [16, 24]. For most states this procedure produces results which are stable with respect to the lattice size. The corresponding results are shown in Table III (a). One observes that small anharmonicities are found except for the  $J = 0$  two-octupole phonon state for which a 15 percent deviation is obtained.

For the other states ( double monopole,  $J = 2$  double dipole and  $J = 0, 2, 4$  double quadrupole phonons) we were not able to calculate the energy shifts by the method described in Sec. II because resonant terms appear during the construction of second order terms. For example, the  $J = 0$  two quadrupole phonon state couples with a resonant mode of the RPA ( $L = 0$ ) matrix so that the inhomogeneous linear equation (2.4) is singular in second order. To study these states we use the modified perturbative construction procedure presented in Ref. [16]. As first order periodic orbit we take a superposition of the  $L$ -mode with energy  $\hbar\omega_L$  and the resonant RPA mode with energy  $\hbar\omega_{L_r} = 2\hbar\omega_L$  instead of the ansatz (2.3). With this modification, the semiclassical quantization procedure generates not only the splitting of the two-phonon states ( $n = 2$ ) but also a splitting of each state  $n, J$  [16]. The results are shown in Table III(b). We have checked that the results in this table change by less than 5 percent when the size of the lattice is increased to 128 mesh points or decreased to 75 mesh points. One remarks first that the energy shifts are small and compatible with zero so that the anharmonicities of these states are negligible, second that for some states the energy shift acquires an imaginary part.

We interpret this result as the signature of an instability of the corresponding orbit.

A comparison with the results of Catara-Chomaz-Van Giai [21] for the modes in Table III is not straightforward. Indeed these authors find large anharmonicities arising from couplings between states such as  $|(0^+, 0^+)0^+ \rangle$  and  $|(2^+, 2^+)0^+ \rangle$  which are out of reach of our semiclassical quantization approach. Further studies of this question are now under way.

## 4 Conclusion

In this paper we have investigated the static and dynamic properties of the alkali-metal cluster  $Na_{21}^+$  in the jellium model. Our results for the static and RPA calculations agree with those of reference [21]. We have determined the splitting of the two-phonon states of multiplicities  $L = 0, 1, 2, 3$  in charged  $Na_{21}^+$ . This was achieved by using a perturbative method of constructing periodic orbits of the mean-field equations recently developed for giant resonances in nuclei [16]. In most cases, we find small anharmonicities. To study the two-phonon states of the monopole and quadrupole modes we had to use a more general method which takes into account the coupling between the two-phonon state and the resonant modes [16]. It turns out that these resonant terms generate anharmonicities which are so small as to be compatible with zero. For the  $J = 2$  two-dipole,  $J = 2$  two-quadrupole and  $J = 4$  two-quadrupole states, we find an imaginary value for the energy shift with respect to the harmonic two-phonon energy. These values are however small and compatible with zero but are nevertheless a signature of an instability of the corresponding orbit. Such instabilities cannot be detected by other methods based on quasi boson expansions [21].

Finally, we wish to emphasize that periodic orbits provide a powerful method to investigate collective energy spectra. This method has the advantage of being rather easy to implement. It was first found useful in the context of giant collective modes in nuclear physics [15, 16] and also in the context of baryonic physics to describe the Roper resonance [17]. In both cases small anharmonic terms were found. This seems to be true also for giant collective modes in metallic aggregates. This is a fortunate situation since expansions in the elongation of periodic orbits

often break down, even for simple systems, because of the appearance of branches or bifurcations at small values of the elongation [18]. Here in contrast the region of interest corresponding to one and two-phonon excitations lies well within the radius of convergence of the series.

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## Table captions

TABLE I. Static properties of charged  $Na_{21}^+$ . The binding energy  $E_{LDA}$  is in eV, the root-mean-square radius  $r_0$  in  $\text{\AA}$  and the single particle energies are in eV.

$E_{LDA}$	$r_0$	$1s$	$1p$	$1d$	$2s$	$1f$
-38.69	4.49	-7.55	-6.82	-5.83	-5.15	-4.64

TABLE II. Low-lying RPA states of charged  $Na_{21}^+$ . For each multipolarity  $L^\pi$  we report the collective energy  $\hbar\omega_0$  (in eV) and the corresponding percentages of the sum rule (SR) and energy weighted sum rule (EWSR).

$L^\pi$	$\hbar\omega_0$	% SR	% EWSR
$0^+$	4.5	23	20
	5.17	22	22
$1^-$	3.04	87	84
$2^+$	3.67	55	54
$3^-$	4.14	33	36

TABLE III. Two-phonon states in charged  $Na_{21}^+$ . For each state are reported its spin and parity and the shift  $\delta E$  (in eV) with respect to the unperturbed two-phonon energy  $E_0^* = 2\hbar\omega_0$  (in eV) (calculated with semiclassical quantization [See Eq. (2.6)]).

(a)				(b)			
$L^\pi \otimes L^\pi$	$E_0^*$	$J^\pi$	$\delta E$	$L^\pi \otimes L^\pi$	$E_0^*$	$J^\pi$	$\delta E$
$1^- \otimes 1^-$	6.08	$0^+$	-0.21	$0^+ \otimes 0^+$	8.98	$0^+$	$\pm 0.01$
$3^- \otimes 3^-$	8.27	$0^+$	-1.24	$0^+ \otimes 0^+$	10.34	$0^+$	0.00
		$2^+$	-0.52	$1^- \otimes 1^-$	6.08	$2^+$	$\pm i0.07$
		$4^+$	-0.20	$2^+ \otimes 2^+$	7.34	$0^+$	$\pm 0.01$
		$6^+$	-0.15			$2^+$	$\pm i0.006$
						$4^+$	$\pm i0.024$

### Figure captions

FIG. 1. Static density  $\rho_0(r)$  ( $\text{\AA}^{-3}$ ) (full line) and transition density  $\rho_1(r)$  ( $\text{\AA}^{-3}$ ) (dashed line) corresponding to dipole state  $1^-$  in the case of charged  $Na_{21}^+$ .

FIG. 2. Static density  $\rho_0(r)$  ( $\text{\AA}^{-3}$ ) (full line) and transition density  $\rho_1(r)$  ( $\text{\AA}^{-3}$ ) (dashed line) corresponding to quadrupole state  $2^+$  in the case of charged  $Na_{21}^+$ .

Fig. 1

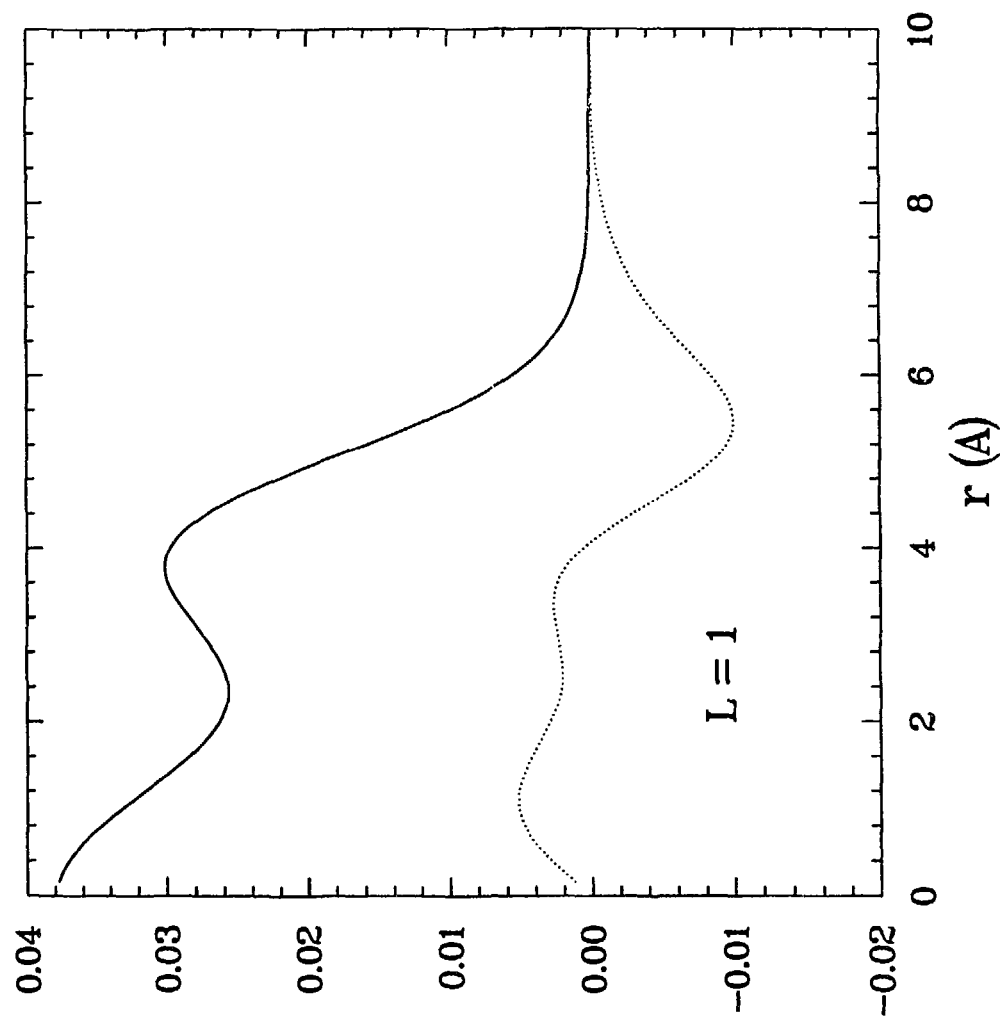




Fig. 2

