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2001 J. Phys.: Condens. Matter 13 L705

(http://iopscience.iop.org/0953-8984/13/29/102)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **13** (2001) L705–L710 PII: S0953-8984(01)25445-9

LETTER TO THE EDITOR

Excitation spectrum of a two-electron 'metal cluster'

F Catara[1,2] **and M Sambataro**[2]

[1] Dipartimento di Fisica, Università di Catania, Catania, Italy
[2] Istituto Nazionale di Fisica Nucleare, Sezione di Catania, Corso Italia 57, I-95129 Catania, Italy

E-mail: catara@ct.infn.it and samba@ct.infn.it

Received 4 June 2001
Published 6 July 2001
Online at stacks.iop.org/JPhysCM/13/L705

Abstract

We study a system of two electrons moving in the Coulomb field generated by a uniform positive charge distribution and interacting with each other. This system, while allowing for an exact calculation of its excitation spectrum, contains several features of a jellium model description of metal clusters. In particular, the interaction is a realistic one. Special attention is devoted to the dipole collective mode and to its multiple excitations. It is shown that, in addition to a quasi-vibrational band based on the ground state, other bands exist whose vibrational character is much less pronounced.

Collective vibrational states are known both in metal clusters and in nuclei. They are interpreted as the excitations of vibrational quanta, the so-called plasmons or phonons. Two questions that have attracted more attention in this context concern the existence of multiple excitations of these quanta and the extent to which their spectrum is harmonic. In nuclei, two- and three-phonon states based both on the low-lying vibrational modes and on giant resonances (GR) have been observed and the influence of their anharmonicities on various processes studied [1]. In metal clusters, instead, the experimental evidence for these multiple excitations is not fully clear as yet [2]. On the other hand, in as much as the dipole plasmon corresponds to the vibration of the centre of mass of the electrons with respect to that of the positive ions, the study of the properties of such states is important since it can give an indication of how harmonic this vibrational mode is. This argument has already been the object of some theoretical analysis [3, 4].

The two theoretical approaches followed so far, to our knowledge, have led to quite different results. In [3], starting from the time-dependent local density approximation and using a boson expansion technique, the fermion Hamiltonian was mapped onto a boson one which included terms up to the fourth order in the boson operators. The anharmonicities were found to be very large. In particular, for Na_{21}^{+}, the states corresponding to the double excitation of the collective dipole plasmon were found to be spread over several eigenstates lying in a large energy range. The same procedure, with the same level of truncation, had already been applied to the study of the spectrum of doubly excited GR in atomic nuclei [5]. In this case, however, small anharmonicities were found, of the order of a few hundred keV.

A completely different approach was used in [4]. It was based on a time-dependent variational principle, with a trial wavefunction generated from the ground state of the system by one single-particle velocity field. This method leads to very small anharmonicities both in the case of metal clusters [4] and nuclei [6]. In the latter case the results are in qualitative agreement with the findings of [5], although the anharmonicities are considerably smaller. On the contrary, for metal clusters, the anharmonicities found in [4] are orders of magnitude smaller than those in [3]. The two approaches were compared with each other and with the nuclear field theory [7] in reference [8] within a solvable two-level model. Very similar results were found using the three different methods.

In order to shed some light on this subject, configuration mixing (CI) calculations could provide an appropriate tool of analysis. In [9] this approach was used to study the ground state and the dipole excited states in small Na clusters with up to 20 electrons, paying special attention to the plasmon excitations. The calculations were done in the jellium approximation, assuming that the electrons interact with each other and with the ionic charge distribution through the Coulomb interaction. Working in a harmonic oscillator basis, fully convergent results were obtained for the two-electron 'cluster'. On increasing the number of electrons, however, it was found that the configuration space required to get stable solutions becomes very rapidly prohibitively large, thus making the calculations quite difficult. These difficulties are even more evident in the case we are interested in, since the states we want to study are quite high in energy, namely at about twice (or more) that of the plasmon.

In this work we will follow the same CI approach of [9] but, wishing to deal with a case where stability problems of the eigenfunctions do not represent a serious hindrance, we will limit ourselves to study a two-electron system which, as said before, allows for essentially exact results while retaining many physical properties of a realistic situation. The analysis we are going to present is an extension of the work done in [9] since we will consider states with multipolarity up to $L = 4$ and lying quite high in energy. This will allow us to study the properties of states which, in the harmonic limit, would correspond to the multiple excitation of the dipole plasmon.

Our starting point is the jellium Hamiltonian which, for a general cluster with Z atoms and N valence electrons ($N = Z$ for neutral clusters), can be written as [9]

$$H = \sum_{i=1}^{N} h_i + \sum_{i<j=2}^{N} v_{ij} \tag{1}$$

with

$$h_i = -\frac{\hbar^2}{2m}\nabla_i^2 + V(r), \qquad v_{ij} = \frac{e^2}{4\pi\epsilon_0}\frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} \tag{2}$$

and

$$V(r) = \frac{Ze^2}{4\pi\epsilon_0}\begin{cases} (1/2r_c)(r^2/r_c^2 - 3) & \text{for } r \leqslant r_c \\ -1/r & \text{for } r \geqslant r_c \end{cases} \tag{3}$$

where r_c is the radius of the jellium sphere.

As is well known, if we consider the extreme case of a highly positively charged cluster ($N \ll Z$), the electron density is well confined within the boundary of the positive jellium background and therefore the interaction of the latter with the electrons can be well approximated by its harmonic part with a frequency coinciding with the Mie classical frequency [10], namely

$$V(r) = \tfrac{1}{2}m\omega_{\text{Mie}}^2 r^2 + \text{const} \tag{4}$$

where $\hbar\omega_{\rm Mie} = 3.45$ eV for Na clusters. In such a case the motion of the system separates exactly into relative and centre-of-mass motion (harmonic) and the Hamiltonian can be written as

$$H = -\left(\frac{\hbar^2}{2Nm}\right)\nabla^2_{\boldsymbol{R}} + \tfrac{1}{2}Nm\omega^2_{\rm Mie}R^2 + H_{\rm int}(\boldsymbol{r}'_i) \tag{5}$$

where $\boldsymbol{R} = \sum_i \boldsymbol{r}_i/N$ is the coordinate of the centre of mass. The part $H_{\rm int}$ depends only on the intrinsic coordinates $\boldsymbol{r}'_i = \boldsymbol{r}_i - \boldsymbol{R}$ and commutes with the centre-of-mass part of H, therefore guaranteeing that all the eigenfunctions are products of the centre-of-mass and intrinsic parts, i.e. $\Psi = \psi_{\rm c.m.}\phi_{\rm int}$.

The electric-dipole operator is proportional to $\boldsymbol{R}$. Therefore for $N \ll Z$ it will excite one quantum of the centre-of-mass motion, leaving unchanged the intrinsic wavefunction. The transition energy is $\hbar\omega_{\rm Mie}$ and the final state defines the plasmon excitation, which then corresponds to an oscillation of the centre of mass of the electron system against the jellium background.

If one neglects in (1) the electron–electron interaction the spectrum is perfectly harmonic and shows multiplets of states at energies $\mathcal{N}\hbar\omega_{\rm Mie}$, where $\mathcal{N}$ is the sum of the numbers of quanta associated with the centre-of-mass motion of the electrons and to their relative motion, which is also harmonic. Assuming this trivial case as a starting point, we have moved towards a more realistic situation by first including the Coulomb interaction between the electrons and then considering the case of a neutral cluster, with the Coulomb interaction of the electrons with the jellium background.

Let us then start our analysis by considering two electrons moving in a harmonic potential in the presence of the Coulomb interaction between them. This problem has also been recently discussed in [12,13]. As the single-particle basis, we have considered the eigenfunctions of the harmonic potential whose frequency is fixed to the Mie value for Na and we have diagonalized the Hamiltonian in the space of antisymmetrized two-particle states constructed with the first 20 harmonic oscillator wavefunctions. Stability against variations of the dimension of the basis has been checked. The resulting spectrum is formed by a series of bands, perfectly vibrational, each one based on a different eigenstate of the relative motion Hamiltonian. In figure 1 we show the levels having spin zero, angular momentum $L \leqslant 4$ and which belong to the three lowest bands. Since the electron–electron interaction mixes different principal quantum numbers of the relative motion the positions of these bands are shifted with respect to the limiting harmonic case. On the other hand, since the dipole operator acts only on the centre-of-mass coordinate of the electrons, the dipole transition probabilities among members of different bands are vanishingly small. Of course, the different bands are connected through higher multipolarity transitions. For example, the quadrupole transitions from the ground state to the states 2^+_1 and 2^+_2 are found to be quite strong, analogously from the first excited 0^+_2 state to 2^+_1, 2^+_3 and 2^+_6. Thus we see that, as expected, the introduction of the electron–electron interaction plays a quite relevant role in the structure of the spectrum. This can still be considered harmonic in the sense that it exhibits a series of perfectly vibrational bands. However, the 'lateral' bands occurring in addition to the ground state one are now strongly shifted with respect to the position they would have in the extreme case of the absence of any electron–electron interaction where, for example, due to the harmonicity of both the centre-of-mass and the relative motion, the states 0^+_2, 0^+_3, 2^+_1 and 2^+_2 form a degenerate quadruplet at twice the Mie energy.

Before moving to the full model with a realistic jellium–electron interaction it might be worth examining some results which refer to an artificial situation where the two electrons are still considered in the same harmonic potential as before but their mutual Coulomb interaction is increased by a factor α. A similar case has recently been discussed in [11] within an analogous

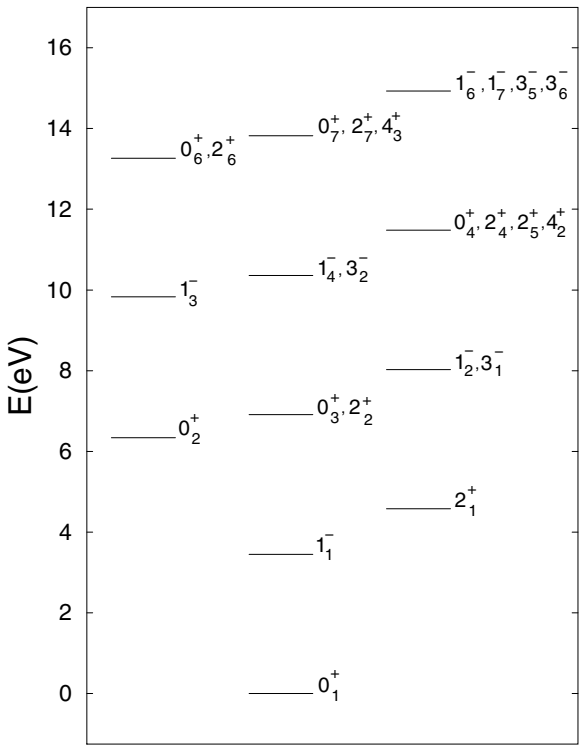

Figure 1. Excitation spectrum for a system of two electrons moving in a harmonic potential in the presence of the Coulomb interaction between them.

Table 1. Energy ratios $R_L^{(\alpha)} = E_L/E_2$ for a system of two electrons moving in a harmonic potential in the presence of the Coulomb interaction increased by a factor α (see text). The ratios refer to the band $0_1^+, 2_1^+, 4_1^+, 6_1^+, 8_1^+$. For comparison, we also show the corresponding ratios in the rotational model.

L	$\alpha = 5$	$\alpha = 10$	$\alpha = 20$	$R_L^{(\mathrm{rotor})}$
2	1.00	1.00	1.00	1.00
4	2.88	3.09	3.22	3.33
6	5.21	5.94	6.46	7.00
8	7.80	9.29	10.53	12.00

model but for a two-dimensional system. Of course, the harmonicity of the vibrational bands is not affected by this artificial change. However, it is interesting to note that, with increasing strength α, the energies of the heads of these bands tend to acquire an $L(L+1)$ dependence typical of rotational bands. This is the case, for instance, for the states $0_1^+, 2_1^+, 4_1^+, 6_1^+, 8_1^+$ whose ratios $R_L^{(\alpha)} = E_L/E_2$ (E_L being the excitation energies) are shown in table 1 for $\alpha = 5$, 10 and 20 and compared with the corresponding ratios of the rotational model. Qualitatively speaking, this behaviour reflects an increasing deformation of the two-electron system which can be associated with a shift toward larger values of the relative distance r at which the minimum in the single-particle potential (sum of the two terms behaving as r^2 and r^{-1}) occurs when one increases the strength α attached to the Coulomb term. The structure of these spectra quite closely resembles that found in [11] where, however, an m^2 ($m = 0, 1, 2\ldots$) law resulted,

which is the appropriate one for a two-dimensional system.

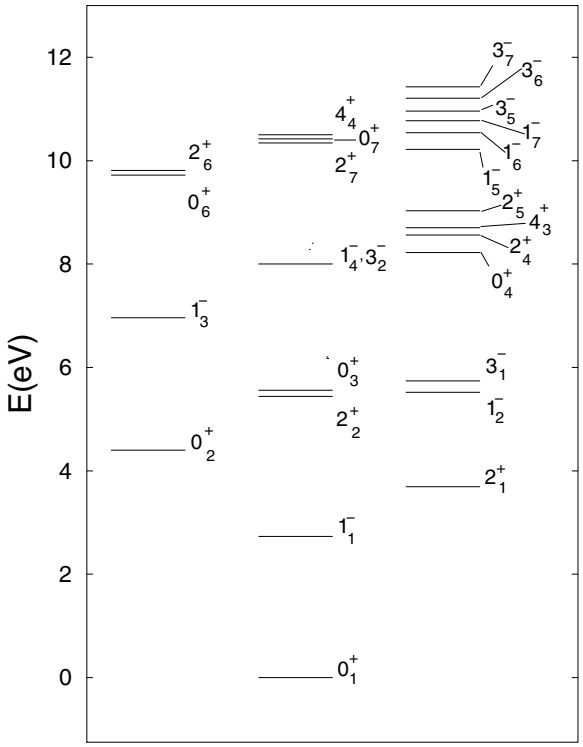

Figure 2. Excitation spectrum for a system of two electrons moving in the Coulomb field generated by a uniform positive charge distribution and interacting with each other.

Let us now turn our attention to the case in which the electrons move in the Coulomb potential generated by the jellium charge distribution. The Hamiltonian has been diagonalized in the same space of antisymmetrized two-particle states described above and the stability of the solutions has been checked also in this case. The results are shown in figure 2, again for the three lowest bands. Concerning this way of ordering the spectrum, it is necessary to point out that the identification of the bands is now not so unambiguous as in figure 1. Unlike that case, in fact, because of the general mixing of the quantum numbers associated with the centre-of-mass and the relative motion of the electrons, non-negligible dipole transitions may now also occur between levels belonging to different bands. We have nevertheless preferred to arrange the levels in such a band scheme in order to make a comparison with the case of figure 1 more transparent. First of all we notice that the energy of the lowest collective dipole state is strongly shifted down with respect to the Mie frequency. This is a well known effect in small metal clusters, related to the spill-out of the electron density outside the jellium sphere [14]. The other members of the band based on the ground state form a spectrum that is essentially harmonic, apart from small splittings. The two 'lateral' bands exhibit instead a less harmonic structure. Namely, in the band associated with the 0^+_2 state, we see that the dipole state 1^-_3 is located at 2.56 eV from the band head (as compared with 2.73 eV in the ground state band) while the next two states are about 2.8 eV above the 1^-_3. More marked deviations can be seen in the other band with a doublet of states at $\sim$2 eV above the 2^+_1 band head and a quadruplet of states $\sim$3 eV above this doublet. A relevant splitting is also observed in this case among the

members of each multiplet.

From a comparison between figures 1 and 2 one may notice that some 'corresponding' levels are labelled with a different index in the two figures. This is the case for the states 4_2^+ and 4_3^+ of figure 1, which become 4_3^+ and 4_4^+, respectively, in figure 2. The reason for such a different classification is simply that in the calculations of figure 2 an extra 4^+ state appears (besides the 4_1^+ state already present also in the calculations of figure 1 but not plotted there because it was the head of an extra band) at an energy lower than that of the quadruplet of states located around 8.5 eV. We have not inserted this state in figure 2 because it is not clear that it belongs to the bands plotted in this figure. In the multiplet of states centred around 11 eV, instead, we have inserted two extra 1^- and 3^- states, with respect to the case of figure 1, since their dipole connections to the other levels of the band are rather relevant.

Summarizing, in this work we have studied a two-electron 'metal cluster' with special attention to the multiple excitations of the dipole plasmon mode. This system, although admittedly simple, has the advantage of retaining many physical aspects of a realistic case while allowing for an exact treatment. Indeed, stable solutions have been found in a configurational mixing calculation. The spectrum obtained by diagonalizing the Hamiltonian in a harmonic oscillator basis has been found to exhibit an interesting structure characterized by a quasi-vibrational dipole band based on the ground state and, in addition, by other dipole bands which, however, do not show such a clear vibrational character. This result therefore appears as intermediate between those of [3, 4] and does help us to improve our understanding of this subject. More complex CI calculations involving larger clusters would actually be necessary to definitively answer the problem of anharmonicities for multiple plasmon excitations. However, getting fully reliable solutions in these systems for the states we are interested in, namely those lying quite high in energy, is still a quite hard task at present.

The authors gratefully acknowledge Nguyen Van Giai for carefully reading the manuscript and for his useful comments.

References

[1] Emling H 1994 *Prog. Part. Nucl. Phys.* **33** 729
Chomaz Ph and Frascaria N 1995 *Phys. Rep.* **252** 275
Aumann T, Bortignon P F and Emling H 1998 *Ann. Rev. Nucl. Part. Sci.* **48**
[2] Schlipper R, Kusche R, von Issendorf B and Haberland H 1998 *Phys. Rev. Lett.* **80** 1194 (see also preprint (2000))
[3] Catara F, Chomaz Ph and Van Giai N 1993 *Phys. Rev.* B **48** 18 207
[4] Hagino K 1999 *Phys. Rev.* B **60** R2197
[5] Catara F, Chomaz Ph and Van Giai N 1989 *Phys. Lett.* B **233** 6
[6] Bertsch G F and Feldmeier H 1997 *Phys. Rev.* C **56** 839
[7] Bes D R, Dussel G C, Broglia R A, Liotta R and Mottelson B R 1996 *Phys. Lett.* B **52** 253
Bes D R, Broglia R A, Dussel G C, Liotta R and Sofia H M 1976 *Nucl. Phys.* A **260** 1
[8] Bertsch G F, Bortignon P F and Hagino K 1999 *Nucl. Phys.* A **657** 59
[9] Koskinen M, Manninen M and Lipas P O 1994 *Phys. Rev.* B **49** 8418
[10] Yannouleas C, Catara F and Van Giai N 1995 *Phys. Rev.* B **51** 4569
[11] Yannouleas C and Landman U 2000 *Phys. Rev. Lett.* **85** 1726
[12] Zhu J L, Li Z Q, Yu J Z, Ohno K and Kawazoe Y 1997 *Phys. Rev.* B **55** 15 819
[13] Lamouche G and Fishman G 1998 *J. Phys.: Condens. Matter* **10** 7857
[14] Kresin V V 1992 *Phys. Rep.* **220** 1