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Wigner distribution function of spherical metal clusters

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We analyze the Wigner distribution function of spherical alkali-metal clusters in the framework of the Density Functional Theory formalism using the jellium and the pseudopotential-jellium models. Nonlocal effects of the interaction between the ionic cores and the set of valence electrons are discussed in comparison with the jellium prediction. We show that simple models like the Slater approach with surface diffuseness give the main features and reproduce the first moments of the Wigner distribution function and can also be used to analyze large clusters.

Keywords: Wigner distribution function; atomic clusters

La función de distribución de Wigner de los agregados esféricos de metales alcalinos ha sido analizada en el esquema de la teoría del funcional de la densidad usando los modelos de *jellium* y de pseudopotencial-*jellium*. Los efectos no locales de la interacción entre los iones y el conjunto de los electrones de valencia se discuten comparando las predicciones del pseudopotencial con las del *jellium*. Se pone de manifiesto que un modelo simple como la aproximación de Slater con difusividad en la superficie da las características principales y reproduce los primeros momentos de la función de distribución de Wigner y puede también ser útil para el análisis de agregados de gran tamaño.

Descriptores: Función de distribución de Wigner; agregados atómicos

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1. Introduction

In the past years the study of the structure of the alkali-metal clusters within the Density Functional Theory (DFT) has provided a reasonable description of some experimental properties for medium clusters [1, 2]. The simplest DFT model based on the quantized motion of the valence electrons in an uniform ionic background, namely the jellium model (JM), provides an appropriate first description for the ground-state and excitation properties of some alkali-metal clusters. Nevertheless, in such a scenario the plasmon resonance energy has a blue shift with respect to the experimental values, especially for lithium clusters [3, 4].

Recently, more elaborated models that account for the ionic core structure have been applied. Reference is to be made, for instance, to the pseudopotential-jellium model (PPJM) that includes the ionic structure using the electron-ion interaction of Bachelet, Hamann, and Schlüter [5]. This model improves the theoretical predictions for polarizabilities as compared to the experimental results, in particular for lithium clusters [6].

Both in the jellium and in the pseudopotential-jellium models, the diagonal part of the electronic one body density matrix plays a central role, as is well known. Much less is known concerning the non diagonal part, which is closely related to the electronic momentum distribution [7, 8] and to the two body correlations. In addition, the one body density matrix provides the starting point to obtain the Wigner distribution function, $f(\vec{r}, \vec{k})$ [9], which is the quantal generalization of the classical phase-space distribution. Although the Wigner distribution function may contain areas of negative "probabilities", its moments are basic observables and it could be the starting point for several approximations to the many body problem [10], such as the time dependent Thomas-Fermi approach for electron dynamics in metal clusters [11]. The Wigner distribution function has recently deserved great attention, both from the theoretical point of view [12, 13] and from the experimental one [14–17]. In particular the Wigner distribution function corresponding to various states of a trapped ion has been experimentally determined by the NIST group [15]. More recently a method for measuring the Wigner function for a vibrational state of a trapped ion or for a molecular vibrational state has been proposed [16, 17].

It appears then useful to complement the study of the electronic one-body density matrix in r-space with that of its Wigner distribution function, and to compare the DFT predictions with some simple models that can be applied to large clusters.

Following these ideas, in this work we focus our attention on the Wigner distribution function for metal clusters predicted by the jellium and the pseudopotential-jellium models. The paper is organized as follows: In Sect. 2 we present the Wigner transform obtained from DFT with the JM and the PPJM. In Sect. 3 we compare the DFT results with the predictions of some simple models based on the Slater approach, and in Sect. 4 we draw some conclusions.

2. DFT results for the Wigner distribution function

Using the Kohn-Sham formalism within the Local Density Approximation for the valence electrons, and the parametrization of Ref. 18 for the exchange-correlation term, we have calculated the Wigner distribution function and its first moments for spherical lithium clusters.

The interaction between the ionic background and the valence electrons has been treated in the local approach with the jellium model, and accounts for the nonlocal effects with the pseudopotential-jellium model.

From the Kohn-Sham selfconsistent wave functions $\psi_j(\vec{r})$ we construct the one body density matrix $\rho(\vec{r}_1, \vec{r}_2)$ in the jellium and in the pseudopotential-jellium models. For a cluster with N valence electrons

$$\rho(\vec{r}_1, \vec{r}_2) = \sum_{j=1}^{N} \psi_j^*(\vec{r}_1)\psi_j(\vec{r}_2)\,. \tag{1}$$

The Wigner distribution function is obtained from the one body density [9]

$$f(\vec{r}, \vec{k}) = \int d\vec{s}\, e^{-i\vec{k}\cdot\vec{s}} \rho\left(\vec{r} + \frac{\vec{s}}{2}, \vec{r} - \frac{\vec{s}}{2}\right), \tag{2}$$

with $\vec{r} = (\vec{r}_1 + \vec{r}_2)/2$ and $\vec{s} = \vec{r}_1 - \vec{r}_2$.

As is well known, $f(\vec{r}, \vec{k})$ is not directly accessible from experiments but its weighted integrals in $\vec{r}$ and $\vec{k}$ space,

$$M_{n,\vec{r}} = \frac{1}{(2\pi)^3} \int d\vec{k}\, k^n f(\vec{r}, \vec{k}) \tag{3}$$

$$M_{n,\vec{k}} = \frac{1}{(2\pi)^3} \int d\vec{r}\, r^n f(\vec{r}, \vec{k}), \tag{4}$$

are basic observables [19]:

$$M_{0,\vec{r}} = \rho(\vec{r}) \tag{5}$$

$$M_{1,\vec{r}} = j(\vec{r}) \tag{6}$$

$$M_{2,\vec{r}} = 2\tau(\vec{r}) + \frac{1}{4}\nabla^2\rho(\vec{r}), \tag{7}$$

where $\rho(\vec{r})$ is the diagonal density matrix, $j(\vec{r})$ the current density and $\tau(\vec{r})$ the kinetic energy density defined as

$$\tau(\vec{r}) = |(\vec{\nabla}_1 \cdot \vec{\nabla}_2)\rho(\vec{r}_1, \vec{r}_2)|_{\vec{r}_1=\vec{r}_2=\vec{r}}, \tag{8}$$

and

$$M_{0,\vec{k}} = n(\vec{k}), \tag{9}$$

$n(\vec{k})$ being the momentum distribution.

When $f(\vec{r}, \vec{k})$ is an even function of $\vec{k}$, its odd moments vanish and $f(\vec{r}, \vec{k})$ is characterized only by the even ones [19], and for a cluster with total spin zero the Wigner distribution function can be determined using three independent variables, r, k and θ (the angle between $\vec{r}$ and $\vec{k}$). With these premises, the Wigner distribution function has been obtained by expanding the selfconsistent single particle wave functions of JM and PPJM in an harmonic oscillator (HO) basis. Using this expansion, $f(\vec{r}, \vec{k})$ can be computed using the method of Ref. 20 for pure HO wave functions by means of the Talmi transformation and the Brody-Moshinsky coefficients. In figure 1 we show the contour plot of $f(\vec{r}, \vec{k})$ (2) obtained within the JM and PPJM for a Li_{92} cluster.

The behavior of the inner structure of $f(\vec{r}, \vec{k})$ as a function of θ can be understood using the analytical expressions for the Wigner distribution function of a harmonic oscillator potential [20]. When the number of occupied single particle levels of the cluster corresponds to that of a harmonic oscillator with closed shells, $f(\vec{r}, \vec{k})$ does not depend on the angle θ. This is the case for Li_{40} for which the JM and PPJM results show only a slight dependence of the Wigner distribution function on θ. In the case of Li_{92} the strong dependence on θ arises from the behavior of the Wigner distribution function corresponding to the open shell $1h$. This behavior is qualitatively the same for the JM, PPJM and HO models as can be appreciated in Fig. 1.

Differences between PPJM and JM can be more clearly seen by looking at the momentum distribution (see Fig. 2). The first moment in k-space of $f(\vec{r}, \vec{k})$ shows that finite size effects are more relevant in PPJM than in the JM, because $n(\vec{k})$ given by PPJM increases for small k values with respect to the jellium prediction. This effect can be understood from the behavior of the density in r-space, where the difference between the finite and the infinite systems is larger in the PPJM than in the JM, due to the non local efects of the PPJM that are included in the effective mass. A simple model for $f(\vec{r}, \vec{k})$, like the Slater approach [7], can explain the behavior of the corresponding momentum distribution $n(\vec{k})$.

3. Comparison with simple models

To have a better understanding of the main features of the Wigner distribution function and its moments we have used a simple model based on the Slater approach, which is exact for a uniform system

$$f_{\mathrm{SL}}(\vec{r}, \vec{k}) = 2\,\theta[\mathrm{k_F}(\vec{r}) - \mathrm{k}], \tag{10}$$

with $k_F(\vec{r})$ determined by the local value of the density $k_F(\vec{r}) = [3\pi^2\rho(\vec{r})]^{1/3}$.

We assume that the diagonal electronic density matrix can be approximated by a Fermi-like density

$$\rho(r) = \rho_0 \left[1 + \exp\left(\frac{r - R_0}{a}\right)\right]^{-1}, \tag{11}$$

with $R_0 = r_s N^{1/3}$ and $r_s = 3.25$ for lithium (Hartree atomic units have been used throughout the text). The diffusivity parameter a is adjusted to reproduce the surface of the Kohn-Sham diagonal density. As is well known [6] the surface diffuseness in r-space is larger in the PPJM ($a = 1.2$) than in the JM ($a = 0.9$).

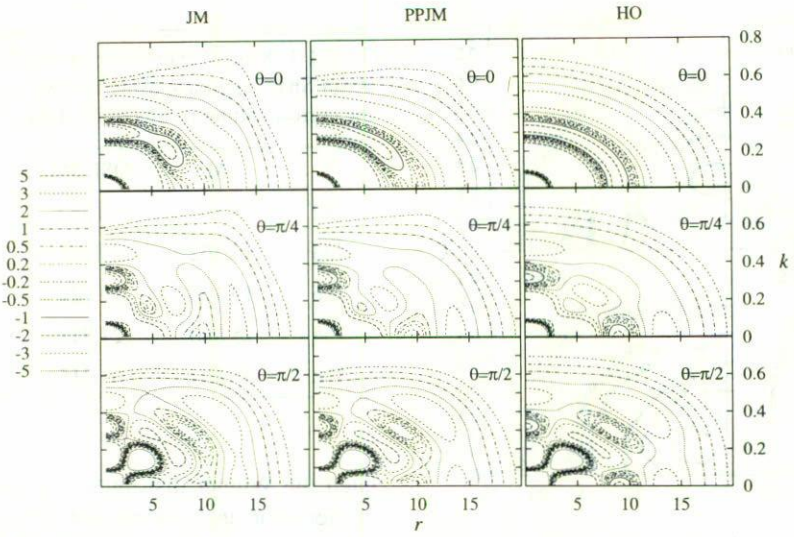

FIGURE 1. Contour plot of $f(\vec{r},\vec{k})$ for $\theta = 0$, $\pi/4$, and $\pi/2$ of a Li_{92} cluster obtained from the selfconsistent Kohn-Sham approach using JM and PPJM. For comparison the HO results are also shown. Hartree atomic units (a.u) are used.

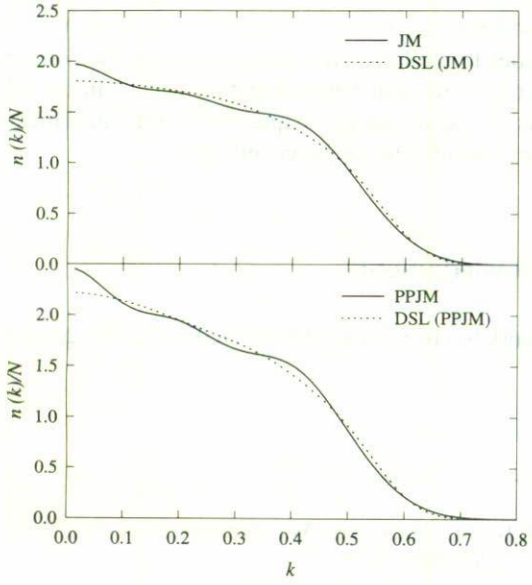

FIGURE 2. Momentum distribution for Li_{92} in a.u. The solid line shows the Kohn-Sham result for the JM (upper panel) and PPJM (lower panel). The dotted line corresponds to the DSL approach for the Wigner distribution function.

The Slater approach (10) with a Fermi-like density lacks of diffusivity in k-space for $f(\vec{r},\vec{k})$ and gives a momentum distribution that diverges at the origin and decreases sharply to zero [7]. In order to obtain a better description of the Wigner distribution function and its moments, as in Ref. 7 we have incorporated a surface diffuseness to the Slater approach (DSL) by convoluting (10) with a normalized gaussian

$$f_{\rm DSL}(\vec{r},\vec{k}) = \int f_{\rm SL}(\vec{r},\vec{k}')\, g(|\vec{k}-\vec{k}'|)\, d\vec{k}', \qquad (12)$$

where $g(x) = \exp(-x^2/\mu^2)/(\pi^{3/2}\mu^3)$.

We have used an r-dependence of the diffuseness parameter μ, taking two values of the diffuseness constant, one in the inner region ($\mu = \mu_1$ for $r < R_0 + \delta$) and other in the outer one ($\mu = \mu_2$ for $r > R_0 + \delta$), where $\delta = 1.2$ is the spill out parameter [2]. We have obtained the two diffuseness constants minimizing the differences between by a least-square fit of the KS and DSL momentum distributions. Closed shell Li clusters with $92 \leq N \leq 338$ have been used for this task. The parameter μ_1 is found to be well reproduced by the following expressions

$$\mu_1 = -1.53 \times 10^{-2} \ln N + 0.155 \quad \text{(JM)} \qquad (13)$$

$$\mu_1 = -1.07 \times 10^{-2} \ln N + 0.126 \quad \text{(PPJM)}; \qquad (14)$$

μ_2 is approximated by a constant obtained as the mean value of the results corresponding to the cluster sizes being considered,

$$\mu_2 = 0.26\,\text{(JM)} \qquad (15)$$

$$\mu_2 = 0.22\,\text{(PPJM)}, \qquad (16)$$

the standard deviation being 0.02 in the first case and 0.01 in the second one.

As shown in Fig. 3 the surface main features of the Wigner distribution are rather well reproduced using the Diffuse Slater approach (12). Reproducing the surface is enough to provide a reasonable fit of the momentum distribution (see Fig. 2) for both the jellium and the pseudopotential-jellium models. In addition, the DSL approach is able to reproduce the integral of $M_{2,\vec{r}}$ (7), that gives the kinetic

$$T = \frac{1}{2}\int M_{2,\vec{r}}\, d\vec{r}, \qquad (17)$$

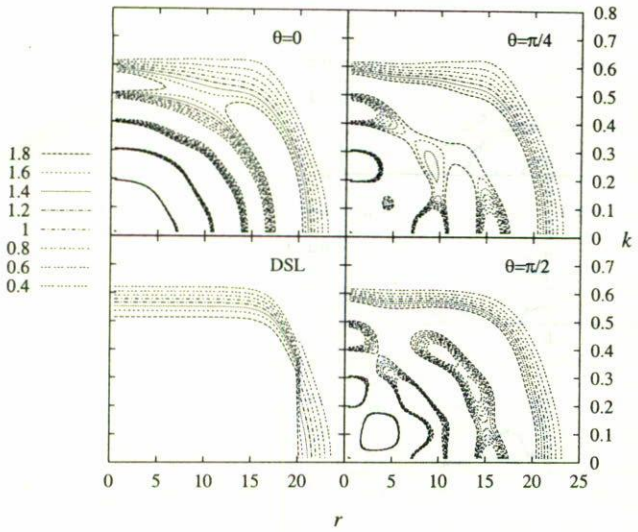

FIGURE 3. Contour plot of $f(\vec{r},\vec{k})$ for a Li_{92} cluster using the PPJM with $\theta = 0$, $\pi/4$, and $\pi/2$. For comparison purposes, the θ-independent DSL approach, obtained with the PPJM fitted parameters, is also shown.

as it is shown in Table I where we have compared the kinetic energy obtained with the JM and the PPJM to that of the corresponding DSL approach for several Li clusters. With the aid of expressions (13) to (16), this model can be used to understand the surface main features of the Wigner distribution function and to reproduce its first moments for large clusters.

4. Conclusions

Using the selfconsistent Kohn-Sham formalism with the jellium and the pseudopotential-jellium models we have calculated the Wigner distribution function for spherical lithium clusters, and analyzed its first moments. In particular, the momentum distribution $n(\vec{k})$ in PPJM is enhanced for small k values with respect to JM. We have proposed a simple approximation, the Diffuse Slater model, which provides a reasonable fit to the surface main features of the Wigner distribution function and reproduces with remarkable agreement its first moments. It can be used for the extrapolation of cluster properties to the large size limit, for which the construction of the one-body distribution function $f(\vec{r},\vec{k})$ in the full six-dimensional space using the quantum-mechanical mean field requires considerable technical efforts.

TABLE I. Kinetic energy for several Li clusters obtained with the Kohn-Sham approach using the JM and the PPJM. For comparison the corresponding results of the DSL model are also shown.

N	JM	DSL JM	PPJM	DSL PPJM
92	8.847	8.747	8.265	8.163
138	13.362	13.355	12.589	12.610
196	19.130	19.122	18.134	18.189
254	25.060	24.818	23.919	23.808
338	33.454	33.315	32.057	32.134

Acknowledgments

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1. M. Brack, *Rev. Mod. Phys.* **65** (1993) 677.
2. W.A. de Heer, *Rev. Mod. Phys.* **65** (1993) 611.
3. A. Puente, Ll. Serra, and M. Casas, *Z. Phys. D* **31** (1994) 283.
4. C. Guet and W.R. Johnson, *Phys. Rev. B* **45** (1992) 11283.
5. G.B. Bachelet, D.R. Hamann, and M. Schlüter, *Phys. Rev. B* **26** (1982) 4199.
6. F. Alasia *et al.*, *Phys. Rev. B* **52** (1995) 8488.
7. A. Rigo *et al.*, *Z. Phys. D* **40** (1997) 294.
8. A. Rigo *et al.*, *Phys. Rev. B* **57** (1998) 11943.
9. E.P. Wigner, *Phys. Rev.* **40** (1932) 749.
10. P. Ring and P. Schuck, *The Nuclear Many Body Problem*, (Springer, New York, 1980).
11. A. Domps, P.G. Reinhard, and E. Suraud, *Phys. Rev. Lett.* **80** (1998) 5520.
12. M. Hug, C. Menke, and W.P. Schleich, *Phys. Rev. A* **57** (1998) 3188; **57** (1998) 3206.
13. S. Nouri, *Phys. Rev. A* **57** (1998) 1526.
14. D. Leibfried, T. Pfau, and Ch. Monroe, *Physics Today* **51** (1998) 22.
15. D. Leibfried *et al.*, *Phys. Rev. Lett.* **77** (1996) 4281.
16. L.G. Lutterbach and L. Davidovich, *Phys. Rev. Lett.* **78** (1997) 2547.
17. L. Davidovich, M. Orszag, and N. Zagury, *Phys. Rev. A* **57** (1998) 2544.
18. J.P. Perdew and A. Zunger, *Phys. Rev. B* **23** (1981) 5048.
19. J. Martorell and E. Moya de Guerra, *Ann. Phys. (N.Y.)* **158** (1984) 1.
20. S. Shlomo and M. Prakash, *Nucl. Phys. A* **357** (1981) 157.