DENSITY-FUNCTIONAL STUDY OF THE STRUCTURE OF PHOTOEXCITED LITHIUM-DOPED NEON CLUSTERS

ESTUDIO DE LA ESTRUCTURA DE CLUSTERS DE NEÓN DOPADOS CON ÁTOMOS DE LITIO FOTOEXCITADOS UTILIZANDO LA TEORÍA DEL FUNCIONAL DE LA DENSIDAD

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We study the rearrangement of a cluster of neon atoms as a consequence of the photoexitation of an impurity (a lithium atom) to its first state of Rydberg, Li (3s←2s). The distribution of neon particles is calculated using the density functional theory for quantum liquids, while introducing a description of the correlation effects based on the London formula for quantum rigid particles. An algorithm was implemented to solve the Schrödinger equation in a self-consistent way, using a damped iteration scheme. The possibility of formation of the structure known as *scolium* in this system is discussed.

Estudiamos el reordenamiento de un cluster de átomos de neón como consecuencia de la fotoexcitación de una impureza (un átomo de litio) a su primer estado de Rydberg, Li (3s←2s). La distribución de partículas de neón se calcula utilizando la teoría del funcional de la densidad para líquidos cuánticos, a la vez que se introduce una descripción de los efectos de correlación basados en la fórmula de London para esferas rígidas cuánticas. Se implementó un algoritmo para resolver la ecuación de Schrödinger de forma autoconsistente, empleando un esquema de iteraciones amortiguadas. Se discute la posibilidad de formación de la estructura conocida como *scolium* en este sistema.

I. INTRODUCTION

In recent years, a large number of theoretical and experimental investigations have been devoted to the study of noble gas clusters. In particular, the rearrangement of aggregates of He atoms due to the implantation of ions inside the cluster has been studied extensively, motivated by the possibility to tune the properties of the superfluid state by modifying the impurity-helium interaction [1]. As a consequence of electrostriction, a strong increase of the He density occurs in the vicinity of the impurity ion, affecting the overall cluster structure. Strongly attractive ions tend to form a solid-like structure known as *snowball*, which is characterized by an inhomogeneous, tightly-bound density of He atoms in the vicinity of the impurity. Due to the presence of strongly attractive impurity-solvent interactions, compared to the He-He interaction, the portion of the helium liquid around the impurity exhibits the inner structure typical of a solid.

The appearance of the so-called *scolium* constitutes an interesting phenomenon closely linked to the snowball formation described above, which has been theorized to occur as a result of the interaction forces between an impurity alkali metal atom and the surrounding He atoms. It is based on the excitation of the dopant atom to one of its Rydberg states. The orbit of the Rydberg electron is spatially distant from the impurity nucleus, and in some cases it may reach the surface of the helium nanodroplet. Since the electron density corresponding to the Rydberg state is spherically symmetric, the short-range impurity-solvent interaction is dominated by the electrostatic attraction between the positively charged ionic core and the He atoms around it. In this way, the helium density is increased locally up to the typical values of solid helium. Alkali atoms constitute ideal candidates to achieve the formation of the *scolium*, since the unpaired electron can be readily photoexcited to one of its Rydberg states. The electron that surrounds the nanodroplet exerts an additional electrostatic pressure that increases the local density of He around the impurity. Theoretical calculations based on density functional theory predict that small clusters of liquid He can solidify via this mechanism [1].

Up to our knowledge, no theoretical predictions have been reported on the feasibility of *scolium* formation in neon clusters. The aim of this work is to study the rearrangement of a Ne cluster as a consequence of the photoexcitation of a Li atom to its first Rydberg state, thus discussing the possibility of *scolium* formation in aggregates of neon atoms. The investigation is carried out within the framework of the density functional theory for quantum fluids [2], to account for the non-negligible quantum delocalization of the noble gas particles.

The paper is structured as follows. The details of the Density Functional Theory (DFT) calculations are presented in the next section. The structural properties of the cluster in its ground electronic state and in the Rydberg state are described in the Results and Discussion section. Finally, some remarks concerning the structural modification of the cluster upon photoexcitation are presented in the Conclusions section.

II. METHODOLOGY

The use of density functional theory allows to reduce the dimensionality of the problem from 3N-6 internal degrees of freedom to 3 degrees of freedom [3, 4]. The solution of the time-independent Schrödinger equation for the effective three dimensional system allows to calculate the distribution of the Ne particles around the Li atom. The spherical symmetry of the alkali metal-neon interaction potential enables further reduction to a one-dimensional problem, with the radius as the dynamical variable and the origin of the coordinate system set at the impurity center.

$$-\frac{\hbar^2}{2m}\nabla^2\phi + v_{eff}[\rho(r)]\phi = E_0\phi \tag{1}$$

Here, $\phi(r)$ is the radial wave function of the reference fluid and m is the mass of the solvent atoms. Equation (1) exploits the fact that, at zero temperature, non-interacting bosons condense in the ground state E_0. The effective potential

$$v_{eff} = v_{Li-Ne}(r) + v_{xc}[\rho(r)] \tag{2}$$

is obtained by adding the Li-Ne interaction potential v_{Li-Ne} and the exchange-correlation contribution v_{xc}. The latter is the functional derivative of the exchange-correlation free energy F_{xc}:

$$v_{xc}[\rho(r)] = \frac{\delta F_{xc}}{\delta \rho(r)}, \tag{3}$$

Within the local density approximation (LDA), the exchange-correlation contribution F_{xc} is expressed as:

$$F_{xc} = \int \rho(r)\varepsilon_{xc}[\rho(r)]d^3\vec{r}, \tag{4}$$

where the exchange-correlation energy density ε_{xc} is a function of the local density $\rho(r)$, and it accounts for the interaction energy between a neon atom and its surroundings. The LDA provides an adequate framework for the approximate evaluation of structural and thermophysical properties of rare gas systems, which are dominated by excluded volume effects due to short-range interactions. Combining equations (4) and (3), the following expression is obtained for the exchange-correlation potential:

$$v_{xc}[\rho(r)] = \varepsilon_{xc}[\rho(r)] + \rho(r)\frac{\delta\varepsilon_{xc}}{\delta\rho(r)}. \tag{5}$$

To evaluate the effective potential v_{eff}, an explicit expression for the exchange-correlation energy density is required. Taking into account the aforementioned dominance of short-range repulsion forces and the influence of quantum delocalization on the structure of neon clusters [6, 7], we choose to evaluate this contribution using the London formula for the energy of a homogeneous system of quantum hard spheres [5]:

$$\varepsilon_{xc} = \frac{E}{N} = \frac{2\pi\hbar^2 d}{m}\frac{\rho_0}{[(\frac{\rho_0}{\rho})^{1/3} - 1]^2}\frac{1}{[(\frac{\rho_0}{\rho})^{1/3} + b]}, \tag{6}$$

which reproduces correctly the low- and high-density limits. In equation (6), $b = \frac{2^{5/2}}{\pi - 1}$ and $\rho_0 = \sqrt{2}/d^3$ represents the high-density limit, while d denotes the hard sphere diameter. The latter was computed using the Barker-Henderson prescription [6]:

$$d = \int_0^{r_e}\left[1 - e^{-\beta v_0(r)}\right]d^3\vec{r}, \tag{7}$$

where $\beta = 1/k_BT$ is the inverse temperature, r_e is the position of the Ne-Ne interatomic potential minimum, and v_0 stands for the repulsive component of interaction potential between Ne atoms according to the Weeks-Chandler-Andersen (WCA) perturbative scheme [6].

The Li-Ne interaction potential correlating to the ground electronic state of the metal is taken as a Lennard-Jones potential:

$$v_{Li-Ne}(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6\right] \tag{8}$$

with parameters $\varepsilon = 9.340$ cm^{-1}, $\sigma = 4.386$ Å, whereas a Morse function

$$v_{Ne-Ne}(r) = D\left[e^{-2\alpha(r-r_e)} - 2e^{-\alpha(r-r_e)}\right] \tag{9}$$

with parameters $D = 29.036$ cm^{-1}, $\alpha = 2.088$ Å^{-1} and $r_e = 3.091$ Å was used for the Ne-Ne interaction potential. In the WCA separation, the short-range repulsive part v_0 of the interaction potential is defined as follows:

$$v_0(r) = \begin{cases} v_{Ne-Ne}(r) + D & , \; r < r_e \\ 0 & , \; r \geq r_e \end{cases}$$
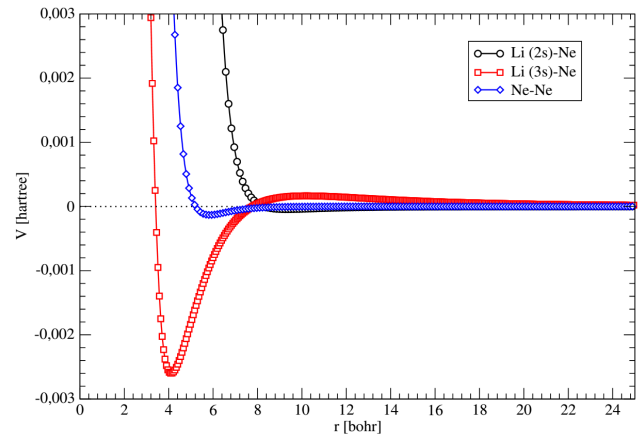

Figure 1. Potential energy curves corresponding to the Ne-Ne (diamonds), Li(2s)-Ne (circles) and Li(3s)-Ne (squares) interactions.

The Li-Ne potential energy curve on the excited electronic state was modeled as a power expansion, as described in Ref. [8]. These interaction potentials are shown in Figure 1.

The time-independent Schrödinger equation was solved self-consistently, using the following damped iterations scheme:

$$\rho_{in}^{i+1}(r) = \alpha\rho_{out}^i(r) + (1-\alpha)\rho_{in}^i(r). \tag{10}$$

At the beginning of the ith iteration, the density profile $\rho_{in}^i(r)$ is used to evaluate the effective potential $v_{eff}(r)$, and the solution of equation (1) results in a new distribution $\rho_{out}^i(r) = |\phi(r)|^2$. The damped density is constructed from these two fields, and it is used to start the next iteration. The damping coefficient employed in the calculations was $\alpha = 0.1$.

III. RESULTS AND DISCUSSION

The rate of convergence of the self-consistent method is illustrated in Figure 2, for the electronic ground state of a lithium-doped cluster containing N=64 neon atoms.
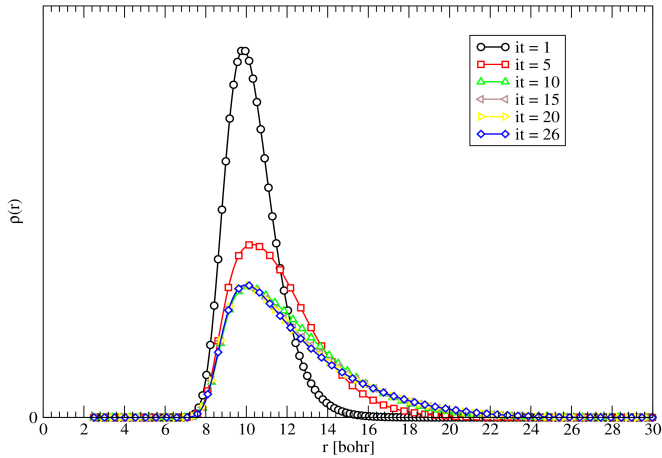

Figure 2. Damped density iterations corresponding to the ground state of a Li(2s)-Ne$_{64}$ cluster.

It can be seen, that the algorithm approaches the stationary probability density in a few iterations (starting from the much more strongly peaked initial distribution). The slowly falling tail of the asymptotic probability distribution also points to the capability of the density-functional calculations to describe the ground vibrational state of the fluid in strongly anharmonic external potentials.
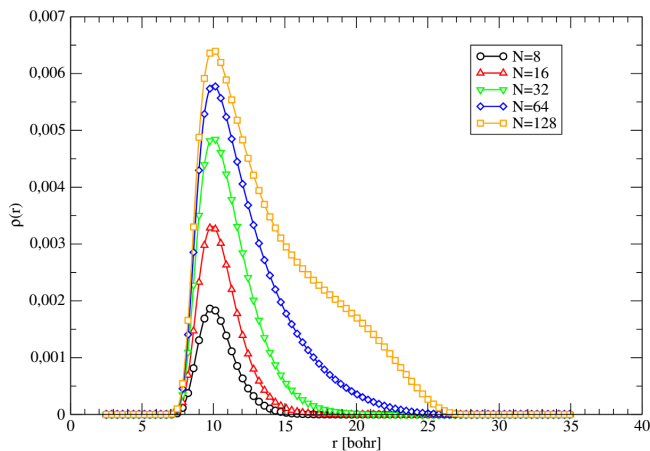

Figure 3. Dependence of the radial density distribution on the number of neon atoms in the cluster.

In Figure 3, we show the evolution of the structure of the cluster in its ground electronic state, as a function of the number of particles in the aggregates. For the smaller clusters, there is a well defined peak in the radial density, centered at about 10 bohr, which is far enough from the impurity center to accommodate up to 64 neon atoms in this first solvation layer. However, for larger cluster sizes additional Ne atoms have to place themselves at larger distances, in order to minimize the interatomic repulsion. The incipient formation of the second layer of rare gas atoms is observed in Figure 3 for the cluster containing 128 particles.

The structural modification of the cluster upon photoexcitation from the ground electronic state to the first Rydberg state is illustrated in Figure 4, for two specific particle numbers (N=8 and N=16). It can be noticed, that the promotion to the Rydberg state causes a major redistribution of the neon atoms surrounding the impurity.
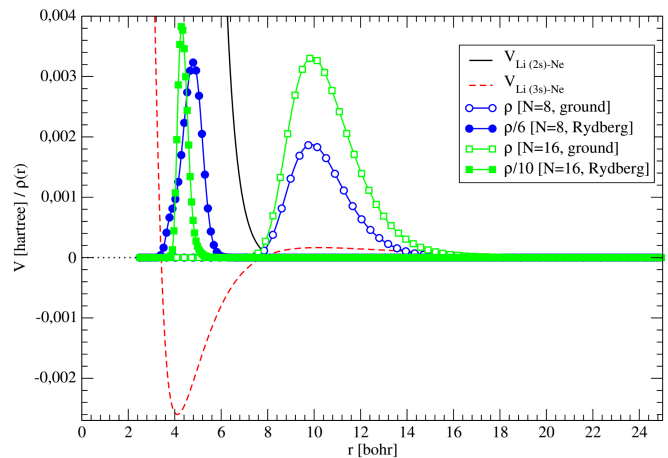

Figure 4. Structural modification of lithium doped clusters upon photoexcitation of the impurity to its first Rydberg state. To facilitate the comparison, the excited state densities have been rescaled.

It is also striking, that this reorganization is chiefly driven by the large differences in the lithium-neon interactions in the ground and the excited states. In the one hand, the ground electronic state is characterized by a predominantly repulsive Li-Ne interaction potential, with a very shallow well located at approximately 9 bohr from the center of mass of the metal atom. As a consequence, the neon atoms tend to pile up at this distance from the origin. On the other hand, the promotion of the alkali atom onto its first Rydberg state is accompanied by a change in the electron density of the metal. The main peak of the radial distribution of the Rydberg electron (whose position is indicated by the outer energy barrier in the Li(3s)-Ne potential energy curve) overlaps with the maxima of the ground-state neon density depicted in Figure 4. Therefore, the equilibrium distribution of the solvent particles in the excited cluster is shifted inwards, to the region where the influence of the spherical density of the Rydberg electron can be neglected, and the positively charged ionic core exerts a strong attraction on the neon atoms.

For the two clusters shown in Figure 4, the picture resulting from the DFT calculations is consistent with the formation of a *scolium*. In the excited clusters, the narrow density peaks indicate that Ne atoms are located in well-defined

positions around the Li center, compared to the much wider distributions of their distances to the impurity in the ground state. Moreover, the maximum of the local density for the aggregate containing N=16 neon atoms (0.038 Å^{-1}) amounts to 83 % of the average density of the neon solid. The *scolium* formation for this cluster needs to be confirmed by fully three-dimensional calculations employing more elaborate density functionals (e.g., the use of non-local exchange-correlation functionals causes the breakdown of the spherical symmetry), and incorporating the weak, long-range attractive tail of the Ne-Ne interaction.

In the Li(3s)-Ne$_8$ complex, the radial distribution density of Ne atoms is broader and the maximum local density is smaller than for the Li(3s)-Ne$_{16}$. These differences originate from the fact that 8 neon atoms are not enough to fill completely the first solvation shell, so their motion is less constrained than for the larger cluster.

IV.   CONCLUSIONS

We presented a density-functional study of the structural reorganization of a neon cluster as a consequence of the photoexcitation of an impurity (Li) atom to its first Rydberg state, within the LDA and exploiting the spherical symmetry of the resulting DFT equations. We implemented and algorithm to solve the time-independent Schrödinger equation in a self-consistent way, using a damped iteration scheme. The efficiency of the method is evidenced by its rapid convergence to the stationary density distribution. The methodology was employed to investigate the structure of the doped cluster in the ground and the excited electronic states, and the relationship between the structural modification and the topology of the lithium-neon interaction potentials.

The photoexcitation of the alkali atom to its first Rydberg state provokes the formation of well-localized peaks in the radial distribution of Ne atoms around the impurity, and for some clusters (e.g., Li(3s)-Ne$_{16}$) it produces local densities which are close to the typical values of the neon solid. These localized peaks suggest the possibility to observe the formation of the structure known as *scolium* for lithium doped neon clusters, which needs to be confirmed by more elaborate DFT calculations (for example, within the weighted-density or the modified weighted-density approximations [6]).

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