Spectrum of a $^3$He atom in a Ca@$^4$He$_{50}$ droplet

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Abstract.
Within density functional theory, we have studied the solvation onset of Ca in a $^4$He droplet to which a small number of $^3$He atoms is being added. In a first step, we have considered the case study of Ca@$^4$He$_{50}$ to which we have added one single $^3$He atom. We have obtained the $^3$He spectrum and probability density distributions. These results are used to infer how many $^3$He atoms are needed to start coating the Ca impurity in that drop.

The absorption spectrum of atomic impurities attached to helium droplets is very sensitive to the structure of the droplet around the foreign atom. Information on the droplet structure, and in particular whether the location of the atom is in the bulk or at the surface of the drop, can be obtained from the analysis of the absorption spectrum [1].

While most impurities present a similar solvation behavior in both helium isotopes, heavy alkaline-earth atoms but magnesium are solvated in $^3$He but not in $^4$He drops, see e.g. Ref. [2] and references therein. For this reason, it has been suggested that Ca atoms may sit in the $^3$He-$^4$He interface of mixed drops hosting several thousand atoms [2], making the Ca atom a possible probe to study the $^3$He-$^4$He interface at very low temperatures. The rationale of this suggestion is that $^3$He has a limited solubility in $^4$He below the tricritical point, segregating for concentrations larger than a critical value. This produces a structure in which a core of $^4$He atoms is coated by a $^3$He shell [3, 4]. Due to the solvation behavior just commented, a Ca atom attached to a mixed droplet will “sink” into the $^3$He shell till reaching the surface of the $^4$He core.

To confirm this scenario, we are studying large mixed helium drops doped with Ca atoms [5] within density functional theory (DFT). To handle the large number of $^3$He atoms found in the actual experimental conditions [1], we have used a Thomas-Fermi approximation to describe them. While this is well justified to describe the experimental situation, it obscures how solvation of Ca proceeds as an increasing number of $^3$He atoms is added to the Ca@$^4$He$_N$ drop. For this reason, we have undertaken the study of the solvation onset of Ca in a $^3$He-$^4$He droplet when it is made attaching the $^3$He atoms one by one. We present here a first step in this direction, describing the spectrum of one single $^3$He atom added to a Ca@$^4$He$_{50}$ drop.

Our starting point is the density functional for liquid helium mixtures of Ref. [6], as well as the method outlooked there (see also Refs. [7, 8]). To assess the reliability of our approach, we compare first in Table 1 the DFT results obtained for $^3$He atoms attached to some spherically symmetric $^4$He$_N$ drops with Diffusion Monte Carlo (DMC) calculations obtained as indicated in Refs. [9, 10]. We want to mention that within DMC, the single particle (s.p.) energies are obtained by subtracting large energy values and consequently, the error bars could be rather...
optimistic. Moreover, the s.p. energies for \( n > 1 \) have been obtained from a sum-rule approach [9, 10] that yields an upper bound to them, and no error bars are provided there. It can be seen that the overall agreement between DMC and DFT results is good.

| \( n, l \) | \( N_1 = 8 \) DMC | \( N_1 = 20 \) DMC | \( N_1 = 40 \) DMC | \( N_1 = 50 \) DMC |
|-----------|----------------|----------------|----------------|----------------|
| 1s        | -0.94(2)      | -0.78          | -1.68(3)       | -1.65          |
| 1p        | -0.46(2)      | -0.38          | -1.27(3)       | -1.38          |
| 1d        | -            | -0.66(3)       | -0.87          |                |
| 1f        | -            | -              | -0.18          |                |
| 1g        | -            | -              | -0.02          |                |
| 2s        | -0.37        | -0.32          | -0.63          | -0.45          |
| 2p        | -0.16        | -0.12          | -0.80          | -0.26          |
| 1h        | -            | -              | -0.19          |                |
| 2d        | -            | -0.27          |                |                |

Table 1. DMC vs. DFT bound state s.p. energies \( \varepsilon_{nl} \) (K) for a \(^3\)He atom in four undoped \(^4\)He\(_N4\) drops. In DMC, the effect of the \(^3\)He atom on the structure of the \(^4\)He drop is included, whereas it is not in DFT. The \((n, l)\) labels correspond to spherically symmetric s.p. levels.

When a Ca atom is added to the pure drop, the complex Ca@\(^4\)He\(_N4\) is no longer spherically symmetric, which renders the numerical problem more involved. We have treated the Ca-drop interaction in the pair potential approximation, as described in detail in Ref. [11], and have used the Ca-He pair potential \( V_{\text{He-Ca}} \) of Ref. [12].

Once the structure of the Ca@\(^4\)He\(_N4\) system has been obtained by solving the appropriate Euler-Lagrange and Schrödinger equations for He and Ca respectively [11], we determine the \(^3\)He s.p. spectrum from the Kohn-Sham equation \( \mathcal{H}_{KS} \varphi_i = \varepsilon_i \varphi_i \). The Kohn-Sham Hamiltonian \( \mathcal{H}_{KS} \) is

\[
\mathcal{H}_{KS} = \left[ -\nabla \frac{\hbar^2}{2m_3^*}(\mathbf{r}) \nabla + \int d^3r' \rho_4(\mathbf{r}') \mathcal{V}_{3-4}(\mathbf{r}' - \mathbf{r}) + \int d^3r' |\Phi(\mathbf{r}')|^2 \mathcal{V}_{He-Ca}(\mathbf{r}' - \mathbf{r}) \right],
\]

where \( \Phi \) is the Ca wave function and \( \rho_4 \) is the \(^4\)He density. The effective mass \( m_3^* \) is defined in Ref. [6], and the mean field \( \mathcal{V}_{3-4} \) is obtained by functional variation from the density functional. Implicit in our approach is the neglect of polarization effects caused by the \(^3\)He atom on the \(^4\)He density and Ca wave function. This is justified by the large mass difference between the \(^3\)He and Ca atoms. In the case of pure \(^4\)He drops, this approximation has been also used in some microscopic approaches, see e.g. Refs. [13, 14], but not in Refs. [9, 10, 15], the effect of this approximation on the DMC results has been discussed in Ref. [9]. To solve all partial differential equations arising in this problem, we have used the imaginary-time method described in Ref. [11] and references therein.

We show in Table 2 the s.p. energies. Comparing with the results shown in Table 1 for the pure \(^4\)He\(_N0\) drop, the first noticeable effect of the presence of Ca is the splitting of the s.p. energies due to the breaking of the spherical symmetry. We recall that in axial symmetry, the projection of the angular momentum on the symmetry axis is the good quantum number, and that states with projected orbital angular momentum \( \pm l \) are degenerate. For instance, the \( 1p \) and \( 2s \) axially symmetric states arise from the splitting of the \( 1p \) spherical state; the \( 1d, 2p \) and \( 3s \) axially symmetric states from the splitting of the \( 1d \) spherical state, and so on. Within a
Table 2. DFT s.p. energies $\varepsilon_{nl}$ (K) corresponding to a $^3$He atom in a Ca@$^4$He$_{50}$ droplet. The effect of the $^3$He atom on the Ca@$^4$He$_{50}$ drop structure has been neglected. The $(n,l)$ labels correspond to axially symmetric s.p. levels.

| $n,l$ | $\varepsilon_{nl}$ |
|-------|--------------------|
| 1s    | –2.53              |
| 1p    | –2.40              |
| 2s    | –2.32              |
| 1d    | –2.11              |
| 2p    | –2.09              |
| 3s    | –1.91              |
| 2d    | –1.69              |
| 1f    | –1.67              |
| 3p    | –1.58              |
| 4s    | –1.30              |
| 5s    | –0.61              |

Given bunch of axially symmetric split states, the less bound states are those with the smallest $l$ values.

Besides this geometrical effect, the presence of a Ca atom changes the s.p. energies by a rather modest amount because the He-Ca interaction is much weaker than the He-He interaction and hence, the $^3$He atom prefers to sit far from the Ca impurity, as can be seen in Fig. 1. Notice that an appreciable number of s-states, the only ones with a large probability density along the symmetry $z$ axis, have to be occupied before the impurity becomes solvated. The structure of the probability densities shown in Fig. 1 indicates that solvation starts to appear when the 5s state is filled. Since the degeneracy of a spin saturated s.p. level is two for $l = 0$ and four otherwise, this would correspond to a number of $^3$He atoms $N_3 \sim 50$ for $N_4 = 50$. This determination is based on the strong assumption that increasing the number of $^3$He atoms for that $N_4$ value, does not change the filling order of the s.p. levels displayed in Table 2. Preliminary Kohn-Sham calculations [16] carried out up to $N_3 = 18$ indicate that this is the case for not too large $N_3$ values.

Figure 1. Probability density distributions $|\varphi(x,0,z)|^2$ in the $y = 0$ plane ($z$ is the symmetry axis) of selected $^3$He s.p. levels in the Ca@$^4$He$_{50}$ droplet. For each s.p. level, we have plotted nine equidensity lines corresponding to 0.9 to 0.1 times the maximum value of the probability density. The dashed line represents the $^4$He dividing surface, where the $^4$He density equals half the bulk liquid value. The cross indicates the point where the Ca probability density has its maximum value.
Finally, we show in Fig. 2 the s.p. energies as a function of the squared orbital angular momentum. It can be seen that they are approximately distributed following rotational-like bands. This feature of the s.p. spectrum has been also found for other geometries, see Ref. [8] and references therein, and it is very robust against increasing the number of $^3$He atoms in the drop [7]. The appearance of this quasi-rotational s.p. spectrum is due again to the non-miscibility of $^3$He in $^4$He, that pushes the lighter helium isotope to the surface of the drop. As a consequence, the centrifugal term is a perturbation to the mean field experienced by $^3$He and this yields the $l^2$ dependence of the s.p. energies for a given principal quantum number $n$.

![Figure 2](image)

**Figure 2.** $^3$He s.p. energies $\varepsilon_{nl}$ (K) in the Ca@$^4$He$_{50}$ droplet as a function of the squared orbital angular momentum. From bottom to top, the rotational-like bands are made of $n = 1, 2$ and 3 s.p. states, respectively. The lines have been drawn as a guide to the eye.

**Acknowledgments**

This work has been performed under Grants No. FIS2005-01414 and FIS2007-60138 MEC-DGI, and No. 2005SGR00343 Generalitat de Catalunya (Spain)

**References**

[1] Stienkemeier F and Lehmann K K 2006 *J. Phys. B: At. Mol. Opt. Phys.* **39** R127.

[2] Hernando A, Mayol R, Pi M, Barranco M, Ancilotto F, Bünemann O and Stienkemeier F 2007 *J. Phys. Chem. A* **111** 7303.

[3] Grebenev S, Toennis J P and Vilesov A F 1998 *Science* **279** 2083.

[4] Pi M, Mayol R and Barranco M 1999 *Phys. Rev. Lett* **82** 3093.

[5] Hernando A, Ancilotto F, Barranco M, Mayol R and Pi M 2008 contribution to LT25.

[6] Barranco M, Pi M, Gatica S M, Hernández E S and Navarro J 1997 *Phys. Rev. B* **56** 8997.

[7] Navarro J, Poves A, Barranco M and Pi M 2004 *Phys. Rev. A* **69** 023202.

[8] Barranco M, Guardiola R, Hernández E S, Mayol R, Navarro J and M. Pi 2006 *J. Low Temp. Phys.* **142** 1.

[9] Fantoni S, Guardiola R and Navarro J 2004 *Phys. Rev. A* **70** 023206.

[10] Fantoni S, Guardiola R, Navarro J and Zuker A 2005 *J. Chem. Phys.* **123** 054503.

[11] Hernando A, Barranco M, Mayol R, Pi M and Krośnicki M 2008 *Phys. Rev. B* **77** 024513.

[12] Hinde R J 2003 *J. Phys. B: At Mol. Opt. Phys.* **36** 3119.

[13] Belić A, Dalfóvo F, Fantoni S and Strigari S 1994 *Phys. Rev. B* **49** 15253.

[14] Krotscheck E and Zillich R 2001 *J. Chem. Phys.* **115** 10161.

[15] Bressanini D, Zavaglia M, Mella M and Morosi G 2000 *J. Chem. Phys.* **112** 717.

[16] Mateo D 2008 unpublished.