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Alkali and alkali-earth ions in ^{4}He systems

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We study with variational Monte Carlo simulations a single ion impurity in nanodroplets and in liquid ^{4}He. Within the shadow wave function (SWF) approach we have studied alkali-earth ion doped ^{4}He systems (Be$^+$ and Mg$^+$) and we have also improved our previous variational results for alkali ion impurities (Na$^+$, K$^+$, and Cs$^+$). The new SWF allows for anisotropic correlations between ^{4}He atoms and the ion. The first shell of ^{4}He atoms around the ions has always a well defined solidlike structure, which is remarkably different for each ion but it does not depend on the ^{4}He system (bulk liquid or cluster). We also give results for the chemical potential, the single particle excitation spectrum, and the effective mass of the ions in the bulk.

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Ions are useful probes on a microscopic scale of the properties of superfluid helium and, in the past decades, a considerable effort has been devoted to the study of these systems.[1,2] Also the properties of molecules or atoms captured inside a ^{4}He cluster have been the object of a large experimental activity.[3] The discovery[4] that also ions can be captured inside helium nanodroplets opens the way to a new class of experiments which will be a unique opportunity for testing the accurancy of the microscopic theories. A charged impurity is expected to strongly modify the local environment of the liquid. For example, a positive alkali ion polarizes the neutral helium atoms giving rise to a region of increased density due to electrostriction. The local density has been estimated to be so large that some kind of solid order should be present; this is the so-called *snowball* model.[5] On the basis of this phenomenological model, the *snowball* does not depend on the specific ion. It was observed[1] that this picture is not correct. In the case of alkali-earth ions it has been suggested that, depending on the ion, the complex could form a *snowball* or a bubble-like structure.[2] The first microscopic computations of these systems have been performed with the shadow wave functions (SWF) and were devoted to the study of some alkali ions in bulk liquid (Li$^+$, Na$^+$, K$^+$, and Cs$^+$)[6] and in nanodroplets (Na$^+$ and K$^+$).[7] We have now improved our previous variational approach giving a better description of the short range He correlations close to the ion in the SWF. In this paper we present our new results for alkali ion doped systems, like Na$^+$, K$^+$, and Cs$^+$ in helium clusters and bulk liquid. In addition we present the first study of ^{4}He systems doped with an alkali-earth ion impurities, Be$^+$ and Mg$^+$. We have described the ion–helium interaction by accurate model potentials developed in the literature;[8–10] for example, in the Na$^+$-^{4}He case,[8] the most attractive, the well is about −445 K deep and the minimum is located at about 2.3 Å, while in the Mg$^+$-^{4}He case,[10] the less attractive, the well is about −94 K deep with the minimum at about 3.6 Å. For the helium–helium interaction we have chosen a standard Aziz potential.[11]

With the SWF variational technique the atoms are correlated not only by standard direct correlations between particles, but also indirectly via coupling to subsidiary (shadow) variables. Integration over the shadows introduces interparticle correlations between the ^{4}He atoms at all orders in an implicit way; this is done so efficiently that it is possible to treat the liquid and the solid phase with the same functional form:[12,13]

$$\Psi(R)=\phi_r(R)\int dS\;\Theta(R,S)\,\phi_s(S). \tag{1}$$

If there is an ion in the ^{4}He system, $R=\{\mathbf{r}_1,\ldots,\mathbf{r}_N,\mathbf{r}_I\}$ and $S=\{\mathbf{s}_1,\ldots,\mathbf{s}_N,\mathbf{s}_I\}$, where $\mathbf{r}_I$ and $\mathbf{s}_I$ are, respectively, the real and the shadow coordinate of the ion, and $\{\mathbf{r}_1,\ldots,\mathbf{r}_N\}$ and $\{\mathbf{s}_1,\ldots,\mathbf{s}_N\}$ are the similar variables of N helium atoms. Notice that in our theory also the ions are treated quantum mechanically. When we study doped helium nanodroplets the self binding of the system is accounted for by a glue factor.[7] As usual with SWF, $\phi_r(R)$, and $\phi_s(S)$ are Jastrow functions. In the previous computations[6,7] the fully optimized local density pseudopotentials were used, here we have used a simpler representation.[12] In ϕ_r, for the ion–^{4}He correlation, we use a McMillan form (for example in the Na$^+$ case the parameters are $m=16$ and $b=2.102$ Å) and in ϕ_s we use as pseudopotential the rescaled and shifted[12] ion–^{4}He potential (in the Na$^+$ case the parameters are $\delta=0.12\ \mathrm{K}^{-1}$ and $\alpha=1.05$). This simplifies the computation without great loss in the description of the neighborhood of the ion. On the other hand we have found that the variational description of these systems is sustantially improved if the kernel $\Theta(R,S)$ contains anisotropic correlations between the ^{4}He atoms and the ion. The kernel $\Theta(R,S)$ has a dominant role in representing the effect of the zero point motion of the ^{4}He atoms[14] and, therefore, the assumption that this kernel has the same form in the whole system implies a similar zero point motion for the ^{4}He atoms close and far from the ion. On the contrary, we might expect that this zero point motion depends on the distance from the ion and, in particular, it should be anisotropic for atoms very close to the ion, such that these atoms undergo a different degree of radial and angular localization. For this reason we have modified the kernel as follows:

$$\Theta(R,S)=e^{-C_I|\mathbf{r}_I-\mathbf{s}_I|^2}\times\prod_{i=1}^{N}e^{-u(\mathbf{r}_i,\mathbf{s}_i,\mathbf{s}_I)}, \tag{2}$$

where

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TABLE I. Variational parameters defined in Eqs. (2) and (3).

Impurity	C (Å^{-2})	g (Å^{-2})	μ_F (Å^{-1})	r_F (Å)	C_I (Å^{-2})
Na$^+$	1.178	19.0	7.629	3.144	15.30
K$^+$	1.056	17.0	7.823	3.067	15.30
Cs$^+$	1.148	48.0	1.956	3.067	15.30
Be$^+$	0.995	9.5	8.411	3.144	13.33
Mg$^+$	1.156	14.0	2.347	3.578	11.94

$$u(\mathbf{r}_i,\mathbf{s}_i,\mathbf{s}_I) = C|\mathbf{r}_i - \mathbf{s}_i|^2 + gf(|\mathbf{s}_{iI}|)\left(\frac{(\mathbf{r}_i - \mathbf{s}_i)\cdot(\mathbf{s}_{iI})}{|\mathbf{s}_{iI}|}\right)^2, \quad (3)$$

where $\mathbf{s}_{iI}=\mathbf{s}_i-\mathbf{s}_I$ and the function $f(|\mathbf{s}_{iI}|)$ is assumed to be a Fermi function with parameters μ_F and r_F. The variational parameters are reported in Table I. This new factor allows to induce a stronger localization along the radial direction centered on the ion subsidiary variable compared to the tangential direction. At large distance from the ion the Fermi function goes to zero and the functional form of the SWF turns out to be again the usual one. Notice that our wave function respects the Bose symmetry. With the present SWF we have achieved better ground state energies than those obtained with the old SWF. For example the ground state energy values for a 64 ^{4}He atoms cluster doped with an alkali ion, which are reported in Table II, are from 1.5% up to 6% lower than the old results, depending on the ion considered. A similar improvement is found for one ion in bulk ^{4}He as represented by 107+1 particles with periodic boundary conditions, and in Table II we give the ion chemical potential. The radial density profile is significantly modified in the present computation and, as an example, in Fig. 1 we plot the result for the ion Na$^+$ in bulk ^{4}He compared to the one obtained with the old SWF.[15] In this case, the radial localization induced by the term (3) is about 3 times greater than the tangential one, which is accounted for by the usual variational parameter C in Eq. (3). As a result the first shell is much more localized and it contains twelve atoms in place of ten of the older computation. The improvement in the *snowball* description is more than evident when we compare the present result with the radial density profile obtained with PIMC simulations.[16] As it can be inferred from the plot, the variational description is now very close to the PIMC one and this is true also for the ground state energy, which is only 5% higher than the PIMC result. This is a typical energy difference between a good variational description and an exact method.

TABLE II. Ground state energy per particle for the doped cluster with 64 ^{4}He atoms E_c, and ion chemical potential μ in bulk ^{4}He computed taking the difference of the total energies of the system when a ^{4}He atom is substituted with an ion plus the pure ^{4}He chemical potential.

Impurity	E_c (K)	μ (K)
Na$^+$	-56.388 ± 0.006	-4134 ± 1
K$^+$	-37.933 ± 0.008	-2885 ± 1
Cs$^+$	-36.498 ± 0.007	-2955 ± 1
Be$^+$	-34.477 ± 0.004	-2680 ± 1
Mg$^+$	-23.998 ± 0.007	-2022 ± 1

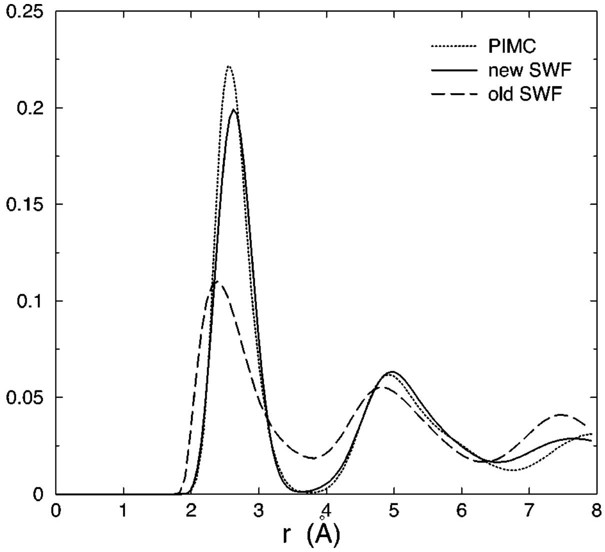

FIG. 1. The radial density profile around Na$^+$ in the bulk liquid, obtained with the new SWF, is compared with the one obtained with the old SWF and the one given by a PIMC (Ref. 16) simulation at $T=1$ K.

Using this new SWF and a smart Monte Carlo (MC) sampling technique as in Ref. 17, we have studied clusters of 32, 64, and 128 ^{4}He atoms and bulk liquid doped with one ion impurity. In the finite systems we find that each positive ion resides stably at the center of the droplets and produces distinctive modulations (shells). All the ions give rise to a *snowball* structure, which depends on the core ion, as indicated by the experimental observations.[1,2] The profiles of the radial density of helium around the ions are plotted in Fig. 2 for a cluster of 64 ^{4}He atoms. The average density in the first shell

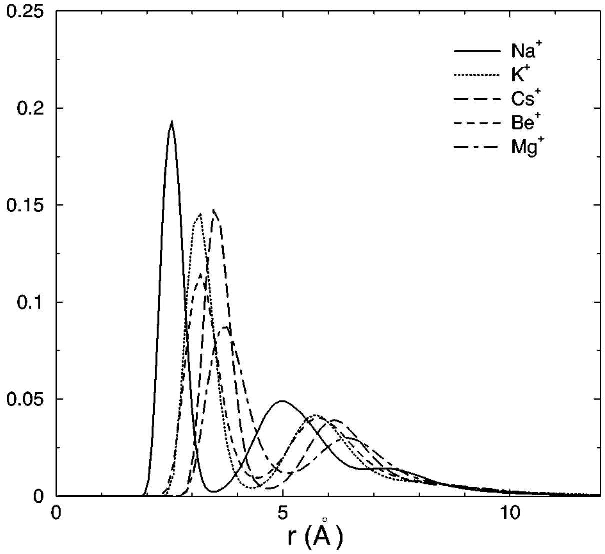

FIG. 2. Radial density profiles for all the ions studied in a cluster with $N=64$ ^{4}He atoms.

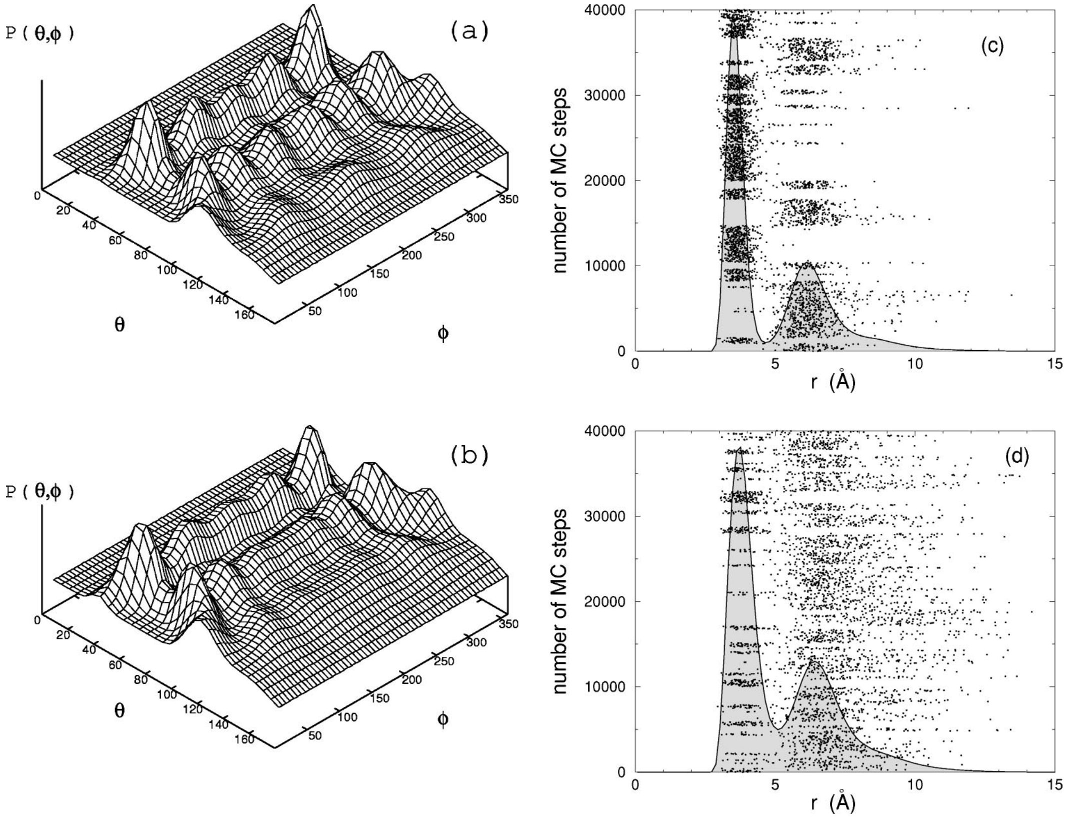

FIG. 3. Angular correlations in the first shell (a), (b) and MC evolution (c), (d) of the distance of one ^{4}He atom from the ion for Cs^+, (a) and (c), and for Mg^+, (b) and (d). In the background the radial density profiles in arbitrary units are shown.

is well above the freezing density of bulk helium, so that some kind of solid order is expected to be present. The shells around the alkali ions are more pronounced (sharper and higher) than the ones around the alkali-earth ions, and the minimum between the first and the second shell is lower for the alkali than for the alkali-earth ions. This means, as we shall see later, that the ^{4}He atoms in the *snowball* of an alkali-earth ion can exchange more easily between the first and the second shell.

The study of the local density is not enough to determine if and which kind of order is present in the first shell. We have then carried out an analysis in terms of the angular correlations within a given shell by introducing an angular probability distribution $P(\theta,\phi)$ that derives from a four body correlation function of the ion and three ^{4}He atoms.[6] The ion is set at the origin of the coordinates, the first He atom is chosen to lie on the z axis and the position of the second atom defines the xz plane. $P(\theta,\phi)$ gives the probability to find a third He atom at angular coordinates θ and ϕ. For all the ions considered, $P(\theta,\phi)$ has modulations extending over the full range of θ and ϕ, revealing the existence of solid-like order in the first shell and this order turns out to be specific to the impurity ion and, as examples, we give the results for Cs^+ and Mg^+ in Figs. 3(a) and 3(b). Local order of the ^{4}He atoms of the first shell does not necessarily mean that the atoms are localized and that they cannot exchange with other atoms. In order to obtain information on the radial localization, one can map the MC evolution of the distance between a helium atom and the ion during the simulation run [Figs. 3(c) and 3(d)]. We find that the solid structure around the ion depends on the position of the minimum of the ion-He potential (for the number of atoms in the first shell N_1 we find that approximately $N_1 \simeq 5.1\ r_{\min}$ with $r_{\min}$ in Å), whereas the degree of localization is a function of the depth of this minimum. For instance, the K^+ and Be^+ *snowballs*, due to close potential minimum positions, have the same number of particles in the first shell (Table III) and a quite similar angular structure, but having a different depth of the potential minimum, the ^{4}He atoms show a different degree of localization. A similar result is found for Cs^+ and Mg^+ *snowballs* (Fig. 3), however the small difference in the minimum positions gives rise to a slightly different angular structure and to different N_1 values. From Fig. 3, it is inferred that, even if ^{4}He atoms in the first shell are radially localized, exchanges between

TABLE III. The effective masses m^* and the excess masses Δm in units of ^{4}He mass for the ions considered and the number N_1 of ^{4}He atoms in the first shell around the ion, obtained by a numerical integration of the radial density profile up to the minimum between the first and the second shell in the bulk.

Impurity	$m^*(m_{\mathrm{He}})$	$\Delta m(m_{\mathrm{He}})$	N_1
Na^+	27.5	22.5	12
K^+	26.0	17.0	15
Cs^+	43.5	10.5	17.5
Be^+	14.6	12.6	15
Mg^+	11.8	5.8	19

different shells in the cluster are frequent. It is worthy to note that for each atom that moves from the first shell to the second there is always a second atom which performs the inverse jump. So these radial exchanges do not destroy or modify the angular and the solid order. An interesting question is if these atoms participate to superfluidity. We find that for Na^+, which has the deeper potential minimum among the the studied ions, the *snowball* has a very pronounced local order both in the first and in the second shells. Of the studied ions Na^+ is the one with the most pronounced local order and this is presumably due to the good matching of the minimum positions of the He–He and He–Na^+ potentials. The angular structure of $P(\theta,\phi)$ is the only one compatible with a platonic solid (icosahedron, $N_1=12$) within the ions studied. For the ions studied, the angular correlations are the same in the bulk system and in a cluster of at least 64 atoms, with the exception of Na^+, whose *snowball* has about 10 atoms in the first shell for such little cluster. In the literature it has been suggested that Mg^+ forms a bubble and not a *snowball*.[2] From our computation we conclude that also Mg^+ forms a *snowball*. However the radial localization of the ^{4}He atoms around Mg^+ is significantly smaller than that due to the other ions and the exchanges between shells are very frequent, as it can be seen in Fig. 3.

An important aspect of an ion in bulk ^{4}He is the characterization of its motion and the value of the effective mass due to the drag of the surrounding liquid. In order to study the single-particle excitation spectra, we have introduced a momentum carrying factor as in Ref. 6 to the wave function (1). We have assumed a new functional form for the explicit back-flow function $\lambda(s)$:

$$\lambda(s)=\begin{cases}\dfrac{[s-(r_0-w)]^2[s-(r_0+w)]^2}{w^4} & \text{if } |s-r_0|\leqslant w\\ 0 & \text{elsewhere}.\end{cases} \tag{4}$$

We find that a more localized back-flow term as given by Eq. (4) leads to an improved variational estimation of the excitation spectrum. The excitation spectrum is very close to a parabola so that the effective mass $m^*(k)$ is essentially a constant. The effective mass can be written as $m^*=m_{\text{ion}}+\Delta m$, the sum of the ion mass and of an excess mass due to the formation of the *snowball* around the ion and the backflow of the surrounding fluid. The results for the effective masses are reported in Table III. We find that the numbers of ^{4}He atoms carried by the impurity (the excess mass Δm in Table III) are related to the depth of the potential well, and, when the exchanges of ^{4}He atoms between the shells are frequent, the excess mass is lower than the number of ^{4}He atoms in the first shell. It is worthy to note that Mg^+ has the greater difference between the number of ^{4}He atoms in the first shell and the excess mass, and that this ion has an expecially low effective mass. This is related to the low degree of radial localization in the *snowball* and very frequent exchanges between shells. We notice that the interaction potentials have a fundamental role in our variational description of the microscopic structure and therefore the reliability of our results depends on the degree of accuracy reached in developing these potentials.

In conclusion, we have presented improved results of alkali ions in helium and the first microscopic study of alkaliearth ions. The present results confirm our previous finding that the *snowball* depends very much on the ion both in terms of local order and of degree of localization. This shows up also in the strong dependence of the effective mass on the ion. The present results indicate the importance of giving an accurate representation of the zero point motion of the ^{4}He atoms close to the ion due to the large intensity of the ion-He potential.

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[1] W. I. Glaberson and W. W. Johnson, J. Low Temp. Phys. **20**, 313 (1975).

[2] M. Foerste, H. Guenther, O. Riediger, J. Wiebe, and G. Putlitz, Z. Phys. B: Condens. Matter **104**, 317 (1997).

[3] J. P. Toennies and A. F. Vilesov, Annu. Rev. Phys. Chem. **49**, 1 (1998); C. Callegari, K. K. Lehmann, R. Schmied, and G. Scoles, J. Chem. Phys. **115**, 10090 (2001).

[4] F. Stienkemeier and S. Mende, Rev. Sci. Instrum. **74**, 4071 (2003).

[5] K. P. Atkins, Phys. Rev. **116**, 1339 (1959).

[6] M. Buzzacchi, D. E. Galli, and L. Reatto, Phys. Rev. B **64**, 094512 (2001).

[7] D. E. Galli, M. Buzzacchi, and L. Reatto, J. Chem. Phys. **115**, 10239 (2001).

[8] R. Ahlrichs, H. J. Bohm, S. Brode, K. T. Tang, and J. P. Toennies, J. Chem. Phys. **88**, 6290 (1988).

[9] A. D. Koutselos, E. A. Mason, and L. A. Viehland, J. Chem. Phys. **93**, 7125 (1990).

[10] D. Bellert and W. H. Beckenridge, Chem. Rev. (Washington, D.C.) **102**, 1595 (2002).

[11] R. A. Aziz, V. P. S. Nain, J. S. Carley, W. L. Taylor, and G. T. McConville, J. Chem. Phys. **70**, 4330 (1979).

[12] T. MacFarland, S. A. Vitiello, L. Reatto, G. V. Chester, and M. H. Kalos, Phys. Rev. B **50**, 13 577 (1994).

[13] S. Moroni, D. E. Galli, S. Fantoni, and L. Reatto, Phys. Rev. B **58**, 909 (1998).

[14] L. Reatto and G. L. Masserini, Phys. Rev. B **38**, 4516 (1988).

[15] The $\rho(r)$ shown here for the old SWF differs from that in Ref. 6 because it comes from a new variational optimization of the old SWF. The old result was obtained with an incorrect optimization biased by MC equilibration problems.

[16] E. Draeger, D. E. Galli, D. M. Ceperley, and L. Reatto (unpublished).

[17] F. Pederiva, G. V. Chester, S. Fantoni, and L. Reatto, Phys. Rev. B **56**, 5909 (1997).