

Binding of electrons to the surface of helium clusters

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A mean-field potential is derived for an excess electron near a $({}^4\text{He})_N$ cluster, which incorporates a realistic description of the cluster surface profile. Calculations of the energies for the ground state and electronically excited surface states were performed. Over a broad cluster size domain ($N=10^7-10^9$) the binding energies are systematically lower (i.e., by 6–10% for the ground state and by 10–20% for electronically excited states) than those based on model potentials, which represented the interaction within the cluster interior in terms of the conduction-band energy of the liquid.

I. INTRODUCTION

The structural, energetic, and dynamic aspects of the binding of an excess electron on a surface of clusters,^{1,2} e.g., $({}^4\text{He})_N$ ($N \geq 3 \times 10^5$),³⁻⁷ $({}^3\text{He})_N$ ($N \geq 5.7 \times 10^5$),⁷ $(\text{Ne})_N$ ($N \geq 1.1 \times 10^4$ for the rigid cluster and $N \geq 1.5 \times 10^4$ for the nonrigid cluster),⁷ and $(\text{H}_2)_N$ ($N \geq 4.6 \times 10^3$ for the rigid cluster and $N \geq 6.3 \times 10^3$ for the nonrigid cluster),⁷ pertain to some interesting phenomena of the following.

(1) The cluster size effects on the onset of the excess electron localization.^{1,2}

(2) The gradual transition from excess electron states on a cluster microsurface to electrons bound to macrosurfaces^{1,2} with increasing cluster size.

(3) The possible utilization of the excess electron as a probe for the interrogation of elementary excitations, e.g., surface and compression modes of molecular clusters,⁸⁻¹⁰ rotons in $({}^4\text{He})_N$ [and possible $(\text{H}_2)_N$] clusters,¹¹⁻¹³ and fermion shell excitation in $({}^3\text{He})_N$ clusters.¹⁴

On the experimental front, large $({}^4\text{He})_N^-$ clusters [which we denote by $(\text{He})_N^-$] were observed by Gspann¹⁵ and subsequently by Northby and co-workers.¹⁶⁻¹⁹ However, the experimental data of Northby and co-workers¹⁶⁻¹⁹ for electron attachment to helium clusters do not provide evidence of surface states, and were interpreted¹⁶⁻¹⁹ in terms of electron localization in interior metastably trapped electron bubbles. In order to provide guidelines for the experimental interrogation of the interesting $(\text{He})_N^-$ surface states, we have explored^{6,7} some of their physical properties, i.e., electronic spectroscopy, field-induced ionization, and (huge) electrical polarizabilities. These calculations rest on an $e-(\text{He})_N$ potential, which consists of a long-range attractive dielectric image potential $V_{\text{IM}}(r)$ and a short-range repulsive potential. The latter was described in terms of a model potential for the cluster interior and a superposition of atomic pseudopotentials $v_{\text{ps}}(r)$ for the surface region, i.e., $V_{\text{SP}}(r) = \int_{\text{S}} d^3r' v_{\text{ps}}(r-r')n(r')$, where $n(r')$ is the surface density profile. Four forms of the potential $V(r)$ were previously employed:⁶ (i) A model potential (MP) $V(r) = V_0$; $r < R$ and $V(r) = V_{\text{IM}}(r)$; $r > R$, where V_0 is

the conduction band energy of liquid He. (ii) A modified model potential (MMP) $V(r) = V_0$; $r < R$, $V(r) = V_{\text{IM}}(a)$; $R < r < R + a$ and $V(r) = V_{\text{IM}}(r)$; $r > R + a$, where the range parameter $a = 1.03$ or 1.25 \AA was fitted from spectroscopic experimental data for the macrosurface. (iii) A step-function profile pseudopotential (PSFP) $V(r) = V_0$; $r < R - r_0$, $V(r) = V_{\text{SP}}(r)$ with $n(r') = 1$ for $(R - r_0) \leq r \leq (R + r_0)$ and $n(r') = 0$ elsewhere (where r_0 is the atom radius), and $V(r) = V_{\text{IM}}(r)$; $r > (R + r_0)$. This form of the boundary potential with a different form of v_{ps} was employed by Rama Krishna and Whaley (RKW).⁵ (iv) A density profile potential (PDP) $V(r) = V_0$; $r < R - t/2$, $V(r) = V_{\text{SP}}(r)$ for $R - t/2 \leq r \leq R + t/2$ where $n(r)$ is the density profile^{20,21} represented by the Gudermannian function, and $V(r) = V_{\text{IM}}(r)$; $r > R + t/2$. For this potential we took⁶ $t = 7 \text{ \AA}$ for the thickness of the $(\text{He})_N$ cluster density profile,^{20,21} which is nearly cluster size independent.^{2,22-26} Theoretical studies of electron binding to macrosurfaces of liquid He incorporated the role of the surface profile, with Huang, Shih, and Woo²⁷ using a nonrealistic profile, while Cheng, Cole, and Cohen²⁸ employed the experimental^{20,21} or theoretical²⁰ surface profile for a complete treatment of the flat surface problem.

These four recipes for the $e-(\text{He})_N$ potential^{6,7} rest on the oversimplified representation of $V(r) = V_0$ in the cluster interior. Of course, the interior repulsive potential in a cluster exceeds V_0 for the infinite medium, as the contribution of the long-range polarization interaction is truncated in the finite system. A heuristic justification for this approximation is that $V_0 (> 0)$ is sufficiently large to satisfy the strength condition for the interior repulsive potential⁵⁻⁷ $[V_0/(e^2/2a_0)](R/a_0)^2 \gg 1$ for the relevant cluster size domain. In view of the availability of experimentally accurate spectroscopic data for electron binding to macroscopic liquid ${}^4\text{He}$ and ${}^3\text{He}$,^{29,30} and the perspectives of obtaining such data for He clusters, a more detailed description of the short-range potential is desirable. In this paper we report on the calculation of the ground and electronically excited state energies of an electron on the surface of $({}^4\text{He})_N$ clusters, employing a realistic short-range repulsive potential in conjunction

with a realistic description of the surface profile, which incorporates the density profile of the cluster. An interesting result emerging from the present calculations pertains to the cluster size dependence of the energy of the quasifree-electron state in clusters.

II. EXCESS ELECTRON-HELIUM CLUSTER POTENTIAL

We consider the interaction potential $V(r)$ exerted on the excess electron by a spherical $(\text{He})_N$ cluster with a radius R , with the coordinate r being measured from the center of the cluster. $V(r)$ corresponds to a mean-field potential provided by the equilibrium density distribution of the cluster. For the surface density profile we shall utilize the Gudermannian function [see Eq. (25)], which represents the experimental profile of Lurio *et al.*²⁰ Our utilization of a mean-field e - $(\text{He})_N$ potential amounts to neglecting polaron effects, which are expected to be negligible in the bulk,³¹⁻³³ as well as the effects of density fluctuations. The nonlocal effective potential will be subdivided into separate interior and exterior contributions in the form

$$V(r) = \begin{cases} V_<(r), & r \leq R - t/2 \\ V_>(r), & r > R - t/2. \end{cases} \quad (1)$$

In the cluster interior range ($r < R - t/2$) the potential $V_<(r)$ is given by the energy of the quasifree electron in the finite system, while in the cluster exterior range ($r > R - t/2$) the potential $V_>(r)$ is given by the superposition of the atomic pseudopotentials exerted on the electron by the He atoms within the surface density profile and the electronic polarization potential exerted by the interior part of the cluster, which is represented in terms of a cluster image potential.

A. Interior contribution

$V_<(r)$ is divided into a repulsive short-range contribution T and an attractive contribution $V_a(r)$, i.e.,

$$V_<(r) = T + V_a(r). \quad (2)$$

The attractive contribution $V_a(r)$, which is due to the polarization energy, is given in the form

$$V_a(r) = U_p^{\text{in}} + U_p^{\text{out}} + V_p^c(r, R), \quad (3)$$

where U_p^{in} is the polarization energy from the atom within the Wigner-Seitz cell, and U_p^{out} represents the polarization energy of the atoms outside the Wigner-Seitz cell in an infinite medium. Finally, $V_p^c(r, R)$ is the correction term for the polarization energy of the final cluster, due to excluded volume effects.

Equations (2) and (3) result in the physically transparent relation for the interior potential

$$V_<(r) = V_0 + V_p^c(r, R), \quad (4)$$

where

$$V_0 = T + U_p^{\text{in}} + U_p^{\text{out}} \quad (5)$$

is the energy in the quasifree electron in the infinite medium. Equation (5) represents a cluster size equation for the quasifree electron in a finite cluster.

We now proceed to evaluate the individual contributions to $V_<(r)$, which appear in Eqs. (4) and (5). The repulsive short-range contribution T is represented by a hard-core pseudopotential with a radius a_c , which is obtained from the Wigner-Seitz approach³⁴⁻³⁶ in the form

$$T = \hbar^2 k^2 / 2m, \quad (6)$$

where the wave vector k is obtained from the equation³⁴⁻³⁶

$$\tan[k(r_s - a_c)] = kr_s, \quad (7)$$

with

$$r_s = (3/4\pi\rho)^{1/3} \quad (8)$$

being the radius of the Wigner-Seitz sphere containing a single atom in a uniform medium, which is determined by the average density ρ .

The calculation of the exterior polarization energy outside the Wigner-Seitz cell in an infinite medium U_p^{out} in Eqs. (3) and (5) follows the procedure of Springett, Jortner, and Cohen,³⁵ which results in

$$U_p^{\text{out}} = -(\alpha e^2 \rho / 2) F \int d\mathbf{r}' g(|\mathbf{r}_0 - \mathbf{r}'|) |\mathbf{r}_0 - \mathbf{r}'|^{-4}, \quad (9)$$

where α is the polarizability of the bare He atom. F is the dielectric screening factor

$$F = (1 + 8\pi\rho\alpha/3)^{-1} \quad (10)$$

and $g(r)$ is the radial distribution function, being expressed by a step function $g(r) = 0$ for $r < r_s$ and $g(r) = 1$ for $r > r_s$. Equations (9) and (10) then result in

$$U_p^{\text{out}} = -(2\pi\rho\alpha e^2 / r_s) F. \quad (11)$$

Utilizing the Clausius-Mossotti relation for the dielectric constant $\epsilon = (2x + 1)/(1 - x)$ with $x = 4\pi\rho\alpha/3$, Eq. (11) can be expressed in the form of the Born charging energy

$$U_p^{\text{out}} = -(e^2 / 2r_s)(1 - 1/\epsilon). \quad (12)$$

It will be also useful to express U_p^{out} in the alternative form,

$$U_p^{\text{out}} = -2\pi(4\pi/3)^{1/3} \alpha e^2 \rho^{4/3} F. \quad (13)$$

The single-atom inner polarization energy was calculated following Cheng, Cole, and Cohen²⁸ from the optical potential attractive scattering length in the form

$$U_p^{\text{in}} = (2\pi\hbar^2 / m) \rho a_a, \quad (14)$$

where $a_a (< 0)$ is the e -He scattering length due to the polarization potential.²⁸

The calculation of the correction term $V_p^c(r, R)$ rests on a continuum dielectric model³⁷ for a charge localized within a sphere of radius r_s at a distance r from the center within the cluster of radius R . The total polarization energy $V_p^B(r, R)$ calculated by Brus is³⁸

$$V_p^B(r, R) = -(e^2/2r_s)(1 - 1/\epsilon) + (e^2/2R) \sum_{j=0}^{\infty} \frac{(\epsilon - 1)(j + 1)}{\epsilon(\epsilon j + j + 1)} (r/R)^{2j}, \quad (15)$$

where the first term on the right-hand side of Eq. (15) $V_p^B(r, \infty) = -(e^2/2r_s)(1 - \epsilon^{-1})$ is

$$V_p^B(r, \infty) = U_p^{\text{out}} \quad (16)$$

according to Eq. (12). The total polarization energy [Eq. (15)] obeys the cluster size equation

$$V_p^B(r, R) = V_p^B(r, \infty) + V_p^c(r, R), \quad (17)$$

where $V_p^c(r, R)$ is the finite-size correction to the interior polarization energy, which appears in Eqs. (3) and (4). Equations (15)–(17) then result in the correction term for the polarization energy in the finite cluster,

$$V_p^c(r, R) = (e^2/2R) \left[\frac{\epsilon - 1}{\epsilon} \right] \times \sum_{j=0}^{\infty} \left[\frac{j + 1}{\epsilon j + j + 1} \right] (r/R)^{2j}, \quad (18)$$

which is portrayed in Fig. 1. Equations (4), (5), (6), (11), (13), and (18) result in the final form

$$V_<(r) = V_0 + (e^2/2R) \left[\frac{\epsilon - 1}{\epsilon} \right] \times \sum_{j=0}^{\infty} \left[\frac{j + 1}{\epsilon j + j + 1} \right] (r/R)^{2j}, \quad (19)$$

with the infinite system value

$$V_0 = \hbar^2 k^2 / 2m + (2\pi\hbar^2 / m)\rho a - 2\pi(4\pi/3)^{1/3} a e^2 \rho^{4/3} F, \quad (20)$$

and the finite-cluster correction term being given by the second term on the right-hand side of Eq. (19).

B. Exterior contribution

$V_>(r)$ is divided into the contribution of the surface density profile $V_{\text{SP}}(r)$ and the image potential $V_{\text{IM}}(R - t/2)$ exerted by the cluster interior

$$V_>(r) = V_{\text{SP}}(r) + V_{\text{IM}}(R - t/2). \quad (21)$$

The contribution from the surface profile region **S** in the range $R - t/2 \leq r \leq R + t/2$ was taken in the form

$$V_{\text{SP}}(r) = \int_{\text{S}} d^3r' v_{\text{ps}}(r' - r) n(r'), \quad (22)$$

where $v_{\text{ps}}(r)$ is the electron–He-atom pseudopotential and $n(r)$ is the surface profile. We have used the e -He pseudopotential of Kestner *et al.*³⁹

$$v_{\text{ps}} = V_{\text{COUL}} + V_{\text{EX}} + V_{\text{POL}} + V_{\text{R}}, \quad (23)$$

where V_{COUL} , V_{EX} , V_{POL} , and V_{R} represent Coulomb, exchange, polarization, and nonlocal contributions, respectively. Although this pseudopotential became less

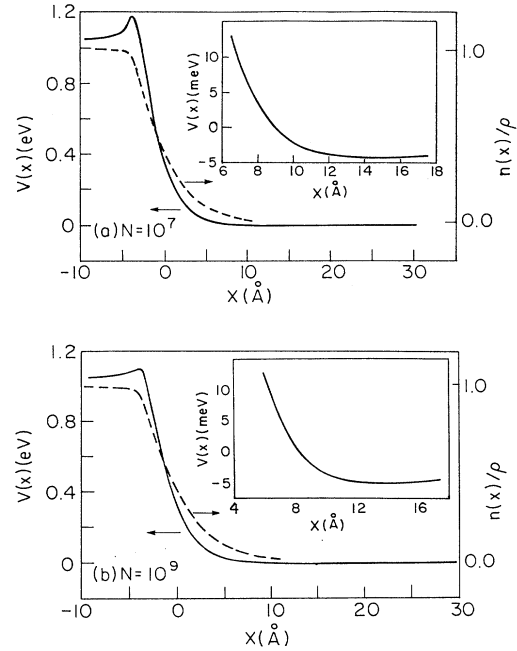


FIG. 1. The excess electron $-(\text{He})_N$ potential, Eqs. (1), (19), and (21), with a realistic description of the surface profile, for $N=10^7$ and 10^9 as marked in (a) and (b). $x = (r - R)$. Dashed lines represent the symmetric surface density profile $n(x)/\rho$, Eq. (25). The insets show the weak attractive part of the potential.

popular, as it systematically underestimates the phase shifts for e -He scattering,⁵ its advantages are (i) It does not contain adjustable parameters, and (ii) it accounts well for the experimental density dependence of the conduction band energy of an excess electron in a macroscopic He fluid.⁴⁰ $n(r)$ in Eq. (22) is the cluster surface density profile. In view of the weak cluster size dependence of the thickness of the calculated $(^4\text{He})_N$ cluster surface profile,^{22,23} which is close to the experimental results of Lurio *et al.*²⁰ and Osborne,²¹ we have represented $n(r)$ by the macrosurface profile. This flat surface density profile, which was obtained from experiment and from quantum-mechanical calculations, was fit by Lurio *et al.*²⁰ to the form

$$\rho_0 - n(x) = \int_0^x dz C / \{ \exp(az/t) + \exp(-bz/t) \}, \quad (24)$$

where ρ_0 is the average atom density of liquid He, $a = 1 + \exp(-\eta)$, $b = 1 + \exp(\eta)$, and $C = \rho_0 (\int_0^\infty dz [\exp(az/t) + \exp(-bz/t)]^{-1})^{-1}$. For the symmetric case, i.e., $\eta=0$ ($a=b=2$), the density profile assumes the form of a Gudermannian function

$$n(x) = (2\rho/\pi) \arctan\{ [\sinh(2x/t)]^{-1} \}, \quad (25)$$

where x is given in \AA and t is the interfacial width, which was defined as the difference between the radii, which correspond to the values of 0.1 and 0.9 of the central value ρ .^{22,23} The experimental data^{21,22} show that $t = 7-8 \text{\AA}$, and we have taken $t = 7 \text{\AA}$.

The contribution of the polarization potential V_{IM} in Eq. (21) was taken as the exterior polarization potential of a uniform dielectric sphere of radius $y = R - t/2$, which was taken in the form

$$V_{\text{IM}}(r) = -(Qe^2/y) \left[\frac{2y^2}{r^2 - y^2} - \left(\frac{y}{r} \right) \sum_{l=0}^{\infty} [l(\epsilon+1)+1]^{-1} \left(\frac{y}{r} \right)^{2l+1} \right], \quad (26)$$

where $Q = (\epsilon - 1)/4(\epsilon + 1)$. Equations (21), (22), and (26) result in the exterior potential

$$V_{>}(r) = \int_{\text{S}} d^3\mathbf{r}' V_{\text{ps}}(r - r') n(r') + V_{\text{IM}}(R - t/2), \quad (27)$$

where V_{IM} is given by Eq. (26).

The e -(He) $_N$ potential $V(r)$ is given by Eqs. (1), (19), and (27). Figure 1 portrays the r dependence of this potential, which provides information on (i) the effects of the surface profile, and (ii) the distance dependence of the interior potential, i.e., the local V_0 .

III. RESULTS AND DISCUSSION

A. Calculation of bound-state energies

The energies were obtained from the solution of the one-dimensional Schrödinger equation with the potential $V(r)$ (Fig. 1). The radial wave function $\chi_{nl}(\rho)$ in reduced units is obtained from the equation⁶

$$-(\partial^2 \chi_{nl} / \partial \rho^2) + [l(l+1)/\rho^2] \chi_{nl} + W(\rho) \chi_{nl} - \epsilon_{nl} \chi_{nl} = 0, \quad (28)$$

where the reduced radial coordinate is $\rho = r/R$, the reduced potential is $W(\rho) = (\gamma^2/E_f)V(\rho R)$, with $\gamma = R/r_f$, $r_f = a_0/Q$, and $E_f = Q^2 e^2 / 2a_0$, and the reduced energies are $\epsilon_{nl} = \gamma^2(E_{nl}/E_f)$, where n and l are the principal and azimuthal quantum numbers. Equation (28) was solved numerically, resulting in the bound energy levels E_{nl} .

B. Parameters

We are interested in electron attachment to (^4He) $_N$ clusters, which are liquid down to 0 K.^{14,22,23} A reasonable estimate for the properties of large ($N > 10^5$) He clusters rests on the physical properties of macroscopic liquid helium. Accordingly we have taken $\rho = 2.18 \times 10^{-2} \text{ \AA}^{-3}$, $r_s = 2.22 \text{ \AA}$, and $\epsilon = 1.0588$. In most of the calculations, except for some tests, a symmetric surface profile was employed. The surface profile, Eq. (25), was characterized by $t = 7 \text{ \AA}$. The properties of an electron on the macrosurface were characterized by the parameters $E_f = 0.695 \text{ meV}$ and $r_f = 74.0 \text{ \AA}$. Finally, the polarizability of the bare He atom was taken as $\alpha = 0.207 \text{ \AA}^3$.

C. Some model calculations for V_0 and energetics for macrosurfaces

The interior potential $V_{<}(r)$ [Eq. (4)] contains the energy V_0 of the quasifree electron in bulk He, which is given by Eqs. (5) and (20). The components T and U_p^{in} are determined by the repulsive hard-core scattering

length a_c [Eqs. (6) and (7)], and the polarization scattering length a_a [Eq. (14)], with the total e -He gas-phase s -wave scattering length being

$$a = a_c + a_a, \quad (29)$$

with the experimental value⁴¹ $a = 0.62 \text{ \AA}$. We slightly extended the calculations of V_0 by Cheng, Cole, and Cohen²⁸ incorporating the role of dielectric screening. In Table I we present the results of model calculations of V_0 for reasonable values of $a_a = -0.08 \text{ \AA}$ to zero. The effect of dielectric screening was incorporated in the screening factor F , Eq. (10). As apparent from the model calculations, the effect of dielectric screening is minor (modifying V_0 by 0.5%). The calculated values of V_0 (Table I) are consistent with the experimental data,^{42,43} which fall in the range 1.0–1.3 eV and are in accord with the original results of Cheng, Cole, and Cohen.²⁸

A simple estimate of the effect of the surface profile on V_0 can be obtained from Eq. (19), which for $r = R - t/2$ in the limit $R \rightarrow \infty$ results in

$$V_{<}(r) = V_0 + \Delta, \quad (30)$$

with

$$\Delta = (e^2/2\epsilon t) \left[\frac{\epsilon - 1}{\epsilon + 1} \right]. \quad (31)$$

The correction Δ to V_0 in the surface domain in the bulk is determined by t^{-1} . The correction term is small. For realistic values of t , Eq. (30) results in $\Delta = 0.028 \text{ eV}$ for $t = 7 \text{ \AA}$ and $\Delta = 0.024 \text{ eV}$ for $t = 8 \text{ \AA}$, providing a 2–3 % change in V_0 .

To explore further the sensitivity of the energetics to the surface thickness, we have tested the effect of the thickness of the surface profile of macroscopic ^4He on the ground-state energy $E_{1,0}(n=1, l=0)$ and electronically excited energies $E_{2,0}$ and $E_{3,0}$ of an excess electron on the macrosurface. These calculations were performed for a reasonable domain of the surface thickness $t = 6.6\text{--}6.8$

TABLE I. Calculations of V_0 for bulk liquid ^4He for different values of the polarization and hard-core scattering lengths a_a and a_c , respectively [Eq. (28)], and exploring the effect dielectric screening incorporated in F [Eq. (10)].

a_c (Å)	a_a (Å)	T (eV)	U_p (eV)		V_0 (eV)	
			F , Eq. (10)	$F=1$	F , Eq. (10)	$F=1$
0.62	0.00	1.180	-0.1726	-0.1790	1.007	1.001
0.63	-0.01	1.207	-0.1831	-0.1895	1.024	1.018
0.65	-0.03	1.275	-0.2042	-0.2105	1.071	1.065
0.68	-0.05	1.383	-0.2251	-0.2315	1.159	1.153
0.70	-0.08	1.458	-0.2566	-0.2630	1.202	1.195

Å. The changes in the binding energies ($\sim 1\%$) are minor, providing justification for the use of the symmetric form [Eq. (25)] of the surface profile.

D. Some model calculations for clusters

We have checked the dependence of the binding energies $E_{n,0}$ ($n=1-3$) for electron binding to $(\text{He})_N$ clusters ($N=10^7-10^{12}$) on the symmetry of the surface profile. We have used Eq. (24) with $a \neq b$ and $\eta = -1.04$ for the potential of the asymmetric surface profile (Fig. 2). We have also performed calculations for the potential with a symmetric surface profile (Fig. 2). With these surface profiles we obtained the energy levels of Table II. The largest change (5%) in the energetics is encountered for the ground state on a relatively small cluster $N=10^7$, while for larger clusters the effect of the surface asymmetry is smaller. Subsequently, the symmetric surface profile was employed.

E. Excess electron binding to clusters

We have performed detailed calculations of the cluster size dependence of the ground-state energy $E_{1,0}$ and the electronically excited state energies $E_{2,0}$ and $E_{3,0}$ of $(\text{He})_N^-$ clusters using the realistic $e-(\text{He})_N$ potential [Eq. (1)] with $t=7$ Å, which we shall denote as $P1$. These results are confronted in Table III with our previous calculations,⁶ using the MP, PSFP, and PDP potentials and with the original (RKW) potential calculations of Rama-Kirshna and Whaley.⁵ For lower cluster sizes ($N=3 \times 10^5-5 \times 10^5$), in the vicinity and just above the localization threshold, the ground-state binding energies $-E_{10}$ calculated by the present $P1$ potential are higher than those calculated by the other potentials. Thus the incorporation of the surface profile in $P1$ results in a somewhat lower localization threshold than obtained using the previous MP,⁶ PSFP,⁶ PDP,⁶ and RKW (Ref. 5) potentials. The minimal cluster size for electron localization in the ground electronic state previously obtained⁶

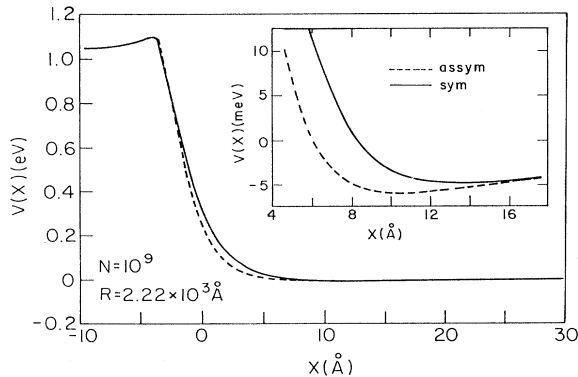


FIG. 2. The $e-(\text{He})_N$ potential for $N=10^9$ for the asymmetric surface profile (dashed line) with $t=7$ Å and $\eta=-1.04$ in Eq. (24) ($a=3.83$ and $b=1.35$), and for the symmetric surface profile (solid line) with $t=7$ Å and $\eta=0$ ($a=b=2$). $x=(r-R)$.

TABLE II. The effect of the asymmetry in the surface profile with $t=6.8$ Å and $\eta=-1.04$ in Eq. (24) (denoted as asym) on the binding energies $E_{n,0}$ for several cluster sizes. These results are compared with the calculations for the symmetric profile with $t=6.8$ Å [Eq. (25)] (denoted as symm). The energies $-E_{n,0}$ for each value of N (and R) are listed in the order of increasing n ($n=1, 2$, and 3).

N	R (Å)	$-E_{n,0}$ (meV)	
		symm	asymm
10^7	578.3	0.2382	0.2522
10^9	2220	0.5328	0.5377
		0.0696	0.0703
		0.0071	0.0082
10^{12}	2.22×10^4	0.6629	0.6673
		0.1600	0.1608
		0.0614	0.0616

from a scaling relation for the MP potential was found to be $R_c^{(1,0)}=148.6$ Å ($N_c^{(1,0)}=3 \times 10^5$). The utilization of the $P1$ potential reveals that the incorporation of the effect of the surface profile results in somewhat lower values of $R_c^{(1,0)}$ and $N_c^{(1,0)}$ for the localization onset. The energies for both the ground and electronically excited states over a broad cluster size domain $N=10^7-10^9$ calculated with the $P1$ potential are systematically lower [by ~ 0.05 meV ($\sim 6-10\%$) for $-E_{10}$ and by ~ 0.01 meV ($\sim 10-20\%$) for higher excited states] than those calculated in previous work. For huge clusters ($N=10^{12}-10^{15}$) and for macrosurfaces, the effect of the surface potential on the energetics is even smaller (Table III). The overall variation of the energetics with respect to the details of the cluster potential is not large. The ground-state charge distribution can be characterized by its first moment $\langle r \rangle$, which diverges near the localization threshold.^{6,7} In Fig. 3 we present the cluster size dependence of $\langle r \rangle$ vs $1/R$ obtained using the realistic $P1$ potential. These values of $\langle r \rangle$ in the size domain $N=10^7-10^9$ are lower by about 7% than those calculated using the MP (Fig. 3), indicating somewhat stronger binding for the $P1$ potential, in accord with the enhanced ground-state energies calculated with the $P1$ potential in this size domain (Table III). For larger cluster sizes $N > 10^{11}$ the values of $\langle r \rangle$ calculated with the $P1$ and MP potentials are close (within 1%), in accord with the closeness of the energetic data (Table III). These detailed calculations reinforce our previous conclusions⁶ that, as long as the $e-(\text{He})_N$ potential incorporates the basic features of the short-range repulsive interactions, the details of the specific potential are not important. Nevertheless, the potential $P1$, introduced herein, which rests on a realistic description of the surface profile, is recommended to be utilized for detailed and reliable future calculations of the energetics and spectroscopy of finite $(\text{He})_N^-$ clusters.

IV. CONCLUDING REMARKS

We advanced and utilized a mean-field $e-(\text{He})_N$ potential, which incorporates a realistic description of the clus-

TABLE III. Energy levels $E_{n,0}$ for the excess electron surface state on $({}^4\text{He})_N$ and on ${}^4\text{He}$ macrosurfaces. The first number for each column for given values of N and R corresponds to the ground-state binding energy ($-E_{10}$), while subsequent numbers in that column represent the energies of bound excited states ($-E_{20}$) and ($-E_{30}$). Calculations were performed using different potentials, as indicated in the columns.

N	R (\AA)	$-E_{n,0}$ (meV)				Present work
		MP ^a	PSFP ^a	PDP ^a	RKW ^b	
3×10^5	148.6	c	c	c	c	0.002 3
4×10^5	163.0	0.001 28	c	0.001 1	c	
5×10^5	176.2	0.004 3			0.005	
10^7	478.3	0.184 6			0.184 7	0.238 2
10^9	2220	0.499 9	0.479 5	0.500 0	0.498 4	0.532 8
		0.057 9	0.055 3	0.058 0	0.058 3	0.069 6
		0.005 6	c	0.005 4	0.006 2	0.007 1
10^{12}	1.11×10^4	0.663 2			0.656 96	0.662 9
		0.149 97			0.150 0	0.160 0
		0.056 97			0.057 0	0.061 4
10^{15}	2.22×10^5	0.689 8	0.667 2	0.689 7	0.685 6	0.684 6
		0.170 3	0.167 2	0.170 4	0.169 9	0.170 5
		0.074 15	0.058 9	0.074 16	0.074 4	0.077 9
6×10^{23}	d	0.694 0	0.671 3	0.694 2	0.690 6	0.696 4
		0.173 7	0.170 6	0.173 7	0.173 6	0.180 4
		0.077 2	0.062 2	0.077 2	0.076 9	0.081 2

^aReference 6.

^bReference 5.

^cBound state not localized.

^dMacrosurface.

ter surface profile, for the calculation of the eigenvalue spectrum of the excess electron surface states. Further refinement of the potential has to rest on transcending the mean-field approximation, incorporating cluster density fluctuations and polaron effects.

Accurate calculations of the energetics of the ground and electronically excited states of $(\text{He})_N^-$ may be of interest in the context of the fascinating problem of long-range Casimir interactions.⁴⁴⁻⁴⁹ Such long-range retarded forces are exhibited between two systems, e.g., atom-atom and atom-electron or wall-electron,⁴⁴⁻⁴⁹ provided that their separation exceeds the typical wavelength λ of a photon emitted by either system, $r \gg (\lambda/2\pi)$, i.e., $r \gg 137a_0$ (Refs. 44-49) (where a_0 is the Bohr radius). The bound excess electron surface states on large $(\text{He})_N$ clusters constitute a giant electronic state with the mean radius $\langle r \rangle \gg 137a_0$. The mean radius for the charge distribution is expected to behave as⁶ $\langle r \rangle = r_f f(R/r_f)$, where $f(R/r_f)$ is a universal function for small values of $Q = (\epsilon - 1)/(\epsilon + 1)$ and $r_f = a_0/Q$.^{6,7} The behavior of $f(r_f/R)$ is characterized by scaling relations near the localization threshold ($R \geq R_c^{(n,l)}$ for nl excess electron states), i.e., $f(r_f/R) \propto (R - R_c^{(n,l)})^{-\eta}$, where $\eta = 1$ for ns ($l = 0$) states and $\eta = 1/2$ for np ($l = 1$) states.⁶ For a given (nl) state for $R \gg R_c^{(n,l)}$, the function $f(r_f/R) (> 1)$ converges to unity for $R \rightarrow \infty$.⁶ Typical values of r_f ($< \langle r \rangle$) are $r_f = 74 \text{ \AA}$ for $({}^4\text{He})_N$ and $r_f = 101 \text{ \AA}$ for $({}^3\text{He})_N$ clusters.^{6,7} Accordingly, long-range ($r > 137a_0$) electron-cluster interactions will be prevalent for this problem. The asymptotic form of the electron-cluster potential, which was calculated on the

basis of the conventional Coulombic interactions, is $V(r \rightarrow \infty) = -\bar{\alpha}e^2/2r^4$, as appropriate for charge-induced dipole interactions, with the effective cluster polarizability being given by $\bar{\alpha} = [(\epsilon - 1)/(\epsilon + 2)]R^3$. Retardation effects for two-polarizable systems⁴⁴⁻⁴⁸ are expected to modify the asymptotic electron-cluster potential in an analogous way to the electron-atom or electron-ion interaction.⁴⁵⁻⁴⁹ The asymptotic potential, including retardation, will be of the form⁴⁵⁻⁴⁹ $V(r) = -\bar{\alpha}e^2/2r^4$

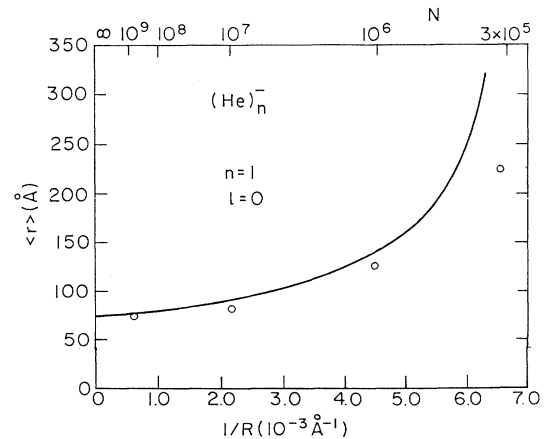


FIG. 3. The cluster size dependence of the first moment $\langle r \rangle$ of the ground-state charge distribution vs $1/R$ of excess electron surface states on $(\text{He})_N$ clusters. Open points represent calculations with the P1 potential (present work). Solid line represents calculations with the MP potential (Ref. 6).

$+C_{e\text{-cluster}}/r^5$, where the numerical constant is $C_{e\text{-cluster}} \simeq e^2 \hbar \bar{\alpha} / mc$, where c is the velocity of light. In contrast to the Casimir-Polder r^{-7} retarded interaction between neutral atoms,^{44,48} which qualitatively modifies the form of the dispersive interactions (at $r \gg 137a_0$), the electron-cluster potential is modified to include a small correction term, being of the asymptotic form $\bar{\alpha} r^{-4} [1 + O((\hbar/mc)r^{-1})]$. Nevertheless, this facet of re-

tardation effects for giant excess electron surface states on clusters is of considerable interest.

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