

Long-Range Potential for Excess Electron Surface States on Helium Clusters*

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An excess electron bound to a (${}^4\text{He}$) $_N$ cluster (number of constituents $N \geq 3 \times 10^5$ and cluster radius $R \geq R_c = 149 \text{ \AA}$) exhibits a divergence of the first moment $\langle r \rangle$ of the charge distribution near the localization threshold ($R = R_c$), obeying the scaling law $\langle r \rangle \propto (R - R_c)^{-1}$. The asymptotic form of the electron-cluster potential has to be modified to include Casimir-Spruch retardation effects, which provide a small repulsive contribution $O(\hbar/mc)r^{-1}$.

1. INTRODUCTION

The advent of the Schrödinger equation in 1926 had a major impact on the development of chemistry, with quantum mechanics being applied to the fundamental problems of the separation of electronic and nuclear motion in molecules [1] and to the structure and energetics of the few-electron molecules H_2^+ [2] and H_2 [3]. Subsequently, the relativistic equations have been introduced to one-electron [4] and two-electron [5] systems. This work culminated in the seminal contributions of Włodzimierz Kołos and his school to the quantum chemistry of the hydrogen molecule [6,7]. Another landmark in the development of the conceptual basis of chemistry was provided in 1930 by the theory of intermolecular forces [8] where Coulomb interaction between two neutral atoms results in the $-r^{-6}$ van der Waals-London long-range potential. It was pointed out by Wheeler [9] in 1941 that when the spatial separation r between two interacting systems is such that the transit time of a photon from one system to the other and back exceeds the characteristic period P of the system, *i.e.*, $2r/c \geq P$ (where c is the speed of light), the interaction cannot be taken as an action-at-distance of the Coulomb interactions. The retarded interactions between a pair of hydrogen atoms sets in at $r \geq 137 a_0$, where the numerical constant $e^2/\hbar c = 1/137$ is the fine structure constant. In 1948 Casimir and Polder [10] derived the first example for a non-classical long-range electromagnetic force, showing that the retarded atom-atom interaction is of the form $V_{\text{CP}}(r) = -(23/4\pi)\hbar c \alpha_D(1)\alpha_D(2)r^{-7}$ where $\alpha_D(1)$ and $\alpha_D(2)$ are the dipole polarizabilities of the two atoms. The familiar van der Waals-London ($-r^{-6}$) potential is replaced by the Casimir-Polder potential for $r \geq 137 a_0$. The broad interest in retarded atom-atom, atom-wall and wall-wall interactions [11] stemmed from two directions. Firstly, the proportionality to Planck's constant \hbar indicates that the retarded interaction constitutes a distinct quantum mechanical phenomenon, in contrast to Coulomb interatomic forces, which

* Dedicated to the memory of Professor Włodzimierz Kołos.

have a classical analogue. Secondly, the speed of light enters the interaction, although the particles are slowly moving. The retarded force originates from interactions with zero-point photons of the electromagnetic field.

A major development in this fascinating field has been advanced by Kelsey and Spruch [12–16] in 1978, who proposed the observation of long-range retarded interactions through their effect on the fine structure of Rydberg states ($n \equiv 10$) of the He atom. They showed that a long-range ($r \gg 137 a_0$) electron-polarizable ion interaction includes a repulsive potential $V_{KS}(r) = (11/4\pi) (\hbar/mc) e^2 \alpha_D r^{-5}$. However, in contrast to the Casimir-Polder potential $V_{CP}(r)$, which constitutes the largest long-range force acting between two neutral atoms, the $V_{KS}(r)$ potential constitutes a small correction to the dominant long-range interaction to the ion-electron potential $V(r) = -e^2/r + V_{dp}(r) + V_{KS}(r)$, with the dipole polarization potential being $V_{dp} = -\alpha_D e^2 / (2r^4)$. $V(r)$ is dominated by the Coulomb potential, which overwhelms the $V_{dp}(r)$ and the $V_{KS}(r)$ contributions. At $r = 137 a_0$, where the Kelsey-Spruch potential begins to hold, the contributions to $V(r)$ are in the ratios $e^2/r : |V_{dp}| : V_{KS} = 1 : 10^{-7} : 10^{-11}$.

We would like to advance a new system for the scrutiny of long-range retardation forces, which involves an excess electron bound on the surface of He clusters [17–21], *i.e.*, $(^4\text{He})_N^-$ ($N \geq 3 \times 10^5$) and $(^3\text{He})_N^-$ ($N \geq 5.7 \times 10^5$) [19,20]. In these large systems the dominating long-range attractive interaction constitutes the cluster dipole polarization, while the retarded interaction will provide the leading repulsive term for the long-range potential.

2. ELECTRON BINDING TO MICROSURFACES OF CLUSTERS

The interaction between an electron and a few-electron closed-shell atom or molecule, *e.g.*, He, Ne or H_2 , is strongly short-range repulsive, with a weak long-range attractive core polarization [22,23]. Accordingly, the conduction band energy V_0 in the corresponding macroscopic dense fluid [23] or in the large cluster [21] is positive (Table 1). When an excess electron interacts with a sufficiently large $(^4\text{He})_N$ cluster (which is liquid down to 0K and which exhibits manifestations of Bose statistics [24]), two types of bound (stable or metastable) excess electron states can be realized. (i) The interior bubble state, with the electron residing in a cavity within the cluster. The “critical” cluster size for the realization of the energetic stability of the electron bubble is $N_B > 6 \times 10^3$ [25]. These states are metastable with respect to electron tunneling [25,26]. (ii) The exterior excess electron surface state with a “critical” cluster size for excess electron binding in a stable state being $N_S > 3 \times 10^5$ [19,20].

The structural, energetic and dynamic aspects of the binding of an excess electron to the surface of He clusters pertains to some interesting phenomena of:

- 1) The cluster size effects on the onset of the excess electron localization [27].
- 2) The gradual “transition” from excess electron states on a cluster microsurface to electrons bound to macrosurfaces [27,28] with increasing the 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 [29–31], rotons in $(^4\text{He})_N$ [24] and fermion shell excitation in $(^3\text{He})_N$ clusters [32].

Table 1. Dielectric constant (ϵ), strength of repulsive potential (V_0), characteristics of flat surface excess electron states (E_f and r_f), together with "critical" cluster radii (R_c) and number of constituents (N_c) for the onset of ground state electron localization. (l) and (s) denote liquid and solid clusters.

System	ϵ	V_0 (eV)	r_f (Å)	E_f (meV)	R_c (Å)	N_c
${}^4\text{He}(l)$	1.0588	1.28	74	0.695	149	3.0×10^5
${}^3\text{He}(l)$	1.0428	0.9	101	0.372	203	5.7×10^5
$\text{Ne}(l)$	1.19	0.45	23.3	7.03	46.3	1.5×10^4
$\text{Ne}(s)$	1.24	0.60	19.8	9.76	39.3	1.1×10^4

Fruitful mutual stimulation between theory and experiment in this interesting field prevails. Large (${}^4\text{He}$) $_N^-$ ($N \sim 10^5$) clusters were experimentally observed [33,34], which could manifest electron surface states. Recent experimental data for (${}^4\text{He}$) $_N$ clusters (with $N \cong 2 \times 10^5$, which is close to the value of N_S) do not provide evidence for electron surface states and were assigned to metastable electron bubble states [26,34,35]. Although not yet experimentally documented, surface excess electron states on large clusters are interesting, as they constitute giant (effective) one-electron states. These giant electron states on Helium (or Neon) clusters (characterized by a radius R and a low-frequency dielectric constant ϵ) are approximated by the ground state ($n = 1, l = 0$) binding energy of an electron to a dielectric sphere [19,20]

$$E_{1,0} = -E_f \Phi(r_f/R) \quad (1)$$

and by the first moment of the charge distribution

$$\langle r \rangle = r_f \Omega(r_f/R) \quad (2)$$

where

$$E_f = (e^2/2a_0)Q^2 \quad (3)$$

$$r_f = a_0/Q \quad (4)$$

and

$$Q = (\epsilon - 1)/4(\epsilon + 1) \quad (5)$$

E_f and r_f represent the ground state binding energy and effective Bohr radius, respectively, for electron binding to a macroscopic dielectric surface. The scaling functions $0 \leq \phi(\cdot) \leq 1$ and $\infty \geq \Omega(\cdot) \geq 1$ change from $\phi = 0^+$ and $\Omega = \infty$ at the localization threshold, i.e., $R = R_c$, to $\phi, \Omega = 1$ at the macrosurface when $R \rightarrow \infty$ (Figures 1 and 2). The localization threshold is characterized by the cluster radius $R = R_c$ where [20]

$$R_c = 2.02(1 - Q)r_f \quad (6)$$

$E_{1,0}$ and $\langle r \rangle$, Eqs. (1) and (2), are specified by the scaling relations near the localization threshold [19,20]

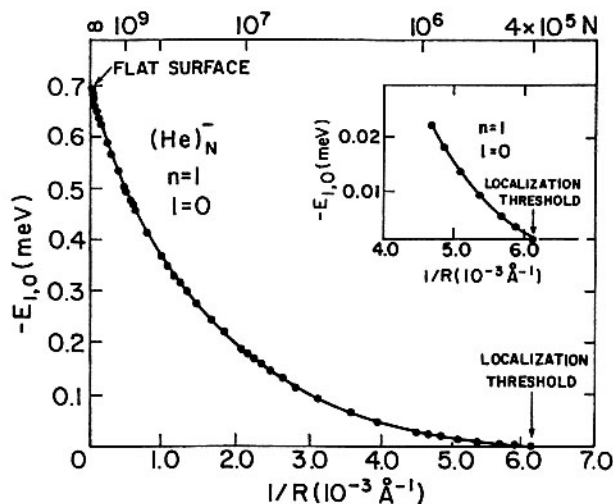


Figure 1. The cluster size dependence of the ground state energy of an excess electron on $({}^4\text{He})_N^-$ clusters. Note the smooth "transition" from the localization threshold to the flat surface with increasing the cluster size.

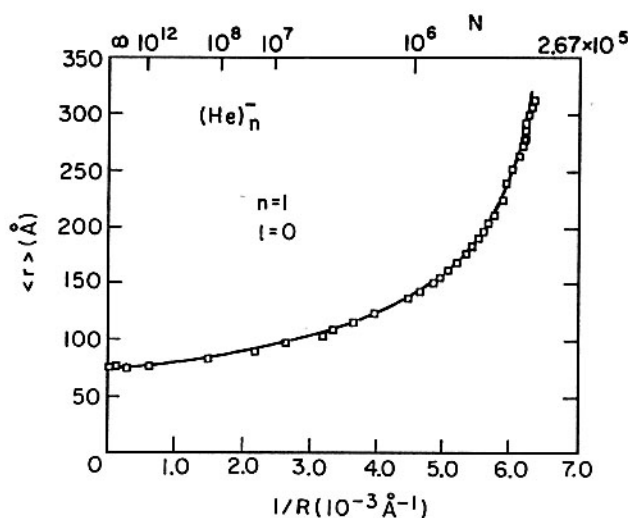


Figure 2. The cluster size dependence of the first moment $\langle r \rangle$ of the charge distribution of an excess electron on $({}^4\text{He})_N^-$ clusters. Note the divergence of $\langle r \rangle \propto (R - R_c)^{-1}$ at the localization threshold.

$$\Phi(r_f/R) = A^2 \left[1 - \frac{R_c}{R} \right] \quad (7)$$

and

$$\Omega(r_f/R) = A^{-1} \left[1 - \frac{R_c}{R} \right]^{-1} \quad (8)$$

where A is a numerical constant of the order of unity. From Eqs. (2) and (8) and Figure 2 it is apparent that $\langle r \rangle$ spans the range of very large values near the localization threshold, which exceeds the distance $137 a_0$ for the onset of long-range retardation forces. Accordingly, the excess electron - He cluster surface states can provide an interesting system for the scrutiny of long-range retardation interactions.

3. ELECTRON-CLUSTER POTENTIAL

The electron - He cluster interaction was treated [21] in terms of a mean-field potential, which incorporates a realistic description of the cluster surface profile. In what follows we shall account for the Coulomb interactions in terms of a model potential [19,20] (Section 2), which will provide the essential ingredients of the problem. The model potential for the $e-(\text{He})_N$ interaction is expressed in the form [19,20]

$$V(\rho) = V_0; \quad \rho \leq 1 \quad (9)$$

$$V(\rho) = -2Q(e^2/R)U(\rho); \quad \rho \geq 1 \quad (10)$$

where $\rho = r/R$ is the reduced distance, r is the distance from the cluster center, Q is given by Eq. (5) and $U(\rho)$ is the distance dependent part of the electron-cluster polarization image potential

$$U(\rho) = (\rho^2 - 1)^{-1} - \sum_{L=0}^{\infty} \left(\frac{b}{L+b} \right) \rho^{-2L-2} \quad (11)$$

with

$$b = \frac{1}{1 + \epsilon} \quad (12)$$

What is of interest for the present discussion is the asymptotic behavior of this image potential ($\rho \gg 1$) when Eq. (11) takes the form $U(\rho) = (1+b)^{-1}\rho^{-4} + 2(2+b)^{-1}\rho^{-6}$ and the long-range attractive potential, Eq. (10), is

$$V(r) = -\frac{A}{r^4} - \frac{B}{r^6} \quad (13)$$

The cluster dipole polarizability term is $A = \alpha_c e^2/2$ with the effective cluster polarizability $\alpha_c = [(\epsilon - 1)/(\epsilon + 2)]R^3$. The cluster quadrupole polarizability term is $B = \beta_c e^2/2$ with $\beta_c = 2[(\epsilon - 1)/(2\epsilon + 3)]R^5$.

The asymptotic Coulomb long-range potential has to be supplemented by the retarded potential. In analogy to the Kelsey and Spruch electron-ion potential [12-14] the electron-cluster retarded potential adds to the electrostatic potential, Eq. (13).

Following the general arguments [9-11] the onset of retardation effects will prevail at $r-R \gtrsim 137 a_0$. To provide a semiquantitative analysis of the retarded

electron-cluster potential, we utilize the approach of Spruch [15,16] for the electromagnetic interaction between two polarizable systems

$$V_{e-c}(r) \equiv (\hbar/c^5 r) \int_0^{c/r} \alpha_c(\omega) \alpha_e(\omega) \omega^5 d\omega \quad (14)$$

The frequency dependent polarizability $\alpha_c(\omega)$ of the cluster is approximated in the Drude form

$$\alpha_c(\omega) = e^2 / (m(\omega_0^2 - \omega^2) + i\gamma\omega) \quad (15)$$

with characteristic frequency ω_0 and (small) damping width γ . Since the range of ω in Eq. (14) is $0 \dots c/r$ and $r \gg c/\omega_0$ for the retarded interactions, we can take the zero-frequency cluster polarizability $\alpha_c(\omega) = e^2/m\omega_0^2 \equiv \alpha_c(0)$. For the frequency dependent polarizability $\alpha_e(\omega)$ of the free electron one sets $\omega_0 = 0$, whereupon $\alpha_e(\omega) = e^2/m\omega^2$. Eq. (14) then results in the retarded interaction

$$V_{e-c}(r) = C e^2 \hbar \alpha_c(0) / m c r^5; \quad r \gg 137 a_0, \quad (16)$$

where the numerical constant is of the order of unity being accurately given by $C = 11/4\pi$ [15,16]. This heuristic argument was presented to emphasize the appearance of the zero frequency cluster polarizability in the retarded interaction.

4. CONCLUDING REMARKS

Retardation effects for two-polarizable systems modify the asymptotic electron-cluster potential in an analogous way to electron-ion or electron-atom interactions [10-16]. The asymptotic electron-Helium cluster potential, including retardation, is given from Eqs. (13) and (16) in the form

$$V(r) = -\frac{A}{r^4} + \frac{D}{r^5} - \frac{B}{r^6}; \quad (r-R) \gg 137 a_0 \quad (17)$$

where the coefficient of the retarded interaction is $D = (11/4\pi)e^2 \hbar \alpha_c / mc$. In view of the large spatial extension of the excess electron charge distribution just above the localization threshold at $R > R_c$ where $\langle r \rangle$ obeys the scaling laws, Eqs. (2) and (8), the condition $(r-R) \gg 137 a_0$ for the onset of retarded interactions is well satisfied, modifying the electron-cluster potential. The retarded interaction in $V(r)$, Eq. (16), provides the leading repulsive interaction in the long-range potential. Nevertheless, the contribution of the retardation term is small. A cursory examination of the first two terms in Eq. (17) reveals that the electron-cluster potential is modified to include a small correction term. The ratio of the retardation and the dipole polarization terms in $V(r)$, Eq. (17), is $\eta = (D/A)r^{-1}$, being $\eta = (\hbar/mc)r^{-1} \equiv (137 r/a_0)^{-1}$. At the relevant distance, where retardation effects set in, $r = (137 a_0 + R)$, this ratio assumes the value of $\eta \sim 10^{-4}$. Nevertheless, this novel facet of retardation effects for giant excess

electron states on clusters is of interest.

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