Rydberg atom at the surface of liquid helium

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The adsorption of highly excited atoms by the surface of liquid helium may lead to the formation of an unusual state, in which the atomic nucleus is bound to the surface and the electron is situated above the helium surface far from the charged complex. The spectrum of such adsorbed atom is analyzed.

The highly excited (Rydberg) atomic states have recently been the subject of active research.[1] Retention of such atoms, producing them in sufficiently high concentrations, and cooling of such an ensemble is a complex technical problem. From this standpoint, the study of highly excited atoms adsorbed on the surface of liquid helium or some other cryogenic dielectric with a dielectric constant close to unity (Ne, N_2, D_2) may prove to be useful.

Separated from the liquid-helium surface a considerable distance, the atom is

attracted to it because of dipole-dipole interaction with its image.[2,3] At short range, the attraction is offset by the rigidity of its electronic shell. In the highly excited state, the sheet is not too rigid and the nucleus or the ionic core of the atom collapses toward the surface and is bound to it. We call the state produced in this manner a strongly adsorbed state.

The exact energy for the adsorption of a proton at the surface of liquid helium is not known. For a crude estimate we can assume that a complex HeH^+ ion with a binding energy $E = 1.85$ eV is produced as a result of adsorption of a proton.[4] The formation of a strongly adsorbed state is therefore desirable from the energy standpoint even for the states with $n \geqslant 4$. The only stable states will, however, be the highly excited states, which are insensitive to small perturbations of the surface. The interaction of an electron with the insulator is described by the image potential

$$U(z) = -Qe^2/z, \tag{1}$$

where for ^{4}He we have $Q = (\epsilon - 1)/(\epsilon + 1) = 6.9 \times 10^{-3}$ ($\epsilon = 1.0572$). The helium surface is virtually impenetrable to electrons: the energy necessary to penetrate the surface is > 1 eV. The surface is substantially ideal and the vapor concentration at low temperatures is exponentially low. All these properties are manifested in the well-known phenomenon known as electron levitation.[5]

Let us consider the change in the electronic state in the case of strong adsorption. In zeroth approximation we ignore the interaction of an electron with the nuclear images and with its self-image. We consider the adsorption in the adiabatic approximation. The coordinates are labeled in Fig. 1. The helium surface is described by the

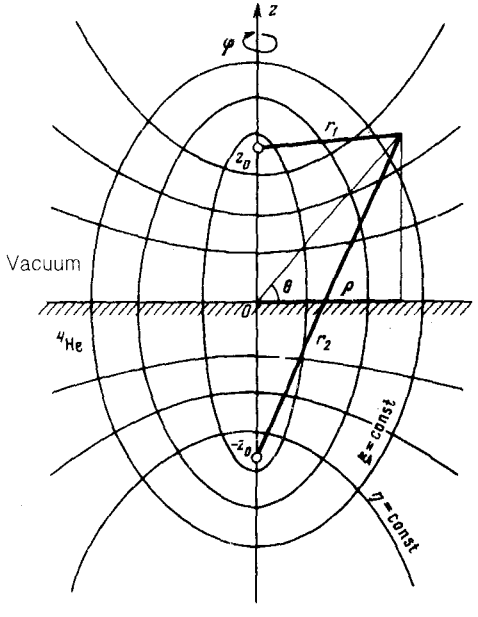

FIG. 1.

boundary condition

$$\psi(z=0)=0. \tag{2}$$

The Schrödinger equation with the potential $U(\mathbf{r}) = -e^2/r_1$ and the boundary condition (2) can easily be solved by analyzing the system which is symmetric with respect to the $z=0$ plane with the potential energy

$$U(\mathbf{r}) = \begin{cases} -e^2/r_1 & \text{for } z>0 \\ -e^2/r_2 & \text{for } z<0 \end{cases}$$

and by singling out its eigenfunctions of odd parity in z. This problem is amenable to a separation of variables in the ellipsoidal coordinates[6] $\xi = (r_1 + r_2/2z_0)$, $\eta = (r_1 - r_2/2z_0)$, φ. The state is characterized by three quantum numbers: the magnetic quantum number, m, and two quantum numbers, n_ξ and n_η, which correspond to the number of zeros of the wave function in the coordinates ξ and η. Condition (2) forces us to assume that $n_\eta = 2k+1$. As $z_0 \to \infty$, the ellipsoidal coordinate system becomes a parabolic coordinate system with the coordinates[6] $\sigma = 2z_0\cdot(1-\xi)$, $\tau = 2z_0(1-\eta)$, φ. The state is characterized by the quantum numbers m, n_σ, and n_τ. As the nucleus approaches the surface adiabatically, these quantum numbers become ellipsoidal numbers: $m = \text{const}$, $n_\xi = n_\sigma$, and $n_\eta = 2n_\tau + 1$. As $z_0 \to 0$, the ellipsoidal coordinate system becomes a spherical coordinate system. Here $m = \text{const}$, $n_r = n_\xi$, and $l - |m| = n_\eta$. The quantity $l - |m|$ is necessarily odd.

In the case of strong adiabatic adsorption, the atom which is initially in the state with parabolic quantum numbers m, n_σ, and n_τ (with principal quantum number $n_1 = n_\sigma + n_\tau + |m| + 1$) thus undergoes a transition to the state with the spherical quantum numbers m, $n_r = n_\sigma$, and $l = 2n_\tau + |m| + 1$, in which the principal quantum number increases to $n_2 = n_1 + n_\tau + 1$ and the energy increases from $E_1 = -(me^4/2\hbar^2 n_1^2)$ to $E_2 = -(me^4/2\hbar^2 n_2^2)$. If the atom in the initial state is in the eigenstate of the angular momentum l, the probability for the increase of the principal quantum number, Δn, is $p(\Delta n) = \Sigma_{\nu=1}^{n-|m|-1}(C_{\mu_1\mu_2}^{lm})^2$, where $C_{\mu_1\mu_2}^{lm}$ are the Clebsch-Gordan coefficients, n is the initial value of the principal quantum number, and $\mu_{1,2} = (m \pm \nu \mp \Delta n)/2$.

The image of the nucleus can be described by the reduction of its effective charge to[7] $qe = (3 - \epsilon/2)e$ and allowance for the interaction of the electron with the self-image leads, in the first order of the perturbation theory, to a level shift

$$\Delta E = a_{lm} QE_n, \tag{3}$$

where $a_{lm} = 2(2l+1)[(l-|m|)!/(l+|m|)!]\int_0^1 [p_l^m(x)]^2(dx/x)$, The function a_{lm} increases monotonically when any one of the following indices increases: $a_{1,0} = 1.50$, $a_{10,9} = 3.70$. As $l \to \infty$, these indices increase logarithmically. The discussion can be restricted to first-order perturbation theory if $n < 10^2/a_{lm}$.

The opposite limiting case, in which the interaction of the electron with the self-image is much stronger than its interaction with the nucleus, is found in other type of states which we call planar states.

In the absence of a nucleus, the electron is situated in one of the levitation levels with an energy $E_k = -(Q^2me^4/2\hbar^2k^2)$: its average distance from the surface is $z_k = (\hbar^2k^2/mQe^2)$, where k is the level number. In the planar state the average distance of the electron from the nucleus is considerably greater than z_k. The potential $u(r) = e(Q/z) + (q/\sqrt{\rho^2+z^2})$, in which the electron is found, becomes the potential $u_\infty(r) = (Qe/z) + (qe/\rho)$, at $\rho \gg z$ and the variables in the Schrödinger equation are separated in the cylindrical coordinates. The motion along z is described by the levitation states and the motion along the surface is described by an equation which has the form $\frac{1}{2}\Delta_{\rho,\varphi}\psi + (1/\rho)\psi = E\psi$ in atomic units. This equation reduces to a hypergeometric equation for $R(\rho)$ through the substitution of $\psi = |\rho|^m e^{-\rho/2} e^{im\varphi} R(\rho)$. The spectrum of the energy eigenvalues is

$$E_n = -\frac{mq^2e^4}{2\hbar^2(n+1/2)^2}. \tag{4}$$

Each state n is multiply degenerate in m. The perturbation $-e(u-u_\infty)$ leads to a correction for the energy, $\Delta E_n \sim E_n Q^{-2}(k/n)^4$, which is small when $n/k > 20$.

Strongly adsorbed atoms, like all highly excited states, have a high degree of polarizability (the polarizability in the z direction is different from the polarizability perpendicular to it) and a highly nonlinear response to the external fields. A considerable advantage of these atoms is that they establish an excellent bond with the helium reservoir.

Since the image potential and the boundary conditions at the helium surface depend on the curvature of the surface, the atom will interact with the surface capillary waves in the helium. This interaction may lead to transitions which are caused by the emission and absorption of a ripplon—a quantum of these vibrations[5]—and to processes involving ripplons and photons.

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NOTE. Yu. E. Lozovik has graciously called our attention to a study by Landau and Lifshitz,[8] in which the classification of the excited states of a surface helium atom is considered. The principal conclusion of this study: that the spectrum of highly excited states is of a Rydberg nature, is incorrect because in it the interaction of the electron with its image is ignored.

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