Electron scattering by a cut-off atomic potential: Application to electron properties in atomic liquids

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(Received 17 August 1995; revised manuscript received 28 May 1996)

The problem of the phase shifts of the cut-off polarization potential is solved exactly by the variable-phase method. The s and p waves are calculated by the method for the Wigner-Seitz cell, which is a unit scatterer of excess electrons in the cellular model of liquids. The phase shifts for the isolated atom are used as input parameters. The accurate form of the short-range part of the electron-atom potential is not required. The general features of the behavior of excess electrons in a dense medium are described by the model. [S0163-1829(96)03339-5]

I. INTRODUCTION

In recent years, interest in the properties of excess electrons in atomic liquids has been renewed.[1,2] This is primarily due to the development of computer simulation of electron movement in a dense medium of scatterers.[3–6] In these works the definition of the electron-atom potential is the main assumption. As a rule, the long-range part of this potential is known and it is the polarization potential

$$V_p(r) = -\frac{e^2\alpha}{2r^4}, \qquad (1)$$

where α is the polarizability of the atoms of the liquid. The short-range part of the potential is constructed in various ways by different authors. Along this line, considerable success has been achieved in calculations of the background energy $V_0(N)$ as a function of the medium density, which are in a good agreement with a large body of experimental data.

Another situation exists with calculation of the excess electron mobility in these liquids. We do not know computer calculations of the mobility in liquid Ar, Kr, and Xe. In the fundamental theory by Cohen and Lekner,[7] the kinetic descriptions of the electron mobility in atomic liquids has been developed with consideration for the spatial correlation of atoms. Two parameters characterizing a liquid are required in this theory. First, is a static structure factor, determined from the neutron and x-ray-scattering experiments and from computer simulations. Second, is an effective electron-scattering cross section in a liquid. As revealed in Ref. 8, the cross section differs considerably from the well-known scattering cross section of an electron in a rarefied gas. The cross section can be calculated by using any model for the interaction between the electron and atom in a liquid. One way is the introduction of an electron-atom pseudopotential for a liquid.[9,10] By using this method the background energy $V_0(N)$, the effective electron mass $m_{eff}(N)$, the zero-field mobility $\mu(N)$, and the effective cross section as a function of the density of medium have been calculated in Refs. 11 and 12. Parameters of the pseudopotential were determined from characteristics of an izolated atom: the polarizability α and the scattering length L_a. The following basic feature of

the electron scattering in liquid Ar, Kr, and Xe, has been obtained. The effective scattering length $L(N)$ as a function of the fluid density passes through zero and becomes positive when the fluid density increases from gas to liquid.[8] The results of the calculations are in good agreement with experimental data. But the weak point in the pseudopotential theory is an unreliable description of scattering of fast electrons with an energy exceeding 0.1 eV. The scattering length of an isolated atom L_a is the basic parameter for this pseudopotential. This quantity is characteristic of slow electron scattering. To construct a theory that will describe the interaction between fast electrons and liquid additional information is required, namely, the partial phase shifts of the wave function of an electron scattered by an isolated atom.

In the present paper a method for calculating characteristics of excess electron scattering in a liquid with high polarizability of atoms is proposed. The method allows us to calculate the partial phase shifts in a wide range of energies of scattered electrons. The initial data for the calculation are the partial phase shifts $\delta_\ell(k)$ of electron scattered by an isolated atom as a function of the wave number k of an electron.

The average field acting on an electron in a liquid is the "muffin-tin" potential. One can model an element of this potential by surrounding each atom of the liquid by the Wigner-Seitz cell with a radius $r_c = (3/4\pi N)^{1/3}$. Here N is the number density of atoms of the liquid. Inside the cell, the potential is a cut-off electron-atom potential. The size of the cell is large enough for the potential to have the form Eq. (1) in much of the cell. For simplicity we shall not take into account the mean potential of environmental atoms. This aspect has been dealt with in earlier papers.[9,10] So the atomic liquid is considered as a set of cells, each of them a unit scatterer for excess electrons. The properties of the electrons, such as electron mobility, conduction-band bottom energy, and effective mass, are determined by the features of the potential. In Refs. 13–15 the Schrödinger equation for the electron wave function in the Wigner-Seitz cell has been solved. It allows us to calculate the background energy V_0 and the effective electron mass m_{eff} of electrons in liquids. But a short-range component of the electron-atom potential has to be assumed.

In the present paper phase shifts for s and p waves are calculated by the variable-phase method[16] for the Wigner-

Seitz cell, which is modeled by the cut-off atomic potential. An accurate form for the short-range part of the potential is not needed. The general information of the short-range electron-atom interaction is contained in the phase shifts $\delta_\ell(k)$ for an isolated atom. The phase shifts for the Wigner-Seitz cell are calculated as the values $\eta_\ell(r_c,k)$ of the partial phase functions at the cell boundary. These effective phase shifts are density dependent since they are a function of the cell radius r_c. We concentrate mostly on the mathematical aspects of the partial phase-shift calculation in a liquid with high atomic polarizability. Some analytical results illustrate the numerical calculations of the phase function. Two terms of the s-wave phase-shift expansion in powers of the wave number k have been obtained. The final result of the work is the s- and p-wave phase shifts $\eta_\ell(r,k)$ for the sufficiently large values of the wave number k, which are required for an electron effective-mass calculation in the liquid. We believe that the calculations in the framework of the pseudopotential approach are not quite reliable in these conditions. Hence, in Sec. IV the calculation of the effective mass in the liquid with the parameters close to liquid Xe has been carried out.

II. THE s-WAVE PHASE SHIFT

There are two known equivalent methods to find the phase shifts for the wave function of a scattered electron. In the first method, the scattering potential is given exactly (with regard to the short-range part of the potential). The Schrödinger equation is solved for the partial wave functions of the scattered electron and the asymptotic form of these wave functions is

$$u_\ell(r\rightarrow\infty)\simeq\sin\left(kr-\frac{\pi\ell}{2}+\delta_\ell(k)\right). \tag{2}$$

Equation (2) contains the partial phase shifts $\delta_\ell(k)$ as a function of the wave number k.

In the second method, the phase function $\eta_\ell(r,k)$ is calculated from the phase equation[16]

$$\frac{d\eta_\ell(r,k)}{dr}=-\frac{2mV(r)}{\hbar^2 k}\left[\cos\eta_\ell j_\ell(kr)-\sin\eta_\ell n_\ell(kr)\right]^2 \tag{3}$$

and the boundary condition $\eta_\ell(0,k)=0$. Here $j_\ell(kr)$ and $n_\ell(kr)$ are the spherical Bessel and Neumann functions, respectively. The asymptote of the phase function is sought for phase shift

$$\lim_{r\rightarrow\infty}\eta_\ell(r,k)=\delta_\ell(k). \tag{4}$$

It is easy to verify that $\eta_\ell(r,k)$ is the phase shift of the partial ℓ-wave function scattered on the potential $V(r)$, which is cut off at a distance r from the atom. In such a manner, the calculation of the phase shifts of the partial waves for the atom potential cut off at the cell boundary r_c is equivalent to the calculation of the phase function $\eta_\ell(r_c)$. Solving the phase equation (3) with a boundary conduction (4), where $\delta_\ell(k)$ are the known partial phase shifts for the isolated atom, the phase shifts for the Wigner-Seitz cell are found exactly, without specific information about the short-range structure of the potential.

The s-wave scattering determines the zero-field mobility of the excess electrons in liquid Ar, Kr, and Xe. For slow electrons the higher partial waves may be neglected. The scattering cross section is determined by the scattering length L, which defines the long-wavelength limit of the s-wave phase shift

$$\delta_0(k)=-Lk. \tag{5}$$

For excess electrons in a gas the cross section is $\sigma=4\pi L_a^2$, where L_a is the scattering length of the isolated atom. This quantity can be measured by the spectrum line-shift method.[17,18] For Ar, Kr, and Xe the L_a values are negative.

The problem of the scattering length of the Wigner-Seitz cell is exactly solved. The phase equation (3) for $\eta_\ell(r,k)$ at $\ell=0$ has the form

$$\frac{d\eta_0}{dr}=-\frac{2mV(r)}{\hbar^2 k}\sin^2(kr+\eta_0), \tag{6}$$

with the boundary condition $\lim_{r\rightarrow\infty}\eta_0(r,k)=-L_a k$. Within the variable-phase method we consider the long-wavelength limit $\eta_0(r,k)=-L(r)k$, where $L(r)$ satisfies the equation

$$\frac{dL}{dr}=-\frac{\alpha}{a_0 r^4}(r-L)^2, \tag{7}$$

with the boundary condition $\lim_{r\rightarrow\infty}L(r)=L_a$. In Eq. (7) we assumed that at large distances from the atom the potential has the form (1). a_0 is the Bohr radius. The Riccati equation (7) has the solution

$$L(r)=\left\{\frac{1}{r}+\sqrt{\frac{a_0}{\alpha}}\tan\left[\arctan\left(\sqrt{\frac{\alpha}{a_0}}\frac{1}{L_a}\right)-\sqrt{\frac{\alpha}{a_0}}\frac{1}{r}\right]\right\}^{-1}. \tag{8}$$

This can be checked by making an immediate substitution. This expression for the scattering length of the Wigner-Seitz cell was obtained in Ref. 10 by an approximate method. Now we have established that this solution is accurate.

It is significant that the scattering length $L(r_c)$ of the Wigner-Seitz cell obtained via this rough model (the average potential of environment is not discounted) qualitatively describes all features that are characteristic for the electron scattering in an atomic liquid (see Fig. 1). For large distances r_c, the function $L(r)$ tends to the value L_a, which is the negative scattering length of the isolated atom. With an increase of the density (decreasing of r_c) the scattering length grows and changes sign: in a liquid near the triple point $L(r)$ is positive.[8] The calculations for Fig. 1 have been made for a Xe-like atom with $L_a=-6a_0$ and $\alpha=27a_0^3$. In dimensionless units [the scale of length is $(\alpha/a_0)^{1/2}$] the atom is characterized by a single parameter such as the dimensionless scattering length $\widetilde{L}_a=(a_0/\alpha)^{1/2}L_a$. In the case under consideration $\widetilde{L}_a=-1.15$. According to Eq. (8), $L(r)$ passes through zero at

$$r_*=\sqrt{\frac{\alpha}{a_0}}\left[\frac{\pi}{2}+\arctan(\widetilde{L}_a^{-1})\right]^{-1}. \tag{9}$$

In a medium with the density N_* appropriate to r_*, s-wave scattering is small and the mobility of the electrons has a
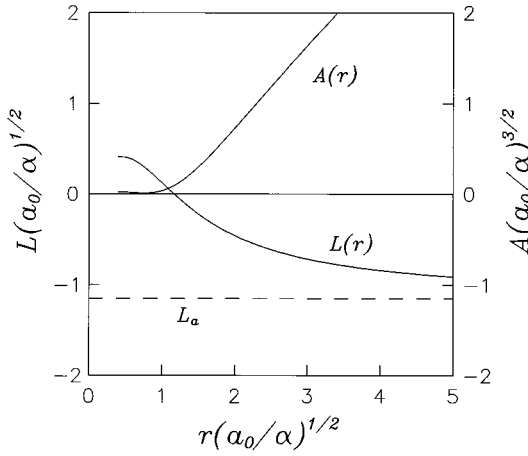
FIG. 1. Scattering length $L(r)$, calculated from Eq. (8), and coefficient $A(r)$ in the expansion of the s-wave phase function for small k, calculated from Eq. (20), versus the cut-off radii r. L_a is the scattering length of the isolated atom.

maximum. We emphasize that it is impossible to obtain expression (8) by the Born approximation, neglecting $\eta_0(r)$ on the right-hand side of Eq. (6).

It is known that for the s-wave phase shift for a potential with a limited radius of action the long-wavelength Bethe-Born expansion (approximation of effective radius) is valid[19]

$$k\,\cot\delta_0 = -\frac{1}{L} + \frac{r_0 k^2}{2} + \cdots ,\qquad (10)$$

where L is the scattering length and r_0 is the effective radius. For the polarization potential (1) of the isolated atom another expansion is valid[20]

$$k\,\cot\delta_0 = -\frac{1}{L} + \frac{\pi\alpha k}{3a_0 L^2} + \frac{2\alpha}{3La_0}\,k^2\ln\!\left(\frac{\alpha k^2}{16a_0}\right) + \cdots .\qquad (11)$$

The appearance of the term proportional to k is the result of a long-range character of the potential (1). For the polarization potential cut off at a distance r_c (it is a short-range potential), expansion (11) should be replaced by expansion (10), where the parameters L and r_0 should be functions of r_c. The problem of obtaining $L(r)$ has been resolved above. Now we shall find the next term of the expansion of the s-wave phase shift in terms of degrees of wave number k.

It has been established that $L(r_*)=0$ at $r=r_*$ [Eqs. (8) and (9)]. When this takes place, expansion (10) loses its meaning. Therefore we shall obtain the $k^{-1}\tan\delta_0$ expansion in terms of powers of a wave number k.

Let $u_0(r,k)$ be an s-wave solution of the radial Schrödinger equation, with the polarization potential (1) cut off at $r=r_c$

$$\frac{d^2 u_0(r,k)}{dr^2} + \left(\frac{\alpha}{a_0 r^4} + k^2\right)u_0 = 0.$$

The well-known property of the Schrödinger equation, belonging to different wave numbers k and k', is used

$$\lim_{r\to\infty}[u_0(k)u_0'(k') - u_0(k')u_0'(k)]$$

$$= (k^2 - k'^2)\int_0^\infty u_0(r,k)u_0(r,k')dr.\qquad (12)$$

Here the notation $u_0'(k)=du_0/dr$ has been introduced and the boundary condition for the wave function $u_0(k,0)=0$ has been used.

At distances $r>r_c$ the cut-off potential is equal to zero and the function $u_0(k,r)$ coincides with its asymptotic form

$$v_0(r,k) = \sin kr + \cos kr\,\tan\eta_0(k,r_c).\qquad (13)$$

For the asymptotic function $v_0(k,r)$ the following relationship can be obtained by the same method:

$$\lim_{r\to\infty}[v_0(k)v_0'(k') - v_0(k')v_0'(k)] - [k'\tan\eta_0(k,r_c) - k\,\tan\eta_0(k',r_c)] = (k^2 - k'^2)\int_0^\infty v_0(k,r)v_0(k',r)dr.\qquad (14)$$

Here $v_0(k,0)=\tan\eta_0(k,r_c)$ and $v_0'(k,0)=k$. The asymptotic values of the function u_0 and v_0 coincide at $r\to\infty$.

Subtracting Eq. (14) from Eq. (12) and then dividing the result by k and k', one has, in the limit of $k'\to0$,

$$k^{-1}\tan\eta_0(k,r_c) + L(r_c) = -k^2\int_0^{r_c}\left[\frac{v_0(k,r)}{k}\lim_{k'\to0}\left(\frac{v_0(k',r)}{k'}\right) - \frac{u_0(k,r)}{k}\lim_{k'\to0}\left(\frac{u_0(k',r)}{k'}\right)\right]dr.\qquad (15)$$

Here we used the definition of the scattering length L for the cut-off potential

$$L(r_c) = -\lim_{k\to0}k^{-1}\tan\eta_0(k,r_c).\qquad (16)$$

The integral on the right-hand side of Eq. (15) is calculated inside a cell, where the function $u_0(k,r)$ differs from its asymptotic form $v_0(k,r)$. From Eq. (14) we obtain the first two terms of the $k^{-1}\tan\eta_0(k,r_c)$ expansion in terms of k

$$k^{-1}\tan\eta_0(k,r_c) = -L(r_c) - k^2\int_0^{r_c}\left[\left(\lim_{k\to0}\frac{v_0(k,r)}{k}\right)^2 - \left(\lim_{k\to0}\frac{u_0(k,r)}{k}\right)^2\right]dr.\qquad (17)$$

The first term of the integrand has the form following from Eq. (13) and the definition (16):

$$\lim_{k \to 0} \frac{v_0}{k} = r - L(r_c). \qquad (18)$$

For the second term we shall use the well-known solution of the radial Schrödinger equation with the polarization potential (1) for $k=0$ and $\ell=0$:

$$\lim_{k \to 0} \frac{u_0(r,k)}{k} = \frac{r_c - L}{r_c} \frac{r \sin\left(\sqrt{\frac{\alpha}{a_0}} \frac{1}{r} - \Delta \right)}{\sin\left(\sqrt{\frac{\alpha}{a_0}} \frac{1}{r_c} - \Delta \right)},$$

$$\qquad (19)$$

$$\cot\left(\sqrt{\frac{\alpha}{a_0}} \frac{1}{r_c} - \Delta \right) = -\sqrt{\frac{a_0}{\alpha}} \frac{L r_c}{(r_c - L)}.$$

This function is normalized according to the condition $u_0(k,r_c) = k(r_c - L)$. The phase Δ is chosen by a smooth join of $u_0(k,r)$ with its asymptotic form $v_0(k,r)$ at $r=r_c$. The integral in Eq. (17) with Eqs. (18) and (19) is taken in an analytical form. For the factor of k^2 in the expansion $k^{-1}\tan\eta_0(k,r_c) = -L(r_c) - A(r_c)k^2$ we have

$$A(r_c) = \frac{\alpha r_c}{3 a_0} \left[b^2 - \left(b^2 - \frac{a_0 L}{\alpha} \right) \beta - \frac{a_0 L r_c}{\alpha} b \gamma \right], \quad (20)$$

where $b = 1 - (L/r_c)$ and β and γ are the well-known functions[21] of the argument $z = 2(\alpha/a_0)^{1/2} r_c^{-1}$,

$$\beta(z) = z \int_0^\infty \frac{\sin t}{t+z} \, dt, \quad \gamma(z) = z^2 \int_0^\infty \frac{\cos t}{t+z} \, dt. \quad (21)$$

The function $A(r_c)$ versus the cut-off radius of the potential is given in Fig. 1. In the domain where r is not significant, $A(r)$ is small and the $\eta_0(k,r)$ depends on the wave-number function linearly up to moderate values of k.

The phase functions $\eta_0(k,r)$ as a function of the wave number k and the radius r are given, respectively, in Figs. 2 and 3. These phase functions have been obtained as the solution of the phase equation (6) with the boundary condition (4). The phase shift $\delta_0(k)$ for the isolated atom potential appears in this boundary condition. In the calculations we used the phase shift calculated for the pseudopotential with a polarization tail and a hard core radius a_c,

$$V(r) = \begin{cases} \infty & \text{if } r \leq a_c \\ -\dfrac{\alpha e^2}{2 r^2} & \text{if } r > a_c. \end{cases} \qquad (22)$$

The size of the hard core is related to the isolated atom scattering length L_a,

$$a_c = \sqrt{\frac{\alpha}{a_0}} \left[\pi + \arctan\left(\sqrt{\frac{\alpha}{a_0}} \frac{1}{L_a} \right) \right]^{-1}. \qquad (23)$$

This pseudopotential describes well electron scattering by the noble-gas isolated atoms. The phase shifts for Xe-like atoms ($L = -6a_0$, $\alpha = 27 a_0^3$, and $a_c = 2.14 a_0$) obtained by the numerical solution of Eq. (6) are compared with the results of the calculation, performed with the realistic electron–Xe-atom potential in[22] in Fig. 2.
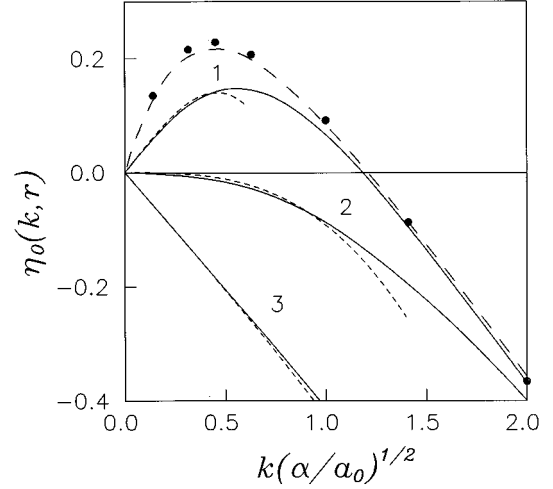
FIG. 2. s-wave phase functions $\eta_0(k,r)$ via the wave number k for different dimensionless cut-off radii $\tilde{r} = r(a_0/\alpha)^{1/2}$: (1) $\tilde{r}=2$, (2) $\tilde{r}=1.167$, and (3) $\tilde{r}=0.5$. Solid lines, calculations by the variable phase method, dotted lines, calculation by the expansion (17). $\delta_0(k)$ for the isolated atom: points, data (Ref. 22); dashed line, the solution of Eq. (6) for infinite r.

A set of the phase functions $\eta_0(r,k)$ is shown in Fig. 2 versus the wave number k. It shows that the contribution of the long-range polarization attraction decays when the cut-off radius of the polarization potential diminishes. The non-monotonic $\delta_0(k)$ dependence, characteristic of the atoms with high polarizability, is replaced by the monotonic dependence $\eta_0(k,r)$ as a result of the change of the scattering length sign.

If the dependence $\delta_0(k)$ is nonmonotonic, the s-wave phase shift becomes zero for the wave-number value k_*. It leads to the Ramsauer effect experiencing electron scattering in the heavier noble gases. The cross section is a nonmonotonic function of the electron energy; it is small at the energy value corresponding to $\hbar^2 k_*^2/2m$. As it follows from Fig. 2, the Ramsauer effect disappears as the cut-off radius is reduced. If the scattering length is positive, the cross section is a monotonic function of the electron energy. There is a critical value $r_* = 1.17(\alpha/a_0)^{1/2}$, where the scattering length changes sign.

For small r the dependence $\eta_0(k)$ on the wave number k is practically linear, resulting from the expansion in terms of k, obtained above. The phase shifts, calculated from the expansion (17), are represented in Fig. 2 by dotted lines.

The dependence of $\eta_0(r,k)$ on r is shown in Fig. 3. At large values of r the phase functions saturate at the $\delta_0(k)$ level, according to the boundary condition. Then the function $\eta_0(r)$ decreases monotonically and becomes negative at smaller r. The sign of the phase function determines the character of the interaction; the attraction predominates if $\eta_0 > 0$. As the polarization potential is cut off, the attraction is reduced and the repulsion begins to play a general part ($\eta_0 < 0$). It should be pointed out that at small k the functions $\eta_0(r)$ become equal to zero at the common value r_*. This is the value at which the scattering length passes through zero.

In Fig. 3 the $\eta_0(r)$ curves are bounded at small r. Actually, the polarization potential (1) is the long-range part of the real electron-atom potential. At short distances the
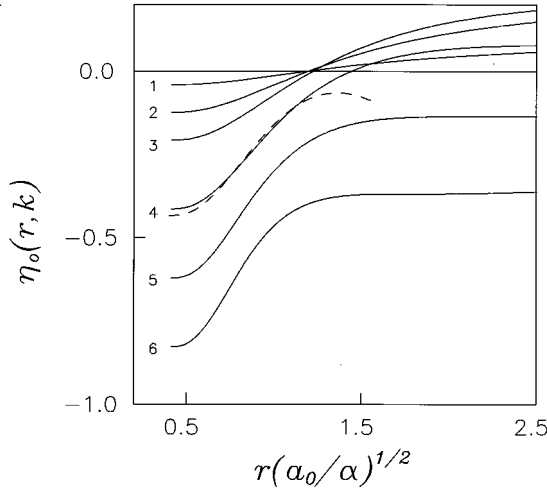
FIG. 3. s-wave phase functions $\eta_0(r,k)$ via the distance r for different dimensionless wave numbers $\tilde{k}=k(\alpha/a_0)^{1/2}$: (1) $\tilde{k}=0.1$, (2) $\tilde{k}=0.3$, (3) $\tilde{k}=0.5$, (4) $\tilde{k}=1$, (5) $\tilde{k}=1.5$, and (6) $\tilde{k}=2$. Solid lines, the solution of Eq. (6); dashed line, expansion (17) for $\tilde{k}=1$.

electron-atomic potential can be simulated by a hard core with the radius a_c [Eq. (23)]. Since we solve the phase equation (6) for the polarization potential only, the validity area of our solutions is $r>a_c$.

As discussed above, expansion (17) in terms of k approximates to the exact phase function $\eta_0(r,k)$ only for small k and not for large r. In Fig. 3 the dashed line gives the result of the calculation following this expansion for $k=(a_0/\alpha)^{1/2}$. One can estimate the boundary of a validity of expression (20) for $A(r)$. For small k the result of the calculation following expression (20) practically coincides with the result of the exact calculation for all r.

III. THE p-WAVE PHASE SHIFT

Let us consider the phase shift of the scattered partial wave with $\ell=1$ for the cut-off potential. The p-wave function is used for the calculation of an electron effective mass in the cellular model media.[15,23] For the p-wave phase function $\eta_1(r,k)$ the equation is valid

$$\frac{d\eta_1}{dr} = -\frac{2m}{\hbar^2}\frac{V(r)}{k}\left[\frac{\sin(kr+\eta_1)}{kr}-\cos(kr+\eta_1)\right]^2. \tag{24}$$

As in the case of the s-wave scattering we used the boundary condition

$$\lim_{r\to\infty}\eta_1(r,k)=\delta_1(k). \tag{25}$$

A few words are in order about the $\delta_1(k)$ function used below. As long as the phase-shift values are small the contributions to the scattering of the long-range and the short-range parts of the potential are additive. Hence, for small k [and small $\delta_1(k)$] we can write

$$\delta_1(k)=\delta_1^{\mathrm{cor}}(k)+\delta_1^{\mathrm{pol}}(k), \tag{26}$$

where $\delta_1^{\mathrm{cor}}(k)$ is the contribution to the phase shift of the scattering by the hard core and $\delta_1^{\mathrm{pol}}(k)$ is the contribution of the polarization scattering.

As is well known, the Born approximation describes the polarization contribution in p-wave scattering well. For the Born approximation one can write, using Eq. (24),

$$\frac{d\eta_1}{dr}=\frac{\alpha}{a_0 kr^4}\left(\frac{\sin kr}{kr}-\cos kr\right)^2. \tag{27}$$

For $\delta_1^{\mathrm{pol}}(k)=\lim_{r\to\infty}\eta_1(k,r)$ using the boundary condition $\delta_1^{\mathrm{pol}}(0)=0$, the following expression can be obtained:

$$\delta_1^{\mathrm{pol}}(k)=\frac{\alpha}{a_0 k}\int_0^\infty\frac{dr}{r^4}\left(\frac{\sin kr}{kr}-\cos kr\right)^2=\frac{\pi}{15}\frac{\alpha k^2}{a_0}. \tag{28}$$

This is the polarization contribution in the p-wave scattering by the isolated atom.

For the short-range potential the Blatt-Jackson expansion[24] of $\delta_1(k)$ in the terms of the wave number k is valid

$$k^3\cot\delta_1=-\frac{1}{a_1}+\frac{b_1 k^2}{2}. \tag{29}$$

Consequently, one can write, for the small values of k,

$$\delta_1^{\mathrm{cor}}(k)=-a_1 k^3, \tag{30}$$

where the coefficient a_1 is characteristic of the p-wave scattering by the isolated atom short-range potential (analogous to the scattering length for s-wave scattering).

The values of $\delta_1(k)$ calculated in Ref. 22 for Xe are shown in Fig. 4. The dependence $\delta_1(k)$ is nonmonotonic and it is proportional to k^2 at $k\to0$, according to Eq. (28). As the wave number is increased, the scattering by the core prevails and the dependence $\delta_1(k)$ decreases according to Eq. (30) and changes its sign. One can find the magnitude of a_1 using
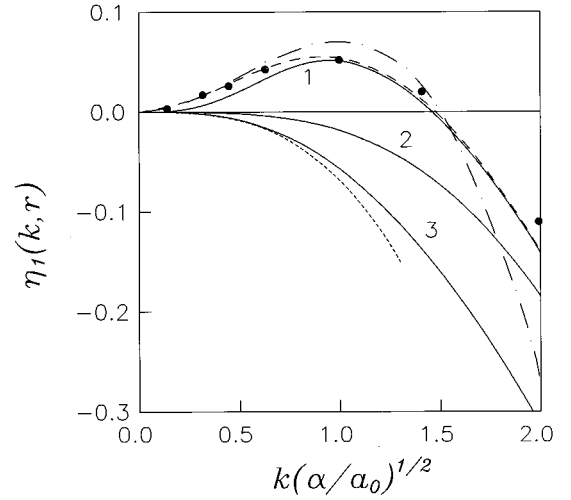

FIG. 4. p-wave phase functions $\eta_1(k,r)$ via the wave number k for different cut-off dimensionless radii $\tilde{r}$: (1) $\tilde{r}=3.5$, (2) $\tilde{r}=1.52$, and (3) $\tilde{r}=0.6$. Solid lines, calculations by the variable phase method; dotted line, expansion (37). $\delta_1(k)$ for the isolated atom: points, data (Ref. 22); dashed line, the solution of Eq. (24) for infinite r; dash-dotted line, expansion (31).

the value k_*, where $\delta_1(k_*)=0$. Thus, for the isolated Xe atom $k_*=0.29a_0^{-1}$ (Ref. 22) and $a_1=19.6a_0^3$. Unfortunately, the expression obtained

$$\delta_1(k)=\frac{\pi}{15}\frac{\alpha k^2}{a_0}-a_1k^3 \qquad (31)$$

is unusable at large values of k. It is not in quantitative agreement with the data[22] (see Fig. 4). Hence, for an approximation of these data over a wide range of wave numbers, we shall use the large-r asymptotic of the Eq. (24) solution $\delta_1(k)=\lim_{r\to\infty}\eta_1(k,r)$. The boundary condition (a scattering by the hard core with radius r_1)

$$\eta_1(k,r_1)=\arctan(kr_1)-kr_1 \qquad (32)$$

simulates the effect of the short-range part of the atom potential. The parameter $r_1=3.07a_0$ is chosen by fitting the calculated $\delta_1(k)$ values to the data.[22] It is seen from Fig. 4 that this approximation is consistent with the data in a wide range of k values.

Let us proceed to discuss the p-wave phase-shift behavior for the atomic potential, cut off at the distance r_c. Because this potential is a short-range one, the representation (29) for small values of k is valid for it. This expansion contains only odd-numbered powers. Polarization contribution (28), which is proportional to k^2 results from the long-range nature of the interaction. This term must be absent in the expansion for the p phase shift of the cut-off potential. In the Born approximation (27) the phase function $\eta_1(k,r)$ for a small k is such that $kr\ll1$; one obtains

$$\eta_1(k,r)=\delta_1(k)-\frac{\pi}{15}\frac{\alpha k^2}{a_0}+\frac{\alpha r}{9a_0}k^3=-\left(a_1-\frac{\alpha r}{9a_0}\right)k^3. \qquad (33)$$

On the right-hand side the contribution of the short-range electron-atom interaction (30) is taken into account.

Unfortunately, the Born approximation does not always give a correct magnitude of the factor coefficient of k^3 terms in Eq. (33). If we write the phase equation (24) for the function $\tan[\eta_1(k,r)]$ the right-hand side of Eq. (24) will be easily expanded in a power series of k

$$\frac{d\tan\eta_1}{dr}=\frac{\alpha}{a_0 k}\frac{1}{r^4}\left[\frac{(kr)^2}{3}+\frac{\tan\eta_1}{kr}\right]^2. \qquad (34)$$

Considering the first term of the expansion $\tan\eta_1(k,r)=-a_1(r)k^3$, we obtain the equation for $a_1(r)$, similar to Eq. (7) for the scattering length,

$$\frac{da_1(r)}{dr}=-\frac{\alpha}{9a_0}\frac{[r^3-3a_1(r)]^2}{r^6}. \qquad (35)$$

The range of validity of the Born approximation results from the inequality $r^3\gg a_1(r)$. The solution of Eq. (35) with the boundary condition

$$a_1(r_1)=\frac{r_1^3}{3} \qquad (36)$$

following from (32) at small values of k is shown in Fig. 5. The range of the $a_1(r)$ function is limited by $r_1=3.07a_0$. The function $a_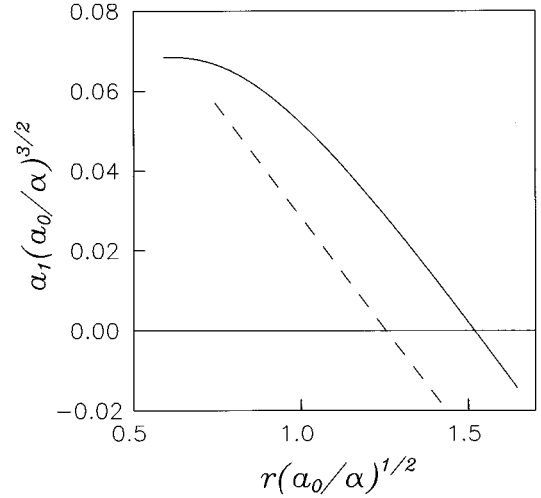1(r)$ tends toward a linear dependence, as predicted by the Born approximation, at $r>(\alpha/a_0)^{1/2}$. However, the $a_1(r)$ values and behavior at small r differ substantially from the values obtained by the Born approximation.

The p-wave phase functions $\eta_1(k)$ shown in Fig. 6 have been obtained by a numerical solution of Eq. (24) with the boundary condition (25). In Eq. (25) the dependence $\delta_1(k)$ for the isolated atom corresponds to the dashed line in Fig. 4. We can see from Fig. 6 that with r values increasing the dependences $\eta_1(k)$ tend to their asymptotic values $\delta_1(k)$. As the magnitude of the wave number increases, this tendency is observed for smaller-r values. In the case where the functions $\eta_1(r,k)$ shown in Fig. 6 have positive limited values, $\delta_1(k)$ and $\eta_1(r,k)$ as a function of r decrease, cross the x axis, and take negative values as r decreases. For small val-
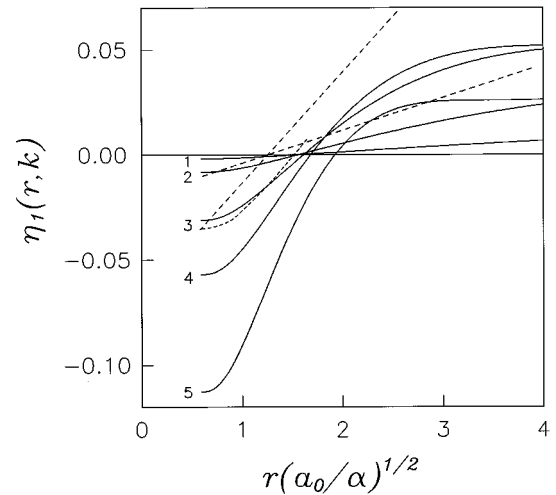

FIG. 5. Coefficient $a_1(r)$ in the expansion of the p-wave phase function for small k. The solid line is the solution of Eqs. (35) and (36) and the dashed line shows the Born approximation Eq. (33).

FIG. 6. p-wave phase functions $\eta_1(k,r)$ via the cut-off radius r for different dimensionless wave number $\tilde{k}$ values: (1) $\tilde{k}=0.3$, (2) $\tilde{k}=0.5$, (3) $\tilde{k}=0.8$, (4) $\tilde{k}=1$, and (5) $\tilde{k}=1.3$. Solid lines, solution of Eq. (24); dashed lines, the Born approximation (33); dotted line, the first term in the small-k expansion (37) with $a_1(r)$ from the solution of Eq. (35) for $\tilde{k}=0.8$.

ues of k, $\eta_1(\tilde{r},k)=0$ at the same point $\tilde{r}=1.52$, where the coefficient $a_1(r)$ becomes zero (Fig. 5).

It follows from Fig. 6 that the straight lines obtained by the Born approximation (33) (dashed lines in Fig. 6) differ significantly from the corresponding $\eta_1(r,k)$ curves. For $kr<1$ a sufficiently good approximation for $\eta_1(r,k)$ is the first term of the expansion

$$\eta_1(r,k)=-a_1(r)k^3, \tag{37}$$

where the function $a_1(r)$ is the solution of Eq. (35) with the boundary condition (36). We finally note that the range of the $\eta_1(k,r)$ function is limited by the value $r_1=0.59(\alpha/a_0)^{1/2}=3.07a_0$ for $\alpha=27a_0^3$. As it follows from Fig. 6, the derivative $d\eta_1/dr$ becomes zero and one obtains, according to Eq. (24),

$$\tan[kr_1+\eta_1(k,r_1)]=kr_1,$$

which corresponds to the boundary condition (32).

The dependences $\eta_1(k,r)$ as a function of the wave number k are shown in Fig. 4. For the isolated atom the dependence $\delta_1(k)=\lim_{r\to\infty}\eta_1(k,r)$ is nonmonotonic; it has positive values at small k as a consequence of the polarization p-wave scattering Eq. (28). The dependence $\eta_1(k,r)$ becomes monotonic and has negative magnitudes as the cut-off radius r decreases. That is, the short-range part of the atom-electron potential begins to predominate over the polarization attraction. At $r=1.52(\alpha/a_0)^{1/2}$ the dependence $\eta_1(k)$ is small for significant k magnitudes, which corresponds to a zero value of a factor the coefficient $a_1(r)$. To draw on the analogy between the s- and p-wave scattering, we have the same situation as when the zero value of the scattering length occurs. The dependences $\eta_1(k,r)$ on r for small k are sufficiently well approximated by the first term of the expansion (37) for $\tilde{r}>1.52$.

IV. THE EFFECTIVE MASS OF EXCESS ELECTRONS IN THE DENSE MEDIUM OF THE ATOMS

In the Wigner-Seitz model, each atom of the medium is replaced by an equivalent unit cell of radius r_c. The potential is assumed to be spherically symmetric and identical in each cell. The ground-state energy of the quasifree excess electron is determined as the sum of the polarization interaction energy and the kinetic energy $\hbar^2 k_0^2/2m$ due to multiple-scattering effects.[25] The wave number k_0 that determines the ground state is obtained by the Wigner-Seitz boundary condition for the electron wave function[26]

$$\left(\frac{d\Psi_0}{dr}\right)_{r=r_c}=0. \tag{38}$$

On the cell boundary the wave function $\Psi_0=r^{-1}u_0(r)$ with the partial s-wave function $u_0(r_c)$ is joined smoothly with its asymptotic form

$$\Psi_0=r^{-1}\sin[k_0r+\eta_0(k_0r_c)].$$

Thus the boundary condition (38) leads to the equation

$$\tan[k_0r_c+\eta_0(k_0,r_c)]=k_0r_c, \tag{39}$$

which determines the wave number k_0 as a function of the cell radius r_c. Equation (39) has a solution only in the case of $\eta_0(k,r)\leq0$. The expansion of the theory to positive $\eta_0(k,r)$ has been proposed in Ref. 27. Here we confine the discussion to the first case, where $r<r_*$ and $\eta_0(k,r)\leq0$, and we shall use Eq. (39) for the wave number k_0 to calculate the electron effective mass m_{eff} as a function of the cell radius r_c. The value of the effective mass m_{eff} can be estimated according to a method proposed by Bardeen[23] in the framework of the cellular model:

$$\frac{m_{\text{eff}}}{m}=\frac{4\pi N\int_0^{r_c}\Psi_0^2(r)r^2dr}{\Psi_0^2(r_c)}\left[\left(\frac{r}{u_1(r)}\frac{du_1}{dr}\right)_{\substack{r=r_c\\k=k_0}}-1\right]^{-1}, \tag{40}$$

where $u_1(r)$ is the p-wave radial function. On a cell boundary one can replace $u_1(r)$ by its asymptotic form

$$u_1(r)=\frac{\sin[kr+\eta_1(k,r_c)]}{kr}-\cos[kr+\eta_1(k,r_c)]. \tag{41}$$

Substituting Eq. (41) into Eq. (40), one obtains

$$\left[\left(\frac{r}{u_1(r)}\frac{du_1}{dr}\right)_{\substack{r=r_c\\k=k_0}}-1\right]$$

$$=\frac{(k_0r_c)^2\tan[k_0r_c+\eta_1(k_0,r_c)]}{\tan[k_0r_c+\eta_1(k_0,r_c)]-k_0r_c}-2. \tag{42}$$

For the first multiplier on the right-hand side of Eq. (40) the well-known polarization wave function

$$\Psi_0=\cos\left[\sqrt{\frac{\alpha}{a_0}}\left(\frac{1}{r}-\frac{1}{r_c}\right)\right]$$

is used, which gives

$$\frac{4\pi N\int_0^{r_c}\Psi_0^2(r)r^2dr}{\Psi_0^2(r_c)}=1-\frac{\alpha}{a_0r_c^2}\left[1-\beta\left(\frac{2}{r_c}\sqrt{\frac{\alpha}{a_0}}\right)\right], \tag{43}$$

where $\beta(z)$ is the function determined in Eq. (21).

Equations (40), (42), and (43) are used to calculate the electron effective mass m_{eff} as a function of the cell radius r_c. The phase functions $\eta_0(k,r)$ and $\eta_1(k,r)$ calculated above are substituted into these equations. The result of the numerical calculations is shown in Fig. 7. The Xe-like parameters $L_a=-6a_0$ and $\alpha=27a_0^3$ are used as input in the calculations. The effective mass is small in the dense medium. We note that the medium density corresponding to the cell radius $r_c=(\alpha/a_0)^{1/2}$ is about $N=10^{22}$ cm^{-3}. With the radius growth the m_{eff}/m ratio increases. In the vicinity of r_*, $\eta_0(k,r)$ and k_0 tend to zero and an analytical expression for m_{eff}/m can be obtained

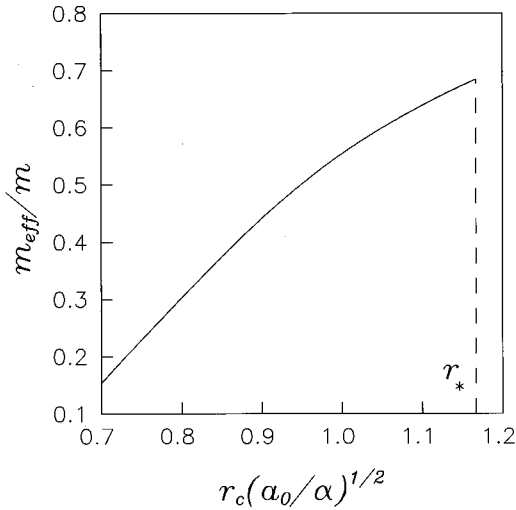FIG. 7. Ratio m_{eff}/m as a function of the cell radius. The calculation is carried out for conditions when $L(r_c) \gtrsim 0$.

$$\left(\frac{m_{\text{eff}}}{m}\right)_{r_c = r_*} = \left(1 - \frac{3a_1(r_*)}{r_*^3}\right)\left(1 - \frac{3A(r_*)}{r_*^3}\right)$$
$$\times \left(1 + \frac{6a_1(r_*)}{r_*^3}\right)^{-1}. \qquad (44)$$

This expression contains the parameters $A(r_*)$ and $a_1(r_*)$, which are those included in the expansions (10) and (29) for $\eta_0(k,r)$ and $\eta_1(k,r)$. The value of m_{eff}/m is close to unity near r_*. This results from the small values of the coefficient $A(r_*)$ and $a_1(r_*)$ in this region.

V. CONCLUSION

In this paper the peculiarities of electron scattering on the cut-off atomic potential was considered when the cutting radius falls at the polarization ''tail'' of this potential. A similar problem arises in the description of the scattering of an excess electron in liquids with a high mobility (such as liquid Ar, Kr, and Xe). The scattering by an isolated atom with high polarizability is characterized by the nonmonotonic dependence of the partial phase shifts $\delta_0(k)$ and $\delta_1(k)$. For s-wave scattering, it is due to the negative sign of the scattering length. For p-wave scattering, it results from the positive contribution of the polarization scattering in the phase shift $\delta_1(k)$. In both cases the partial phase shifts are positive at small k, suggesting that the long-range polarization attraction is the dominant component in the interaction between the electron and the atom.

As the action radius of the atom-electron potential (for the cut-off potential) is limited, the contribution of the polarization part in the scattering decreases. The partial phase function $\eta_\ell(k,r)$ gives information about the phase shifts on the cut-off potential. The parameters determining the phase shifts are functions of the cut-off radius. For s-wave scattering these parameters are the coefficients in the expansion $\eta_0(k,r)$ in terms of wave number k powers, such as the scattering length $L(r)$ and the ''effective volume'' $A(r)$. For $L(r)$ the analytical expression (8) is obtained. It shows how the transition from the negative scattering length of the iso-

lated atom to the positive one of the cell occurs with a cell radius decrease. Our study of the phase function $\eta_0(r,k)$ shows that for small values of k, the set of $\eta_0(r,k)$ as a function of r changes their sign at the same value r_* (Fig. 3). It means that s-wave scattering of slow electrons is weak in a fluid with the density $N_* = (4\pi r_*^3/3)$. At this density the mobility of thermalized electrons $\mu(N)$ as a function of liquid density has a maximum.[28–30] This striking qualitative effect is a result of weakening of the long-range polarization interaction between an electron and an atom in the liquid. In the present paper this weakening is simulated by cutting the electron-atom potential on the Wigner-Seitz cell boundary.

Another feature of the scattering by the cut-off potential is a small value of the effective volume $A(r)$ for $r \lesssim (\alpha/a_0)^{1/2}$. As a consequence, the phase function $\eta_0(k)$ is almost linear in the wide range of wave-number values. For a slow electron the s-wave scattering determines the scattering cross section $\sigma = 4\pi\eta_0^2/k^2$, which is constant for the cut-off potential. This behavior simulates an almost constant scattering cross section of excess electrons in liquids near the triple points.[12,31] In gaseous Ar, Kr, and Xe the scattering cross section for slow electrons decreases as a function of electron energy. In corresponding liquids this cross section is constant up to considerable values of the energy. As a result, the mobility of hot electrons (the electrons whose mean energy is higher than a fluid temperature) $\mu(E)$ as a function of the external electric-field strength E is different in liquids and gases.[28–30] We plan to study this problem in a future paper.

For the isolated atom with high polarizability, the dependence $\delta_1(k)$ is nonmonotonic and positive for small k. It follows from the polarization attraction between an electron and an atom. The diminution of the polarization part of the potential leads to the change in sign of the $\eta_1(r,k)$ phase function. For small-r values the phase function $\eta_1(r,k)$ is negative for all values of k, which results from the short-range character of the cut-off potential. Hence there is the vicinity of a point $\tilde{r} = 1.5$ where the phase function $\eta_1(r,k)$ passes through zero. At this point the coefficient of the first term of the $\eta_1(r,k)$ expansion becomes zero. The coefficient characterizes the behavior of the p-wave phase shift for small k.

The effective mass of excess electrons in dense media is calculated by using the p-wave phase function in the framework of the Bardeen theory[23] in the Wigner-Seitz model. In a dense medium (small r_c) the ratio m_{eff}/m is small and increases with increasing r_c.

Recently, the effective mass has been calculated[11,15] within the framework of the Wigner-Seitz model of a liquid. The results of this calculation are different. In the paper of Ref. 15 the relatively slow growth of the m_{eff}/m ratio with decreasing density was observed. For the liquid the m_{eff}/m changes are small and the ratio tends to unity only for the dilute gas. The steeper increase of m_{eff}/m as a function of density has been obtained in Ref. 11. The m_{eff}/m values approach unity at the liquid density near the N_* point. The p-wave phase shift has been calculated in Ref. 11 using the Born approximation.

Our calculation demonstrates the strong growth of m_{eff}/m as a function of medium density. We used the accurate p-wave phase shifts obtained by the variable-phase method.

The analytical expression for m_{eff}/m is obtained for the point r_*, where the effective scattering length of excess electrons in the liquid equals zero. The ratio m_{eff}/m is close to unity in the vicinity of r_*. This is a result of small magnitudes of the coefficients $A(r_*)$ and $a_1(r_*)$ of the s- and p-wave phase functions.

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