

Conduction Band Energy of Excess Electrons in Liquid Argon.

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Abstract. – The energy V_0 of the quasi-free electron state in liquid argon is calculated as a function of the number density n in the range $(0.001 \div 0.021) \text{ \AA}^{-3}$. In the calculation, Lekner's theory for the scattering of excess electrons in liquid argon is followed, but modern, first-principles pseudopotentials are used. By comparing to experiment, it is shown that our results correctly describe not only the order of magnitude of $V_0(n)$, but also the shape of the curve, which shows a minimum at $n = 1.2 \cdot 10^{22} \text{ atoms/cm}^3$. These new results are in much closer agreement with experimental data than other existing calculations.

There is a considerable interest in the behaviour of excess electrons in dielectric fluids [1]. Transport of electrons injected in nonpolar insulating liquids is characterized by electron mobilities similar to those encountered in crystalline solids [2]. However, the behaviour of the electron mobility over a wide range of liquid densities is still not fully understood. In particular, there is no theoretical model providing a precise and comprehensive explanation of this behaviour even for the case of liquid argon, which is simpler than most others, because extra electrons in it are in the quasi-free state.

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REININGER *et al.* [3] measured the quasi-free electron energy V_0 in liquid argon as a function of the liquid density n and observed a minimum in $V_0(n)$ at a density very near that corresponding to the well-known mobility maximum. BASAK and COHEN [4] interpreted these results by relating the mobility to a deformation potential produced by local density fluctuations. These authors suggested that, at the minimum of V_0 , the potential fluctuations were minimal causing a minimum in the electron scattering and a maximum in the mobility. They also calculated the density dependence of the conduction band minimum using Lekner's potential [5] in the framework of the Wigner-Seitz approximation. However, the minimum of $V_0(n)$ they obtained was shifted towards lower densities in comparison to that found from experiment. On the other hand, values of the ground-state energy relative to the vacuum level were systematically too low by about 0.2 eV.

As noticed by JAHNKE *et al.* [6], LEKNER [5] used in his calculations the modified static Holtmark [7] potential. The core part of this potential cannot be considered very accurate. In fact, Lekner's requirement that the potential reproduce the experimental low-energy electron-atom scattering cross-sections is not a sufficient constraint for the quality of the core part, since it is well known that the long-range polarizability interaction dominates such cross-sections.

The density dependence of the quasi-free electron ground-state energy calculated by REININGER *et al.* [3] using another simple hard-core pseudopotential previously introduced by SPRINGETT *et al.* [8] does not compare well with the experimental data either. In that case, the theoretical curve describing the variation of the ground-state energy with density is monotonic without any minimum.

We suspected that some of the above problems could derive from the rather primitive pseudopotentials used to simulate the neutral argon atoms in the previous work, and decided to perform a new calculation of $V_0(n)$ in liquid argon, using recently developed, norm-conserving pseudopotentials [9], which describe well the core part of the atom. These pseudopotentials are first-principles ones, in that they are derived from all-electron, local density-functional atomic calculations. In the local density-functional approximation [10], the ground-state energy of a system of interacting electrons in an external (nuclear) potential is expressed as a functional of the electron density $\rho(r)$

$$E(\rho) = T(\rho) + E_{\text{Coul}}(\rho) + \int V_{\text{ext}}(r)\rho(r) dr + E_{\text{xc}}(\rho), \quad (1)$$

where $T(\rho)$ is the kinetic energy of the noninteracting electrons,

$$E_{\text{Coul}}(\rho) = \frac{1}{2} \iint \frac{\rho(r)\rho(r')}{|r-r'|} dr dr' \quad (2)$$

is the usual electrostatic Coulomb energy of the electrons,

$$V_{\text{ext}}(r) = -\frac{Z}{r} \quad (3)$$

is the nuclear potential (Z being the nuclear charge), and $E_{\text{xc}}(\rho)$ is the exchange-correlation energy. In the construction of norm-conserving pseudopotentials for the periodic table, the Ceperley-Alder results for the homogeneous electron gas [11, 12] were adopted for the exchange-correlation energy, and smooth, nonlocal (l -dependent) bare-ion pseudopotentials were extracted from the full-core atomic calculations. Once these bare-ion potentials are self-consistently screened by their valence electrons, they yield identical valence eigenvalues and nodeless valence wave functions which exactly agree with the full-atom ones

outside the core region [9]. Most relevant to our task is the related ability of these potentials to reproduce the scattering properties of the full-core atom over a wide energy range around the valence eigenvalues (~ 20 eV, typically) [9]. In addition to the tabulation of bare-ion potentials, a fit to neutral-ion, screened pseudopotentials was also obtained [13] in the following parametrized form:

$$V_{\text{ps}}^l(r) = \sum_{i=1}^6 A_i \exp[-\alpha_i r^2] + \sum_{i=1}^8 (B_i^l + r^2 B_{i+3}^l) \exp[-\beta_i^l r^2]. \quad (4)$$

Roughly speaking, the first term in eq. (4) describes the screened Coulomb potential and the second one the short-range, angular-momentum-dependent part related to the orthogonality to the inner core. The parameters A_i , B_i^l , α_i , and β_i^l (in atomic units), describing the neutral-argon pseudopotential for $l = 0$, are listed in table I.

TABLE I. – List of the $l = 0$ neutral-argon pseudopotential parameters (in atomic units) used in eq. (4).

A_i	α_i	B_i	β_i
– 406.606 649 7	0.70	– 41 516.481 283 2	4.67
2641.300 757 4	0.84	27 994.623 884 0	5.28
– 5602.331 795 8	0.95	13 544.887 928 4	6.26
6000.089 283 2	1.06	8 595.351 284 1	4.67
– 2642.854 755 5	1.13	26 122.872 231 5	5.28
– 4.418 327 1	3.15	3 945.668 725 3	6.26

Since the aim of our work was to accurately describe an excess electron in liquid argon, it seemed reasonable to us to smoothly match to the neutral-argon pseudopotential a polarization tail just described in the form

$$V_{\text{pol}}(r) = -\frac{1}{2} \left(\frac{\alpha}{r^4} \right) \exp[-(r_0/r)^\eta], \quad (5)$$

using r_0 and η as adjustable parameters i) to optimize the fit to the gas-phase, low-energy electron-argon total scattering cross-section data, and ii) to maintain the smoothness of our single-atom pseudopotential $V_t^l = V_{\text{ps}}^l + V_{\text{pol}}$ in the sewing region of the two terms. This correction is necessary because the local density approximation for exchange and correlation does not give the correct long-range behaviour of neutral atomic potentials. The way we introduce it, on the other hand, is such that this empirical correction does not spoil the quality of the core part of the potential, since our polarizability tail takes off quite far from the core region. r_0 and η used in the present calculations were equal to 3.90 a.u. and 3.95, respectively.

Using $V_t^{l=0}$ and the atomic polarizability $\alpha = 11$ a.u. for the argon atom [14], the calculated scattering length related to the zero-energy cross-section was found to be equal to -1.4 a.u., which agreed well with that obtained recently from experiment (-1.45 ± 0.02 a.u.) [15].

In order to find the effective potential acting on the excess electron in the liquid, we followed the method given by LEKNER [5]. The potential is calculated within the muffin-tin approximation and is taken to be the superposition of the single-site potentials inside each

muffin-tin sphere and as zero outside, namely

$$U_{\text{eff}}(r) = \begin{cases} V_t^{l=0}(r)f(r) + \frac{2\pi n}{r} \int_0^\infty ds sg(s) \int_{|r-s|}^{r+s} dt tf(t) V_t^{l=0}(t) - U_0, & r < r_m, \\ 0, & r > r_m. \end{cases} \quad (6)$$

In view of the facts that i) the excess electron in the bottom of the conduction band is of purely s character and ii) the contribution from nearest and farther neighbours to the central cell potential comes from potential tails which are the same for all angular momenta, it seemed reasonable to use just the s -potential in eq. (6). U_0 is the value of the first maximum of the first two terms in eq. (6) (corresponding to the fact that the electron only sees differences in the potential), which occurs at the muffin-tin radius r_m . r_m and U_0 are thus fixed simultaneously here. The Lorentz screening function, which approximately includes the effect of induced atomic polarization when the electron is between the atoms, was calculated self-consistently according to the following formula [5]:

$$f(r) = 1 - \pi n \alpha \int_0^\infty ds \frac{g(s)}{s^2} \int_{|r-s|}^{r+s} dt \frac{f(t)}{t^2} \Theta(r, s, t), \quad (7)$$

where

$$\Theta(r, s, t) = \left(\frac{3}{2s^2} \right) (s^2 + t^2 - r^2)(s^2 + r^2 - t^2) + (r^2 + t^2 - s^2), \quad (8)$$

s is the distance between two atoms, r and t are the distances of these two atoms from the electron, $g(s)$ is the pair correlation function given by

$$g(s) = 1 + \frac{1}{2\pi^2 ns} \int_0^\infty [S(k) - 1] \sin(ks) k dk, \quad (9)$$

and $S(k)$ is the structure factor calculated according to the theory given by ASHCROFT and LEKNER [16]. In the calculation, Lekner's hard-core diameter was taken to be equal to 3.44 Å [5].

In the Wigner-Seitz approximation, the ground-state energy of an excess electron is the energy at which the s -wave single-site radial wave function has zero derivative at the Wigner-Seitz radius r_s , which is defined by the relation

$$r_s = \left(\frac{3}{4\pi n} \right)^{\frac{1}{3}}. \quad (10)$$

At all densities considered in the present work, we have $r_s > r_m$. Consequently, the s -wave radial wave function in this case may be written as

$$\psi_0(r) = \left(\frac{\text{const}}{kr} \right) [\sin(kr) - k \langle a \rangle \cos(kr)], \quad (11)$$

where $\langle a \rangle$ is the scattering length, obtained from the numerical integration of the $l=0$

Schrödinger equation for U_{eff} . Then k_0 may be calculated by solving the equation

$$k_0 \operatorname{tg}(k_0 r_s) = \frac{r_s + \langle a \rangle}{(1/k_0^2) - r_s \langle a \rangle}. \quad (12)$$

In fig. 1, we show the results of our calculation for the ground-state energy $V_0 = \hbar^2 k_0^2 / 2m_0 + U_0$ of an excess electron in liquid argon as a function of liquid density in the range $(0.001 \div 0.021) \text{ \AA}^{-3}$. The effective electron mass at the bottom of the conduction band was assumed to be equal to the free-electron mass m_0 . The solid curve *b*) of fig. 1 represents our theoretical results, while the broken line *c*) is a fit to the experimental data of Reininger *et al.* [3]. The various symbols shown in fig. 1 give the experimental results obtained by

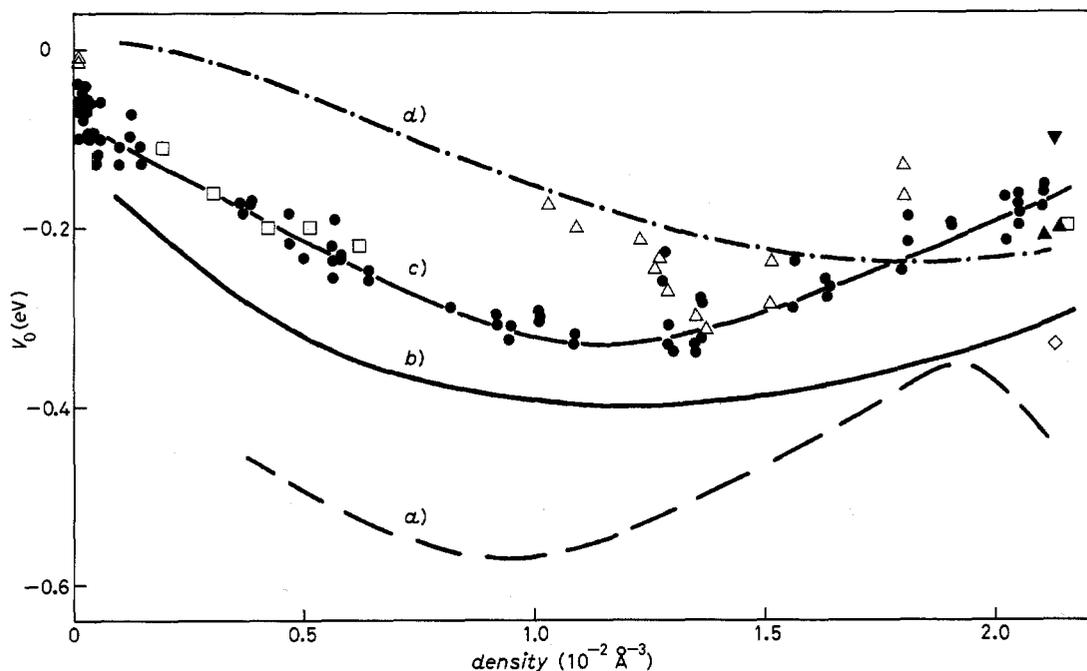


Fig. 1. – Density dependence of the conduction band energy V_0 in liquid argon: *a*) theoretical results obtained by BASAK and COHEN in ref. [4]; *b*) present work; *c*) smooth curve representing the experimental data (●) by REININGER *et al.* (ref. [3]); *d*) theoretical results obtained by REININGER *et al.* (ref. [3]) using the simple pseudopotential model proposed by SPRINGETT *et al.* (ref. [8]) with a constant hard-core radius of 0.918 Å. The experimental results of $V_0(n)$ obtained at certain densities by other authors are also presented in the figure: □ MESSING and JORTNER (ref. [17]); ▲ TAUCHERT *et al.* (ref. [18]); ▼ VON ZDROJEWSKI *et al.* (ref. [19]); △ ALLEN and SCHMIDT (ref. [20]); ◇ HALPERN *et al.* (ref. [21]).

different authors [17-21] as listed in ref. [3]. As we can see, our calculated $V_0(n)$ curve compares well with experiment. In particular, a minimum of $V_0(n)$ is found at a density equal to 0.012 \AA^{-3} , which is in excellent agreement with the experimental results. The discrepancies existing between the calculated and experimental $V_0(n)$ curves are observed to be much smaller than those resulting from Basak and Cohen [4] or Reininger *et al.* [3] calculations. For the sake of comparison, we have also shown in fig. 1 the $V_0(n)$ curves calculated by these authors (curves *a*) and *d*)).

In conclusion, we would like to emphasize the importance of using a potential which adequately describes the core region of the atom. The simple calculation presented here, which differs from previous ones for a more accurate pseudopotential, is enough to yield a dependence of the quasi-free-electron energy V_0 on the density n in much closer agreement with measured data.

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