Table I. Rayleigh-to-Raman cross-section ratios and absolute Raman cross sections from benzene at 6328 Å. $\Delta\nu$ = wave number displacement, δ_0 = absolute Rayleigh cross section, δ_R = absolute Raman cross section.

$\Delta\nu$ (cm^{-1})	δ_0/δ_R	$10^{28}\delta_R$ (cm^2)
992	220	0.56
1583-1606	1980	0.062
3049-3062	250	0.50

Together with the present measurements this allows for precise calculation of both Raman- to Rayleigh cross-section ratios and absolute Raman cross sections. Results are summarized in Table I for the aforementioned benzene Raman frequencies; the values of the total cross sections carry an uncertainty of about 20%. We are presently improving the apparatus for extensive measurements on other molecular liquids.

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NEGATIVE IONS IN LIQUID HELIUM II†

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This Letter presents a calculation which supports the conjecture that negative ions in liquid helium II are self-trapped electrons.[1,2] The mechanism responsible for this trapping is the electron-helium interaction produced by the requirement that the electron wave function be orthogonal to the 1s core states of a helium atom and modified by the long-range attraction due to polarization. A self-trapped electron occupies a cavity or bubble whose surface is a shell of polarized helium atoms. To test the validity of this model one must know how effectively an electron repels helium from a volume in the liquid. A measure of this ability is the energy of repulsion between electrons and helium atoms which is calculated here.

To investigate the properties of such an electron moving in liquid helium, the model of an electron propagating in a periodic lattice is used for calculation from first principles. In replacing the liquid structure by a solid structure, one hopes to estimate the behavior of an electron in a dense fluid. Only for certain energies will an electron be able to move through this periodic array without attenuation. The lowest energy satisfying this condition will be the kinetic energy required for an electron to penetrate into liquid helium. Such an energy barrier has been found experimentally by Sommer.[3]

The wave equation is written down for the scattering of a particle of energy k^2 by a lattice of Fermi pseudopotentials[4] representing the electron-helium interaction (units of $\hbar = 1$, $2m = 1$ are used). Only the S-wave, low-energy term of the pseudopotential is retained:

$$(\nabla^2 + k^2)\psi(\vec{r}) = 4\pi l \sum_{\vec{a}} \delta(\vec{r}-\vec{a}) \frac{\partial}{\partial|\vec{r}-\vec{a}|}[|\vec{r}-\vec{a}|\psi(\vec{r})], \quad (1)$$

where l is the scattering length. Now write

$$\psi(\vec{r}) = \sum_{\vec{b}} \varphi_{\vec{b}} e^{i\vec{b}\cdot\vec{r}}, \quad (2)$$

where the $\vec{b}$ are 2π times the reciprocal lattice vectors generated by the lattice $\vec{a}$. Thus,

$$\psi(\vec{r}) = -\frac{16\pi^2 l}{\Delta} \sum_{\vec{b}} \frac{e^{i\vec{b}\cdot\vec{r}}}{b^2 - k^2}, \quad (3)$$

where Δ is the volume of the unit cell of the lattice $\vec{a}$. An integral representation for the

Fourier coefficients is introduced:

$$\frac{1}{b^2-k^2}=\int_0^\theta \exp[(k^2-b^2)t]dt+\frac{\exp[(k^2-b^2)\theta]}{b^2-k^2}, \tag{4}$$

and an Ewald[5] transformation is performed yielding sums which are rapidly convergent. Thus,

$$\psi(\vec{r})=-\frac{16\pi^2 l}{\Delta}\Bigg\{2\Delta(4\pi)^{-3/2}\Bigg[\sum_{\vec{a}}\frac{\pi^{1/2}}{|\vec{r}-\vec{a}|}\operatorname{erfc}\left(\frac{|\vec{r}-\vec{a}|}{2\theta^{1/2}}\right)+\sum_{n=1}^{\infty}\frac{(-k^2)^n}{2n!}\Bigg\{\sum_{\vec{a}}(-|\vec{r}-\vec{a}|^2)^n$$

$$\times\Bigg[\frac{\pi^{1/2}}{|\vec{r}-\vec{a}|}\operatorname{erfc}\left(\frac{|\vec{r}-\vec{a}|}{2\theta^{1/2}}\right)-\frac{2\theta^{1/2}}{|\vec{r}-\vec{a}|^2}\exp\left(\frac{|\vec{r}-\vec{a}|^2}{4\theta}\right)\sum_{m=0}^{n-1}\left(\frac{-\theta}{|\vec{r}-\vec{a}|^2}\right)^m\frac{(2m)!}{m!}\Bigg]\Bigg\}\Bigg]$$

$$+\sum_{\vec{b}}\frac{\exp[(k^2-b^2)\theta]e^{i\vec{b}\cdot\vec{r}}}{b^2-k^2}\Bigg\}, \tag{5}$$

where

$$\operatorname{erfc}(x)=1-\operatorname{erf}(x)=1-\frac{2}{\pi^{1/2}}\int_0^x e^{-u^2}du.$$

The application of the boundary condition at the surface of the hard cores yields an algebraic equation for k^2.

If the wave function is generalized to a Bloch wave function with nonzero wave vector, the same analysis is performed and the reciprocal mass tensor is calculated. Thus k^2 and m^* are obtained as a function of the number density n of liquid helium.

For this model to be effective in calculating the properties of an electron in liquid helium, the ground-state energy should not depend too strongly on the particular lattice selected. To date, calculations have been performed on the sc, bcc, and fcc lattices with the hcp and diamond structures to be done in the future. The values of k^2 for $l=1.46a_0$ and liquid-helium density for the sc, bcc, and fcc cases are 1.71, 1.76, and 1.77 eV, respectively. Thus k^2 is fairly insensitive to lattice structure which confirms the expectation that a lattice model would be a good replacement for a liquid.

The results of this calculation are illustrated in Fig. 1 by a plot of k^2/nl versus $n^{1/3}l$ as suggested by Huang and Yang.[6]

Calculations have also been done using two values of the scattering length: (1) Moiseiwitch's[7] value of $1.46a_0$, which includes exchange, and (2) a value of $1.13a_0$ which is obtained by using the results of O'Malley, Spruch, and Rosenberg[8] to correct Moiseiwitch's value for the effect of polarization as follows:

O'Malley, Spruch, and Rosenberg define a short-range potential

$$\Delta V(r)\equiv V(r)+(\hbar^2/2\mu)\beta^2/r^4,$$

where $\beta^2=\alpha/a_0$, α = atomic polarizability, a_0 = Bohr radius, and μ = mass of incident particle, and solve

$$\left[\frac{d^2}{dr^2}-\frac{L(L+1)}{r^2}+\frac{\beta^2}{r^4}-\frac{2\mu}{\hbar^2}\Delta V(r)+k^2\right]u(r)=0, \tag{6}$$

subject to the boundary conditions

$$u(0)=0,\quad u(r)\underset{r\to\infty}{\longrightarrow}v_{ps}(r)+Bv_{pc}(r),$$

where $v_{ps}(r)$ and $v_{pc}(r)$ are the polarization-

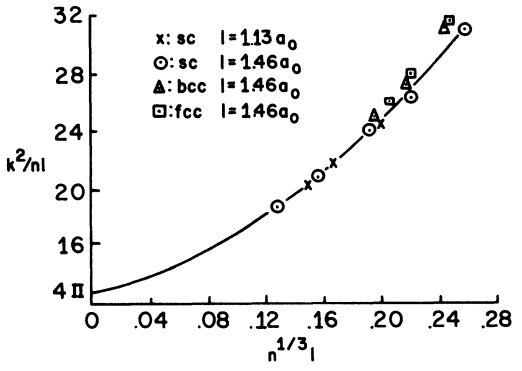

FIG. 1. Ground-state energy of an electron in a lattice as a function of number density and scattering length.

potential analogs of the usual free solutions $j_L(kr)$ and $n_L(kr)$ of scattering theory. But if the short-range potential is the pseudopotential $4\pi l\delta(\vec{r})(\partial/\partial r)(r\ )$, this is equivalent to the boundary condition $u(l)=0$, and thus one may replace Eq. (6) by

$$\left[\frac{d^2}{dr^2}-\frac{L(L+1)}{r^2}+\frac{\beta^2}{r^4}+k^2\right]u(r)=0, \tag{7}$$

subject to $u(l)=0$ and

$$u(r) \underset{r>l}{=} v_{ps}(r)+Bv_{pc}(r).$$

For the case $k^2=0$,

$$v_{ps}(r)+Bv_{pc}(r)=j_L(\beta/r)-B_0n_L(\beta/r).$$

Thus equation (5.6) of reference 8 defining the scattering length A which includes the effect of polarization in terms of the S-wave phase shift $\eta(0)$,

$$\lim_{k\to 0}[\tan\eta(0)/k]\equiv -A=\beta/B_0,$$

leads to

$$A=-\beta\frac{n_0(\beta/l)}{j_0(\beta/l)}. \tag{8}$$

Using the value of 0.203 Å^3 for the atomic polarizability of helium[9] in $\beta=(\alpha/a_0)^{1/2}$, one finds $A=1.13a_0$. Thus the scattering length of $1.13a_0$ which includes the polarization effect agrees with O'Malley[10] and LaBahn and Callaway.[11]

At liquid helium densities, and for a simple cubic lattice $l=1.46a_0$ yields $k^2=1.71$ eV and $l=1.13a_0$ yields $k^2=1.09$ eV. These values are to be compared with Sommer's[3] experimental value of 1.3 eV which may be in error by 30%.

This large potential barrier thus appears to rule out the model of an essentially free electron.[12] The process of thermalization whereby electrons with this large energy slow down to bubbles with energies of about 0.2 eV is not understood. As Fig. 1 suggests, low-density regions in helium are associated with low energies for the electron. Since helium is a liquid, there are density fluctuations and the electron will prefer a site of low density. Presumably, the extra energy of the electron will be radiated away as phonons as it disturbs the liquid helium in its pursuit of thermalization.

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