radiation through the inverse bremsstrahlung processes and ionize the gas by excitational collisions with the gas atoms as described in Phelps's work.[15] By using the concept of the mutual absorption coefficient for the photon-electron interaction given by Wheeler and Wildt[16] and the elastic and excitational collision cross section given by Massey and Burhop,[17] and assuming the rate of ionization to be limited by the rate of excitation to the first excited state, the electron density has been computed for the conditions shown in Fig. 2. The results (solid lines, Fig. 2) are in qualitative agreement with the experimental data and show similar pressure dependence. The possibility of production of a small amount of high-energy electrons by photon ionization which ionize the gas by impact without the inverse bremsstrahlung process can also be excluded by cross-section considerations.[9]

It is therefore concluded that the ionization process in the argon gas irradiated by a laser beam is inverse bremsstrahlung and electron inelastic collisions. The evidence supporting the electron impact process in high-pressure gases has recently been published.[18]

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ELECTRON-HYDROGEN IONIZATION: THE ASYMPTOTIC FORM OF THE WAVE FUNCTION AND THE THRESHOLD BEHAVIOR OF THE CROSS SECTION

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The problem of the ionization of atomic hydrogen by electron impact is a fundamental problem involving the wave function of three separated charged particles. In addition to its theoretical interest, the problem is of considerable current importance because recent observations of the elastic resonances in electron-hydrogen scattering[1] are limited in accuracy as a result of the theoretical uncertainty of the true shape of the ionization cross section, whose starting point is a key reference point in determining the experimental energy scale.

Although there have been numerous approximate calculations of the ionization cross section of atomic hydrogen by electron impact, it is only comparatively recently that attempts have been made to put this problem on a more

rigorous theoretical footing. Peterkop[2] and later, but largely independently, Rudge and Seaton[3,4] have derived an asymptotic form of the wave function. This asymptotic form can be used to determine a phase factor which must be known in order that an independently derived relation between direct and exchange ionization amplitudes[2] be useful. In addition, this asymptotic form is, in the important region of configuration space, proportional to the complex conjugate of a function Φ, a product of two Coulomb waves whose charges depend on the vector velocities of the outgoing particles. This is the underlying basis upon which the latter[3,4] have derived a linear threshold law for ionization.

The purpose of this note is to point out inadequacies in the above asymptotic form, and to show by means of a simpler model that the neglect of certain terms which must be made in deriving it is not justified. The two arguments taken together indicate that the asymptotic form is not correct. This in turn has obvious negative implications about the aforementioned phase factor and about the validity of a linear threshold law.[5] Finally, we shall propose an asymptotic form of the wave function which is more acceptable, albeit less explicit, than the above.

We restrict ourselves to the total S-wave system. The previous analyses[2,3] have been made in terms of hyperspherical coordinates:

$$\rho \equiv (r_1^2 + r_2^2)^{1/2}, \tag{1}$$

$$\alpha \equiv \tan^{-1}(r_2/r_1). \tag{2}$$

In terms of these coordinates, the S-wave Schrödinger equation becomes

$$\left[\frac{\partial^2}{\partial\rho^2}+\frac{1}{\rho}\frac{\partial}{\partial\rho}+\frac{1}{\rho^2}\frac{\partial^2}{\partial\alpha^2}+\frac{2}{\rho}W(\alpha,\theta_{12})+\frac{4}{\rho^2\sin^2 2\alpha}\times\frac{1}{\sin\theta_{12}}\frac{\partial}{\partial\theta_{12}}\sin\theta_{12}\frac{\partial}{\partial\theta_{12}}+E\right]\psi(\rho,\alpha,\theta_{12})=0, \tag{3}$$

where energies are in rydbergs, lengths in Bohr radii; ψ is $r_1 r_2$ times the complete S-wave function, and

$$W(\alpha,\theta_{12}) = (\sin\alpha)^{-1}+(\cos\alpha)^{-1}-(1-\sin 2\alpha\cos\theta_{12})^{-1/2}. \tag{4}$$

The asymptotic form of Refs. 2 and 3 can be derived from (3) by neglecting all terms which depend on ρ^{-2}. In this way Eq. (3) becomes an ordinary differential equation in ρ whose solution depends only parametrically on the remaining coordinates α and θ_{12}. In particular, that solution which represents an outgoing radial current in this approximation is

$$\lim_{\rho\to\infty}\psi_c = \frac{f(\alpha,\theta_{12})}{\rho^{1/2}}\exp\left\{i\left[E^{1/2}\rho+\frac{W\ln(2E^{1/2}\rho)}{E^{1/2}}\right]\right\}, \tag{5}$$

where $f(\alpha,\theta_{12})$ is a function whose specification we need not here consider. If one operates on this function with the ρ^{-2} terms that were neglected in Eq. (3), one finds that the leading order term is

$$-\frac{1}{\rho^2}\left[\left(\frac{\partial W}{\partial\alpha}\right)^2+\frac{4}{\sin^2 2\alpha}\left(\frac{\partial W}{\partial\theta_{12}}\right)^2\right]\left(\frac{\ln 2E^{1/2}\rho}{E^{1/2}}\right)^2\psi_c. \tag{6}$$

This remainder term being also essentially of order ρ^{-2} appears consistent with the neglect of such terms in the first place.

It should be noted that this consistency argument is not foolproof, because it is possible that (a) a solution with asymptotic form of Eq. (5) satisfying all other required boundary conditions does not exist, (b) there is another solution for which the terms in question cannot be neglected. Indeed if (a) is the case, then (b) follows.

If (5) were the correct asymptotic form, it would have to be valid for both space-symmetric (singlet) and space-antisymmetric (triplet) solutions. We shall consider the singlet case in this paragraph. The phase in (5) depends on W. But from (4), W is proportional to the total potential energy and therefore has singularities where the potential has singularities; one of these is at $r_{12}=0$, which can occur for large values of $\vec{r}_1$ and $\vec{r}_2$ where Eq. (5) is supposed to be valid. Nor can anything in $f(\alpha,\theta_{12})$ cancel this singularity since the W term is multiplied by a function of ρ. However, a correct quantum mechanical solution has a cusp where the potentials are singular.[6] Secondly, the quantity by which this function differs from being an exact solution, the expression (6), is (for a given ρ) even more infinite than the potential itself at $\vec{r}_1=\vec{r}_2$. Rudge and Seaton[3,4] have not mentioned these difficulties. Peterkop[7] has stated that this singularity recedes to infinity by which we presume he means that since (5) represents an asymptotic expansion, the region where the asymptotic form becomes valid demands that ρ be indefinitely large as $\vec{r}_1\to\vec{r}_2$. This argument is circular: There is a correct asymptotic form of the wave function including the region $\vec{r}_1=\vec{r}_2$; the problem is, given the Schrödinger equation as a partial differential

equation, to find that solution. When one has found that solution, one can inquire as to whether it is close to another (approximate) solution of (3) which does not obey that boundary condition. In fact the form of (5) is reminiscent of a WKB type of approximation, and the diverging phase along singularities of the potential is a characteristic defect of that approximation. The crucial question of whether a WKB description is valid depends on the energies and masses of the particles involved. We shall talk of the energy dependence below, but it is clear that the approximation is much more compelling for, say, proton-hydrogen ionization than for e-H ionization.

We shall next show by considering a simplified model that there almost certainly are solutions of (3) for which one cannot neglect ρ^{-2} terms even in the asymptotic region. The model consists of replacing W in Eq. (3) by its spherical average $W_0 = \frac{1}{2}\int W \sin\theta_{12} d\theta_{12}$:

$$W_0 = 1/\sin\alpha, \quad r_1 > r_2, \qquad = 1/\cos\alpha, \quad r_1 < r_2. \tag{4a}$$

It is clear that going through the same arguments which led to ψ_C would in this case lead to a solution with asymptotic form

$$\lim_{\rho\to\infty} \psi_C^{(0)} = f_0(\alpha)\rho^{-1/2}\exp\{i[E^{1/2}\rho + E^{-1/2}W_0 \ln(2E^{1/2}\rho)]\}. \tag{5a}$$

Here the diverging phase along $\vec{r}_1 = \vec{r}_2$ is transformed into a cusp (discontinuity of slope) along $r_1 = r_2$, but in essence inadequacy remains.[6] Here, however, we can write down exact solutions neglecting no terms in the W_0 equation. An example of such a solution is ($\cos\alpha > \sin\alpha$)

$$\psi^{(0)}_{q_1 q_2} = e^{iq_1\rho\cos\alpha} F_{q_2}(\rho\sin\alpha), \tag{7}$$

where

$$q_1^2 + q_2^2 = E, \tag{8}$$

and $F_{q_2}(x)$ is the $l = 0$ regular Coulomb wave function[8]:

$$\lim_{x\to\infty} F_q(x) = \sin(qx + q^{-1}\ln 2x + \sigma_0). \tag{9}$$

Note that for $\psi^{(0)}_{q_1 q_2}$ to be a solution, one cannot neglect the $\rho^{-2}\partial^2/\partial\alpha^2$ term in the model Schrödinger equation. In particular, $\partial^2/\partial\alpha^2$ brings down ρ^2 which cancels the ρ^{-2} factor making this term nonvanishing even in the asymptotic region. (Thus this term, in spite of being formally of the order ρ^{-2}, is in fact more important than the Coulombic potential term.)

Considering the totality of solutions (all q_1, q_2 for a given E), one cannot say beforehand whether the sum [cf. the expression (14)] yields a function for which one can neglect the $\partial^2/\partial\alpha^2$ term. In the case of short-range forces the elementary ionization (S-wave) solutions are[8]

$$e^{ik_1 r_1}\sin k_2 r_2 = e^{ik_1\rho\cos\alpha}\sin(k_2\rho\sin\alpha), \tag{10}$$

for which one can also not neglect the $\partial^2/\partial\alpha^2$ term. Nevertheless, when one sums the totality of such solutions, one arrives at a function[3]

$$\lim_{\rho\to\infty} \psi_S = f_S(\alpha, \theta_{12})\rho^{-1/2}\exp(iE^{1/2}\rho), \tag{11}$$

for which one can neglect the $\rho^{-2}\partial^2/\partial\alpha^2$ derivative. In the case of the Coulomb forces, however, the inadequacy of (5) and (5a) along $\vec{r}_1 = \vec{r}_2$ ($r_1 = r_2$) shows that the composite solution will not allow this second derivative to be neglected. [Notice that (11) does not contain these difficulties along the line $\vec{r}_1 = \vec{r}_2$. If there is a short-range singularity between particles 1 and 2, the cusp condition can nicely be incorporated in f_S.]

When the model Schrödinger equation is written in terms of r_1 and r_2,

$$(\partial^2/\partial r_1^2 + \partial^2/\partial r_2^2 + 2/r_2 + E)\Phi_0^{(0)}(r_1 r_2) = 0, \quad r_1 > r_2, \tag{12}$$

it can be seen to be the zeroth-order problem of the nonadiabatic theory of electron-hydrogen scattering.[9] For energies below the ionization threshold ($E < 0$), the exact solution can be written in terms of exact separable solutions:

$$\Phi_0^{(0)} = A\frac{\sin kr_1}{k}R_{1s}(r_2) + \sum_{n=1} C_n \exp(ik_n r_1)R_{ns}(r_2) + \int_0^\infty C(\kappa_2)e^{-\kappa_1 r_1}F_{\kappa_2}(r_2)d\kappa_2, \tag{13}$$

where

$$E = k_n^2 - n^{-2} = -\kappa_1^2 + \kappa_2^2. \tag{8a}$$

The point is that the coefficients in (13) are determined by the condition that the singlet or triplet boundary condition along $r_1 = r_2$ be smoothly satisfied.[6] Utilizing the continuity conditions, and conservation of current, we have analytically shown in both the singlet and

triplet cases that for energies near ionization threshold, $C_n \propto n^{-3/2}$, which implies that the threshold ionization dependence is proportional to $E^{3/2}$ for the zeroth-order problem.[10]

Above threshold one must augment (13) with terms of the form

$$\int_0^{\sqrt{E}} C(q_2) e^{iq_1 r_1} F_{q_2}(r_2) dq_2. \tag{14}$$

The boundary condition along $r_2 = 0$ is automatically satisfied, and the coefficients $C(q_2)$ are still determined by the boundary condition at $r_1 = r_2$. This boundary condition having been satisfied, the resultant solution will not be subject to the criticism of (and therefore will be different from) Eq. (5a). Peterkop[11] has used an argument of stationary phase to reduce (14) to (5a); however, unlike the case of short-range forces, the resultant expression cannot satisfy Kato's theorem. This would seem to indicate that the method of stationary phase needs further examination in this case.

The individual solutions in (14) describe, in a clear way, the quantum mechanics of the physical situation. The scattered particle moves as an outgoing (free) spherical wave whereas the inner particle moves in the Coulomb field of the nucleus. That this continues to be the case when one considers the full (W) interaction has not been proven. In fact, the semiclassical argument (which corresponds to the function Φ^*) contends that the outer particle sees an r_1^{-1} potential coming from the fact it sees (in the first approximation) a multipole field of the nucleus and the inner electron, the moment of which expands as r_1 itself (due to the inner and outer particle coming out with a constant ratio of their velocities). We, however, consider this argument to be questionable, because quantum mechanically in order to prepare an incident beam of a given energy, one requires a longer and longer wave train. Thus the emerging particles are described by spherical waves, and what the outer particle sees is not an inner particle in a definite orbit but a smeared out probability amplitude which we would expect ultimately to screen the outer electron from the nucleus. This consideration is particularly relevant near threshold where the wavelengths of both emergent particles are large. This is the physical basis upon which we believe that not only is the asymptotic form of ψ_C in Eq. (5) not completely correct, which we have already shown, but not even a very good approximation in the threshold region.

Finally, these considerations indicate that one cannot neglect the term $\rho^{-2}\sin^{-1}\theta_{12}\partial/\partial\theta_{12} \times(\sin\theta_{12})\partial/\partial\theta_{12}$ in the full S-wave problem any more than one can neglect the term $\rho^{-2}\partial^2/\partial\alpha^2$ in the zeroth-order problem. We can find solutions in the presence of this term providing we retain W_0 in place of W. A typical solution is $r_1 h_l(q_1 r_1) F_{lq_2}(r_2) P_l(\cos\theta_{12})$, where h_l and F_{lq_2} are the lth spherical Hankel and Coulomb wave functions, respectively. The most general such wave function incorporates the features of the previous mathematical and physical arguments, and thus we believe it represents the correct asymptotic form of the S-wave function:

$$\lim_{r_1 > r_2 \to \infty} \psi = \sum_{l=0}^{\infty} P_l(\cos\theta_{12}) \int_0^{\sqrt{E}} C_l(q_2) r_1 h_l \times(q_1 r_1) F_{lq_2}(r_2) dq_2. \tag{15}$$

This form is θ_{12} dependent, of course, but being a product of free (spherical) waves and Coulomb waves, it strongly suggests a nonlinear threshold law for ionization.

I would like to thank Professor J. Sucher for incisive and invaluable consultations on this problem. I am indebted to the following colleagues: Dr. K. Omidvar, Dr. R. Drachman, and Dr. I. Cheshire, for valuable discussions. I am also indebted to many visitors to this division for patiently listening to our ideas on this subject and for their own comments. Finally, I would like to thank Dr. J. W. McGowan and M. A. Fineman for very valuable conversations on the experimental aspects of the problem. Although their initial results were obtained before this work was undertaken, it is significant that they do reveal a nonlinearity of the threshold ionization behavior.[12]

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although believable, is not rigorous. It is somewhat unfortunate that in Refs. 3 and 4 the argument is never given nor is any statement made of how rigorously the result is considered to have been derived.

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[11]R. K. Peterkop, private communication.

[12]J. W. McGowan, M. A. Fineman, E. M. Clarke, and H. P. Hanson, to be published. Wannier, Ref. 3, also derived a nonlinear threshold dependence. The experimental nonlinearity that is in question here occurs within a tenth of an electron volt of threshold.

COLLECTIVE MOTION IN LIQUID ARGON†

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Recently Chen et al.[1] have observed well-defined inelastic peaks in the energy distribution of slow neutrons scattered by liquid argon. These inelastic peaks were not resolved by earlier experiments.[2,3] In this note we present independent evidence that the observed inelastic peaks are a real manifestation of collective motion in liquid argon.

Rahman[4] has carried out a classical molecular-dynamics calculation of the Van Hove correlation functions $G_S(r,t)$ and $G_d(r,t)$ for liquid argon. We have used his results to compute the expected inelastic neutron scattering under the conditions of Ref. 1 and find a structure in the energy distribution of scattered neutrons similar to that reported by Chen et al.

We need the double Fourier transforms $S_S(\kappa,\omega)$ and $S_d(\kappa,\omega)$ of the Van Hove correlation functions. This is not feasible on a completely numerical basis from Rahman's results, but Rahman has already given us enough information to carry out the spatial transform analytically. He has found that his data are well fitted by a delayed convolution approximation. For the intermediate scattering function [transform of $G(r,t)$ with respect to r] this implies

$$F_d(\kappa,t) = [S(\kappa)-1]F_S(\kappa,t'), \tag{1}$$

where $S(\kappa)$ is the usual structure factor. The time t' is given by Rahman as

$$t' = t-\tau[1-\exp(-t/\tau)-(t^2/\tau^2)\exp(-t^2/\tau^2)] \tag{2}$$

with $\tau = 1.0\times10^{-12}$ sec. It should be emphasized that this is a fit to the computed correlation functions, and not an approximate theoretical construct. The physical origin of this approximation is not well understood. Furthermore, $F_S(\kappa,t)$ is almost a Gaussian function of κ and can be written in terms of the spatial moments of $G_S(r,t)$ in the form

$$F_S(\kappa,t) = \exp[-\kappa^2\gamma_1(t)]\left\{1+\alpha_2(t)\frac{[\kappa^2\gamma_1(t)]^2}{2!}-[\alpha_3(t)-3\alpha_2(t)]\frac{[\kappa^2\gamma_1(t)]^3}{3!}\right.$$
$$\left.+[\alpha_4(t)-4\alpha_3(t)+6\alpha_2(t)]\frac{[\kappa^2\gamma_1(t)]^4}{4!}-\cdots\right\}, \tag{3}$$