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Low-Energy Elastic Scattering of Electrons and Positrons from Helium Atoms

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In this paper we calculate the electron-helium atom pseudopotential, and from that pseudopotential the cross section for low-energy elastic scattering of electrons from helium atoms. The agreement between experiment and theory is good. In addition, the scattering of low-energy positrons from helium atoms is considered. The case of electron-helium atom scattering is chosen only as an example of the use of the pseudopotential as a natural tool for the study of scattering problems. The numerical calculations demonstrate that the results obtained in this way are of comparable accuracy with the results of more tedious and less instructive approaches. In particular, the use of pseudopotential arguments leads to an easily understood physical description. Moreover, because the pseudopotential approach permits the use of variational procedures, even in the presence of bound (i.e., core) states, the necessary calculations are not difficult to carry through.

I. INTRODUCTION

THE calculation of the cross section for low-energy electron-atom elastic scattering is a subject of continuing interest, both theoretically and experimentally. Now, even the scattering of an electron from a helium atom requires solution of a three-electron problem. The analysis may be simplified on physical grounds by noting that the scattered electron is, to a large extent, independent of the two tightly bound electrons. But in contrast with electron-ion scattering, it does not seem possible to invent a simple potential which accurately describes the scattering. There are primarily three sources of difficulty: These arise from the Pauli exclusion principle and the indistinguishability of electrons, the requirement that the wave function of the scattered electron be orthogonal to the orbitals of the atom, and the necessity to account for distortion of the atom (represented primarily by polarization effects). Of course, it is always possible to solve the atom-plus-electron problem completely, without making the atom-scattered electron separation, by using a large computer. However, exact solutions of the type cited are not known even for small atoms and molecules. In addition to the difficult computational problems which arise in such an approach, there are other reasons for searching for simple methods. It is easier to understand a scattering process when the interaction can be expressed in terms of a potential. This feeling leads to the search for some sort of quasipotentials (possibly energy-dependent) with which to describe the scattering. It is obviously desirable for these quasipotentials to have simple forms and to correspond to well-defined model systems. This last point is of considerable importance since, for electron-atom or electron-molecule scattering in larger systems, the present prospects for obtaining "exact" solutions are very small. In this paper we show how the pseudopotentials first introduced in solid-state physics[1] may be used to describe electron-atom scattering, and make a specific calculation for the case of low-energy electron scattering from helium atoms.

II. PREVIOUS WORK ON ELECTRON-ATOM SCATTERING

Early studies of electron-atom scattering, typified by MacDougall's paper[2] on electron-helium atom scattering, attempted to solve the virtual orbital problem for the atom in the Hartree approximation. Later work, such as that of Morse and Allis,[3] emphasized the importance of the Pauli exclusion principle and the antisymmetry of the total wave function, while the most recent work[4–6] has involved attempts to solve the full atom-plus-electron problem. In attempting to solve the full problem, all many-electron effects (distortion polarization, correlation of the electrons in the atom, and distortion of the wave function of the scattered electron) are included in some sense. The electron-hydrogen (e-H) atom and the electron-helium (e-He) atom systems have been studied in most detail, and excellent reviews are available (for e-H see Refs. 4–6 for e-He see Ref. 6).

In the case of electron-helium atom scattering, most attention has been focused on the exchange and distortion effects. Moreover, because of the agreement between calculation and experiment (±15%), Moiseiwitsch[7] has concluded that all other (neglected) effects lead to small corrections. The calculations cited[8] have

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[8] H. S. W. Massey and B. L. Moiseiwitsch, Proc. Roy. Soc. (London) **A205**, 483 (1951); B. L. Moiseiwitsch, *ibid.* **A219**, 102 (1953).

involved both numerical integration of the proper integrodifferential equation and the use of variational procedures. The latest result leads to a scattering length of 1.442 atomic units (a.u.), to be compared with O'Malley's[9] extrapolated scattering length of 1.19 a.u., or the mean of the scattered experimental results, which is 1.32 a.u.[9] The difference between experiment and theory may reasonably be assigned to the neglected polarization effects. Hurst,[10] Hashino and Matsuda,[11] and Kolos and Pecul[12] have considered correlation effects within the atom and conclude that these are not very important. At high energies (>100 eV) it seems likely that correlation may become more important since in this energy range the electron does not "see" a spherically averaged two-electron atom, i.e., there is a breakdown of the adiabatic approximation.

To examine the influence of atomic polarization it is interesting to compare electron and positron scattering, since no exclusion principle operates in the latter case. While few low-energy positron scattering data are available, the theoretical results show that polarization effects are very important at low energies (the inclusion of polarization may even lead to a change of the sign of the scattering length). Accurate calculations for this system are difficult because to obtain significant results trial wave function must include the possibility of virtual positronium formation.

The increased importance of atomic polarization in electron–rare-gas atom scattering may be observed by examining the sequence He, Ne, Ar, Kr, Xe. For, He has a large positive scattering length, Ne has a small slightly positive scattering length, but the heavier rare gases have large negative scattering lengths[9] and also exhibit the Ramsauer effect. The only attempts to include polarization in the description of the scattering have used the very elementary potential[13–15]

$$-[P/(S^2+r^2)^2], \qquad (1)$$

where P is a constant, and S is a cutoff distance. This form for the potential is somewhat superior to that first used by Holtzmark[16] in his classic papers ($S=0$). Klein and Brueckner[17] used Eq. (1) for electron-oxygen atom scattering, fitting P and S so as to obtain the correct atom electronegativity, while Mittleman and Watson[18] have used variational techniques together with model calculations fo find the best values of the constants appearing in Eq. (1).

For small systems, at least, there exists a method to obtain a better form for the polarization potential. First derived by Bethe[19] in studies of core polarization in the excited states of helium, modifications of this method have been used by Dalgarno,[20] Martin,[21] Temkin,[22] and others. The method is now referred to as the polarized orbital approach, and thus far has only been used to study electron-hydrogen atom scattering.[4] Herein we extend this approach to electron-He scattering in a fashion similar to that of LaBahn and Callaway.[23]

Several investigators have attempted to construct an effective potential theory of electron scattering. In particular, Watson and co-workers[24] have developed an approach to the calculation of such a potential for the scattering of both electrons and ions, but their perturbation theory must be carried to high order before the orthogonality corrections appear. Mittleman and Watson[18] did consider the orthogonality problem in their study of the scattering of an electron from a Thomas-Fermi atom [using Eq. (1)]. A unified view of the theory and basic philosophy has been presented by Goldberger and Watson.[25]

In this paper we shall present an approach to electron-atom scattering in which an effective potential which contains both orthogonality and exclusion effects is defined as a pseudopotential.[26–28] The pseudopotential we use also contains polarization effects in an adiabatic form, and is employed to calculate electron- and positron-helium atom scattering cross sections in the limit of low energies. The agreement between theory and experiment is very good.

It is important to emphasize that it is not the purpose of this paper to restrict attention to the particular case of e-He scattering. Rather, it is our intention to present the pseudopotential method as a natural tool for the study of scattering problems and to show that the results obtained in this way are of comparable accuracy with the results of more tedious and less instructive approaches. What we demonstrate in this paper is that the use of pseudopotential arguments leads to an easily understood physical description, while because it

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permits the use of variational procedures even in the presence of bound (i.e., core) states, the necessary calculations are not difficult to carry through.

III. THE PSEUDOPOTENTIAL

In an atom, molecule, or solid there is extensive cancellation between the large negative potential energy V of a valence electron inside the core of an atom, and the large positive kinetic energy which is characteristic of the oscillations of the one-electron-valence wave function ϕ in that region. These oscillations arise from the restrictions imposed by the Pauli exclusion principle. Calculations which involve the wave function of the valence electron may be considerably simplified by introduction of a formalism which explicitly uses the orthogonality imposed by the Pauli principle to simplify the form of the wave function, albeit by the introduction of a new potential. The new potential inherently contains the cancellation of energies already mentioned, so that the resultant wave function is "smooth."

Now, the one-electron self-consistent field (SCF) eigenvalue equation

$$(T+V)\psi=\epsilon\psi \tag{2}$$

can be transformed to read

$$(T+V+V_R)\phi=\epsilon\phi\,, \tag{3}$$

where V_R is a nonlocal repulsive potential, and ϕ is a pseudo wave function which is equal to ψ at large distances from the core, but inside the core has the oscillations of ψ removed. The potential (V_R+V) defines the pseudopotential,

$$V_{\mathrm{ps}}=V+V_R \tag{4}$$

which can now be used as the scattering potential or effective potential for ϕ, since almost all of the complex many-electron effects and exclusion-principle effects are included in the defined potential.

If the eigenvalues of Eq. (3) are to be the same as those of the untransformed Eq. (2), Austin, Heine, and Sham have shown that V_R must take the general form

$$V_R\phi=\sum_c \chi_c\langle\chi_c|F|\phi\rangle\,, \tag{5}$$

where the χ_c are core orbitals, and F is any arbitrary operator. It should be noted that F can be chosen so as to satisfy any one of many independent criteria related to the orbitals.

Cohen and Heine[28] have examined the various criteria which could be used to define the new valence orbitals. In particular, they have shown that the smoothest orbitals (in the sense of having the lowest kinetic energy) are given by the following potential:

$$V_R^{\mathrm{CH}}\phi=-\sum_c \langle\chi_c|V|\phi\rangle\chi_c+\bar{V}\sum_c \langle\chi_c|\phi\rangle\chi_c\,, \tag{6}$$

where

$$\bar{V}=\langle\phi|V+V_R|\phi\rangle/\langle\phi|\phi\rangle\,. \tag{7}$$

The second term on the right-hand side of Eq. (6) is small and will be neglected in this paper. The neglect of $\bar{V}$, while still leading to a "smooth" valence-electron wave function and the same eigenvalues, is equivalent to choosing the Austin, Heine, Sham pseudopotential defined by $F=-V$.[26] Hereafter in this paper when referring to the pseudopotential, we shall specifically mean

$$V_R^A\phi=-\sum_c \chi_c\langle\chi_c|V|\phi\rangle\,. \tag{8}$$

There are many computational advantages derived from this procedure. Actually, the calculation of V_R^A or V_R^{CH} involves a self-consistency condition, since V_R^A is used to determine ϕ but V_R^A is calculated using ϕ. The smoother the wave function, the more rapid is the convergence to the correct wave function. The pseudopotential $V+V_R$ is influenced by ϕ in three ways. Because of the self-consistency conditions implicit in the Hartree-Fock equations, the core orbitals depend on the valence-electron orbitals or the scattered electron wave function, as well as on each other. However, a comparison of the wave functions of Na with those of Na^+, or of K with K^+, shows that the core orbitals are insensitive to the presence of the outer electron,[29] much less to the exact form of the wave function. Thus, $V+V_R$ depends on ϕ *explicitly* in two places: in the exchange potential, and in V_R.

Because the wave function obtained in this way is smooth, we can bypass the complete self-consistent calculation of ϕ by simply assuming a form for ϕ in the calculation of the potential. The resulting energy or scattering length is then even more insensitive to the exact form of ϕ. Indeed, since ϕ resembles a simple plane wave, $V+V_R$ is calculated for the case of a plane wave. The total effective Hamiltonian is then used to determine ϕ. The self-consistency of the calculation can easily be carried further, if that proves necessary.

The effective core potentials for electron-helium atom scattering are constructed from a potential V which is the sum of the nuclear, Coulomb, and exchange potentials, plus the polarization potential arising from the small distortion of the atom by the electronic charge:

$$V=-\frac{2}{r_3}+2\int\frac{\chi^2(r_1)}{r_{13}}d\tau_1-\int\frac{\chi(r_1)\chi(r_3)}{r_{13}}d\tau_1 P_{13} +V_{\mathrm{pol}}(r_3)\,, \tag{9}$$

where r_3 is the distance of the scattered electron from the nucleus, r_{13} is the distance between two electrons, χ is a Hartree-Fock atomic wave function (very similar to the correct self-consistent field core orbital), P_{13} is an

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[29] D. R. Hartree and W. Hartree, Proc. Cambridge Phil. Soc. 34, 550 (1948), and recent papers by C. C. J. Roothaan and collaborators (unpublished).

operator which permutes electrons one and three in functions to its right, and V_{pol} is the polarization potential evaluated below.

IV. POLARIZATION POTENTIAL BY CORE POLARIZATION METHODS

For the study of low-energy electron scattering, it is sufficiently accurate to use the adiabatic approximation to calculate the polarization potential. By this we mean that at each distance r_3 the scattered electron is assumed to be at rest relative to the core electrons of the atom, i.e., the core electrons of the atom adjust to any movement of the scattered electron before appreciable displacement occurs. The adiabatic assumption is poorest for very small electron-atom separations, when the electron is "well within the atom," but even in this domain two factors tend to limit the error made. First, the potential itself approaches zero, so that any error cannot be very large. Second, in calculations by Temkin and Lamkin on electron-hydrogen atom scattering using various potentials all of which differ at short distances, similar results are obtained in all cases.[30,22]

To study the two-electron atom it is necessary to make another assumption before core polarization potentials may be used directly. To be specific, it must be assumed that the electrons polarize independently, so that each electron reacts as if it were in the field of an effective nuclear charge, z_{eff}. This approximation can be tested using the calculations of Dalgarno[31] and others. Dalgarno has computed the polarizability both in the uncoupled (independent electrons) and the coupled approximations. The difference between the results is less than 10% for the helium atom. In the beryllium atom the error is larger, but the error appears to become smaller again for neon and similar large systems.[32]

Many forms for the core polarization potential have been proposed.[22] However, most of the analyses published to date have been based on the assumption that the electron cannot penetrate the atom. The form originally used by Bethe[19] does include penetration in the dipole ($l=1$) contribution. Recently, two papers have extended Bethe's work. Callaway[33] has calculated the no penetration, $l=1$, $l=2$, potential for s orbitals and Reeh[34] has calculated the complete $l=0$, 1, 2 potential for s and p electrons. In our calculations we shall use the Reeh $l=0$ component, the Bethe $l=1$ component, and only one nonpenetration component, namely that computed by Callaway for $l=2$. LaBahn and Callaway[23] have used only the Bethe potential. In explicit form, the potential we use is

$$V_{\text{pol}}=V_0+c_1V_1+V_2\,, \tag{10}$$

$$V_1=-\frac{4.5}{x^4}\left[1-\frac{e^{-2x}}{3}\left(1+2x+6x^2+(20/3)x^3+\tfrac{4}{3}x^4\right)-\tfrac{2}{3}e^{-4x}(1+x)^4\right], \tag{11}$$

$$V_2=-\frac{15}{x^6}\left[1-e^{-2x}\left(1+2x+2x^2+\tfrac{4}{3}x^3+\tfrac{2}{3}x^4+\frac{4}{15}x^5+\frac{4}{45}x^6+\frac{4}{225}x^7\right)\right], \tag{12}$$

$$\begin{aligned}V_0=2e^{-2x}\Bigg[&-\frac{2}{x^2}+\frac{1}{2x}+\tfrac{5}{2}+x+2(\ln 2+c)\left(\frac{1}{x^2}+\frac{1}{x}\right)+\text{Ei}(-2x)\left(1-\frac{1}{x^2}\right)+\ln x\left(-2x+1+\frac{2}{x}+\frac{1}{x^2}\right)\\&-\alpha\left(\frac{2}{x}+4+4x\right)+\beta(2+4x)\Bigg]+\frac{4\alpha}{x}+2\left(1-\frac{1}{x}\right)\text{Ei}(-2x)+2e^{-4x}\Bigg[\frac{2}{x^2}+\frac{7}{2x}+\tfrac{5}{2}+x-\overline{\text{Ei}}(2x)\\&\times\left(\frac{1}{x^2}+\frac{3}{x}+4+2x\right)+\left(\frac{1}{x^2}+\frac{2}{x}+1\right)\ln x\Bigg],\end{aligned} \tag{13}$$

where

$$\alpha=-(1+1/x)e^{-2x}(\ln 2+c+\tfrac{1}{2}\ln x)+\tfrac{1}{2}(1/x-1)\,\text{Ei}(-2x)+e^{-2x}(1/4x+\tfrac{1}{2}-\tfrac{1}{2}x)\,,$$

$$\beta=(1+1/x)[e^{-2x}(\tfrac{1}{2}\,\overline{\text{Ei}}(2x)-\tfrac{1}{2}\ln x-\ln 2-c)-\tfrac{1}{4}]+\tfrac{1}{2}(1/x-1)[(\text{Ei}(-2x)-\ln x)+e^{-2x}(1/4x+\tfrac{1}{2}-\tfrac{1}{2}x)]\,,$$

$$c=0.577215665\cdots=\text{Euler's constant},$$

$$\text{Ei}(-x)=-\int_x^{\infty}\frac{e^{-t}}{t}dt\,,\quad \overline{\text{Ei}}(x)=\mathcal{P}\int_{-\infty}^{x}\frac{e^{t}}{t}dt$$

and in each case $x=r_3z_{\text{eff}}$, the product of the distance of the scattered electron from the nucleus and the effective nuclear charge. For helium a value of z_{eff} of 1.6875 is used, since this corresponds to the best single Slater orbital approximation to the wave function. It might be argued that z_{eff} should be selected to give the correct asymptotic behavior of the wave function.

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[30] A. Temkin and J. C. Lamkin, Phys. Rev. **121**, 788 (1961).

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[32] H. Cohen, Laboratory of Molecular Structure and Spectra, University of Chicago (private communication).

[33] J. Callaway, Phys. Rev. **106**, 868 (1957).

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However, the asymptotic behavior of the wave function has little influence on the polarization potential, since the potential varies as r_3^{-4}. We have forced the polarization potential to be correct at large distances by adjusting the constant c_1 (which is 1.1219 for our choice of z_{eff}, and is 1.000 for the LaBahn and Callaway[23] choice). We shall treat all parts of the polarization, including the pseudopotential part, as though they correspond to a wave function with an effective nuclear charge of 1.6875. This approximation is not serious, as shown by the results of Temkin andLamkin.[30,35]

V. TOTAL EFFECTIVE POTENTIAL

As Hartree-Fock orbitals in Eqs. (8) and (9), except for the polarization calculation, we shall use the Bagus-Gilbert nominal basis set[36]

$$\chi=0.18159\varphi_{1s}(2.906)+0.84289\varphi_{1s}(1.453)\,, \tag{14}$$

where $\varphi_{1s}(z)$ is a normalized Slater $1s$ function with orbital exponent z. We evaluate the exchange part of the potential in the limit of zero-electron energy, assuming that the scattered-electron wave function in the pseudopotential formalism is sufficiently smooth that the spatial variation contributions to the exchange are small. Then

$$\int \frac{\chi(r_1)\phi(r_1)}{r_{13}}d\tau_1\,\chi(r_3)\rightarrow\int\frac{\chi(r_1)}{r_{13}}d\tau_1\,\chi(r_3)\phi(r_1) \tag{15}$$

in the limit as $k\rightarrow 0$, where k is the magnitude of the wave vector of the scattered electron. There is then obtained the local potential[37]

$$\begin{aligned}V_A=V-V_{\text{pol}}=&-6.116632e^{-\Lambda r}/r+0.535625e^{-2\Lambda r}/r\\&+3.3831894e^{-3\Lambda r}/r+0.1978492e^{-4\Lambda r}/r\\&+2.2064609e^{-2\Lambda r}+2.026883e^{-3\Lambda r}\\&+0.191650e^{-4\Lambda r}\end{aligned} \tag{16}$$

with $\Lambda=1.453$. To complete the potential,

$$V_R\phi=-\int\chi V\phi d^3r_1\chi(r_3) \tag{17}$$

must be computed. Again taking the limit $k\rightarrow 0$ so as to obtain a local potential, we find

$$V_R=-\int\chi(r_1)V(r_1)d^3r_1\chi(r_3)\,. \tag{18}$$

Substituting $V=V_A+V_{\text{pol}}$, then,

$$\begin{aligned}V_R=5.634646e^{-1.453r_3}&+3.434869e^{-2.906r_3}\\&+1.107442e^{-1.6875r_3}.\end{aligned} \tag{19}$$

The total effective potential is, of course,

$$V_T=V_A+V_{\text{pol}}+V_R \tag{20}$$

which is easily obtained from Eqs. (16), (10), and (19). Because of the assumptions made in calculating this local potential, it is valid only near $k=0$. However, for $k\rightarrow 0$, most contributions vary as, e.g., $1/[k^2+(1.453)^2]$, and the error in the potential is small even for electron energies of 0.5 eV ($k\sim 0.2$). The validity of this conclusion is easily checked using the calculations of LaBahn and Callaway.

In Fig. 1 is displayed the total potential for the electron-helium atom scattering. The maximum of this potential occurs at about 1.15 a.u., an interesting observation since the scattering length is 1.19 a.u. accord-

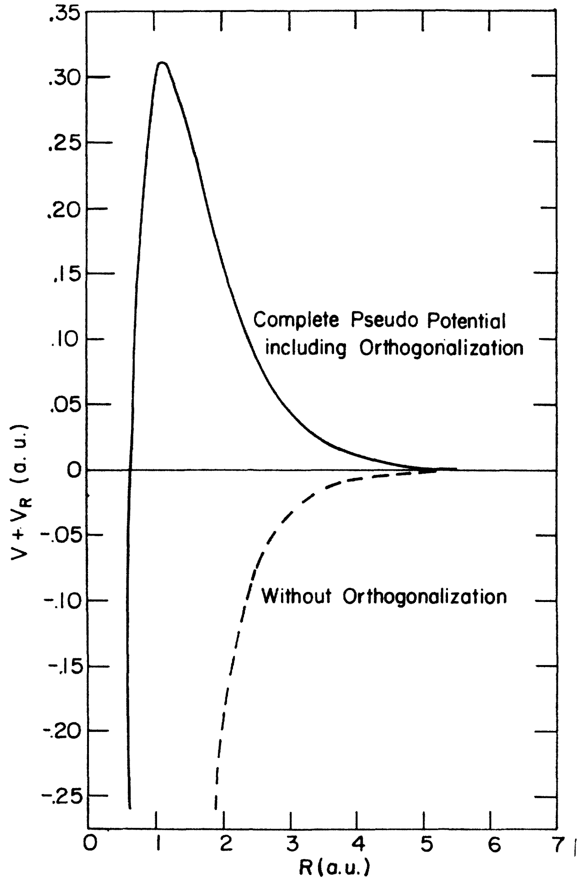

FIG. 1. The electron-helium atom pseudopotential as a function of electron-atom separation.

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[35] Preliminary versions of the next section were presented at the Istanbul International Summer School of Quantum Chemistry, August-September, 1964, and will be published in the proceedings of the conference.

[36] P. Bagus, T. L. Gilbert, C. C. J. Roothaan, and H. Cohen (to be published). These results were supplied by Gilbert of Argonne National Laboratory and by Roothaan of the Laboratory of Molecular Structure and Spectra, University of Chicago.

[37] The local pseudopotential approximation implies that the variation of the pseudo wave function $\phi(r_1)$ over the atomic-core region is small. We can then replace the repulsive pseudopotential $V_R{}^A$ [Eq. (8)] by a local potential

$$V_R{}^A\phi\approx-\sum_c\chi_c\langle\chi_c|V\rangle\phi. \tag{8a}$$

ing to O'Malley. The potential does not become negative until 6.7 a.u., and has a well depth of -0.0001109 a.u. at 7.8 a.u. From these observations alone, it is obvious that the polarization interaction is not very important in electron-helium atom scattering. LaBahn and Callaway,[23] using effective-range theory, estimate that the short-range potential has a range of 3.7 a.u., and this agrees closely with our results.

VI. SCATTERING LENGTH

Before presenting our variational calculations of the scattering length, it is advantageous to examine the Born-approximation estimate of the cross section in the limit of zero energy. We examine the Born approximation not because it is good (indeed, one *cannot* use the Born approximation), but because the relative magnitudes of the various contributions are nicely and simply represented in this way. In Table I there is displayed the Fourier transform of the potential subdivided into the various contributions. We note again the relatively small contribution of the polarization interaction to the total cross section. It is also important to note that the contribution of the polarization interaction is very small primarily because of the orthogonalization implicit in the pseudopotential (only the tail of the polarization contributes), and therefore it is to be expected that the polarization interaction will make a much larger contribution in positron-atom scattering where orthogonality requirements are absent. We shall later present some simple calculations verifying this remark.

The magnitude of the potential makes the use of the Born approximation inappropriate. There are two alternative ways to calculate the zero-energy cross section: the integrodifferential equation, which reduces to a one-dimensional equation because of our local potential assumption, may be integrated (see LaBahn and Callaway[23]), or standard variational procedures may be used to determine directly the scattering length. Several numerical integrations were tried, but difficulty was encountered in the small-k region and we, therefore, used instead the variational method. A variational calculation is also more accurate, since the extrapolation of the cross section to zero energy can be difficult. (It should be remembered that the k dependence of the repulsion and polarization components of the cross section are very different.[38]

Ohmura has developed a method for obtaining the scattering length using the Kohn variational procedure. This method converges monotonically to the correct scattering length with increasing parameterization, provided that the wave function has a few simple properties. A general discussion of these required properties is to be found in the text by Wu and Ohmura.[39]

Table I. Zero-energy Fourier transforms (in a.u./4π).

	Potential	Pseudopotential contribution	Total
V_A	-2.4281	$+3.9510$	1.5229
V_0	-0.0597	0.1661	0.1064
V_1	-0.5034	0.2550	-0.2484
V_2	-0.0484	0.0398	-0.0086
			1.3723

Given the asymptotic conditions

$$\lim_{r_3\to\infty} \Phi(r_3) \to \sin(kr_3+\delta)\,, \qquad \Phi(0)=0 \tag{21}$$

and letting a_t be the variational approximation to the scattering length,

$$\lim_{k\to 0} \Phi(r_3) \to r_3 - a_t\,. \tag{22}$$

The stationary value of the scattering length, here denoted μ, then satisfies the condition

$$\mu \leq a_t + \int_0^\infty \Phi(r_3) L\Phi(r_3) d^3r_3 \tag{23}$$

with a_t determined by actually taking the limit (21), and where

$$L = -(d^2/dr^2) + 2V_T\,. \tag{24}$$

The factor of 2 in Eq. (24) arises from the change from atomic units to Rydberg units. Ohmura shows that for the correct choice of trial wave function, there is a monotonic convergence to the scattering length from above provided that no bound states exist. Notice that there is no possibility for bound states to occur in the pseudopotential formalism, since the wave function for the scattered electron must be orthogonal to the bound states of the atom.

The choice of trial function is fraught with difficulty and our choice was dictated by computational convenience. As an n function approximation we take

$$\Phi_n(r_3) = u_0 + \sum_{m=1}^{n} b_m u_m\,, \tag{25}$$

where

$$u_0 = r\,, \qquad u_m = \exp[-(m-1)r][1-\exp(-r)]\,. \tag{26}$$

These terms represent the spatial variation of the phase shift. While individual terms in this expression vary rapidly with distance, the net spatial variation of (25) near the nucleus is small.

The scattering length was evaluated using Eq. (23) for V_A, $V_A + V_R(A)$, and V_T for $n=1$, 2, 3 [Eq. (25)], i.e., using up to three variational parameters. $V_R(A)$

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[38] T. F. O'Malley, L. Spruch, and L. Rosenberg, J. Math. Phys. 2, 491 (1961).

[39] T. Y. Wu and T. Ohumura, *Quantum Theory of Scattering* (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1962), p. 76ff.

Table II. Variational calculations of scattering lengths for electron-helium scattering using the Kohn-Ohmura procedure. $\Phi=r-\alpha(1-e^{-r})-\beta e^{-r}(1-e^{-r})-\gamma e^{-2r}(1-e^{-r})$.

Potential	$\mu(0)$ (a.u.)	$\mu(1)$ (a.u.)	$\mu(2)$ (a.u.)	$\mu(3)$ (a.u.)
1. No pseudopotential or polarization: V_A	-4.887 $(\alpha=0)$	undefined		
2. No polarization effects: $V_A+V_R(A)$	3.0425 $(\alpha=0)$	1.713 $(\alpha=1.230)$	1.5056 $(\alpha=1.500)$ $(\beta=-1.686)$	1.5016 $(\alpha=1.5721)$ $(\beta=-2.1011)$ $(\gamma=0.6156)$
3. Total potential	2.7412 $(\alpha=0)$	1.473 $(\alpha=1.204)$	1.278 $(\alpha=1.468)$ $(\beta=-1.647)$	1.193 $(\alpha=1.436)$ $(\beta=-1.428)$ $(\gamma=-0.315)$
4. Experimental[a]				(1.19)
5. LaBahn-Callaway[b] calculation using only dipole polarization but more elaborate methods				1.132

[a] See Ref. 9 in text.
[b] See Ref. 23 in text.

represents the repulsive potential without polarization terms. The results obtained are listed in Table II. Agreement with other calculations, when these exist, is good. Without the polarization interaction, i.e., $V=V_A+V_R(A)$, our calculated scattering length is 1.502 a.u. versus 1.442 a.u. obtained from a more elaborate (and more precise) calculation by Moiseiwitsch.[7] The agreement between our calculated scattering length and experiment may be misleading since the "experimental" results are based on a drastic extrapolation using effective-range theory,[9] and the associated error may be as large as 10% since exchange effects may not be properly accounted for by the extrapolation procedure used. The scattering length reported herein has probably converged to within a few percent of the correct result. The scattering length computed by LaBahn and Callaway is in good agreement with our value, even though they have neglected the $l=0$ terms defined in Sec. IV. Although we may have overestimated these terms, they probably contribute less than 10% (in a positive sense) to the scattering length computed by LaBahn and Callaway[23] (see Table I). The good agreement between the results of our calculations and those of more elaborate calculations is very encouraging. However, it will be shown that the cross section as a function of energy is not given very accurately by our potential.

Table III. Phase shifts δ and cross sections σ for s-wave electron-helium scattering.

		Complete pseudopotential		Pseudopotential without monopole distortion term	
E eV	k a.u.	$\sin\delta/k$ a.u.	σ a.u.	$\sin\delta/k$ a.u.	σ a.u.
0.00	0.00	(-1.193)[a]	(17.885)[a]	...	...
0.005	0.02	-1.275	20.42	-1.228	18.95
0.022	0.04	-1.310	21.57	-1.270	20.27
0.049	0.06	-1.340	22.57	-1.297	21.14
0.087	0.08	-1.342	22.64	-1.297	21.14
0.136	0.10	-1.346	22.77	-1.301	21.27
0.196	0.12	-1.357	23.12	-1.300	21.24

[a] From previous section by variational calculation.

A plot of $\Phi(r_3)/r_3$ from Eq. (25) shows that the function is smooth and deviates from unity by less than 17% out to 0.3 a_0, i.e., the rapid variations of the individual terms are removed in the sum of terms. Indeed, some of the remaining variation of $\Phi(r_3)/r_3$ would be removed upon adding further terms to the trial function. The computed scattering length may be expected to vary only slightly with increasing number of terms while the wave function may vary greatly. It should be noted that the constancy of $\Phi(r_3)/r_3$ implies that only minor errors are introduced by not completing the iterative procedure.

We estimate that the scattering length calculated herein is accurate to 5% in the limit of zero energy. The error, unfortunately, increases rapidly with energy, since the potential is more sensitive to k than at first suspected.

VII. SCATTERING CROSS SECTION AS A FUNCTION OF ENERGY

The cross section as a function of energy can be determined from our total potential by integrating

$$(L-k^2)\Phi=0. \tag{27}$$

In assuming that there exists a local potential, we have removed the energy dependence of the operator L. As stated earlier, this k dependence is weaker than that of the principal scattering process. However, we shall see that for scattering with nonzero incident energy our results deviate significantly from the more exact calculations of LaBahn and Callaway. It is possible to include, with relative ease, some of the k dependence of the potential. We have not, for reasons of consistency,

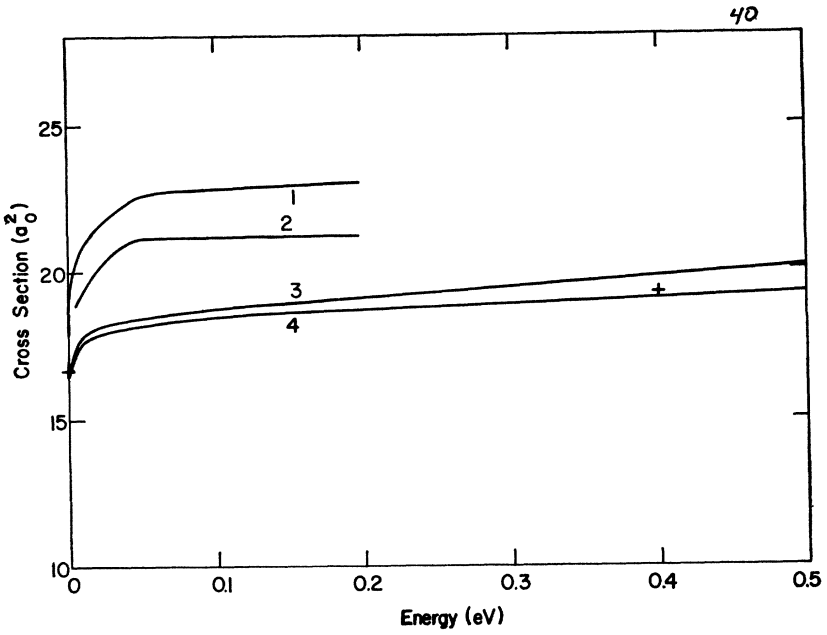

FIG. 2. The electron-helium atom elastic-scattering cross section as a function of energy. 1. This work based on a pseudopotential formalism including all adiabatic polarization effects. 2. This work, pseudopotential formalism without monopole distortion term. 3. LaBahn and Callaway adiabatic-exchange results including dipole polarization effects. 4. Modified-effective-range theory using only dipole polarization effects. Plus sign represents experimental data of Golden and Bandel.

made this extension herein, but other studies of electron-hydrogen atom scattering[40] will consider this energy dependence in more detail.

Equation (27) was integrated outward, using standard procedures,[41] on the IBM 7094 computer at the University of Chicago.

For the low-energy region of interest the numerical integration was carried out to 50 a.u. The mesh size Δr used was varied from 0.01 to 0.1 in the following way: $\Delta r=0.01$ for $0\leq r\leq 0.15$, $\Delta r=0.05$ for $0.15\leq r\leq 2.0$ and $\Delta r=0.1$ for $2.0\leq r\leq 50.0$. The phase shifts were evaluated from the zeros and the maxima of the resulting wave function. As a check, the procedure of LaBahn and Callaway[23] was also used by matching the wave function to spherical Bessel functions of the form $k^{-1}(C\cos kr+D\sin kr)$ from which the s-wave phase shift is found to be $\delta_0=\cot^{-1}(D/C)$. From the phase shifts, the cross section as a function of energy for the s wave was constructed (Table III and Fig. 2).

For the low energies considered, p-wave scattering is small. To calculate the magnitude of p-wave scattering we need another potential, since when $l=1$ the exchange potential changes and V_R disappears. The p-wave phase shift should vary approximately as k relative to the s-wave phase shift. Since in our calculations $k^2<0.04$ a.u. (approximate) calculations indicate that p-wave scattering contributes less than 1% to the total cross section even at $k=0.2(0.54$ eV).

To obtain accurate zero-energy cross sections experimental points are required in the region $0.06>k>0.01$ a.u. (0.048 to 0.001 eV). The scattering cross section in this region changes rapidly with energy. In this regard, we are in agreement with the calculations of LaBahn and Callaway.[23] We also agree that the cross section from 0.15 to 0.6 eV (at least) is relatively flat, but our calculations only hint at the maximum found by LaBahn and Callaway, and are not accurate enough to unambiguously establish the existence of the maximum. The calculations reported in this paper deviate by about 20% from those of LaBahn and Callaway, and by a slightly larger amount from the results of effective-range theory.

It should be noted that at one point we have included an effect omitted by LaBahn and Callaway, i.e., the short-range zero-angular-momentum effects of polarization [V_0 in Eq. (13)]. While it is difficult to estimate how accurate our one-electron model is as a description for this effect, we have shown that this particular contribution is of the order of one-third the dipole polarization contribution. The quadrupole term is much smaller. The effects of the spherically symmetric polarization term extend to larger k because of the short range of the polarization potential. Indeed, some of the discrepancy between our values and those of LaBahn and Callaway, but probably not the major fraction, might be thus accounted for. We estimate that the terms included by us but omitted by LaBahn and Callaway would contribute an increase of the order of 10% to their cross sections (see Table I). It is then necessary to re-examine the modified effective-range theory, but our work had been completed before we learned of these results, and thus we have not evaluated the effect of V_0 alone.

Both this paper and the paper of LaBahn and

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[40] N. R. Kestner (to be published).

[41] J. Irving and N. Mullineux, *Mathematics in Physics and Engineering* (Academic Press Inc., New York, 1959), p. 697; J. B. Scarborough, *Numerical Mathematical Analysis* (Johns Hopkins Press, Baltimore, 1962), p. 56.

Callaway have established two features of the energy dependence of the cross section which should be studied experimentally: there is predicted a rapid change in cross section with energy below 0.05 eV, and a maximum in the cross section somewhere between 0.4 and 0.9 eV, our value being on the lower side but less accurate.

In the recent experimental work of Golden and Bandel [D. E. Golden and H. W. Bandel, Phys. Rev. **138**, A14 (1965)],[42] the electron-helium atom cross sections at low energies (to 0.3 eV) were determined. The modified effective-range formula[23] yields a scattering length of 1.15±0.02 a.u., in good agreement with the value 1.193 a.u. calculated herein. At higher energies (0.4 eV) there exists a discrepancy of about 15–20% between our calculated values and the experimental results of Golden and Bandel, which are in very good agreement with the calculation of LaBahn and Callaway.[23] This discrepancy does not arise from the use of the monopole distortion term, which contributes only about 5% to the calculated cross section (Table III). There are two possible ways of improving our results for higher values of k: (a) The k dependence of the pseudopotential should be included; (b) A nonlocal potential should be used.

It should be noted that even if it proves rather difficult to apply the pseudopotential formalism to the calculation of electron-scattering cross sections for finite (nonzero) k, this method should be useful in conjunction with the effective-range theory.[23] The combination of the calculated scattering length and the polarizability correction should lead to scattering cross sections at energies up to 1 eV which are reliable within 5%.

VIII. POSITRON-HELIUM SCATTERING

The description of the scattering of positrons by helium atoms is, in many ways, a much simpler problem than the description of electron scattering, since we have no difficulty with constructing an effective potential. Indeed,

$$V_{Tp} = -V_A{}^{\mathrm{NE}} + V_{\mathrm{pol}} \tag{28}$$

where $V_A{}^{\mathrm{NE}}$ is the nonexchange part of V in Eq. (16), i.e., it does not contain the term displayed in Eq. (15).

TABLE IV. Zero-energy Fourier transforms of the positron-helium potential (in atomic units).

Potential	Contribution
$V_A{}^{\mathrm{NE}}$	4.969
V_0	−0.750
V_1	−6.696
V_2	−0.610
Total	−3.088

This potential is not k-dependent. The sign change arises from the sign of the positron charge.

There are several reasons for examining positron-atom scattering in this paper. Although our calculations are not accurate enough (due to the neglect of virtual positronium formation)[43,44] to be regarded as a substitute for experimental data, they are of interest in comparison with the electron-atom scattering results because of the large contribution by the polarization interaction. In addition, we find a Ramsauer effect if s waves alone are included in the representation of the cross section, in agreement with Schwartz's[43] calculations of positron hydrogen-atom scattering. In the following we also estimate the p-wave contribution to the cross section, and show that the Ramsauer effect is then not to be expected, except in a very mild form.

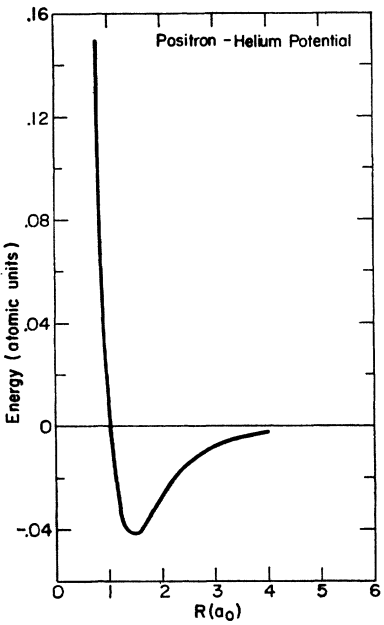

FIG. 3. The positron-helium atom potential as a function of distance.

In Table IV we list the zero-energy Fourier transform for the potential of Eq. (28), where $V_A{}^{\mathrm{NE}}$ is

$$\begin{aligned} V_A{}^{\mathrm{NE}} = {} & 1.420928\frac{e^{-2.906r_3}}{r_3} + 2.064608e^{-2.906r_3} \\ & + 0.5130906\frac{e^{-4.359r_3}}{r_3} + 1.118281e^{-4.359r_3} \\ & + 0.065950\frac{e^{-5.812r_3}}{r_3} + 0.191650e^{-5.812r_3}. \end{aligned} \tag{29}$$

The results are strikingly different from the case of electron-helium atom scattering where the contribu-

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[42] This paper was published after this manuscript had been submitted for publication. Hence the present authors were not biased by knowledge of the experimental facts when these calculations were performed.

[43] C. Schwartz, Phys. Rev. **124**, 1468 (1961).

[44] L. Spruch and L. Rosenberg, Phys. Rev. **117**, 143 (1960); W. J. Cody, J. Lawson, H. Massey, and K. Smith, Proc. Roy. Soc. (London) **A278** (1963).

tions from the exchange potential and the pseudopotential dominated. Here neither exists, and thus we get an entirely different picture of the scattering. In fact, without inclusion of the polarization interaction, the wrong sign is obtained for the transform and, as we show below, also of the scattering length. This is to be expected from the potential shown in Fig. 3.

The scattering length was calculated in the same manner as for the previously discussed electron-atom scattering. The results are displayed in Table V. The change in sign agrees with the calculations of other authors.

Again the differential equation was integrated numerically for values of k to 2.0 a.u. The s-wave phase shift is shown in Fig. 4. We see clearly that a "Ramsauer" effect exists for the s-wave scattering, i.e., the cross section goes to zero at about 4.9 eV. This also occurs in the case of positron-hydrogen atom scattering.[43,44] For a true Ramsauer effect, however, the contributions from higher partial waves must also vanish. Several authors have compared the $k=0$ cross section with the experimental estimate of Teutsch and Hughes[45] for 18-eV positrons. Clearly this is not a value comparison, as is easily deduced from Fig. 4.

TABLE V. Zero-energy scattering lengths for positron-helium scattering (in atomic units).

$$\Phi=r-\alpha(1-e^{-r})-\beta e^{-r}(1-e^{-r})-\gamma e^{-2r}(1-e^{-r}).$$

Potential	$\mu(0)$	$\mu(1)$	$\mu(2)$	$\mu(3)$
V_A^{NE} (No polarization)	0.795 ($\alpha=0$)	0.448 ($\alpha=0.615$)	0.426 ($\alpha=0.439$) ($\beta=0.392$)	
Total potential V_{TP}	−0.430 ($\alpha=0$)	−0.440 ($\alpha=0.0988$)	−0.5751 ($\alpha=-0.4079$) ($\beta=1.0433$)	−0.5754 ($\alpha=-0.4209$) ($\beta=1.146$) ($\gamma=-0.1221$)

The p-wave cross section was calculated using a one parameter ($\tan\eta$) variational equation[46]

$$\Phi_1=-\cos kr+\sin kr/kr+\tan\eta\,\sin kr. \tag{30}$$

Using the Kohn variational method,[46] set

$$I_l\equiv\int_0^\infty \Phi_l\left(L+\frac{l(l+1)}{r^2}-k^2\right)\Phi_l d^3r, \tag{31}$$

where the stationary condition is

$$\delta(I_l-k\tan\eta)=0 \tag{32}$$

$$k\tan\delta_l=k\tan\eta_l-I_l. \tag{33}$$

The results of this analysis are displayed in Table VI in terms of the partial cross section σ_l, where

$$\sigma_T=\sum_{l=0}\sigma_l=4\pi k^{-2}\sum_{l=0}(2l+1)\sin^2\delta_l. \tag{34}$$

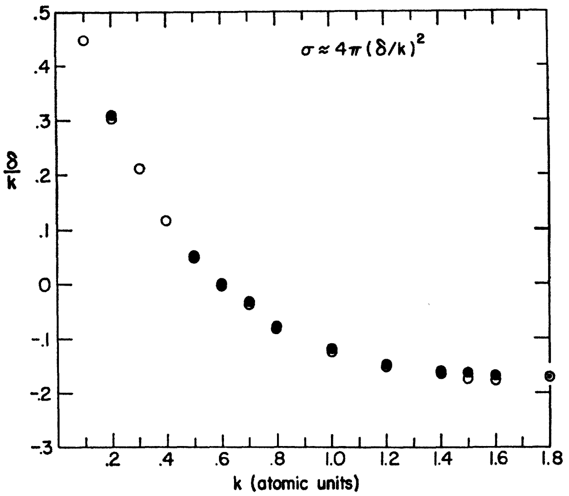

FIG. 4. The positron-helium atom phase shift as a function of the magnitude of the wave vector.

As clearly shown in Fig. 5, there is no Ramsauer effect because of the large p-wave scattering. The p-wave phase shift is clearly not as accurate as the s-wave phase shift, but any comparison between the cross section computed for zero energy and that measured at 18 eV is impossible, and the assumption that the cross section is independent of energy is also not correct. Unfortunately, the agreement between calculation and experiment at $k=1.14\ a_0$ is not good, since Teutsch and Hughes find $\sigma_T=0.07\pm0.02$ (a.u.). The experimental values are hard to obtain and may be in error. Our values are much larger than those of other authors, possibly due to differences in the method of introducing the polarization interaction: our cross section without polarization is in good agreement with that of Allison, McIntyre, and Moiseiwitsch.[47] Their value, including

TABLE VI. Total and partial cross sections (a.u.) for positron-helium scattering (s- and p-wave contributions).

k	s-wave partial cross section	p-wave partial cross section	Total cross section
0.0	(4.161)	0.000	(4.161)
0.1	2.518		
0.2	1.194	0.044	1.238
0.3	0.583		
0.4	0.180	0.175	0.355
0.5	0.035		
0.6	0.000	0.214	0.214
0.7	0.012		
0.8	0.068	0.185	0.253
0.9			
1.0	0.174	0.126	0.301
1.2	0.261	0.070	0.331
1.4	0.316	0.031	0.347
1.6	0.342	0.009	0.351
1.8	0.355	0.001	0.356

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[45] W. B. Teutsch and V. W. Hughes, Phys. Rev. **103**, 1266 (1956).

[46] See, for example, a thorough discussion in Ref. 39, pp. 57–60.

[47] D. C. S. Allison, H. A. J. McIntyre, and B. L. Moiseiwitsch, Proc. Phys. Soc. (London) **78**, 1169 (1961).

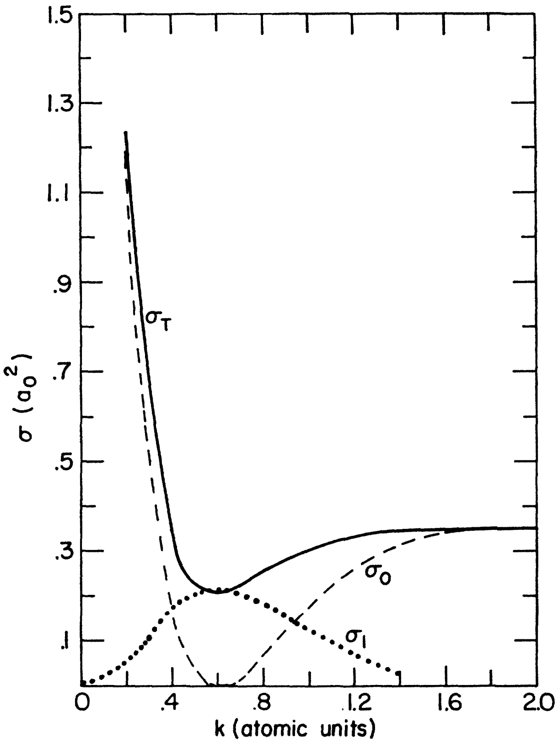

FIG. 5. The positron-helium atom elastic-scattering cross section as a function of the magnitude of the wave vector.

polarization, is only −0.16, indicating that they have greatly underestimated polarization effects.

IX. CONCLUSIONS

In this paper, by using a pesudopotential formalism and an adiabatic-core-polarization method for the introduction of polarization effects, we have calculated an effective potential for low-energy electron scattering from helium atoms. The zero-energy cross section agrees with the "experimental" value and with the more elaborate, though incomplete calculations of LaBahn and Callaway[23] to within 5%. In agreement with the last authors we find the scattering cross section to be energy-dependent below 0.05 eV and relatively flat above, with a maximum possible near 0.4 eV. Polarization effects contribute about 20% to the scattering length. At finite energies our values are substantially higher than those of LaBahn and Callaway since we have included the effect of symmetrical distortion of the atom by the scattered electron. This accounts for a sizeable part of the discrepancy between the two calculations.

Our calculations show that the concept of a potential can be used, even in this extreme case, if care is taken to define the situation in which this effective potential is to be used. The simplicity of our calculations attest to the advantages of this method. Knowledge of the potential also enables us to understand better the qualitative features of our scattering results. It appears that most properties of the potential are given within 10% by this useful approximation.

The cross section for positron-helium atom scattering was found to have a large polarization contribution. The energy dependence of the cross section is complex, for while the *s* wave has a zero-phase shift at $k=0.6$ a.u., the total cross section (*s* and *p* waves) has only a small dip at this point. Thus *no* Ramsauer effect is to be expected.

We feel confident that the methods discussed herein can be applied with reasonable confidence to other electron–rare-gas and inert-molecule-scattering problems without some of the parameterizations often used in the past for the exchange, orthogonalization, and polarization effects.

ACKNOWLEDGMENTS

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