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Sir David Bates Benjamin Bederson

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ADVANCES IN ATOMIC AND MOLECULAR PHYSICS, VOL 22

POSITRONIUM—ITS FORMATION AND INTERACTION WITH SIMPLE SYSTEMS

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I. Introduction

During the past few years very significant developments have taken place in the study of the interactions of positrons with atoms and molecules. Progress has been particularly impressive on the experimental front where the availability of more intense positron beams and improved detectors have made possible much more sophisticated experiments, and this in turn has stimulated further associated theoretical investigations. Recent experimental developments are reviewed by Griffith in another chapter in this volume, and a more comprehensive review by Charlton (1985) has also recently been published.

One of the most interesting processes to occur in positron–atom collisions is positronium formation, a simple example of a rearrangement collision in which the incident positron combines with one of the electrons in the target atom to produce a bound positron–electron system, positronium (Ps), and a residual ion; thus

$$e^+ + A \rightarrow \mathrm{Ps} + A^+$$

Positronium formation cross sections have recently been measured directly (Charlton *et al.*, 1983; Fornari *et al.*, 1983) over a wide range of incident positron energies for several target systems, and a significant discrepancy is found between the results of the two experiments which becomes increasingly pronounced as the positron energy is raised. The possibility of resolving this discrepancy provides an added incentive to study positronium formation theoretically, and it is this topic which will form the major part of this

article. We shall also discuss the interaction of positronium with simple systems.

Other theoretical aspects of positron collisions in gases, and particularly elastic scattering and annihilation, are treated in the review articles of Fraser (1968), Bransden (1969), Massey (1971), Drachman (1972a), Massey *et al.* (1974), Humberston (1979), and Ghosh *et al.* (1982).

II. Positronium Formation in Positron–Atom Scattering

Positronium has the structure of a hydrogenic atom with a reduced mass of half the electron mass. The ground-state energy is therefore -6.8 eV and the dipole polarizability is $36\, a_0^3$. The two spin states are referred to as parapositronium ($S = 0$) and orthopositronium ($S = 1\,\hbar$), and annihilation is into two and three γ rays respectively with lifetimes in the ground state of 1.251×10^{-10} s and 1.418×10^{-7} s (Gidley *et al.*, 1982). We shall neglect spin-dependent forces and generally make no distinction between ortho- and parapositronium. Consequently, of all the positronium formed in the collisions of positrons with the target system, one-quarter is assumed to be parapositronium and three-quarters orthopositronium.

If the ionization energy of the target atom is E_i, the energy of the positron at the threshold for ground-state positronium formation is

$$E_{Ps} = E_i - 6.8 \text{ eV}$$

For atomic hydrogen and helium, the two target atoms with which we shall be most concerned, the positronium formation thresholds are 6.803 and 17.6 eV, respectively. If the ionization potential is less than 6.8 eV, as is the case for the alkali atoms, the positronium formation channel is open even at zero positron energy; indeed the reaction is exothermic.

The energy interval between the positronium formation threshold and the first excitation threshold of the target atom, E_1 (assuming $E_1 > E_{Ps}$), is referred to as the Ore gap. Within this energy gap positrons can either be elastically scattered or form positronium. Direct annihilation of the positron with one of the electrons in the target atom is also possible, but the cross section for this process is very much smaller than that for either elastic scattering or positronium formation. The Ore gaps for atomic hydrogen and helium are 6.8–10.2 and 17.8–20.6 eV, respectively.

Positronium formation can of course occur at energies beyond the upper limit of the Ore gap, and it continues to make a significant contribution to the total cross section at positron energies as high as 100 eV, but it then

competes with many other inelastic processes and it becomes almost impossible to treat the process in a very precise manner. Within the Ore gap only two channels are open and very accurate results can be obtained, at least for simple target atoms, using rather similar techniques to those employed to calculate the essentially exact values of the scattering parameters for low-energy elastic scattering of positrons by hydrogen (Schwartz, 1961a; Humberston and Wallace, 1972; Armstead, 1968; Register and Poe, 1975) and helium (Humberston, 1973; Campeanu and Humberston, 1975; Humberston and Campeanu, 1980).

Detailed theoretical investigations of positronium formation in the Ore gap have so far only been made for atomic hydrogen. No experimental results are yet available for this system, although the development of much more intense positron beams may make such an experiment possible in the near future. Nevertheless, the study of the process in the relatively simple positron–hydrogen system is expected to lead to a better understanding of positronium formation in more complex systems.

A. Positron–Hydrogen Scattering

Many different approximation methods have been used to calculate positronium formation cross sections, and we will not attempt to review them all here. Instead we shall concentrate mainly on the more elaborate methods which have yielded the most accurate results within the Ore gap. References to other simpler methods are given in the review of Ghosh *et al.* (1982).

The Hamiltonian of the positron–hydrogen system can be written in atomic units (using the nomenclature in Fig. 1 and assuming an infinitely massive proton) as

$$H = -\tfrac{1}{2}\nabla_{r_1}^2 - \tfrac{1}{2}\nabla_{r_2}^2 + \frac{1}{r_1} - \frac{1}{r_2} - \frac{1}{r_3} \tag{1}$$

which is appropriate when considering the system as positron–hydrogen, or as

$$H = -\tfrac{1}{4}\nabla_{\rho}^2 - \nabla_{r_2}^2 + \frac{1}{r_1} - \frac{1}{r_2} - \frac{1}{r_3} \tag{2}$$

which is appropriate when considering the system as positronium–proton.

For each partial wave the total wave function can be written in the two-component form as

$$\begin{pmatrix} \Psi_1 \\ \Psi_2 \end{pmatrix}$$

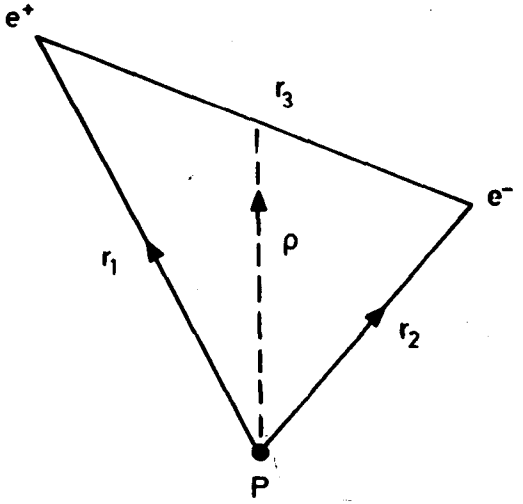

FIG. 1. The positron–hydrogen system.

where the first component, Ψ_1, represents positron–hydrogen elastic scattering with positronium formation, and the second component, Ψ_2, represents positronium–proton elastic scattering with electron attachment to the proton. The asymptotic forms of the two components are

$$\begin{aligned}
\Psi_1 &\underset{r_1\to\infty}{\sim} Y_{l,0}(\hat{r}_1)k^{1/2}\phi_{\mathrm{H}}(r_2)[j_l(kr_1) - K_{11}n_l(kr_1)] \\
&\underset{\rho\to\infty}{\sim} -Y_{l,0}(\hat{\rho})(2\kappa)^{1/2}\phi_{\mathrm{Ps}}(r_3)K_{21}n_l(\kappa\rho) \\
\Psi_2 &\underset{\rho\to\infty}{\sim} Y_{l,0}(\hat{\rho})(2\kappa)^{1/2}\phi_{\mathrm{Ps}}(r_3)[j_l(\kappa\rho) - K_{22}n_l(\kappa\rho)] \\
&\underset{r_1\to\infty}{\sim} -Y_{l,0}(\hat{r}_1)(k)^{1/2}\phi_{\mathrm{H}}(r_2)K_{12}n_l(kr_1)
\end{aligned} \tag{3}$$

where K_{ij} $(i, j = 1, 2)$ are the elements of the K matrix (reaction matrix), and $\phi_{\mathrm{H}}(r_2)$ and $\phi_{\mathrm{Ps}}(r_3)$ are the wave functions of the hydrogen atom and the positronium. The wave numbers of the positron and positronium are k and κ, respectively, and energy conservation gives

$$2E = k^2 - 1 = \tfrac{1}{2}(\kappa^2 - 1) \tag{4}$$

The cross section for scattering between channels v and v' is

$$\sigma_{vv'} = \frac{4(2l+1)}{k_v^2}\left|\left(\frac{K}{1-iK}\right)_{vv'}\right|^2 \tag{5}$$

in units of πa_0^2, where subscripts 1 and 2 refer to the positron–hydrogen and positronium–proton channels, respectively, and $k_1 = k$ and $k_2 = \kappa$. Thus, the cross sections for positron–hydrogen elastic scattering and positronium formation are σ_{11} and σ_{12}, respectively.

The most accurate results for the s-, p-, and d-wave contributions to the positronium formation cross section are believed to be those obtained by Humberston (1982, 1984) and Brown and Humberston (1984, 1985) using the Kohn variational method with very elaborate trial functions containing many variational parameters. Although it is not a bounded variational method, and very anomalous results can sometimes be obtained (Schwartz, 1961a), the method is simple to use and has yielded very accurate results for the elastic scattering of positrons by hydrogen and helium atoms below the positronium formation threshold.

For the present two-channel problem the stationary Kohn functional takes the matrix form

$$\begin{vmatrix} K_{11} & K_{12} \\ K_{21} & K_{22} \end{vmatrix} = \begin{vmatrix} K_{11}^t & K_{12}^t \\ K_{21}^t & K_{22}^t \end{vmatrix} - \begin{vmatrix} (\Psi_1, \mathcal{L}\Psi_1) & (\Psi_1, \mathcal{L}\Psi_2) \\ (\Psi_2, \mathcal{L}\Psi_1) & (\Psi_2, \mathcal{L}\Psi_2) \end{vmatrix} \tag{6}$$

where $\mathcal{L} = 2(H - E)$, and Ψ_1 and Ψ_2 are suitably chosen trial functions with the asymptotic forms given by Eq. (3), namely

$$\begin{aligned} \Psi_1 = {} & Y_{l,0}(\hat{r}_1)\phi_H(r_2)k^{1/2}\{j_l(kr_1) - K_{11}^t n_l(kr_1)[1 - \exp(-\lambda r_1)]^p\} \\ & - Y_{l,0}(\hat{\rho})\phi_{Ps}(r_3)(2\kappa)^{1/2}K_{21}^t n_l(\kappa\rho)[1 - \exp(-\mu\rho)]^q \\ & + Y_{l,0}(\hat{r}_1,\hat{r}_2)\sum_i c_i \exp[-(\alpha r_1 + \beta r_2 + \gamma r_3)]r_1^{k_i}r_2^{l_i}r_3^{m_i} \\ \Psi_2 = {} & Y_{l,0}(\hat{\rho})\phi_{Ps}(r_3)(2\kappa)^{1/2}\{j_l(\kappa\rho) - K_{22}^t n_l(\kappa\rho)[1 - \exp(-\mu\rho)]^q\} \\ & - Y_{l,0}(\hat{r}_1)\phi_H(r_2)k^{1/2}K_{12}^t n_l(kr_1)[1 - \exp(-\lambda r_1)]^p \\ & + Y_{l,0}(\hat{r}_1,\hat{r}_2)\sum_i d_i \exp[-(\alpha r_1 + \beta r_2 + \gamma r_3)]r_1^{k_i}r_2^{l_i}r_3^{m_i} \end{aligned} \tag{7}$$

For each value of l there are $(l + 1)$ different angular functions $Y_{l,0}(\hat{r}_1,\hat{r}_2)$ with the parity of l (Schwartz, 1961b), and associated with each such function is a summation over the index i in Eq. (7), which includes all terms with $k_i + l_i + m_i \leq \omega$, where k_i, l_i, m_i, and ω are non-negative integers. Further details of the method of calculation are given by Humberston (1982).

Very accurate results can be obtained if sufficient short-range correlation terms are included, but in order to establish the precision of a particular result it is necessary to investigate the convergence with respect to systematic improvements in the trial function. Increasing the value of ω provides such a systematic improvement, and the numbers of terms generated by the above scheme for $\omega = 1, 2, \ldots, 7$ are 4, 10, 20, 35, 56, 84, and 120, respectively.

Although, as mentioned earlier, the Kohn variational method is not a bounded method, it is almost invariably found in practice to give lower bounds on the diagonal elements of the K matrix. As the trial function is improved by increasing ω, these matrix elements increase monotonically and converge to the (presumably) exact values. Indeed the convergence is often sufficiently smooth that extrapolation to infinite ω is possible, giving even more accurate results (Humberston, 1984). No such bound principle applies to the off-diagonal K-matrix element $K_{12}(=K_{21})$ and accordingly the variation with ω can be somewhat erratic, although for sufficiently large values of ω the results do seem to converge.

We will now consider the results obtained by the above procedure for each partial wave in turn.

1. s Wave

The variations of the elastic scattering and positronium formation cross sections with ω at four positron energies within the Ore gap are shown in Figs. 2 and 3. The lower and upper boundaries of the Ore gap correspond to $k = 1/\sqrt{2} = 0.7071 a_0^{-1}$ and $k = \sqrt{3/4} = 0.8660 a_0^{-1}$, respectively. The con-

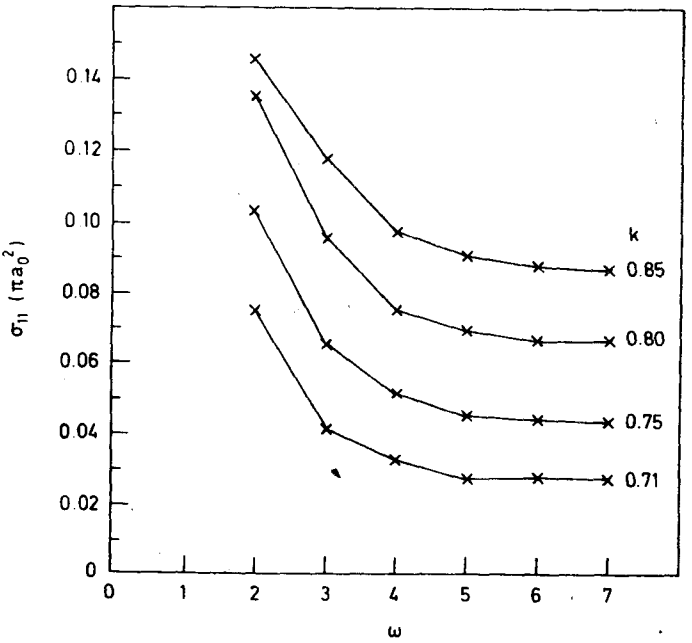

FIG. 2. Variation of the s-wave elastic cross section with ω.

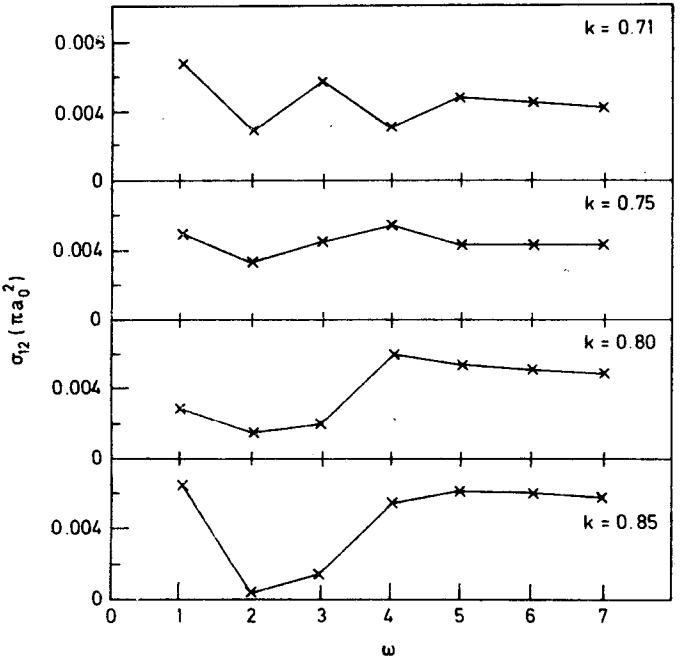

FIG. 3. Variation of the *s*-wave positronium formation cross section with ω.

vergence of the elastic scattering cross sections is particularly impressive, and even the positronium formation cross sections have probably converged to within 10% of their exact values. Details of the convergence of the individual *K*-matrix elements are given by Humberston (1984).

The energy dependence of the *s*-wave contribution to the positronium formation cross section is plotted in Fig. 4. A conspicuous feature, which has been examined in detail by Humberston (1982), is the initial very rapid rise from zero at the threshold, but the magnitude of the cross section remains very small relative to the elastic cross section and, as we shall see, also to higher partial-wave contributions to the positronium formation cross section.

Also plotted in Fig. 4 are the results from other calculations using a variety of approximation methods. The extraordinarily wide range of values, spanning several orders of magnitude, illustrates the sensitive dependence of the results on the quality of the trial function. Even some of the other elaborate variational calculations, such as those of Stein and Sternlicht (1972), Chan and Fraser (1973), and Winick and Reinhardt (1978), give significantly different results.

Stein and Sternlicht also used the Kohn variational method with a similar,

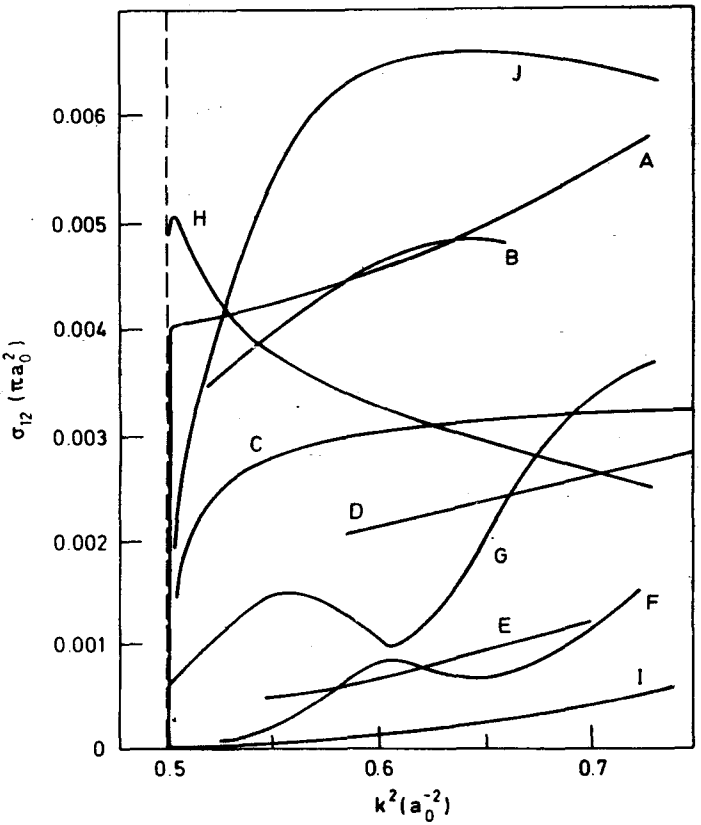

FIG. 4. Results for the *s*-wave positronium formation cross section in positron–hydrogen scattering: (A) Humberston (1982); (B) Stein and Sternlicht (1972); (C) Chan and Fraser (1973); (D) Winick and Reinhardt $\times 10^{-1}$ (1978); (E) Fels and Mittleman (1967); (F) Dirks and Hahn (1971); (G) Wakid and La Bahn $\times 10$ (1972); (H) Bransden and Jundi $\times 10^{-2}$ (1967); (I) coupled static approximation; (J) Born approximation $\times 10^{-2}$.

but slightly less flexible, trial function to that of Humberston. Up to 84 correlation terms ($\omega = 6$) were included and very satisfactory agreement with the results of Humberston was obtained except at energies close to the positronium formation threshold. Their values of the diagonal elements of the K matrix then fall slightly below those of Humberston, strongly suggesting that their results are less accurate.

Chan and Fraser used a method based on the formulation of the coupled static approximation with the addition of several short-range correlation terms, ϕ_i. The method amounts to using the Kohn variational method with

trial functions of the form

$$\Psi_1 = F_1(r_1)\phi_H(r_2) + G_1(\rho)\phi_{Ps}(r_3) + \sum_i c_i\phi_i$$
$$\Psi_2 = F_2(r_1)\phi_H(r_2) + G_2(\rho)\phi_{Ps}(r_3) + \sum_i d_i\phi_i \qquad (8)$$

and allowing the variational method to determine the forms of the functions $F_i(r_1)$ and $G_i(\rho)$ $(i = 1, 2)$. These emerge as numerical solutions to a set of coupled integrodifferential equations with boundary conditions at infinity given by Eq. (3). Although the method is more complicated than the purely algebraic Kohn method, it has the advantage of yielding rigorous lower bounds on the diagonal elements and eigenvalues of the K matrix provided the total energy of the system is below the lowest eigenvalue of the operator **QHQ**, where **Q** is the closed channel projection operator (Hahn, 1966);

$$\mathbf{Q} = \begin{pmatrix} 1 - |\phi_H\rangle\langle\phi_H| & 0 \\ 0 & 1 - |\phi_{Ps}\rangle\langle\phi_{Ps}| \end{pmatrix}$$

and

$$\mathbf{H} = \begin{pmatrix} H & H \\ H & H \end{pmatrix}$$

The eigenvalues of **QHQ** are related to the positions of Feshbach resonances and such resonances are known to exist just below the $n = 2$ excitation threshold of the hydrogen atom (Doolen *et al.*, 1978), although none has yet been found in a direct calculation of the type being described here. The three resonances found by Seiler *et al.* (1971) have been shown to be artifacts of their method of calculation, which neglected the open positronium channel. When this channel was included in the trial function the resonances disappeared (Drachman, 1975).

Only 26 short-range correlation terms of a rather restricted form were used by Chan and Fraser, and, not surprisingly, the values of their diagonal K-matrix elements and eigenphases are somewhat less positive than those of Humberston. However, their results are significantly better than those obtained from earlier rigorous lower-bound calculations such as those of Dirks and Hahn (1971) and the coupled static approximation.

A somewhat less conventional method of calculation has been used by Winick and Reinhardt (1978). They calculated the various partial-wave elastic scattering amplitudes, t_l, from the off-shell elastic scattering T matrix and hence the elastic scattering across sections

$$\sigma_{el}^{l} = \frac{4}{k^2}(2l + 1)|t_l|^2 \qquad (9)$$

Then, using the optical theorem, they also obtained the partial-wave total cross sections

$$\sigma_{\text{tot}}^{l} = \frac{4}{k^2}(2l+1)\,\text{Im}\,t_l \tag{10}$$

The difference between σ_{tot} and σ_{el} is the cross section due to all inelastic processes, and within the Ore gap the only such process is positronium formation.

The matrix representation of the total Hamiltonian that is required for the calculation of the T matrix was generated using basis functions of the form, using the same nomenclature as in Fig. 1,

$$\phi_i = \exp[-(\alpha r_1 + \beta r_2)] r_1^{k_i} r_2^{l_i} r_3^{m_i} Y_{l_1,l_2,L}(\hat{r}_1, \hat{r}_2) \tag{11}$$

Again all functions with $k_i + l_i + m_i \leq \omega$ were included with the exception of a few terms when $\omega = 7$, so that the maximum number of functions was 105. Given the similarity of these basis functions in form and number to those used by Humberston, one might have expected the two sets of results to

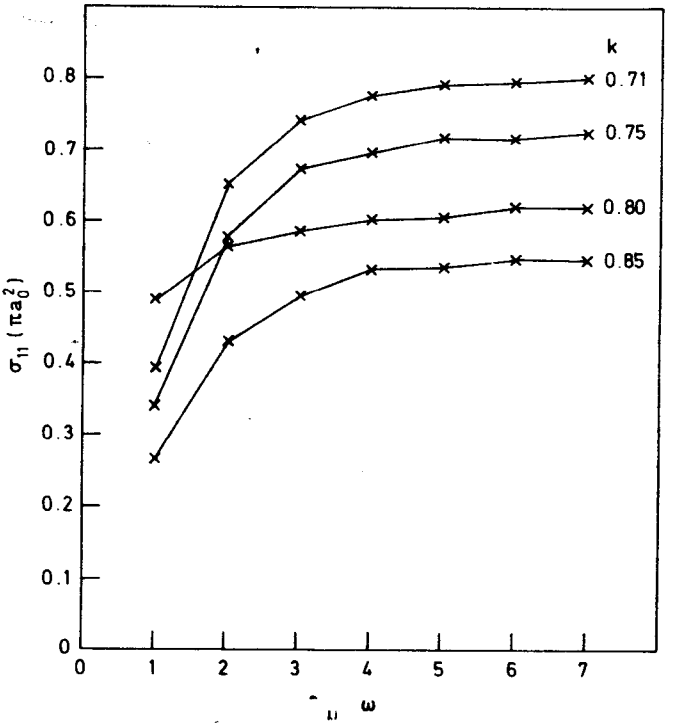

FIG. 5. Variation of the p-wave elastic scattering cross section with ω.

be in good agreement. This is indeed so for the elastic scattering cross section, but the positronium formation cross section is approximately five times larger than Humberston's. The discrepancy is most probably due to the smallness of the positronium formation cross section in relation to the elastic cross section. The elastic and total cross sections are therefore very similar in magnitude, and, as both cross sections are slightly in error, the subtraction procedure is very likely to introduce a large percentage error into the positronium formation cross section.

2. *p Wave*

The convergence of the *p*-wave elastic scattering and positronium formation cross sections with respect to ω, as obtained by Brown and Humberston, is shown in Figs. 5 and 6. These results are slightly different from those already published by Brown and Humberston (1984) and correspond to an improved choice of values of the nonlinear parameters in the trial function that gives much better convergence to well within 10% of the exact values. Except at energies very close to the threshold, the *p*-wave contribution to the

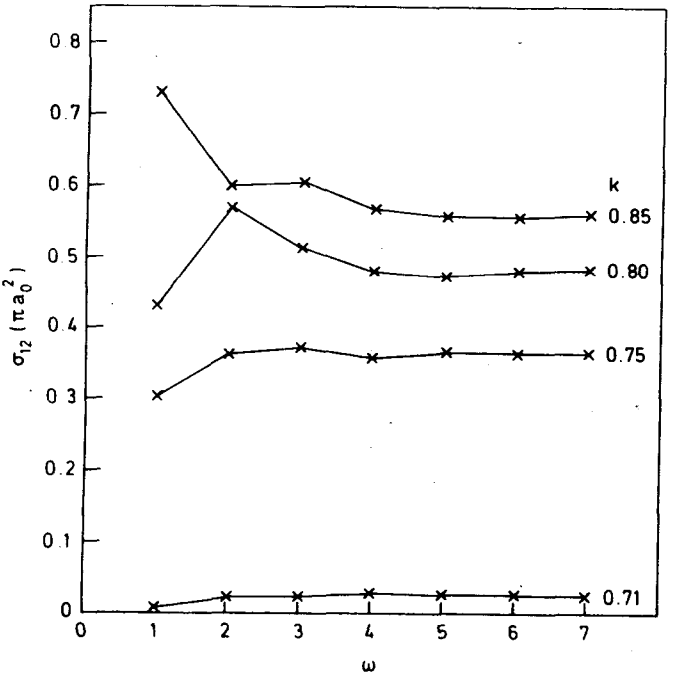

FIG. 6. Variation of the *p*-wave positronium formation cross section with ω.