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Semiempirical polarization potential for low-energy positron-atom and positron–atomic-ion interactions. I. Theory: Hydrogen and the noble gases

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A simple model for the effects of polarization is introduced for the study of positron-atom interactions. The model is also used to study positronium-atom interactions by treatment of such systems as the interactions of positrons with polarizable anions. The model depends upon the average dipole polarizability of the atom (or ion) and one disposable parameter, an effective radius. The effective radius is determined by fitting calculated scattering lengths for H and He and the calculated positronium affinity of H to their well-established values, and by interpolating on the ionization potentials for other atoms. The model produces quite satisfactory phase shifts and cross sections for positrons scattering elastically off H, He, Ne, Ar, Kr, and Xe. The model appears to be equal or superior in predictive power to the much more elaborate polarized-orbital model recently formulated by McEachran *et al.* The model predicts that none of the rare-gas atoms studied will bind a positron. As a measure of how far from binding they are, negative values of the positron affinity are devised by appealing to effective-range theory and a heuristic argument involving the dependence of the calculated scattering length on the disposable parameter in the model.

INTRODUCTION

The concept of modeling the response of a complicated electronic system to an external perturbation has attracted attention from the early days of quantum mechanics. The attractive features of the concept include its numerical and conceptual simplicity, and the great variety of systems to which it can be applied. In the present series of papers we are concerned with a particular application: the interactions of the positron and of positronium with neutral atoms.

Our understanding of the chemistry of positronium has been advanced very markedly in the last decade, principally by experimentalists who are measuring the rate constants for the ortho-to-para conversion of positronium by a large number of molecules in a variety of gaseous and liquid environments. A detailed theoretical understanding of this process is just beginning to appear,[1,2] but progress in this area is slow and uncertain owing to our extremely limited knowledge of the interactions of positron and positronium with simpler systems—atoms.

This is what we know well about binding energies and phase shifts for low-energy ($\lesssim 10$ eV) positron- and positronium-atom interactions: the binding energy of positronium hydride (1.02 eV)[3]; the s-, p-, and d-wave phase shifts for positron-hydrogen elastic scattering,[4-7] and s- and p-wave phase shifts for positron-helium elastic scattering.[8,9] These values are probably accurate to within 1%. Less well known (5%–20% probable uncertainty) are the cross sections for positrons scattering off neon, argon, krypton, and xenon,[10-15] and the positronium binding energies for the halogen atoms.[16]

In the present series of papers we use some of this information to calibrate a model which we can apply to other atoms, calculating binding energies and scattering cross sections of (hopefully) about the same quality. Specifically, we calibrate the model with three well-known numbers: the binding energy of positronium hydride, and the scattering lengths for positrons off hydrogen and helium atoms. The utility of the model is then established by calculations of the cross sections for positrons off hydrogen and the noble gases (this paper) and calculations of the positronium affinities of the halogen atoms (next paper in this series). In subsequent papers, the model will be applied to many other atoms, thus mapping out the main features of positron-atom interactions for the bulk of the Periodic Table with a uniform theory. We will then be in a position to improve our initial attempt at understanding positron-molecule interactions.[1,2]

MODEL

We integrate a Schrödinger equation for the positronic-orbital/scattering wave ϕ_p:

$$\left(-\tfrac{1}{2}\nabla^2+\frac{Z}{r}-\sum_i J_i(r)+V_{\text{pol}}(r)-\epsilon_p\right)\phi_p(\vec{r})=0\,. \qquad (1)$$

J_i is the Coulomb potential for the ith electronic orbital of the isolated atom,

$$J_i(r_p)=\int\frac{|\phi_i(\vec{r}_e)|^2}{|\vec{r}_e-\vec{r}_p|}d\vec{r}_e\,; \qquad (2)$$

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ϵ_p is either the (−) binding energy of the positron to the atom or $1/2k^2$, the positron incident energy, depending upon whether a bound or scattering positron is being considered; and V_{pol} is a potential to account for the distortion of the electronic orbitals due to the presence of the positron. This polarization potential embodies the model. We calculate the static part of the potential, $-\sum_i J_i$, from tabulated Hartree-Fock wave functions,[17-20] and we model the polarization part: a specification of V_{pol} constitutes a model. Positronium-atom interactions are investigated by applying this procedure to atomic mononegative ions.

The long-range behavior of V_{pol} is well known. Its dominant term is $-\frac{1}{2}\alpha/r^4$, where α is the average static dipole polarizability of the atom. The next most important term is of the order of r^{-6}, which we ignore. The short-range behavior of V_{pol} is not well known. It has important nonadiabatic components, and its determination, even approximately and for simple atoms, requires a major computational effort.[21,22]

Our model is extremely simple:

$$V_{\mathrm{pol}}(r) = \begin{cases} -\alpha/2r^4 & r \geq r_0 \\ -\alpha/2r_0^4 & r \leq r_0 \,. \end{cases} \tag{3}$$

The polarizability is the best value available[23,24] and r_0 is a disposable parameter determined for each atom as described below.

Any number of other functional forms than (3) above might have been used. The most important feature of any model for positron-atom interactions is to have the correct long-range behavior, as in (3). This was recognized very early by Ore[25]; it was applied in further calculations by Lee,[26] and it has been emphasized more recently by several other groups.[27-30]

The only question has to do with the short-range behavior of V_{pol}. In some exploratory calculations we used, instead of Eq. (3), a form $-\alpha w(r)/2r^4$ where w, a cutoff function, was taken to be

$$w(r) = (1 - e^{-(r/r_0)^N})^{4/N}. \tag{4}$$

We found that, for each fixed value of $N > 0$, we could find a value for r_0 which gave the desired scattering length for positron-hydrogen scattering. However, the agreement between our calculated s-wave phase shifts and those of Bhatia *et al.*[5] for hydrogen for $k < 1$ a.u. improved as N was made larger; we therefore took the form of w as N increases without limit:

$$w \xrightarrow{N \to \infty} \begin{cases} (r/r_0)^4 & r \leq r_0 \\ 1 & r \geq r_0 \,. \end{cases} \tag{5}$$

This choice gives Eq. (3), the polarization potential used in the rest of our calculations.

Equation (1) is integrated outward from the origin with the method of Bulirsch and Stoer,[31] using a subroutine coded by Ramaker. For the scattering calculations, the integration is carried out until the scattering wave achieves its asymptotic form as determined by the convergence of phase shifts to five significant figures. Calculations are performed with our model for the waves $l = 0$ to 3 (exception: 2 for H and He) and the rule of O'Malley *et al.*[32] is used for $l = 4$ to 6 (3 to 6 for H and He). For bound-state calculations the integration is carried out until the positronic orbital achieves its asymptotic form.[33] The value of ϵ_p in Eq. (1) which eliminates the diverging component of ϕ_p is determined by a method due to Schrader and Prager.[34]

HYDROGEN-POSITRON

Hydrogen does not bind a positron[35,36]; the scattering is only elastic from $k = 0$ up to $k = 0.707$ a.u., the threshold for positronium formation. The s-wave phase shifts were given with good accuracy by Schwartz[4] whose numbers were later confirmed and refined by Bhatia *et al.*[5] We take these results together with those of Bhatia, Temkin, and Eiserike[6] for the p wave and those of Register and Poe[7] for the d wave, and the approximation of O'Malley *et al.*[32] for $l = 3$ to 6, and from them calculate the cross section for comparison with our model. For the scattering length, we take as our standard −2.1036 a.u., the value of Houston and Drachman.[37]

The value of α, the dipole polarizability in our model [Eq. (3)], is known from elementary atomic theory; the value of r_0 which reproduces the scattering length is 2.399 a.u.

Our results for hydrogen are shown in Figs. 1 and 2 where they are compared with the accurate values, and with those given by the adiabatic and polarized-orbital approximations. (A key to all the figures is given in Table I.) Our cross sections in Fig. 2 cannot be distinguished from the accurate values from $k = 0$–0.25 a.u. beyond which they are close to the polarized orbital results. No bound state exists for our potential.

HELIUM-POSITRON

We know that helium is definitely not able to bind a positron[39,40] despite some confusion on this point.[41,42] The positronium formation threshold is $k = 1.145$ a.u.

Following Campeanu and Humberston,[9] we take as our standard for comparison the s-wave phase shifts of Humberston,[8] the p-wave results of

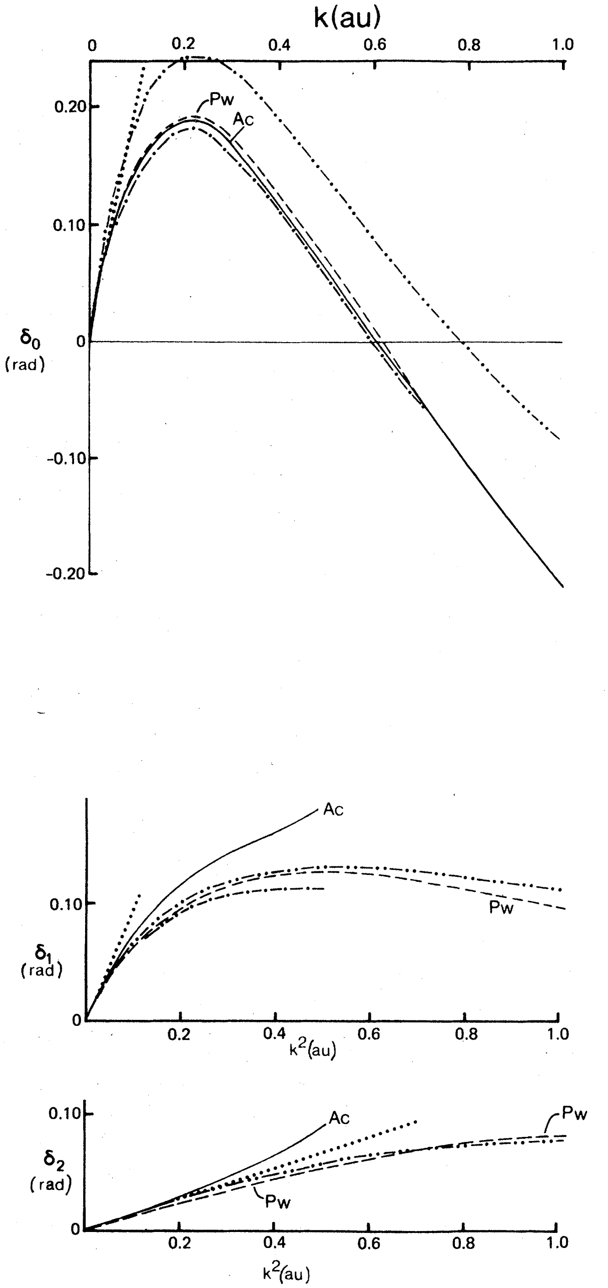

FIG. 1. The s-, p-, and d-wave phase shifts for positron-hydrogen elastic scattering as functions of positron momentum k (s wave) or k^2 (p and d waves). See Table I for a key.

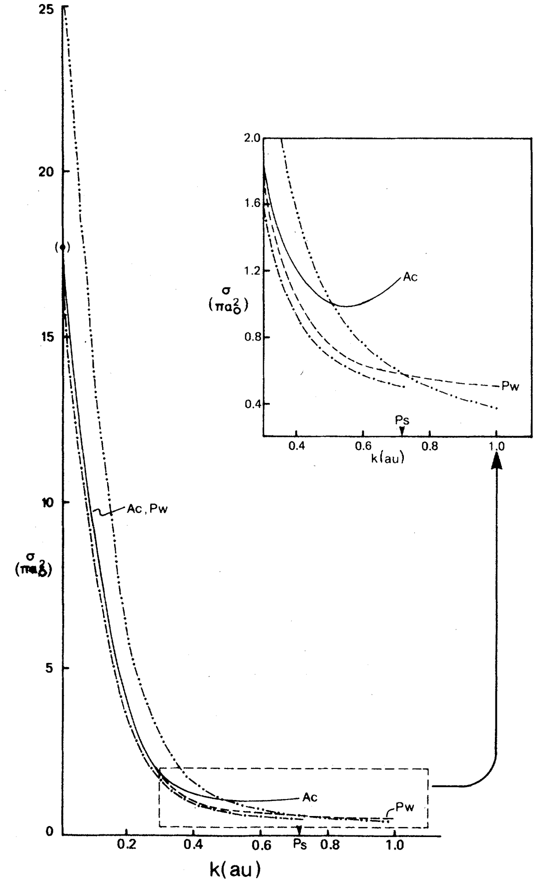

FIG. 2. Cross section for positron-hydrogen elastic scattering. The point indicated by (•) is fitted; the remainder of the PW curve is calculated from our model. Ps indicated the threshold for positronium formation. See Table I for a key.

Campeanu and Humberston,[9] and the highest d-wave results of Drachman.[43] For the cross-section calculation, we augment these with phase shifts for $l = 3$ to 6 with the rule of O'Malley *et al.*[32] Although the resulting cross sections are in good agreement with the observed values of Canter *et al*,[10,11,44] these results should not necessarily be regarded as the ultimate choice, for there remains significant disagreement between these results and other apparently accurate calculations and observations.[15,45-50] The somewhat confusing state of affairs, portrayed in Fig. 3, has been analyzed by Humberston[51] who argues that the results of Canter *et al.*[10,11] and of Campeanu and Humberston[8,9] are the most accurate. The calculations of Amusia *et al.*[47] seem to agree closely with the calculations of Humberston and Campeanu[8,9] and the measurements of Canter *et al.*[10,11] The measurements of Stein *et al.*[15] seem to be in good agreement with those of Burciaga *et al*,[50] the calculations of Aulenkamp *et al.*,[46] and the observations of Jaduszliwer and Paul[45] are somewhat at variance with each other and the other results as well. All these results are shown in Fig. 3. {Some new experimental results [W. G. Wilson, J. Phys. B 11, L629 (1978)] and analysis [T. C. Griffith *et al.*, J. Phys. B 11, L635 (1978)]

TABLE I. Key to Figs. 1–10.

Symbol	Description	H (Figs. 1 and 2)	He (Figs. 3 and 4)	Ne (Figs. 5 and 6)	Ar (Figs. 7 and 8)	Kr (Fig. 9)	Xe (Fig. 10)
——AC	Accurate results	Refs. 5–7	Ref. 9				
———PW	Present work						
–·–·–	Polarized orbital	Ref. 38	Ref. 52	Ref. 74	Ref. 83		
–··–··–	Adiabatic	Ref. 38	Ref. 43				
–···–···–	Other theoretical		Ref. 47	Refs. 72 and 73[b]	Refs. 72 and 73		
–····–····	Other theoretical		Ref. 46	Ref. 70	Ref. 70	Ref. 70	
+	Other theoretical			Ref. 71	Ref. 71		
········	Limiting slopes[a]	Ref. 37	Ref. 8				
||||| ⊙	Experimental		Ref. 15	Ref. 15	Ref. 14	Ref. 12	Ref. 12
\\\\\ ⊡	Experimental		Refs. 10,11,44	Refs. 10,11,44	Refs. 10,11,44	Refs. 10,11	Refs. 10,11
≣ △	Experimental		Refs. 50,53	Ref. 53	Preliminary results (Ref. 53)		Ref. 53
▽	Experimental		Refs. 13,45	Refs. 13,45	Ref. 13		

[a] s-wave limiting slopes are (–) the accurately determined scattering lengths, for which references are given above. For p-waves, the limiting slopes are $\pi\alpha/15$; for d waves, $\pi\alpha/105$.

[b] The $(2s\text{-}p) + (2p\text{-}d)$ normalized results are given for neon; $(3p\text{-}d) + (3p\text{-}s) + (3s\text{-}p)$ results for argon.

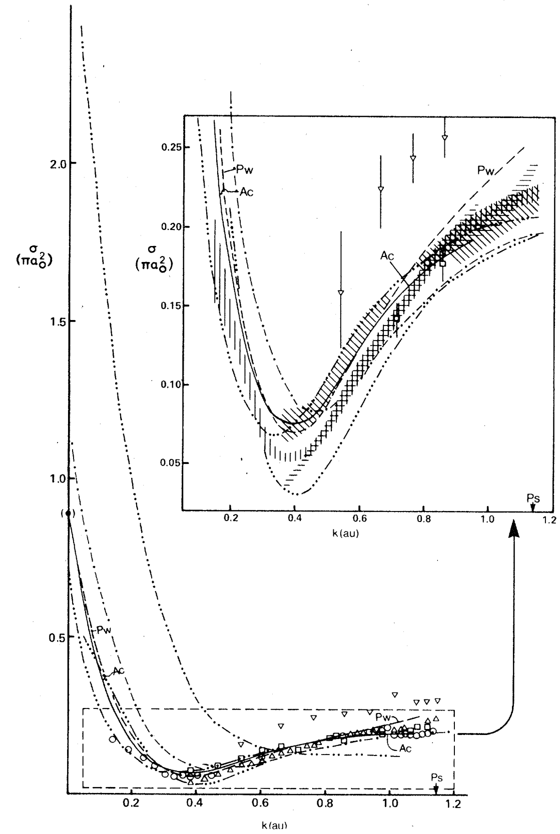

FIG. 3. Cross section for positron-helium elastic scattering. The point indicated by (•) is fitted, the remainder of the PW curve is calculated from our model. Ps indicates the threshold for positronium formation. See Table I for a key. The adiabatic results are not shown in the inset for clarity.

indicates the result of Refs. 8–11 are best.}

The polarizability of helium is well known from quantum calculations: $1.383a_0$.[54-58] The value of r_0 which reproduces Humberston's[8] scattering length ($-0.472a_0$) is $1.774a_0$. This parameter produces cross sections (Fig. 3) and phase shifts (Fig. 4) in quite remarkable agreement with the results of Humberston[8] and Campeanu and Humberston[9] from $k=0$ (the one fitted point) clear through the Ramsauer minimum and up to the positronium formation threshold. The agreement is particularly apparent in the phase shifts, Fig. 4. One should note that the Campeanu-Humberston phase shifts for $l=1$ can probably be improved a little by including p-type targets in the wave function for the scattering problem.[9]

We find no bound state for our potential.

HYDROGEN-POSITRONIUM

The positron will bind to any negative ion, of course. The question is, is the bound state below the threshold for positronium split-off? If so, the positronium-atom complex is stable to dissociation, and the positronium affinity A_{Ps}

$$A_{\text{Ps}} = A_e - \epsilon_p - 6.8 \text{ eV} \qquad (6)$$

is positive. A_e above is the electron affinity of the atom in question, ϵ_p is the eigenvalue calculated by solving Eq. (1) for the lowest bound state, and 6.8 eV is the binding energy of positronium, Ps.

The electron affinity of the hydrogen atom is

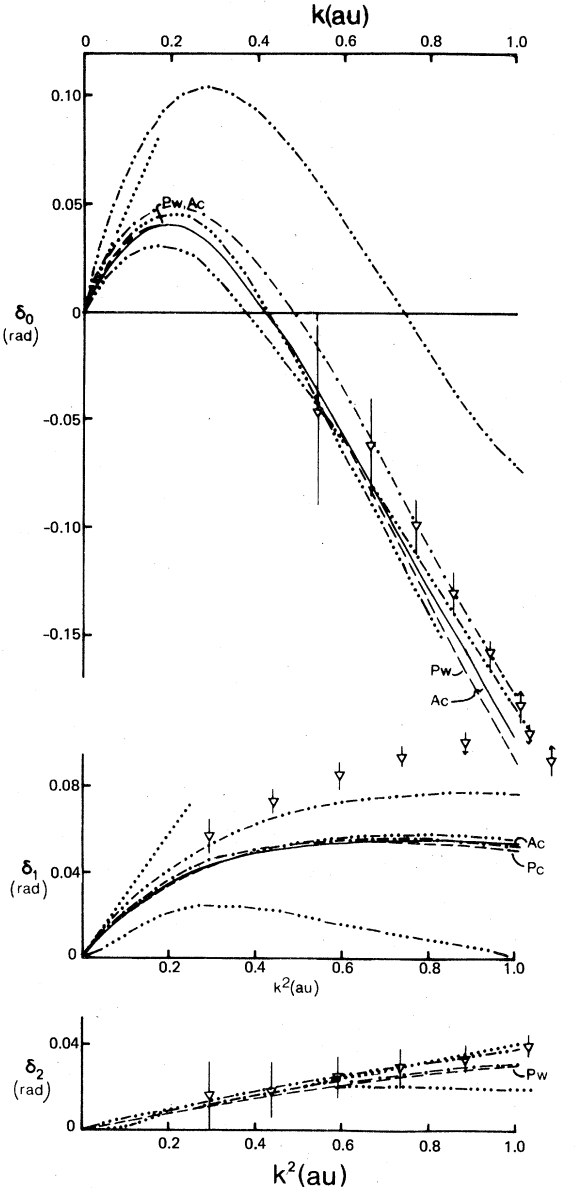

FIG. 4. The s-, p-, and d-wave phase shifts for positron-helium elastic scattering as functions of positron momentum k (s wave) or k^2 (p and d wave). See Table I for a key.

extremely well known from quantal calculations.[59] It is 0.754 eV. Similarily, an accurate value for the polarizability of H$^-$ is also provided by calculations[54]: 206.1a_0^3. The positronium affinity in Eq. (6) is known with good accuracy from the calculations of Ho[3] and Page and Fraser[60]; it is 1.02 eV. These numbers and Eq. (6) lead one to −0.25982 a.u. as the desired value of ϵ_p in Eq. (1). This number is obtained if the parameter r_0 is given the value 5.621a_0.

This value gives $\epsilon_p = -0.17545$ for the lowest $l = 1$ solution of Eq. (1). Equation (6) then gives the positronium affinity for a $2p$ positron as −1.27 eV; this indicates there is no bound excited state of positronium hydride.

The Hartree-Fock wave function for H$^-$, needed to calculate the term $-\sum_i J_i$ in Eq. (1), is not available in the literature as far as we know. None of the standard tabulations of negative ion wave functions[17-20] include H$^-$, presumably because the self-consistent-field iterative process diverges for this system. A function purported to be the Hartree-Fock wave function for H$^-$,[61] is in fact not, being infinite at the origin. Making an obvious correction in the reported parameters (changing each reported parameter n_i to $n_i - 1$) gives a function which is finite at the origin but does not accurately satisfy the cusp condition for electron-proton coalescense there, and hence does not satisfy the Hartree-Fock equation at that point.

For this reason we have calculated a Hartree-Fock wave function for H$^-$. For a wave function of the Hartree-Fock form

$$\Psi(\vec{r}_1, \vec{r}_2) = \phi(r_1)\phi(r_2),$$

$$\phi(r) = \sum_i X_i(r) C_i, \tag{7}$$

$$X_i(r) = \frac{(2\rho_i)^{n_i+1/2}}{[4\pi(2n_i)!]^{1/2}} r^{n_i-1} e^{-\rho_i r},$$

we minimize the quantity $\langle\Psi|H|\Psi\rangle/\langle\Psi|\Psi\rangle$ directly as a function of the parameters C_i, thus avoiding any self-consistency instabilities. H is

$$H = -\tfrac{1}{2}\nabla_1^2 - \tfrac{1}{2}\nabla_2^2 - 1/r_1 - 1/r_2 + 1/r_{12}. \tag{8}$$

Our function is given in Table II. The basis set is that of Curl and Coulson,[61] with their n_i values increased by one each. Our function is normalized to unity.

TABLE II. Hartree-Fock wave function for H$^-$.

	Parameters [Eq. (7)]	
n_i	ρ_i	C_i
1	0.3	0.256 42
1	0.7	0.489 01
2	0.7	0.134 48
1	1.3	0.248 19
2	1.3	−0.032 65
Total energy		= −0.487 909 2
$\frac{\text{Potential energy}}{\text{Kinetic energy}}$		= −2.000 090
Orbital eigenvalue		= −0.046 306
Orbital cusp		= −0.999 179

HELIUM-POSITRONIUM

This system, as well as the other noble-gas atom-positronium systems, is beyond the scope of our model. In order to study atom-positronium systems with our model, we must first solve Eq. (1) for the positron interacting with the polarizable mononegative atomic ion, and then we must use Eq. (6) to calculate the positronium affinity of the neutral atom. It follows that the atom must have a stable mononegative ion, and that the Hartree-Fock wave function for this ion must be known in order for our model to be applicable. For helium, these necessary conditions are not satisfied, so we have nothing to say about this system.

It has been the object of only one quantum-mechanical calculation to our knowledge, that of Clary,[62] that gives an extensive correlated configuration-interaction wave function appropriate for a bound state. However, Clary's calculated energy for the system is 1.51 eV above that for separated He and Ps atoms.

EXTENDING THE MODEL TO OTHER ATOMS

The values of r_0 obtained as described above are (1.774a_0, 2.399a_0, 5.621a_0) for (He, H, H$^-$). These do not correlate well with any measure of the sizes of these systems which are also available for most other atoms and their mononegative ions. For example, the accepted values of the "chemical" radii (crystalline radius for He, covalent radius for H, ionic radius for H$^-$) are (1.76a_0, 0.65a_0, 2.91a_0).[63] The electrical polarizabilities and diamagnetic susceptibilities of atoms can be shown on the basis of simple and approximate arguments to vary as the cube and square of the atomic radii, respectively.[64] The radii calculated from polarizabilities are 0.69a_0, 1.02a_0, 3.71a_0 and those from susceptibilities are 1.55a_0, 1.93a_0, 3.98a_0, respectively; the latter set of values correlates fairly well with those of our parameter r_0; unfortunately, the diamagnetic susceptibilities are not generally available for atoms and their mononegative ions, which are usually paramagnetic. A similar problem obviates the use of radii from kinetic theory.

It appears that we must search further for a physical property to which we can relate our values of the parameter r_0. To be useful in determining r_0 for other atoms and mononegative ions, the property must be accurately determined for these species. The polarizability is already a part of our model; another property which is a measure of how strongly a polarizable atom (or ion) attracts a positron is the ionization potential: a loosely bound electron (low ionization potential) contributes more to attracting a positron than does an electron tightly bound to its atom (high ionization potential).

The depth of the polarization potential well at the origin, $-\alpha/2r_0^4$, should relate directly to the ionization potential, and $\alpha \sim r_0^2$,[64] so we might reasonably look for an empirical relationship between r_0^{-2} and the ionization potential which is linear. Fitting our three values of r_0 ($1.774a_0$, $2.399a_0$, $5.621a_0$) to such a relationship,

$$r_0^{-2} = A + B(P_I)^C \tag{9}$$

we find, for the ionization potentials 24.586, 13.599, 0.754 eV,[59] the values

$$A = 0.026\,37,\; B = 0.007\,308,\; C = 1.1510, \tag{10}$$

for P_I in electron volts and r_0 in atomic units. Our three systems (He, H, H$^-$) are very different from each other in size, polarizability, and ionization potential. Therefore, the near linearity ($C \sim 1$) found in Eq. (9) suggests our heuristic notions leading to it have some merit, and that our interpolation scheme is reasonably safe. We are encouraged to proceed.

First ionization potentials of neutral atoms and electron affinities of mononegative ions are well-known and tabulated,[65-69] so this property, together with the polarizabilities[23,24] and Hartree-Fock wave functions,[17-20] provides us with all the information we need for applying our model to the upper half of the Periodic Table. Our model is well conditioned in the sense that the three values (two ionization potentials and one electron affinity) used to evaluate the constants in Eq. (9) very nearly span the set of these quantities for the whole Periodic Table, and one (the ionization potential of H) is near the middle of that range.

NEON-POSITRON

There is no experimental evidence that neon binds a positron, and there is a strong theoretical evidence that a bound state does not exist.[40] The elastic-scattering cross section has been measured recently below the positronium threshold ($k = 1.0416$ a.u.) by four groups: Canter *et al*,[10,11,44] Jaduszliwer and Paul,[13] Stein *et al*,[15] and McNutt and Coleman.[53] There is a little disagreement among these results, which are shown in Fig. 5.

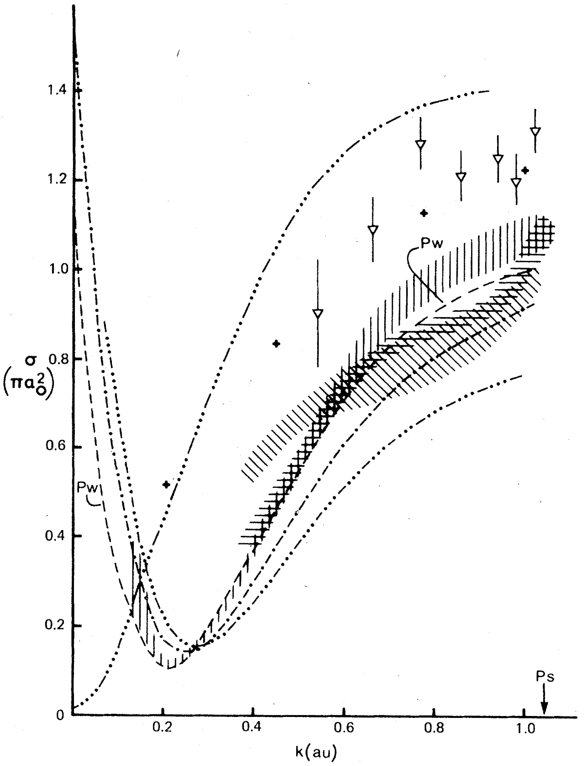

FIG. 5. Cross section for positron-neon elastic scattering. Ps indicates the threshold for positronium formation. See Table I for a key.

Several variants of the polarized-orbital approximation for the positron-neon problem are in the literature, and elastic-scattering phase shifts below the positronium threshold are reported by Massey *et al*,[70] Gillespie and Thompson,[71] Montgomery and LaBahn,[72,73] and McEachran *et al.*[74] Among these polarized-orbital calculations, the formulation of McEachran *et al* is seen to be the most accurate. These results are also shown in Fig. 5.

The polarizability of neon, $2.663a_0^3$, is very well established[23,75,76] as is the ionization potential, 21.564 eV. The value of r_0 from Eq. (9) above is $1.90a_0$. These values produce the curve labeled "PW" in Fig. 5, which is in very good agreement with the observations of Stein *et al*,[15] up to the positronium formation threshold. {New theoretical results by Campeanu and Dubau [J. Phys. B 11, L567 (1978)] are slightly higher than ours and also in good agreement with experiment[15] for $k \geq 0.4$, but are significantly below all other results for $0.1 \leq k \leq 0.3$.}

Exploratory calculations show that there is essentially no freedom in adjusting the value of r_0. Variations of only 1% or 2% do not change the agreement on one side of the Ramsauer minimum but make it worse on the other side.

No bound state exists for this potential. The calculated scattering length $-0.542a_0$ is in exact agreement with the value given by Tsai *et al,*[77] $(-0.53 \pm 0.15)a_0$.

Jaduszliwer and Paul[13] have extracted from their data values of the phase shifts for the *s, p,* and *d* waves for five positron energies below the positronium formation threshold. These are compared with our calculations in Fig. 6, where a disagreement is seen only for the *p* wave; this is necessarily the source of the discrepancy between the two sets of cross sections (Fig. 5). The same pattern is shown for helium, Figs. 3 and 4.

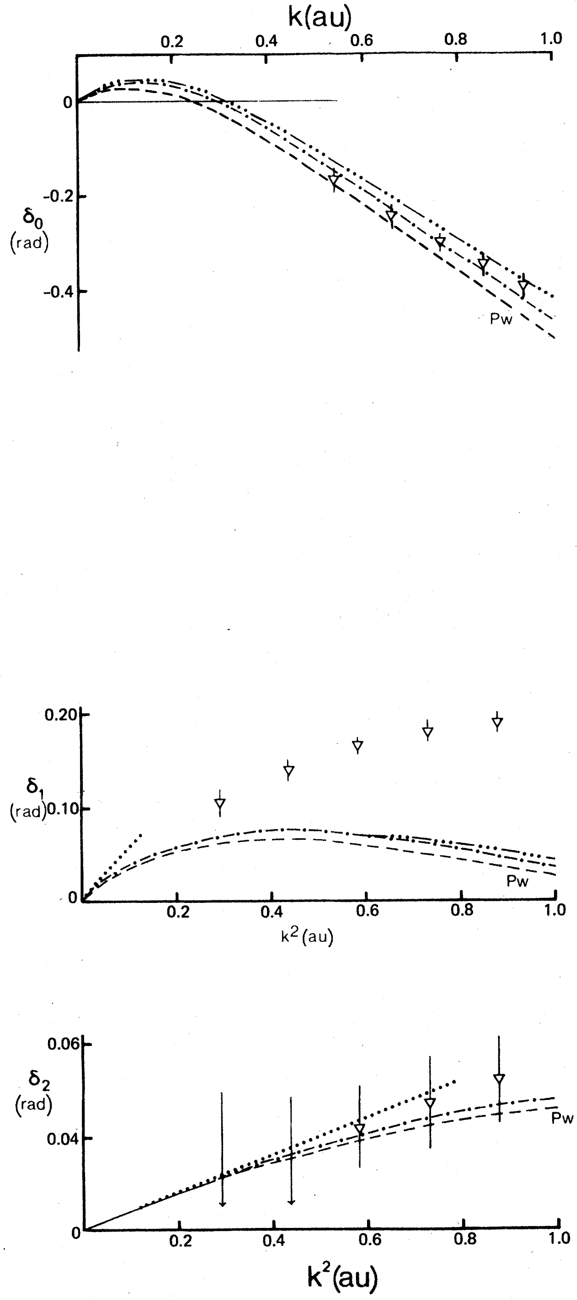

FIG. 6. Phase shifts for positron-neon elastic scattering. The *d*-wave phase shifts of Montgomery and LaBahn (Refs. 72, 73) are close to those calculated in the present work. See Table I for a key.

ARGON-POSITRON

Existence of a shoulder in the positron lifetime curve for argon at certain temperatures and pressures has prompted several experimentalists to conjecture that the positron forms a bound state with one or more argon atoms.[78-80] Elastic-scattering cross sections below the positronium formation threshold have been measured by several groups: down to $k = 0.543$ a.u. by Jaduszliwer and Paul[13]; down to $k = 0.383$ a.u. by Canter *et al.*[10,11,44]; and down to $k = 0.169$ a.u. by Kauppila *et al.*[14] Only the observations of Kauppila *et al.* go to an energy sufficiently low to reveal a pronounced Ramsauer minimum.

The polarizability[23] is accurately known[75,76] to be $11.06a_0^3$, and the ionization potential, 15.759 eV, yields the value [Eq. (9)] $2.23a_0$ for r_0.

We calculate a scattering length of $-4.11a_0$, and find no bound state. The analysis of Orth and Jone's[29] measured lifetime dependence on density and dc electric field gives the cross section for thermal positrons as 33 ± 5 in units of πa_0^2 which suggests $\pm(2.80 \pm 0.20)a_0$ for the scattering length. Tsai *et al.*[77] report $(-2.8 \pm 0.7)a_0$; recent data and analysis by Lee and Jones[81] gives a scattering length of $(-4.4 \pm 0.5)a_0$; and analysis by Hara and Fraser[82] of experimental data gives $(-3.5 \pm 0.5)a_0$. Our value, $-4.11a_0$, is seen to be in good to excellent agreement with these experimental values, and we take this and the failure of our potential to support a bound state to be very good evidence that one does not exist for a single argon atom. The polarized orbital method of McEachran *et al.*[83] gives $a_0 = -5.30a_0$.

Our calculated cross sections and the several experimental measurements are shown in Fig. 7. Agreement between our results and the measurements of Kauppila *et al.*[14] are seen to be perfect below $k \sim 0.4$ a.u. and about 5% too low from there out to the positronium formation threshold. Agreement between our results and recent preliminary measurements of McNutt and Coleman[53] are excellent. There is some leeway in the value of r_0; agreement with the measurements of Kauppila *et al.* does not deteriorate significantly until r_0 rises above $2.33a_0$, which is almost 5% larger than the value given by Eq. (9). The dot-dash curve in Fig. 7 is for $r_0 = 2.33a_0$.

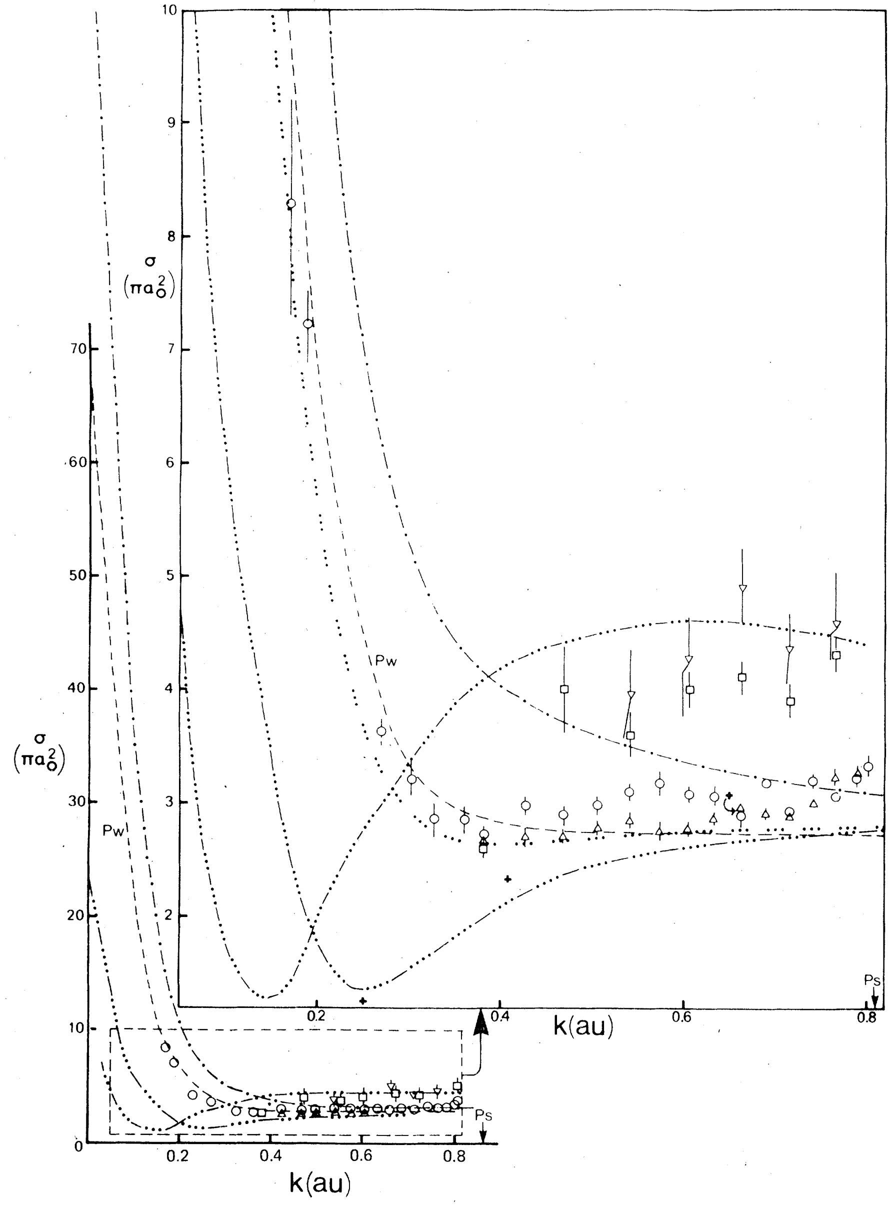

FIG. 7. Cross section for positron-argon elastic scattering. The dot-dash curve (... — ...) is the result of the present model if the parameter r_0 is increased about 5%. The experimental results of McNutt and Coleman (Ref. 53) are preliminary. See Table I for a key.

A polarized-orbital calculation by Gillespie and Thompson[71] has only three calculated points in the inelastic region; an older polarized-orbital calculation by Massey *et al.*[70] shows a rather deep minimum of $\sigma \sim 1.2\pi a_0^2$ at $k \sim 0.25$ a.u. and a scattering length of $\pm 2.5a_0$, somewhat unlike our results or those of Kauppila *et al.* in Fig. 7. The cross-section curve of Montgomery and LaBahn[72,73] shows a pronounced Ramsauer minimum but is otherwise unlike our present results or the observations of Kauppila *et al.* Very recent polarized-orbital results[83] are also shown in Figs. 7 and 8.

Phase shifts for the *s*, *p*, and *d* waves are displayed in Fig. 8; the data of Jaduszliwer and Paul[13] and Hara and Fraser[82] are based on the older experimental work. The discrepancy between our cross sections and this older work, evident in Fig. 7, is reflected in Fig. 8.

KRYPTON-POSITRON

If argon binds a positron then krypton does perforce because of its greater polarizability ($16.74a_0^3$, Refs. 23 and 24); similarly, krypton may bind even if argon does not.

Cross sections have been measured by two groups[11,12,44] and have been calculated by only one

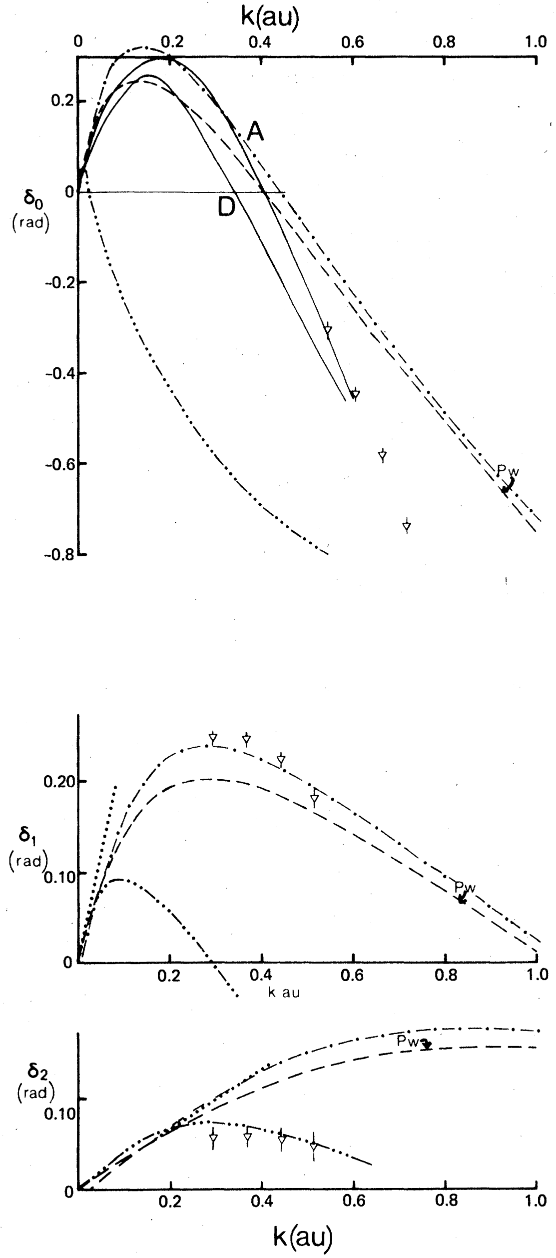

FIG. 8. Phase shifts for positron-argon elastic scattering. The solid curves labeled *A* and *D* are extreme models of Hara and Fraser (Ref. 82). See Table I for a key.

group.[70] The experimental work is recent, but the theoretical work is older—a polarized-orbital calculation. The agreement between the observations of Kauppila *et al.* and the calculation of Massey *et al.* is good above $k \sim 0.3$ a.u. and only modest below that.

The polarizability and ionization potential (13.999 eV) gives $r_0 = 2.37a_0$ from Eq. (9), the curve "PW" in Fig. 9 results. Our cross sections, like those of Massey *et al.*, are the right magnitude but disagree in trend with those of Canter *et al.* A roughly similar relationship between our cross section and those of Canter *et al.* is seen for argon, Fig. 7; neon, Fig. 5; and helium, Fig. 3; so the repetition for krypton is not discouraging. The present work agrees with the observations of Kauppila *et al.* better than with that of Canter *et al.* The present model gives a scattering length of $-7.69a_0$.

As r_0 is decreased, the resulting scattering length falls without limit, and around $r_0 \sim 1.7$ it changes sign and continues to fall. This singularity marks the appearance of a bound state, and it is accompanied by a large and sudden increase in the calculated cross section. Values for $r_0 = 1.18a_0$, $1.11a_0$, and $1.05a_0$ (for which the scattering lengths are $\sim 2.5a_0$, $0.6a_0$, and $-1.1a_0$) are shown in Fig. 9 for the range of momentum $k = 0.3$ to 0.7 a.u. (the inelastic part of the observation of Canter *et al.*) They are markedly larger ($\sigma \sim 30\pi a_0^2$ to $60\pi a_0^2$) then the observed values ($\sigma \sim 3.5\pi a_0^2$ to $8\pi a_0^2$), and one might reasonably doubt the existence of a bound state on the basis of this discrepancy.

XENON-POSITRON

We know of no previous calculations on this system. Measured cross sections are reported by Canter *et al.*[10,11] and by Stein *et al.*[12] The polarizability is $27.29a_0^3$ (Refs. 23 and 24) and ionization potential (12.130 eV) gives $r_0 = 2.54a_0$ from Eq. (9), which yields curve "PW" in Fig. 10. Figure 10 does not show the preliminary measurements of McNutt and Coleman,[53] which lie about 10% below the points of Canter *et al.* The present work agrees more closely with the preliminary results of McNutt and Coleman than with the other observations.

The situation is similar to that for krypton in that calculated and observed cross sections agree in general but not in detail, although the overall agreement between the present results and the experimental results is rather better in the case of xenon compared to krypton. The calculated scattering length $-20.3a_0$ is so large (negative) that one knows the onset of a bound state is not far away. Our calculations show this occurs as r_0 falls below ~ 2.0 a.u.; and our calculations give cross sections for r_0 below the critical binding value which are very much greater than those observed. As for krypton, we take this as evidence that a bound state for the positron-xenon system does not exist.

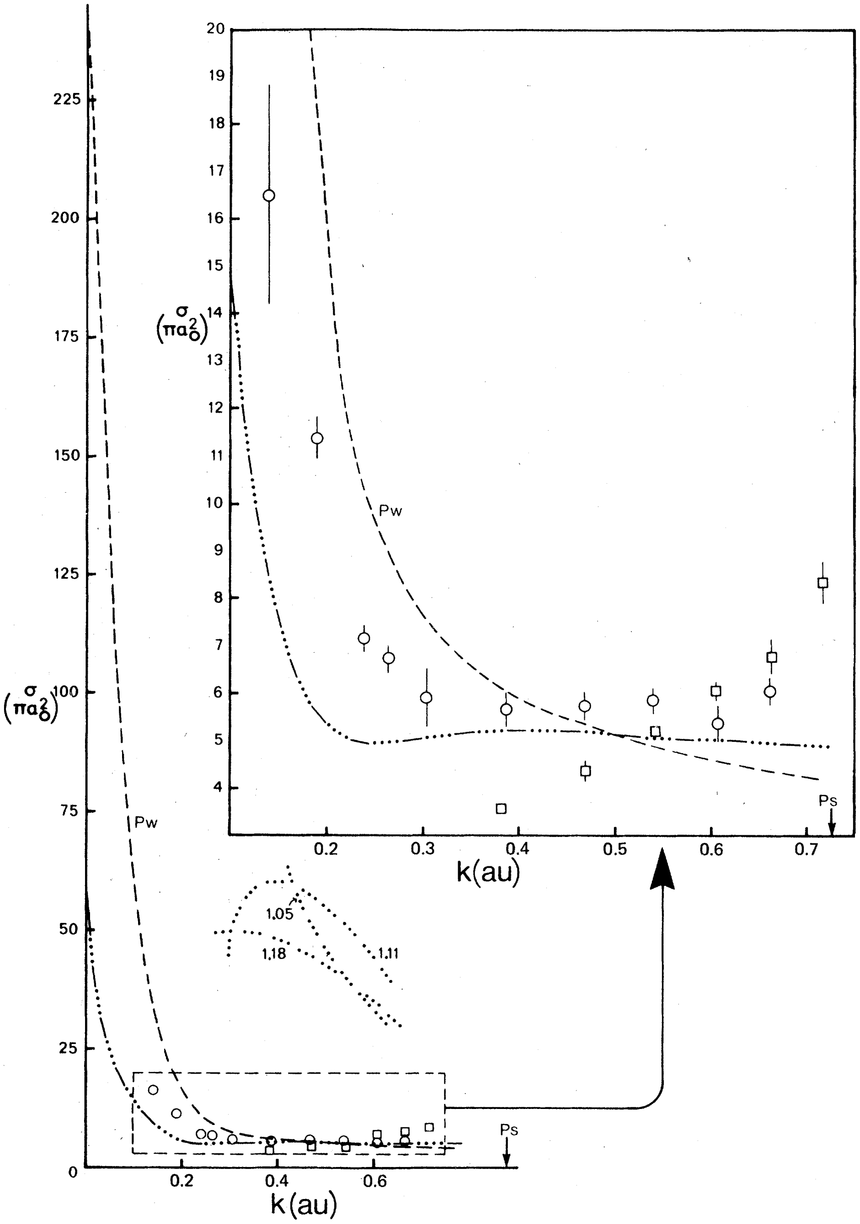

FIG. 9. Cross sections for positron-krypton elastic scattering. The dot-dash curves (... — ...) are test calculations for a possible bound state (see text). See Table I for a key.

NEGATIVE POSITRON AFFINITIES

There is only limited physical content in the notion of "electron affinity" for an unbound electron, yet many negative values may be found in the compendia of Massey[84] and Hotop and Lineberg.[68] Negative values arise in model-dependent studies, such as isoelectronic extrapolations, where a parameter in a formula has a value defining a system which itself is physically unbound; quantal calculations on an atom and its mononegative ion can yield a negative electron affinity upon subtraction of the two calculated energies. Within this limited context, the notion of negative affinities has some utility as a relative measure of how far an atom is from binding. Another measure is the critical mass for binding, but this measure is not of interest to us here because r_0 is mass dependent. Consequently, r_0 values for positrons should not be expected to "work" (i.e., give the known values of critical masses correctly) for heavier particles.

Positron and positronium affinities, both positive and negative, are an essential ingredient in the parameterization of a theory of the structures of positron-molecule and positronium-molecule

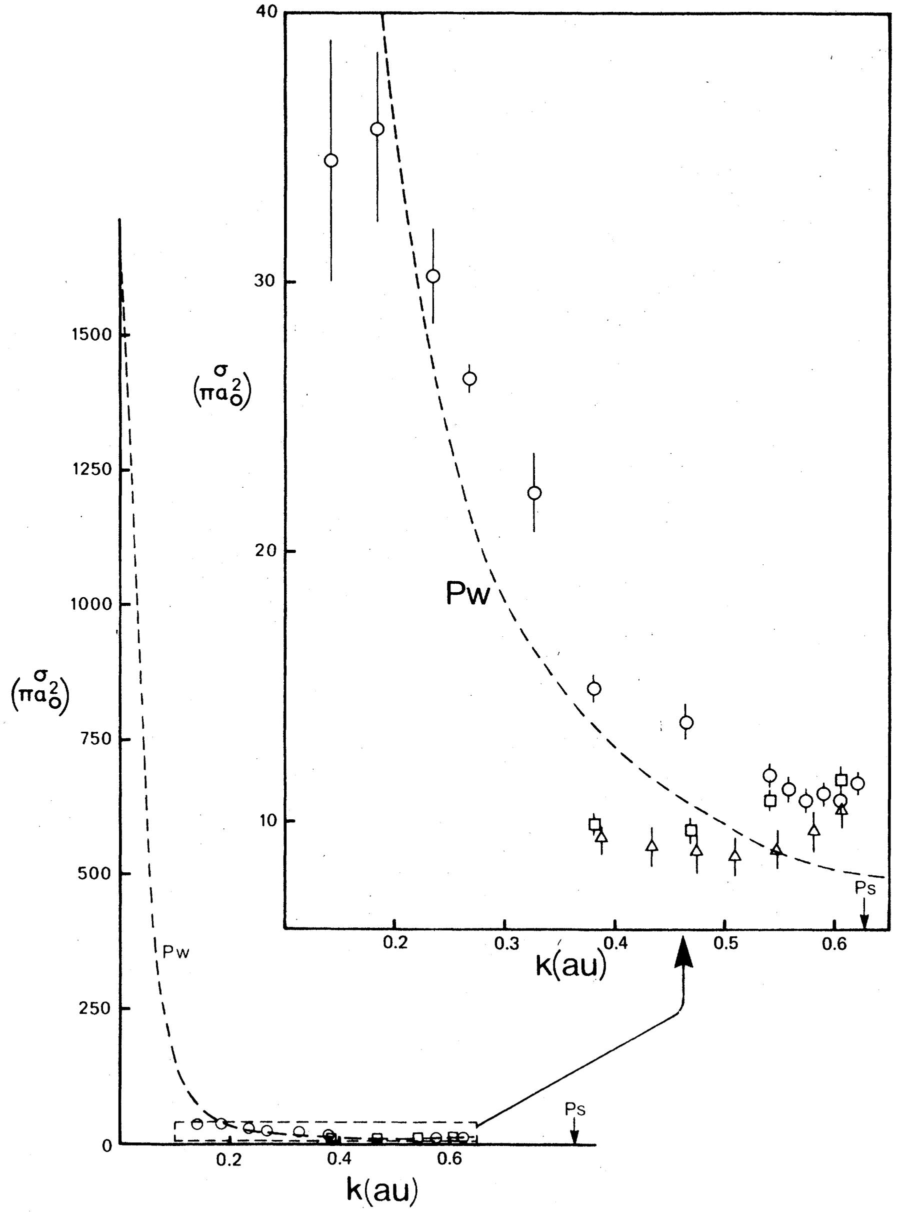

FIG. 10. Cross sections for positron-xenon elastic scattering. See Table I for a key.

complexes.[1,2] Therefore, these quantities have some significance.

Our approach to calculating negative positron affinities starts with effective range theory[85,86] and the observation that the calculated scattering length for positron-hydrogen is nearly a periodic function of the inverse of our parameter r_0. Figure 11 shows this relationship. Each singularity marks the onset of another bound s state; to the left of the point X there is no bound state, between X and Y there is one, and so on.

We know from effective-range theory[85,86] that the binding energy to the right of X is approximately $1/2A_0^2$, where A_0 is the scattering length. The closer r_0 is to the singularity (point X), the better this approximation. Our simple thought is as follows: for unbound systems (to the left of X), the closer r_0 is to the critical binding value (at point X), the closer the system is to binding. It is sensible to take $-1/2A_0^2$ as our positron affinity.

A complication arises because this approximation is accurate only for very large absolute values of the scattering length.[87] Our remedy follows: The approximate periodicity of the scattering length in Fig. 11 gives rise to an approximate local inversion symmetry in the curve about point X. We find the value of r_0 for a point (in the neighborhood of A inverted through X) which has a scattering

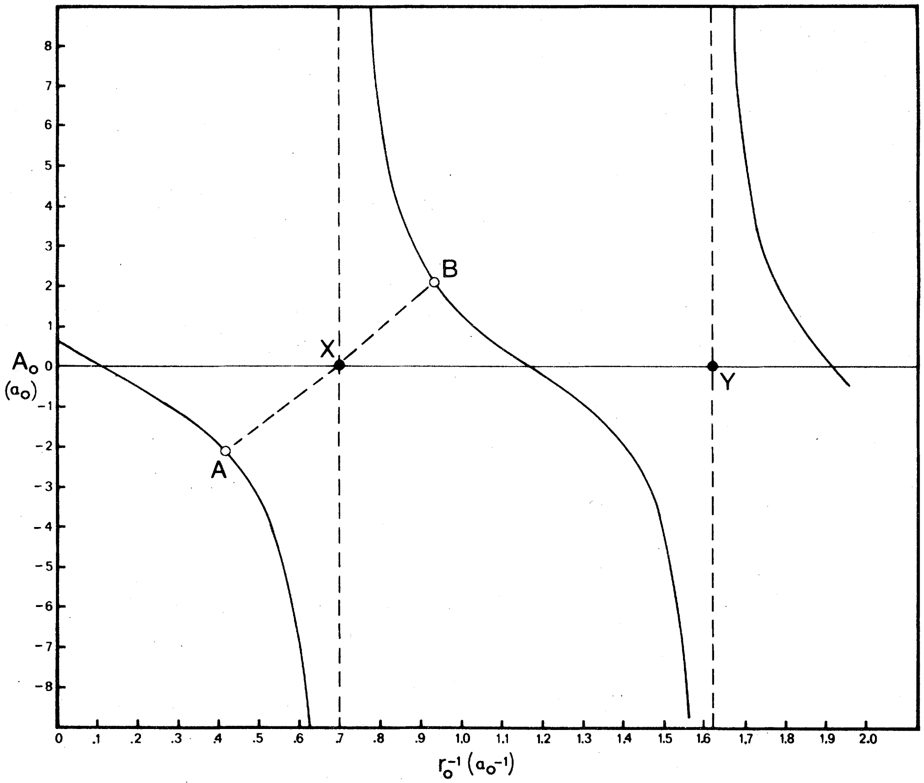

FIG. 11. Scattering length A_0 for positron-hydrogen elastic scattering as a function of r_0^{-1}. Atomic units are used throughout. The vertical dashed lines indicate the onset of an additional bound s state as one moves from left to right. Point A is the model of Figs. 1 and 2, and B has the same scattering length but for sign.

length equal to the negative of that for point A. This point B corresponds to a fictitious system, a hydrogen atom which is artificially overpolarized at short range, and which has one bound s state for a positron. We take the positron affinity of hydrogen to be the negative of this binding energy.

For the atoms H, He, Ne, Ar, Kr, and Xe, the inverted point has $r_0 = 1.07a_0$, $0.52a_0$, $0.56a_0$, $1.07a_0$, $1.30a_0$, and $1.73a_0$, respectively and the resulting positron affinities are −4.34, −43.9, −23.3, −1.18, −0.35, and −0.037 eV, respectively. Thus we see the expected trend in the noble gases; perhaps not so expected are the magnitudes: helium is extraordinarily repulsive to a positron, and xenon comes very close indeed to binding.

TABLE III. Summary of results.[a]

	r_0, Eq. (9)[b]	Scattering length (a_0)	Positron affinity (eV)	Positronium affinity (eV)
H	2.399	(−2.1036[c])	−4.34	(1.02[d])
He	1.774	(−0.472[e])	−43.9	f
Ne	1.90	−0.542	−23.3	f
Ar	2.23	−4.11	−1.18	f
Kr	2.37	−7.69	−0.35	f
Xe	2.54	−20.3	−0.037	f

[a] Values in parentheses are fitted; all others are calculated in the present work.

[b] Values in the first column are r_0 for the neutral atom. The only negative ion considered here, hydride, has $r_0 = 5.621a_0$.

[c] Reference 37.

[d] Reference 3.

[e] Reference 8.

[f] Not available from our model; one needs a stable mononegative ion in order to calculate a positronium affinity.

CONCLUSIONS

The results of this work are summarized in Table III. Three numbers have been fitted, the rest calculated. Two of the fitted numbers are indicated by (•) in Figs. 2 and 3; in Figs. 1 and 4 the initial slopes of the PW curves for *s* waves are fitted. Otherwise all other PW curves are calculated in the present work from our model.

The predictive ability of our model may be gauged by comparing the accurate results (curves AC) with our results (curves PW) in Figs. 1–4, and recent experimental results with our results in Figs. 5, 7, 9, and 10. The agreement for hydrogen is good for positron momenta below ~0.4 a.u. and no worse above that than other models (adiabatic and polarized orbital), which require much more elaborate and expensive calculations.

Our model agrees satisfactorily with the observations of Canter *et al.*[10,11,44] for helium; (Fig. 3) very well with the observations of Stein *et al.*[15] for neon (Fig. 5); very well with the observations of Stein *et al.* and of McNutt and Coleman[53] for argon (Fig. 7); a little less satisfactorily with the observations of Stein *et al.*[12] for krypton; and satisfactorily with the three sets of observations available for xenon.

Of the several variants of the polarized orbital model in the literature, the formulation of McEachran *et al.*[52] is the most rigorous; our results show that our model is at least its equal in predictive power. Our model is extremely simple because no electronic equations are solved; it requires at least an order of magnitude less computation than the polarized orbital method of McEachran *et al.*

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