Binding Energy Predictions of Positron- and Positronium-Atom System

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BINDING ENERGY PREDICTIONS OF POSITRON- AND POSITRONIUM-ATOM SYSTEMS

by

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A Thesis submitted to the Faculty of the Graduate School,
Marquette University,
in Partial Fulfillment of the Requirements for
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ABSTRACT

BINDING ENERGY PREDICTIONS OF POSITRON- AND POSITRONIUM-ATOM SYSTEM

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Marquette University, 2011

There has been a large amount of work studying positron and positronium (Ps) binding to atoms. Twelve atoms (including Ps) are known to bind with a positron and 14 atoms won’t. For Ps binding, 12 atoms are found to bind with Ps and 2 atoms do not. For both positron and Ps binding to atoms, we find that the known binding energy can be fitted to a simple expression involving several common physical properties. Positron binding energies can be fitted using the parameters of ionization potentials, polarizabilities, and the number of *s* electrons of the atoms; while Ps binding energies can be fitted using the covalent radii, the number of *s* electrons, and the product of ionization potentials and electron affinities. The fitted relationships are tested on the unbound atoms and bound atoms not involved in the fitting. Then these two best-fit equations are used to predict the binding energies of positron-atom and Ps-atom systems for all other unstudied atoms through Bi. The results are discussed and analyzed theoretically. The models and the results appear to be reliable.

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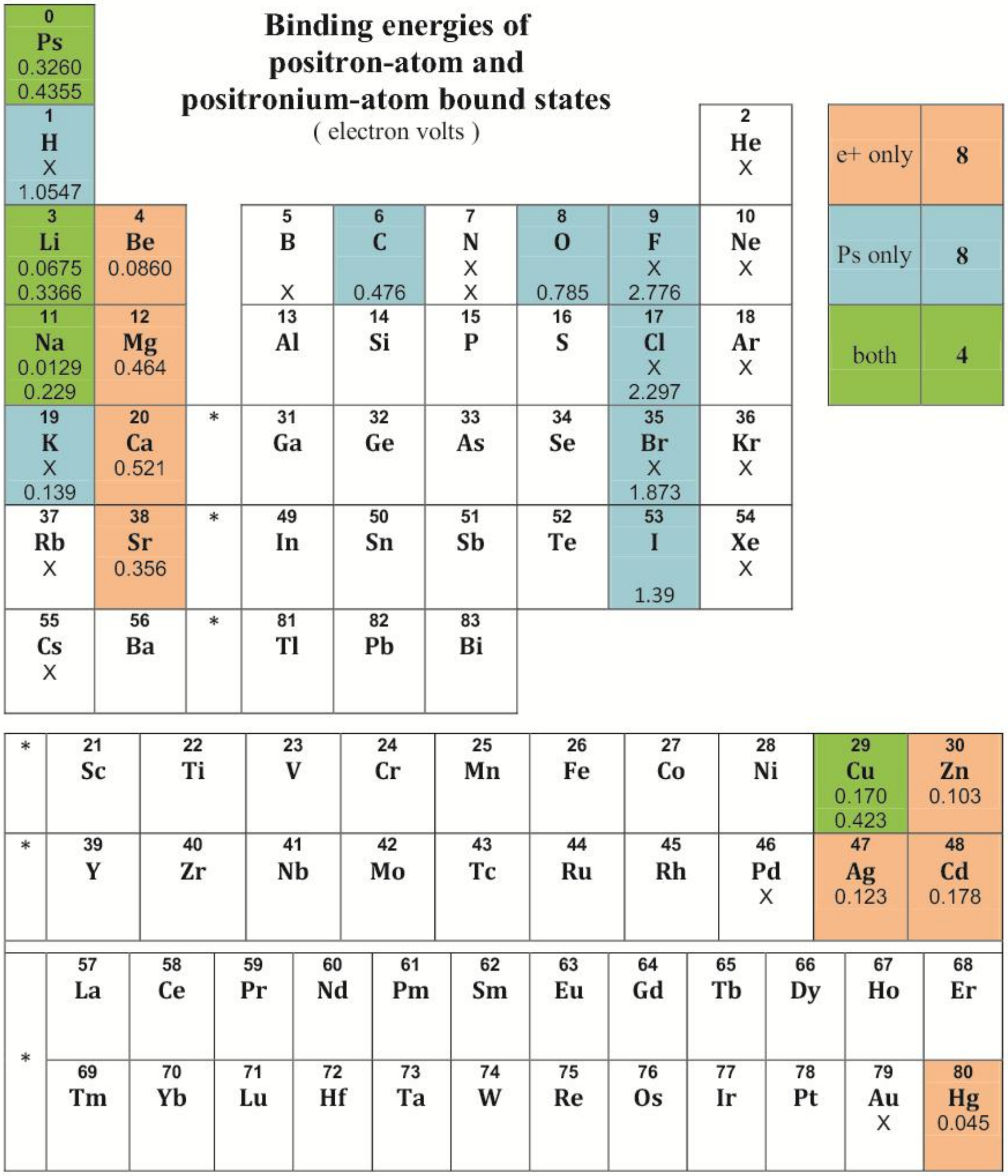
I. INTRODUCTION

The positron e^+ is the antiparticle of the electron. It was theoretically predicted by Paul Dirac [1] in 1928, and experimentally observed by Carl Anderson [2] in 1932. One positron can bind with one electron to form the atom positronium (Ps). Positronium was predicted by Croatian scientist Stjepan Mohorovicic [3], and experimentally discovered by Martin Deutsch at MIT in 1951. In 2007 David Cassidy and Allen Mills [4] reported the observation of molecular positronium Ps_2. Modern sources of positrons [5-7] have new applications to several fields, such as quantum dots [8], superconductors [9], surfaces and coatings [10], and so on. These applications will be enriched by the knowledge of accurate binding energies of positrons and positronium atoms to atoms and molecules. A large amount of research work shows that a positron or positronium can form a bound state with some atoms and molecules and not with others. The presently known data of binding energies between atoms and positrons or positronium atoms are shown in Fig. I.1. All of them come from quantum calculations. But there are still many atoms remaining unstudied. This subject has been reviewed recently by D. M. Schrader [11].

Theoretically determining the binding energies with reasonable accuracy requires extensive calculations. Several scientists have resorted to approximations [12, 13] to increase the calculation efficiency and provide useful estimates at the same time. M. W. Karl *et al.* [12] assumed that Morse potential parameters for protonic diatoms are transferrable to the corresponding positronic molecules, and they found that over half of the 42 atoms tested by their method show positronium binding. V. A. Dzuba *et al.* [14]

used many-body perturbation theory, examined the interaction of positrons with atoms, and predicted the binding energies of positrons with Mg, Zn, Cd and Hg. Using the Monte Carlo method, Nan Jiang and David M. Schrader [15] proved the stability of positronic water Ps_2O and calculated the binding energy of PsH.



Binding energies of positron-atom and positronium-atom bound states
(electron volts)

0 Ps 0.3260 0.4355								
1 H X 1.0547								2 He X
3 Li 0.0675 0.3366	4 Be 0.0860		5 B X	6 C 0.476	7 N X X	8 O 0.785	9 F X 2.776	10 Ne X
11 Na 0.0129 0.229	12 Mg 0.464		13 Al	14 Si	15 P	16 S	17 Cl X 2.297	18 Ar X
19 K X 0.139	20 Ca 0.521	*	31 Ga	32 Ge	33 As	34 Se	35 Br X 1.873	36 Kr X
37 Rb X	38 Sr 0.356	*	49 In	50 Sn	51 Sb	52 Te	53 I 1.39	54 Xe X
55 Cs X	56 Ba	*	81 Tl	82 Pb	83 Bi			

e+ only	8
Ps only	8
both	4

*	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu 0.170 0.423	30 Zn 0.103
*	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd X	47 Ag 0.123	48 Cd 0.178

*	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er
	69 Tm	70 Yb	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au X	80 Hg 0.045

Figure I.1. The binding energies of e^+A and PsA are given under the atomic number and chemical symbol of each atom. “X” means the atom does not bind a positron or Ps, and a blank means no information is found. All the binding energies are in electron volts.

There are some other methods used in the past few years for the calculation of binding energies. Danielson *et al.* [16] used regression analysis on data for 30 molecules to identify the molecular properties that affect the binding energies. Also V. A. Dzuba and V. V. Flambaum [17] detected positron-atom bound states by observing enhanced positron annihilation. Their method is applicable to a range of open-shell transition-metal atoms, and they present estimates to the binding energies of 13 such atoms.

In this study, no quantum mechanical calculations or approximations are used. Instead, the approach here is entirely empirical: known positron- and Ps-atom binding energies are related to certain atomic parameters, and the unknown binding energies are predicted for unstudied atoms. The inspiration is drawn from the work by Danielson *et al.* [16]. A review article by J. Mitroy *et al.* [18] gives the underlying physical idea for the present work. Here this idea is extended to quantitative predictions.

First this thesis gives a general summary and analysis of current data for positron and positronium binding to atoms. Then the dependence of positron- and positronium-atom binding energies on some physical properties is examined. These atomic physical properties include ionization potential (IP), electron affinity (EA), static electric dipole polarizability (α), atomic radius, electronegativity, and the numbers and types of valence electrons. A MATLAB code is written to find the best combinations of these parameters for fitting known binding energies. Using these combinations, linear regressions are carried out to fit positron- and positronium-atom binding energies, and new binding energies for unstudied atoms are calculated from the equations of the the linear regressions studies.

II. POSITRON BINDING TO ATOMS

Although there is still no experimental observation of positron binding with atoms, the existence of electronically stable e^+A bound states is well established by rigorous quantum calculations. The data used in the data analysis are from these quantum calculations. The current data of one-positron, one-atom systems show some interesting patterns. A reasonable linear equation is found, and 60 stable atoms are predicted using the equation. The detailed work is shown in the following sections.

A. Data analysis

The binding energies, thresholds, and methods of calculations for e^+A systems are listed in Table II.1. For positron binding to atoms, only 24 atoms have been studied, and 12 of them have been found to form bound states with positrons. The binding energies appear to correlate with several well-known atomic physical properties. It is easy to find ranges of atomic properties within which the binding of positrons is confined. These ranges shown in Figure. II.1 are each bracketed by K on one side and some other atom (Xe, Br, or H) on the other. In all cases the separation of binding and nonbinding atoms is perfect with the exception of Au.

For a bound state of a positron-atom system, there are two channels for the dissociation. For the atoms whose ionization potentials are less than 6.803 eV, the lowest dissociation threshold is

$$e^+A \rightarrow A^+ + Ps$$

and for the others, it is

$$e^+A \rightarrow A + e^+$$

System	Threshold	BE/eV	Method
Binding Atoms			
e^+Ps	e^+ +Ps	0.3260	$Hyll_{rel}$ [19]
e^+Li	Ps + Li^+	0.0675(3)	SVM [20]
e^+Be	e^+ + Be	0.0860(3)	SVM [21]
e^+Na	Ps + Na^+	0.0129(5)	$SVMFC_2$ [22]
e^+Mg	e^+ + Mg	0.464(6)	$SVMFC_3$ [23]
e^+Ca	Ps + Ca^+	0.521(10)	$CI_\infty FC_3$ [23]
e^+Cu	e^+ + Cu	0.170(15)	$MBPT_{rel}$ [24]
e^+Zn	e^+ + Zn	0.103(2)	$CI_\infty FC_3$ [25]
e^+Sr	Ps + Sr^+	0.356(13)	$CI_\infty FC_3$ [23]
e^+Ag	e^+ + Ag	0.123(16)	$MBPT_{rel}$ [26]
e^+Cd	e^+ + Cd	0.178(3)	$CI_\infty FC_3$ [27]
e^+Hg	e^+ + Hg	0.045(20)	MBPT [13]
Nonbinding Atoms			
e^+H	e^+ + H	Unbound	FNC [28]
e^+He	e^+ + He	Unbound	FNC [29]
e^+N	e^+ + N	Unbound	FNC [29]
e^+F	e^+ + F	Unbound	$ModPot_1$ [30]
e^+Ne	e^+ + Ne	Unbound	FNC [29]
e^+Cl	e^+ + Cl	Unbound	$ModPot_1$ [30]
e^+Ar	e^+ + Ar	Unbound	$ModPot_1$ [31], PO [32]
e^+K	Ps + K^+	Unbound	$SVMFC_2$ [33]
e^+Br	e^+ + Br	Unbound	$ModPot_1$ [30]
e^+Kr	e^+ + Kr	Unbound	$ModPot_1$ [31], PO [34]
e^+Rb	e^+ + Rb	Unbound	$SVMFC_2$ [33]
e^+Xe	e^+ + Xe	Unbound	$ModPot_1$ [31], PO [34]
e^+Cs	Ps + Cs^+	Unbound	$SVMFC_2$ [33]
e^+Au	e^+ + Au	Unbound	$MBPT_{rel}$ [26]

Table II.1. The binding energies, thresholds, and methods of calculation for all studied positron-atom systems. Hyll means an expansion in a Hylleraasian basis, rel = relativistic treatment, SVM = stochastic variational method, FC_n = fixed core with *n* particles treated explicitly, CI = configuration interaction, ∞ indicates an extrapolation to convergence of a basis expansion, MBPT = many body perturbation theory, $ModPot_n$ indicates a model potential with *n* particles explicitly treated, FNC indicates the atom fails a necessary test for binding a positron, and PO indicates the method of polarized orbitals.

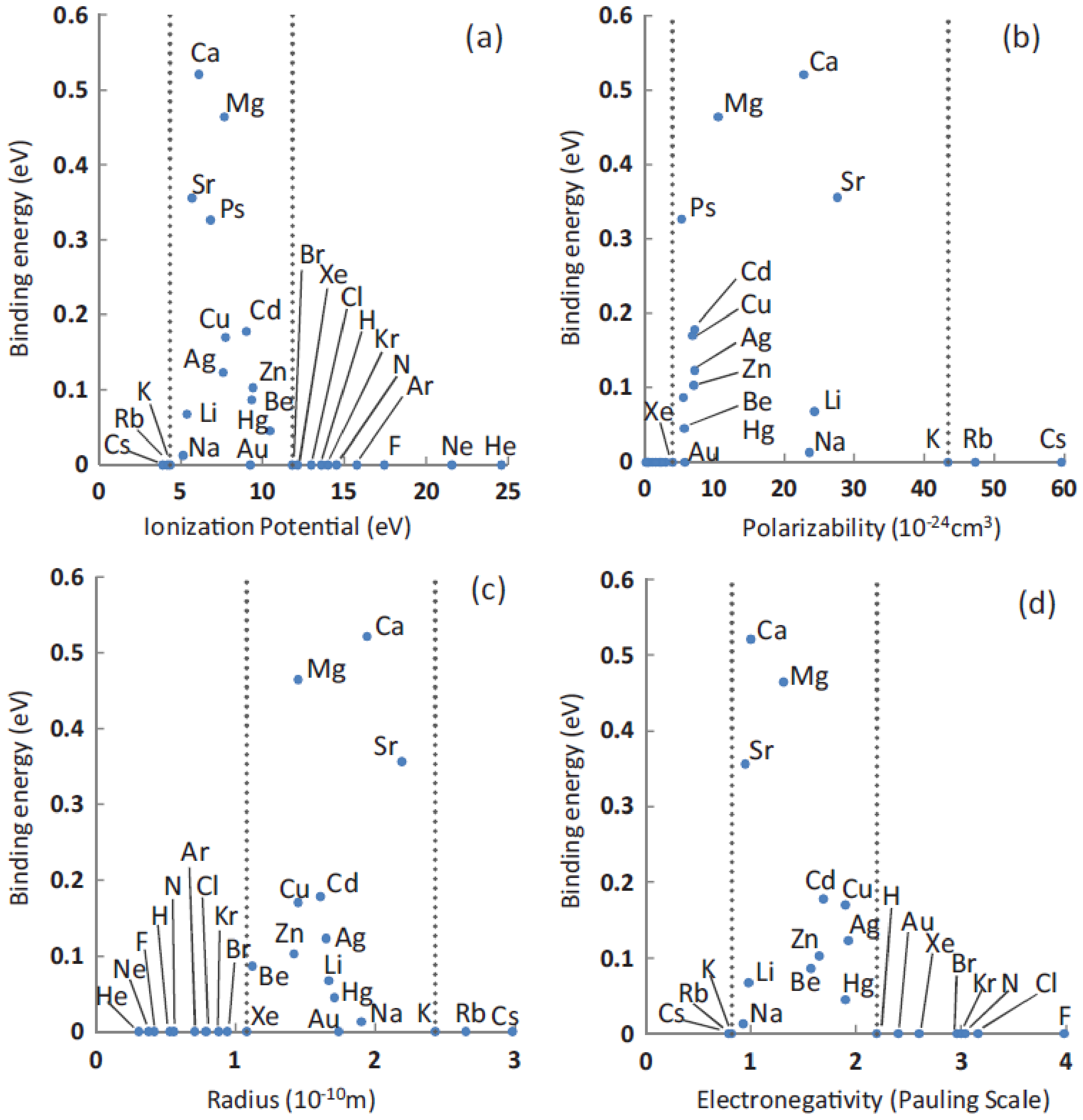


Figure II.1. Positron-atom binding energy vs. different physical properties, with ranges indicated with vertical dotted lines. (a) Ionization potentials are from ref. [35]. The range is bracketed by K (4.341 eV) and Br (11.814 eV). (b) The source of polarizabilities is ref. [36]. The range is bracketed by Xe (4.01 Å^3) and K (43.4 Å^3). The points to the left of Xe are (from left to right) He, Ne, F, H, N, Ar, Cl, Kr and Br. (c) The source of radii is ref. [37]. The bracketing atoms are Xe (1.08 Å) and K (2.43 Å). (d) The bracketing atoms are K (0.82) and H (2.2).

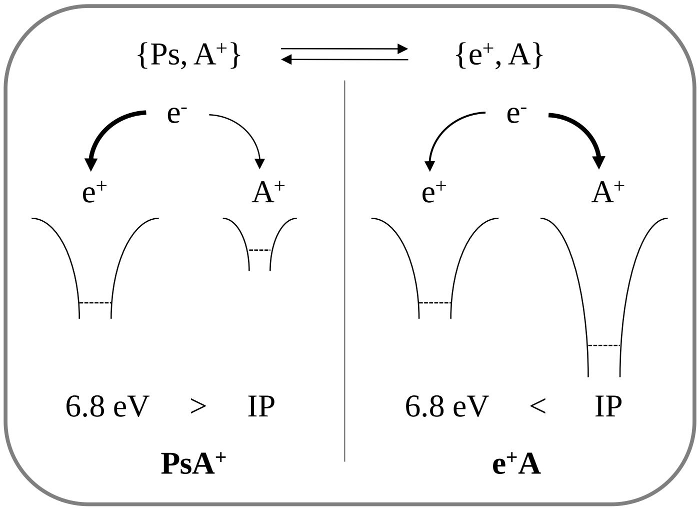


Figure II.2. Resonance stabilization.

It can be regarded as a resonance interaction as shown in Fig. II.2, where a valence electron e^- in atom A interacts with its own parent ion and a nearby positron. The interaction is stronger the closer the depths of the two wells, which are *IP* of atom A and 6.8 eV, the *IP* of Ps.

Consequently, the positron binding energy as a function of ionization potential has a discontinuity in its slope at 6.803 eV owing to the crossing of the levels associated with the two processes above. Danielson *et al.* [16] fitted the binding energy directly, but all the molecules in their sample have ionization potentials greater than 6.803. His method will not work for this study, because our systems have IPs that span 6.803 eV. First, this work is for positron binding to atoms which should be different from the case of molecules. Second, a smoothly varying indicator of the binding energy is preferred in this work. So the binding is described as resulting from the quantum mechanical mixing of the structures of $\{e^+A\}$ and $\{PsA^+\}$. The eigenvalues are given by

$$\begin{vmatrix} -IP-\varepsilon & \gamma \\ \gamma & -6.803-\varepsilon \end{vmatrix} = 0 \tag{1}$$

where *IP* is the atomic ionization potential, 6.803 is the ionization potential of positronium, ε is the eigenvalue, and γ is the interaction energy, all in electron volts. The overlap between the two interacting structures is ignored. The eigenvalue ε and the interaction energy γ are both smooth functions of the ionization potential and other parameters, but γ^2 is fitted because then we can treat atoms that do not bind positrons and those that do. For those nonbound atoms, γ^2 will be negative. The eigenvalue ε has two roots, the lower of which is the ground-state energy:

$$\varepsilon_1 = \frac{-6.803-IP-\sqrt{(IP-6.803)^2+4\gamma^2}}{2} \tag{2}$$

Then the binding energy is

$$BE = -\varepsilon_1 - \max\{IP, 6.803\} \tag{3}$$

All the units are electron volts. In Eq. (II.2), the upper root ε_2 with plus sign in front of the radical may indicate resonances.

To further prove the reliability of our conversion and show the relationship among *IP*, ε_1, *BE*, and γ, a graph is shown as Figure II.3. The x-axis is the ionization potential in electron volts; while y stands for the energies of *IP*, ε_1, ε_2, and *BE*. The green line and the violet line are the lower root ε_1 and the upper root ε_2 as a function of *IP*, respectively. The blue line is the *BE* as a function of *IP*. The cusp is evident.

A MATLAB program was written to carry out the data analysis and calculation. The algorithm is shown in Figure II.4. The parameters used in the calculation are shown in Table II.2. *Z* is the atomic number.

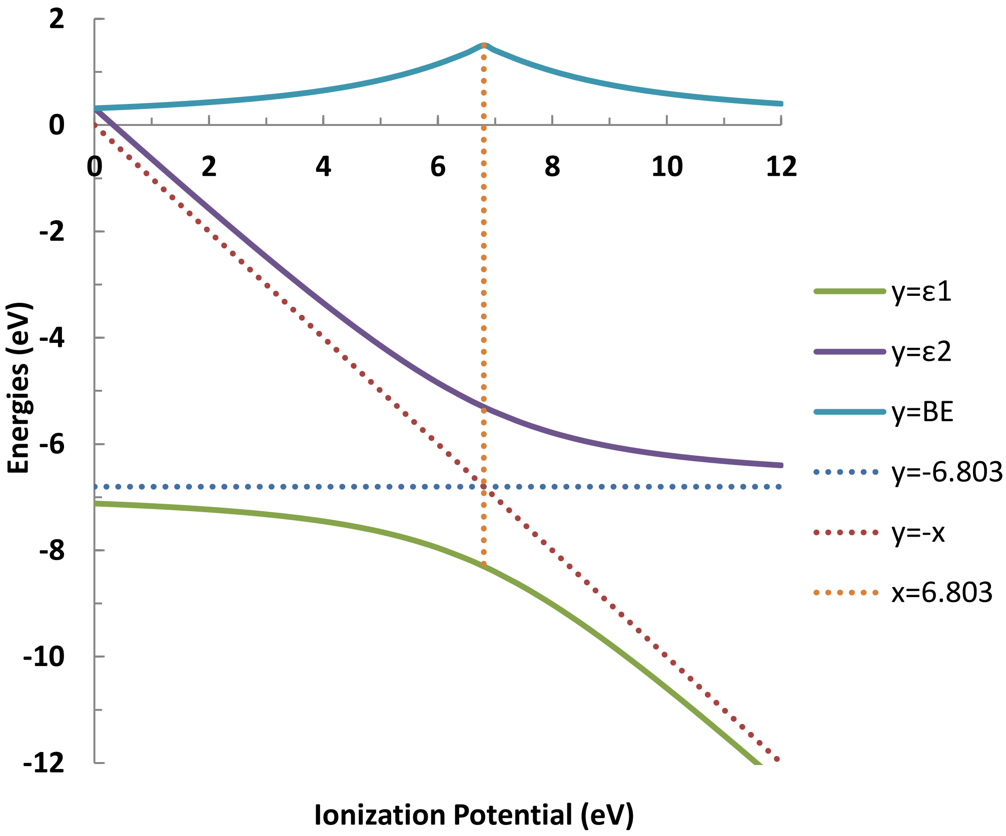


Figure II.3. The relationship among *IP*, ε_1, and *BE* while γ=1.5.

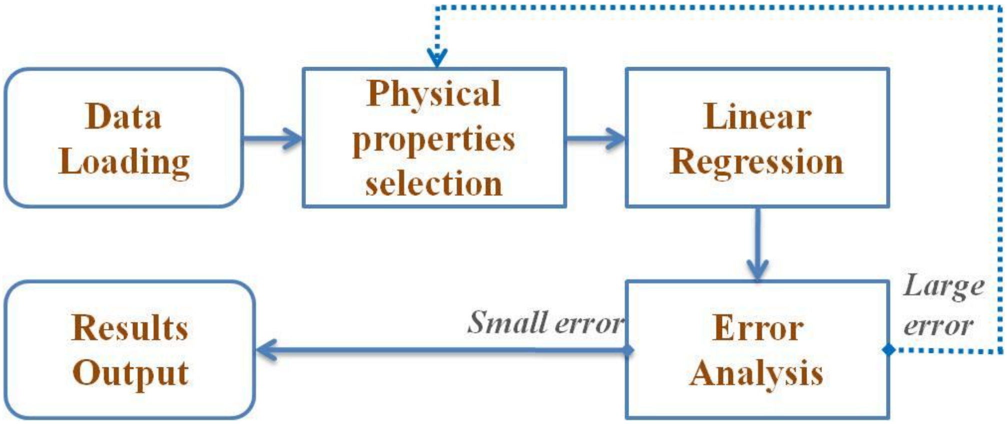


Figure II.4. Flowchart of data analysis and calculation.

$1/x$	x	x^2	$x_1 \cdot x_2$	x^3
$1/IP$	IP	IP^2	$IP \cdot \alpha$	IP^3
$1/\alpha$	α	α^2	$\alpha \cdot EA$	α^3
$1/EA$	EA	EA^2	$EA \cdot IP$	EA^3
$1/Ns$	Ns	Ns^2		
$1/Np$	Np	Np^2		
$1/Nd$	Nd	Nd^2		
$1/Z$	Z	Z^2		

Table II.2. Parameters of physical properties tested in positron binding part.

In the step of data loading, twenty-eight atomic parameters (Table II.2) are loaded. Then from this large set, plus a constant term, a sequence of subsets of fixed number are randomly chosen. For 2-, 3-, 4-, 5-, and 6-parameter fits, there are $\binom{28}{2} + \binom{28}{3} + \binom{28}{4} + \binom{28}{5} + \binom{28}{6} = 499{,}177$ distinct subsets. To make sure all the distinct subsets are attempted, five million random selection and fitting are carried out. For every subset-fitting, the result will be examined in the step of Error Analysis. Good results will be saved in the output file, while results with large error will be ignored. After 5 million iterations, all the good results will be outputted.

B. Results

Until now, 12 atoms have been found to bind with positrons (Table II.1). The binding energy of Hg is not included in this fitting because of its great uncertainty. Instead, artificial negative binding energies of K and Br are introduced from effective-range theory into order to tie down the two ends of the binding range (Figure II.1).

Negative binding energies are unphysical, but they are useful for our present purposes. For K and Br we take the binding energy to be $-1/a^2$, where a is the positron scattering length. Then the binding energy for K and Br will be -0.5442 [38] and -0.1048 eV [30], respectively. According to the binding energies, the corresponding values of γ^2 are easily calculated. The fitting uses K, Br and all the binding atoms, except Ps (an atypical atom) and Hg.

After comparison among numerous sets of fitting with various combinations of different physical properties, the fitting of γ^2 with IP, α, $\alpha \cdot IP$, and the number of valence s electrons (N_S) is the best. The fitting equation is

$$\gamma^2 = -0.2793 \cdot IP - 0.1466 \cdot \alpha + 0.0238 \cdot IP \cdot \alpha + 0.3646 \cdot Ns + 1.6757 \qquad (4)$$

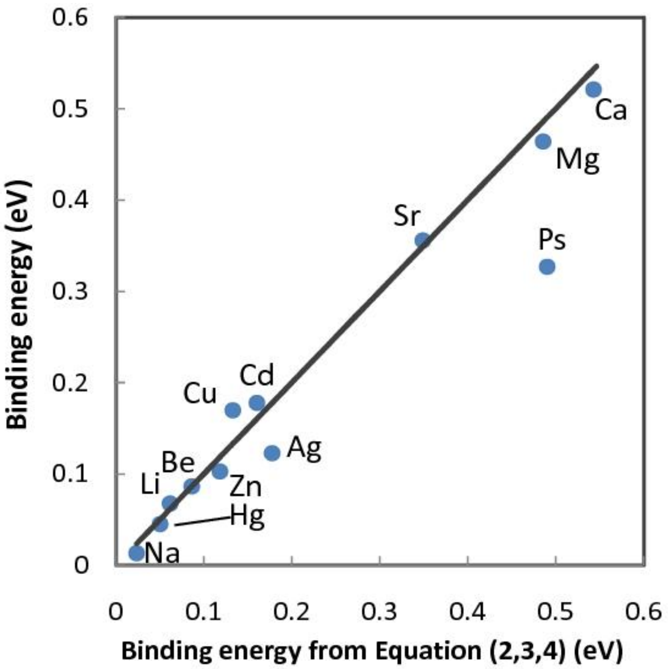


Figure II.5.The solid line is the binding energy calculated from the best fit equation (eq. (4)) and Eq. (2, 3). The solid circles are binding energies from the literature. Ps was not used in the fit but is shown here for reference purposes.

The fitting results are shown in Fig. II.5. Units of the numerical coefficients above follow from the units of γ^2, α, and IP, which are eV^2, Å^3, and eV, respectively. The data used for the fit and our calculated binding energies are compared in Table II.3. The principal source of uncertainties in our calculated binding energies is the polarizabilities, which are not precisely known for all atoms.

The binding energies of all binding atoms are close to the actual values. Although Hg is not included in the fitting, it is still close to the line. It is also acceptable that Ps, an atypical atom, is far away from the line. The fitting equation is tested with the atoms which have been determined not to bind with a positron. If the model is valid, then γ^2 of unbound atoms will be negative; for Hg, it will be positive. The results (Table II.4) are in accordance with the predictions. The model appears to be reliable.

Atoms	***IP*(eV)**	**α(Å^3)**	***BE*(eV)** **(Present work)**	***BE*(eV)** **(Literature values)**	***Error***	***Tolerance***
Na	5.1391	23.6(5)	0.023(8)	0.0129(5)	0.0101	0.0085
Li	5.3917	24.3(5)	0.0617(61)	0.0675(3)	–0.0058	0.0064
Sr	5.6949	27.6(22)	0.349(14)	0.356(13)	–0.007	0.027
Ca	6.1132	22.8(8)	0.543(22)	0.521(10)	0.022	0.032
Ag	7.5762	7.2(2)	0.177(6)	0.123(16)	0.054	0.022
Mg	7.6462	10.6(5)	0.486(12)	0.464(6)	0.022	0.018
Cu	7.7264	6.9(5)	0.135(21)	0.170(15)	–0.035	0.036
Cd	8.9938	7.2(2)	0.159(6)	0.178(4)	–0.019	0.01
Be	9.3227	5.6(1)	0.0858(28)	0.0860(3)	–0.0002	0.0031
Zn	9.3942	7.1(5)	0.118(20)	0.103(2)	0.015	0.022

Table II.3. Data and Results. The *Error* is the difference between present work and literature values of *BE*. The *Tolerance* is the sum of the uncertainties of present work and literature values. The predictions of Li, Sr, Ca, Cu, Be, and Zn are within our tolerances.

Atoms	**IP(eV)**	**α(Å^3)**	**γ^2(eV^2)**
H	13.5984	0.6668(5)	-1.65
Rb	4.1771	46.83(5)	-1.32
Cs	3.8939	59.42(5)	-2.22
N	14.5341	1.13(5)	-1.44
F	17.4228	0.548(5)	-2.34
Cl	12.9676	2.159(5)	-0.88
He	24.5874	0.2049(5)	-4.43
Ne	21.5645	0.3957(10)	-3.52
Ar	15.7596	1.640(2)	-1.65
Kr	13.9996	2.5303(2)	-1.05
Xe	12.1298	4.0099(2)	-0.43
Au	9.2255	5.35(10)	-0.15
Hg	10.4375	5.098(10)	0.04

Table II.4. Equation (4) for known nonbinding atoms and Hg.

Fifty-eight atoms not previously studied are tested with Eq. (4). It is predicted that 24 will bind a positron, 6 will not, and 28 are indeterminate. The latter are those with uncertainties larger than or equal to our predicted binding energies. All the predictions are shown in Table II.5 and Fig. II.6. Figure II.6 shows the cusp in binding energies as a function of ionization potentials, which we find also in Ref. [18]. The very large positron affinities of atoms with ionization potentials close of 6.803 eV is evident and was predicted earlier [13].

The energies of present work are calculated by Eqs. (1), (2), (3), and (4). The uncertainties in the predicted binding energies are from uncertainties in polarizabilities. We calculate uncertainties of the *BE*s from the largest and smallest values of α. We also include the predictions of ref. [17].

Positronium is an atom and so is correctly treated as such here. Ps_2 is also an atom, but it is not treated here because the addition of a positron gets one involved in exclusion effects that are not present for any other atom.

Table II.5. Positron binding energies predictions of all other atoms up to Bi.

Atomic Number	**Atoms**	***IP* (eV)**	***α* (Å^3)**	**γ^2 (eV^2)**	***BE* (present work. eV)**	***BE* (ref. [17]], eV)**
5	B	8.298	3.03(5)	0.2404	0.16(1)	
6	C	11.2603	1.76(5)	-0.5274	Unbound	
8	O	13.6181	0.802(5)	-1.2569	Unbound	
13	Al	5.9858	6.8(1)	0.7033	0.54(2)	
14	Si	8.1517	5.38(5)	0.3815	0.25(1)	
15	P	10.4867	3.63(5)	-0.1517	Unbound	
16	S	10.36	2.9(1)	-0.2000	Unbound	
21	Sc	6.5615	17.8(1)	0.7382	0.75(2)	
22	Ti	6.8281	14.6(1)	0.7264	0.84(3)	
23	V	6.7462	12.4(1)	0.6907	0.81(3)	
24	Cr	6.7665	11.6(2)	0.3151	0.54(8)	
25	Mn	7.434	9.4(1)	0.6111	0.53(3)	
26	Fe	7.9024	8.4(1)	0.5437	0.37(3)	0.28
27	Co	7.881	7.5(1)	0.5088	0.36(3)	0.26
28	Ni	7.6398	6.8(1)	0.5087	0.42(3)	0.24
31	Ga	5.9993	8.12(5)	0.6964	0.54(1)	
32	Ge	7.8994	6.07(12)	0.4481	0.33(3)	
33	As	9.7886	4.31(5)	0.0415	0.01(1)	
34	Se	9.7524	3.77(5)	0.0019	0.001(9)	
39	Y	6.2173	22.7(79)	0.6944	0.6(19)	
40	Zr	6.6339	17.9(45)	0.7497	0.8(11)	
41	Nb	6.7589	15.7(39)	0.3726	0.6(14)	
42	Mo	7.0924	12.8(1)	0.3402	0.45(4)	
43	Tc	7.28	11.4(1)	0.6725	0.62(4)	0.46
44	Ru	7.3605	9.6(24)	0.2563	0.30(95)	0.21
45	Rh	7.4589	8.6(22)	0.2206	0.24(86)	0.20

Table II. 5 continued on next page.

46	Pd	8.3369	4.8(12)	-0.4056	Unbound	
49	In	5.7864	10.2(5)	0.6959	0.48(16)	
50	Sn	7.3439	7.7(5)	0.5686	0.54(1)	0.02
51	Sb	8.6084	6.6(5)	0.3831	0.19(11)	0.05
52	Te	9.0096	5.5(5)	0.2597	0.11(4)	
53	I	10.451	5.35(10)	0.0302	0.01(3)	
56	Ba	5.2117	39.7(5)	0.0460	0.03(1)	
57	La	5.5769	31.1(78)	0.4096	0.3(16)	
58	Ce	5.5387	29.6(74)	0.4145	0.3(16)	
59	Pr	5.473	28.2(70)	0.4097	0.3(15)	
60	Nd	5.525	31.4(78)	0.3811	0.3(17)	
61	Pm	5.582	30.1(75)	0.4259	0.3 (16)	
62	Sm	5.6437	28.8(72)	0.4690	0.3(16)	
63	Eu	5.6704	27.7(69)	0.4928	0.4(15)	
64	Gd	6.1498	23.5(59)	0.6765	0.6(14)	
65	Tb	5.8638	25.5(64)	0.5821	0.4(14)	
66	Dy	5.9389	24.5(61)	0.6121	0.5(14)	
67	Ho	6.0215	23.6(59)	0.6403	0.5(14)	
68	Er	6.1077	22.7(57)	0.6659	0.5(15)	
69	Tm	6.1843	21.8(55)	0.6855	0.6(12)	
70	Yb	6.2542	21(53)	0.7005	0.6(12)	
71	Lu	5.4259	21.9(55)	0.5026	0.2(11)	
72	Hf	6.8251	16.2(41)	0.7512	0.8(10)	
73	Ta	7.5496	13.1(33)	0.7260	0.6(8)	0.45
74	W	7.864	11.1(28)	0.6555	0.4(7)	0.46
75	Re	7.8335	9.7(5)	0.6006	0.42(12)	
76	Os	8.4382	8.5(21)	0.5064	0.3(5)	0.47
77	Ir	8.967	7.6(19)	0.4057	0.2(4)	0.46
78	Pt	8.9588	6.5(16)	-0.0310	Unbound	0.27
81	Tl	6.1082	7.6(5)	0.6878	0.57(11)	
82	Pb	7.4167	6.8(5)	0.5349	0.50(15)	
83	Bi	7.2855	7.4(5)	0.5663	0.56(15)	

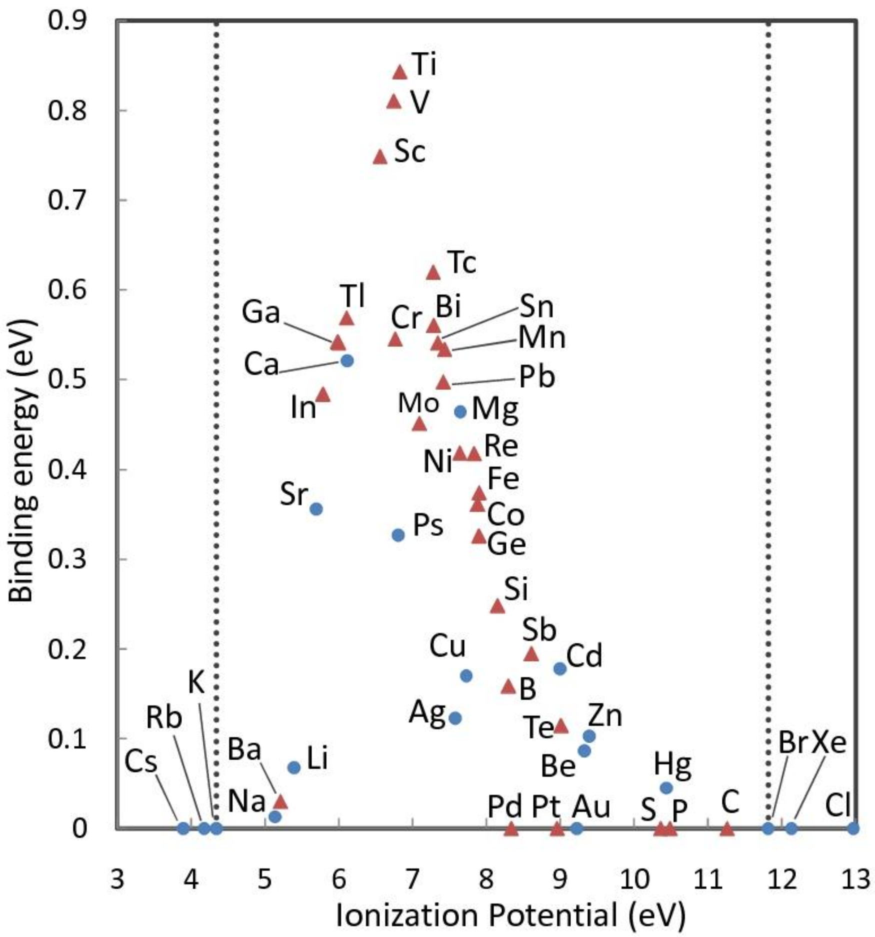


Figure II.6. This is the bonding region of Fig. II.1(a) with our predictions added (triangles). The cusp in the binding energy at 6.803 eV is evident. All the predicted binding atoms are in the range of *IP*s of K and Br.

C. Discussion

From the fitting results, it is evident that the binding energies of atoms and positrons are governed by the *IP*, α, and the electron configuration. The influence of polarizability is profound, simple, and always attractive at long range:

$$\lim_{r\to\infty} V = \frac{-\alpha}{2r^4} \tag{5}$$

where r is the distance between the atom and the positron, and V is the interaction potential of an atom and a positron. This has been understood for a very long time [39] and has been commented on by many authors. The short-range interaction, that of the positron and nucleus, is also profound and simple, but it is always repulsive:

$$\lim_{r\to 0} V = \frac{Z}{r} \tag{6}$$

where Z is the atomic number.

The intermediate interaction, much more complicated, arises because of the correlation of the motions of the positron and the atomic electrons. The interplay among these three influences is different for each atom and determines whether a positron can bind. For atoms with ionization potentials less than 6.803 eV, short-range correlation effects are more significant and lead to the formation of virtual positronium that is bound by its large polarizability (5.33 Å^3) to the atomic cation. Ionization potentials are significant in that their propinquity to 6.803 eV is a measure of the strength of the interaction energy γ.

In a new work by V. A. Dzuba *et al.* [40], many-body perturbation theory is used to devise a nonlocal potential that accounts for the long-range positron-induced polarization effects discussed above but not for the effects of virtual positronium formation. The latter is accounted for approximately and empirically by multiplying the nonlocal potential by the factor 2. Binding energies are predicted for several atoms, mostly transition metals, with ionization potentials greater than about 7.5 eV; the method does not seem to be applicable to atoms with smaller *IP*s. The results of Dzuba *et al.* are consistent with our work, with only two exceptions: Sn and Pt. These authors ignore relativistic effects and do not provide uncertainties in their predictions. Nevertheless, their predictions for atoms with open *d* subshells are at least as authoritative as this work. Their predictions are included in Table II.5 for comparison.

There is no data on positron binding to atoms with open *d* and *f* subshells, so the predictions for these atoms are less authoritative. No atom that has unpaired *p* electrons is known to bind a positron, but the entire boron family is predicted to bind a positron. Good calculations for e^+B, e^+Al, and e^+Si would be valuable tests.

Relativistic effects cannot be ignored for atoms with atomic numbers greater than about 30. Dzuba *et al.* [26] compare e^+Ag and e^+Au with nonrelativistic and relativistic calculations that are otherwise comparable. They find that relativistic effects lower the binding energies of e^+Ag by about 0.020 eV and of e^+Au by over 10 times that amount, which is larger than the calculated binding energy in the nonrelativistic approximation.

Eq. (4) is generally applicable to the stable atoms. But it might apply to nearly spherical nonpolar molecules, such as methane and neopentane, and to homonuclear diatomics. Eq. (4) is used to the calculation of the binding energies for CH_4, neo-C_5H_{12}, H_2, O_2, N_2, F_2, Cl_2, or Br_2. No indication of binding is found. But for C_{60}, Eq. (4) gives a enormous binding energy for positron, ~40 eV, by virtue of its huge polarizability (550 – 600 Å^3). However the binding energy for e^+C_{60} should be treated with great skepticism, since the polarizability of C_{60} is far outside the parameter region used for the fit (Eq. (4)).

D. <u>Summary</u>

The relationship between e^+A binding energies and atomic physical properties has been studied using all the available data. Good fitting results are obtained with the parameters *IP*, α, and number of valence *s* electrons. The model is established to be reliable using the unbound atoms and Hg. The binding energies for 23 other atoms are predicted. The largest predicted binding energy, 0.84 eV for Ti, is a reflection of the maximum mixing of the structures $\{e^+A\}$ and $\{PsA^+\}$ at the crossover point. Positronic titanium, e^+Ti, with five light particles outside its core, is well within reach of present-day high-level codes.

Measurements of positron-atom binding energies are possible with current laboratory technology [11, 39, 41 – 43]. Hopefully the present work will provide motivation to carry out such experiments.

III. POSITRONIUM BINDING TO ATOMS

Positronium is an atom as well as a quantum particle. It has a rich chemistry, engaging in chemical bonding and exchange reactions [11]. Compared to the positron, a single basic physical particle, positronium is much more complicated because each particle in Ps interacts with an atom and each other. The work that has been done for Ps binding is shown in the following sections.

A. Data analysis

System	*BE* / eV	Method	Literature
Binding atoms			
Ps_2	0.4355	SVM	[44]
PsH	1.0547	SVM	[45]
LiPs	0.3366	$SVMFC_3$	[46, 47]
NaPs	0.229	$SVMFC_3$	[46, 47]
KPs	0.139	$SVMFC_3$	[46, 48]
PsCu	0.423	$CI_\infty FC_3$	[49]
PsC	0.476	DMC, $CI_\infty FC_3$	[50, 51]
PsO	0.785	DMC, $CI_\infty FC_6$	[51, 52]
PsF	2.776	DMC, $CI_\infty FC_9$	[50, 53]
PsCl	2.297	$CI_\infty FC_9$	[53]
PsBr	1.873	$CI_\infty FC_9$	[53]
PsI	1.39	$CI_\infty FC_9$	[53]
Nonbinding atoms			
PsB	Unbound	DMC, CI	[50, 51]
PsN	Unbound	$CI_\infty FC_5$	[51]

Table III.1. The binding energies and methods of calculation for all studied Ps-atom systems. SVM = stochastic vibrational method, CI = configuration interaction, ∞ indicates an extrapolation to convergence of a basis expansion, DMC = Diffusion Monte Carlo. In all cases, the threshold is Ps + A.

For Ps binding, all the studied atoms are shown in Table III.1 and Figure III.1. In Ps binding, there are three contributing resonance schemes instead of just one as in positron binding to atoms. These three schemes are:

Scheme 1: {A, Ps} ↔ {A^+, Ps^-} — an electron moderates the A^+ – Ps interaction;

Scheme 2: {A^-, e^+} ↔ {A, Ps} — an electron moderates the A – e^+ interaction;

Scheme 3: {e^+A, e^-} ↔ {A, Ps} — a positron moderates the A – e^- interaction;

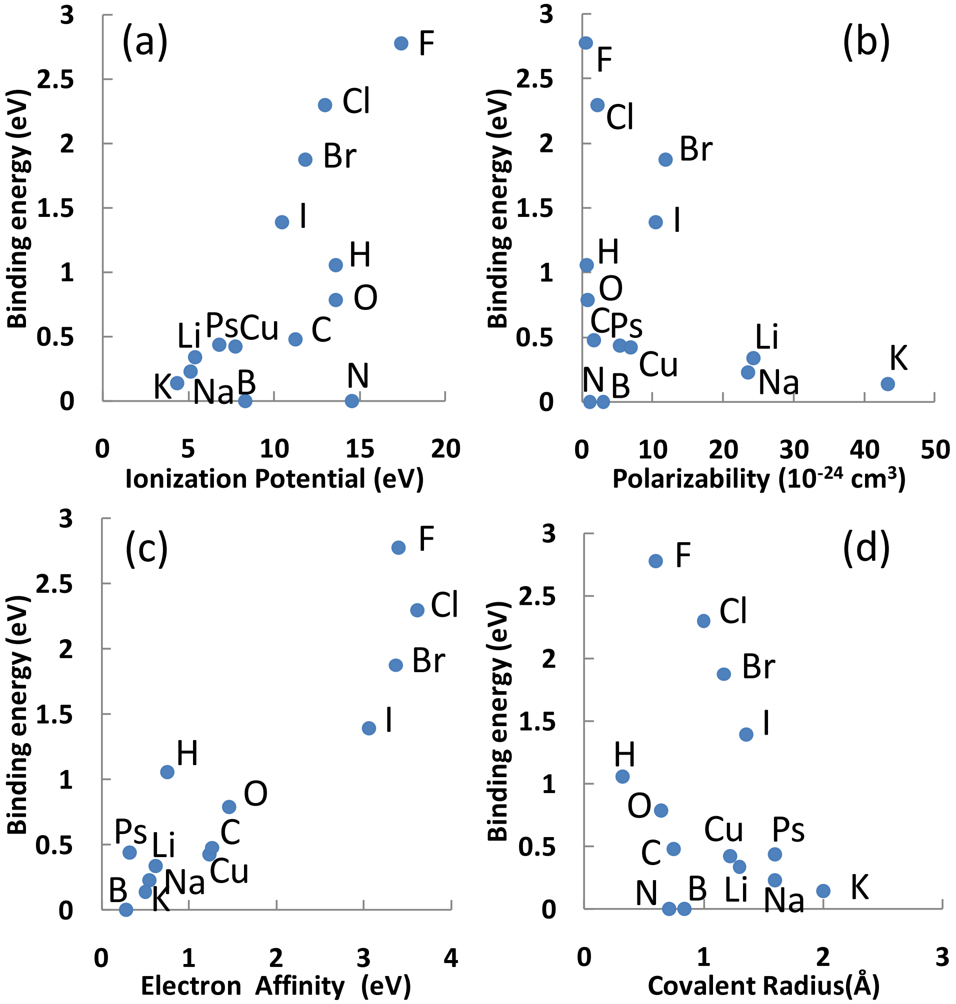


Figure III.1. Ps-atom binding energy vs. different physical properties. (a) Ionization potentials are from Ref. [35]. (b) The source of polarizabilities is Ref. [36]. (c) The source of electron affinities is Ref. [54]. (d) The source of covalent radius is Ref. [55].

If scheme 1 were important, there should be a maximum in binding energy as a function of *IP* at 0.326 eV (the binding energy of e^{-}Ps), but none of the *IP*s are that small. If scheme 2 were important, there would be a maximum in *BE* vs. *EA* at 6.803 eV, but none of our *BE*s are that large. If scheme 3 were important, there would be a maximum in *BE* vs. *PA* at 6.803 eV, but none of our *PA*s [52] is that large. Thus a resonance stabilization model similar to that for e^{+} binding does not apply to Ps binding.

The binding energy is found to be approximately proportional to the cross term *IP·EA*, as shown in Figure III.2. The work left now is to improve the fitting. B and N are found not to bind with Ps. These atoms, together with Ps, will provide an important test of the reliability of our model.

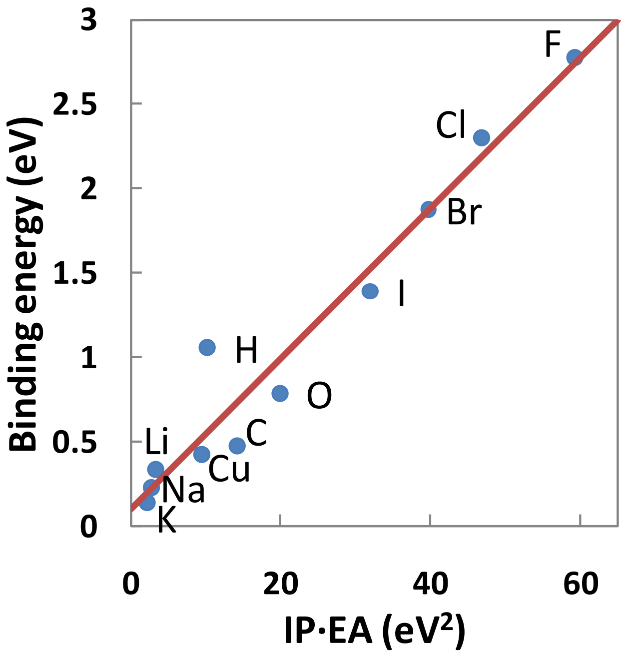


Figure III.2. Binding energy vs. *IP·EA*.

$1/x$	x^2	x^3	$x_1 \cdot x_2$	x^3
$1/IP$	IP	IP^2	$IP\alpha$	IP^3
$1/\alpha$	α	α^2	$\alpha \cdot EA$	α^3
$1/EA$	EA	EA^2	$EA \cdot IP$	EA^3
$1/R_{\mathrm{cov}}$	R_{cov}	$R_{\mathrm{cov}}{}^2$		
$1/Ns$	Ns	Ns^2		
$1/Np$	Np	Np^2		
$1/Nd$	Nd	Nd^2		
$1/Z$	Z	Z^2		

Table III.2. Parameters of physical properties tested in Ps binding part.

In the data analysis, the same MATLAB program for e^+ binding is used. The only difference is the pool of atomic parameters. Thirty parameters (Table III.2) are included, and there are $\binom{30}{2} + \binom{30}{3} + \binom{30}{4} + \binom{30}{5} + \binom{30}{6} = 767{,}746$ distinct subsets. Ten million iterations are carried out. The results are shown in the following section.

B. Results

As shown in Table III.1, 12 atoms have been found to bind with positronium. All the binding atoms, except Hg and the atypical atom Ps, are used in the fitting. The parameters of physical properties included in the fitting are shown in Table III.2.

After numerous sets of fitting with different physical properties and various combinations, we find that a fitting of binding energies with $IP \cdot EA$, covalent radius R_{cov} and the number of valence s electrons (Ns) is the best. The fitting equation is

$$BE = 0.875928 + 0.052314 \cdot IP \cdot EA - 0.207273 \cdot R_{\mathrm{cov}} - 0.466741 \cdot Ns \qquad (7)$$

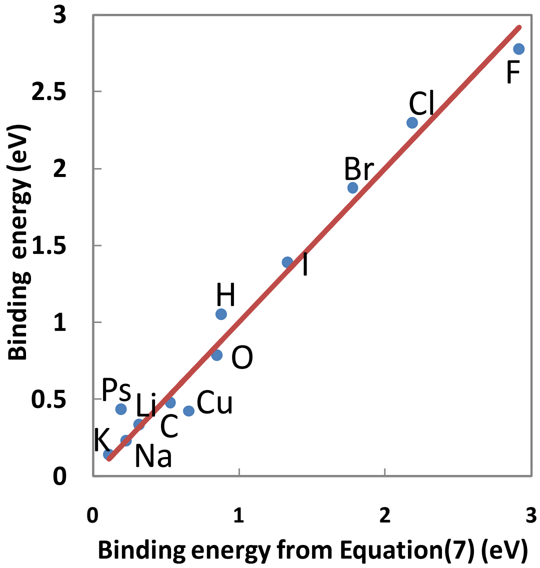


Figure III.3. The solid line is the binding energy calculated from the best-fit equation (Eq. (7)). The solid circles are the binding energies from the literature. Ps was not used in the fit but is shown here for reference purposes.

The fitting results are shown in Figure III.3. The units of $IP{\cdot}EA$ and R_{cov} are eV^2 and Å, respectively. The root-mean-square deviation is only 0.12, and the normalized root-mean-square deviation is as small as 4%. The uncertainties in the calculated binding energies are all from electron affinities and covalent radii. The equation of the uncertainties is

$$\Delta BE = \sqrt{(0.0523142 \cdot IP \cdot \Delta EA)^2 + (0.207273 \cdot \Delta R_{\mathrm{cov}})^2} \tag{8}$$

The detailed data and results are shown in Table III.3.

Also the fitting equation is tested by Ps and the nonbinding atoms. The bond length or covalent radius of Ps is from Ref [56]. The predicted binding energies are shown in Table III.4. All these values are in good agreement with theoretical predictions. The model appears to provide a reliable predictor.

Using the best-fit equation (Eq. (7)), the binding energies of 67 other atoms not previous studied are predicted. The atoms that cannot form a stable state with electron have negative *EA*s from Ref [57]. In the prediction, 23 will bind a positronium, 33 atoms will not, and 11 atoms are indeterminate because of *EA* data missing or have large uncertainties. The results are shown in Table III.5.

	IP	*EA*	R_{cov}	Literature values	Present work	*Error*	*Tolerance*
H	13.5984	0.754195(19)	0.32(3)	1.0547(0)	0.8794(66)	-0.1753	0.0066
Li	5.3917	0.618049(20)	1.3(1)	0.3366(30)	0.3141(269)	-0.0225	0.0299
Na	5.1391	0.547926(25)	1.6(2)	0.229(15)	0.2249(332)	-0.0041	0.0482
K	4.3407	0.50147(10)	2.0(2)	0.139(10)	0.1085(415)	-0.0305	0.0515
Cu	7.7264	1.235(5)	1.22(12)	0.423(80)	0.6555(254)	0.2325	0.1054
C	11.2603	1.262119(20)	0.75(8)	0.476(30)	0.5305(155)	0.0545	0.0455
O	13.6181	1.461114(1)	0.64(6)	0.785(60)	0.8507(133)	0.0657	0.0733
F	17.4228	3.401190(3)	0.60(6)	2.776(2)	2.9181(124)	0.1421	0.0144
Cl	12.9676	3.612724(27)	1.0(1)	2.297(180)	2.1860(207)	-0.1110	0.2007
Br	11.8138	3.363588(2)	1.17(12)	1.873(60)	1.7787(249)	-0.0943	0.0849
I	10.4513	3.059037(10)	1.36(14)	1.39(20)	1.3331(282)	-0.0569	0.2282

Table III.3. Data and results. The error is the difference between the present work and literature values. The tolerance is the sum of the uncertainties of the present work and literature values.

	IP	*EA*	R_{cov}	Present work
Ps	6.803	0.326(0)	1.59(16)	0.1944(415)
B	8.298	0.279723(25)	0.84(8)	-0.1102(174)
N	14.5341	-0.21(5)	0.71(7)	-0.3644(147)

Table III.4. Ps and nonbinding atoms results

Table III.5. All other atoms up to Bi.

Atomic Number	**Atoms**	***IP* (eV)**	***EA* (eV)**	**R_{cov}(Å)**	***BE* of Present work (eV)**	**Result**
2	He	24.5874	-0.22(5)	0.37(4)	-0.42(1)	Unbound
4	Be	9.3227	-0.65(7)	0.99(10)	-0.58(2)	Unbound
10	Ne	21.5645	-0.3(1)	0.62(6)	-0.52(1)	Unbound
12	Mg	7.6462	-0.52(5)	1.4(1)	-0.56(3)	Unbound
13	Al	5.9858	0.43283(5)	1.24(12)	-0.18(3)	Unbound
14	Si	8.1517	1.389521(1)	1.14(11)	0.30(2)	**Bound**
15	P	10.4867	0.7465(3)	1.09(11)	0.13(2)	**Bound**
16	S	10.36	2.077104(7)	1.04(10)	0.85(2)	**Bound**
18	Ar	15.7596	-0.37(4)	1.01(10)	-0.57(2)	Unbound
20	Ca	6.1132	0.02455(10)	1.9(2)	-0.41(3)	Unbound
21	Sc	6.5615	0.188(20)	1.59(16)	-0.32(3)	Unbound
22	Ti	6.8281	0.079(14)	1.48(15)	-0.33(3)	Unbound
23	V	6.7462	0.525(12)	1.44(14)	-0.17(3)	Unbound
24	Cr	6.7665	0.666(12)	1.3(1)	0.38(3)	**Bound**
25	Mn	7.434	-1.07(10)	1.29(13)	-0.74(3)	Unbound
26	Fe	7.9024	0.151(3)	1.24(12)	-0.25(3)	Unbound
27	Co	7.881	0.662(3)	1.18(12)	-0.03(2)	Unbound
28	Ni	7.6398	1.156(10)	1.17(12)	0.16(2)	**Bound**
30	Zn	9.3942	-0.67(7)	1.2(1)	-0.64(2)	Unbound
31	Ga	5.9993	0.43(3)	1.23(12)	-0.18(3)	Unbound
32	Ge	7.8994	1.232712(15)	1.2(1)	0.20(2)	**Bound**
33	As	9.7886	0.804(2)	1.2(1)	0.11(2)	**Bound**
34	Se	9.7524	2.020670(25)	1.18(12)	0.73(2)	**Bound**
35	Br	11.8138	3.363588(2)	1.17(12)	1.78(2)	**Bound**
36	Kr	13.9996	-0.42(4)	1.16(12)	-0.61(2)	Unbound
37	Rb	4.1771	0.48592(2)	2.15(22)	0.07(4)	**Bound**
38	Sr	5.6949	0.048(6)	1.9(2)	-0.44(4)	Unbound
39	Y	6.2173	0.307(12)	1.76(18)	-0.32(4)	Unbound
40	Zr	6.6339	0.426(14)	1.64(16)	-0.25(3)	Unbound
41	Nb	6.7589	0.916(5)	1.56(16)	0.41(3)	**Bound**
42	Mo	7.0924	0.748(2)	1.46(15)	0.38(3)	**Bound**
43	Tc	7.28	0.55(20)	1.38(14)	-0.13(8)	Unbound
44	Ru	7.3605	1.05(15)	1.36(14)	0.53(6)	**Bound**
45	Rh	7.4589	1.137(8)	1.34(13)	0.58(3)	**Bound**
46	Pd	8.3369	0.562(5)	1.3(1)	0.85(3)	**Bound**
47	Ag	7.5762	1.302(7)	1.36(14)	0.64(3)	**Bound**
48	Cd	8.9938	-0.78(8)	1.4(1)	-0.71(3)	Unbound

Table III. 5 continued on next page.

49	In	5.7864	0.3(2)	1.42(14)	-0.26(7)	Unbound
50	Sn	7.3439	1.112067(15)	1.4(14)	0.08(3)	**Bound**
51	Sb	8.6084	1.046(5)	1.4(1)	0.12(3)	**Bound**
52	Te	9.0096	1.970876(7)	1.37(14)	0.59(3)	**Bound**
54	Xe	12.1298	-0.45(5)	1.36(14)	-0.63(3)	Unbound
55	Cs	3.8939	0.471626(25)	2.38(24)	0.01(5)	Indeterminate
56	Ba	5.2117	0.14462(6)	2.06(21)	-0.45(4)	Unbound
57	La	5.5769	0.48(2)	1.94(19)	-0.32(4)	Unbound
58	Ce	5.5387	0.65(3)	1.84(18)	-0.25(4)	Unbound
59	Pr	5.473	0.962(24)	1.9(2)	-0.18(4)	Unbound
60	Nd	5.525	>1.916(383)	1.88(19)	0.11(12)	Indeterminate
61	Pm	5.582	no data	1.86(19)	no data	Indeterminate
62	Sm	5.6437	no data	1.85(19)	no data	Indeterminate
63	Eu	5.6704	0.864(24)	1.83(18)	-0.18(4)	Unbound
64	Gd	6.1498	>1.165(230)	1.82(18)	-0.06(8)	Indeterminate
65	Tb	5.8638	no data	1.81(18)	no data	Indeterminate
66	Dy	5.9389	>0	1.8(2)	>-0.43(16)	Indeterminate
67	Ho	6.0215	no data	1.79(18)	no data	Indeterminate
68	Er	6.1077	no data	1.77(18)	no data	Indeterminate
69	Tm	6.1843	1.029(22)	1.77(18)	-0.09(4)	Unbound
70	Yb	6.2542	-0.02(1)	1.78(18)	-0.43(4)	Unbound
71	Lu	5.4259	0.34(1)	1.74(17)	-0.32(4)	Unbound
72	Hf	6.8251	0.017(2)	1.64(16)	-0.39(3)	Unbound
73	Ta	7.5496	0.322(12)	1.58(16)	-0.26(3)	Unbound
74	W	7.864	0.815(2)	1.5(2)	-0.03(3)	Indeterminate
75	Re	7.8335	0.15(15)	1.41(14)	-0.29(7)	Unbound
76	Os	8.4382	1.1(2)	1.36(14)	0.15(9)	**Bound**
77	Ir	8.967	1.5638(50)	1.32(13)	0.40(3)	**Bound**
78	Pt	8.9588	2.128(2)	1.3(1)	1.14(3)	**Bound**
79	Au	9.2255	2.30863(3)	1.3(1)	1.25(3)	**Bound**
80	Hg	10.4375	-0.67(7)	1.32(13)	-0.70(3)	Unbound
81	Tl	6.1082	0.377(13)	1.44(14)	-0.24(3)	Unbound
82	Pb	7.4167	0.364(8)	1.45(15)	-0.27(3)	Unbound
83	Bi	7.2855	0.942362(13)	1.5(2)	-0.01(3)	Indeterminate

C. Discussion

The fitting results and predictions are generally reasonable. We can conclude that the binding energy of positronium and atom is governed by *IP*, *EA*, the covalent radius R_{cov}, and the electron configuration.

	EA **(eV)**	***IP*** **(eV)**	***IP·EA*** **(eV^2)**	***BE*****(eV)**	**Literature**
CH	1.238	10.64	13.17	0.44(2)	[58]
OH	1.82767	13	23.76	0.28(3)	[58]
CN	3.821	14.09	53.84	0.83(80)	[59]
NH_2	0.771	11.14	8.59	0.15(2)	[58]
N_3	2.7			0.14(10)	[59]
CH_3	0.08	9.84	0.79	0.2(20)	[60]
NO_3	3.937			0.3(3)	[61]

Table III.6. Ps binding to molecules.

As shown in Fig. III.2, the cross term of *IP* and *EA* is a very important factor. It can be simply regarded as an indicator of the magnitude of the binding energy. This is easy to understand from the definitions of the ionization potential and electron affinity. The ionization potential is the energy needed to remove an electron from an atom. The greater the *IP* is, the more difficult it is to remove an electron from the atom. The electron affinity is the energy change when an electron is added to the neutral atom to form a negative ion. The greater the *EA* is, the more eager the atom is to add an electron. Thus the cross term is a good parameter to indicate the binding energy between atoms and positronium (e^+e^-). In short, in positronium binding, both of the atom's eagerness to gain an electron (scheme 2) and its reluctance to lose one (scheme 1) are important. Moreover, it is qualitatively true for the studied molecules binding to positronium as shown in Table

III.6. These molecules are not so adequate to prove *IP·EA*’s influence because they can be regarded as e^+M^- instead of PsM (M=molecule). The IP and EA are all about the electron. It may indicate that the electron from positronium is closer to the bound atom than is the positron.

The covalent radius and N_s can be both regarded as parameters of electron configuration. Atoms that can attain a more stable configuration by adding an electron tend to bind with Ps, because the electron in Ps completes the subshell [11]. This idea finds support from the alkali metals and the halogens, two families that are otherwise starkly different both strongly bond to Ps. The positronium binding is sensitive to electron configuration. In our predictions above, most atoms with half-filled *s* subshells will bind with Ps. Positive binding energies are obtained for the following such atoms: Rb ([Ar]5*s*), Cr([Ar]$3d^5 4s$), Mo ([Kr]$4d^4 5s$), Ag ([Kr]$4d^{10} 5s$), Pt ([Xe]$4f^{14} 5d^9 6s$), and Au ([Xe]$4f^{14} 5d^{10} 6s$). Moreover, most atoms with 3 or 5 electrons on *p* subshell will also bind with positronium. They are P ([Ne]$3s^2 3p^3$), As ([Ar]$3d^{10} 4s^2 4p^3$), Sb ([Kr]$4d^{10} 5s^2 5p^3$) and Br ([Ar]$3d^{10} 4s^2 4p^5$). Among these atoms, only Cs and Bi are indeterminate because of large uncertainties. The unbound predictions are good too. All atoms in the beryllium family are predicted not to bind with positronium. For noble gases, none of them is predicted to bind with Ps. These results will further prove the reliability and value of our model and prediction.

There is no data on positronium binding to atoms with open *d* and *f* subshells, so the predictions for these atoms are less authoritative.

D. Summary

The relationship between PsA binding energies and atomic physical properties has been studied. Good results [Eq. (7)] are obtained using the parameters $IP \cdot EA$, covalent radius R_{cov} and the number of valence *s* electrons *Ns*. Then using the best-fit equation, other stable atoms are calculated and predicted. Twenty-three other atoms are predicted to bind with Ps, and the predicted binding energies are shown in Table III.5.

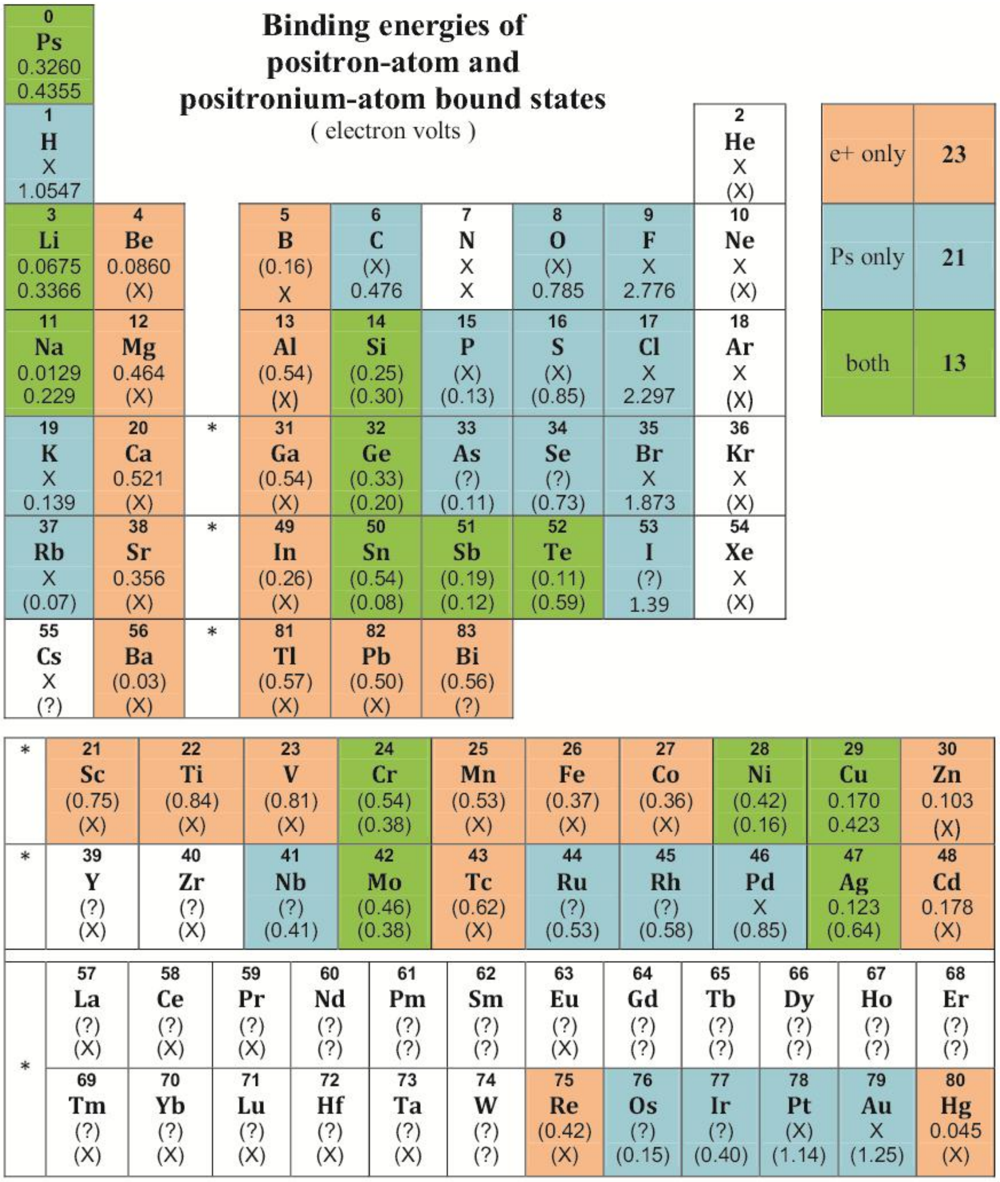
We hope the present work will provide motivation for experimental measurement and the high-quality calculation of Ps binding to atoms.

IV. CONCLUSION AND SUMMARY

The relationship between positron- and positronium-atom binding energies and atomic physical properties has been studied. Two best-fit equations give good predictions for atoms. They are Eq. (4) for positron binding and Eq. (7) for positronium binding. We can conclude that the binding energy of one positron and one atom is governed by the ionization potential, polarizability, the cross term of ionization potential and polarizability, and the number of valence *s* electrons; while the binding energy of one positronium and one atom is governed by the cross term of ionization potential and electron affinity, covalent radius, and the number of valence *s* electrons. These relationships between binding energies and atomic physical parameters are examined using the atoms studied by quantum calculations in others' work. The agreement is very good for both the binding atoms and nonbinding atoms. Also these fitting equations are discussed, and seem to be theoretically reasonable.

Based on the work above, all the unstudied stable atoms are calculated using all the available data of physical properties. It is found that there are 24 new atoms that will bind with positron, and 23 new atoms that will bind with positronium. All the results are shown in Figure IV.1.

We hope the present work will provide motivation to carry out more high-quality calculations and experimental measurements on both atoms and molecules. Overlap between theoretical calculation and experiment will better support the study of positron and positronium binding.



Binding energies of positron-atom and positronium-atom bound states

(electron volts)

0 **Ps** 0.3260 0.4355								
1 **H** X 1.0547								2 **He** X (X)
3 **Li** 0.0675 0.3366	4 **Be** 0.0860 (X)		5 **B** (0.16) X	6 **C** (X) 0.476	7 **N** X X	8 **O** (X) 0.785	9 **F** X 2.776	10 **Ne** X (X)
11 **Na** 0.0129 0.229	12 **Mg** 0.464 (X)		13 **Al** (0.54) (X)	14 **Si** (0.25) (0.30)	15 **P** (X) (0.13)	16 **S** (X) (0.85)	17 **Cl** X 2.297	18 **Ar** X (X)
19 **K** X 0.139	20 **Ca** 0.521 (X)	*	31 **Ga** (0.54) (X)	32 **Ge** (0.33) (0.20)	33 **As** (?) (0.11)	34 **Se** (?) (0.73)	35 **Br** X 1.873	36 **Kr** X (X)
37 **Rb** X (0.07)	38 **Sr** 0.356 (X)	*	49 **In** (0.26) (X)	50 **Sn** (0.54) (0.08)	51 **Sb** (0.19) (0.12)	52 **Te** (0.11) (0.59)	53 **I** (?) 1.39	54 **Xe** X (X)
55 **Cs** X (?)	56 **Ba** (0.03) (X)	*	81 **Tl** (0.57) (X)	82 **Pb** (0.50) (X)	83 **Bi** (0.56) (?)			

e+ only	**23**
Ps only	**21**
both	**13**

*	21 **Sc** (0.75) (X)	22 **Ti** (0.84) (X)	23 **V** (0.81) (X)	24 **Cr** (0.54) (0.38)	25 **Mn** (0.53) (X)	26 **Fe** (0.37) (X)	27 **Co** (0.36) (X)	28 **Ni** (0.42) (0.16)	29 **Cu** 0.170 0.423	30 **Zn** 0.103 (X)
*	39 **Y** (?) (X)	40 **Zr** (?) (X)	41 **Nb** (?) (0.41)	42 **Mo** (0.46) (0.38)	43 **Tc** (0.62) (X)	44 **Ru** (?) (0.53)	45 **Rh** (?) (0.58)	46 **Pd** X (0.85)	47 **Ag** 0.123 (0.64)	48 **Cd** 0.178 (X)

*	57 **La** (?) (X)	58 **Ce** (?) (X)	59 **Pr** (?) (X)	60 **Nd** (?) (?)	61 **Pm** (?) (?)	62 **Sm** (?) (?)	63 **Eu** (?) (X)	64 **Gd** (?) (?)	65 **Tb** (?) (?)	66 **Dy** (?) (?)	67 **Ho** (?) (?)	68 **Er** (?) (?)
	69 **Tm** (?) (X)	70 **Yb** (?) (X)	71 **Lu** (?) (X)	72 **Hf** (?) (X)	73 **Ta** (?) (X)	74 **W** (?) (?)	75 **Re** (0.42) (X)	76 **Os** (?) (0.15)	77 **Ir** (?) (0.40)	78 **Pt** (X) (1.14)	79 **Au** X (1.25)	80 **Hg** 0.045 (X)

Figure IV.1. All available results. Binding energies for atoms with uncertainties larger than our predicted values are indicated with question marks. All the binding energies are in electron volts.

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APPENDIX

MATLAB code for data analysis and calculation

```
clc
clear all
warning off all

% Global data for graphing and so on.
global NCoeff NIter BEmin BEmax;          %NC is number of coefficients;
IPL=1;                                    %The column of IP;
NCoeff=3;                                 %Parameter number besides constant
NIter=100000;                             %NR is number of repeation of the fitting;
BEmin=0;
BEmax=3.0;

% Data Input
disp('Instruction about the factor of every column:');
disp('You have to make sure the last 2 columns are constant and BE.');
disp('Now calculating......');
DATA=[];                                  %The data for nonbound atom for N and B;
NAcoeff=size(DATA,2)-2;                   %number of all the parameters
NboundA=size(DATA,1);                     %number of bound atoms
NunboundA=size(DATA2,1);                  %number of nonbound atoms

% Variables that will be used in each fitting.
FittingX=zeros(size(DATA,1),NCoeff+1);
FittingY=DATA(:,NAcoeff+2);
BestF=zeros(NCoeff+2,16);   %Save the best 8 fittings
BestBE=zeros(size(DATA,1),8); % Save the best 8 fitting BE
BestBE2=zeros(size(DATA2,1),8);
FittingS=zeros(NCoeff+1,1); % Store the coefficient sequence
FittingC=zeros(NCoeff+1,1); % Store the coefficients of every items
FittedBE=zeros(size(DATA,1),1);
Progress2=0;

% Start Fitting
n=0;
while n<NIter
  n=n+1;
% Parameter Sletion
FittingS(1,1)=NAcoeff+1;
i=2;
    while i<=NCoeff+1
        signflag=0;
        rn=randi(NAcoeff,1);
```

```
        FittingS(i)=rn;
        for j=2:i
            if i==j;
            elseif FittingS(j)==FittingS(i)
                signflag=1;
            end
        end
        if signflag==0
         i=i+1;
        end
    end
%Load FittingX
    for i=1:NCoeff+1
        FittingX(:,i)=DATA(:,FittingS(i));
    end
%Linear regression
    FittingC=inv((FittingX'*FittingX))*FittingX'*FittingY;

%Error Calculation
    error=0;
    for i=1:size(DATA,1)
        BE=0;
        for j=1:NCoeff+1
            BE=FittingC(j)*DATA(i,FittingS(j));
        end
        FittedBE(i)=BE;
        error=error+(BE-FittingY(i))^2;
    end
    error=sqrt(error);

%Decide whether to keep the result
    DecisionC=0;
    Sign=0;
    if n<=8
      DecisionC=n;
    else
      %check whether equal error
      for i=1:8
        if abs(error-BestF(NCoeff+2,2*i))<1e-6
            Sign=1;
        end
      end
      if Sign==0
      % decide the maxmium error
        maxError=BestF(NCoeff+2,2);
        maxC=1;
```

```
         for i=2:8
                if maxError<=BestF(NCoeff+2,2*i)
                    maxError=BestF(NCoeff+2,2*i);
                    maxC=i;
                end
         end
         if maxError-error>1e-5
            DecisionC=maxC;
         end
      end
    end

%do the transfer or not
    if DecisionC~=0
        for i=1:NCoeff+1
            BestF(i,DecisionC*2-1)=FittingS(i);
            BestF(i,DecisionC*2)=FittingC(i);
        end
        BestF(NCoeff+2,DecisionC*2)=error;
        BestBE(:,DecisionC)=FittedBE;
    end
    Progress1=fix(n/NIter*100);
    if Progress1-Progress2>=20
        Progress2=Progress1;
        fprintf('Percentage completed: %d%%',Progress1);
        fprintf('\n');
    end
end
%Calculation for unbound atoms
for i=1:8
    for j=1:NunboundA
        BE=0;
        for k=1:NCoeff+1
            BE=BE+BestF(k,2*i)*DATA2(j,BestF(k,2*i-1));
        end
        BestBE2(j,i)=BE;
    end
end

%Output data and figures
fid=fopen('Ps_May26_1.txt','wt');
fprintf(fid,'Instruction about the factor of every column:');
fprintf(fid,'You have to make sure the last 2 columns are constant and BE.');
fprintf(fid,'Bound atoms of the 8 best combinations, coefficients, and error:\n');
fprintf(fid,'%-3d %-11.6f %-3d %-11.6f %-3d %-11.6f %-3d %-11.6f %-3d %-11.6f %-
3d %-11.6f %-3d %-11.6f %-3d %-11.6f\n',BestF');
```

```
fprintf(fid,'Bound atoms predicted: \n');
fprintf(fid,'%-11.6f %-11.6f %-11.6f %-11.6f %-11.6f %-11.6f %-11.6f %-11.6f \n',
BestBE');
fprintf(fid,'Bound atoms predicted: \n');
fprintf(fid,'%-11.6f %-11.6f %-11.6f %-11.6f %-11.6f %-11.6f %-11.6f %-11.6f \n',
BestBE');
fprintf(fid,'Unbound atoms predicted: \n');
fprintf(fid,'%-11.6f %-11.6f %-11.6f %-11.6f %-11.6f %-11.6f %-11.6f %-11.6f \n',
BestBE2');
    % Output figures
x=BEmin:0.1:BEmax;
for i=1:8
    figure(i):plot(x,x);
    hold all
    figure(i):plot(BestBE(:,i),FittingY,'o');
end
fclose(fid);

disp('Done. Please check TXT file');
```