Binding-energy predictions of positronium-atom systems

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A large amount of work has been performed on positron and positronium (Ps) binding to atoms. Positron binding was treated in our last paper [Phys. Rev. A **83**, 032504 (2011)], of which the present paper is a continuation. For Ps binding, 12 atoms have been found to bind with Ps, and 2 atoms have been found not to bind with Ps. We fit the known binding energies to a simple expression involving a few common physical properties and then use it to predict the Ps-binding energies of the other atoms. The model and results appear to be reliable.

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I. INTRODUCTION

Positronium (Ps) is an atom consisting of a positron and an electron. Ps and positrons have some practical applications, such as serving as sensitive probes of free volume and defects in polymers and semiconductors [1,2], characterization of thin films, quantum dots [3,4], and more [1,5]. They are potentially as useful as neutrons, electrons, and x rays as probes of matter; in order to reach that potential, we must have more accurate and extensive information on the interactions of positrons and Ps atoms with ordinary matter [6].

Recent advances in the development of positron sources [7,8] and traps [9–11] have led to an interest in multipositron physics and chemistry [12]. These advances provide the technology required to accurately measure positron- and Ps-binding energies to atoms and molecules [6]. This field, bound states of positrons and Ps atoms to *koino* atoms and molecules, is unusual in that the theory is ahead of the experiments [6]. We hope the present paper will stimulate and will promote laboratory work in this area.

Recently, the entire field of positron- and Ps-atom and Ps-molecule-bound systems was reviewed [6]. An updated list of all known Ps-binding energies of atoms is given in Table I.

First, we give a general summary and analysis of the current status of Ps binding to atoms. Then, we examine the dependence of Ps-atom-binding energies (E) on parameters derived from a few physical properties, such as ionization potential (V_i), static electric dipole polarizability (α), electron affinity (E_a), covalent radius (R_{cov}), numbers and types of valence electrons, and so on. We employ MATLAB to test about 30 combinations of these. We pick the most accurate and reasonable combination, demonstrate its validity, and use it to predict binding energies for all the unstudied atoms up to bismuth.

II. CURRENT STATUS OF THE PROBLEM

All our knowledge of positron and Ps binding to atoms and molecules comes from quantum-mechanical calculations. Several experimental methods have been suggested for measuring these quantities [25–28], but only two have been used so far, the more fruitful of which has been exploited skillfully in Professor Surko's laboratory [29]. Considerable experimental work was performed there on positron binding to small organic molecules [26], which were inferred from the redshifts of certain infrared vibrational spectral features upon the capture of positrons into vibrational Feshbach resonances [30]. The method gives binding energies with precisions of 20–25 meV. It does not appear to be applicable to Ps binding to atoms and molecules nor to positron binding to atoms. It has been used to measure positron-binding energies of about 30 molecules, mostly hydrocarbons and halosubstituted hydrocarbons. In addition, about ten such molecules were found not to bind positrons, which is also useful knowledge.

The other method, dissociative attachment, appears to be potentially more general, but it has been used in only one measurement so far, that of the Ps-H bond strength [25]. With available equipment at the time of the experiment (about 20 yr ago), a precision of 200 meV did not compare with much superior precision from quantum calculations. Nevertheless, the experiment was significant because it was a laboratory demonstration that showed dissociative attachment can provide the desired binding energies. Today, cryogenic moderation of positron beams [31] coupled with high-precision recoil ion momentum spectroscopy (RIMS) [32] can provide a precision in binding energies of a few meV. The experiment entails crossed pulsed beams of positrons and molecular targets and the detection of a signature ion and the measurement of its kinetic energy by RIMS.

A positron colliding with a molecule AB has four possible dissociative attachment outcomes that have two products,

Products	Appearance potentials (eV)	
$\mathrm{Ps}A + B^+$	$E_{\mathrm{AB}} + V_{i\mathrm{B}} - V_{i\mathrm{Ps}} - E_{\mathrm{Ps}A}$	
$A + e^+B$	$E_{\mathrm{AB}} - E_{e^+\mathrm{B}}$	(1)
$A^+ + \mathrm{Ps}B$	$E_{\mathrm{AB}} + V_{i\mathrm{A}} - V_{i\mathrm{Ps}} - E_{\mathrm{PsB}}$	
$e^+A + B$	$E_{\mathrm{AB}} - E_{e^+\mathrm{A}}$	

A and B above may be complex and/or identical. The right-hand column gives the appearance potentials of the signature ions; this energy is provided by the incident positron. The product species above that contain a positron, which annihilates on a much shorter time scale than ion extraction and detection, so B^+ is detected in the first two reactions but at different positron energies and is similarly for the last two reactions. In the case of $A = \mathrm{CH_3}$ and $B = \mathrm{H}$, the new compounds, thresholds (in eV) and signature ions are in the order above,

New compounds	Appearance potentials (eV)	Signature ions	
$\mathrm{PsCH_3}$	$11.342 - E_{\mathrm{Ps-CH_3}}$	$\mathrm{H^+}$	
$e^+\mathrm{H}$	$4.543 - E_{\mathrm{e^+H}}$	$\mathrm{H^+}$	(2)
PsH	6.53	$\mathrm{CH_3^+}$	
$e^+\mathrm{CH_3}$	$4.543 - E_{\mathrm{e^+CH_3}}$	$\mathrm{CH_3^+}$	

TABLE I. The binding energies and methods of calculation for all studied Ps-atom systems. Stochastic variational method (SVM), configuration interaction (CI), ∞ indicates an extrapolation to convergence of a basis expansion, diffusion Monte Carlo (DMC) method. In all cases, the threshold is Ps + A.

System	E (eV)	Method	References
	Binding atoms		
Ps_2	0.4355	SVM	[13]
PsH	1.0547	SVM	[14,15]
LiPs	0.3366	$SVMFC_3$	[16]
NaPs	0.229	$SVMFC_3$	[17,18]
KPs	0.139	$SVMFC_3$	[17,19]
PsCu	0.423	$CI_\infty FC_3$	[20]
PsC	0.476	DMC, $CI_\infty FC_3$	[21,22]
PsO	0.785	DMC, $CI_\infty FC_6$	[22,23]
PsF	2.776	DMC, $CI_\infty FC_9$	[21,24]
PsCl	2.297	$CI_\infty FC_9$	[24]
PsBr	1.873	$CI_\infty FC_9$	[24]
PsI	1.39	$CI_\infty FC_9$	[24]
	Nonbinding atoms		
PsB	Unbound	DMC, CI	[21,22]
PsN	Unbound	$CI_\infty FC_5$	[22]

The two signals for mass 1 cannot be confused because they are far apart in energy. The first appearance of a proton signal is at 4.543 eV since e^+H is known not to be bound [33]. The binding energy for Ps-CH_3 is unknown, so an observation of a second appearance of H^+ at 10.00 eV, say, would indicate a binding energy for Ps-CH_3 of 1.34 eV. The energy that supplies the appearance potential comes from the kinetic energy of the positron, $(E_{\mathrm{kin}})_{e^+}$, so the binding energies are as follows:

$$\begin{aligned} E_{\mathrm{Ps}A} &= E_{\mathrm{AB}} + V_{i\mathrm{B}} - V_{i\mathrm{Ps}} - (E_{\mathrm{kin}})_{e^+} + (E_{\mathrm{kin}})_{\mathrm{prod}}, \\ E_{e^+\mathrm{B}} &= E_{\mathrm{AB}} - (E_{\mathrm{kin}})_{e^+} - (E_{\mathrm{kin}})_{\mathrm{prod}}. \end{aligned} \tag{3}$$

The kinetic energy of the products is, of course, zero at the threshold, but the cross sections of the attachment processes are also zero there [25]; therefore, a RIMS determination of $(E_{\mathrm{kin}})_{\mathrm{prod}}$ is desirable—without this determination, only a lower bound of the binding energy is obtained. Here, we ignore possible internal excitation of products (also zero at threshold) for simplicity, although this is of interest in its own right [6].

The method of Surko and co-workers and the method of dissociative attachment are nicely complementary: Surko's method provides positron-binding energies to whole molecules, and the dissociative attachment method can give positron- and Ps-binding energies to fragments of molecules including atoms.

The theoretical methods that have given us all our knowledge of Ps-atom binding are as follows: the stochastic variational method (SVM), the configuration interaction (CI) method, the quantum Monte Carlo method (QMC), and the many-body perturbation theory (MBPT).

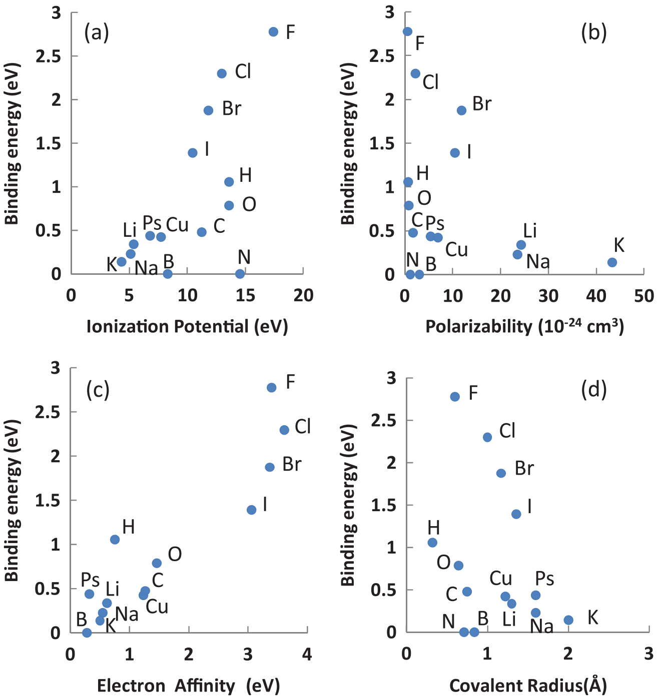


FIG. 1. (Color online) Ps-atom-binding energy vs different physical properties. (a) Ionization potentials are from Ref. [46]. (b) The source of polarizabilities is Ref. [47]. (c) The source of electron affinities is Ref. [48]. (d) The source of covalent radius is Ref. [49].

SVM has been applied to hydrogen, to the three lighter alkali metals, and to Ps itself. All four particles of PsH and Ps_2 were treated explicitly as were all five particles of e^+Li and the three outer light particles of Na and K. The core electrons of the latter were subsumed into a sophisticated model polarization potential [34]. The trial wave function was expressed as a linear sum of Gaussian functions that correlate the relative motions of the particles [35]. These basis functions are inapt to account for correlation between light particles, but the Hamiltonian matrix elements are very easy to calculate, permitting the use of large numbers of terms in the expansion, a few thousand in some cases [16]. The wave functions were built up by choosing values for the nonlinear parameters that appear in the arguments of the Gaussian functions in an automated random manner with some constraints. As terms were added to the sum, they were retained or were discarded according to their effect on the calculated energy. The linear parameters in the expansion were obtained by solving a secular equation. Five of the twelve known Ps-atom-binding energies have been obtained with this method, mostly by Mitroy and Ryzhikh [36], with accuracies on the order of up to several meV. The method

TABLE II. Parameters of physical properties tested in the Ps-binding part. Z is the atomic number.

$1/x$	x	x^2	x_1x_2	x^3
$1/V_i$	V_i	V_i^2	$V_i\alpha$	V_i^3
$1/\alpha$	α	α^2	αE_a	α^3
$1/E_a$	E_a	E_a^2	E_aV_i	E_a^3
$1/R_{cov}$	R_{cov}	R_{cov}^2		
$1/N_s$	N_s	N_s^2		
1/Np	Np	Np^2		
1/Nd	Nd	Nd^2		
$1/Z$	Z	Z^2		

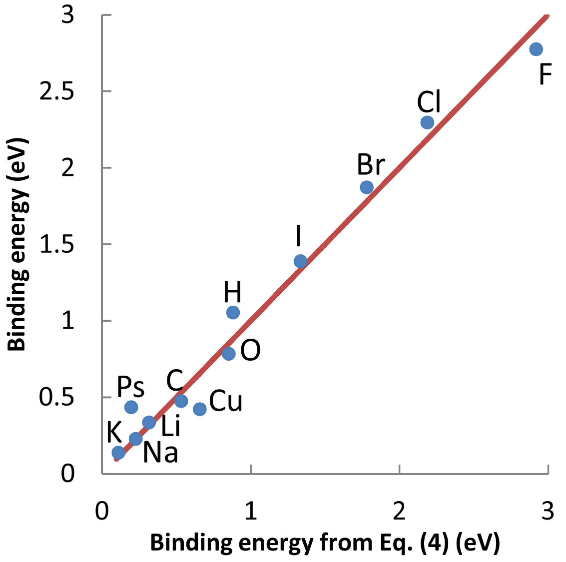


FIG. 2. (Color online) Binding energies from literature vs binding energies of the present paper. The solid line is the binding energy calculated from the best-fit equation [Eq. (4)]. The solid circles are the binding energies from the literature. Ps is not used in the fit but is shown here for reference purposes.

TABLE IV. Prediction using Eq. (4) for Ps and nonbinding atoms.

	V_i (eV)	E_a (eV)	R_{cov} (Å)	N_s	E (eV), present paper
Ps	6.803	0.326(0)	1.59(16)	1	0.1944(415)
B	8.298	0.279723(25)	0.84(8)	2	−0.1102(174)
N	14.5341	−0.21(5)	0.71(7)	2	−0.3644(147)

also has been used to predict positron binding to atoms. So far, it has been used for S and P states with up to six explicit particles; see Ref. [6] for a review of this paper.

The CI method has been used mainly by Saito [24] for Ps binding to atoms with only a few vacancies in their valence shells (i.e., atoms on the right side of the periodic chart) and by Mitroy *et al.* [37] for positron binding to atoms with only a few electrons in their valence shells (on the left side of the periodic chart). The method consists of building up an approximate wave function by adding other configurations that resemble excited states that can be single excitations (using helium as an example, $1s2s$) and double ($2s^2$, $2p^2$, etc.) excitations to a ground-state configuration. The choice of configurations is unlimited, and accuracy improves as more are added. Each configuration is composed of products of orbitals that are themselves expansions in some primitive basis set. Thus, two expansions are involved, one within the other. These are necessarily finite, and sophisticated methods of extrapolation have been devised to estimate the effects of incompleteness [38,39]. For the primitive basis functions, Saito uses natural orbitals (NOs) expressed in terms of B-splines; otherwise, his approach is known in modern quantum chemistry as multireference configuration interaction with the single- and double-excitations method. He has performed calculations on PsB, PsC, PsN, PsO, as well as on the Ps halides that have from 11 to 53 light particles, all of which he treated explicitly [23]. Taking PsF and PsI as representative examples, Saito used NOs with orbital angular momentum l up to 9 that were coupled into the total $L = 0$ symmetry. Forty-four reference configurations for PsF (38 for PsI) were constructed from NOs using an iterative bootstrap process; altogether, the total number of configurations used in the final calculations were ∼40 000 to ∼60 000 for PsF to PsI. Saito's results agree with predictions from the MBPT calculations of Ludlow and Gribakin [40] within a few tens of meV. Relativistic corrections were included in both these papers and were found to significantly reduce predicted binding energies from nonrelativistic predictions by a few tens of meV for the lightest species to a few hundreds of meV for the heaviest.

The CI approach of Mitroy and coworkers differs from that of Saito in two ways: Mitroy and coworkers do not treat core electrons explicitly but use carefully crafted potentials [34] to mimic the effects of core electrons on the outer particles; and the atomic orbitals are constructed from mixtures of Slater-type orbitals and Laguerre-type basis functions. For CuPs, a sequence of calculations using about 100 atomic orbitals with increasing values of atomic orbital angular momentum l from 0 to 10 were performed, with increasing numbers of $L = 0$ configurations up to about 64 000 to give a calculated Ps-Cu-binding energy of 0.292 eV. The truncation error was estimated, by extrapolation, to be 0.132 eV,

TABLE III. Input data and results for the binding energies. The error is the difference between the present paper and the literature values. The tolerance is the sum of the uncertainties of the present paper and literature values.

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

TABLE V. Predictions using Eq. (4) for all other atoms up to Bi.

Atomic number	Atoms	V_i (eV)	E_a (eV)	R_{cov} (Å)	N_s	E (eV), present paper	Result
2	He	24.5874	−0.22(5)	0.37(4)	2	−0.42(1)	Unbound
4	Be	9.3227	−0.65(7)	0.99(10)	2	−0.58(2)	Unbound
10	Ne	21.5645	−0.3(1)	0.62(6)	2	−0.52(1)	Unbound
12	Mg	7.6462	−0.52(5)	1.4(1)	2	−0.56(3)	Unbound
13	Al	5.9858	0.43283(5)	1.24(12)	2	−0.18(3)	Unbound
14	Si	8.1517	1.389521(1)	1.14(11)	2	0.30(2)	Bound
15	P	10.4867	0.7465(3)	1.09(11)	2	0.13(2)	Bound
16	S	10.36	2.077104(7)	1.04(10)	2	0.85(2)	Bound
18	Ar	15.7596	−0.37(4)	1.01(10)	2	−0.57(2)	Unbound
20	Ca	6.1132	0.02455(10)	1.9(2)	2	−0.41(3)	Unbound
21	Sc	6.5615	0.188(20)	1.59(16)	2	−0.32(3)	Unbound
22	Ti	6.8281	0.079(14)	1.48(15)	2	−0.33(3)	Unbound
23	V	6.7462	0.525(12)	1.44(14)	2	−0.17(3)	Unbound
24	Cr	6.7665	0.666(12)	1.3(1)	1	0.38(3)	Bound
25	Mn	7.434	−1.07(10)	1.29(13)	2	−0.74(3)	Unbound
26	Fe	7.9024	0.151(3)	1.24(12)	2	−0.25(3)	Unbound
27	Co	7.881	0.662(3)	1.18(12)	2	−0.03(2)	Unbound
28	Ni	7.6398	1.156(10)	1.17(12)	2	0.16(2)	Bound
30	Zn	9.3942	−0.67(7)	1.2(1)	2	−0.64(2)	Unbound
31	Ga	5.9993	0.43(3)	1.23(12)	2	−0.18(3)	Unbound
32	Ge	7.8994	1.232712(15)	1.2(1)	2	0.20(2)	Bound
33	As	9.7886	0.804(2)	1.2(1)	2	0.11(2)	Bound
34	Se	9.7524	2.020670(25)	1.18(12)	2	0.73(2)	Bound
35	Br	11.8138	3.363588(2)	1.17(12)	2	1.78(2)	Bound
36	Kr	13.9996	−0.42(4)	1.16(12)	2	−0.61(2)	Unbound
37	Rb	4.1771	0.48592(2)	2.15(22)	1	0.07(4)	Bound
38	Sr	5.6949	0.048(6)	1.9(2)	2	−0.44(4)	Unbound
39	Y	6.2173	0.307(12)	1.76(18)	2	−0.32(4)	Unbound
40	Zr	6.6339	0.426(14)	1.64(16)	2	−0.25(3)	Unbound
41	Nb	6.7589	0.916(5)	1.56(16)	1	0.41(3)	Bound
42	Mo	7.0924	0.748(2)	1.46(15)	1	0.38(3)	Bound
43	Tc	7.28	0.55(20)	1.38(14)	2	−0.13(8)	Unbound
44	Ru	7.3605	1.05(15)	1.36(14)	1	0.53(6)	Bound
45	Rh	7.4589	1.137(8)	1.34(13)	1	0.58(3)	Bound
46	Pd	8.3369	0.562(5)	1.3(1)	0	0.85(3)	Bound
47	Ag	7.5762	1.302(7)	1.36(14)	1	0.64(3)	Bound
48	Cd	8.9938	−0.78(8)	1.4(1)	2	−0.71(3)	Unbound
49	In	5.7864	0.3(2)	1.42(14)	2	−0.26(7)	Unbound
50	Sn	7.3439	1.112067(15)	1.4(14)	2	0.08(3)	Bound
51	Sb	8.6084	1.046(5)	1.4(1)	2	0.12(3)	Bound
52	Te	9.0096	1.970876(7)	1.37(14)	2	0.59(3)	Bound
54	Xe	12.1298	−0.45(5)	1.36(14)	2	−0.63(3)	Unbound
55	Cs	3.8939	0.471626(25)	2.38(24)	1	0.01(5)	Indeterminate
56	Ba	5.2117	0.14462(6)	2.06(21)	2	−0.45(4)	Unbound
57	La	5.5769	0.48(2)	1.94(19)	2	−0.32(4)	Unbound
58	Ce	5.5387	0.65(3)	1.84(18)	2	−0.25(4)	Unbound
59	Pr	5.473	0.962(24)	1.9(2)	2	−0.18(4)	Unbound
60	Nd	5.525	1.916(383)	1.88(19)	2	0.11(12)	Indeterminate
61	Pm	5.582	No data	1.86(19)	2	No data	Indeterminate
62	Sm	5.6437	No data	1.85(19)	2	No data	Indeterminate
63	Eu	5.6704	0.864(24)	1.83(18)	2	−0.18(4)	Unbound
64	Gd	6.1498	1.165(230)	1.82(18)	2	−0.06(8)	Indeterminate
65	Tb	5.8638	No data	1.81(18)	2	No data	Indeterminate
66	Dy	5.9389	0	1.8(2)	2	−0.43(16)	Indeterminate
67	Ho	6.0215	No data	1.79(18)	2	No data	Indeterminate
68	Er	6.1077	No data	1.77(18)	2	No data	Indeterminate
69	Tm	6.1843	1.029(22)	1.77(18)	2	−0.09(4)	Unbound
70	Yb	6.2542	−0.02(1)	1.78(18)	2	−0.43(4)	Unbound

TABLE V. (*Continued.*)

Atomic number	Atoms	V_i (eV)	E_a (eV)	R_{cov} (Å)	N_s	E (eV), present paper	Result
71	Lu	5.4259	0.34(1)	1.74(17)	2	−0.32(4)	Unbound
72	Hf	6.8251	0.017(2)	1.64(16)	2	−0.39(3)	Unbound
73	Ta	7.5496	0.322(12)	1.58(16)	2	−0.26(3)	Unbound
74	W	7.864	0.815(2)	1.5(2)	2	−0.03(3)	Indeterminate
75	Re	7.8335	0.15(15)	1.41(14)	2	−0.29(7)	Unbound
76	Os	8.4382	1.1(2)	1.36(14)	2	0.15(9)	Bound
77	Ir	8.967	1.5638(50)	1.32(13)	2	0.40(3)	Bound
78	Pt	8.9588	2.128(2)	1.3(1)	1	1.14(3)	Bound
79	Au	9.2255	2.30863(3)	1.3(1)	1	1.25(3)	Bound
80	Hg	10.4375	−0.67(7)	1.32(13)	2	−0.70(3)	Unbound
81	Tl	6.1082	0.377(13)	1.44(14)	0	−0.24(3)	Unbound
82	Pb	7.4167	0.364(8)	1.45(15)	0	−0.27(3)	Unbound
83	Bi	7.2855	0.942362(13)	1.5(2)	0	−0.01(3)	Indeterminate

giving a predicted binding energy of 0.424 eV [20]. The very large truncation error suggests an accuracy of several tens of meV at best in the calculated energy. Binding energies for NaPs and KPs were calculated in this way with accuracies of probably a few tens of meV [18,19]. LiPs was treated as a six-particle system in extensive calculations [16] that are probably accurate in calculated energies to better than 1 meV.

In the QMC (more specifically, the DMC) method, one transforms the Schrödinger equation into a diffusion equation by the substitution $t \rightarrow it$. Diffusion equations can be solved by stochastic methods in $3n$-dimensional space, where n is the number of particles being treated explicitly; each point in this $3n$-dimensional space represents one possible arrangement of the real particles. The $3n$-dimensional particles are called walkers, and a great many of them, 1000 or more, are allowed to perform random walks under the influence of the quantum-mechanical potential of the system. After a large number of steps, the distribution of walkers approaches a state of dynamic equilibrium that approximates the quantum-mechanical wave function of the system, from which the eigenvalue of the original Schrödinger equation easily is extracted. Accuracy improves with the number of walkers, the number of their steps, and the small size of steps. Typically, 1000 walkers are used and are made to take 10 000 to 100 000 steps to produce acceptable precision, which currently is 20 meV.

Not surprisingly, some refinements are required, for solutions of conventional diffusion equations (e.g., distributions of temperature and concentrations of components) are necessarily positive while quantum-mechanical wave functions have parts that are positive or negative as well as imaginary or real. An artifice has been invented to deal with this distinctly nonclassical behavior: An approximate wave function $\tilde{\Psi}$ from outside the QMC is combined with the desired solution Ψ into a product $f = \tilde{\Psi}\Psi$, and a new diffusion equation is written that has f as its solution. At the nodes of $\tilde{\Psi}$, f is necessarily zero; elsewhere f is positive and real. The nodes of $\tilde{\Psi}$ are not only the familiar orbital nodes in elementary quantum theory, but also $(3n-3)$-dimensional nodes that arise from the exclusion principle. For good results, $\tilde{\Psi}$, called the trial function, must be accurate in regions of space near singularities of the potential. To achieve this, Jastrow factors [41] are attached to the trial function.

The method naturally is variational in nature, thus, preserving the comforting boundedness in calculated energies that quantum chemists rely upon. The QMC requires no integrations, no matrix inversions, no complications related to wave function completeness, and gives a good account of the correlation of light-particle motion. Accuracy and precision are limited only by computational resources and by discrepancies in the nodes of the trial function. Aside from calculations that ignore correlation, the QMC was the first *ab initio* method to be applied to bound systems containing positrons and more than five electrons [42,43]. Later, it was used in extensive calculations by Mella *et al.* [44].

The important thing to remember is that the technology exists for the measurement of positron- and Ps-binding energies to atoms with a precision of a few meV. This precision would empower laboratory measurements to challenge calculations for all but the very few simplest systems.

III. DATA ANALYSIS

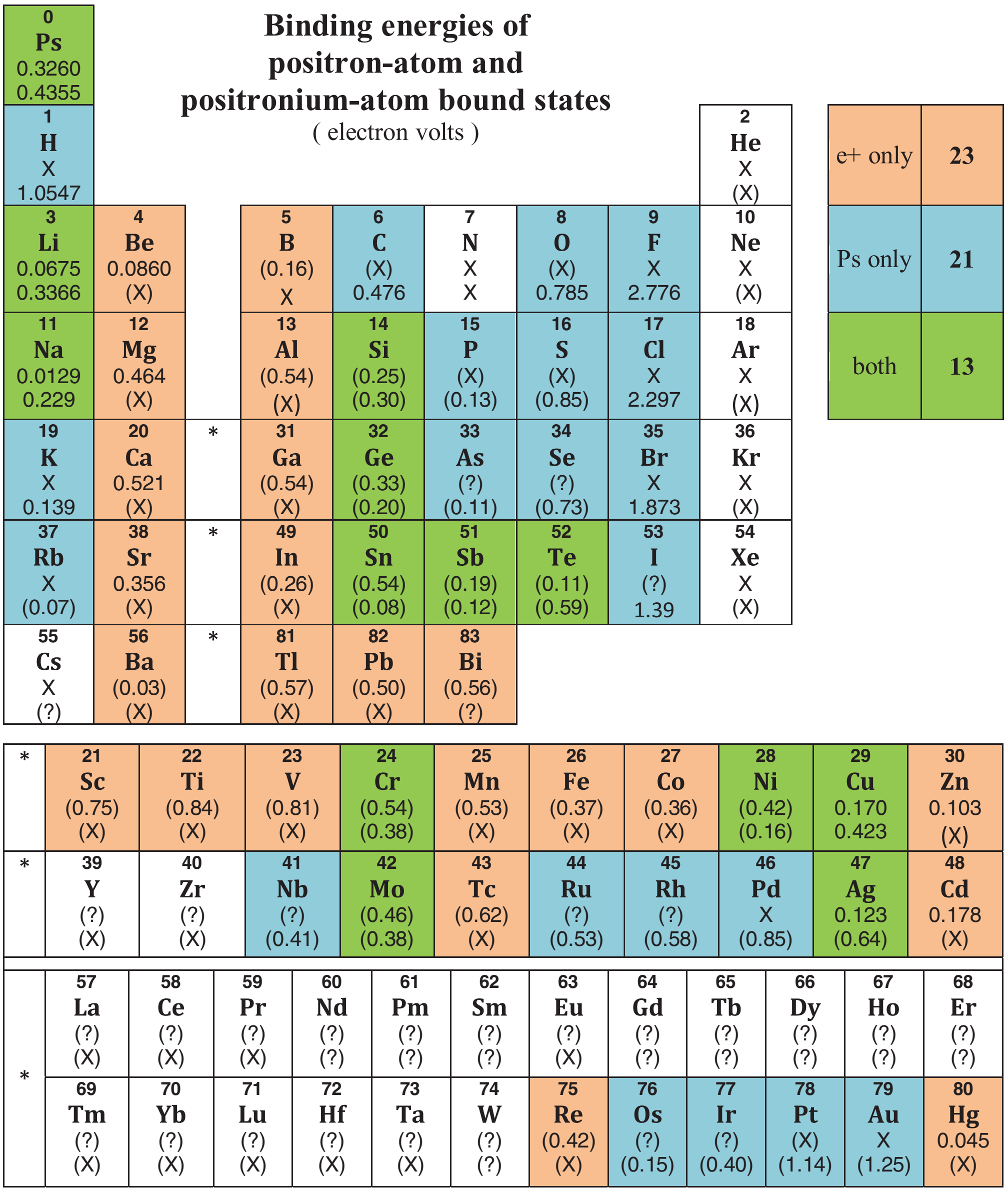
For Ps binding to atoms, only 14 atoms have been studied so far. As in our first paper [45], we present four graphs of binding energies vs ionization potentials, static electric dipole polarizabilities, electron affinities, and covalent radii. They are shown in Fig. 1. There are three contributing resonance schemes instead of just one as in positron binding to atoms. These three schemes are as follows:

(1) Scheme 1. $\{A,\mathrm{Ps}\} \leftrightarrow \{A^+,\mathrm{Ps}^-\}$—an electron moderates the A^+-Ps interaction.

(2) Scheme 2. $\{A^-,e^+\} \leftrightarrow \{A,\mathrm{Ps}\}$— an electron moderates the A-e^+ interaction.

(3) Scheme 3. $\{e^+A,e^-\} \leftrightarrow \{A,\mathrm{Ps}\}$—a positron moderates the A-e^- interaction.

If Scheme 1 was important, there should be a maximum in Ps-binding energy as a function of ionization potential at 0.326 eV (the binding energy of e^-Ps), but none of the ionization potentials was that small [as shown in Fig. 1(a)]. If Scheme 2 was important, there would be a maximum in Ps-binding energies vs electron affinity at 6.803 eV, but none of our positron-binding energies was that large [as shown in Fig. 1(c)]. If Scheme 3 was important, there would be a maximum in Ps-binding energy vs positron affinity at



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)

FIG. 3. (Color online) All available results on the binding of positron and Ps to atoms. The binding energies (in electron volts) 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. All the predictions in the present paper and our last paper are in parentheses. Binding energies for atoms with uncertainties larger than our predicted values are indicated with question marks.

6.803 eV, but none of our positron affinities was that large. Thus, a resonance stabilization model similar to that for e^+ binding [45] does not lend itself to Ps binding. However, we expect the Ps-binding energies, unlike the positron-binding energies, to be a smooth function of all parameters, permitting a good fit with a simple polynomial function. To find the function, we used the MATLAB program written for our last paper [45] to carry out the data analysis. We consider 30 parameters (Table II), from which

$$\binom{30}{2}+\binom{30}{3}+\binom{30}{4}+\binom{30}{5}+\binom{30}{6}=767746$$

distinct combinations of two to six members can be created. The best combination is shown in the following section.

IV. RESULTS

As shown in Table I, 12 atoms are known to bind with Ps. All these, 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 II. After numerous sets of fitting with different physical properties and various combinations, we find that a fitting of binding energies with $V_i E_a$, covalent radius $R_{\rm cov}$ (from Ref. [49]), and the number of valence s electrons (N_s) is the best compromise between good accuracy and a small number of parameters. The fitting equation for the binding energy E is

$$\begin{aligned} E =&\ 0.875928 + 0.052314 V_i E_{\rm a} \\ & - 0.207273 R_{\rm cov} - 0.466741 N_s. \end{aligned} \tag{4}$$

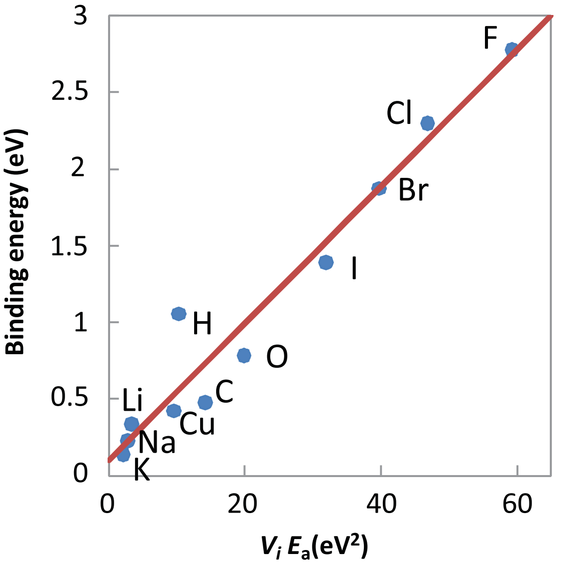


FIG. 4. (Color online) Binding energy vs $V_i E_a$.

The fitting results are shown in Fig. 2. The units of V_i E_a and R_{cov} are eV^2 and angstroms, 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 mostly from electron affinities and covalent radii. The uncertainties of the predicted Ps-binding energies are calculated from

$$\Delta E = \sqrt{(0.052314 V_i \Delta E_a)^2 + (0.207273 \Delta R_{cov})^2}. \qquad (5)$$

These are verified by calculating E from Eq. (4), whereas, E_a and R_{cov} are varied to the maximum of their uncertainties. The detailed data and results are shown in Table III.

The fitting equation is tested on the nonbinding atoms B and N and is found to predict negative-binding energies as shown in Table IV. This is a significant confirmation of our predictor function [Eq. (4)]. The bond length or covalent radius of Ps is from Ref. [50]. The Ps affinity of Ps itself is given poorly by our predictor, but this is not surprising since Ps is an atypical atom. B and N are known not to bind, and the predictor correctly gives negative values. The model appears to provide a reliable predictor.

Using the best-fit equation [Eq. (4)], the binding energies of 47 other atoms not previously studied are predicted. The atoms that cannot form a stable state with an electron have negative electron affinities from Ref. [51]. In the prediction, 23 atoms will bind with a Ps, 33 will not, and 11 are indeterminate because their electron affinities are unknown or they have uncertainties that are larger than the predicted binding energies. These results are shown in Table V.

Together with the predictions in our last paper [45], all the current data are shown in Fig. 3. We predict that 24 new atoms will bind with a positron [45], and 23 new atoms will bind with Ps (present paper).

V. DISCUSSION

It is important to understand that Eq. (4) does not have a physical basis—it is merely curve fitting. Other sets of fitting parameters give results that are only slightly inferior to these, and in that sense, there is some arbitrariness in our selection. However, some of these other sets have more parameters than our set.

It is curious that the only energies in the chosen set, the ionization potential and the electron affinity, only appear in a product. Relativistic terms are important in calculated Ps-binding energies for the heavier atoms [23], and these effects are included in experimental ionization potentials and electron affinities also, of course. Our approach, therefore, should give good results for both light and heavy atoms, and it is probably more reliable than other attempts to predict positron- and Ps-binding energies [52] including quantum calculations made with dubious approximations [27].

As shown in Fig. 4, the cross term of V_i and E_a is a very important factor. It can be regarded simply 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 V_i, the more difficult it is to remove an electron from an 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 E_a, 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 Ps. In short, in Ps 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 Ps as shown in Table VI. These molecules are not so adequate to prove V_i E_a's influence because they can be regarded as e^+M^- instead of PsM ($M =$ molecule). The V_i's and E_a's are all about the electron. It may indicate that the electron from Ps is closer to the bound atom than is the positron.

TABLE VI. The energies of Ps binding to molecules. The sources of E_a's and V_i's are from Refs. [53,54], respectively.

	E_a (eV)	V_i (eV)	$V_i E_a$ (eV^2)	E (eV)	References
CH	1.238(8)	10.64(1)	13.17(9)	0.44(2)	[55]
OH	1.8276487(11)	13.0170(2)	23.79(0)	0.28(3)	[55]
CN	3.862(4)	13.5984	52.51(5)	0.83(80)	[56]
NH_2	0.771(5)	11.14(2)	8.59(6)	0.15(2)	[55]
N_3	2.70(12)			0.14(10)	[56]
CH_3	0.08(3)	9.843(2)	0.79(30)	0.2(20)	[57]
NO_3	3.937(14)			0.3(3)	[58]

The covalent radius and N_s can both be 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 a subshell [6]. This idea finds support from the alkali metals and the halogens, two families that are otherwise starkly different that both strongly bind to Ps. The Ps 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]$5s$), 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 three or five electrons in the p subshell also will bind with Ps. 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 Ps. None of the noble gases are predicted to bind with Ps. These results further substantiate the reliability and value of our model and prediction.

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

VI. SUMMARY

The relationship between PsA-binding energies and atomic physical properties has been studied. Good results [Eq. (4)] are obtained using the parameters $V_i E_a$, the covalent radius R_{cov}, and the number of valence s electrons N_s. Then, using the best-fit equation, other stable atoms are calculated and are predicted. Twenty-three other atoms are predicted to bind with Ps, and the predicted binding energies are shown in Table V.

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

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