Relativistic linearized coupled-cluster single-double calculations of positron-atom bound states

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Relativistic linearized coupled-cluster single-double approximation with third-order corrections is used to calculate positron-atom bound states. The method is tested on closed-shell atoms such as Be, Mg, Ca, Zn, Cd, and Hg, where a number of accurate calculations are available. It is then used to calculate positron binding energies for a range of open-shell transition metal atoms from Sc to Cu, from Y to Pd, and from Lu to Pt. These systems possess Feshbach resonances, which can be used to search for positron-atom binding experimentally through resonant annihilation or scattering.

I. INTRODUCTION

In this paper we apply the relativistic linearized coupled-cluster single-double (SD) approximation to calculate positron binding energies for a number of atoms, including open-shell transition metal atoms. Positron-atom bound states are characterized by strong electron-positron correlation effects. These effects for the positron-bound states are even stronger than for their electron counterparts, i.e., the atomic negative ions. This is due to the electron-positron *attraction* and, in particular, the large role of virtual positronium (Ps) formation [1–3]. This makes calculations of positron-atom bound states a challenging theoretical problem. Using the SD method allows us to include all of the main correlation effects for atoms with several electrons in the open valence shell.

The existence of positron-atom bound states was predicted by many-body theory calculations [4] and verified variationally [5,6] more than a decade ago. Since then, positron binding energies have been calculated for many ground-state and excited atoms: He $2\,^3S$, Li, Be, Be $2\,^3P$, Na, Mg, Ca, Cu, Zn, Sr, Ag, Cd, and Hg (see Refs. [7–12] and references therein). There are strong indications that many more atoms, possibly over a quarter of the whole Periodic Table, should be able to bind positrons [4,9,13,14]. Such conclusions are based on the analysis of the atomic ionization potentials and dipole polarizabilities, which are relevant for positron binding, and on the calculations of positron binding to a "model alkali atom" [15] (see also review on positron compounds [16]). In spite of this wealth of predictions, experimental verification of positron binding to neutral atoms is still lacking.

Recently, we proposed [13] that positron binding to many open-shell atoms could be studied experimentally by measuring resonant positron-atom annihilation. Such resonant annihilation is similar to the resonant annihilation observed for positrons in many polyatomic molecules [17]. In this process the incident positron is captured into a bound state with the target, with the excess energy being transferred (in the case of molecules) to vibrations. Since the vibrational motion of the molecules is quantized, these transitions can only take place at specific positron energies, which means they have a *resonant* character. These energies correspond to vibrational Feshbach resonances of the positron-molecule complex [17–19]. The majority of the resonances observed are associated with individual vibrational modes of the molecule.

The negative energy of the positron-bound state ϵ_0 is then related to the downshift of the resonance energy,

$$\varepsilon_\nu = \omega_\nu + \epsilon_0, \tag{1}$$

with respect to the energy ω_ν of the vibrational excitation [20,21]. Hence, by observing the resonances, the positron binding energy $\varepsilon_b = |\epsilon_0|$ can be found. In this way, binding energies for over 60 polyatomic species have been determined [22–25] by measuring positron annihilation using a high-resolution, tunable, trap-based positron beam [26]. In our previous paper [13] we suggested that one can search for a similar effect in atoms. In this case the resonances will be associated with low-lying electronic excitations. These can be found in open-shell atoms, where they often have the same configuration as the ground state. If the positron can bind to such an atom in the ground state, then it can likely bind to this atom in an excited state as well. One can then consider the following process:

$$A + e^+ \rightarrow A^*e^+ \rightarrow A^+ + 2\gamma. \tag{2}$$
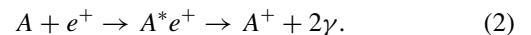
Here the positron first loses energy by exciting the atom and becoming trapped in the bound state with the excited atom. It then annihilates with one of the electrons, and the resulting γ quanta can be detected. The first step of the process (2) is obviously reversible. Hence, to estimate the efficiency of resonant annihilation one needs to evaluate the rates of both positron annihilation and autodetachment [13].

To prove the feasibility of such a process one also needs to estimate the positron binding energies to open-shell atoms in their ground and excited states. At the moment, there is no simple, universal theoretical method to do this. All previous calculations deal with a positron interacting with either a closed-shell atom or an atom with a single electron above a closed-shell core. Positron interaction with a many-electron system is a challenging problem due to strong electron-positron attraction. This attraction leads to virtual Ps formation, which is difficult to describe using a single-center basis with the origin on the atomic nucleus. In particular, to achieve convergence one needs to include basis states with large values of the orbital angular momentum l. The required maximum value should satisfy $l_{max} > d/R_{Ps}$, where R_{Ps} is the radius of Ps and d is the distance between Ps and the atomic nucleus. This can easily lead to $l_{max} \gtrsim 10$. Large values of l_{max} required to describe the total wave function

at small electron-positron separations lead to large sizes of the electron and positron single-particle bases. While there are many methods for accurate treatment of various many-electron systems, their application to the positron-atom problem is not straightforward due to much larger basis sizes needed to achieve similar accuracy. Development of methods for accurate calculations of positron binding to many-electron open-shell atoms is an important direction for future studies, but one that goes beyond the scope of the present work. Our aim is to survey a large number of open-shell atoms. We want to demonstrate that many of them can bind positrons not only in the ground state but also in excited states, and to provide rough estimates of the corresponding binding energies.

In Ref. [13] we used a simple approach in which the second-order correlation potential of the positron-atom interaction was scaled up to account for the effect of higher-order electron-positron correlations (i.e., virtual Ps formation). It was assumed that the scaling factor is the same for all atoms, and its value was chosen by fitting the results for those atoms where accurate positron binding calculations are available. Open shells were treated by using fractional occupation numbers in the standard expressions for a closed-shell system. It is well known that the fractional occupation numbers approach works very well on the Hartree-Fock level. For example, such calculations were used as a starting point for the configuration interaction (CI) calculations for many-valence-electron atoms [27–29]. It looks even more reasonable in the positron-atom problem, because the positron is not affected by the Pauli principle. The positron-atom interaction has, thus, no direct sensitivity to the valence shell being open or closed (unlike the electron-atom interaction in the negative ion problem).

In the present paper we use a more sophisticated fully *ab initio* approach in which the strong electron-positron correlations are included explicitly through the use of an all-order technique.

Accurate treatment of the strong electron-positron correlations is the main challenge in the calculation of positron-atom interaction. It calls for the use of nonperturbative approaches. For systems with few active electrons accurate results were obtained using the stochastic variation method [5,9]. The most obvious choice for a generic many-electron atom is the CI technique. It was successfully employed in a number of previous calculations for atoms with one or two electrons in the valence *s* shell (see, e.g., Refs. [7,8,30,31]). However, it becomes too complicated for more than two valence electrons and, in particular, for atoms with open *d* shells, which we want to consider in the present work. Another suitable all-order technique is the coupled-cluster approach. In this approach the interparticle interaction is included to all orders via an iterative procedure. The corresponding subset of terms includes the so-called *ladder* diagrams [32]. This class of diagrams is very important in the positron-atom problem, as it describes the effect of virtual Ps formation. Summation of the electron-positron ladder-diagram series was performed earlier by solving a linear matrix equation for the electron-positron vertex function for hydrogen [33], noble gas atoms [34], and halogen negative ions [35].

The coupled-cluster approach in its linearized single-double approximation has been widely used for atoms and ions with one external electron above closed shells (see, e.g.,

Refs. [36–40]). It is relatively easy to modify the corresponding equations for the case of a positron interacting with a closed-shell atom. We will do this in the next section.

To test the method we first apply it to positron binding to closed-shell atoms: Be, Mg, Ca, Zn, Cd, and Hg, for which a number of accurate calculations are available. We then apply the same approach to open-shell atoms, treating them in a simplified manner similar to that of Ref. [13]. Fractional occupation numbers are used to rescale the terms containing contributions from the open shells. The main advance of the present method compared with Ref. [13] is the all-order treatment of the positron-electron interaction in the correlation potential. No further fitting is used or needed. Remarkably, the results of the all-order calculations turn out to be close to the estimates obtained in our previous work. These calculations lend further support to the proposal to search for positron-bound states with open-shell atoms through resonant annihilation or scattering.

II. THEORY

A. Electron and positron basis sets

The use of the coupled-cluster technique requires construction of a single-particle basis. For a positron interacting with an atom one must have two separate basis sets: one for electron states and one for positron states. We use a standard *B*-spline technique in both cases [41]. The electron basis states are constructed by diagonalizing the matrix of the relativistic Hartree-Fock (RHF) Hamiltonian in the *B*-spline basis. The positron basis states are constructed using the same set of *B* splines and the RHF Hamiltonian in which the sign of the direct potential is changed and the exchange potential is omitted. Below we will use the following notation for the basis states: Indices a, b, c refer to electron states in the core, indices m, n, k, l refer to electron states above the core, indices v, r, w refer to positron states, and indices i, j refer to any states. Numerical results reported in Secs. III and IV were obtained using the basis sets built from 30 *B* splines of order 7 spanning the radial coordinate from the origin to $R = 30$ a.u., with angular momenta between 0 and 10.

B. Single-double equations

The wave function of an atom with a positron in state v can be written in the SD approximation as an expansion

$$|\Psi_v\rangle = \left[1 + \sum_{na} \rho_{na} a_n^\dagger a_a + \frac{1}{2} \sum_{mnab} \rho_{mnab} a_m^\dagger a_n^\dagger a_a a_b \right.$$
$$\left. + \sum_{r \neq v} p_{rv} a_r^\dagger a_v + \sum_{rna} p_{rnva} a_r^\dagger a_v a_n^\dagger a_a \right] |\Phi_v\rangle, \quad (3)$$

where $|\Phi_v\rangle$ is the zeroth-order wave function of the frozen-core atom in the relativistic Hartree-Fock approximation with the positron in state v. It can be written as

$$|\Phi_v\rangle = a_v^\dagger |0_C\rangle, \quad (4)$$

where $|0_C\rangle$ is the RHF wave function of the atomic core.

The expansion coefficients ρ_{na} and ρ_{mnab} in Eq. (3) represent single- and double-electron excitations from the

core. The coefficients p_{rv} represent excitations of the positron, and the coefficients p_{rnwa} represent simultaneous excitations of the positron and one of the electrons.

The SD equations for the core excitation coefficients do not depend on the external particle and are the same in the electron and positron cases. They are written as a set of equations for the single-excitation coefficients ρ_{ma} and double-excitation coefficients ρ_{mnab} (see, e.g., Ref. [36]):

$$(\epsilon_a - \epsilon_m)\rho_{ma} = \sum_{bn} \tilde{g}_{mban}\rho_{nb} + \sum_{bnk} g_{mbnk}\tilde{\rho}_{nkab}$$
$$- \sum_{bcn} g_{bcan}\tilde{\rho}_{mnbc} \qquad (5)$$

and

$$(\epsilon_a + \epsilon_b - \epsilon_m - \epsilon_n)\rho_{mnab}$$
$$= g_{mnab} + \sum_{cd} g_{cdab}\rho_{mncd} + \sum_{kl} g_{mnkl}\rho_{klab}$$
$$+ \sum_{k} g_{mnkb}\rho_{ka} - \sum_{c} g_{cnab}\rho_{mc} + \sum_{kc} \tilde{g}_{cnkb}\tilde{\rho}_{mkac}$$
$$+ \sum_{k} g_{nmka}\rho_{kb} - \sum_{c} g_{cmba}\rho_{nc} + \sum_{kc} \tilde{g}_{cmka}\tilde{\rho}_{nkbc} . \qquad (6)$$

In these equations $\tilde{g}_{mnkl} \equiv g_{mnkl} - g_{mnlk}$ and $\tilde{\rho}_{mnkl} \equiv \rho_{mnkl} - \rho_{mnlk}$, and the coefficients g are the Coulomb integrals,

$$g_{mnkl} = \iint \psi_m^\dagger(\mathbf{r}_1)\psi_n^\dagger(\mathbf{r}_2)\frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}\psi_k(\mathbf{r}_1)\psi_l(\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2, \qquad (7)$$

involving electron states ψ_k, ψ_l, etc.

The core SD equations (5) and (6) are solved iteratively until convergence is achieved. This is controlled by the correlation correction to the energy of the core:

$$\delta E_C = \frac{1}{2}\sum_{mnab} g_{abmn}\tilde{\rho}_{nmba}. \qquad (8)$$

After solving the SD equations for the core one can start iterating the SD equations for the external particle. The SD equations for the positron can be obtained by substituting the state $|\Psi_v\rangle$ from Eq. (3) into the relativistic many-body Schrödinger equation:

$$H|\Psi_v\rangle = \epsilon_0|\Psi_v\rangle. \qquad (9)$$

Projecting the Schrödinger equation onto $a_w^\dagger|0_C\rangle$ gives the equation for p_{wv},

$$(\epsilon_0 - \epsilon_w)p_{wv} = -\sum_{bm} q_{wbvm}\rho_{mb} + \sum_{bmr} q_{wbrm}p_{rmvb}, \qquad (10)$$

Projecting Eq. (9) onto $a_w^\dagger a_n^\dagger a_a|0_C\rangle$ gives the equation for the double-excitation coefficient p_{wnva},

$$(\epsilon_0 + \epsilon_a - \epsilon_w - \epsilon_n)p_{wnva}$$
$$= q_{wnva} - \sum_{rm} q_{wnrm}p_{rmva} + \sum_{m} q_{wnvm}\rho_{ma}$$
$$- \sum_{b} q_{wavb}\rho_{nb} + \sum_{mb} p_{wmvb}\tilde{g}_{mabn}$$
$$+ \sum_{rb} q_{warb}p_{rbvn} + \sum_{mb} q_{wmvb}\tilde{\rho}_{mabn} . \qquad (11)$$
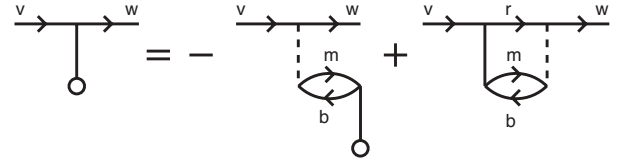

FIG. 1. Diagrammatic form of the SD equation (10) for the positron single-excitation coefficient. Lines with arrows to the right are positron and excited electron states, and those with arrows to the left are core electron states ("holes"). The vertical solid line is the double-excitation coefficient, and the solid line terminated by a circle is the single-excitation coefficient. Dashed lines are the Coulomb interactions.

Here q_{wnva} is the Coulomb integral (7) involving positron states.

Equations (10) and (11) are presented graphically in Figs. 1 and 2. When solving these equations, the correction to the energy of the positron state v,

$$\delta\epsilon_v = -\sum_{mb} q_{vbvm}\rho_{mb} + \sum_{bmr} q_{vbrm}p_{rmvb}, \qquad (12)$$

is used to control convergence.

C. Positron-bound state

Apart from the absence of the exchange terms involving the positron, there is another important difference between the SD equation (11) for the positron and those for external electrons in atoms or ions. In the latter cases the SD equation for the double-excitation coefficient also contains a term $\sum_r q_{wnra}p_{rv}$. The corresponding diagram is "reducible," i.e., it contains two parts connected by the single line of the excited valence particle. Including it ensures that the correction to the energy of the valence state v is determined in all orders.

When using the SD method for the positron, its eigenstate and energy eigenvalue ϵ_0 are obtained by matrix diagonalization (see below). The need for this procedure arises because of the absence of a good zeroth-order approximation for the wave function of the bound positron. In the RHF approximation
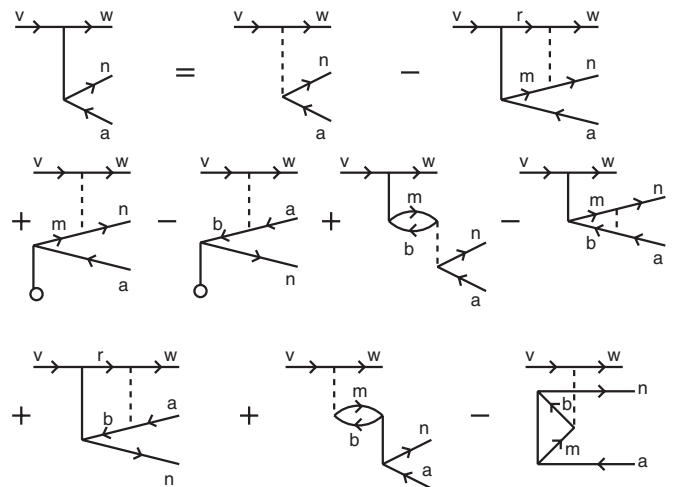

FIG. 2. Diagrammatic form of the SD equation (11) for the positron double-excitation coefficient.

the positron-atom interaction is repulsive, and all of the single-particle positron basis states lie in the continuum. On the other hand, the *B*-spline basis is effectively complete for the positron-bound state to be obtained by matrix diagonalization. To do this, the SD equations (10) and (11) should be iterated for every positron basis state used to construct an effective single-particle Hamiltonian matrix. A similar situation occurs for negative ions [42,43] and when combining the SD method with the CI technique to obtain many-electron wave functions [44]. In all of these cases the term $\sum_r q_{wnra} p_{rv}$ should be removed from the SD equations, as it is taken into account via matrix diagonalization.

The wave function of the bound positron is found as an expansion over the positron basis states:

$$\psi_p = \sum_v c_v \psi_v. \tag{13}$$

Equations (10) and (11) are iterated for every basis state v in the expansion (13). The energy parameter ϵ_0 in these equations is the (unknown) energy of the positron state (13). The energy ϵ_0 and the expansion coefficients c_v are found by solving the eigenvalue problem

$$\hat{\Sigma} X = \epsilon_0 X, \tag{14}$$

where X is the vector of expansion coefficients c_v, ϵ_0 is the lowest eigenvalue (which must be negative), and the elements of the effective Hamiltonian matrix $\hat{\Sigma}$ are given by

$$\sigma_{vw} = \epsilon_v \delta_{vw} - \sum_{mb} q_{wbvm} \rho_{mb} + \sum_{bmr} q_{wbrm} p_{rmvb}. \tag{15}$$

The first term on the right-hand side of Eq. (15) represents the positron energies in the static RHF approximation. The second and third terms describe the effect of electron-positron correlations. These two terms are the positron-atom *self-energy*, which is given by right-hand side of the diagrammatic equation in Fig. 1.

Since the SD equations (10) and (11) depend on the energy ϵ_0 which is found later from Eq. (14), we start with an initial guess for ϵ_0. The calculations are then performed iteratively, solving the SD equations (10) and (11) and diagonalizing the matrix (15) several times until ϵ_0 has converged. In practice this takes about five global iterations.

D. Third-order corrections

The SD equations account for the second-order contribution and selected classes of higher-order correlation diagrams in all orders. In particular, the electron-positron ladder diagram series, which describes virtual Ps formation, is included in full. However, beginning with the third order, the SD approximation misses certain terms. It is well known that the missing third-order terms can give sizable corrections to the energy in atomic systems (see, e.g., Ref. [38]). Including these terms can lead to significant improvements in the accuracy of the results, and we include these contributions for the positron-bound states with atoms.

The third-order terms not included in the SD approximation are listed in Ref. [38] for the case of an electron interacting with a closed-shell ion. Similar terms for the positron case can be obtained by changing the sign of Coulomb integrals
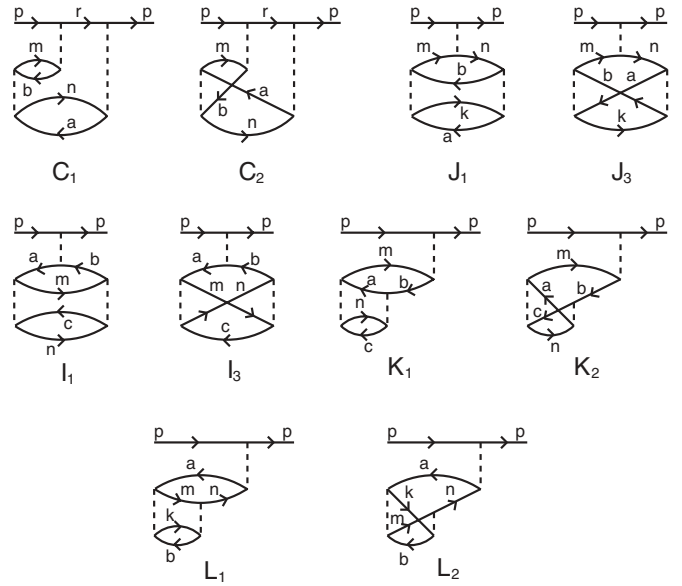

FIG. 3. Third-order positron-atom interaction diagrams not included into the SD equations. Notation of Ref. [45] is used.

involving the positron and removing exchange. All resulting third-order diagrams are shown in Fig. 3. The corresponding perturbation theory corrections to the energy of the positron state p are

$$E_C^{(3)} = \sum_{abmnr} \frac{q_{pmrb} q_{rnpa} \tilde{g}_{bamn}}{(\epsilon_{0a} - \epsilon_{rn})(\epsilon_{ab} - \epsilon_{mn})}, \tag{16}$$

$$E_I^{(3)} = \sum_{abcmn} \frac{q_{papb} g_{acmn} \tilde{g}_{mnbc}}{(\epsilon_{bc} - \epsilon_{mn})(\epsilon_{ab} - \epsilon_{mn})}, \tag{17}$$

$$E_J^{(3)} = -\sum_{abmnk} \frac{q_{pmpn} g_{bamk} \tilde{g}_{bank}}{(\epsilon_{ab} - \epsilon_{mk})(\epsilon_{ab} - \epsilon_{nk})}, \tag{18}$$

$$E_K^{(3)} = \sum_{abcmn} \frac{q_{pmpb} g_{acmn} \tilde{g}_{acnb}}{(\epsilon_{ac} - \epsilon_{nm})(\epsilon_b - \epsilon_m)}, \tag{19}$$

$$E_L^{(3)} = -\sum_{abmnk} \frac{q_{papn} g_{abmk} \tilde{g}_{mbnk}}{(\epsilon_{ab} - \epsilon_{mk})(\epsilon_a - \epsilon_n)}. \tag{20}$$

Here $\epsilon_{ij} = \epsilon_i + \epsilon_j$, ϵ_0 is the positron energy found by solving the eigenvalue problem (14), and the positron state p is given by Eq. (13).

III. CLOSED-SHELL ATOMS

For a positron interacting with a closed-shell atom, all sums over the projections of angular momenta of electron and positron states in the SD equations (5), (6), (10), and (11) and third-order corrections (16)–(20) are done analytically, together with the angular reduction of the Coulomb integrals. Such systems are easiest from the computational point of view. There are also a number of other calculations of positron binding of different levels of sophistication for several such atoms. We use these systems to test our approach. The results of calculations of positron *s*-wave bound states with Be, Mg, Ca, Zn, Cd, and Hg are shown in Table I. These six atoms share the following features. First, they have closed electronic shells. Second, the dipole polarizabilities α_d of these atoms are sufficiently large to provide strong attraction and ensure

TABLE I. Positron binding energies (BE, in meV) for closed-shell atoms obtained using the SD equations (SD) with third-order correction (E3), and by other methods, with best available predictions in bold.

Atom (Z)		I (eV)	α_d[a] (a.u.)	BE, this work			BE from other calculations
				SD	E3	Total	
4	Be	9.32	38	157	26	184	45.90 [46], **85.63** [47], **83.8** [48], 3.0 [50], 33 [51]
12	Mg	7.64	72	475	37	512	870 [4], 425 [47], **439** [30], 985 [52], 15 [50], 457 [51], 125 [53]
20	Ca	6.11	154	1114	50	1164	**1139**[b] [30]
30	Zn	9.39	42	143	40	183	230 [4], 39 [54], **103** [31], 0.01 [55], 53 [53]
48	Cd	8.99	49	204	70	274	350 [4], **166** [31], 1.5 [55]
80	Hg	10.43	38	59	53	112	**45** [4]

[a]Static dipole polarizabilities from Ref. [56].
[b]Positron-atom BE obtained from the calculated BE of 449 meV with respect to the $Ca^{++}Ps$ threshold.

positron binding. Finally, the ionization potentials I of these atoms (with the exception of calcium) are greater than the Ps binding energy (6.8 eV). Hence, the Ps-formation channel is closed at low positron energies, and the positron-atom bound states are stable against dissociation into positive ion + Ps.

The SD column of Table I shows the binding energies (BE) $|\epsilon_0|$ (in meV) found by solving the eigenvalue problem (14). The E3 column gives the third-order corrections (16)–(20). The next column is the total obtained by adding the third-order correction to the BE from the SD calculations. We also examined the effect of finite box size on the binding energy [7] and found it negligible. The rest of the table shows the results of earlier calculations. The most accurate among them are probably the calculations by the Mitroy group [30,31,46–48]. Our results are generally slightly larger, but within 100 meV of the best earlier predictions. Adding third-order corrections increases the BE in all the systems, and in most cases increases the difference between the present and best earlier results.

Note the scatter of the results between different groups and even between different calculations by the same group. This reflects the fact that the positron-atom binding energy is very sensitive to the correlations. In the static field RHF approximation the positron is repelled from the neutral atom. The binding is solely due to correlations. Most of the correlation energy is required to get the system across the threshold for binding, while the final binding energy is a result of a relatively small "surplus" of the correlation energy. For this reason, absolute difference in binding energies is the better indication of the accuracy of the calculations. This difference between ours and best earlier results is roughly the same for all atoms (~100 meV). We take this value as an estimate of the accuracy of our method.

IV. OPEN-SHELL ATOMS

In this section we consider open-shell atoms, which were suggested in our previous work [13] as good candidates for experimental detection of positron-atom bound states via resonant annihilation or scattering. We treat open-shell systems in an approximate way, by introducing fractional occupation numbers. For example, the ground-state electron configuration of neutral iron is $3d^6 4s^2$ above the Ar-like core. We treat it as a closed-shell system but reduce the contribution

of the $3d$ subshell to the correlation potential by the factor 0.6. Both members of the fine-structure multiplet, $3d_{3/2}$ and $3d_{5/2}$, are treated identically, and the corresponding terms are rescaled by the same factor 0.6.

Note, however, that the SD equations (11) are left unchanged. There is strong cancellation between different terms in these equations, and rescaling of the core contribution is an insufficiently accurate procedure. It breaks the delicate balance between different terms, leading to unreliable results. The rescaling is done when constructing the correlation potential matrix σ_{vw}, by reducing the terms corresponding to the open subshells when summing over the hole states b in Eq. (15). The fact that this procedure works well is supported by good agreement between the present calculations of positron binding to copper with our previous calculations (see Table II). In the table we also compare the positron binding energy obtained for Li with the accurate variational calculation of Mitroy [49]. The difference is larger than for the closed-shell systems in Table I and for Cu. This is mostly due to poor convergence with respect to l_{max}. Since the ionization potential of Li is smaller than the Ps binding energy, this system is best described as Ps bound to the Li^+ ion. Its accurate description requires even higher values of the maximum angular momentum l_{max}. The results shown in Table II are obtained using $l_{max} = 10$. We have checked that for Li the binding energy obtained for $l_{max} = 8$ is significantly smaller (670 meV), which means that convergence has not been achieved for this system. Recall also that for atoms with ionization potentials smaller than 6.8 eV, the Ps formation channel is open at all incident positron energies. Even if such systems could form electronic Feshbach resonances with the positron, these resonances will likely be too broad to be observed.

The present approach does not distinguish between different states of the same configuration. This means that if the positron is found to be bound to an atom in a given electronic configuration, it is predicted to be bound to all states of this configuration. This should be expected at least for the states where the excitation energy is smaller than the binding energy. However, this may still be true for higher-lying states. The ability of an atom in an excited state to bind the positron is what is needed for the resonant process proposed in Ref. [13]. As it was argued in Ref. [13] and as we will see below, there are many such atoms.

TABLE II. Positron binding energies (BE, in eV) for open-shell atoms obtained using the SD equations (SD) with third-order correction (E3). In this table I is the ionization energy from the lowest state of a given configuration. The last column shows semiempirical values from Ref. [14].

Atom (Z)		Valence configuration	I (eV)	α_d[a] (a.u.)	BE, this work			BE, other predictions	
					SD	E3	Total	Ref. [13]	Ref. [14]
3	Li	$1s^2 2s$	5.39	164	0.800	0.044	0.845	1.341[b]	
21	Sc	$3d4s^2$	6.56	120	0.908	0.129	1.037		0.75(2)
		$3d^2 4s$	5.13		0.849	0.109	0.958		
22	Ti	$3d^2 4s^2$	6.83	98.5	0.785	0.110	0.896		0.84(3)
		$3d^3 4s$	6.02		0.727	0.097	0.825		
23	V	$3d^3 4s^2$	6.74	83.7	0.678	0.097	0.775		0.81(3)
		$3d^4 4s$	6.48		0.602	0.086	0.689		
24	Cr	$3d^5 4s$	6.76	78.3	0.488	0.077	0.565		0.54(8)
		$3d^4 4s^2$	5.80		0.590	0.086	0.676		
25	Mn	$3d^5 4s^2$	7.43	63	0.496	0.077	0.574		0.53(3)
		$3d^6 4s$	5.32		0.382	0.068	0.450		
26	Fe	$3d^6 4s^2$	7.90	56.7	0.429	0.069	0.498	0.28	0.37(3)
		$3d^7 4s$	7.04		0.315	0.061	0.376	0.09	
27	Co	$3d^7 4s^2$	7.88	50.7	0.360	0.061	0.422	0.26	0.36(3)
		$3d^8 4s$	7.45		0.243	0.053	0.297	0.08	
28	Ni	$3d^8 4s^2$	7.64	45.9	0.295	0.055	0.350	0.24	0.42(3)
		$3d^9 4s$	7.61		0.173	0.046	0.220	0.07	
29	Cu	$3d^{10} 4s$	7.72	41	0.125	0.040	0.166	0.17(2)[c]	0.152(2)[d]
39	Y	$4d5s^2$	6.22	153	0.845	0.256	1.102		0.6(19)
		$4d^2 5s$	4.86		0.683	0.258	0.942		
40	Zr	$4d^2 5s^2$	6.63	121	0.729	0.209	0.939		0.8(11)
		$4d^3 5s$	6.12		0.623	0.208	0.831		
41	Nb	$4d^4 5s$	6.76	106	0.527	0.172	0.699		0.6(14)
		$4d^3 5s^2$	6.62		0.658	0.178	0.836		
42	Mo	$4d^5 5s$	7.09	86.4	0.442	0.145	0.587		0.45(4)
		$4d^4 5s^2$	5.73		0.583	0.155	0.739		
43	Tc	$4d^5 5s^2$	7.28	76.9	0.461	0.133	0.594	0.46	0.62(4)
		$4d^6 5s$	6.96		0.355	0.124	0.479	0.23	
44	Ru	$4d^7 5s$	7.36	65	0.310	0.109	0.419	0.21	0.30(95)
		$4d^6 5s^2$	6.43		0.461	0.121	0.583		
45	Rh	$4d^8 5s$	7.46	58	0.260	0.095	0.355	0.20	0.24(86)
46	Pd	$4d^{10}$	8.34	32	<0	−	<0		<0
		$4d^9 5s$	7.52		0.205	0.083	0.288		
		$4d^8 5s^2$	5.23		0.361	0.097	0.459		
71	Lu	$5d6s^2$	5.43	148	0.188	0.221	0.410		0.2(11)
72	Hf	$5d^2 6s^2$	6.83	109	0.305	0.198	0.503		0.8(10)
		$5d^3 6s$	5.08		0.349	0.190	0.539		
73	Ta	$5d^3 6s^2$	7.55	88.4	0.274	0.166	0.441	0.45	0.6(8)
		$5d^4 6s$	6.34		0.126	0.147	0.273		
74	W	$5d^4 6s^2$	7.86	74.9	0.235	0.141	0.377	0.46	0.4(7)
		$5d^5 6s$	7.50		0.083	0.118	0.201	0.30	
75	Re	$5d^5 6s^2$	7.83	65	0.202	0.121	0.324		0.42(12)
		$5d^6 6s$	6.38		0.051	0.096	0.147		
76	Os	$5d^6 6s^2$	8.44	57	0.167	0.105	0.273	0.47	0.3(5)
		$5d^7 6s$	7.80		0.025	0.079	0.105	0.29	
77	Ir	$5d^7 6s^2$	8.97	51	0.137	0.091	0.229	0.46	0.2(4)
		$5d^8 6s$	8.62		0.005	0.067	0.072	0.28	
78	Pt	$5d^9 6s$	8.96	44	<0	−	<0	0.27	<0
		$5d^8 6s^2$	8.86		0.111	0.080	0.191	0.46	
		$5d^{10}$	8.20		0.020	0.023	0.044	0.23	

[a]Ground-state atomic static dipole polarizabilities from Ref. [56].
[b]Stochastic variation method, Ref. [49].
[c]Configuration-interaction with many-body theory, Ref. [7].
[d]Stochastic variation method, Ref. [9].

Table II shows the results of our calculations of positron binding energies for a number of atoms with an open d shell. These values are compared with the binding energies calculated in Ref. [13] and with semiempirical estimates of Ref. [14]. Within the accuracy of the current approach all results appear to be in good accord with each other. There is a correlation between the occupation of the d shell and the binding energies. In most cases the closer the occupation is to 100% the smaller is the binding energy, and the smaller are the differences between the values obtained using different approaches. In the end, the results of the present work confirm the claim of Ref. [13] that many open-shell atoms do bind the positron not only in the ground state but also in excited states. Note that according to our calculations, positrons do not bind to either Pd or Pt in their ground states. However, both atoms bind in excited states.

The final energies of positron-bound states and resonances are presented in Table III. The resonant energy is the energy of the incident positron ε for which capture into a bound state with an excited atom is possible. The resonant and binding

TABLE III. Final binding and resonant energies (ε_b and ε_r, in eV) for the detection of positron-atom bound states through resonant annihilation or scattering.

Atom (Z)		Valence configuration	Excited states	E_{ex}[a]	ε_b	ε_r[b]
22	Ti	$3d^2 4s^2$	$^1D_2$	0.90	0.90	0.0
		$3d^3 4s$	$^5F_1, ^5F_2$	0.813, 0.818	0.825	$-0.012, -0.007$
27	Co	$3d^8 4s$	$^4F_{9/2}, ^4F_{7/2}, ^4F_{5/2}, ^4F_{3/2}$	0.43, 0.51, 0.58, 0.63	0.30	0.13, 0.21, 0.28, 0.33
			$^2F_{7/2}$	0.92	0.30	0.62
28	Ni	$3d^9 4s$	$^1D_2$	0.42	0.22	0.20
43	Tc	$4d^6 5s$	$^6D_{5/2}, ^6D_{3/2}, ^6D_{1/2}$	0.46, 0.50, 0.52	0.48	$-0.02, 0.02, 0.04$
44	Ru	$4d^7 5s$	$^5F_1$	0.39	0.42	-0.03
			$^3F_4, ^3F_3$	0.81, 1.00	0.42	0.39, 0.58
			$^5P_2$	1.00	0.42	0.58
45	Rh	$4d^8 5s$	$^4F_{5/2}, ^4F_{3/2}$	0.322, 0.43	0.355	$-0.033, 0.08$
			$^2F_{7/2}, ^2F_{5/2}$	0.71, 0.96	0.36	0.35, 0.60
46	Pd	$4d^9 5s$	$^2[5/2]_3, ^2[5/2]_2$	0.81, 0.96	0.29	0.52, 0.67
72	Hf	$5d^2 6s^2$	$^3F_4$	0.57	0.50	0.07
73	Ta	$5d^3 6s^2$	$^4F_{7/2}, ^4F_{9/2}$	0.49, 0.70	0.44	0.05, 0.26
			$^4P_{1/2}, ^4P_{3/2}, ^4P_{5/2}$	0.75, 0.75, 1.15	0.44	0.31, 0.31, 0.71
			$^2G_{7/2}$	1.20	0.44	0.76
74	W	$5d^4 6s^2$	$^5D_2, ^5D_3$	0.41, 0.60	0.38	0.03, 0.22
			$^4D_3$	0.77	0.38	0.39
			$^3P2_0$	1.18	0.38	0.80
		$5d^5 6s$	$^7S_3$	0.36	0.20	0.16
75	Re	$5d^5 6s^2$	$^4P_{5/2}$	1.44	0.32	1.12
76	Os	$5d^6 6s^2$	$^5D_2, ^5D_3, ^5D_1, ^5D_0$	0.34, 0.52, 0.71, 0.76	0.27	0.07, 0.25, 0.44, 0.49
			$^3H_5, ^3H_4, ^3H_6$	1.78, 1.84, 1.84	0.27	1.51, 1.57, 1.57
		$5d^7 6s$	$^5F_5, ^5F_4$	0.64, 1.08	0.10	0.54, 0.98
77	Ir	$5d^7 6s^2$	$^4F_{3/2}, ^4F_{5/2}, ^4F_{7/2}$	0.51, 0.72, 0.78	0.23	0.28, 0.49, 0.55
			$^2G_{9/2}, ^2G_{7/2}$	1.73, 2.20	0.23	1.50, 1.97
			$^4P_{5/2}, ^4P_{3/2}, ^4P_{1/2}$	2.00, 2.30, 2.51	0.23	1.77, 2.07, 2.27
			$^2H_{11/2}$	2.43	0.23	2.20
		$5d^8 6s$	$^4F_{9/2}, ^4F_{7/2}, ^4F_{5/2}, ^4F_{3/2}$	0.35, 0.88, 1.22, 1.47	0.07	0.28, 0.81, 1.15, 1.40
			$^2P_{3/2}, ^2P_{1/2}$	1.31, 1.55	0.07	1.24, 1.48
			$^2F_{5/2}, ^2F_{7/2}$	1.51, 1.62	0.07	1.44, 1.55
			$^4P_{5/2}$	1.60	0.07	1.53
78	Pt	$5d^8 6s^2$	$^3F_3, ^3F_2$	1.25, 1.92	0.19	1.06, 1.73
			$^3P_2$	0.81	0.19	0.62
		$5d^{10}$	$^1S_0$	0.76	0.04	0.72

[a]Atomic excitation lenergy with respect to the ground state from Ref. [57].
[b]Resonance energy from Eq. (21).

energies are related to each other by

$$\varepsilon_r = E_{\text{ex}} - \varepsilon_b, \tag{21}$$

where E_{ex} is the atomic excitation energy measured with respect to the ground state. To observe the resonance, one requires $\varepsilon_r > 0$, which means that the excitation energy must be greater than binding energy ($E_{\text{ex}} > \varepsilon_b$). In lighter atoms, the fine-structure splitting of the ground state is too small to satisfy this condition. However, in the heavier atoms, the fine structure can be larger than ε_b, and the corresponding low-lying excited states can form resonances. There is also another condition for observing narrow resonances. The resonance energy should be smaller than the Ps formation threshold, $\varepsilon_r < I - 6.8$. For resonances lying above this energy, the Ps formation channel will be open. This can reduce the resonance lifetimes and make the resonances too broad to be observed. Also, at these energies the positron-atom annihilation signal due to resonances will be "drowned" by the annihilation within the positronium. Table III shows resonances which satisfy or approximately satisfy these two conditions. Note that we also show some

states with negative ε_r values, which correspond to weakly bound positron states. Given the uncertainty in our calculation, they may in fact turn out to be low-lying resonances.

V. CONCLUSION

The coupled-cluster single-double approach has been used to calculate positron binding energy for a number of open-shell atoms. The binding energies are in good agreement with previous estimates and indicate that atoms with open d shells can bind positron not only in their ground but also in excited states. Many of the atoms considered appear to be good candidates for studying positron binding to atoms through resonant annihilation or resonant scattering.

ACKNOWLEDGMENTS

[1] W. J. Cody, J. Lawson, H. S. W. Massey, and K. Smith, Proc. R. Soc. London A **278**, 479 (1964).
[2] M. Ya. Amusia, N. A. Cherepkov, L. V. Chernysheva, and S. G. Shapiro, J. Phys. B **9**, L531 (1976).
[3] V. A. Dzuba, V. V. Flambaum, W. A. King, B. N. Miller, and O. P. Sushkov, Phys. Scr., T **46**, 248 (1993).
[4] V. A. Dzuba, V. V. Flambaum, G. F. Gribakin, and W. A. King, Phys. Rev. A **52**, 4541 (1995).
[5] G. G. Ryzhikh and J. Mitroy, Phys. Rev. Lett. **79**, 4124 (1997).
[6] K. Strasburger and H. Chojnacki, J. Chem. Phys. **108**, 3218 (1998).
[7] V. A. Dzuba, V. V. Flambaum, G. F. Gribakin, and C. Harabati, Phys. Rev. A **60**, 3641 (1999).
[8] V. A. Dzuba, V. V. Flambaum, and C. Harabati, Phys. Rev. A **62**, 042504 (2000).
[9] J. Mitroy, M. W. J. Bromley, and G. G. Ryzhikh, J. Phys. B **35**, R81 (2002).
[10] M. W. J. Bromley and J. Mitroy, Phys. Rev. A **73**, 032507 (2006).
[11] M. W. J. Bromley and J. Mitroy, Phys. Rev. A **75**, 042506 (2007).
[12] J. Mitroy, J. Y. Zhang, M. W. J. Bromley, and S. I. Young, Phys. Rev. A **78**, 012715 (2008).
[13] V. A. Dzuba, V. V. Flambaum, and G. F. Gribakin, Phys. Rev. Lett. **105**, 203401 (2010).
[14] X. Cheng, D. Babikov, and D. M. Schrader, Phys. Rev. A **83**, 032504 (2011).
[15] J. Mitroy, M. W. J. Bromley, and G. G. Ryzhikh, J. Phys. B **32**, 2203 (1999).
[16] D. M. Schrader, in *Physics with Many Positrons*, edited by A. Dupasquier and A. P. Mills, Jr., International School of Physics Enrico Fermi, Vol. 174 (IOS, Amsterdam, 2010).
[17] G. F. Gribakin, J. A. Young, and C. M. Surko, Rev. Mod. Phys. **82**, 2557 (2010).
[18] G. F. Gribakin, Phys. Rev. A **61**, 022720 (2000).

[19] G. F. Gribakin, in *New Directions in Antimatter Chemistry and Physics*, edited by C. M. Surko and F. A. Gianturco (Kluwer Academic, Dordrecht, 2001), p. 413.
[20] S. J. Gilbert, L. D. Barnes, J. P. Sullivan, and C. M. Surko, Phys. Rev. Lett. **88**, 043201 (2002).
[21] L. D. Barnes, S. J. Gilbert, and C. M. Surko, Phys. Rev. A **67**, 032706 (2003).
[22] J. R. Danielson, J. A. Young, and C. M. Surko, J. Phys. B **42**, 235203 (2009).
[23] J. R. Danielson, J. J. Gosselin, and C. M. Surko, Phys. Rev. Lett. **104**, 233201 (2010).
[24] A. C. L. Jones, J. R. Danielson, J. J. Gosselin, M. R. Natisin, and C. M. Surko, New J. Phys. **14**, 015006 (2012).
[25] J. R. Danielson, A. C. L. Jones, J. J. Gosselin, M. R. Natisin, and C. M. Surko, Phys. Rev. A **85**, 022709 (2012).
[26] S. J. Gilbert, C. Kurz, R. G. Greaves, and C. M. Surko, Appl. Phys. Lett. **70**, 1944 (1997); C. Kurz, S. J. Gilbert, R. G. Greaves, and C. Surko, Nucl. Instrum. Methods Phys. Res., Sect. B **143**, 188 (1998).
[27] V. A. Dzuba, V. V. Flambaum, and M. V. Marchenko, Phys. Rev. A **68**, 022506 (2003).
[28] V. A. Dzuba and V. V. Flambaum, Phys. Rev. A **77**, 012514 (2008).
[29] V. A. Dzuba and V. V. Flambaum, Phys. Rev. A **77**, 012515 (2008).
[30] M. W. J. Bromley and J. Mitroy, Phys. Rev. A **65**, 062505 (2002).
[31] M. W. J. Bromley and J. Mitroy, Phys. Rev. A **65**, 062506 (2002).
[32] V. A. Dzuba, Phys. Rev. A **78**, 042502 (2008).
[33] G. F. Gribakin and J. Ludlow, Phys. Rev. A **70**, 032720 (2004).
[34] J. Ludlow, Ph.D. thesis, Queen's University, Belfast, 2003.
[35] J. A. Ludlow and G. F. Gribakin, Int. Rev. At. Mol. Phys **1**, 73 (2010).
[36] S. A. Blundell, W. R. Johnson, Z. W. Liu, and J. Sapirstein, Phys. Rev. A **40**, 2233 (1989).

[37] S. A. Blundell, W. R. Johnson, and J. Sapirstein, Phys. Rev. A **43**, 3407 (1991).

[38] M. S. Safronova, A. Derevianko, and W. R. Johnson, Phys. Rev. A **58**, 1016 (1998).

[39] M. S. Safronova, W. R. Johnson, and A. Derevianko, Phys. Rev. A **60**, 4476 (1999).

[40] V. A. Dzuba and W. R. Johnson, Phys. Rev. A **76**, 062510 (2007).

[41] W. R. Johnson and J. Sapirstein, Phys. Rev. Lett. **57**, 1126 (1986).

[42] V. A. Dzuba and G. F. Gribakin, Phys. Rev. A **49**, 2483 (1994); **50**, 3551 (1994).

[43] V. A. Dzuba, V. V. Flambaum, G. F. Gribakin, and C. Harabati (unpublished).

[44] M. S. Safronova, M. G. Kozlov, W. R. Johnson, and D. S. Jiang, Phys. Rev. A **80**, 012516 (2009).

[45] S. A. Blundell, W. R. Johnson, and J. Sapirstein, Phys. Rev. A **42**, 3751 (1990).

[46] G. G. Ryzhikh, J. Mitroy, and K. Varga, J. Phys. B **31**, 3965 (1998).

[47] J. Mitroy and G. G. Ryzhikh, J. Phys. B **34**, 2001 (2001).

[48] M. W. J. Bromley and J. Mitroy, Phys. Rev. A **65**, 012505 (2001).

[49] J. Mitroy, Phys. Rev. A **70**, 024502 (2004).

[50] R. Szmytkowski, J. Phys. II **3**, 183 (1993).

[51] M. Mella, M. Casalegno, and G. Morosi, J. Chem. Phys. **117**, 1450 (2002).

[52] G. F. Gribakin and W. A. King, Can. J. Phys. **74**, 449 (1996).

[53] R. P. McEachran and A. D. Stauffer, Nucl. Instrum. Methods Phys. Res., Sect. B **143**, 199 (1998).

[54] J. Mitroy and G. G. Ryzhikh, J. Phys. B **32**, 1375 (1999).

[55] R. Szmytkowski, Acta Phys. Pol. A **84**, 1035 (1993).

[56] T. M. Miller, in *Handbook of Chemistry and Physics*, edited by D. R. Lide (CRC, Boca Raton, 2000).

[57] Yu. Ralchenko, A. E. Kramida, and J. Reader, NIST ASD Team (2011). NIST Atomic Spectra Database (ver. 4.1.0) [online], February 21, 2012. National Institute of Standards and Technology, Gaithersburg, MD; http://physics.nist.gov/asd.