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Calculation of positron binding to silver and gold atoms

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Positron binding to silver and gold atoms was studied using a fully *ab initio* relativistic method, which combines the configuration-interaction method with many-body perturbation theory. It was found that the silver atom forms a bound state with a positron with binding energy 123 (±30%) meV, while the gold atom cannot bind a positron. Our calculations reveal the importance of the relativistic effects for positron binding to heavy atoms. The role of these effects was studied by varying the value of the fine-structure constant α. In the nonrelativistic limit, $\alpha=0$, both systems e^+Ag and e^+Au are bound with binding energies of about 200 meV for e^+Ag and 220 meV for e^+Au. Relativistic corrections for a negative ion are essentially different from that for a positron interacting with an atom. Therefore the calculation of electron affinities cannot serve as a test of the method used for positron binding in the nonrelativistic case. However, it is still a good test of the relativistic calculations. Our calculated electron affinities for silver (1.327 eV) and gold (2.307 eV) atoms are in very good agreement with corresponding experimental values (1.303 and 2.309 eV, respectively).

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I. INTRODUCTION

Positron binding by neutral atoms has not been directly observed yet. However, intensive theoretical study of the problem undertaken in the last few years strongly suggests that many atoms can actually form bound states with a positron (see, e.g. [1–8]). Most of the atoms studied so far were atoms with a relatively small value of the nuclear charge Z. It is important to extend the study to heavy atoms. The main obstacle in this way is the rapid rise of computational difficulties associated with increasing the number of electrons. However, as we show in this paper, an inclusion of relativistic effects is also important. The role of these effects in positron binding to atoms has not been properly investigated. Indeed, one can say that due to strong Coulomb repulsion, a positron cannot penetrate to short distances from the nucleus and remains nonrelativistic. However, the positron binding is due to interaction with electrons that have large relativistic corrections to their energies and wave functions. The binding energy is the difference between the energies of a neutral atom and an atom bound with a positron. This difference is usually small. On the other hand, relativistic contributions to the energies of both systems are large and there is no reason to expect they are the same and cancel each other. Therefore, some relativistic technique is needed to study positron binding by heavy atoms.

For both light and heavy atoms, the main difficulty in calculations of positron interaction comes from the strong electron-positron Coulomb attraction. This attraction leads to virtual positronium (Ps) formation [9]. One can say that it gives rise to a specific short-range attraction between the positron and the atom, in addition to the usual polarizational potential, which acts between a neutral target and a charged projectile [1,9–12]. This attraction cannot be treated accurately by perturbations and some all-order technique is needed. In our earlier works [1,9–12] we used the Ps wave function explicitly to approximate the virtual Ps-formation contribution to the positron-atom interaction and predicted e^+Mg, e^+Zn, e^+Cd, and a few other bound states. The same physics may also explain the success of the stochastic variational method in positron-atom bound-state calculations (see, e.g., [3] and references therein). In this approach, the wave function is expanded in terms of explicitly correlated Gaussian functions that include factors $\exp(-\alpha r_{ij}^2)$ with interparticle distances r_{ij}. Using this method, Ryzhikh and Mitroy obtained positron bound states for a whole range of atoms (Be, Mg, Zn, Cu, Ag, Li, Na, etc.). This method is well suited for few-particle systems. Its application to heavier systems is done by considering the Hamiltonian of the valence electrons and the positron in the model potential of the ionic core. However, for heavier atoms, e.g., Zn, the calculation becomes extremely time consuming [5], and its convergence cannot be ensured.

Another nonperturbative technique is the configuration interaction (CI) method widely used in standard atomic calculations. This method was applied to the positron-copper bound state in [6]. In this work, the single-particle orbitals of the valence electron and positron are chosen as Slater-type orbitals, and their interaction with the Cu$^+$ core is approximated by the sum of the Hartree-Fock and model polarization potentials. The calculation shows slow convergence with respect to the number of spherical harmonics included in the CI expansion, $L_{\max}=10$ being still not sufficient to extrapolate the results reliably to $L_{\max}\rightarrow\infty$. In their more recent work, the same authors applied the CI method to a preliminary analysis of such systems as PsH, e^+Cu, e^+Li, e^+Be, e^+Cd, and CuPs.

In our previous paper, we developed a different version of the CI method for the positron-atom problem [13]. The method is based on the relativistic Hartree-Fock method (RHF) and a combination of the CI method with many-body perturbation theory (MBPT). This method was first developed for pure electron systems [14], and its high effectiveness was demonstrated in a number of calculations [16–18]. In the paper [13], it was successfully applied to the positron binding by copper. There are several important advances in the technique as compared to the standard nonrelativistic CI method that make it a very effective tool for the investigation of positron binding by heavy atoms:

(1) The method is relativistic in the sense that the Dirac-

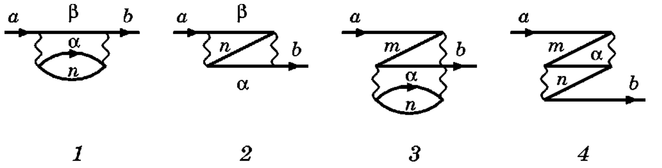

FIG. 1. Second-order diagrams for the self-energy of the valence electron ($\hat{\Sigma}_e$ operator). Summation over excited electron states α and β and core hole states m and n is assumed.

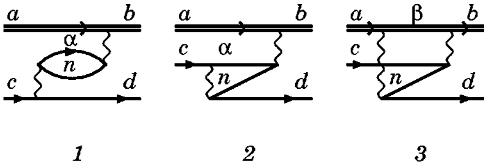

FIG. 3. Screening of the positron-electron Coulomb interaction ($\hat{\Sigma}_{ep}$ operator).

Hartree-Fock operator is used to construct an effective Hamiltonian for the problem and to calculate electron and positron orbitals.

(2) B splines [19] in a cavity of finite radius R were used to generate single-particle basis sets for an external electron and a positron. The B-spline technique has the remarkable property of providing fast convergence with respect to the number of radial functions included in the calculations [20,21]. Convergence can be further controlled by varying the cavity radius R while the effect of the cavity on the energy of the system is taken into account analytically [13]. Convergence was clearly achieved for the e^+Cu system in Ref. [13] and for the e^+Ag and e^+Au systems as presented below.

(3) We use MBPT to include excitations from the core into the effective Hamiltonian. This corresponds to the inclusion of the correlations between core electrons and external particles (electron and positron) and of the effect of screening of the electron-positron interaction by core electrons. These effects are also often called the polarization of the core by the external particles. We include them in a fully *ab initio* manner up to the second order of the MBPT.

In the present paper we apply this method to the problem of positron binding by silver and gold atoms. Using a similar technique we also calculate electron affinities for both these atoms. Calculations for negative ions serve as a test of the technique used for positron-atom binding. We also study the role of the relativistic effects in neutral silver and gold, silver and gold negative ions, and silver and gold interacting with a positron. This is done by varying the value of the fine-structure constant α towards its nonrelativistic limit $\alpha=0$.

II. THEORY

A detailed description of the method was given in Ref. [13]. We briefly repeat it here, emphasizing the role of the relativistic effects. We use the relativistic Hartree-Fock method in the V^{N-1} approximation to obtain the single-particle basis sets of electron and positron orbitals and to construct an effective Hamiltonian.

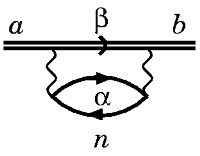

FIG. 2. Second-order diagram for the positron self-energy ($\hat{\Sigma}_p$ operator). Double line denotes positron states.

The two-particle electron-positron wave function is given by the CI expansion,

$$\Psi(\mathbf{r}_e,\mathbf{r}_p)=\sum_{i,j} C_{ij}\psi_i^e(\mathbf{r}_e)\psi_j^p(\mathbf{r}_p), \tag{1}$$

where ψ_i^e and ψ_j^p are the electron and positron orbitals, respectively. The expansion coefficients C_{ij} are determined by the diagonalization of the matrix of the effective CI Hamiltonian acting in the Hilbert space of the valence electron and the positron,

$$\begin{aligned} H_{\text{eff}}^{\text{CI}}&=\hat{h}_e+\hat{h}_p+\hat{h}_{ep},\\ \hat{h}_e&=c\boldsymbol{\alpha}\cdot\boldsymbol{p}+(\beta-1)mc^2-\frac{Ze^2}{r_e}+V_d^{N-1}-\hat{V}_{exch}^{N-1}+\hat{\Sigma}_e,\\ \hat{h}_p&=c\boldsymbol{\alpha}\cdot\boldsymbol{p}+(\beta-1)mc^2+\frac{Ze^2}{r_p}-V_d^{N-1}+\hat{\Sigma}_p,\\ \hat{h}_{ep}&=-\frac{e^2}{|\mathbf{r}_e-\mathbf{r}_p|}+\hat{\Sigma}_{ep}, \end{aligned} \tag{2}$$

where $\hat{h}_e$ and $\hat{h}_p$ are the effective single-particle Hamiltonians of the electron and positron, and $\hat{h}_{ep}$ is the effective electron-positron two-body interaction. Apart from the relativistic Dirac operator, $\hat{h}_e$ and $\hat{h}_p$ include the direct and exchange Hartree-Fock potentials of the core electrons V_d^{N-1} and $\hat{V}_{exch}^{N-1}$, respectively. The additional $\hat{\Sigma}$ operators account for correlations involving core electrons. Σ_e and Σ_p are single-particle operators that can be considered as a self-energy part of the correlation interaction between an external electron or positron and core electrons. These operators are often called "correlation potentials" due to the analogy with the nonlocal exchange Hartree-Fock potential. $\hat{\Sigma}_{ep}$ represents the screening of the Coulomb interaction between external particles by core electrons (see [14,13] for a detailed discussion).

We use many-body perturbation theory to calculate $\hat{\Sigma}$. All second-order diagrams in the residual Coulomb interaction are included. Diagrams for $\hat{\Sigma}_e$ are presented in Fig. 1. The only second-order diagram for $\hat{\Sigma}_p$ is presented in Fig. 2. Diagrams for $\hat{\Sigma}_{ep}$ are presented in Fig. 3. We include $\hat{\Sigma}$ in s,p, and d states only. The $\hat{\Sigma}$ in higher waves practically does not contribute to the CI energy. Calculation of $\hat{\Sigma}$ involves summation over intermediate electron or positron states. We restrict this summation to states with $l \leqslant 5$. Convergence is very fast and states with $l > 5$ do not contribute to the $\hat{\Sigma}$ in s,p,d states. Note that the polarization potential $-\alpha/(2r^4)$ is often used as a local energy-independent approximation for the correlation potential $\hat{\Sigma}$. However, one needs only a dipole multipole in the Coulomb interaction in $\hat{\Sigma}$ to obtain the expression for this potential. According to the calculations, the dipole term really dominates in $\hat{\Sigma}$. However, the contributions of the higher multipolarities are not small and we include them as well. Note also that the fast convergence in the wave expansion of $\hat{\Sigma}$ is in contrast with the very slow convergence of the CI expansion of the two-particle electron-positron wave function. As was discussed above, this slow convergence is caused by strong attraction between positron and valence electrons, which leads to the virtual positronium formation. There is no such interaction in the $\hat{\Sigma}$ operator. Indeed, $\hat{\Sigma}_e$ has no positron-electron interaction at all. $\hat{\Sigma}_p$ and $\hat{\Sigma}_{ep}$ do include positron-electron interaction but with the core electrons only. The effect of attraction of positron to core electrons is not as strong as that for a valence electron and practically does not lead to the virtual positronium formation. This problem was also considered in Ref. [15].

To study the role of the relativistic effects we use the form of the operators h_e and h_p in which the dependence on the fine-structure constant α is explicitly shown. Single-particle orbitals have the form

$$\psi(\mathbf{r})_{njlm}=\frac{1}{r}\begin{pmatrix} f_n(r)\Omega(\mathbf{r}/r)_{jlm} \\ i\alpha g_n(r)\tilde{\Omega}(\mathbf{r}/r)_{jlm} \end{pmatrix}. \tag{3}$$

Then the RHF equations

$$(h_i-\epsilon_n)\psi_n^i=0, \quad (i=e,p)$$

take the following form:

$$\begin{aligned} f_n'(r)+\frac{\kappa_n}{r}f_n(r)-[2+\alpha^2(\epsilon_n-\hat{V})]g_n(r)=0,\\ g_n'(r)-\frac{\kappa_n}{r}g_n(r)+(\epsilon_n-\hat{V})f_n(r)=0, \end{aligned} \tag{4}$$

where $\kappa=(-1)^{l+j+1/2}(j+1/2)$ and $\hat{V}$ is the effective potential. For the core electron states $\hat{V}$ is the sum of direct and exchange Hartree-Fock potentials

$$\hat{V}=-\frac{Ze^2}{r_e}+V_d^{N-1}-\hat{V}_{exch}^{N-1}. \tag{5}$$

For the states above core (electron or positron), $\hat{\Sigma}$ is the sum of the Hartree-Fock potential and correlation potential Σ:

$$\hat{V}=-\frac{Ze^2}{r_e}+V_d^{N-1}-\hat{V}_{exch}^{N-1}+\hat{\Sigma}_e \quad \text{(for an electron)}, \tag{6}$$

$$\hat{V}=\frac{Ze^2}{r_p}-V_d^{N-1}+\hat{\Sigma}_p \quad \text{(for a positron)}.$$

The nonrelativistic limit can be achieved by reducing the value of α in Eq. (4) to $\alpha=0$.

The relativistic energy shift in atoms with one external electron can also be estimated by the following equation [22]:

$$\Delta_n=\frac{E_n}{\nu}(Z\alpha)^2\left[\frac{1}{j+1/2}-C(Z,j,l)\right], \tag{7}$$

where E_n is the energy of an external electron, ν is the effective principal quantum number ($E_n=-0.5/\nu^2$ a.u.). The coefficient $C(Z,j,l)$ accounts for many-body effects. Note that formula (7) is based on the specific expression for the electron density in the vicinity of the nucleus and therefore is not applicable for a positron.

III. SILVER AND GOLD NEGATIVE IONS

We calculated electron affinities of silver and gold atoms mostly to test the technique used for positron-atom binding. The calculation of a negative ion Ag^- or Au^- is a two-particle problem technically very similar to positron-atom binding. The effective Hamiltonian of the problem has a form similar to that of Eq. (2):

$$H_{\text{eff}}^{\text{CI}}=\hat{h}_e(r_1)+\hat{h}_e(r_2)+\hat{h}_{ee},$$

$$\hat{h}_{ee}=\frac{e^2}{|\mathbf{r}_e-\mathbf{r}_p|}+\hat{\Sigma}_{ee},$$

where $\hat{\Sigma}_{ee}$ represents the screening of the Coulomb interaction between external electrons by core electrons (see Refs. [14,13] for a detailed discussion). Electron affinity is defined when an electron can form a bound state with an atom. In this case the difference between the energy of a neutral atom and the energy of a negative ion is called the electron affinity to this atom. Energies of Ag, Ag^-, Au, Au^- obtained in different approximations and corresponding electron affinities are presented in Table I together with experimental data. The energies are given with respect to the cores (Ag^+ and Au^+). Like in the case of Cu^- [13], the accuracy of the Hartree-Fock approximation is very poor. The binding energies of the $5s$ electron in neutral Ag and the $6s$ electron in neutral Au are underestimated by about 21% and 23%, respectively, while the negative ions are unbound. Inclusion of either core-valence correlations (Σ) or valence-valence correlations (CI) does produce binding but the accuracy is still poor. Only when both these effects are included does the accuracy for the electron affinities improve significantly, becoming 20% for Ag^- and 11% for Au^-. Further improvement can be achieved by introducing numerical factors before $\hat{\Sigma}_e$ to fit the lowest $s,p,$ and d energy levels of the neutral atoms. These factors simulate the effect of higher-order correlations. Their values are $f_s=0.88$, $f_p=0.97$, $f_d=1.08$ for the Ag atom and $f_s=0.81$, $f_p=1$, $f_d=1.04$ for the

TABLE I. Ground state energies (in a.u.) of silver, gold and their negative ions calculated in different approximations.

	Neutral atom	Negative ion	Electron affinity [a]
		Silver	
RHF [b]	−0.229 52	−0.201 56	−0.027 95
RHF+Σ [c]	−0.279 90	−0.302 31	0.022 41
CI [d]	−0.229 52	−0.256 75	0.027 22
CI+Σ_e [e]	−0.285 64	−0.335 60	0.049 96
CI+Σ_e+Σ_{ee} [f]	−0.285 64	−0.342 98	0.057 34
CI+$f\Sigma_e$+Σ_{ee} [g]	−0.278 41	−0.327 21	0.048 80
Experiment [h]	−0.278 41	−0.326 26	0.047 84
		Gold	
RHF [b]	−0.274 61	−0.261 69	−0.012 92
RHF+Σ [c]	−0.349 00	−0.410 46	0.061 46
CI [d]	−0.274 61	−0.313 69	0.039 08
CI+Σ_e [e]	−0.355 36	−0.439 13	0.083 76
CI+Σ_e+Σ_{ee} [f]	−0.355 36	−0.449 43	0.094 07
CI+$f\Sigma_e$+Σ_{ee} [g]	−0.339 03	−0.423 89	0.084 86
Experiment [h]	−0.339 03	−0.423 86	0.084 83

[a] Negative affinity means no binding.

[b] Relativistic Hartree-Fock; a single-configuration approximation, no core-valence correlations are included.

[c] Single-configuration approximation, core-valence correlations are included by means of MBPT.

[d] Standard CI method.

[e] Self-energy part of core-valence correlations are included by adding the Σ_e operator to the CI Hamiltonian.

[f] CI+MBPT method, self-energy and screening correlations are included by Σ operators while valence-valence correlations are included by configuration interaction.

[g] Σ_e in different waves are taken with factors to fit energies of a neutral atom.

[h] Refs. [23,24].

TABLE II. Electron affinities of Ag and Au (eV). Comparison with other calculations and experiment.

Ag	Au	Ref.	Method
	Theory		
1.008	1.103	[25]	Nonrelativistic quadratic configuration interaction method
1.199	2.073	[25]	Relativistic quadratic configuration interaction method
1.254	2.229	[26]	Relativistic coupled cluster method
1.022		[4]	Nonrelativistic stochastic variational method
	2.28	[27]	Fock-space relativistic coupled-cluster method
	2.26	[28]	Fock-space coupled-cluster method with Douglas-Kroll transformation (relativistic)
1.327	2.307		Present work
	Experiment		
1.303	2.309	[29]	

Au atom in the *s*, *p*, and *d* channels, respectively. As is evident from Table I, the fitting of the energies of neutral atoms also significantly improves electron affinities. Results of other calculations of the electron affinities of silver and gold are presented in Table II together with the experimental values.

IV. POSITRON BINDING TO SILVER AND GOLD AND THE ROLE OF RELATIVISTIC EFFECTS

As for the case of copper [13], we have performed calculations for two different cavity radii $R=30a_0$ and $R=15a_0$. For a smaller radius, convergence with respect to the number of single-particle basis states is fast. However, the effect of the cavity on the converged energy is large. For a larger cavity radius, convergence is slower and the effect of the cavity on the energy is small. When the energy shift caused by the finite cavity radius is taken into account both calculations come to the same value of the positron binding energy. Table III illustrates the convergence of the calculated energies of e^+Ag and e^+Au with respect to the maximum value of the angular momentum of single-particle orbitals. Energies presented in the table are two-particle energies (in a.u.) with respect to the energies of Ag$^+$ and Au$^+$. The number of radial orbitals n in each partial wave is fixed at $n=16$. Figures 4 and 5 show the convergence of the calculated energy with respect to n when maximum momentum of the single-particle orbitals was fixed at $L=10$. The cavity radius in both cases was $R=30a_0$. Table III and Figs. 4 and 5 show that even for a larger cavity radius, convergence was clearly achieved. Table III also shows the convergence in different approximations, namely, with and without core-valence correlations (Σ). One can see that while inclusion of Σ does shift the energy, the convergence is not affected.

Table IV shows how positron binding by silver and gold is formed in different approximations. This table is very similar to Table I for the negative ions except there is no RHF approximation for the positron binding. Indeed, the RHF approximation for the negative ions means a single-configuration approximation: $5s^2$ for Ag$^-$ and $6s^2$ for Au$^-$. These configurations strongly dominate in the two-electron wave function of the negative ions even when a large number of configurations are mixed to ensure convergence. In contrast, no single configuration strongly dominates in the positron binding problem. Therefore we present our results in Table IV starting from the standard CI approximation. In this approximation the energy of the positron and an atom is lower than the energy of a neutral atom for both silver and gold atoms. Note, however, that the absolute value of the energy 0.2488 a.u. of the e^+Ag system is smaller than that of positronium, which is 0.25 a.u. This makes the system unstable against dissociation in the silver positive ion and positronium. In their nonrelativistic calculations, Ryzhikh and Mitroy get 0.260 a.u. for the CI energy [3]. The difference between this and our results is most likely due to relativistic effects (see Table V and the discussion of the relativistic effects in the end of this section).

Inclusion of core-valence correlations through the introduction of Σ_e, Σ_p, and Σ_{ep} operators shifts the energies

TABLE III. Convergence of the calculation of the energies of e^+Ag and e^+Au with respect to the number of included partial waves (a.u.). (Finite box size correction is not included.)

	$L_{\max}$	CI [a]	CI+Σ [b]	CI+fΣ [c]
e^+Ag	0	−0.223 272 9	−0.280 022 3	−0.272 903 8
	1	−0.227 170 9	−0.283 836 0	−0.274 959 1
	2	−0.230 920 7	−0.286 837 5	−0.276 512 4
	3	−0.235 082 3	−0.289 569 1	−0.278 057 1
	4	−0.238 831 5	−0.291 680 0	−0.279 378 4
	5	−0.241 925 1	−0.293 238 1	−0.280 448 7
	6	−0.244 321 8	−0.294 347 0	−0.281 267 8
	7	−0.246 074 5	−0.295 108 5	−0.281 860 3
	8	−0.247 281 2	−0.295 610 0	−0.282 264 7
	9	−0.248 047 7	−0.295 918 9	−0.282 519 9
	10	−0.248 474 9	−0.296 082 9	−0.282 659 6
	11	−0.248 669 8	−0.296 144 4	−0.282 714 3
	12	−0.248 755 4	−0.296 168 2	−0.282 736 7
	13	−0.248 792 8	−0.296 177 8	−0.282 745 9
	14	−0.248 809 0	−0.296 181 7	−0.282 749 8
e^+Au	0	−0.268 404 9	−0.350 044 7	−0.333 016 3
	1	−0.270 658 2	−0.352 660 2	−0.333 950 0
	2	−0.271 981 3	−0.353 974 5	−0.334 456 4
	3	−0.273 270 5	−0.355 048 1	−0.334 876 5
	4	−0.274 390 5	−0.355 803 0	−0.335 178 7
	5	−0.275 322 2	−0.356 328 9	−0.335 397 3
	6	−0.276 053 9	−0.356 688 3	−0.335 552 5
	7	−0.276 594 3	−0.356 928 3	−0.335 659 0
	8	−0.276 968 6	−0.357 083 7	−0.335 729 4
	9	−0.277 207 4	−0.357 179 1	−0.335 373 3
	10	−0.277 339 0	−0.357 229 3	−0.335 797 2
	11	−0.277 392 5	−0.357 244 9	−0.335 804 9
	12	−0.277 414 6	−0.357 250 5	−0.335 807 8
	13	−0.277 423 9	−0.357 252 7	−0.335 809 1
	14	−0.277 427 8	−0.357 253 6	−0.335 809 5

[a] Standard CI method.

[b] CI+MBPT method, Σ_e and Σ_p are included while Σ_{ep} is not.

[c] Same as before but Σ_e and Σ_p are taken with fitting parameters as explained in the text.

significantly. The e^+Ag system becomes bound and stable while the e^+Au system is unbound.

As was discussed in our previous paper [13], the dominating factor affecting the accuracy of the calculations is higher-order correlations that mostly manifest themself via the value of the Σ operator. An introduction of the fitting parameters as described in the preceding section can be considered as a way to simulate the effect of higher-order correlations. Also, the energy shift caused by the fitting can be considered as an estimation of the uncertainty of the calculations. We use the same rescaling parameters for $\hat{\Sigma}_p$ and Σ_e (see preceding section). $\hat{\Sigma}_{ep}$ is not rescaled. Shift of the energy caused by rescaling is 0.0015 a.u. in the case of silver and 0.0003 a.u. in the case of gold (see Table IV). Note that these values are considerably smaller than energy shifts for the silver and gold negative ions (0.008 54 and 0.009 21 a.u., respectively; see Table I). This is because of the cancellation of the effects of the variation of Σ_e and Σ_p. In particular, for gold it is accidentally very small. One can see that even if the value of 0.0015 a.u. is adopted as an upper limit of the uncertainty of the calculations, the e^+Ag system remains bound while the e^+Au system remains unbound. However, the actual accuracy might be even higher. We saw that the fitting procedure significantly improves the accuracy of the calculations for the silver and gold negative ions. It is natural to assume that the same procedure works equally well for the positron binding problem. The final result for the energy of positron binding by the silver atom as presented in Table IV is 0.0043 a.u. This result does not include the effect of the finite cavity size. When this effect is taken into account, by means of the procedure described in Ref. [13], the binding energy becomes 0.004 52 a.u. or 123 meV. If we adopt the value of 0.0015 a.u as an estimation of the uncertainty of the result, then the accuracy we can claim is about 30%.

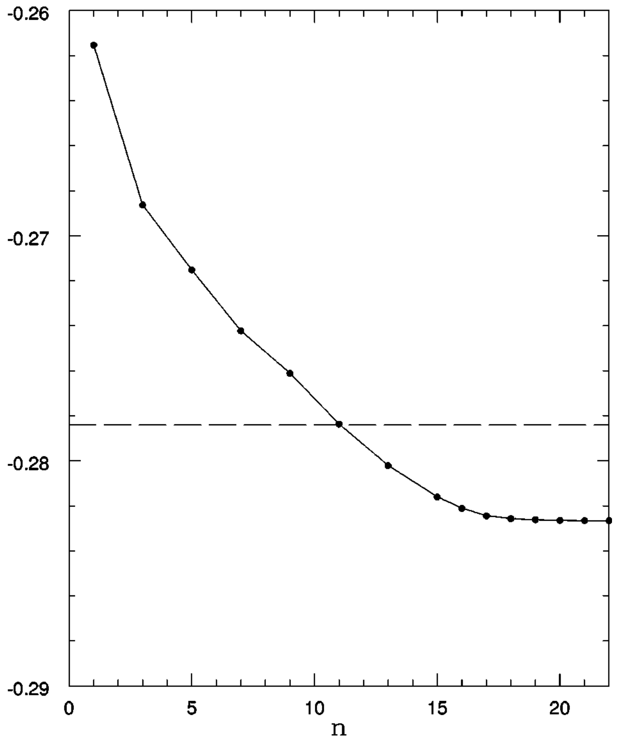

FIG. 4. Energy of e^+Ag as a function of the number of radial electron and positron basis functions in each partial wave ($L_{\max}=10$) in the cavity with $R=30a_0$. Dashed line represents the energy of neutral silver.

The calculation of the positron binding by copper [13], silver, and gold reveal an interesting trend. All three atoms have a very similar electron structure. However, the positron binding energy for silver (123 meV) is considerably smaller than that for copper (170 meV [13]), while gold atoms cannot bind positrons at all. We believe that this trend is caused by relativistic effects. An argument that the positron is always nonrelativistic does not look very convincing because electrons also contribute to the binding energy. Relativistic effects are large for heavy atoms and electron contributions to the positron binding energy could be very different in the relativistic and nonrelativistic limits. Indeed, we demon-

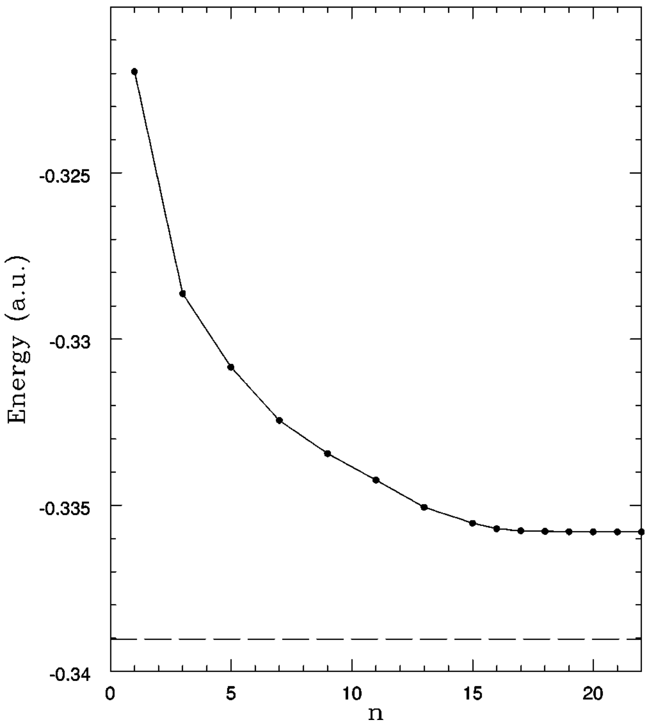

FIG. 5. Same as Fig. 4 but for e^+Au.

TABLE IV. Positron binding by silver and gold calculated in different approximations (all energies are in a.u.; finite box size correction is not included).

	Neutral atom	Atom with e^+	Binding energy [a]
		Silver	
CI	−0.2295	−0.2488	0.0193
CI+Σ_e+Σ_p	−0.2856	−0.2962	0.0105
CI+Σ_e+Σ_p+Σ_{ep}	−0.2856	−0.2884	0.0028
CI+$f\Sigma_e$+$f\Sigma_p$+Σ_{ep}	−0.2784	−0.2828	0.0043
		Gold	
CI	−0.2746	−0.2774	0.0028
CI+Σ_e+Σ_p	−0.3554	−0.3573	0.0019
CI+Σ_e+Σ_p+Σ_{ep}	−0.3554	−0.3519	−0.0035
CI+$f\Sigma_e$+$f\Sigma_p$+Σ_{ep}	−0.3390	−0.3358	−0.0032

[a] Negative energy means no binding.

strated in Ref. [22] that the relativistic energy shift considerably changes the values of the transition frequencies in Hg^+ ions and sometimes even changes the order of the energy levels. If we use formula (7) with the contribution of the many-body effects $C=0.6$, as suggested in Ref. [22], to estimate the relativistic energy shift for neutral Au, then the result is -0.037 a.u. This is about an order of magnitude larger than the energy difference between Au and e^+Au. If the relativistic energy shift in e^+Au is different from that in Au then the positron binding energy may be strongly affected.

To study the role of the relativistic effects in positron binding in more detail we performed the calculations for Ag, Ag^-, e^+Ag, Au, Au^-, and e^+Au in the relativistic and nonrelativistic limits. The latter corresponds to the zero value of the fine-structure constant α (see Sec. II). In the nonrelativistic case we start the calculations from the very beginning, putting $\alpha=0$ in the Hartree-Fock calculations of the core states. Then the electron states above the core and positron states are also calculated with $\alpha=0$. This means that our nonrelativistic calculations are equivalent to the fully nonrelativistic calculations of other authors (like Mitroy and Ryzhikh, see, e.g. [2]). Note that there are ''direct'' and ''indirect'' relativistic effects. The direct effect describes the difference between the Dirac and Schrödinger solution of the one-body equations for an external electron and a positron and the two-body CI equations for the electron-positron pair. The indirect relativistic effect describes the differences due to different electron-charge distributions arising from the use of Dirac-Hartree-Fock equations or Schrödinger-Hartree-Fock equations for the atomic core. In our relativistic calculations both effects are included, while in the nonrelativistic limit ($\alpha=0$) both effects are neglected. The comparison between the relativistic and non-relativistic calculations is presented in Table V. One can see that the actual relativistic energy shift for neutral Au is even bigger than is suggested by formula (7) with $C=0.6$. The shift is 0.0805 a.u., which corresponds to $C=0.08$. Formula (7) with $C=0.08$ also reproduces the relativistic energy shift for neutral Ag. The rela-

TABLE V. Energies (in a.u.) of Ag, Ag^-, e^+Ag, Au, Au^-, and e^+Au with respect to the energy of the core in relativistic and nonrelativistic cases.

	Neutral atom	Negative ion	Atom with a positron	Electron affinity	Positron binding energy [a]
			Silver		
Nonrelativistic	−0.2558	−0.2974	−0.2640	0.0416	0.0073
Relativistic	−0.2784	−0.3272	−0.2827	0.0488	0.0043
Δ	0.0226	0.0298	0.0187	−0.0072	0.0030
			Gold		
Nonrelativistic	−0.2537	−0.3040	−0.2665	0.0503	0.0080
Relativistic	−0.3390	−0.4239	−0.3358	0.0849	−0.0032
Δ	0.0853	0.1199	0.0693	−0.0346	0.0112

[a] Positive energy means bound state.

tivistic energy shift for an atom with a positron is of the same order of magnitude but a little different in value. This difference turned out to be enough to affect the positron binding energy significantly. In particular, the e^+Au system, which is unbound in relativistic calculations, becomes bound in the nonrelativistic limit with binding energy 0.0080 a.u or 218 meV. In the case of silver, the positron binding energy is considerably higher in the nonrelativistic limit. It is 0.0073 a.u. or 199 meV. It is interesting to compare this value with the value of 150 meV obtained by Mitroy and Ryzhikh using the nonrelativistic stochastic variational method [4]. Since the convergence was achieved in both calculations, the remaining difference should probably be attributed to the different treatment of the core-valence correlations. We use many-body perturbation theory for an accurate calculation of the Σ operator, which accounts for these correlations. Mitroy and Ryzhikh use an approximate semiempirical expression for the Σ operator that is based on its long-range asymptotic behavior.

Note that the relativistic energy shift for negative ions is also large. However, electron affinities are less affected. This is because electron affinities are many times larger than positron binding energies and therefore less sensitive to the energy shift. Apart from that there is a strong cancellation between relativistic energy shifts in the negative ion and neutral atom. This means in particular that the calculation of the electron affinities cannot serve as a test of a nonrelativistic method chosen for the positron binding problem. However, it is still a good test of the relativistic calculations. Note also that our calculated relativistic energy shifts for neutral and negative silver and gold are in very good agreement with calculations performed by Schwerdtfeger and Bowmaker by means of relativistic and nonrelativistic versions of the quadratic configuration interaction method (see Table VI and Ref. [25]).

TABLE VI. Comparison of the relativistic energy shift with other calculations (energies are in a.u.).

Atom/Ion	Present work	Schwerdtfeger and Bowmaker [a]
Ag	0.0226	0.0200
Ag^-	0.0072	0.0070
Au	0.0853	0.0714
Au^-	0.0346	0.0357

[a] Quadratic configuration interaction method, Ref. [25].

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