Work Functions for Positrons in Metals*

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Positron work functions have been calculated for a number of simple metals and the noble metals. Three separate contributions were estimated: the positron zero-point energy and the positron-electron correlation energy, which together constitute the internal positron chemical potential, and the contribution from the surface-dipole layer. The effect of the ionic lattice was included in the zero-point energy and the surface-dipole barrier. The correlation energy was calculated taking into account the nonlinear response of the electron system to the positron. Of all the metals considered only Au and Cu were calculated to have negative work functions. Positronium work functions were also calculated and in all cases they are smaller than the corresponding positron work function and are negative for several metals.

I. INTRODUCTION

There has recently been considerable interest[1-4] in the possibility of positrons having negative work functions for some metals. A negative work function would imply that work has to be done on the positron in fetching it from infinity into the metal or, alternatively, that positrons will leave the metal with a minimum kinetic energy which has the magnitude of the work function. Experiments have been reported that indicate that positrons, thermalized in a moderator coated with ~ 200-Å Au, leave the Au surface with a distribution that peaks at an energy between 0.75 and 2.90 eV. This low-energy emission of positrons was taken to be evidence for a negative positron work function in Au. Theoretical estimates of positron work functions have been made by Tong for the uniform-positive-background or jellium model of a metal. We present here calculations of the positron work function, for a number of simple metals and the noble metals, which take into account the effect of the ionic lattice. Our results, in general, differ considerably from those of Tong.[2]

The positron work function ϕ_p, by analogy with the electron case,[5] can be separated into two terms,

$$\phi_p = -D - \mu_p ,$$

where D is the potential barrier against electron escape due to the surface-dipole layer, which acts to expel the positron because of its opposite charge. The second term, μ_p, is strictly a bulk property; it is the positron chemical potential in the interior of the metal. We have measured μ_p from the electrostatic potential at the radius of the Wigner–Seitz sphere; if the ions are smeared out in a uniform positive-charge background, as in the jellium model, then our procedure is equivalent to measuring μ_p from the mean electrostatic potential.

Our estimates of D for the simple metals are taken from the work of Heine and Hodges,[6] in which they derive the dipole-layer contribution to the electron work function from calculated internal Fermi levels and experimental work functions. Their estimates take account of the electron-ion interaction. Tong[2] took his estimates of D from the first-principles calculations of Lang and Kohn[5] based on the jellium model; his values differ substantially from the results we have adopted, especially for the metals with large attractive pseudo-potentials. We have slightly modified the procedure of Heine and Hodges in the case of the noble metals to take account of the d bands.

We have split up the internal chemical potential into two parts and calculated each part separately. The first contribution arises from the positron-ion interaction. The positron is strongly repelled from the ions and in some cases the lowest single-particle state lies several electron volts above the electrostatic potential in the interstitial region—this energy has been termed the positron zero-point energy and we denote it by E_0. We have used the Wigner–Seitz approximation to estimate E_0 for some simple metals and the noble metals; in other cases we have used results from an earlier paper of Hodges.[7] This contribution does not appear in calculations based on the jellium model. The second contribution to μ_p is the positron-electron correlation energy, E_{corr}. We define this as the difference between the ground-state energy of the metal and positron and the ground-state energy calculated in the Hartree approximation. For this contribution, including the ionic lattice in the calculation is prohibitively difficult, and, in common with all other attempts to calculate this quantity, we find it necessary here to use the jellium model. Apart from raising the positron energy by E_0, the strong ion-positron repulsion still leaves the positron energy band remarkably free-electron-like and we feel that use of the jellium approximation

for this problem ought not to be very much worse than its use for the electron-electron correlation energy in a simple metal. We calculate the positron-electron correlation energy for a uniform electron gas using a method that takes into account the nonlinear response of the electron system to the positron. The method breaks down for low electron densities, but we extrapolate our curve to the low-density limit guided by the positron-annihilation-rate-vs-density curves obtained from experiment and from the nonlinear-response theory[8] used here. In his calculations Tong[2] obtained estimates of the correlation energy from the linear response of the electron gas to the positron using a static effective interaction between the electron and positron.

No attention has previously been paid to the work function for positronium for metals. Using a simple argument we are able to conclude that in all the cases we have considered the positronium work function is less than the positron work function.

In Secs. II–IV we discuss, in turn, the zero-point energy, the positron-electron correlation energy, and the surface-dipole contribution, and in Sec. V we discuss the work functions for bare positrons and positronium.

II. POSITRON ZERO-POINT ENERGY

The positron zero-point energy arising from the positron-ion interaction has been calculated previously by Berko and Plaskett[9] for Cu and Al using the Wigner–Seitz approximation and numerically integrating the Schrödinger equation. Hodges[7]

performed calculations for a variety of metals also using the Wigner–Seitz approximation, but using a variational method with an analytic trial wave function. We have calculated the positron zero-point energy E_0 in the Wigner–Seitz approximation by numerical integration of the Schrödinger equation for the cases of Li, Na, Mg, Al, In, Pb, Cu, Ag, and Au. The results are given in column 3 of Table I and in all cases the zero of energy was taken to be the electrostatic potential at the Wigner–Seitz cell radius. Apart from the noble metals, the Hartree potentials used in our calculations above were constructed from the charge density due to the ions[10] and uniformly distributed valence electrons. There is excellent agreement with Hodges's results[7] in all cases except Li. The disagreement in this case is due to a poor trial wave function in the variational calculation. [Hodges's trial wave function vanished at the center of the cell. This is not strictly valid but, except for Li, it is a good approximation in all the cases we have considered because $\psi(0)/\psi(r_{WS})$ < 0.02, where r_{WS} is the radius of the Wigner–Seitz sphere; for Li, however, $\psi(0)/\psi(r_{WS}) \approx 0.15$.] We have adopted Hodges's values for E_0 in the cases of K, Rb, Cs, Zn, Cd, Hg, Ga, Tl, and Sn.

The potentials for the noble metals were constructed in a similar manner except that the outermost d-electron distribution was renormalized[11] so that 10 d electrons were within the Wigner–Seitz sphere.

The calculations indicate that the zero-point energy for the noble metals is considerably great-

TABLE I. Positron zero-point energy E_0, the positron-electron correlation energy E_{corr}, and the dipole-layer contribution D. The last two columns list the estimated values for the positron work function ϕ_p and the positronium work function ϕ_{ps}.

	r_s (a.u.)	E_0 (Ry)	E_{corr} (Ry)	D (Ry)	$\phi_p = -E_{corr} - E_0 - D$ (Ry)	$\phi_{ps} = \phi_e + \phi_p - 0.5$ (Ry)
Li	3.26	0.13	−0.54	0.09	+0.32	+0.05
Na	3.93	0.13	−0.52	0.05	+0.34	+0.04
K	4.86	0.10	−0.51	0.02	+0.38	+0.06
Rb	5.20	0.09	−0.51	0.01	+0.40	+0.06
Cs	5.63	0.08	−0.51	−0.00	+0.42	+0.08
Mg	2.65	0.23	−0.58	0.15	+0.20	−0.03
Zn	2.30	0.34	−0.62	0.21	+0.07	−0.11
Cd	2.59	0.32	−0.59	0.14	+0.13	−0.06
Hg	2.66	0.31	−0.58	0.06	+0.21	+0.04
Al	2.07	0.35	−0.65	0.25	+0.05	−0.14
Ga	2.19	0.33	−0.63	0.15	+0.15	−0.02
In	2.41	0.31	−0.60	0.10	+0.19	−0.02
Tl	2.48	0.30	−0.59	0.03	+0.26	+0.04
Sn	2.21	0.34	−0.63	0.09	+0.20	+0.02
Pb	2.30	0.32	−0.62	0.02	+0.28	+0.07
Cu	2.67	0.31	−0.58	0.34	−0.07	−0.23
Ag	3.01	0.31	−0.55	0.22	+0.02	−0.19
Au	3.01	0.34	−0.55	0.33	−0.12	−0.24

er than that for the alkali metals. The positron is repelled from the ions but is not completely confined to the interstitial regions because of the ensuing unfavorable increase in kinetic energy. However, penetration of the positron into the rather diffuse outer d shell of the noble metals exposes it to a much larger repulsive potential than is experienced in the alkali metals. For similar reasons a decrease in atomic volume and an increase in valency both lead to a larger zero-point energy in the simple metals.

In the case of aluminum a slightly modified plane-wave expansion has been used to calculate the zero-point energy taking into account the full lattice symmetry. There is very good agreement between this and the result of the Wigner–Seitz calculation (the two differ by only ~0.01 Ry), and this gives us confidence in our simple Wigner–Seitz calculations.

III. CORRELATION ENERGY

Estimates of the correlation energy of a positron in an electron gas have been made by Bergersen,[12] Tong,[2] and Bergersen and Carbotte.[13] Bergersen studied the low-electron-density region, performing a variational calculation using a model Hamiltonian. As expected on physical grounds, the positron-electron binding energy (the negative of the correlation energy) approaches the binding energy of free positronium, 0.5 Ry, as the electron density is decreased. However, we feel that the method fails in the metallic range of electron density and at higher density because it accounts only for the interaction between the positron and one privileged electron. The calculations of Tong and Bergersen and Carbotte are based on the linear response of the electron system to the positron. Tong assumed a static effective interaction between the positron and an electron, whereas Bergersen and Carbotte used the full wave-number- and frequency-dependent random-phase-approximation (RPA) dielectric function in constructing their effective interaction. The results of Bergersen and Carbotte are therefore asymptotically correct in the high-density limit and should be reasonable for $r_s \lesssim 1$ a.u. However, for lower densities we feel that the positron-electron interaction is strong and must be treated beyond linear response. We present a method for calculating the positron-electron binding energy that gives the correct behavior for high densities but also treats the positron and the electron as strongly interacting particles.

Consider a system consisting of N electrons and one additional particle, an impurity particle, with the electron mass and charge Ze. The Z dependence of the total Hamiltonian is contained in the interaction term

$$H_{\text{int}} = \frac{-Ze^2 \int d\vec{r} \int d\vec{r}\,' [\rho^+(\vec{r})\rho^-(\vec{r}\,') - \rho^+\rho^-]}{|\vec{r} - \vec{r}\,'|}, \quad (1)$$

where $\rho^-(\vec{r})$, ρ^- are the electron-density operator and mean electron density, respectively, and similarly $\rho^+(\vec{r})$, ρ^+ relate to the impurity. The second term arises from the uniform charge background that we have included to ensure total charge neutrality. If $E_0(Z)$ is the ground-state energy of the system then from Feynman's theorem

$$\frac{dE_0(Z)}{dZ} = \frac{-e^2 \int d\vec{r} \int d\vec{r}\,' [\langle 0| \rho^+(\vec{r})\rho^-(\vec{r}\,')|0\rangle - \rho^+\rho^-]}{|\vec{r} - \vec{r}\,'|}, \quad (2)$$

where $|0\rangle$ is the ground state. Simplifying (2) we have

$$\frac{dE_0(Z)}{dZ} = \frac{-e^2\rho^- \int d\vec{r}\, [g^{+-}(\vec{r}, Z) - 1]}{r}, \quad (3)$$

where $g^{+-}(r, Z)$ is the static-partial-pair distribution function giving the distribution of electrons around the impurity particle for a given charge Z.[8] Integrating (3) with respect to Z from 0 to 1, we have for E_{corr} the positron-electron correlation energy,

$$E_{\text{corr}} = E_0(1) - E_0(0)$$

and, finally, in terms of g^{+-},

$$E_{\text{corr}} = -\frac{3e^2}{r_s^3} \int_0^1 dZ \int_0^\infty dr\, r [g^{+-}(r, Z) - 1]. \quad (4)$$

We see a close relation between the form of the electron polarization cloud around charged impurity particles and the positron correlation energy. We have calculated the $g^{+-}(r, Z)$ following the method of Sjölander and Stott.[8] The integral equation

$$\gamma^{+-}(\vec{q}, Z) = f(\vec{q}) + f(\vec{q}) \int \frac{d\vec{q}\,'}{(2\pi)^3} \left(\frac{\vec{q} \cdot \vec{q}\,'}{q'^2} \right) \gamma^{+-}(\vec{q} - \vec{q}\,', Z), \quad (5)$$

was solved numerically for $\gamma^{+-}(\vec{q}, Z)$ and, using the relation

$$g^{+-}(r, Z) - 1 = \int \frac{d\vec{q}}{(2\pi)^3} \gamma^{+-}(\vec{q}, Z) e^{-i\vec{q}\cdot\vec{r}}, \quad (6)$$

$g^{+-}(r, Z)$ was calculated for values of Z between 0 and 1. In the integral equation (5), $f(\vec{q})$ is just the leading term in a series expansion of $\gamma^{+-}(\vec{q}, Z)$ in powers of Z. It would therefore be the result obtained for γ^{+-} in a perturbation calculation taken to first order in the positron-electron interaction. Explicitly, we have

$$f(\vec{q}) = \frac{Z\hbar}{\pi\rho^+\rho^-} \int_0^\infty d\omega \, \text{Im}\left[\left(\frac{1}{\epsilon(\vec{q}, \omega)} - 1 \right) \chi_0^+(\vec{q}, \omega) \right], \quad (7)$$

where $\epsilon(q, \omega)$ is the frequency- and wave-number-dependent dielectric function for the electron gas

which we take from Singwi et al.[14] and $\chi_0^+(\vec{q}, \omega)$ is the free-particle response function for the odd particle given by

$$\chi_0^+(\vec{q}, \omega) = \frac{\rho^+}{\hbar}\left(\frac{1}{\omega - (\hbar^2 q^2/2m) + i\eta}\right.$$

$$\left. - \frac{1}{\omega + (\hbar^2 q^2/2m) + i\eta}\right) , \quad (8)$$

η being a positive infinitesimal.

The correlation energy has been calculated for a number of values of r_s using (4) and the $\gamma^{+-}(\vec{q}, Z)$ obtained from the integral equation. Similar calculations have been performed with $\gamma^{+-}(\vec{q}, Z) = f(\vec{q})$ taking account only of the linear response of the electron system to the positron. The results are illustrated in Fig. 1. We have plotted positron-electron binding energy against r_s where r_s is an electron-density parameter defined by $\rho^- = [\frac{1}{3}(4\pi r_s^3)]^{-1}$. Our linear-response and nonlinear-response results are plotted. The results from linear response are almost equivalent to those of Bergersen and Carbotte; where the latter authors used the RPA dielectric function we used the im-

proved dielectric function of Singwi et al.[14] The results of Tong[2] are also included for comparison.

Linear and nonlinear responses give similar results for small r_s, the positron-electron binding energy being large due to the piling up of electrons around the positron in the region of large attractive potential. The binding energies calculated by Tong[2] are very much smaller than even the linear-response results. Bergersen and Carbotte[13] have shown that this discrepancy has arisen because the static effective positron-electron interaction adopted by Tong results in the omission of the large plasmon contribution to the positron-electron binding energy.

For values of r_s somewhat larger than 1 a.u., linear response gives too small a value for the binding energy, which falls below the positronium binding energy of 0.5 Ry. It is clear how this has happened. From a comparison of the positron-annihilation rate λ calculated from linear-response theory and the experimental results[15] illustrated in Fig. 2, since $g^{+-}(r = 0) \propto \lambda$, we see that linear-response theory underestimates the electron density at the position of the positron.
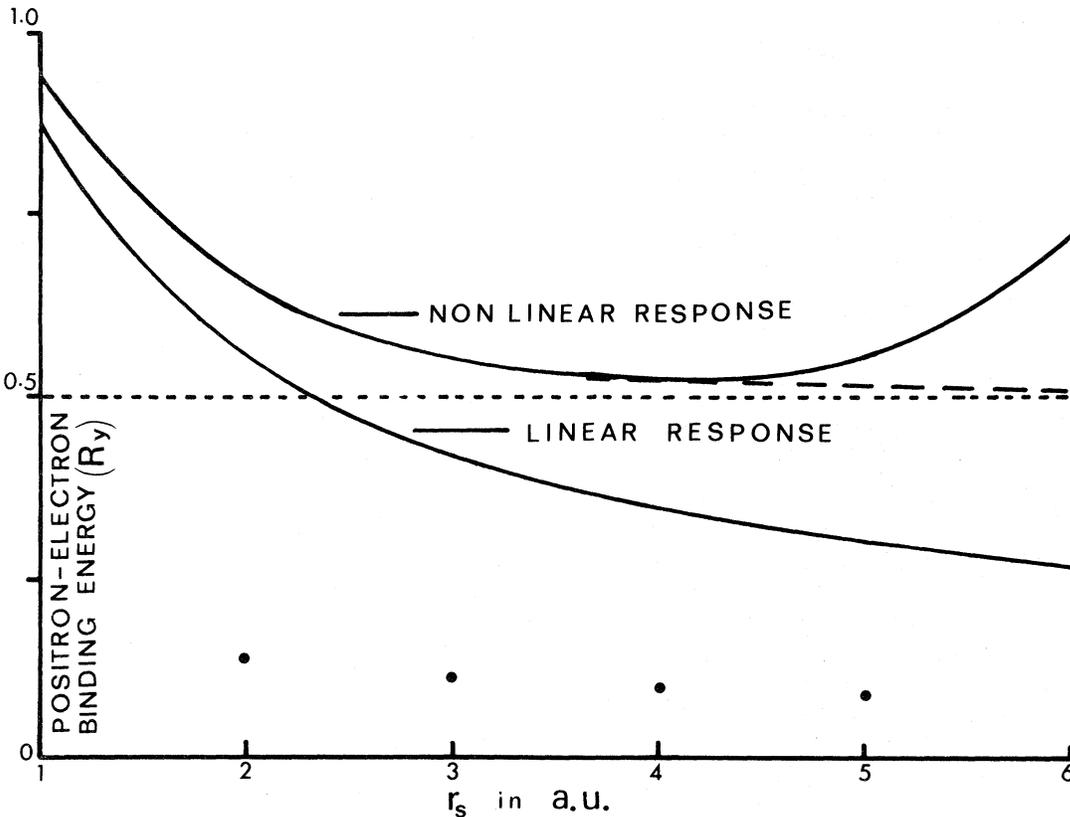
FIG. 1. Positron-electron binding energy ($= -E_{corr}$) plotted against r_s for linear and nonlinear response within the jellium model. The dashed curve is the extrapolation to the low-density limit. The points (●) are the results of Tong (Ref. 2).

Now charge is conserved so that

$$\int d\vec{r}\,[g^{+-}(\vec{r})-1] = \tfrac{1}{3}(4\pi r_s^3)\,,$$

and we conclude that linear response underestimates the electron density in the region of large attractive potential near the positron and hence underestimates the binding energy.

The binding energy calculated from nonlinear response lies above and close to 0.5 Ry over most of the metallic-density region. However, it increases rapidly beyond $r_s = 5$ a.u.; this behavior is unphysical and is remarkably similar to the behavior of the positron-annihilation rates in the same region of electron density calculated using the integral equation (5).[8] It is clear that for these larger values of r_s the electron density near to the positron is overestimated by the theory of Sjölander and Stott[8] and this results in an overestimate of the potential energy contribution to the positron binding energy. We have discarded the values of the binding energy for $r_s > 3.5$ a.u. calculated from the nonlinear-response theory and instead, influenced strongly by the similarity between the binding-energy curve and the positron-annihilation-rate curve both calculated from the integral equation (5), we have sketched in the binding energy for $r_s > 3.5$ a.u., by comparison with the experimental annihilation rates, as an asymptote from above to 0.5 Ry.

In column 4 of Table I are values of the correlation energy appropriate to the mean valence electron density of the metals listed. The simple metals, apart from those with the highest electron densities, namely, Zn, Al, Ga, Sn, and Pb, are in a region of r_s where we believe the correlation energy is slowly varying and our extrapolation procedure for $r_s > 3.5$ a.u. should lead to little error. Those metals with high electron densities are in a region of r_s where the method of calculating $g^{+-}(r)$ beyond linear response leads to good values for the annihilation rate, and we are confident that this implies good correlation energies.

We have neglected completely lattice effects and effects due to core electrons, since we do not at present see a convenient way of incorporating them into our theory for the correlation energy. A rough estimate of the effect of positron-core-electron correlation may be obtained for the simple metals by comparing the core to conduction-electron annihilation rates. The arguments used above to explain the close correspondence between the conduction-electron–positron annihilation rate and binding energy in Figs. 1 and 2 would also suggest that the core-to-conduction correlation energies ought to scale very roughly as the core-to-conduction annihilation rates (strictly speaking, the enhanced parts of these annihilation rates). An estimate of the core annihilation rate may be obtained from Fig. 2 as the difference between the experimental points and the theoretical curves representing the conduction-electron contribution to the annihilation rate.

We have least confidence in our results for the noble metals since positron-core-electron correlations must be important in these cases. It is clear from the bell-like shape of the angular-correlation
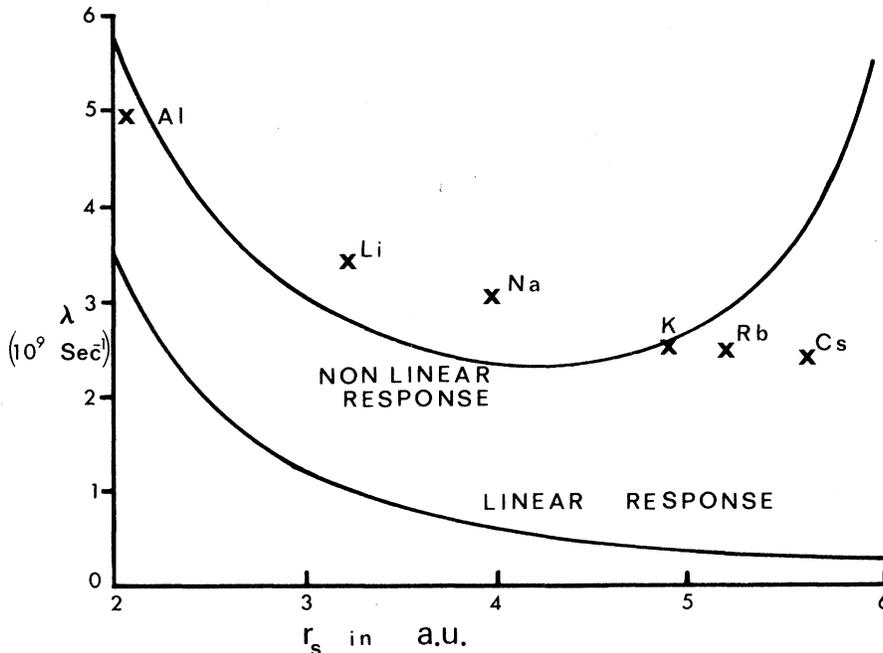
FIG. 2. Positron annihilation rate λ plotted against r_s for linear and nonlinear response taken from Sjölander and Stott (Ref. 8). The experimental points are taken from Weisberg and Berko (Ref. 15).

curves[16] and the size of the annihilation rate that the positron penetrates far into the d shell and does not sample the s electron only. Our estimates of the positron-electron correlation energy for the noble metals are based on one free electron per atom and therefore should give upper limits for the correlation energy.

IV. SURFACE CONTRIBUTION

In this section we shall discuss estimates of the surface-dipole barrier contribution D to the positron work function. In his calculation of positron work functions, Tong[2] has used values of D calculated by Lang and Kohn[5] for the uniform-positive-background, or jellium model. However, as Heine and Hodges[6] have shown, for simple metals other than the alkalis and alkaline earths the surface-dipole-layer potential may be considerably different from the value calculated in the jellium model. This is because the pseudopotential of these elements is considerably more attractive than the jellium potential, and the electron Fermi level, or internal chemical potential μ_e, becomes more negative than that for jellium. This reduces the tendency of the electrons to "spill over" into the vacuum and thus reduces the magnitude of the dipole barrier D. In fact, the change in D almost cancels the change in μ_e, leaving the electron work function relatively insensitive to the strength of the electron pseudopotential, a result which is also borne out by the work of Lang and Kohn. Since the value of D is much more sensitive to the electron pseudopotential than is the electron work function, we have for the purposes of the present calculation used the values of D given by Heine and Hodges, where the strength of the pseudopotential is taken into account through the experimental metallic cohesive energies used in their calculations. These values of D, given in Table I, column 5, are probably accurate to within 0.05 Ry.

Estimation of D for the noble metals is complicated by the effects of s-d hybridization. We have modified the method of Heine and Hodges for these elements as follows.

First, we calculate the value of the internal Fermi level μ_e in the absence of s-d hybridization by using the cohesive energies calculated by Watson and Ehrenreich[11] for renormalized noble atoms in which the s-d interaction has not yet been "switched on." At this stage we take the effective mass ratio $m^*/m = 1$ and the valence $Z = 1$. For gold, which was not treated by Watson and Ehrenreich, we have simply corrected the experimental cohesive energy by a guess at the hybridization energy, which we take to be the same as for Cu, i.e., 2.25 eV/atom. The results are presented in column 4 of Table II. The values of μ_e are fairly large and negative, as we might expect for

TABLE II. For the noble metals—the electron work function ϕ_e, the cohesive energy U, and internal Fermi level μ_e in the absence of s-d interaction; the band broadening Δ and the internal Fermi level μ_e^* and dipole barrier D taking hybridization into account.

	ϕ_e (Ry)	U (Ry)	μ_e (Ry)	Δ (Ry)	μ_e^* (Ry)	D (Ry)
Cu	0.34	0.07	-0.11	0.11	0.00	0.34
Ag	0.29	0.09	-0.22	0.15	-0.07	0.22
Au	0.38	0.11	-0.33	0.28	-0.05	0.33

metals which are relatively electronegative and attract electrons strongly.

On switching on the s-d hybridization interaction, the conduction band broadens in energy considerably over the free-electron width. Since the bottom of the conduction band Γ_1 does not hybridize, the effect is to raise the Fermi level by the amount of band broadening due to s-d hybridization. We have estimated the amount of band broadening from the band-structure calculations of Ballinger and Marshall[17] for Cu and Ag and Christensen and Seraphin[18] for Au (see column 5, Table II). The new values of the Fermi level (μ_e^*) are given in column 6 of Table II. In column 2 of this table we list the experimental electron work function ϕ_e for the noble metals quoted by Lang and Kohn[5] which we use to calculate the dipole-moment barrier $D = \phi_e + \mu_e^*$. The values of D taking into account s-d interaction are given in column 7. They seem surprisingly large for these electronegative metals (compare, for example, the values of D for Hg, Tl, and Pb). A large contribution to D in the noble metals probably comes from the d band which contains 10 times the number of electrons in the s-p band. However, we should caution against placing too much confidence in these results for the noble metals, especially in view of our guess at the hybridization energy of gold and the fact that bandwidths vary considerably between different band-structure calculations. Our values of D are probably only accurate to within 0.1 Ry or so for these metals.

V. DISCUSSION

Our estimates of the positron work function are listed in column 6 of Table I. The positron-electron correlations tend to bind the positron to the metal, whereas the positron-ion interaction and the surface-dipole layer both tend to squeeze the positron out of the metal. We have obtained positive work functions for the positron for all the simple metals we have considered. The smallest work functions are those for Al and Zn, and in these cases we do not have complete confidence in the sign of ϕ_p. However, our greatest source of error will be the neglect of positron-core-electron correlation, and this should tend to further increase

the magnitude of E_{corr}, that is, increase our estimate of ϕ_p. The variation of ϕ_p from metal to metal can easily be understood. Polyvalent metals with high valence-electron density, e.g., Zn, Al, and In, generally have smaller ϕ_p because of the large zero-point energy and dipole-layer potential; a more negative correlation energy balances this to some extent. Exceptions to this rough rule are Pb, Sn, and Tl; in these cases the electron pseudopotential is strongly attractive, leading to a reduced dipole-layer potential, and consequently ϕ_p is large.

The noble metals all appear to have smaller positron work functions than any of the simple metals we have considered. The large E_0 and large D both contribute to this. The d bands in the noble metals appear to give rise to an effective valence larger than unity as far as ϕ_p is concerned. The errors are large in the case of the noble metals; however, we feel fairly confident that gold has a negative work function. We are unable to conclude the sign of ϕ_p with any confidence for Cu or Ag.

In the case of gold the three contributions to the positron work function are approximately of the same magnitude and the negative work function results from considerable cancellation between these different contributions. In view of this we feel that it would be misleading to attribute the negative work function for gold to any one mechanism.

So far we have been concerned with the positron work function, that is, the work needed to strip the positron of its electron polarization cloud and take it far from the metal. We have concluded that this process is probably energetically unfavorable for all metals except Au. We have seen that the positron-electron binding energy is roughly 0.5 Ry: This large energy prompts us to ask whether it is necessary to strip the positron of its polarization cloud in order to take it from the metal. The polarization cloud may be dragged along as the positron is taken from the metal, and if it consists of one electron only we will have removed the con-

stituents of a positronium atom. What are the energetics of such a process or, in other words, what is the work function for positronium? To take a bare positron from the metal requires an amount of work ϕ_p; to take out an electron requires, in addition, the electron work function ϕ_e. However, on forming positronium we recover 0.5 Ry, the positronium binding energy. Denoting the positronium work function by ϕ_{ps} we have

$$\phi_{ps} = \phi_p + \phi_e - 0.5 \text{ Ry}.$$

None of the metals considered here has an electron work function as large as 0.5 Ry, and so it requires less work to remove positronium from these metals than just the bare positron. In column 7 of Table I we have listed values for ϕ_{ps}; the values of ϕ_e are those quoted by Heine and Hodges,[6] and, for the noble metals, by Lang and Kohn.[5] Now for emission of positronium we estimate that in addition to the noble metals several of the simple metals have negative work functions. The positronium work functions are all small in magnitude compared with the E_0 and, consequently, there is uncertainty in cases such as Mg, In, Ga, and Sn, and we hesitate to conclude the sign of ϕ_{ps} for these metals.

Finally, we mention one effect of a negative positronium work function related to defects in metals. It is clear that if there is a negative positronium work function for a particular metal, as seems likely for Al, to take one example, then it will be energetically favorable for positronium to be formed in voids in the material. The limiting value of the binding energy of positronium to the void as the magnitude of the void increases is simply the negative of the positronium work function.

ACKNOWLEDGMENT

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