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Positronium at surfaces

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We analyze the problem of a positron at a jellium surface assuming that it is a weakly physisorbed positronium.

Recently there has been a great deal of interest in the behavior of modest energy ($E \cong 1$ keV) positron beams interacting with solids.[1] These positrons when implanted in a metal stop within a few hundred angstroms of the surface, thermalize, and then diffuse to the surface. At the surface they can be and are (with some branching ratio) emitted as positrons (small negative work function) or positronium (bigger negative work function), or are trapped in a surface state. When the metal, exposed to the positron beam, is heated the trapped positrons are desorbed as Ps whose binding energy, E_{Ps}, to the surface is typically several tenths of an eV.[2] ($E_{\mathrm{Ps}} \leq 0.5$ eV for A1.)

The positron (positronium) trapped at the surface of a simple metal is a very interesting quantum-mechanical object. It is light and it clearly has very strong correlations with the inhomogeneous electron fluid at the surface. To date theoretical descriptions[3] have started with an image potential at large distances and used the calculated electron charge density at the surface in a metal in the absence of the positron as a starting point for calculating energies at small distances. The positron is then assumed to exist in this *slowly varying* inhomogeneous electron gas. Such descriptions encounter some difficulty since the electron density is rapidly varying (on the scale of the energies involved), outside a metal surface,[4] and realistically the charge density in such a picture would be severely distorted by the interaction with the positron.

In a low density electron gas it is known that it is more appropriate to think of the positron as forming positronium[5] Ps with an electron which rapidly exchanges with the host material. This approach works very well at densities which are about a factor of ten lower than those in ordinary metals. However, even at metallic densities it gives some qualitatively accurate results for the lifetime and angular correlation.[5]

The density outside a metal falls off from the surface dropping to one tenth its value at about 0.7 Å from the end of the jellium background. In this case it is certainly sensible to assume that most of the correlation between e^+ and the electrons in the metal may be accounted for by thinking of the e^+ surface state as Ps. Of course the Ps at large distances is attracted to the surface by a weak $1/Z^3$ van der Waals polarization potential.[6] At short distances the effective potential (if it exists) is more complicated. The singular potential begins to level off[7] and ultimately becomes repulsive. The repulsion comes from the short-range repulsion between electrons in the metal of the same spin as the one on the Ps.[8] Electrons of the opposite spin feel a net weak attraction characteristic of Ps^-. Of course the bound e^- exchanges rapidly with the bulk electrons. Unlike the long-range part, the short-range part, as we shall see, can only be estimated.

This picture, despite its drawbacks, leads to a new and physically consistent picture of the surface state whose properties may be related to experiments. The reason we believe that such a picture is consistent is that $E_{\mathrm{Ps}} \cong 0.5$ eV implies, by simple uncertainty principle arguments (small Ps mass), that the mean distance from the surface of Ps is about 2.5 Å. In addition $E_{\mathrm{Ps}} < E_B \cong 6.5$ eV, the binding energy of Ps. Thus Ps in its surface state can be thought of as a well-defined object. A rough picture of the physical situation is shown in Fig. 1.

In general the coupling of the Ps system (no exchange of the e^- in the Ps atom) to the metal is simply the sum of direct Coulomb interactions between e^+ and the e^- in Ps and the e^- in the metal. However at large distances $Z > 1$ Å (roughly the diameter of the Ps atom) the potential energy of interaction between Ps and the surface is determined by the coupling to the density fluctuations of the unperturbed metal. The Ps atom has an effective coupling to surface plasmons with a Hamiltonian[9] ($\hbar = 1$),

$$H = H_p' + \sum_{k_+} \sigma_{k_+} a_{k_+}^\dagger a_{k_+} + e\Phi(\mathbf{R} - \mathbf{r}/2) - e\Phi(\mathbf{R} + \mathbf{r}/2). \tag{1}$$

In Eq. (1) H_p' is the Hamiltonian for vacuum Ps with a center of mass (CM) coordinate $\mathbf{R} \equiv Z\hat{\mathbf{z}}$ and a relative coordinate $\mathbf{r}$. The operator a_{k_+} ($a_{k_+}^\dagger$) is the annihilation (creation) operator for surface plasmons (two-dimensional wave vector k_+ and frequency σ_{k_+}). The electrostatic potential $\Phi(r)$ of the surface plasmon is[6,8]

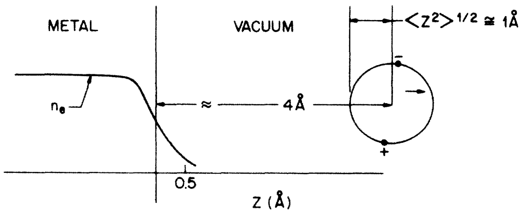

FIG. 1. Schematic of the surface Ps and the electron density profile of the metal.

$$\Phi(r) = \sum_{\mathbf{k}_+} f(k_+)(a_{k_+} e^{-k_+ z + i\mathbf{k}_+\cdot\mathbf{r}} + \mathrm{H.c.}) \tag{2}$$

with

$$f^2(k_+) = \pi\omega_p^2(2k_+\sigma_{k_+})^{-1} \tag{3}$$

and ω_p is the bulk plasmon frequency. At large R,

$$\Phi(\mathbf{R}-\mathbf{r}/2) - \Phi(\mathbf{R}+\mathbf{r}/2) \cong \mathbf{r}\cdot\nabla_{\mathbf{R}}\Phi(\mathbf{R}) \,. \tag{4}$$

This approximation gives the leading large distance behavior.

To obtain the effective Ps atom potential we calculate the second-order shift in energy of the Ps atom due to ϕ assuming that the CM coordinate of Ps is fixed, i.e.,

$$\Delta E_2(Z) = -\sum_{n,k_+} \frac{|\langle n,k_+ | e\mathbf{r}\cdot\nabla_{\mathbf{R}}\Phi(\mathbf{R}) | 0,0\rangle|^2}{E_n - E_0 + \sigma_{k_+}} \tag{5}$$

In this expression $|n,k_+\rangle$ specifies the internal state of positronium, i.e., $n=0$ is the ground state and k_+ the momentum of the one surface plasmon with energy σ_{k_+}. The internal coordinate $\mathbf{r}$ connects $n=0$ to all internal states with angular momentum one. The positronium atom in its ground state at $R=Z$ emits a surface plasmon and goes to an excited P state eventually reabsorbing the surface plasmon and returning to the ground state.

This procedure, "nailing down" the CM and calculating to lowest order in perturbation theory, is only valid at large Z (small E_{Ps}) where the important surface plasmon momenta are small. In this case we take $\sigma_{k_+} \cong \omega_p/\sqrt{2} \equiv \omega_s$ and Eq. (5) becomes

$$\Delta E_2(Z) = -(e^2\omega_s/2)\int dk_+ k_+^2 e^{-2k_+Z}\alpha(\omega_s). \tag{6}$$

In addition if we approximate the polarizability,

$$\alpha(\omega_s) = 2\sum_n \frac{\langle 0|z|n\rangle\langle n|z|0\rangle}{\omega_s + E_n - E_0} \,. \tag{7}$$

by

$$\alpha \cong \frac{2}{\omega_s + \bar{E}_{n0}}\langle 0|z^2|0\rangle = \frac{8r_0^2}{\omega_s + \bar{E}_{n0}} \tag{8}$$

with $r_0 = \hbar/me^2 \cong 0.5$ Å then,

$$\Delta E_2 \cong -\left[\frac{e^2}{r_0}\right]\left[\frac{r_0}{Z}\right]^3\left[\frac{\omega_s}{\omega_s + \bar{E}_{n0}}\right] \,. \tag{9}$$

The quantity $\bar{E}_{n0}$ is slightly larger than the $1S-2P$ energy difference for Ps. A rough calculation shows that $\bar{E}_{n0} \cong \frac{3}{16}me^4 \cong 5$ eV.

At shorter distances we cannot "nail" the CM down. We must include the CM kinetic energy, i.e., larger k_+ does lead to a recoil of the CM. The problem is more complicated. However, because of the fact that the coupling [Eq. (12)] is exponential in character, we know that typical k_+ are of order $1/Z$, i.e., the CM recoil parallel to the plane will be comparable to the kinetic energy perpendicular to the surface after the Schrödinger equation is solved. In addition, since the energy E_n and σ_{k_+} increase with k_+ we expect, at distances of roughly 1 Å, a softening of the $1/Z^3$ potential. Such softening has been considered by other authors.[7]

In this 1-Å regime and at still shorter distances several new physical effects characteristic of weak physisorption come into play.[6,8] The edge of the rather large "rigid" Ps atom begins to encounter a very dilute electron gas. The interaction is best described by adding up an effective metallic electron Ps atom pseudopotential.[10] The screening of the e^-e^+ interaction in the Ps atom may be neglected.[11] This potential is made up of two parts. A rather weak long range attractive (van der Waals) part which in vacuum accounts for the Ps$^-$ and in this problem is correctly taken into account by the coupling to surface plasmons of shorter wavelengths. In addition there is a short-range repulsive pseudopotential. The repulsive part of the potential comes from the fact that for a dilute electron gas ($E_F \ll E_B$) the conduction electrons, with spins parallel to the electron in the pseudo-Ps atom, must orthogonalize their wave function with respect to the tightly bound electron.

The repulsive part of the interaction is well simulated by a Gaussian pseudopotential,

$$U(r) = U_0 e^{-r^2\eta^2} \tag{10}$$

where U_0 is 4—8 eV (of the order of E_B) and η^{-1} is of the order of the electron positronium atom scattering length, i.e., of order r_0,[10] the size of the Ps atom. The exact functional form of $U(r)$ is unimportant since it will be included phenomenologically. To obtain the Ps atom surface potential we must add up the effects of $U(r)$ from all the electrons in the metal. Assuming that they are noninteracting and contained in a box whose height is determined by the work function we may very roughly, since the important energies are small compared to internal Ps binding energy or the electron work function, calculate the effects of $U(r)$ in second-order perturbation theory. Such a procedure, since the electrons in the metal have a rapidly varying wave function compared to η^{-1}, yields

$$\Delta E_1(Z) = V_0 e^{-(Z+Z_0)^2\eta^2}, \quad Z > 1\ \text{Å} \,. \tag{11}$$

In Eq. (11), Z is again the CM coordinate of Ps and Z_0 characterizes the ambiguities in measuring the origin in the real material relative to our simple model. The spatial dependence of the energy ΔE_1 is determined by the size of the Ps atom (scattering length) and not by the characteristic fall off length of the electron gas. This results from the fact that the electron density fall off distance is much shorter than the Ps diameter, and thus the overlap integral of the electron density with the pseudopotential has a characteristic fall off distance equal to the size of the Ps atom. V_0 is proportional to U_0 and some function of η and the work function of the metal which can be calculated in simple models. However, it is most appropriate to think of V_0 and Z_0 and η as parameters which are known only approximately and express our *ignorance* of the short-range many-body aspects of the Ps metal interactions. High-order effects will still result in a potential of the form given in Eq. (11). They will also lead a dramatic decrease of the electron density in the neighborhood of the edge of the Ps atom which should make our surface Ps model even better.

Combining ΔE_1 with ΔE_2, the attractive part of the potential, gives a total $V(Z)$ which is sketched in Fig. 2 (dashed curve). In this figure we have taken $Z_0 \cong 1$ Å, $V_0 = 6$ eV to fit the correct (for Al) work function for Ps, $\eta = 4$ Å^{-1}, and have cut off the incoming $1/Z^3$ potential at 1 Å. This procedure is consistent with the flattening of the $1/Z^3$ due to recoil effects and plasmon dispersion as discussed earlier. In order to calculate properties of surface Ps we have replaced the dashed potential by the solid potential and treated d as a single parameter to *fit* the binding energy. Since the "short-range" potential is surely sharply rising above zero energy for all those metals which emit Ps and since we know that $1/Z^3$ is softened, the proposed form is probably as accurate a description as we can get. For $d = 1.08$ Å we obtain a binding energy of 0.5 eV, the known E_{Ps} for Al.[2]

The important point here is *not* agreement of binding energies since we have *at least* one parameter in our model but the *other* predictions one makes when considering such a picture.

(i) The van der Waals potential is almost universal for most simple metals and even for insulators. The softening region and the position of the hard core is mostly in the 1 Å range, so that we can simply understand why $|E_{Ps}|$ is always a few tenths of an eV.[1,12] Thinking about a single e^+ bound to a surface with energy $|E_{e^+}|$ by the combination of a universal image potential and a repulsive self-energy effect leads to some difficulties. In such a picture $|E_{e^+}| = |E_{\text{Ps}}| - |W_{e^-}| + 6.5$ eV with W_{e^-} the work function for the electron. When submonolayers of, for example, alkalis are chemisorbed onto the surface of Ni (Ref. 12) the work function of the electron is changed by several eV yet the E_{Ps} is still roughly a few tenths of an eV. This would imply that the binding of e^+ must change by several volts and mirror the changes in the electron work function, a phenomenon, while not impossible, is not simply understood.

(ii) Recent very beautiful measurements of the lifetime of e^+ trapped at the surface of Al seem to substantiate our model.[13] The observed surface e^+ lifetime τ was found to be 580 ± 10 psec; about 15% *longer than the spin-averaged vacuum Ps lifetime* $\tau_0 \cong 500$ psec.[14] In our picture Ps is rattling back and forth on a very short time scale ($t_R \cong \hbar / E_{\text{Ps}} \cong 10^{-15}$ sec). When it is in the core region its electron will spin exchange with the unpolarized e^- of the solid. Since the Ps is mostly in a region of very low electron density the lifetime should be close to τ_0.

While the binding energy is quite sensitive to d, the positronium atom spends most of its time in the van der Waals potential region where it experiences a $1/Z^3$ potential, i.e., $\int_1^\infty \psi^2(Z)dz \cong 0.8$ for $E_{\text{Ps}} = 0.5$ eV. In this region the electric field from the image potential polarizes the Ps atom, i.e., mixes in excited P states and, as suggested in Ref. 13, lengthens the lifetime. For $Z > 1$ Å we can reliably calculate the probability δ of surface Ps being in the excited P state, i.e.,

$$\delta = \frac{e^2}{r_0} \frac{\hbar\omega_s}{(\hbar\omega_s + \bar{E}_{n0})^2} \left[\frac{r_0}{\bar{Z}} \right]^3 . \tag{12}$$

Here

$$\bar{Z}^{-3} \equiv \int_1^\infty \frac{\psi^2(Z)dz}{Z^3} \sim E_{\text{Ps}}^{3/2} . \tag{13}$$

and $\tau/\tau_0 \cong 1 + \delta$. We have found $\delta \cong 9\%$ for $E_{\text{Ps}} = 0.5$ eV for Al ($\omega_p \cong 15$ eV). We can also predict the functional form for low E_{Ps} of τ/τ_0 (see Fig. 3). We conjecture that the lifetime should show a maximum, decreasing at large E_{Ps} to the positron lifetime in a metal. While we cannot calculate the exact position of the maximum in τ we expect it to occur for $E_{\text{Ps}} > 1$ eV. The experimental value for Al is shown as the solid dot in Fig. 3 in good (possibly too good) agreement with the theory.

(iii) If this picture (Ps weakly bound to the surface) is correct, then angular correlation of the 2γ annihilation radiation (ACAR) can yield important information about it. Recent experiments[15] on clean Al(100) show an isotropic ACAR with a full width at half maximum of $7.1 \pm 0.5 \times 10^{-3}$ radians. This is about 50% narrower than the bulk ACAR curves. If the main correlation is Ps the CM motion will be the only thing which will show up

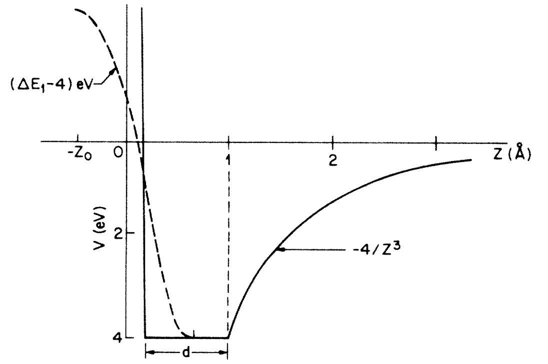

FIG. 2. The effective potential for Ps interacting with a surface. The solid curve is the parametrized version of the more accurate dashed curve.

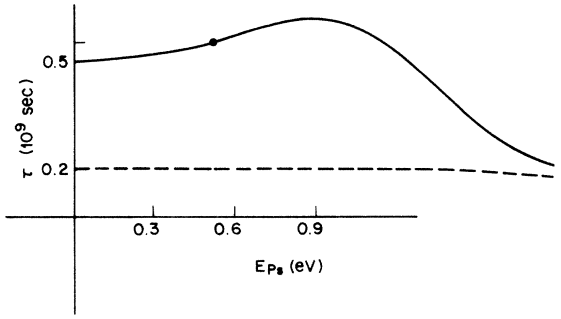

FIG. 3. The curve is meant to indicate the qualitative behavior of the surface Ps lifetime as a function of E_{Ps}. The value 0.5×10^{-9} sec in the rough spin-averaged value, while 0.2×10^{-9} is an approximate lifetime in a metal like Al. The dot is the experimental point of Ref. 12.

in the width of the ACAR curves. In our Ps model, looking parallel to the surface we see the CM motion in $V(Z)$ (Fig. 2) and the shape of the angular correlation is simply related to the Fourier transform of the wave function in $V(Z)$, i.e., approximately a Lorentzian squared with $\langle k^2\rangle_\perp^{1/2}=0.6$ Å^{-1}, which converts to

$$\Delta\theta_{\parallel}=2\langle k^2\rangle_\perp^{1/2}\frac{\hbar}{mc}\cong 4.8\times 10^{-3}\text{ rad.} \tag{14}$$

Perpendicular to the surface the situation is more complicated. We have pointed out that the average recoil momentum of the CM due to emission of a surface plasmon [Eq. (5)] is comparable to the Z momentum. However in our picture (dipole coupling) this plasmon emission leads to an excited P state of Ps which does *not* annihilate. Fortunately there are other processes, which are of the same order and which do contribute to the ACAR (see Fig. 4). Such virtual plasmon processes are higher order in the metal-electron Ps interaction. They lead to an intermediate state with a metallic electron correlated to Ps in its ground state. These processes give rise to a parallel spread of CM momentum comparable to $\langle k^2\rangle_\perp^{1/2}$. These effects can in fact be thought of as a Ps$^-$ like, i.e., polaronic (electron polarization) in the plane.[16] This picture then suggests a rather isotropic Lorentzian-squared angular distribution with a 2.4 mrad half-width. This is about 40% narrower than the observed profile. However, in the experiment, other effects at the surface, steps, etc. could lead to an experimental width which is broader and a line which is more isotropic than the intrinsic width on a perfect surface.

The conventional e^+ model at the surfaces has its difficulties. It is hard to make the binding independent of work-function changes due to the addition of monolayer coverages of the surface. Estimates of the lifetime are complicated and the angular correlation is broader than the experiment. The Ps model is appealing because it is easy to understand why the binding is universal and weak, and why the lifetime should be longer than the spin-averaged vacuum value. The fact that the angular correlation is narrower than experiment is also encouraging. Most important though is that the Ps model agrees with one's physical intuition that at low electron densities the major correlations between e^+ and e^- are accounted for by vacuum Ps. This does *not* mean that the Ps picture is completely accurate, but merely that it is a good starting point. The correct picture of the e^+ surface state probably lies between these two extreme starting points. Clarification of this rather basic absorption problem will involve a strong interplay between theory and experiment.

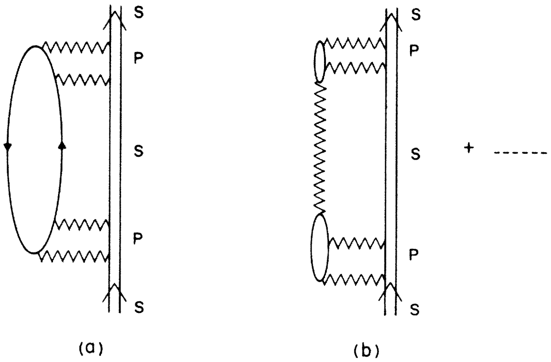

FIG. 4. Feynman diagrams which give rise to in-plane recoil effects which broaden the annihilation angular width looking perpendicular to the surface. The double line is Ps, the single solid line an electron or hole in the Fermi sea, and the wiggly line a surface plasmon.

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[1] A. P. Mills, Jr., *Lecture Notes for 83rd Session of the International School of Physics, "Enrico Fermi", Varenna, Italy, 1981,* edited by W. Brandt and A. Dupasquier (North-Holland, Amsterdam, 1983).

[2] A. P. Mills and L. N. Pfeiffer, Phys. Rev. Lett. **43**, 1961 (1979).

[3] J. Oliva, Phys. Rev. B **21**, 4925 (1980); R. M. Niemenen and M. J. Puska, Phys. Rev. Lett. **50**, 218 (1983); R. M. Niemenen, M. J. Puska, and M. Manninen, *ibid.* **53**, 1298 (1984).

[4] H. D. Lang and W. Kohn, Phys. Rev. B **1**, 4550 (1970).

[5] A. Maldague, Phys. Rev. B **20**, 21 (1979).

[6] E. Zaremba and W. Kohn, Phys. Rev. B **15**, 1769 (1977).

[7] J. R. Manson and R. H. Ritchie, Phys. Rev. B **29**, 1084 (1984).

[8] M. Manninen, J. K. Noreskov, M. J. Puska, and C. Umrigar, Phys. Rev. B **29**, 2314 (1984).

[9] R. H. Ritchie, Phys. Lett. **38A**, 189 (1972); G. D. Mahan, Phys. Rev. B **5**, 739 (1972).

[10] See the articles by M. Cohen and V. Heine in *Solid State Physics,* edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1970), Vol. 24. Equation 10 is adequate for a non-magnetic material since there are always equal numbers of spin-up and spin-down electrons. In magnetic materials where electrons near the Fermi surface have predominantly one spin direction it may be possible to stabilize surface triplet Ps.

[11] A. Held and S. Kahana, Can. J. Phys. **42**, 1908 (1964).

[12] A. Köymen, D. W. Gidley, and W. Capehart (unpublished).

[13] K. G. Lynn, W. E. Frieze, and P. J. Schulz, Phys. Rev. Lett. **52**, 1137 (1984).

[14] The best theoretical value was $\tau=400$ psec (Ref. 3). Recently this calculation was corrected by a somewhat *ad hoc* procedure to give a larger τ.

[15] K. G. Lynn, A. P. Mills, Jr., R. N. West, S. Berko, K. F. Canter, and L. O. Roellig, Phys. Rev. Lett. **54**, 1702 (1985).

[16] We would like to thank K. Lynn, S. Berko, and A. Mills for mentioning this idea to us.