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Positron states in vacancies and voids

G M Dunn†, Kjeld O Jensen‡ and Alison B Walker‡

† Physics Department, Royal Holloway and Bedford New College, University of London, Egham Hill, Egham, Surrey TW20 OEX, UK

‡ School of Physics, University of East Anglia, Norwich NR4 7TJ, UK

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Abstract. We have calculated the positron wavefunctions and annihilation rates in voids in aluminium as functions of void radius using density functional theory with the non-local approximation to the positron–electron correlation potential developed by Jensen and Walker. Our calculations show the gradual evolution of the positron state, as the radius increases, from a state extending over the whole of the defect volume in monovacancies to a state localized at the void surface in large voids. We find that for voids with radii larger than about 5 Å the lifetime is independent of void size.

1. Introduction

Understanding the behaviour of open volume defects in metals is an area of immense technological importance, for instance in studies of radiation damage. In this area, positron lifetime spectroscopy makes an important contribution as a non-destructive technique that is uniquely capable of detecting voids throughout the size range, from monovacancies to large cavities, even at very low concentrations (Sharpe 1985). Examples of applications of this technique are in studies of vacancy clustering (Eldrup *et al* 1976) and the influence of temperature on processes involved in gas bubble growth and dynamics (Nieminen 1989).

For unambiguous comparisons of lifetime data with model predictions of the defect behaviour, theoretical modelling of positron states is required. Such theories exist but only in certain limits. One limit is where the void is so small (i.e. only a few atoms are missing) that the positron state extends throughout the void, with a maximum probability for the positron being in the void centre. In this case, the positron lifetime increases with cavity size, so can be used directly to estimate these sizes (Hautojärvi *et al* 1977). The other limit is for voids that are sufficiently large for the positron to be localized at the surface of the void. Here, the lifetime is independent of the size and will be that of a positron at a planar surface (Hodges and Stott 1973). In this case, information about the void can be obtained by deviations of the measured lifetime from the value it would have for a planar surface, which would be due to effects like the presence of gas inside the cavity (Jensen and Nieminen 1987, Jensen *et al* 1988, Rajainmäki *et al* 1988) or impurity layers on the cavity surface (Linderoth 1989). Hence, knowledge of the saturation radius above which the lifetime is independent of size is essential for adequate interpretation of the measurements.

Experiments on voids in molybdenum (Thrane *et al* 1977) have shown that the saturation radius is below 9 Å but a more precise determination is essentially impossible due to the difficulty of obtaining independent measurements of void sizes for radii below about 10 Å. Therefore, a theory that is valid between the two limits of small and large void sizes, that can be used to estimate the saturation radius, is much needed.

Theories only exist in the two limits since in earlier studies of positron states, the modelling of positron–electron correlations has been treated quite differently for bulk solids compared with surfaces. In bulk solids, the correlation can be approximated by a local density approximation (LDA) (Puska and Nieminen 1983). However, the LDA breaks down in the case of the positron surface state, since this state arises from the image potential outside the surface and the image potential is the result of non-local correlations of the positron outside the surface with electrons within the surface. The conventional answer to this difficulty has been to attach a classical image potential outside the surface to the correlation potential calculated with the LDA near and inside the surface (Nieminen and Puska 1983). This method has the clear disadvantages that there is no prescription for interpolation between the bulk and surface limits, and the results are sensitive to the position of the image plane (Brown *et al* 1987).

Fortunately, the formalism developed by Jensen and Walker (1988) for calculating positron–electron correlations in strongly inhomogeneous systems is readily adaptable to this problem. It has been shown to give realistic results for the surface state in that, for example, it gives good agreement with the measured lifetime of 580 ps (Lynn *et al* 1984) without empirically adjustable parameters that influence the surface state. Furthermore, it is equivalent to the LDA for nearly homogeneous systems. Previous calculations for positron states in metal voids at varying radii (Hautojärvi *et al* 1977, Jena and Rao 1985) have used the LDA, so that the state obtained for large voids is incorrect, since the image potential has been ignored, giving rise to a state for which probability for the positron being in the centre of the void is a maximum. Hence, our calculations are the first to give a realistic treatment of positron states at all void radii.

Below, we outline the theoretical formalism in section 2, present and discuss the results in section 3 and conclude in section 4. The appendix describes our calculation of electron densities. Atomic units (energies in Hartrees or, where appropriate, converted to eV) are used throughout.

2. Methods

We describe the voids by a jellium model in which the positive background charge is given by

$$N_+ = n_0 \theta(r - R) \quad (1)$$

where r is the distance from the centre of the void, n_0 the bulk electron density, R the void radius and θ is the step function. The self-consistent electron density with the external potential due to N_+ was found by density functional theory (Manninen *et al* 1975) using a local density approximation for exchange and correlation (Ceperley 1978). Further details are given in the appendix.

According to the weighted density approximation (WDA) of Jensen and Walker (1988) the positron–electron correlation potential for a single positron in a system of

electrons may be expressed in terms of the electron density $n_-^0(\mathbf{r}')$ of the electronic system without the positron and the pair distribution function $g_d^h(|\mathbf{r} - \mathbf{r}'|; n_+, n_-, \lambda)$ for a homogeneous system with positron density n_+ , actual electron density n_- , and a positron-electron interaction scaled by the coupling constant λ :

$$V_{\text{corr}}^+(\mathbf{r}) = \frac{\partial E_{\text{corr}}}{\partial n_+} = \int d\mathbf{r}' \frac{1}{|\mathbf{r} - \mathbf{r}'|} n_-^0(\mathbf{r}') \int_0^1 d\lambda [g_d^h(|\mathbf{r} - \mathbf{r}'|; n_+, \tilde{n}_-, \lambda) - 1]. \quad (2)$$

In all equations \mathbf{r} and \mathbf{r}' refer to the positron and electron coordinates, respectively. For the pair distribution function $g_d^h(r; n_+, n_-, \lambda)$, we have used the scaled positronium approximation

$$g_d^h(r; n_+, n_-, \lambda) = \lambda^3 \exp(-\lambda r/a(n_-)) / [8\pi(a(n_-))^3 n_-] + 1 \quad (3)$$

where the scaling length $a(n_-)$ is given by

$$a(n_-) = (1 + 41.87n_-)^{-1/3} \quad (4)$$

which can be derived from the Brandt-Reinheimer formula for the positron annihilation rate in an electron gas (Brandt and Reinheimer 1971) and is found to reproduce values for the correlation potential in good agreement with those of Arponen and Pajanne (1979) when used in equation (2) for a homogeneous system (Jensen and Walker 1988). The electron density \tilde{n}_- is for each positron coordinate \mathbf{r} defined by requiring the sum rule

$$\int d\mathbf{r}' n_-^0(\mathbf{r}') \int_0^1 d\lambda \frac{\lambda^3 \exp(-\lambda|\mathbf{r} - \mathbf{r}'|/a(\tilde{n}_-))}{8\pi(a(\tilde{n}_-))^3 \tilde{n}_-} = 1 \quad (5)$$

to be satisfied. This equation is solved numerically and the resulting \tilde{n}_- is inserted into equation (2) to obtain the correlation potential.

Our approximation to the correlation potential implicitly assumes that the positron density throughout the system is vanishing. This is valid for delocalized states, such as the states at a planar surfaces and in defect-free bulk systems, but is violated for localized states like those found in voids. However, calculations using the LDA for monovacancies, in which the effects of finite positron density is expected to be largest, have shown that the differences between binding energies and positron lifetimes obtained with the vanishing density approximation and with the full two-component density functional theory, taking the finite positron density into account, are fairly small (Boronski and Nieminen 1986). We therefore expect that this approximation will not affect the results significantly.

The total effective positron potential in and near the void is given by

$$V_{\text{eff}}^+(r) = \phi(r) + V_{\text{corr}}^+(r) + E_0\theta(r - R) \quad (6)$$

where ϕ is the electrostatic potential from electrons and positive background charge and the E_0 term shifts the potential outside the void to take into account the zero-point energy due to the repulsion from the ion cores which is not included in a jellium model. The value of $E_0 = 1.1$ eV is adjusted to produce the correct positron work function for a planar surface, -0.19 eV (Mills 1983).

The positron wavefunction was obtained by a numerical solution of the positron Schrödinger equation:

$$\left(-\frac{1}{2} \frac{d^2}{dr^2} + V_{\text{eff}}^+(r)\right)U(r) = \epsilon_+ U(r) \quad (7)$$

where U is defined in terms of the spherically symmetric positron wavefunction Ψ as

$$U(r) = (4\pi)^{1/2} r \Psi(r) \quad (8)$$

and ϵ_+ is the positron energy eigenvalue.

The annihilation rate is given within the WDA by

$$\Gamma = \pi r_0^2 c \int n_+(r) n_-^0(r) g_d^h[0, n_+, n_-^*, \lambda = 1] dr \quad (9)$$

where the density n_-^* is determined by numerical solution of the sum rule equation

$$\int dr' n_-^0(r') \frac{\exp(-|r - r'|/a(n_-^*))}{8\pi(a(n_-^*))^3} = 1 \quad (10)$$

(Jensen and Walker 1988). The positron lifetime τ , which is the quantity measured in experiments, is given by Γ^{-1} . This lifetime represents only annihilation with conduction electrons. However, the contribution from core electrons is expected only to be a few per cent (Jensen and Weiss 1990) and will be assumed negligible in the present work.

3. Results and discussion

We have performed calculations for voids of radii ranging from 3.0 atomic units, corresponding to a monovacancy, to 30 au. Figure 1 shows the correlation potential, the total effective potential and the positron wave function for void radii from 3 to 18 au. As the cavity radius increases the positron wavefunction evolves, as seen in the figure, from a volume state peaking at the centre of the cavity to a state localized at the void surface approaching the wavefunction at a planar surface. At $R = 18$ au the difference between the void state and the state at a planar surface is negligible. The evolution from volume to surface state is found to be gradual with no evidence of a sharp transition between the two types of state.

The non-local nature of the positron-electron correlation in large voids is demonstrated by figure 2 which shows the correlation cloud, i.e. the pair distribution function defined as

$$n_{\text{corr}}(\mathbf{r}, \mathbf{r}'; \lambda = 1) = n_-^0(\mathbf{r}') [g_d^h(|\mathbf{r} - \mathbf{r}'|; n_+, \tilde{n}_-, \lambda = 1) - 1] \quad (11)$$

as a function of the electron coordinate \mathbf{r}' for different positron coordinates \mathbf{r} in the void. For \mathbf{r} well inside the void n_{corr} is located at the void surface forming an image charge while it is centred on the positron for \mathbf{r} near and outside the void radius.

The binding energy of the positron, with respect to the positron energy in bulk Al, was found to vary from 1.5 eV at a radius of 3 au (monovacancy), to a maximum

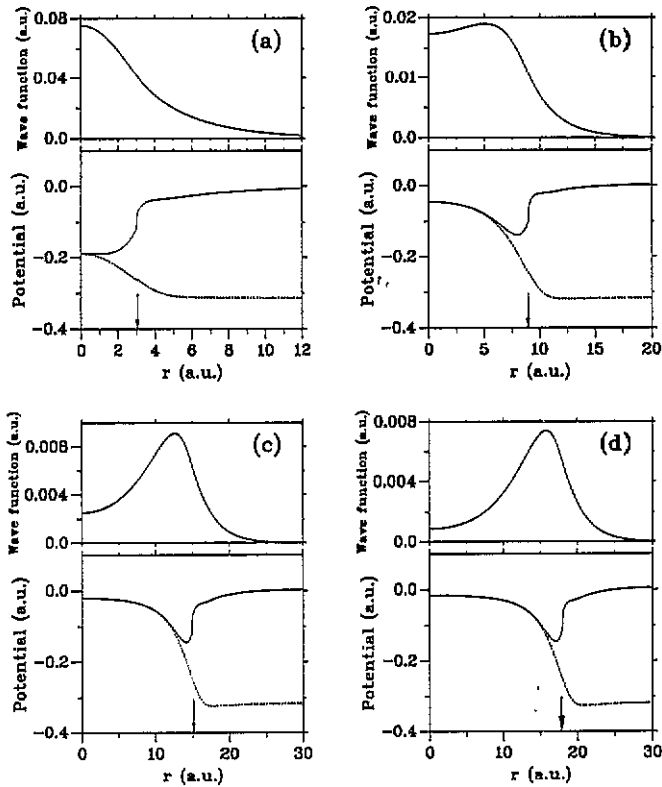


Figure 1. Positron wavefunction, effective potentials (full curves) and correlation potentials (broken curves) corresponding to voids of radii (a) 3 au, (b) 9 au, (c) 15 au and (d) 18 au. The arrows indicate the void radius.

of 2.5 eV by 9 au, as shown in figure 3. The monovacancy result is similar to what is found by other theoretical methods employing the LDA for the positron-electron correlation (Boronski and Nieminen 1986).

Figure 4 presents our results for the positron lifetime. The lifetime is seen to increase from the monovacancy value, 250 ps, to a value of 565 ps for large voids. The saturation radius above which the lifetime does not depend on void size is found to be about 5 Å which is consistent with the experiments of Thrane *et al* (1977) who were able to set an upper limit for the saturation size in molybdenum of about 9 Å.

The work of Jensen and Nieminen (1987) and Dunn *et al* (1991) has shown that, for both small and large cavities, the introduction of inert gas into the cavity modifies the positron wavefunction locally around each gas atom but does not change the overall shape of the wavefunction significantly. This indicates that the saturation radius for gas bubbles with a given gas density is the same as for empty cavities, i.e. about 5 Å. Thus, the present results vindicate the use of the relationships between density of inert gas inside cavities and positron lifetime, derived for nominally large cavities (Jensen and Nieminen 1987, Dunn *et al* 1991), for cavities with radii as small as 5 Å.

The lifetime results in the present work are qualitatively similar to those of Hautojärvi *et al* (1977), see figure 4. Their results are based on the local density approximation for the positron-electron correlation and thus does not describe the positron state in large voids correctly since the non-local image effects are neglected. This

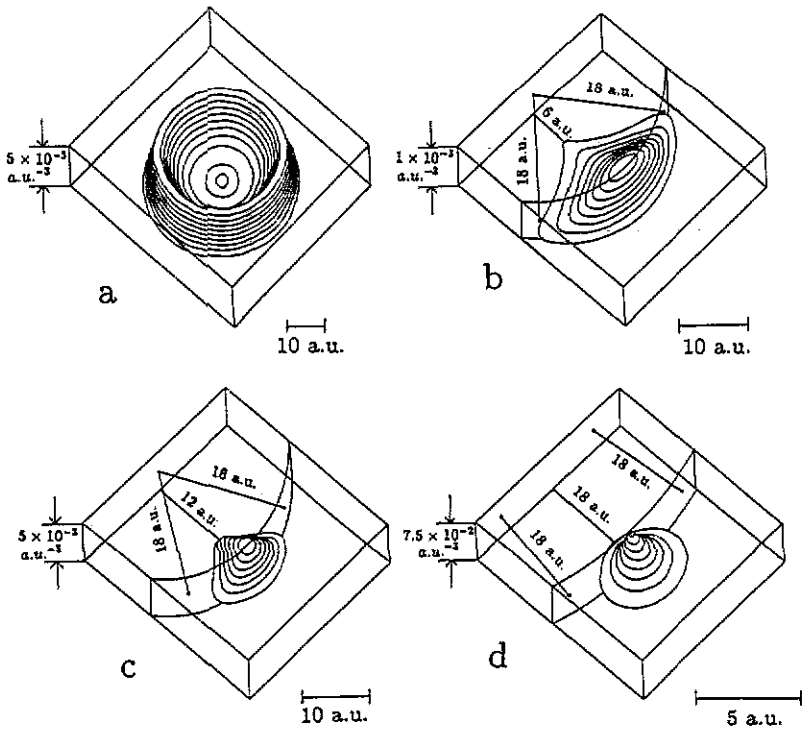


Figure 2. The correlation cloud of electrons for different positron coordinates in a void of radius 18 au: (a) centre of void, (b) 6 au from centre (c), 12 au from centre and (d) at the surface of the void.

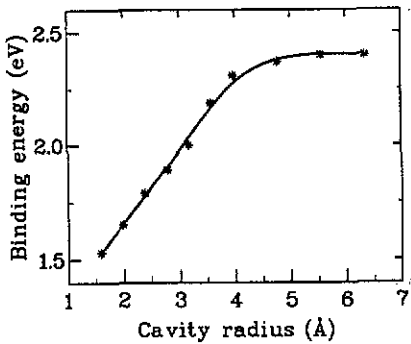


Figure 3. The binding energies relative to the positron energy in bulk Al as a function of void radius. The curve is a spline fit to the calculated data.

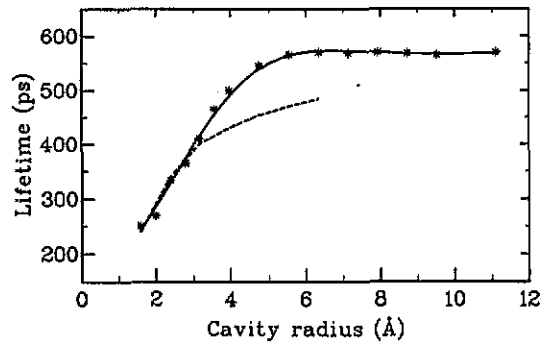


Figure 4. Positron lifetimes as a function of void radius. The markers indicate the results of the present work using the weighted density approximation to the positron-electron correlation. The full curve is a spline fit to these results. The broken curve shows the values calculated by Hautojärvi *et al* (1977) using the local density approximation.

accounts for the difference at large void sizes. However, for small vacancy clusters, in which non-local effects are unimportant, the two sets of results are in good agreement.

The lifetime value found for a monovacancy agrees well with the experimental

value of about 240 ps (Jackman *et al* 1987). The value for large voids is consistent with the lifetime of 580 ps measured for an external Al(110) surface (Lynn *et al* 1984). However, there is a discrepancy between this lifetime and the measured lifetimes close to 500 ps in large voids (Lindberg *et al* 1977, Nieminen *et al* 1979, Linderoth *et al* 1985, Eldrup and Jensen 1987). The inherent difficulty in modelling the positron-electron correlations in strongly inhomogeneous systems means that it is difficult for any theory that relies on a series of assumptions and approximations to provide quantitatively accurate values for the surface state lifetime. We are therefore not in a position to resolve this discrepancy. It will be interesting to see if future experiments, especially on the lifetime at external surfaces, will be able to shed more light on this issue.

4. Conclusion

We have calculated the positron states and the associated positron binding energies E_B and lifetimes τ for cavities in Al ranging in size from monovacancies to large voids employing a non-local approximation to the positron-electron correlation. Our model is the first to provide a realistic description of the positron-electron correlation throughout the range of cavity sizes and it shows the gradual evolution from a volume state, extending over the whole of the cavity, to a state localized at the cavity surface with increasing cavity radius. We find that E_B and τ both increase with cavity size for small radii and saturate at the values for a positron bound to a planar surface at a cavity radius of about 5 Å.

Appendix. Calculation of electron densities

Our electron densities were calculated by the usual iterative self-consistency procedure employed in density functional theory (see, e.g., Lundquist and March 1983). Each successive iteration cycle consists of (i) inserting the effective potential into the electron Schrödinger equation which is solved for the electron wavefunctions and hence the electron density; (ii) evaluating a new effective potential consisting of a Coulomb potential (from the Poisson equation) and an exchange-correlation potential (from the local density approximation); (iii) solving the Schrödinger equation with the new potential.

We found, like Manninen *et al* (1975), that the newly evaluated Coulomb potential, if used directly in the next iteration, caused the solution to become unstable with the electron densities going through successively greater oscillations. There are several methods of stabilizing the solution (see, e.g., Manninen *et al* 1975, Lang and Kohn 1970). In these calculations we elected to average the new potential with the old, weighting each according to the present convergence of the electron densities (found by calculating the sum of the squared differences of the electron densities at each mesh point of two successive iterations). As the convergence increases, so does the weighting of the new potential. Normally, starting with a weighting of about 10% for the newly evaluated potential, the electron densities converge quickly and the weighting of the new potential may be increased by about 5% on each iteration. Sometimes, this increment proves to be too large and the electron density starts to oscillate. In this eventually the program detects the oscillation, reduces the weighting factor of the new potential to its initial value and re-assigns a lower increment factor. Satisfactory convergence is usually achieved after about 40 iterations.

Values of angular momentum up to $l = 30$ for larger voids were found to contribute significantly in the region of evaluation (we normally evaluated for 15 au into the jellium surrounding the void), the total number of wavefunctions used being of the order of 300.

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