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Local density calculation of positron annihilation in metals

Kjeld O Jensen

Department of Physics, The University of Texas at Arlington, Box 19059, Arlington, Texas 76019, USA and School of Physics, University of East Anglia, Norwich NR4 7TJ, UK†

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Abstract. A comprehensive set of calculations of positron lifetimes in bulk metals demonstrate that experimental lifetimes are reproduced well by a simple first-principles theory in which the annihilation rate (the inverse of the lifetime) is evaluated in a local density approximation. It is shown that the method presented here avoids assigning unrealistic enhancement factors for annihilation with valence and d-band electrons, in contrast to previous calculations in which partial annihilation rates with different types of electrons are evaluated separately.

Theoretical calculations of positron states and their annihilation characteristics play an increasingly important role in the interpretation of experiments employing positron tehniques, see e.g. the review by Puska [1]. The annihilation characteristics commonly measured are the positron lifetime (the inverse of the annihilation rate), which yields unique information about defects in materials [2], and Angular Correlation of Annihilation Radiation (ACAR) spectra, giving the momentum distribution of the annihilating electron–positron pairs that can be used to study electronic structure [3]. In the positron calculations an effective positron potential is first constructed followed by solution of the positron Schrödinger equation. The annihilation characteristics can then be calculated from the positron and electron densities and/or wave functions. When calculating lifetimes it is essential to include the effects of electron–positron correlations which lead to an enhancement of the annihilation rate due to the pile-up of electrons around the positron. It is common to divide the electrons in the system into different classes, i.e. valence-band, d-band and core electrons, which allows different descriptions of the correlation effects to be employed for each class. This strategy is, for example, used in the atomistic model of Puska and Nieminen [4], which has been used extensively for calculations of positron states and positron lifetimes for defects in metals [4–10], semiconductors [11–13], and recently also high-temperature superconductors [14, 15] and for metallic surfaces [8, 16–20].

In this paper I show that it is not necessary to treat different classes of electrons differently when calculating positron lifetimes. This conclusion is reached by a comprehensive calculation of lifetimes for delocalised positron states in a large number of

† Present address.

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metals which shows that the experimental lifetimes are reproduced well when the annihilation rate is calculated in a local density approximation based on the total electron density. Unlike in the Puska–Nieminen model [4], no adjustable parameters are involved in the calculation of annihilation rates. The results show that the variation of positron lifetimes across the periodic table, which so far has been accounted for only by semi-empirical models [21, 22] can be reproduced accurately by a first-principles theory. The theory also allows predictions of the average enhancement factors for the different classes of electrons to be made. Comparing these enhancement factors to ACAR results shows that the local density approach provide a more realistic description of the relative contributions from different types of electrons to the total annihilation rate than the Puska–Nieminen model.

The calculations of bulk positron states were made in a Wigner–Seitz approximation, in which the unit cell is approximated by a sphere and the gradient of the positron wave function is required to vanish at the sphere boundary. The positron potential is a sum of an electrostatic (Hartree) component $V_H(\boldsymbol{r})$ and a correlation component $V_{corr}(\boldsymbol{r})$:

$$V^+(\boldsymbol{r}) = V_H(\boldsymbol{r}) + V_{corr}(\boldsymbol{r}). \tag{1}$$

$V_{corr}(\boldsymbol{r})$ is constructed using a local density approximation (LDA) where it becomes a function of the electron density $n(\boldsymbol{r})$. For the density-dependence of V_{corr} the parametrisation by Boronski and Nieminen [23] is used. The electron densities and the Hartree potential are obtained by superposing free-atom charge densities and Hartree potentials using the Lowdin alpha expansion [24]. The free-atom results needed for this construction were calculated using the Local-Spin-Density Approximation [25] using the exchange-correlation potential of Ceperly and Alder [26]. Electronic configurations, crystal structures, and lattice constants were all taken from Ashcroft and Mermin [27]. The choice of electronic configurations involves a certain arbitrariness since actual band structures of metals, in particular transition metals, do not correspond to unique free-atom configurations. However, different choices, e.g. $3d^94s^1$ and $3d^84s^2$ in the case of Ni and $4d^{10}5s^0$ and $4d^95s^1$ in the case of Pd, yield identical lifetimes to within a few ps. The positron energy eigenvalues and the potential and kinetic energies obtained from the solution of the positron Schrödinger equation agree well with the results of similar Wigner–Seitz calculations in reference 4.

The total annihilation rate λ_{LDA} is calculated using a local-density approximation:

$$\lambda_{LDA} = \int d\boldsymbol{r} |\Psi_+(\boldsymbol{r})|^2 \Gamma(n(\boldsymbol{r})) \tag{2}$$

where Ψ_+ is the (normalised) positron wave function and $\Gamma(n)$ is the annihilation rate of a positron in an electron gas of density n [23]:

$$\Gamma(n) = \pi r_0^2 \, cn(1 + 1.23r_s + 0.8295r_s^{3/2} - 1.26r_s^2 + 0.3286r_s^{5/2} + r_s^3/6) \tag{3}$$

where r_0 is the classical electron radius ($= 2.818 \times 10^{-15}$ m), c is the velocity of light and $r_s = (3/4\pi n)^{-3}$. The integration in equation (2) is performed over the unit cell. The values of the lifetimes $\tau_{LDA} = 1/\lambda_{LDA}$ calculated using this model for different metals with FCC, BCC or HCP crystal structures are given in table 1 which also shows the experimental lifetimes τ_{expt} taken from the recent compilation of Seeger *et al* [28]. In order to facilitate the comparison of theory and experiment, τ_{LDA} is plotted against τ_{expt} in figure 1. It is seen that the agreement of τ_{LDA} with experiment is remarkably good with the deviation only in a few cases exceeding 10%.

Table 1. Experimental and calculated bulk positron lifetimes for different metals. The crystal structure is indicated for each element and lattice constants a and (in the case of HCP structures) c are given. The experimental lifetimes are denoted by τ_{expt}. The theoretical values denoted by τ_{LDA} have been calculated using the LDA for all electrons in the metal, while the τ'_{LDA} values were obtained by calculating the core electron contribution separately using the Independent Particle model. The average enhancement factors, γ_v, $\gamma_d(\gamma_f)$, and γ_c for valence, d-band (f-band in the case of lanthanides), and core electrons, respectively, were calculated from equations 4–6.

Element	a (au)	c (au)	τ_{expt} (ps)†	τ_{LDA} (ps)	τ'_{LDA} (ps)	γ_v	$\gamma_d(\gamma_f)$	γ_c
Li BCC	6.597		291	295	313	8.07	—	2.96
Be HCP	4.329	6.783	142	134	140	3.63	—	2.24
Na BCC	7.996		338	317	350	11.67	—	3.13
Mg HCP	6.068	9.855	225	228	245	5.64	—	2.59
Al FCC	7.656		163	163	171	4.09	—	2.33
K BCC	9.887		397	363	395	18.10	—	4.76
Ti HCP	5.577	8.856	147	141	160	4.05	3.47	2.65
V BCC	5.709		130	112	126	3.58	3.09	2.47
Cr BCC	5.444		120	99	112	3.49	3.04	2.36
Fe BCC	5.425		106	98	106	3.39	2.81	2.23
Ni FCC	6.654		110	94	100	3.46	2.83	2.10
Cu FCC	6.824		110	103	109	3.64	2.87	2.06
Zn HCP	5.028	9.333	148	130	135	3.94	2.85	2.04
Rb BCC	10.567		406	372	405	20.49	—	5.53
Zr HCP	6.106	9.727	165	153	174	4.21	3.80	2.87
Nb BCC	6.238		118	119	137	3.72	3.40	2.66
Mo BCC	5.955		103	103	116	3.47	3.15	2.52
Pd FCC	7.353		96	101	108	—	3.06	2.27
Ag FCC	7.732		131	119	125	3.96	3.07	2.24
Cd HCP	5.633	10.624	175	148	153	4.33	3.09	2.23
Cs BCC	11.437		418	383	414	23.54	—	6.71
Ce FCC	9.754		235	196	241	5.29	3.66	3.54
Gd HCP	6.881	10.927	230	195	223	5.19	4.09	3.24
Ta BCC	6.257		116	112	129	3.58	3.28	2.55
W BCC	5.974		105	96	109	3.32	3.04	2.44
Pt FCC	7.410		99	92	99	—	2.99	2.25
Au FCC	7.713		117	105	112	3.65	3.00	2.23
Tl HCP	6.541	10.459	229	174	178	4.66	3.11	2.23
Pb FCC	9.357		194	178	181	4.53	2.95	2.20

† from [28].

Table 1 also gives the calculated values of the average enhancement factors for different types of electrons defined as

$$\gamma_x = \lambda_x/\lambda_x^{IPM} \tag{4}$$

where x stands for either v (valence), d (d-band), f (f-band—in the case of lanthanides), or c (core). The partial annihilation rate λ_x is given by

$$\lambda_x = \int d\boldsymbol{r}|\Psi_+(\boldsymbol{r})|^2\Gamma(n(\boldsymbol{r}))(n_x(\boldsymbol{r})/n(\boldsymbol{r})) \tag{5}$$

where n_x is the density of electrons of type x, and the partial independent particle model

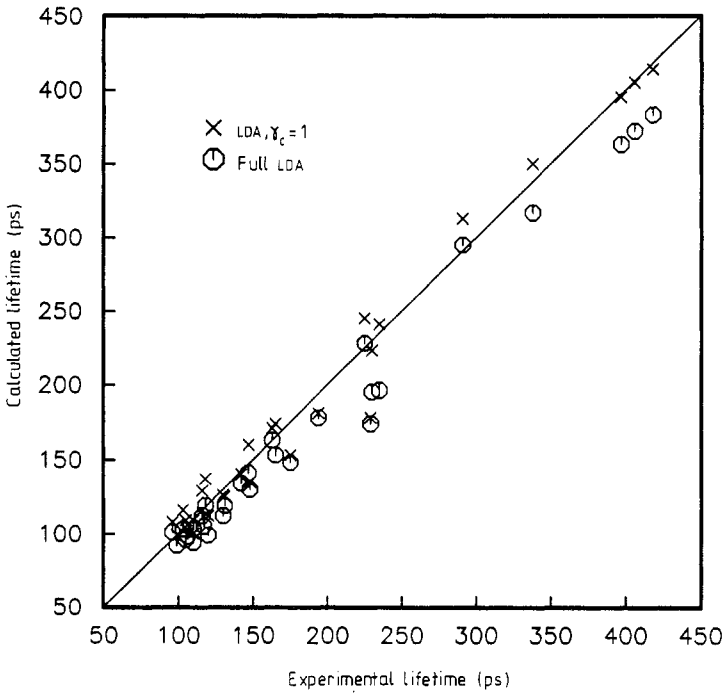

Figure 1. Comparison of experimental and theoretical positron bulk lifetimes. Octagonal markers and crosses denote τ_{LDA} and τ'_{LDA}, respectively, see table 1. Perfect agreement between theory and experiment corresponds to points on the diagonal line.

(IPM) annihilation rate which is the partial annihilation rate calculated without any enhancement is given by

$$\lambda_x^{IPM} = \pi r_0^2 c \int d\boldsymbol{r} |\Psi_+(\boldsymbol{r})|^2 n_x(\boldsymbol{r}). \tag{6}$$

Equation (5) relies on the assumption that the relative contribution to the annihilation rate at each point $\boldsymbol{r}$ of the unit cell from electrons of a given type x is given simply by the ratio between $n_x(\boldsymbol{r})$ and $n(\boldsymbol{r})$. This assumption is equivalent to neglecting the electron-energy dependence of the enhancement factor in the electron gas. However, both theory and experiment indicate that the enhancement in electron gas at high energies near the Fermi level is roughly 50% higher than at low energies [29]. The neglect of energy dependent enhancement therefore implies that the relative contribution from core electrons, which may be associated with the low-energy electrons in the local-density electron gas picture, is lower than predicted by equation (5). Thus, the enhancement factors given in table 1 for core electrons are upper estimates to the true values which could be up to 50% lower than those tabulated. Similarly, valence enhancement factors are likely to be higher than the values in table 1 while it is less clear how the d-electron enhancements are affected.

In the Puska–Nieminen model [4] the contribution from valence electrons to the annihilaton rate is calculated in a local-density approximation and both d-band and core electron contributions are calculated using the independent particle model with constant enhancement factors, γ_d and γ_c, respectively. A value of 1.5 is used for γ_c [30] while γ_d

is treated as an adjustable parameter for each metal chosen so that the experimental bulk lifetime is reproduced in the calculations. This leads to γ_d values typically in the range 1.5–3.0 [4]. This construction means that the average enhancement for annihilation with valence electrons γ_v is implicitly assumed to be much larger than that for d-band electrons, e.g. for Cu $\gamma_v \approx 5.5$ compared to $\gamma_d \approx 1.8$. However, no preferential enhancement of the valence relative to d-band electrons of this magnitude is observed in ACAR experiments since analyses of ACAR spectra for transition metals [31–35] indicate that the average enhancement for valence electrons is only roughly 50% higher than for d electrons, although the precise values obtained are quite sensitive to the details of the analysis [33, 34]. Table 1 shows that the present calculations yield γ_v values typically about 25% greater than γ_d. In view of the uncertainties associated with the theoretical estimates, mentioned in the previous paragraph, and the difficulty of extracting enhancement factors from the experimental results, the consistency between theory and ACAR experiments is surprisingly good. In particular, it shows that the present model for calculating annihilation rates avoids the gross overestimate of the valence electron enhancement relative to d-band electrons of the Puska–Nieminen model [4].

It should be noted that average enhancement factors for different types of electrons, like those presented here, do not give a full description of the enhancement effects in ACAR spectra since there is appreciable variation of the enhancement with electron energy or momentum within each band [36]. It has recently been proposed that these effects can be taken into account using a local density approximation based on energy-dependent enhancement factors for the electron gas [37, 38]. This approximation is a direct equivalent to the present model for calculating total annihilation rates, since integrating the momentum dependent annihilation rates within the LDA model over all momenta leads directly to equation (2) above. Reasonably good agreement between experimental ACAR spectra and the momentum-dependent LDA model has been found for Cu [37] and Zn [38] which confirms the conclusion of the simpler analysis based on a comparison of average enhancements factors given above, namely that the local density approach yields partial annihilation rates for different types of electrons that are consistent with experiment.

The average core enhancement factors presented in table 1 are somewhat higher than other theoretical predictions [30, 39] that are supported by experimental results for high electron–positron momenta [40]. This may be related to the neglect of energy-dependent enhancements, as discussed above. However, it is interesting to note that the γ_c values for alkali metals agree quite well with values derived from the intensity of the broad (high-momentum) component of ACAR spectra [41] which shows that the high γ_c values for these metals are in fact realistic. Within the present theory the high core enhancements result from a low total electron density in the region of the unit cell with high positron–core-electron overlap. It was noted in [41] that there is a correlation between γ_c and the polarisabilities of the ion cores of simple metals and this correlation was used to predict γ_c values for a range of other metals [42]. These predictions follow the same trends as the results in table 1. Thus, the phenomenological model of reference 42 and the present first-principles theory yield similar predictions for γ_c.

Because of the uncertainty related to the core enhancement a set of lifetimes was calculated where the LDA, equation (2), was used only for the sum of valence and d-band electon densities (valence and f-band electron densities in the case of lanthanides) while the core contribution was calculated using the IPM, equation (6). The calculated values are shown as τ'_{LDA} in table 1 and are plotted against the experimental values τ_{expt} in figure 1. It is seen that the difference between the two theoretical lifetime estimates is

Table 2. Calculated lifetimes for bulk and mono-vacancy-trapped positron states in Cu and Mo using the atomistic model of Puska and Nieminen. τ_{LDA} and τ_{PN} are, respectively, calculated using the local-density approximation and the method used by Puska and Nieminen.

	Bulk		Vacancy	
Element	τ_{LDA} (ps)	τ_{PN} (ps)	τ_{LDA} (ps)	τ_{PN} (ps)
Cu	106	110	168	174
Mo	107	103	197	208

fairly small in most cases, and although the results show that the values of τ'_{LDA} give slightly better overall agreement with τ_{expt} than the pure LDA values τ_{LDA}, it is not possible to establish conclusively which method gives the most realistic description of the core enhancement, because of the additional assumptions used in the calculations, i.e. the Wigner–Seitz and atomic-superposition approximations. It should also be noted that the results depend on which data are used for the positron annihilation rate as a function of electron gas density since different theories give slightly different results, see e.g. reference 29. However, it is clear from the overall agreement between theory and experiment that the contributions from valence and d-band electrons, which account for most of the total annihilation rate, are represented accurately by the LDA formula, cf equations (2, 3).

The preceding discussion has shown that the LDA approach works well for metallic systems. However, in semiconductors and insulators the model is expected to break down because the effect of the band gap on the positron-electron correlations, which leads to a reduction of the annihilation enhancement [12], is ignored. This is illustrated by calculations for noble gas solids which yield lifetime values more than 100 ps lower than the experimental values [43]. It thus appears essential to go beyond the present model by incorporating band-gap effects in calculations of positron states in non-metals, which at present can only be done in a semi-empirical way [12].

In order to examine whether the present approach yields lifetime values for positron defect-states substantially different from earlier results, a calculation of bulk and mono-vacancy-trapped states in Cu and Mo was made using the atomistic model of Puska and Nieminen [4]. In each case two estimates of the lifetimes are calculated, one using the approach used in reference 4 with the contribution from different electrons calculated separately, denoted τ_{PN}, and one using the LDA formula, equation (2), denoted τ_{LDA}. The results are shown in table 2. The bulk values for τ_{PN} agree with the experimental values (see table 1) by construction, since the d-electron enhancement is adjusted to obtain the correct bulk lifetime. The present τ_{PN} values differ slightly from those of reference 4, since different values are used for the experimental bulk lifetimes. It is seen that the vacancy lifetimes calculated with the two approaches are in fairly close agreement. This indicates that, although the relative contributions from different types of electrons is misrepresented (see discussion above), the Puska–Nieminen model provides reasonably accurate values for the total annihilation rate (and thus the lifetime) and replacing it with the more realistic LDA model will not produce lifetimes significantly different from those published in [4–20].

In summary, I have presented a simple first-principles theory based on the local density approximation which reproduces accurately experimental lifetimes for defect-free metals. The average enhancement factors for different classes of electrons implied in this model were shown to be consistent with ACAR experiments. The results thus suggest a parameter-free prescription for calculating positron lifetimes in inhomogeneous systems which is both simpler and physically more realistic than the approach of Puska and Nieminen [4] in which the partial annihilation rates with different types of electrons were evaluated separately. Nevertheless, the two prescriptions were shown to yield similar values for lifetimes of defect-trapped positrons.

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