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γ-ray spectra and enhancement factors for positron annihilation with core electrons

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Many-body theory is developed to calculate the γ-spectra for positron annihilation in noble-gas atoms. Inclusion of electron–positron correlation effects and core annihilation gives spectra in excellent agreement with experiment [Iwata et al., Phys. Rev. Lett. 79, 39 (1997)]. The calculated correlation enhancement factors γnl for individual electron orbitals nl are found to scale with the ionization energy Imnl (in eV), as γnl = 1 + √(A/Imnl) + (B/Imnl)β, where A ≈ 40 eV, B ≈ 24 eV and β ≈ 2.3.

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Introduction.—This Letter shows that many-body theory (MBT) provides accurate γ-ray spectra for positron annihilation with valence and core electrons of noble-gas atoms, and establishes firmly the fractions of core annihilation. It uncovers a simple scaling of the enhancement factors, which increase the annihilation probability beyond the independent-particle approximation (IPA), with the electron ionization energy.

Low-energy positrons annihilate predominantly on the valence electrons in atoms. Small fractions of positrons can, however, tunnel through the repulsive nuclear potential and annihilate with core electrons [1]. The two-photon annihilation γ-ray spectrum is Doppler-broadened by the electron velocity distribution in the states involved. In particular, annihilation on tightly-bound core electrons results in distinct features at larger Doppler shifts [2, 3]. Its signal shows high elemental specificity [4], allowing to study vacancies and other defects in metals and semiconductors [5–7]. Annihilation on core electrons enables positron-induced Auger-electron spectroscopy (PAES) [8–11] and time-resolved PAES [12], to study the dynamics of catalysis, corrosion, and surface alloying [13]. Coincident measurements of the γ-rays and Auger electrons yields γ-ray spectra for individual core orbitals [14, 15].

Interpretation of experiments relies heavily on theoretical input, e.g., the relative annihilation probabilities for core electrons of various atoms in PAES [16]. However, positron annihilation in many-electron systems is characterised by strong electron–positron correlations, which affect the positron wave function and electron-positron annihilation vertex. Correlations lead to dramatic enhancements of positron annihilation rates in heavier noble-gas atoms, compared with the single-particle approximation (see [17] and references therein), and influence the shapes of the γ-ray spectra [18–20]. For atomic systems correlations can be included systematically by MBT methods [17, 21]. MBT provided early insights into positron annihilation in metals by considering positrons in an electron gas [22, 23]. These works introduced the concept of enhancement factors (EF), which measure the increase of the electron density at the positron. Subsequently, density functional theories were developed for condensed-matter systems [24, 25]. They describe positron states and annihilation in real materials, often using parametrisations of the correlation energy and EF for the positron in electron gas from MBT [26]. The EF are particularly large (~10) for the valence electrons, but also significant for the core electrons [27]. They correct the IPA annihilation probabilities and γ-spectra [2, 16]. However, they also lead to spurious effects in the spectra [6], and show deficiencies when benchmarked against accurate calculations [28].

Positron interaction with noble-gas atoms has been studied thoroughly in experiment by measuring the scattering cross sections and annihilation rates. This system is ideal for testing the ability of theory to account for correlations. An extensive comparison with the data attests the accuracy of our MBT approach [17]. One outstanding issue is the annihilation γ-ray spectra of Ar, Kr and Xe [3], that have till now eluded theoretical description. In this work we extend the MBT approach to the γ-ray spectra. The calculation of the valence and core annihilation yields excellent agreement with experiment, including the large Doppler shifts where the core contribution dominates. The MBT also provides “exact” EF γnl for individual electron orbitals nl [29].

Theory.—In the dominant process, a positron annihilates with an electron in state n to form two γ-ray photons of total momentum P [30]. In the centre-of-mass frame the two γ-rays have equal energies mc^2 = 511 keV (neglecting the initial positron and electron energies ε and ε_n). In the laboratory frame the photon energies are Doppler shifted by ε ≤ Pc/2, and their spectrum is

\[ w_n(\epsilon) = \frac{1}{c} \int_{2|\epsilon|/c}^{\infty} \int_{4\pi} |A_{ne}(P)|^2 \frac{d\Omega_p}{(2\pi)^3} P dP, \] (1)

where \( A_{ne}(P) \) is the annihilation amplitude [18]. Figure 1 shows the main contributions to this amplitude: the zeroth-order vertex (IPA), and the first- and higher-order (‘Γ-block’) corrections, which account for the attractive electron-positron interaction at short range (see [17–19, 24–25].

\[ P \approx (mc^2)^2 = 511 \text{ keV}, \]

\[ A_{ne}(P) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{-\frac{P^2}{2(\epsilon - \epsilon_n)^2}} \frac{d\epsilon}{4\pi}, \]
The fully-correlated incident positron quasiparticle wave function $\psi_z$ is obtained from the Dyson equation $(H_0 + \Sigma_z)\psi_z = \varepsilon\psi_z$, where $H_0$ is the positron Hamiltonian in the field of the Hartree-Fock (HF) ground state atom, and $\Sigma_z$ is the positron self-energy operator which represents the positron-atom correlation potential. This potential accounts for polarization of the atom by the positron and for virtual positronium formation (represented by the $\Gamma$-block), both of which contribute to the positron-atom attraction (see [17, 21] for details).

The positron annihilation rate in a gas is parameterized by the dimensionless effective number of electrons, $Z_{\text{eff}}$ [33]. For an orbital $nl$, it is $Z_{\text{eff},nl} = \int_{-\infty}^{\infty} w_{nl}(\varepsilon) d\varepsilon$. $Z_{\text{eff},nl}$ for valence orbitals is usually greater than the actual number of electrons, owing to the positron-atom attraction and vertex corrections.

The positron self-energy diagrams and the annihilation amplitude contain sums over the intermediate excited electron and positron states. We calculate them numerically using a basis set 40 B-splines of order 6, in a spherical box of radius 30 a.u. The maximum angular momentum of the intermediate states is $l_{\text{max}}=15$, and we extrapolate to $l_{\text{max}} \rightarrow \infty$ as in [18] (see [17, 31, 32] for details).

Results.—The annihilation $\gamma$-ray spectra for Ar, Kr and Xe were measured with room-temperature positrons in a Penning-Malmberg trap [3]. That work also showed that the IPA [Fig. 1 (a)] overestimates both the full width at half maximum (FWHM) of the spectra and the fraction of core annihilation. Ref. [18] showed that the first-order correction [Fig. 1 (b)] narrowed the spectrum, but was insufficient to describe the experiment.

The full calculation presented in this work highlights the importance of higher-order corrections [Fig. 1 (c)], especially for the valence electrons. The MBT also shows that the self-energy that affects the positron wave function (double line in Fig. 1) and the correlation corrections to the vertex [diagrams (b) and (c)] have strikingly different effects on the spectra. As an example, Fig. 2 presents the spectra for the valence 4p orbital and a core 3p orbital in Kr [34]. It shows that the vertex corrections enhance the annihilation by almost an order of magnitude for the valence electrons and by about 50% for the core orbital. The higher-order corrections [Fig. 1 (c)] are much more prominent for the valence electrons. Vertex corrections also lead to a significant narrowing of the spectrum for the valence electrons.

In contrast, improving the positron wave function (i.e., using the Dyson orbital instead of the static HF state) uniformly increases the annihilation signal. This increase is due to the build-up of the positron density in the vicinity of the atom caused by the positron-atom attraction. The magnitude of this effect is similar for the valence and core electrons. However, unlike the vertex corrections, it is sensitive to the atomic environment and the positron energy (e.g., the low-energy annihilation in Ar, Kr and Xe is strongly enhanced by the positron virtual states [17]).

Figure 3 shows the spectra for positron annihilation on individual subshells of Ar, Kr and Xe, calculated with the full amplitude (Fig. 1) using the Dyson s-wave positron state of thermal momentum $k = 0.04$ a.u. The narrowly peaked valence spectra dominate the total spectra at low Doppler shifts. The tightly-bound and faster moving core electrons produce broader $\gamma$-ray spectra. Note also that most individual spectra include multiple ‘shoulders’. They are caused by the oscillations of the electron or-
FIG. 3. Calculated $\gamma$-spectra for positron annihilation on individual subshells $nl$ in Ar, Kr and Xe: valence $ns$, $np$, (solid black and red lines); core $(n-1)s$, $(n-1)p$, and $(n-1)d$ (dashed lines); inner core $(n-2)s$, $(n-2)p$, and $(n-2)d$ (dash-dash-dotted lines); and total spectra (thick solid green line). All spectra are obtained using the full annihilation vertex (Fig. 1) and Dyson positron wave function.

FIG. 4. $\gamma$-spectra for positron annihilation in Ar, Kr and Xe. Experiment: red circles. Theory: valence (dashed line); core (dash-dash-dotted line); and total (solid line), calculated with the full annihilation vertex and Dyson positron wave function. Dotted line is the static calculation of [3] (blue dots).

The IPA $\gamma$-spectra obtained for the positron in the static atomic field (dotted lines in Fig. 4) are significantly broader than the experiment. Such calculation also overestimates the fraction of core annihilation by a factor of two. However, when this fraction is used as a free parameter to fit the experimental data [3], the core annihilation fractions for Kr and Xe (1.3% and 2.4%, respectively) are close to the above $ab\ initio$ values.

Enhancement factors.—In the MBT approach, the en-
enhancement factors due to the correlation corrections to the annihilation vertex (Fig. 1), are found from the ratio of the annihilation rate obtained with the full vertex to that of the zeroth-order (IPA), for each electron orbital \( nl \):

\[
\gamma_{nl} = \frac{Z^{(0+1+\Gamma)}_{\text{eff},nl}}{Z^{(0)}_{\text{eff},nl}}.
\]

Figure 5 shows the EF \( \gamma_{nl} \) for the core and valence orbitals in Ar, Kr and Xe, for both static HF and Dyson incident positron states. Also shown are values of \( \gamma_{1s} \) for hydrogen and hydrogen-like ions, from the MBT calculations [19, 21].

The values of \( \gamma_{nl} \) obtained from the positron wave function in the static atomic field are slightly larger that those found using the fully correlated Dyson wave functions (although this effect is negligible for the positive ions). This difference aside, Fig. 5 displays a near-universal scaling of the EF for the neutral atoms with the orbital ionization energy \( I_{nl} \). This scaling can be parametrized by the formula

\[
\gamma_{nl} = 1 + \sqrt{A/I_{nl}} + (B/I_{nl})^{\beta},
\]

where \( A, B \) and \( \beta \) are constants found by fitting the numerical data. The second term on the right-hand side of (3) describes the effect of the first-order correction, Fig. 1 (b). Its scaling with \( I_{nl} \) is motivated by the \( 1/Z \) scaling of the EF in hydrogen-like ions [19]. The third term is phenomenological; it accounts for the higher-order corrections which are important for the valence electrons (cf. Fig. 2).

**Summary.**—Many-body theory has been used to calculate the contribution of individual subshells to the \( \gamma \)-spectra of positron annihilation in noble gases. Inclusion of core annihilation gives excellent agreement with experiment and yields accurate core annihilation probabilities. The calculated “exact” vertex enhancement factors are found to follow a simple scaling with the electron ionization energy. This result can be used to improve simple IPA calculations of core annihilation on atoms across the periodic table and in condensed matter.

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[29] The theory also allows one to extract momentum-dependent EF [19, 20].
[33] $Z_{\text{eff}}$ is the ratio of the positron annihilation rate in an atomic or molecular gas to the Dirac annihilation rate in the electron gas of the same number density.
[34] All calculations are done for the s-wave incident positron with room-temperature momentum $k = 0.04$ a.u.
[35] In Kr and Xe the theoretical spectrum slightly underestimates the measurements at large $\epsilon$. This could be due to the neglect of relativistic effects on the electron wave functions [38]. However, a recent work [39] which employs model potentials to describe positron-atom interactions, shows that the relativistic effect on the $\gamma$-spectra is small, e.g., increasing the FWHM in Xe by only 1.4%.
[36] The uncertainty of these numbers is about 5%, comparable to effect of nonladder 3rd-order diagrams on the valence annihilation rates [17].