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Electron shell contributions to gamma-ray spectra of positron annihilation in noble gases

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Abstract

Gamma-ray positron annihilation spectra of the noble gases are simulated using computational chemistry tools for the bound electron wavefunctions and plane-wave approximation for the low-energy positron. The present annihilation line shapes, i.e. the full width at half maximum, $\Delta\varepsilon$, of the γ -ray annihilation spectra for He and Ar (valence) agree well with available independent atomic calculations using a different algorithm. For other noble gases they achieve moderate agreement with the experimental measurements. It is found that the contributions of various atomic electron shells to the spectra depend significantly on their principal quantum number n and orbital angular momentum quantum number l . The present study further reveals that the outermost ns electrons of the noble gases exhibit spectral line shapes in close agreement with those measured, indicating (as expected) that the measurements are not due to a simple sum over the momentum densities for all atomic electrons. The robust nature of the present approach makes it possible for us to proceed to more complex molecular systems using the tools of modern computational chemistry.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

A positron (e^+) is the antiparticle of the electron (e^-). Electron–positron annihilation occurs when an electron collides with a positron and produces detectable gamma rays with the total energy of $2mc^2$, where m is the electron mass and c is the speed of light [1, 2]. In an atom or a molecule, positron annihilation leads to the removal of one electron from the system. Thus positron annihilation is an ionization process, but it is qualitatively different from conventional ionization processes [3, 4] such as those involved in conventional mass spectroscopy and in $(e, 2e)$ scattering. As a result of the motion of the annihilating electron–positron pair, the energies of the annihilation γ -rays are Doppler shifted [4]. The γ -ray energy

spectrum carries information about the electron momentum distribution in the bound-state orbitals [5, 6].

The emission of two 511 keV γ -rays is a unique aspect of the positron–matter interactions. This signal provides information which forms the bases of many types of measurements [6]. Among these measurements, one is the observation of the emitted γ -ray directions and another is the study of the γ -ray energies, both of which provide the momenta of annihilating pairs. In the case of bound electrons, the momentum distribution is dominated by that of the electron orbitals [4, 7]. The γ -ray energies can be measured directly using high-resolution γ -ray spectroscopy [4].

Positrons annihilate predominantly with valence electrons in insulators or with conduction electrons in metals because of the repulsive potential exerted on the positron by the nuclei [6]. However, a small fraction of the positrons can tunnel through

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this repulsive potential and annihilate with electrons in other shells, such as the inner shell [7–9]. The objectives of the present study are twofold: one is to explore various electron shell contributions to the γ -ray spectra using a plane-wave approximation for the positron, and the other is to gauge the applicability of modern computational chemistry methods that can later be applied to the study of a broad range of molecular species.

2. Methods and computational details

A positron with momentum \mathbf{k} annihilates with an electron in an orbital i to produce two photons with a total momentum \mathbf{P} . In the mean-field approximation the photon spectrum is determined by the annihilation amplitude [5]

$$A_{i\mathbf{k}}(\mathbf{P}) = \int e^{-i\mathbf{P}\cdot\mathbf{r}} \psi_i(\mathbf{r}) \varphi_{\mathbf{k}}(\mathbf{r}) d\mathbf{r}, \quad (1)$$

where $\psi_i(\mathbf{r})$ is the wavefunction of the electron and $\varphi_{\mathbf{k}}(\mathbf{r})$ is the positron wavefunction. If one describes the positron as a plane wave, $\varphi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}$, then for low positron momenta, $k \ll 1$ au, one has $\varphi_{\mathbf{k}}(\mathbf{r}) \cong 1$ for the range of positron coordinates where annihilation occurs. This is equivalent to disregarding the positron wavefunction in equation (1), so that the γ -ray spectrum $w(\varepsilon)$ is given by [5]

$$w(\varepsilon) = \frac{1}{c} \int_{2|\varepsilon|/c}^{\infty} \sigma_{\text{EMS}}^{\text{total}}(p) p dp. \quad (2)$$

Here ε is the shift of the γ -ray energy relative to $mc^2 = 511$ keV [4], and $\sigma_{\text{EMS}}^{\text{total}}(p)$ is the total electron momentum density obtained by the summation of the momentum distributions for the occupied orbitals in the system [10]. (Note that $\sigma_{\text{EMS}}^{\text{total}}(p)$ is related to the cross section measured using the electron–momentum spectroscopy technique [11].) The total annihilation rate in positron collisions is conventionally expressed in terms of the dimensionless parameter [5]:

$$Z_{\text{eff}} = \int w(\varepsilon) d\varepsilon = \sum_i \int |A_{i\mathbf{k}}(\mathbf{P})|^2 \frac{d^3\mathbf{P}}{(2\pi)^3}. \quad (3)$$

It relates to the measured annihilation rate λ by $Z_{\text{eff}} = \lambda / (\pi r_0^2 c n_m)$, where r_0 , c and n_m are the classical electron radius, the speed of light and the density of the molecular gas, respectively. Theoretically, in the approximation of equation (2), Z_{eff} in equation (3) satisfies [12]

$$Z_{\text{eff}} = N^e, \quad (4)$$

where N^e is the total number of electrons in the shell or in the atomic system (depending on the orbitals included in the sum over i in equation (3)).

As indicated by Iwata *et al* [4] and Van Reeth *et al* [13], in the case of bound electrons, the γ -ray momentum distribution is dominated by the electron contribution. If $\sigma_{\text{EMS}}^{\text{total}}(p)$ contains only the contribution of an individual orbital of the atom or molecule, then equation (2) produces the corresponding orbital contribution to the γ -ray spectra under the plane-wave approximation for the positron. In this approximation, we can readily quantify the atomic or molecular electron shell contributions to the positron annihilation γ -ray spectra.

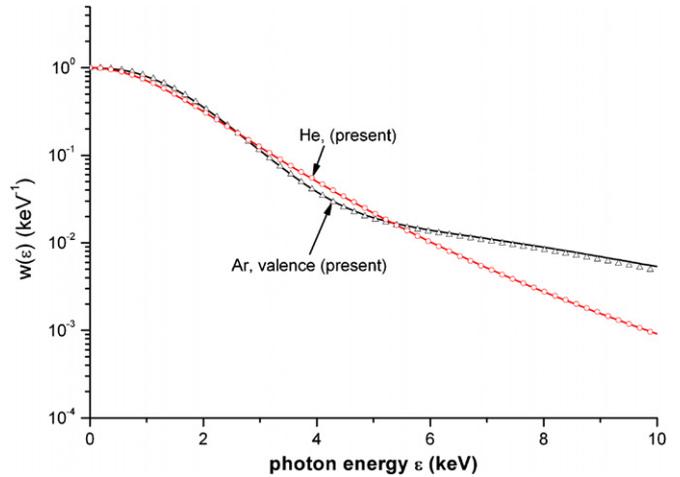


Figure 1. Comparison of the annihilation γ -ray spectra in the outermost shell of He and Ar calculated based on the PW approximation using the standard Hartree–Fock method [4, 7] (solid lines) with the present study: He (circles) and Ar (triangles). All spectra are normalized to unity at $\varepsilon = 0$.

In this study, the atomic electron wavefunctions are calculated quantum mechanically, using the Hartree–Fock (HF) theory [14]. The basis set employed is the Godbout density functional triplet zeta with valence polarized orbitals (TZVP) [15], which is found to produce good agreement with the experimental measurements for the molecular orbital momentum distributions [16] and is a basis set small enough to be used for larger molecules. All of the electronic wavefunction calculations are performed using the computational chemistry package GAUSSIAN03 [17].

The HF electron orbitals for the atomic or molecular system are then Fourier transformed. In addition to the mean-field (independent-particle) approximation, for molecules this also implies the use of the Born–Oppenheimer approximation. In fact, the process of electron–positron annihilation is instantaneous compared with typical nuclear motion times, so the nuclei may be regarded as being at their equilibrium positions. The overlap between the neutral target and the ion gives the triple differential cross section for the orbital in momentum space [10]:

$$\sigma_i \propto \int d\Omega |\phi_i(\mathbf{p})|^2, \quad (5)$$

where \mathbf{p} is the momentum of the target electron at the instant of ionization (annihilation). In density-functional theories used widely for molecules, the orbital $\phi_i(\mathbf{p})$ in momentum space is approximated by the Kohn–Sham (KS) orbitals of the ground electronic state [18]. A momentum cut-off is required for the numerical calculations, and it is taken to be 10 au.

3. Results and discussion

Figure 1 presents the annihilation γ -ray spectra for He (1s orbital) and Ar (3s and 3p orbitals) as a function of the photon energy shift ε . The spectra shown by the solid lines are calculated using the unit positron wavefunction (which corresponds to the plane-wave (PW) approximation

Table 1. Comparison of the FWHM of the annihilation γ -ray spectra, $\Delta\varepsilon$ (keV), for noble gases based on the HF/TZVP model for the atomic electrons.

Noble gases	$\Delta\varepsilon$ (PW) total	$\Delta\varepsilon$ (PW) valence	$\Delta\varepsilon$ experiment [4]	$\delta(\Delta\varepsilon)^a$	$\Delta\varepsilon$ (HF) [5, 7]	$\Delta\varepsilon$ (PW) ^d	$\langle R^2 \rangle$ (au)	$\langle R \rangle_{nl}^c$ (au)
He	2.99	(2.99)	2.50	0.16	2.53	2.95	2.35	0.927
Ne	5.14	4.94	3.36	0.32	3.82	–	9.33	0.965
Ar	3.85	3.31	2.30	0.31	2.65	3.30	25.94	1.663
Kr	4.07	2.93	2.09	0.29	2.38	–	39.45	1.952
Xe ^b	– ^c	2.48	1.92	0.22	2.06	–	62.83	2.338

^a $\delta(\Delta\varepsilon) = (\Delta\varepsilon \text{ (PW, valence)} - \Delta\varepsilon \text{ (experiment)}) / \Delta\varepsilon \text{ (PW, valence)}$.

^b For Xe the basis set is DGDZVP as TZVP is not available for Xe.

^c The current program is unable to access the inner shells of Xe due to the large number of shells.

^d Produced by one of the authors (GG) using standard atomic HF codes.

^e Mean radius of the outer valence orbital from [20].

at low positron momenta) using standard atomic HF codes [7], and the circles and triangles show the present calculations for He and Ar, respectively. As the annihilation γ -ray spectra are symmetric, $w(-\varepsilon) = w(\varepsilon)$, only positive photon energies ($\varepsilon > 0$ keV) are shown in figure 1. All spectra are normalized to unity at $\varepsilon = 0$. It is seen in figure 1 that in the PW approximation, the momentum distributions of the atomic electrons in the outermost shells of He and Ar are reproduced well using completely different algorithms. This is a significant result, as it tests the capacity of the present approach to reproduce the shapes of the γ -ray spectra in noble gases. Hence we believe that the method of using modern computational chemistry techniques can be readily applied to more complex systems such as molecules [19].

Table 1 compares the annihilation line shape parameter, namely, the full width at half maximum (FWHM), $\Delta\varepsilon$, of the γ -ray annihilation spectra for noble gases with available atomic HF calculations (where the positron orbital is treated by both HF and PW models) and the results from experiment. The atomic electron wavefunctions are calculated using the HF/TZVP model. The electronic spatial extent $\langle R^2 \rangle$ and the mean-squared radii of the outer valence orbitals, $\langle R \rangle_{nl}$ of the noble gases (1s for He and np for heavier atoms [20]) are also tabulated as an indicator of atomic size. Here $\langle R^2 \rangle$ is a single number that attempts to describe the size of an atom or a molecule. It is computed as the expectation value of the electron density times the squared distance from the centre of mass of a molecule (or atom) [17]. The annihilation spectral width $\Delta\varepsilon$ of the noble gases exhibits an opposite trend with respect to size; that is, $\Delta\varepsilon$ decreases as $\langle R^2 \rangle$ increases (except for He) or $\langle R \rangle_{nl}$ increases.

As observed previously in insulators and metals, as well as noble gases [7], the annihilation spectra are basically determined by the momentum distributions of the valence electrons, which are described well by the HF model. The calculated $\Delta\varepsilon$ values for the *total* electron contributions, namely 5.14 keV (Ne) > 3.85 keV (Ar) < 4.07 keV (Kr), do not agree with the measured values of 3.36 keV (Ne) > 2.30 keV (Ar) > 2.09 keV (Kr). However, as shown in table 1, the $\Delta\varepsilon$ values for the *outer valence* electron shell agree well with the measurements and also follow the trend. Note that the values for Xe in this table are only listed for completeness, as the basis set for Xe is the double zeta with

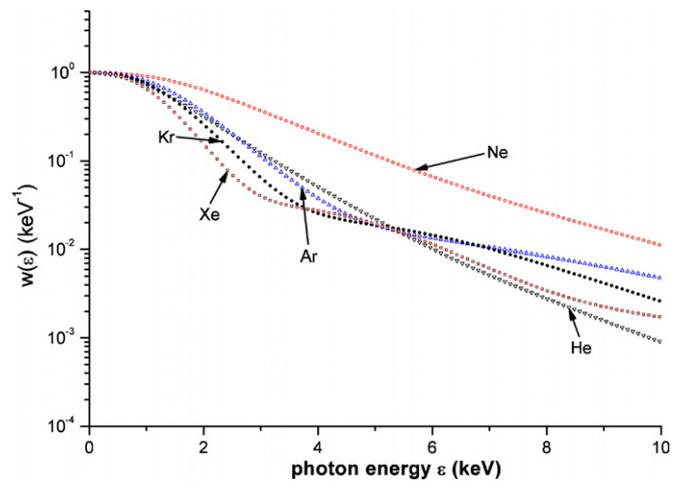


Figure 2. Comparison of the annihilation γ -ray spectra of the outermost shells of noble gases calculated using the HF/TZVP model for atomic electron wavefunctions (HF/DZVP for Xe) in the PW approximation: He (∇), Ne (\circ), Ar (Δ), Kr (\bullet) and Xe (\square). All spectra are normalized to unity at $\varepsilon = 0$.

valence polarized orbitals (DZVP) (i.e. the TZVP basis set is not available for Xe).

Figure 2 compares the γ -ray spectra for the outer valence electrons ($ns + np$) of the noble gases calculated in the PW approximation. As can be seen in this figure, He and Ne exhibit certain similarities in their γ -ray spectra in which they can be fitted well using a single Gaussian function. On the other hand, the γ -ray spectra of heavier noble gas atoms, such as Ar, Kr and Xe, have a ‘shoulder’ (inflection point) and may be fitted better as the sum of two Gaussian distributions (this approximation was used for determining detector-broadening-free spectra in [7]). Such a shoulder is usually related to high-momenta contributions from the inner shells. In particular, comparison between the measured and calculated spectra in [4] permitted the identification of contributions from the outermost inner shell (i.e. $(n-1)s$, $(n-1)p$, and $(n-1)d$, for Kr and Xe), in addition to that from the valence ns and np electrons. The present spectra in figure 2 contain the contributions from the outer shell only, i.e. ns and np electrons. The shoulder structure evident here is a manifestation of the fact that these orbitals in Ar, Kr and Xe are *orthogonal* to the inner-shell orbitals; hence they contain some high-momentum components.

Table 2. Bound electron shell contributions to the positron annihilation γ -ray spectra ($\Delta\varepsilon$ in keV) of noble gases based on the HF/TZVP model for atomic electron wavefunctions.

Shell	He		Ne		Ar		Kr		Xe ^a	
	$\Delta\varepsilon$	Z_{eff}								
1s	2.99	2.00	16.27	1.48	22.03	0.67	25.31	0.13		
2s	–	–	3.52	1.95	7.90	1.79	16.90	1.54	<i>21.84</i>	<i>0.91</i>
3s	–	–	–	–	2.39	1.98	6.43	1.80	<i>10.67</i>	<i>1.44</i>
4s	–	–	–	–	–	–	2.15	1.98	<i>4.89</i>	<i>1.87</i>
5s	–	–	–	–	–	–	–	–	1.80	<i>1.98</i>
2p	–	–	5.86	5.98	15.77	5.39	26.86	1.80	<i>29.42</i>	<i>0.44</i>
3p	–	–	–	–	3.77	5.94	11.86	5.34	<i>20.68</i>	<i>4.73</i>
4p	–	–	–	–	–	–	3.30	5.95	<i>8.68</i>	<i>5.56</i>
5p	–	–	–	–	–	–	–	–	<i>2.80</i>	<i>5.95</i>
3d	–	–	–	–	–	–	16.25	8.97	<i>27.09</i>	<i>4.25</i>
4d	–	–	–	–	–	–	–	–	<i>10.89</i>	<i>9.14</i>
S($l = 0$)	–	–	3.98	3.43	2.94	4.43	2.77	5.44	–	–
P($l = 1$)	–	–	5.86	5.98	4.29	11.33	3.90	13.09	<i>3.53</i>	<i>16.68</i>
Core	–	–	16.27	1.48	12.62	7.84	13.08	19.57	–	–
Valence	–	–	4.94	7.93	3.31	7.92	2.93	7.93	<i>2.48</i>	<i>7.93</i>
Total	2.99	2.00	5.14	9.41	3.85	15.76	4.07	27.50	–	–
Experiment ^b	2.50		3.36		2.30		2.09		1.92	

^a The basis set for Xe is DZVP whereas the other noble gases use the TZVP basis. As a result, the last two columns (italic) of Xe can be considered for reference.

^b See [4].

Positron–electron annihilation spectra are very sensitive to the atomic electron shells where the bound electrons reside (i.e. to the principal quantum number n and the orbital angular quantum number l). Table 2 reports the bound electron contributions to the spectra of the noble gases. It is always the innermost shells, either 1s or 2p, that have the largest FWHM $\Delta\varepsilon$, and they are significantly larger than the measured $\Delta\varepsilon$ values. Thus these contributions are less likely to dominate the γ -ray spectra. This is in agreement with previous findings that the contributions from the inner shells are very small, never exceeding a few per cent [4]. In addition, the wavefunctions (orbitals) of the innermost s and p electrons in heavier noble gas atoms (i.e. Ar and beyond) extend to significantly larger momentum regions, namely, greater than the 10 au cut-off momentum in the present study. As a result, it is the innermost electrons that are associated with a most significant ‘electron density loss’ at this cut-off momentum. For example, for the 1s orbital of Ar, $\Delta\varepsilon = 22.03$ keV from the HF/TZVP model, but the theoretically calculated Z_{eff} (with an upper limit of 2.0) is only 0.67, which accounts for only 33.5% of total electron density in the Ar 1s shell. The $\Delta\varepsilon$ for the 2p orbital of Ar is 15.77 keV using the same model, while the theoretical Z_{eff} value (upper limit of 6.0) is 5.39, thus including almost 90% of the 2p electron density in this orbital.

For other atomic electrons, the $\Delta\varepsilon$ values vary considerably from shell to shell, that is, with the quantum numbers n and l , which is in agreement with previous studies [5, 7]. For example, for the same orbital angular momentum, e.g., $l = 0$, $\Delta\varepsilon$ decreases as the principal quantum number n is increased, whereas for the same n , e.g., $n = 3$, the trend is the opposite; $\Delta\varepsilon$ increases as the orbital quantum number l is increased. As seen in table 2, the outermost ns electrons of the noble gases have γ -ray annihilation line shape parameters $\Delta\varepsilon$ closest to the measured FWHM values, that is, the 1s orbital

for He, 2s for Ne, 3s for Ar, 4s for Kr and 5s for Xe (highlighted in table 2).

Figure 3 shows the bound electron contributions to the γ -ray spectra of Ar with (a) collective contributions from s electrons, p electrons, core electrons, valence electrons and all electrons; and (b) the orbital (subshell, n and l) based contributions. It is seen from figure 3(a) that the shape of the total spectrum (solid line) is very similar to the contribution from the p electrons (dot–dash line), whereas the contributions from the s-electrons (long-dashed line) is much smaller, and have a weaker effect on the shape of the total spectrum. The γ -ray spectra of the s and p electrons of Ar are almost ‘parallel’ except in the larger photon energy region above 5 keV. However, the outer valence electrons of Ar, which include 3s and 3p (short-dashed line), exhibit apparent differences in shape to the contribution of the other orbitals of Ar (dotted line).

Figure 3(b) shows the individual orbital contributions to the γ -ray spectrum of Ar. The outer valence shell indeed behaves very differently from the shells with smaller quantum numbers, such as the 1s, 2s and 2p shells. The $\Delta\varepsilon$ values for the atomic electrons in other than the outermost shell are very different from the experimental $\Delta\varepsilon$ values, indicating their relatively small contributions to the γ -ray spectrum of Ar. The fact that the $\Delta\varepsilon$ of the calculated total contribution from all atomic electrons of Ar exhibits less similarity to the experiment than do either the 3s or 3p orbitals indicates that the measured spectra are not the result of a simple direct sum over the contributions of all atomic electrons. Rather, the annihilation measurements reflect contributions from particular orbitals in the outer valence shell, such as the ns electrons. This is largely due to the positron repulsion from the nucleus which suppresses the contribution of the inner orbitals and reduces their effect on $\Delta\varepsilon$.

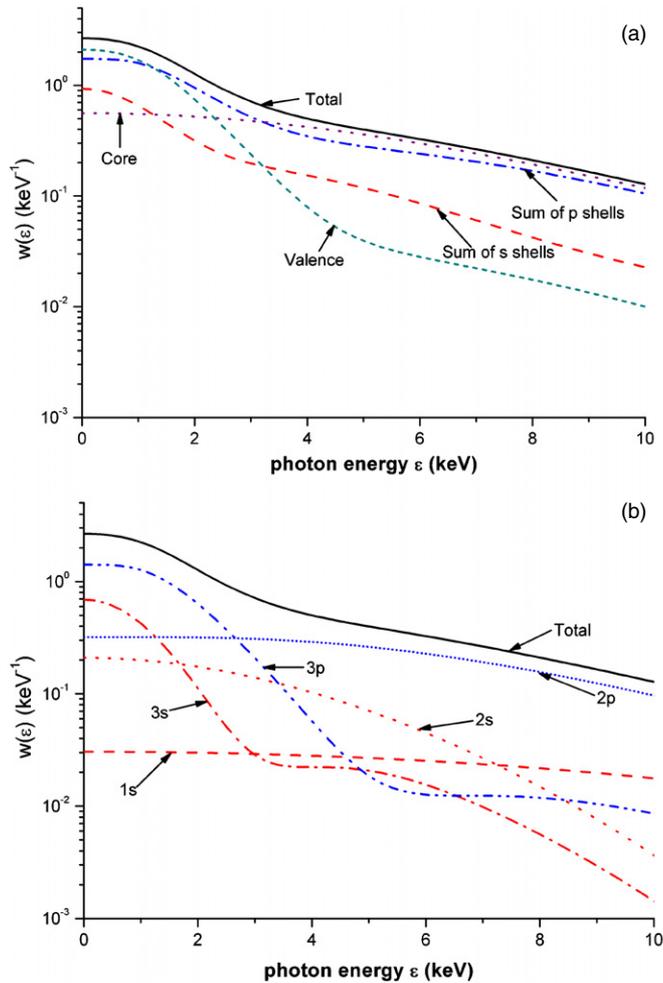


Figure 3. Comparison of atomic electronic shell contributions to the annihilation γ -ray spectra of Ar calculated using the HF/TZVP model for atomic wavefunctions in the plane-wave approximation for the positron: (a) summed by orbital type and (b) specific orbitals.

Figures 4(a) and (b) compare the contributions of the outer valence electrons of Ar (3s, 3p and 3s + 3p) and Kr (4s, 4p and 4s + 4p), respectively, with the experimental two-Gaussian fits to the spectra for these atoms [7]. Here, all spectra normalized to unity at $\epsilon = 0$. For small photon Doppler shifts, namely $\epsilon < 2$ keV, the experimental spectra agree well with the PW approximation spectra for the ns electrons (i.e. the 3s electrons in Ar and 4s in Kr). This similarity was seen earlier in the FWHM parameters in table 2. For larger Doppler shifts, the calculated spectra lie higher than those from the experiment. This feature is related to the overestimate of the high-momentum components (which come from small distances) due to neglect of the positron–nuclear repulsion by the PW approximation.

Finally, figure 4(c) shows the γ -ray spectra of the outer valence ns electrons of the noble gases, together with their $\Delta\epsilon$ values. Although the spectral shapes and therefore the FWHM $\Delta\epsilon$ of the noble gases are quite different, certain trends are observed. Starting with Ne, inflection points are observed in these spectra. For example, inflection points are observed at 6 keV for Ne, 3 keV for Ar and 2.5 keV for Kr. These

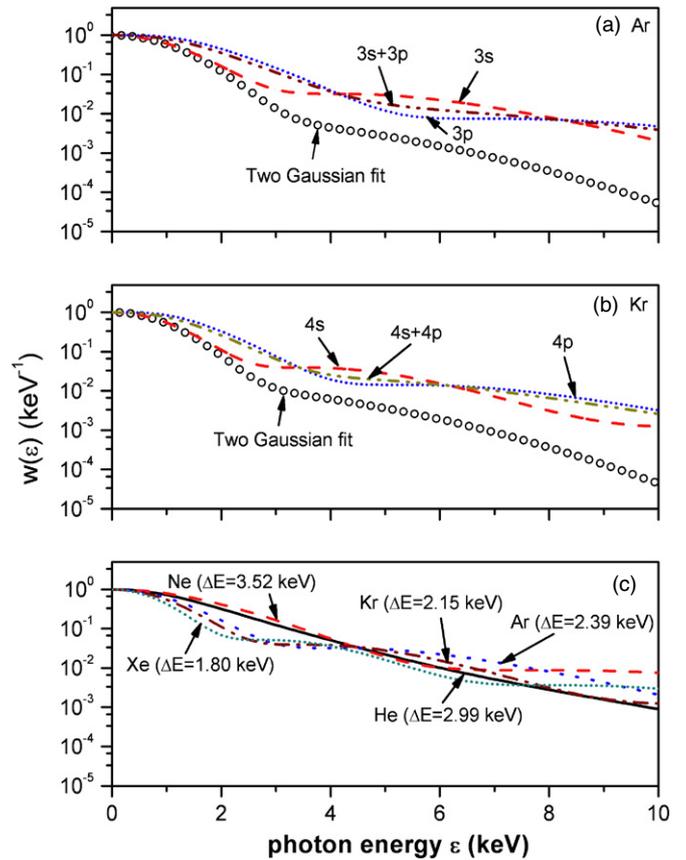


Figure 4. Comparison of the contributions of outer electron shells (ns , np and $ns+np$) to the annihilation γ -ray spectra (curves) with the experimental data represented by two-Gaussian fits (open circles) [7] for (a) Ar, and (b) Kr; shown in (c) are the ns electron contributions to the annihilation γ -ray spectra of He, Ne, Ar, Kr and Xe. All atomic electron wave functions are calculated using the HF/TZVP (HF/DZVP for Xe) model and the spectra are normalized to unity at $\epsilon = 0$.

features are related to the nodes in the spatial wavefunctions of the ns orbitals with $n > 1$. Such changes in the shapes of the spectra suggest that more than one Gaussian function is needed to appropriately fit the spectra. For Xe, two such inflection points, at 2 keV and 6.5 keV, are visible, indicating that more than two Gaussian fitting functions would be required in this case to represent the spectrum over a wider range of energies. As compared with Kr, the position of the first minimum in Xe has moved towards smaller energy shifts ϵ , leading to a decrease in the corresponding $\Delta\epsilon$. Note, however, that the np contributions (e.g., see figures 4(a) and (b)) are increased at energies close to the minima of the ns spectra, so that these features become less prominent in the total spectrum.

4. Concluding remarks

In this work positron annihilation γ -ray spectra of the noble gases have been calculated using modern computational chemistry tools for the bound electron wavefunctions and plane-wave approximation for the low-energy positron. The

results agree well with independent atomic calculations using a different algorithm and they achieve moderate agreement with the experimental spectral line shapes, e.g. the full-width at half maximum parameter $\Delta\varepsilon$. It is found that the contributions of various electron shells to the spectra depend significantly on the principal quantum number n and the orbital angular momentum quantum number l . The present study further reveals that the outermost ns electrons of the noble gases exhibit the spectral shapes in close agreement with those measured. It is also observed that the measured spectra are not simple sums of the momentum densities for all atomic electrons. This is mostly due to the effect of positron repulsion from the nucleus, which suppresses the inner-shell (and more generally, high-momentum) contributions to the spectra.

The present study, however, does not address the absolute magnitudes of the measured annihilation rates Z_{eff} . The theoretical values, $Z_{\text{eff}} < N^c$, in the valence shells indicate that the electron momentum cut-off at 10 au in the calculations is not sufficiently large for some cases, and thus this criterion needs to be extended beyond this momentum region to ensure sufficient electron density in further calculations. Also, unlike the *shapes* of the γ -ray spectra, the absolute values of the annihilation rates are strongly affected by electron–positron correlations (see, e.g., [5]) and for molecules, by positron capture in vibrational Feshbach resonances [6]. Nevertheless, the robust nature of the present approach makes it possible for us to proceed to more complex molecular systems using tools of modern computational chemistry, and to study electronic structure effects on the γ -ray positron annihilation spectra of other atoms and molecules.

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