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Theoretical analysis of the binding of a positron and pair-annihilation in fluorinated benzene molecules[⋆]

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Abstract. The binding of a positron to fluorobenzene molecules was theoretically demonstrated at Hartree-Fock level of multi-component molecular orbital theory. We confirmed that (i) 1,2-difluorobenzene, 1,2,3-trifluorobenzene, 1,2,3,4-tetrafluorobenzene molecules have bound states for a positron, and (ii) their positron affinity (PA) and two photon pair-annihilation rate (Γ_2) are strongly correlated with their dipole moment. Analyzing the Γ_2 values for each electronic molecular orbital in all the fluorobenzene molecules, we found that the electronic valence orbitals, consisting of $2p$ atomic orbitals of fluorine atoms, have the dominant contribution to the total Γ_2 value.

1 Introduction

The positron (e^+) is the anti-particle of the electron and has the same mass and spin, but opposite charge. When the positron collides with an electron, it undergoes a pair-annihilation with two or three gamma-rays emitted. Positron spectroscopy using the gamma-ray is now used in a wide range of areas, such as detection of lattice defect in material science and positron emission tomography in medical technology [1–3]. A positron injected into a gas, a liquid or solid induces processes such as ionization, electronic excitation, the formation of positronium (a temporary bound state of a positron and an electron), and the formation of positron-molecular complex before the pair-annihilation with an electron.

Recently, Surko and coworkers experimentally measured a pair-annihilation rate (Z_{eff}) and positron affinity (PA), which is the binding energy of positron to an atom or molecule, using vibrational Feshbach resonance technique for various molecules such as aldehydes, alcohols, and aromatics [4–6]. Although they also reported the PA values for some kinds of aromatic compounds [7,8], the PA values for some fluorobenzene molecules are the predicted values based on a statistical approach that holds for other molecular species [9]. The positron annihilation spectra for this molecule have been measured by Iawata et al. [10] and the difference in the Doppler broadenings among difluo-

robenzene isomers has been discussed. From a theoretical side, Wang et al. [11] have analyzed the Doppler shifts in the γ-ray spectra for positron annihilation for benzene and its fluoro-derivatives under a low energy plane wave positron (LEPWP) approximation, in which the wave function of a positron is assumed as unity. To our knowledge, however, the bound state of a positron to fluorobenzene molecules has not been demonstrated both experimentally and theoretically, yet.

In this study, thus, in order to demonstrate the positron binding to fluorobenzene molecules, we theoretically analyzed the PA values and two photon pair-annihilation rate (Γ_2) of them using first-principles calculations. The PA values were analyzed using multi-component molecular orbital (MC_MO) theory [12] which allows us to solve electronic and positronic wavefunctions on equal footing. In order to elucidate the mechanism of the pair-annihilation, we also report the Γ_2 values for each electronic molecular orbital.

2 Method

We assume the atomic unit ($m_e = 1, \hbar = 1, e = 1$) throughout this paper. We here show a brief outline of Hartree-Fock (HF) level of MC_MO theory. The details are described in reference [12]. The non-relativistic Hamiltonian operator for a molecular system containing N_e electrons, N_{nuc} nuclei, and a positron is

$$\hat{H} = -\frac{1}{2}\sum_i^{N_e} \nabla_i^2 - \frac{1}{2}\nabla_p^2 + \sum_i^{N_e}\sum_{j>i}^{N_e}\frac{1}{r_{ij}}$$
$$- \sum_i^{N_e}\sum_I^{N_{\text{nuc}}}\frac{Z_I}{r_{iI}} - \sum_i^{N_e}\frac{1}{r_{ip}} + \sum_I^{N_{\text{nuc}}}\frac{Z_I}{r_{pI}}, \quad (1)$$

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where the first and second terms are the kinetic energy operators of the electrons and positron, respectively. The other terms are the Coulomb interactions: Z_I is the charge of the I-th nucleus and the variables of r_{ij}, r_{ip}, etc. are the distances between particles.

The total wave function at HF level of the theory can be written as

$$\Psi_{\text{MC\_MO}} = \Phi^{(e)}\left(\mathbf{R}_e\right) \times \varphi^{(p)}\left(\mathbf{r}_p\right), \qquad (2)$$

where $\Phi^{(e)}$ and $\varphi^{(p)}$ are an electronic Slater determinant and a positronic orbital, respectively. Expanding molecular orbitals of electrons and a positron with a linear combination of basis functions, one can obtain a multi-component electron-positron wave function by solving the corresponding Roothaan equations simultaneously.

The total energy of positron-attached system $[X; e^+]$ at the HF level of MC_MO theory is given by

$$E^{[X;e^+]} = 2 \sum_{i}^{N_e/2} h_{ii}^e + \sum_{i,j}^{N_e/2} \left[2\left(ii|jj\right) - \left(ij|ij\right)\right]$$
$$+ h_{pp}^p - 2 \sum_{i}^{N_e/2} \left(ii|pp\right) + \sum_{I,J}^{N_{\text{nuc}}} \frac{Z_I Z_J}{r_{IJ}} \qquad (3)$$

where h_{ii}^e is one-electronic integral, h_{pp}^p one-positronic integral, $(ii|jj)$ Coulomb two-electronic integral, $(ij|ij)$ the exchange two-electronic integral, and $(ii|pp)$ Coulomb integral between an electron and a positron. We here assumed a closed shell system for electrons. A theoretical PA value of parent molecule is simply defined by the total energy difference of the parent molecule and its positron-attached system as $\text{PA} \equiv E^X - E^{[X;e^+]}$, where E^X is the total energy of parent molecule X with a conventional HF calculation.

The Γ_2 values were calculated with the general formula [14] as

$$\Gamma_2 = \pi \alpha^4 c a_0^{-1} \langle \delta_{ep} \rangle, \qquad (4)$$

where α, c, and a_0 are the fine-structure constant, the speed of light, and Bohr radius, respectively. The electron-positron collision probability $\langle \delta_{\text{ep}} \rangle$ is the expectation value of the δ function, and can be analyzed with the MC_MO wave function as

$$\langle \delta_{ep} \rangle = \langle \Psi_{\text{MC\_MO}} \left| \sum_{i}^{N_e} \delta\left(\mathbf{r}_i^e - \mathbf{r}^p\right) \right| \Psi_{\text{MC\_MO}} \rangle / \langle \Psi_{\text{MC\_MO}} | \Psi_{\text{MC\_MO}} \rangle. \qquad (5)$$

At HF level of MC_MO theory for electronic closed shell systems, $\langle \delta_{ep} \rangle$ can be also reduced to the following formula with electronic molecular orbitals $\varphi_i^{(e)}$:

$$\langle \delta_{ep} \rangle = 2 \sum_{i}^{N_e/2} \int \varphi_i^{(e)}\left(\mathbf{r}\right) \varphi_i^{(e)}\left(\mathbf{r}\right) \varphi^{(p)}\left(\mathbf{r}\right) \varphi^{(p)}\left(\mathbf{r}\right) d\mathbf{r}. \qquad (6)$$

This formula clearly shows that the total Γ_2 values can be computed as the sum of contributions from each electronic molecular orbital. One of the authors, Oyamada, implemented a code to calculate the electron-positron collision probability of equation (5) for both the Hartree-Fock and the configuration interaction methods, using the Obara-Saika scheme [15].

3 Computational details

The geometries of all fluorobenzene molecules analyzed in this study are shown in Figure 1. The other possible structural isomers and mono-, penta-, and hexa-fluorobenzene molecules are out of our present study, since they have no bound states for a positron at the present HF level of MC_MO theory. Geometry optimizations for all parent molecules were performed at HF level of theory with 6–31++G(d,p) basis set. PA and Γ_2 values were calculated at the optimal geometry of the parent molecules. In the calculation of positron attached systems, we employed multi-centered Gaussian-type functions (GTFs) as positronic basis sets, where a set of $[11s11p]$ GTFs having identical basis center were placed on each fluorine atom. The exponent in the positronic GTFs were determined by the even-tempered scheme of $\alpha_{i+1} = c \times \alpha_i$, where $c = 3.1623$. For s- and p- type GTFs, $\alpha_1 = 1.0 \times 10^{-5}$. Since the positronic basis set we employed was considerably diffuse, the multi-centered basis sets could cause significant linear dependence problems. To avoid such problems, we eliminated redundant basis sets having small eigenvalues in its overlap matrix less than 1.0×10^{-4} with the canonical orthogonalization technique. All calculations for parent molecules and those positron-attached systems were performed with a modified version of GAMESS package [16].

4 Results and discussion

4.1 Positron affinity and annihilation rate

The PA and Γ_2 values for all fluorobenzene molecules are shown in Table 1. We obtained the bound state of a positron, or positive PA values, only for 1,2-difluoro-, 1,2,3-trifluoro-, and 1,2,3,4-tetrafluoro-benzene molecules. The 1,2,3-trifluorobenzene molecule has the largest PA and Γ_2 values among these three molecules. Other two fluorobenzene molecules have relatively small PA and Γ_2 values, and then the lowest values were found for the 1,2,3,4-tetrafluorobenzene molecule. We found that the similar tendency was also found for the dipole moment of those molecules, and confirmed that other possible structural isomers of fluorobenzene molecules have the dipole moment smaller than of 1,2,3,4-tetrafluorobenzene molecule. Figure 2 shows the results of linear regression analysis for PA and Γ_2 values with molecular dipole moments as an explanatory variable. In fact, the PA and Γ_2 values have a strong correlation with the dipole moment of parent molecules, where the coefficients of determination for the PA and Γ_2 values are 0.979 and 0.910, respectively.

As shown in Table 1, our PA values of 1,2-difluoro- and 1,2,3,4-tetrafluorobenzene molecules are significantly smaller than the binding energies predicted from the empirical formula proposed by Danielson et al. [9]. The present calculations also give negative PA values for other fluorobenzene molecules, although positive binding energies have been predicted for those molecules by the empirical formula. A part of the reason for such qualitative and quantitative inconsistency could be due to
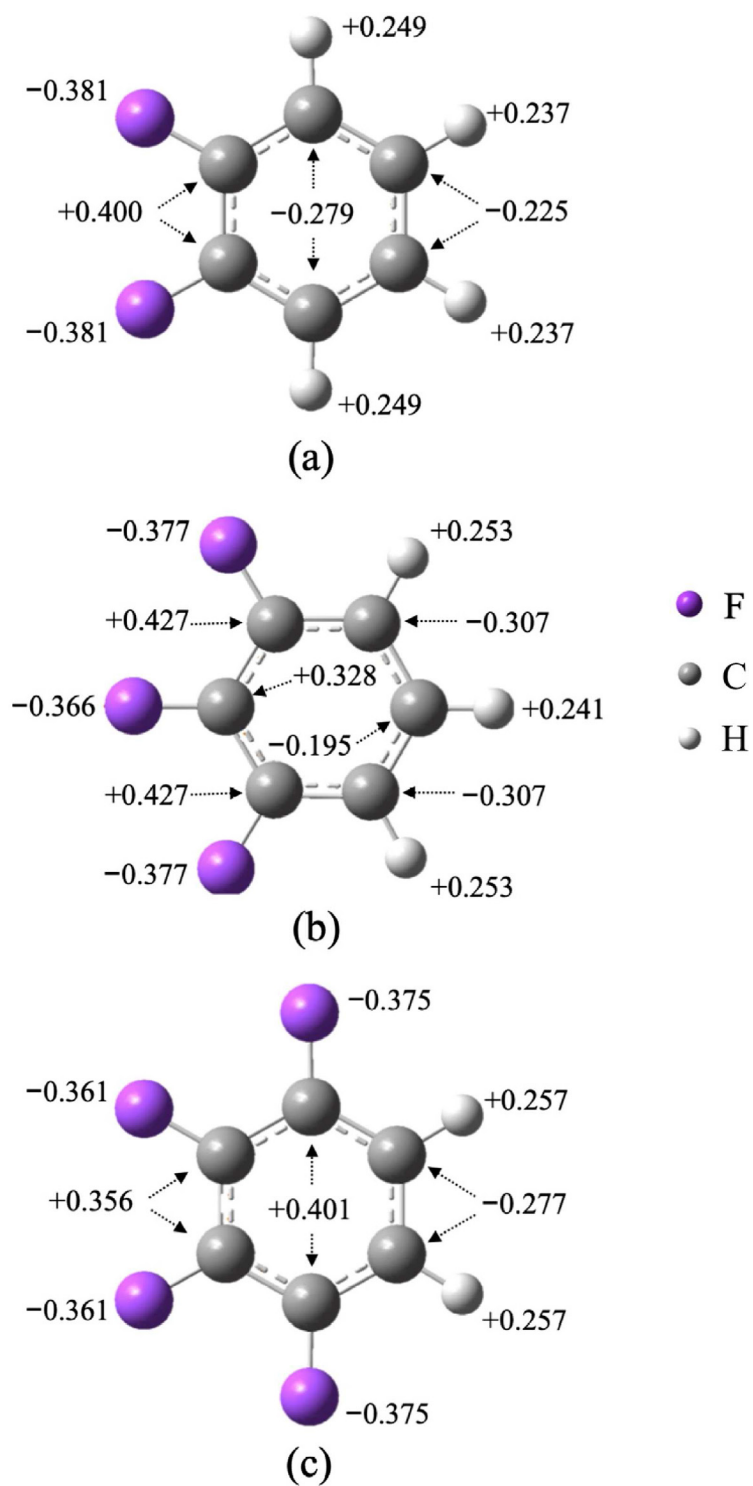
Fig. 1. The structures of fluorobenzene molecules analyzed in this study: (a) 1,2-difluorobenzene, (b) 1,2,3-trifluorobenzene, and (c) 1,2,3,4-tetrafluorobenzene molecules. Numbers mean the net atomic charge obtained with the natural population analysis.

Table 1. The dipole moment (μ), positron affinities (PA) and two-photon pair-annihilation rate (Γ_2) of fluorobenzene molecules. The predicted binding energies of a positron (ϵ_b) from the empirical formula proposed by Danielson et al. [9] are also shown. [a]The predicted binding energy from the empirical linear equation, $\epsilon_b = 12.4 \, (\alpha + 1.6\mu + 2.4N_\pi - 5.6)$, proposed by Danielson et al. [9]. The variable N_π is the number of π bonds; $N_\pi = 3$ for all molecules listed in this table. [b]The μ and/or α values are unavailable in literatures. [c]The μ and α values used in calculating ϵ_b are taken from reference [17].

Molecules	Formula	μ [debye]	PA [meV]	Γ_2 [ns^{-1}]	$\epsilon_{(b)}$ [meV][a]
Fluorobenzene	C_6H_5F	1.83	<0	–	176
1,2-difluorobenzene	$C_6H_4F_2$	3.08	0.39	9.49×10^{-5}	189
1,3-difluorobenzene		1.81	<0	–	173
1,4-difluorobenzene		0.00	<0	–	141
1,2,3-trifluorobenzene	$C_6H_3F_3$	3.51	0.98	1.80×10^{-4}	–[b]
1,2,4-trifluorobenzene		1.75	<0	–	–[b]
1,3,5-trifluorobenzene		0.00	<0	–	–[c]
1,2,3,4-tetrafluorobenzene	$C_6H_2F_4$	3.00	0.12	2.62×10^{-5}	188[c]
1,2,3,5-tetrafluorobenzene		1.71	<0	–	–[b]
1,2,4,5-tetrafluorobenzene		0.00	<0	–	140[c]
1,2,3,4,5-pentafluorobenzene	C_6HF_5	1.70	<0	–	–[b]
Hexafluorobenzene	C_6F_6	0.00	<0	–	139[c]
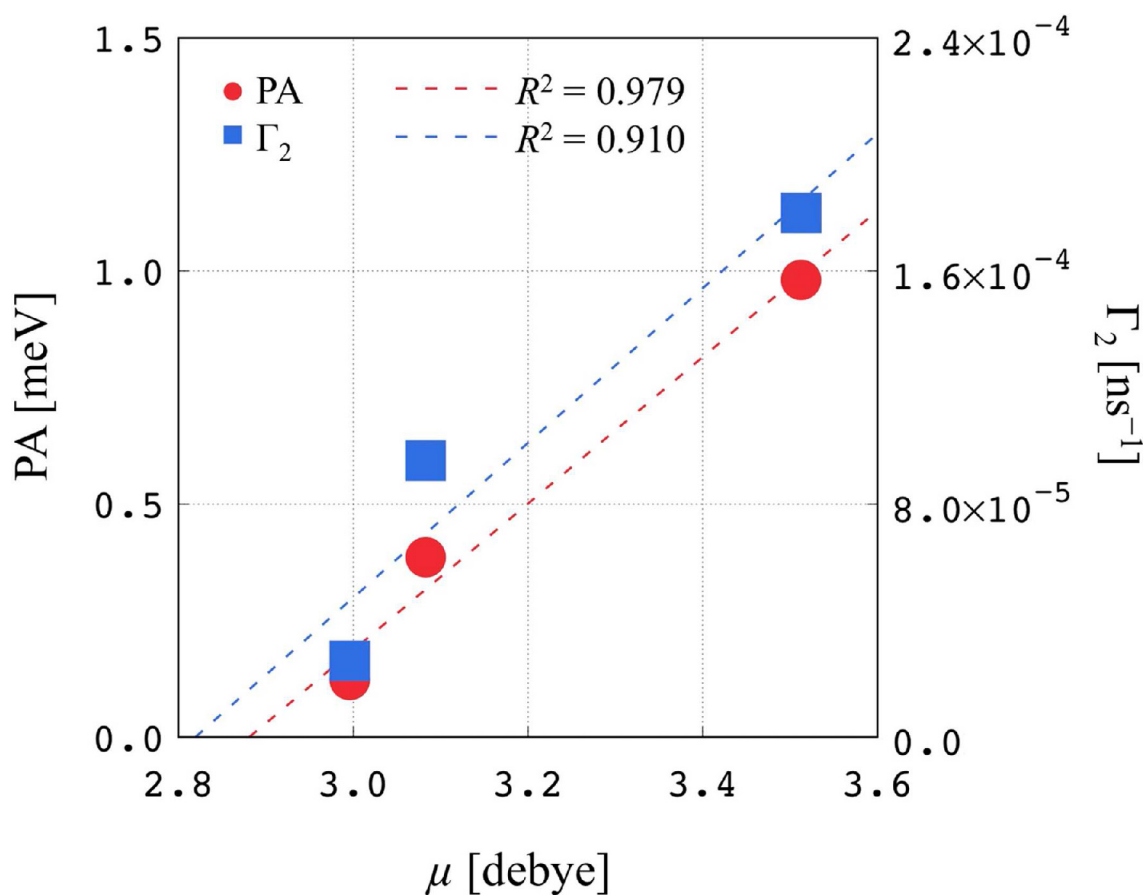
Fig. 2. The results of linear regression analysis for the positron affinity (PA) (red circle) and the two-photon pair annihilation rate (Γ_2) (blue square) with the dipole moment (μ). The red (blue) dash line is a fitted line for PA (Γ_2). The coefficients of determination (R^2) for PA and Γ_2 are 0.979 and 0.910, respectively.
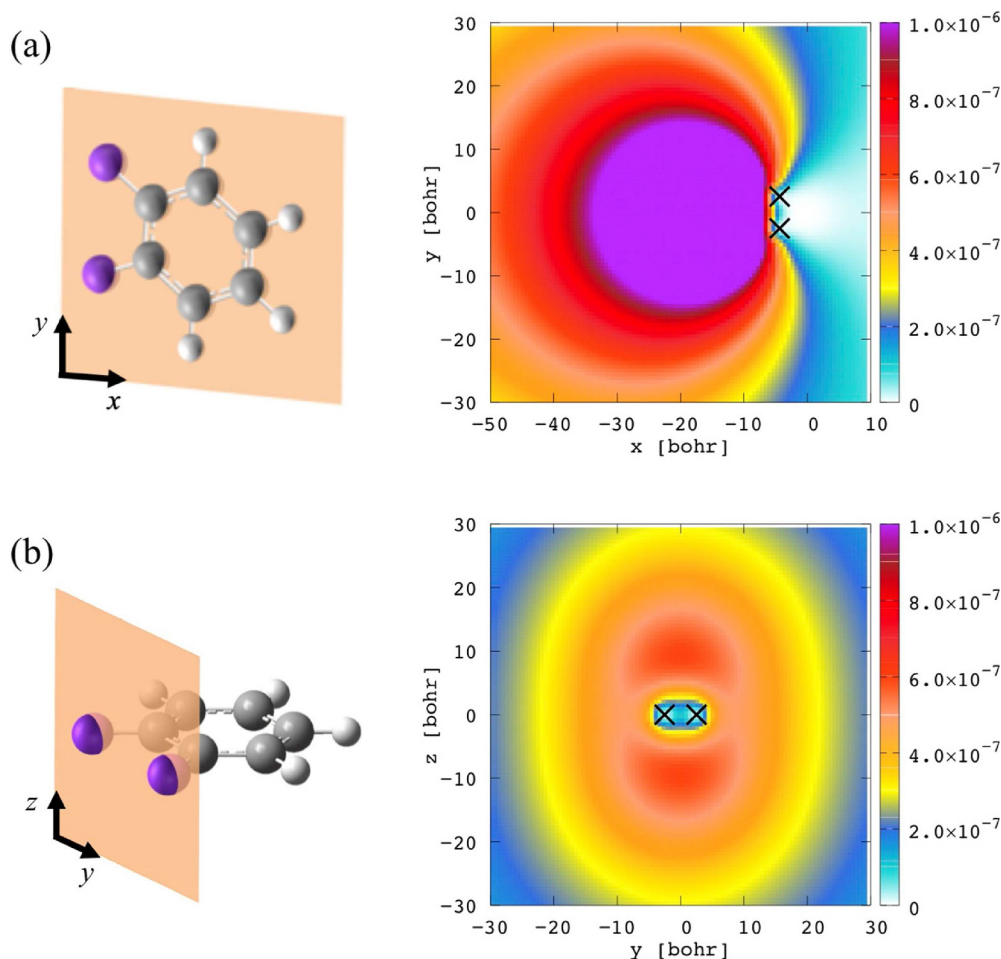
Fig. 3. The density distribution of positron attached to 1,2-difluorobenzene molecule: (a) in the molecular plane (xy-plane) and (b) in the perpendicular plane to the molecular plane through two fluorine atoms (yz-plane). The symbols "$\times$" means the position of fluorine atoms. The color bar shows the value of positron density.

the lack of both electron-positron correlations [18,19] and the effects of molecular vibrations [20,21] in the present theoretical approach. Thus, further investigations based on more sophisticated theoretical ways would be required to explain these discrepancies.

### 4.1.1 Density distributions of the attached positron

We show the density distribution of the positron attached to fluorobenzene molecules in Figures 3–5. For all molecules, the positron density becomes high at the fluorine atom side in the outside region of the molecule as shown in Figures 3a, 4a, and 5a. These uniform behaviors of the attached positron would be easily understood with the net atomic charges obtained with the natural population analysis shown in Figure 1, where fluorine atoms are the most negatively charged among all other atoms. As shown in Figures 3b, 4b, 4c, 5b, and 5c, the positron densities are also spread into the out-of-molecular plane direction (or in a plane perpendicular to the molecular plane), and those behaviors are slightly different among three fluorobenzene molecules. For instance, the positron density is mainly spread into the z-direction for 1,2-difluorobenzene molecule

and into the y-direction for 1,2,3,4-tetrafluorobenzene molecule, while that is spherically spread on the yz-plane for 1,2,3-trifluorobenzene molecule. Such density distributions of the attached positron in the out-of-molecular plane can contribute to the variation of Γ_2 values for each molecular orbital, because the orbital Γ_2 value is proportional to the spatial overlap between the positronic and electronic densities as clearly described in equation (6).

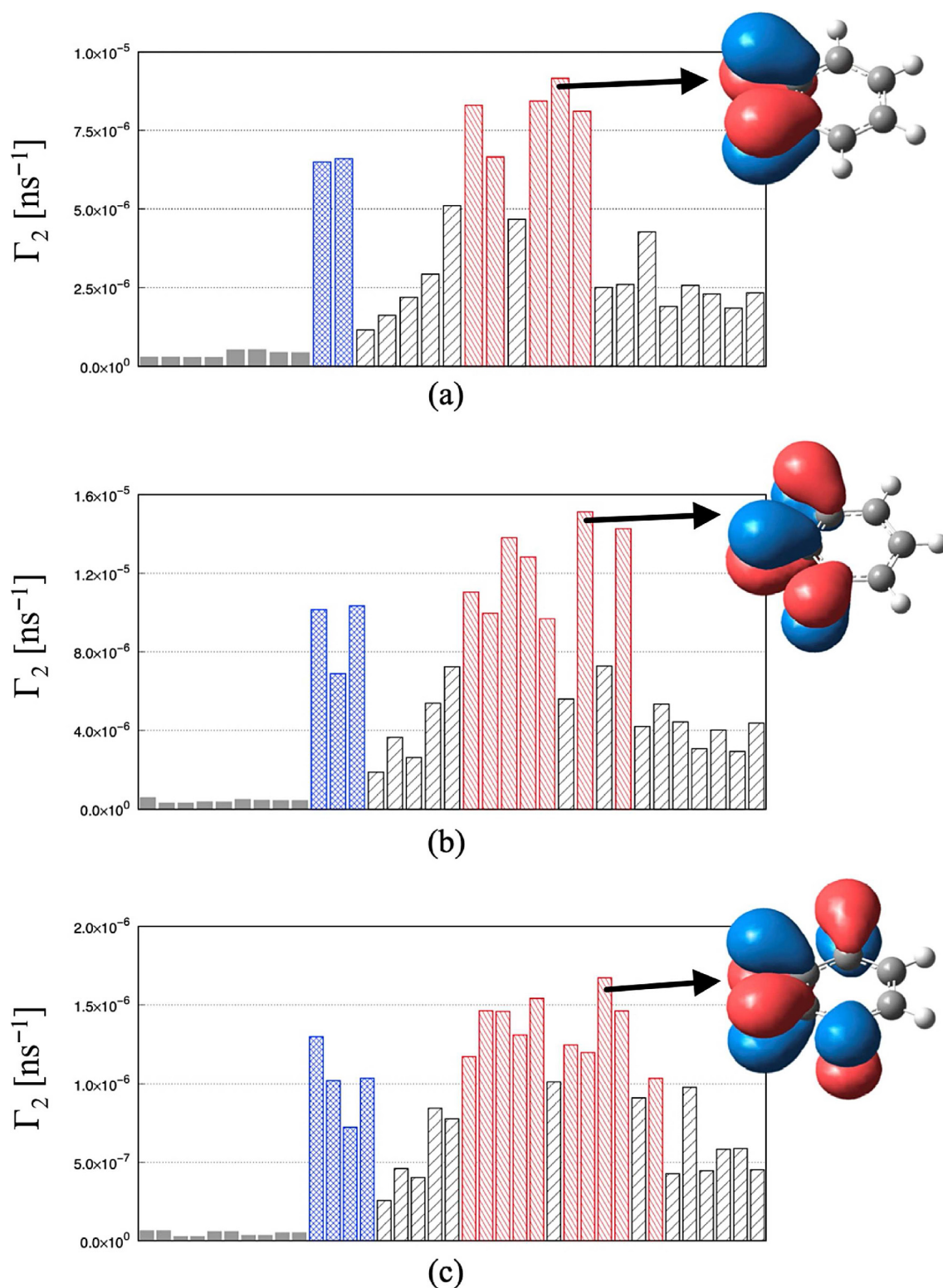## 4.2 Pair-annihilation rate of each molecular orbital

We show the Γ_2 values of each molecular orbital for three fluorobenzene molecules in Figure 6. For all molecules, the Γ_2 values of the electronic core orbitals mainly consisting of $1s$ atomic orbitals of fluorine and carbon atoms are relatively small compared to those of the valence orbitals. The contributions from core orbitals to the total Γ_2 value for di-, tri-, and tetra- fluorobenzene molecules are 3.2%, 2.1%, and 1.8%, respectively. This could be because a positron is generally subjected to strong electrostatic repulsion from nuclei, and thus the probability density of the attached positron becomes lower around nuclei.
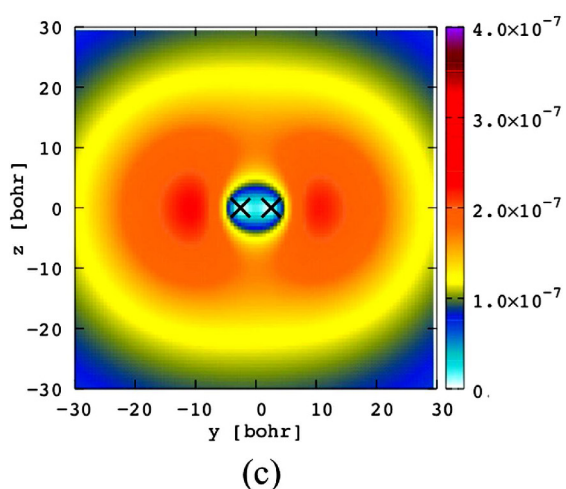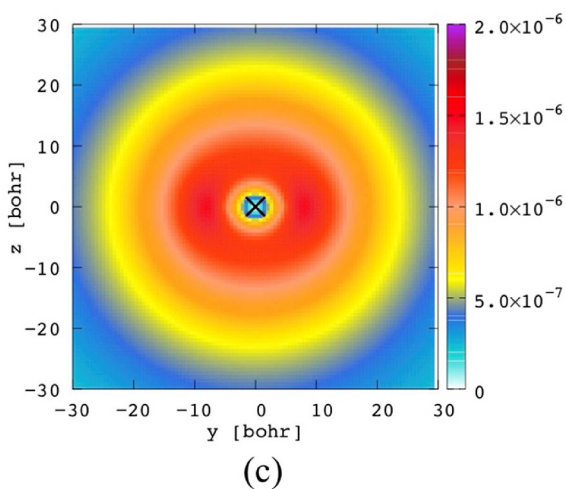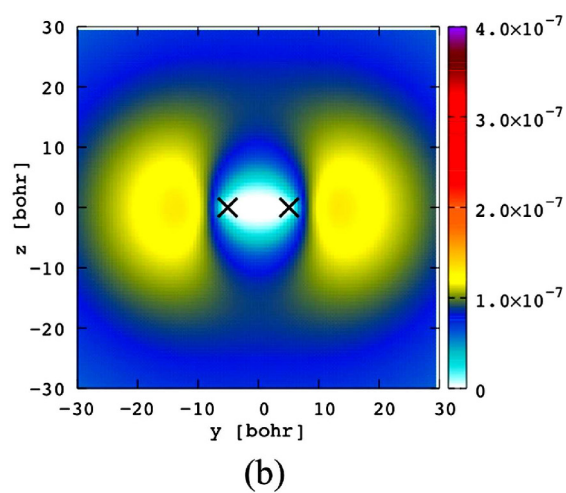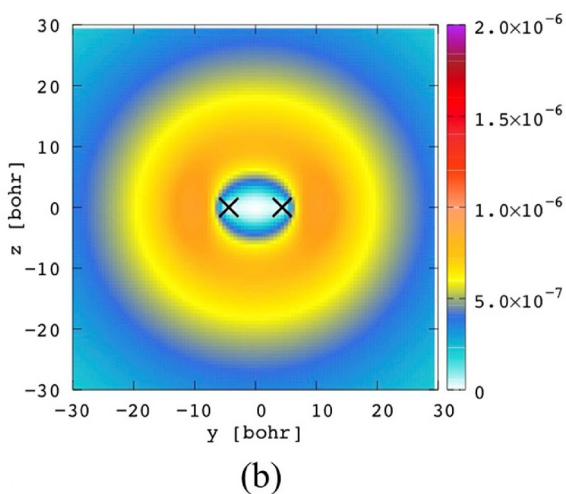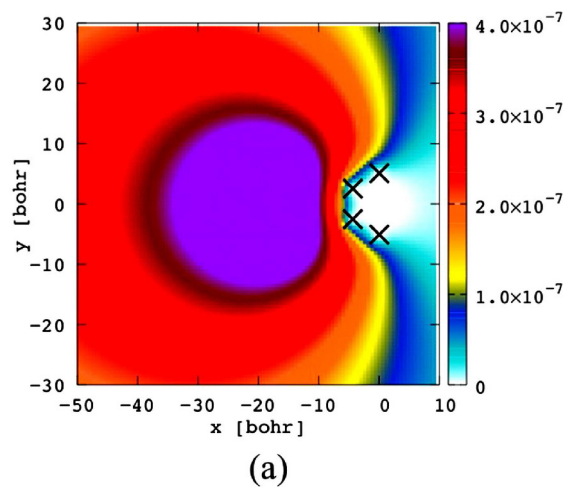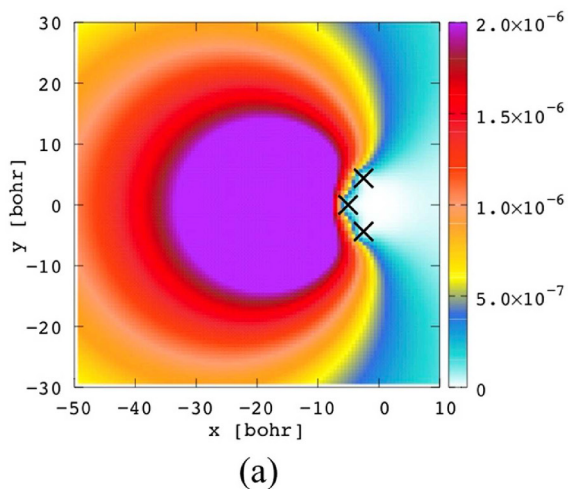
Fig. 4. The density distribution of positron attached to 1,2,3-trifluorobenzene molecule: (a) in the molecular plane (xy-plane), (b) in the perpendicular plane to the molecular plane through outer two fluorine atoms (yz-plane 1), and (c) in another perpendicular plane through the inner fluorine atom (yz-plane 2). The symbols "×" means the position of fluorine atoms. The color bar shows the value of positron density.

Fig. 5. The density distribution of positron attached to 1,2,3,4-tetrafluorobenzene molecule: (a) in the molecular plane (xy-plane), (b) in the perpendicular plane to the molecular plane through outer two fluorine atoms (yz-plane 1), and (c) in another plane through inner two fluorine atoms (yz-plane 2). The symbols "×" means the position of fluorine atoms. The color bar shows the value of positron density.

Fig. 6. Two-photon pair-annihilation rates (Γ_2) for each electronic molecular orbital for (a) 1,2-difluorobenzene, (b) 1,2,3-trifluorobenzene, and (c) 1,2,3,4-tetrafluorobenzene molecules. Each bar is arranged in the increasing order of those orbital energies from the left-hand side. The solid gray bars correspond to the core ($1s$) orbitals of the fluorine and the carbon atoms, the blue (red) meshed bars the valence orbitals consisted of $2s$ ($2p$) orbitals of the fluorine atoms, and the gray meshed bars other valence orbitals. The molecular orbital having the highest Γ_2 value has also been shown for each molecule.

On the other hand, the electronic valence orbitals, mainly consisting of $2s$ and $2p$ atomic orbitals of fluorine atoms, have the relatively large Γ_2 values. The dominant contribution to the total Γ_2 value arises from the $2p$ fluorine orbitals: the ratio from the $2p$ ($2s$) orbitals are 42.8% (13.8%) in 1,2-difluorobenzene molecule, 48.2% (15.2%) in 1,2,3-trifluorobenzene molecule, and 51.7% (15.5%) in 1,2,3,4-tetrafluorobenzene molecule. For all molecules, the valence orbitals having the largest Γ_2 value for each molecule consist of $2p_z$ atomic orbitals of fluorine atom as drawn in Figure 6. Although the density distribution of the attached positron to the fluorobenzene molecules is dominantly distributed at the region away from the molecule, as mentioned in the previous subsection, the positron density is also slightly spread into the out-of-molecular plane region. The enhancement of Γ_2 values in the $2p$ fluorine orbitals could be due to the positron density spreading in the out-of-molecular plane regions. The significant contributions from the valence electrons of fluorine atom in fluorobenzene molecules have been first discussed experimentally by Iwata et al. [10]. They have shown that the observed γ-ray spectra can be reasonably decomposed into the two line shapes of fluorinated and hydrogenated components, and the linewidths of the spectra of fluorobenzene molecules increase linearly as increasing the fraction of valence electrons of the fluorine atoms [8,10]. Wang et al. [11] have also reported theoretically that the valence electrons of fluorine atom give the significant contributions to the Doppler shifts in γ-ray spectra of fluorobenzene molecule. The dominant contributions of $2p$ valence electrons shown in the present study are consistent with these previous works.

5 Conclusions

In order to demonstrate the binding of a positron to fluorobenzene molecules, we theoretically analyzed the positron affinity (PA) and two photon pair annihilation rate (Γ_2) of them at Hartree-Fock level of multi-component molecular orbital theory. Only 1,2-difluorobenzene, 1,2,3-trifluorobenzene, 1,2,3,4-tetrafluorobenzene molecules have a positive PA value, while other possible structural isomers and penta- and hexa-fluorobenzene molecules have no bound states for a positron at the present level of calculations. The PA and Γ_2 values of three fluorobenzene molecules are strongly correlated with their dipole moment values, and then the 1,2,3-trifluorobenzene molecule has the largest PA and Γ_2 values among them. Analyzing Γ_2 values for each electronic orbital, we found the electronic valence molecular orbitals consisting of $2p$ atomic orbitals of fluorine atoms have the dominant contribution to the total Γ_2 value for all molecules. The enhancement of Γ_2 values in the $2p$ fluorine orbitals is relevant to the positron density spreading in the out-of-molecular plane regions. The mechanism of the pair-annihilation to the fluorobenzene molecules takes origin from the molecular orbitals consisted of the orbitals of fluorine atom, especially molecular orbitals consisted of $2p$ atomic orbitals of fluorine atoms.

Author contribution statement

Kuniaki Ono: investigation, calculation, writing, Takayuki Oyamada: part of implimentation of our program code, Yukiumi Kita: writing original draft, visualization, data curation, Masanori Tachikawa: project administration, supervision, verification.

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