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The first-principles multi-component molecular orbital approach to bound states of positron with the 2-deoxyglucose molecule as a reagent of positron emission tomography

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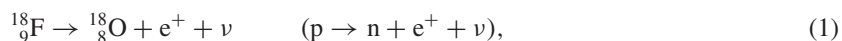
Abstract

Characteristic features of the positron binding properties of 2-deoxyglucose molecules of $C_6H_{11}O_5F$ and $C_6H_{11}O_6^-$, which are used as reagents of positron emission tomography (PET), are discussed based on the results obtained by a first-principles multi-component molecular orbital calculation. This method can take the positron–electron coupling into account under the mean-field approximation. Due to the large electronic polarization, the positron affinity of anionic $C_6H_{11}O_6^-$ is much greater than that of neutral $C_6H_{11}O_5F$.

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

1. Introduction

A positron (e^+) is the antiparticle of an electron; it has the same mass as an electron, and opposite charge. A positron is generated by pair creation or β^+ decay of the radioisotope species, e.g.,



with 109.8 min lifetime. Recently, positron spectroscopy has become a remarkable tool in studying the properties of surface and vacancy-type defects of metals and semiconductors [1].

A positron is used for a non-invasive technique for brain studies, prostate cancer detection, and mammography, known as positron emission tomography (PET). For oncological investigations, one often uses fluorodeoxyglucose (FDG, $C_6H_{11}O_5F$) labelled with the positron emitter ${}^{18}F$, which is a radioisotope of a biologically active substance,



which actively concentrates in cancer cells [2]. After positrons travel a short distance, they collide with electrons and both particles annihilate by emitting two 511 keV γ photons in opposite directions. By measuring the coincidence of the two photons, the origin of the photon emitter can be located, and PET can reveal the presence of cancer by recording an increased rate of glucose metabolism. In this study, we have calculated positron complexes of FDG species by the first-principles multi-component molecular orbital method, in which we have modelled that a positron emitted from FDG can capture another FDG.

With the recent development of experimental techniques, some stable systems containing a positron have been detected for some small molecules [3] before a pair annihilation between a positron and an electron. A positron should be able to form an infinite number of bound states with molecules if the molecule has a dipole moment with a value greater than 1.625 Debye (D) (the critical dipole moment, D_c) [4]. In fact, there are some experimental reports that may imply the formation of a bound state at least temporarily [5–8]. These are:

- (i) the results of Surko's group [5] for extremely large annihilation rates for hydrocarbons compared to those for fluoro-hydrocarbons,
- (ii) the results of Sueoka and Kimura [6] for larger positronium (Ps) formation rates for hydrocarbons than for fluoro-hydrocarbons, and
- (iii) the detection of various fragmented species from large hydrocarbons by slow positron impact below the Ps formation threshold by Xu *et al* [7].

These three experimental results superficially appear to be different physical events. If, however, one assumes a positron bound state, then all three results can be interpreted uniformly.

In order to investigate such positronic compounds with a theoretical approach, it is necessary to develop a computational method which treats both electron and positron on an equal footing quantum-mechanically. It is not possible to calculate a positron–electron compound with a conventional first-principles calculation, since it has been developed for the description of *only* electronic structures employing a quantum wavefunction based upon the Born–Oppenheimer approximation. There have been some theoretical attempts to investigate a possible formation of positron bound states based on mean-field [9–12], Møller-Plesset perturbation [13, 14], configuration interaction (CI) [15–20], multireference single- and double-excitation CI (MRD-CI) [22–24], and quantum Monte Carlo [14, 25, 26] schemes. Most calculations have shown that molecules with strong dipole moments (>3 – 4 D) can indeed bind a positron.

In this report, we focus on the 2-deoxyglucose molecules of $C_6H_{11}O_5F$ and $C_6H_{11}O_6^-$ as a reagent of positron emission tomography (PET). We demonstrate the binding of a positron to these species, and propose a possibility for positron bound states. In the next section, we give an outline of the numerical calculation for a positronic compound with the mean-field approximation. In section 3 we show the numerical calculation, and we present some computational results and discussion for these positronic compounds in section 4. Finally in section 5, concluding remarks are given.

2. Theory

The Hamiltonian of a system containing M nuclei, N electrons, and a positron is written as

$$H = \sum_{a=1}^N h^e(a) + \sum_{a>b}^N \frac{1}{r_{ab}} + h^p(p) - \sum_{a=1}^N \frac{1}{r_{pa}}, \quad (3)$$

where

$$h^e = -\frac{1}{2}\nabla_a^2 - \sum_{\alpha}^M \frac{Z_{\alpha}}{r_{a\alpha}},$$

$$h^p = -\frac{1}{2}\nabla_p^2 + \sum_{\alpha}^M \frac{Z_{\alpha}}{r_{p\alpha}},$$

and Z_{α} is the charge of the α th nucleus. $r_{a\alpha}$ is the distance of the a th electron from the α th nucleus, and $r_{p\alpha}$ is that of the positron from the a th nucleus. r_{ab} is the distance between the a th and b th electrons, and r_{pa} is that between the positron and the a th electron.

The total wavefunction (Ψ) of the species is given by a configuration interaction (CI) formalism as

$$|\Psi\rangle = \sum_L |\Phi_L\rangle C_L = |\Phi_0^e\rangle |\Phi_0^p\rangle C_0 + \left(\sum_{L_e} \sum_{L_p} \right)' |\Phi_{L_e}^e\rangle |\Phi_{L_p}^p\rangle C_{(L_e, L_p)}, \quad (4)$$

where C_L is the L th CI coefficient of the L th configuration ($|\Phi_L\rangle$), which consists of products of the L_e th electronic configuration ($|\Phi_{L_e}^e\rangle$) and the L_p th positronic one ($|\Phi_{L_p}^p\rangle$).

If one treats only the first term of equation (4), one can derive the mean-field equations [9–12]. We denote the set of spatial orbitals of electrons and a positron as $\{\phi_i\}$ and φ_p , respectively. Considering a closed shell electronic structure, the one-particle electronic and positronic mean-field operators are given as

$$f^e = h^e + \sum_j^{N/2} \{2J_j - K_j\} - J_p, \quad (5)$$

$$f^p = h^p - \sum_j^{N/2} 2J_j, \quad (6)$$

where J_j and K_j are Coulomb and exchange operators, respectively. The molecular orbitals (MOs) of the electron and positron are expanded by the set of IAO^e and IAO^p basis functions $\{\chi_r^e\}$ and $\{\chi_r^p\}$ as

$$\phi_i = \sum_{r=1}^{\text{IAO}^e} \chi_r^e C_{ri}^e, \quad (7)$$

$$\varphi_p = \sum_{r=1}^{\text{IAO}^p} \chi_r^p C_{rp}^p, \quad (8)$$

and the following multi-component Roothaan equations are obtained for electrons and a positron,

$$\mathbf{F}^e \mathbf{C}^e = \mathbf{S} \mathbf{C}^e \boldsymbol{\epsilon}^e, \quad (9)$$

$$\mathbf{F}^p \mathbf{C}^p = \mathbf{S} \mathbf{C}^p \boldsymbol{\epsilon}^p. \quad (10)$$

The energy of this system is given finally as

$$E_{\text{HF}} = \sum_{rs}^{\text{IAO}^e} P_{sr}^e (h_{rs}^e + F_{rs}^e) + \frac{1}{2} \sum_{rs}^{\text{IAO}^p} P_{sr}^p (h_{rs}^p + F_{rs}^p), \quad (11)$$

where P_{rs}^e and P_{rs}^p are density matrices defined as

$$P_{rs}^e = 2 \sum_i^{N/2} C_{ri}^e C_{si}^{e*}, \quad (12)$$

$$P_{rs}^p = C_{r1}^p C_{s1}^{p*}. \quad (13)$$

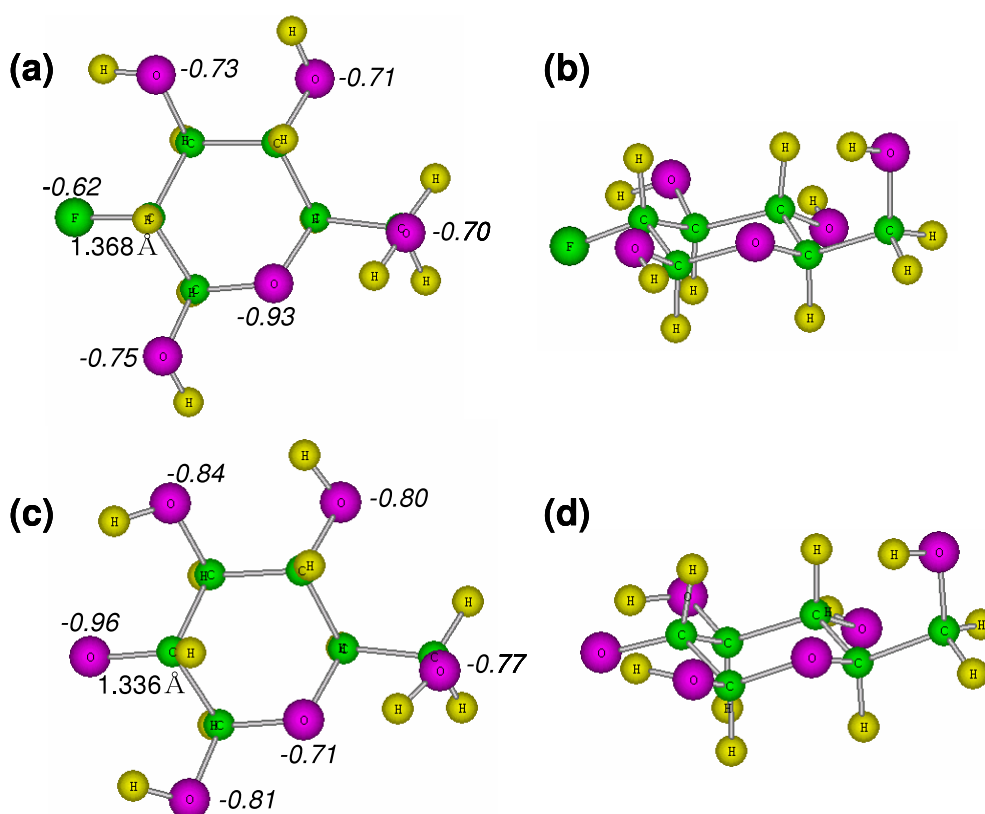


Figure 1. Optimized structure of $C_6H_{11}O_5F$ ((a) top view and (b) side view) and $C_6H_{11}O_6^-$ ((c) top view and (d) side view). Bold and italic characters denote internuclear distance and Mulliken population.

3. Numerical calculation

We have employed Gaussian-type functions (GTFs) as basis functions; these are known to possess an advantageous feature for the numerical evaluation of molecular integrals, particularly for computations of many-electron systems. The method by McMurchie and Davidson [27] is utilized to evaluate the integrals and derivatives. The 6-31G* basis set, commonly used in *ab initio* MO calculations, with additional diffuse and polarization GTFs has been used for electronic parts. For the positron basis set, very diffuse-type GTFs are taken into account. We have employed positronic [10s7p2d1f] GTFs in which the s- and p-type exponents are determined by the even-tempered scheme as $\alpha_{i+1} = c \times \alpha_i$, where $\alpha_1 = 0.00001$ and $c = 3.0$ are chosen and the exponents of the two d-type and one f-type GTFs as polarization functions are 0.001, 0.0001, and 0.001, respectively. The positronic GTFs are set on the centre of mass of the molecule.

4. Results and discussion

4.1. Electronic properties

Figure 1 summarizes the optimized equilibrium geometries of the $C_6H_{11}O_5F$ and $C_6H_{11}O_6^-$ molecules at the mean-field 6-31G* level of approximation. From the italic characters which

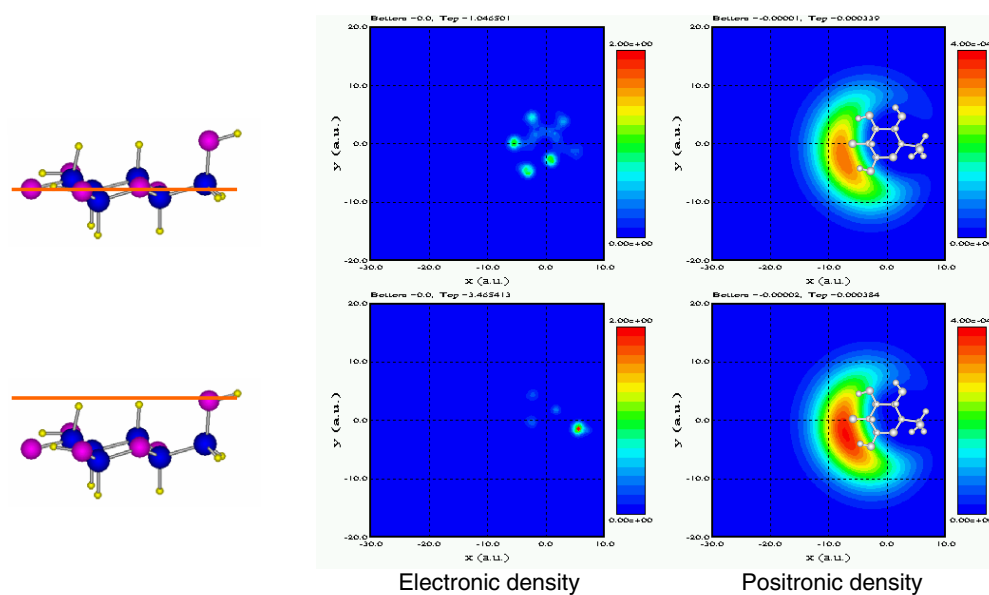


Figure 2. Electronic and positronic densities of the $C_6H_{11}O_6^-$ anion.

Table 1. Energy and positron affinity (PA) for each species.

	A = $C_6H_{11}O_5F$	A = $C_6H_{11}O_6$
$E(A)$ (Hartree)	-707.360 808	-682.772 4066
$E([A; e^+])$ (Hartree)	-707.360 707	-682.853 4688
PA (kcal mol^{-1})	-0.06	50.87

denote the Mulliken population in figure 1 it can be seen that the electronic population on the oxygen atom of $C_6H_{11}O_6^-$ (-0.96) is greater than that on the fluorine of $C_6H_{11}O_5F$ (-0.62). This means that electrons are polarized toward the oxygen atom from the carbon atom in the $C_6H_{11}O_6^-$ anion, though the electronegativity of oxygen ($O = 3.5$) is smaller than that of fluorine ($F = 4.0$).

4.2. Positronic properties

Next, we have calculated the positronic complexes of $C_6H_{11}O_5F$ and $C_6H_{11}O_6^-$ with the fixed geometry as shown in figure 1. Table 1 summarizes the energy and their positron affinity (PA). The PA is calculated as the difference between the energies of the parent species and the positron-attached compound. The PA of the $C_6H_{11}O_6^-$ anion is found to be positive, which indicates that a stable positronic bound state is present. Indeed, the positronic orbital energy of the $[C_6H_{11}O_6^-; e^+]$ species is negative. On the other hand, the PA of $C_6H_{11}O_5F$ is a very small negative value at the present level of calculation.

Figure 2 shows the electronic and positronic densities of the $C_6H_{11}O_6^-$ anion. We can find the electronic density near the oxygen atoms, since the carbonyl group tends to form an ionic structure. The positron density is found near three oxygen atom, especially above the sugar plane. Figure 2 clearly shows that the positron is captured by the strong Coulombic interaction with the negative charge on the oxygen atom, although there is no direct

experimental observation. It should be noted that a positron can form a bound state in the anion case, even though the geometrical relaxation effect due to the presence of a positron is not taken into account.

At the present level of calculation, we have found no stable positronic complexes for $C_6H_{11}O_5F$ shown in table 1. The calculated dipole moment of $C_6H_{11}O_5F$ is 2.42 D, which is greater than the critical dipole moment D_c . As has been pointed out previously [21], it is not possible for conventional methods to obtain similarly good results for many-electron molecules because of inherent restrictions in the types of basis sets that can be realistically employed in our calculations. If much more diffuse and polarization-type GTFs are included, a positive PA value may be obtained. For more quantitative discussion further theoretical development, such as multi-component quantum Monte Carlo method, would be indispensable.

5. Conclusion

Using first-principles mean-field multi-component molecular orbital calculations, we have calculated the positron-attached structures of 2-deoxyglucose molecules of $C_6H_{11}O_5F$ and $C_6H_{11}O_6^-$, which are used as reagents of positron emission tomography (PET). The positron affinity of the $C_6H_{11}O_6^-$ anion is positive, while that of the neutral $C_6H_{11}O_5F$ is negative at the present level of calculation. The positron distribution of the $C_6H_{11}O_6^-$ anion is largely concentrated behind the oxygen atom of the carbonyl group due to the strong Columbic interaction between the positron and the excess electron.

The electronic and positronic wavefunctions obtained here should be useful for the theoretical prediction of annihilation rates for biological molecules. For a more quantitative calculation, we are now developing a multi-component quantum Monte Carlo method, and some results will be given in the near future.

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