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Molecular Structure of Water-Like Positronium Complexes

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We resort to a previously introduced molecular model for positron complexes to study the molecular structures of Ps_2O and PsOH and to explore their analogies and differences from the molecular structure of water.

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1. Introduction: the molecular model for positron complexes

It is well known that positrons can live long enough to form complexes with atoms. The theoretical study of these complexes is important to interpret experimental data from both positron scattering by atoms and molecules and positron annihilation spectroscopy.

There are typically two different kinds of positron complexes. In one of them a positron attaches to a neutral or ionic atom or molecule A with a positive positron affinity, yielding the formation of the complex $[e^+;A]$. In the other kind, a pair (e^-,e^+) (the positronium (Ps) atom) acts as a light isotope of hydrogen and binds to matter in almost the same way as the H atom does. Examples considered here are the two different species of positronic water, $[\text{PsOH}]$ and $[\text{Ps}_2\text{O}]$.

Most theoretical studies of positron complexes consider the three different types of particles: heavy nuclei, light electrons and positrons in the same footing and aim to treat all the correlations between any pair of them. As a consequence, these calculations are computationally quite hard and limited to very small systems. We have found, on the other hand, that treating a positron as a light nucleus and performing an adiabatic separation of the electronic and nuclear motions, a lot of valuable information can be obtained from the potential energy surface (PES)

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for nuclei and positron motions [1, 2]. Despite the need of a large adiabatic correction to positron motion, everything else works as in standard molecular structure calculations. Of course we have to be careful in analyzing the outputs, when comparing with typical molecular calculations. For example, for a general complex $[e^+;A]$ the point of minimum energy of the PES gives the geometry of the parent A system but just an approximation to the average position of the positron. Even though, predictions of positron bonding sites and geometry relaxation [2] and estimative of annihilation rates [1] are available within the molecular model.

In what follows we consider a complex containing just one positron, the extension to more positrons being trivial. We drop the notation for the nuclear coordinates \mathbf{R} , for simplicity, but the nuclear degrees of freedom are considered anyway in the Born–Oppenheimer (BO) approximation. The symbol A represents a neutral parent atomic or molecular system and r stands for positron coordinates. Atomic units (a.u.) are used throughout.

The non-relativistic N -electron Hamiltonian, in which the kinetic energy terms of heavy particles are disregarded, is written as

$$H = -\frac{\nabla_r^2}{2} - \sum_i^N \frac{\nabla_i^2}{2} + V, \quad (1)$$

with conventional notation, V representing the Coulomb potential energy of all particles.

Let us consider a general complex divided in two sub-systems. To keep the previous notation we call the positron and the n_B electrons occupying orbitals ϕ_B as “sub-system B ”, so that “sub-system A ” is composed by the heavy nuclei and the remaining n_A electrons occupying orbitals ϕ_A . The procedure of considering momentum conservation just in sub-system B lead to $\nabla_r = -\sum_{i=1}^{n_B} \nabla_i$. Due to the smallness of the positron mass, crossing (mass polarization) terms could be relevant but, since the positron can hardly attach more than one electron, they become negligible so that $\nabla_r^2 \simeq -\sum_{i=1}^{n_B} \nabla_i^2$. This result will be taken into Eq. (1) to generate the model electronic Hamiltonian. This procedure would however distinguish electrons, so that we perform just a single sum over all N electrons but impose no interaction of sub-systems A and B in calculations involving this term, a procedure that is symbolized by multiplying it by a δ_{AB} , so that

$$H = \sum_i^N \left(-\frac{\nabla_i^2}{2} \delta_{AB} - \frac{\nabla_i^2}{2} \right) + V. \quad (2)$$

In practice, this means that matrix elements of the first operator between orbitals of different sub-systems are forced to vanish, that is, $\langle \phi_A | -\frac{\nabla_i^2}{2} \delta_{AB} | \phi_B \rangle = 0$.

In consequence, the Hamiltonian becomes a pure electronic operator and the positron is treated on a common footing with the other nuclei except that a large mass correction is introduced for its motion, as a consequence of the form (2) for the Hamiltonian. In the variational adiabatic approximation, the PES for nuclear motion is obtained by

$$\epsilon(\mathbf{R}, r) = \frac{\langle \Phi | H | \Phi \rangle}{\langle \Phi | \mathbf{1} | \Phi \rangle}, \quad (3)$$

where Φ is a variational electronic wave function which depends parametrically on \mathbf{R} and r in the sense that Φ is normalizable for all values of these coordinates. As a matter of fact, for present applications, the parametric dependence of ϵ and Φ on the nuclear coordinates \mathbf{R} is taken as in the usual BO approximation.

To solve this equation for general molecules, an electronic self-consistent-field-molecular-orbital-configuration-interaction (SCF-MO-CI) method has been implemented as a simple modification of the Gamess code [3, 4]. All the calculations reported here use this code.

2. The molecular structure of [Ps₂O] and [PsOH]

Complexes with two positrons seem unreliable in practical work, but are the interesting matter to theoretical study. The fact that the *positronic water*, Ps₂O, could be bound was predicted by Jiang and Schrader [5] with the use of fully correlated diffusion Monte Carlo (DMC) method, yielding the total energy of -75.6270 a.u. and a binding energy of 1.67 ± 0.08 eV relative to the products O + Ps. They suggest the system to have a spherical symmetry with the two positrons occupying outer $1s$ orbitals centered on the O atom (the atomic model). The stability of [PsOH] against dissociation of positron and positronium was predicted in Ref. [6], keeping frozen the geometries of the parent OH or OH⁻ and with no other structure considerations. First tests with the molecular model show shallow minima of the PES against variation of bond distances (Ps–O being the more relevant) and the bond angle Ps–O–Ps(H). To explore analogies with the structure of the water molecule we study first the barrier to linearity. We first perform a geometry optimization of each system. Then keeping constant the bond distance we vary the angle. Our results are displayed in Fig. 1 and the Table, and can be interpreted in terms of the molecular model. For the water molecule, it is well known that the localization of the bonds forces them to repel each other, including the lone pair, leading to its definite geometry and a large barrier to linearity. In the case of Ps₂O no barrier has been found, see Fig. 1c. The explanation is that the two positrons (and thus the two Ps atoms) present a large deal of delocalization, so that bond repulsion takes no effect. On the other hand, the two Ps atoms must have their motion strongly correlated, occupying symmetric positions relative to the central O atom, in classical words. This explains the “linear configuration” in internal coordinates, advanced by the vanishing barrier, and a spherical picture of

TABLE
Bond angles and barriers to linearity for water and water-like positronium complexes.

Complex	OH bond	OPs bond	Angle	Barrier
H ₂ O	1.810	–	104.5	0.0556
PsOH	1.779	1.853	119.3	0.0089
Ps ₂ O	–	1.810	180.0	0.00

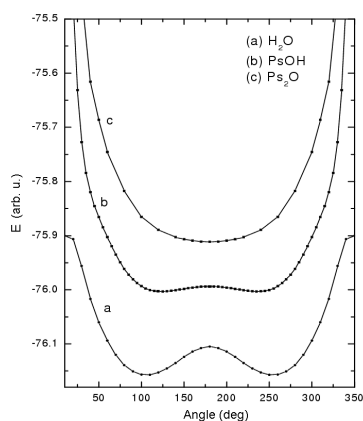


Fig. 1. C_{2v} cuts of the potential energy surfaces for water and water-like positronium complexes showing barriers to linearity.

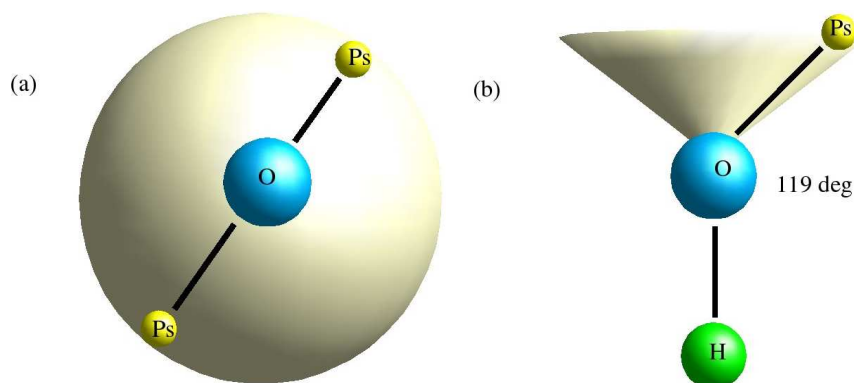


Fig. 2. Proposed molecular structures of (a) Ps₂O and (b) PsOH.

the system from outside, see Fig. 2a, which turns out to be in agreement with the spherical atomic model of Ref. [5].

The concept of molecular structure of Ps complexes becomes more meaningful in the case of PsOH. Geometry optimization leads to a bend structure with the bond angle of 119.3°, that is, a small but finite barrier to linearity appears, see

Fig. 1b, and the O–H bond distance is somewhat reduced as well. The two heavy nuclei define a reference axis, which prevents spherical symmetry of Ps motion, leading to the cone model of Fig. 2b as our picture for this system. We found this to be a general rule, that is, as the parent molecule becomes larger, a single positron tends to be localized in some molecular site [2, 7], instead of occupying an outer molecular orbital.

The minimum of the PES of PsOH is -76.0175 a.u. Comparing with the DMC value of -75.9815 a.u. [6] we note that the difference is very small, about 10% of the ground state Ps energy, -0.25 a.u. This feature is unexpected, and could be related to the fact that in the calculation of the O–H bond is kept frozen [6]. Anyway, a general property is that the experimental result (or exact calculations) will be an upper bound to our minimum point energy. In the same way, the minimum point energy of the corresponding common molecule (H_2O in this case) will be a lower bound. This property can be explored in the study of larger complexes.

Finally, in Ref. [1], we proposed that the pair annihilation rate of Ps, $\Gamma = 2.0 \times 10^9 \text{ s}^{-1}$, is a lower bound to the annihilation rate per positron in any complex in a state that breaks in one or more Ps atoms. Thus for Ps_2O we predict $\Gamma \gtrsim 4.0 \times 10^9 \text{ s}^{-1}$ which is in consonance with the calculation of Ref. [5]. In the case of PsOH, any state supported by the ground state PES will dissociate in Ps + OH, as discussed in Ref. [8]. We have really found it by stretching the coordinate Ps–OH, allowing the bond OH to relax. We can thus propose for the annihilation rate of such a state the value $\Gamma \gtrsim 2.0 \times 10^9 \text{ s}^{-1}$.

3. Further remarks

We have discussed the application of the molecular model for positron complexes to $[\text{Ps}_2\text{O}]$ and $[\text{PsOH}]$. The molecular structure that comes out, when we take the positron as a light nucleus, permits us to get a “chemical” picture of the complexes that can be further explored in the predictions of their properties.

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