1) 86(8): Some Orbital Calculations in Positronium

i.e.s

In some cases, the p orbitals of the positronium wave functions vanish, but in other cases they do not.

Mixing Among p Orbitals

In this case all of the orthopositronium wavefunctions vanish, for example:

$$\psi_-(1,2) = \left(\frac{1}{2}\right)^{1/2}\left(\psi_{2p_z}(r_1)\psi_{2p_y}(r_2) - \psi_{2p_z}(r_2)\psi_{2p_y}(r_1)\right)$$

$$= \left(\frac{1}{2}\right)^{1/2}\left(\frac{r_1}{a}\cos\theta \exp\left(-\frac{r_1}{2a}\right)\frac{r_2}{a}\sin\theta\, e^{-i\phi}\exp\left(-\frac{r_2}{2a}\right)\right.$$

$$\left. - \frac{r_2}{a}\cos\theta\exp\left(-\frac{r_2}{2a}\right)\frac{r_1}{a}\sin\theta\, e^{-i\phi}\exp\left(-\frac{r_1}{2a}\right)\right)$$

$$= 0 \qquad -(1)$$

Mixing between 2s and $2p_z$ Orbitals

In this case the orbital is non-zero as follows:

$$\psi_-(1,2) = \left(\frac{1}{2}\right)^{1/2}\left(\psi_{2s}(r_1)\psi_{2p_z}(r_2) - \psi_{2s}(r_2)\psi_{2p_z}(r_1)\right)$$

$$= \left(\frac{1}{2}\right)^{1/2}\left(\left(2-\frac{r_1}{a}\right)\exp\left(-\frac{r_1}{2a}\right)\frac{r_2}{a}\cos\theta\exp\left(-\frac{r_2}{2a}\right)\right.$$

$$\left. - \left(2-\frac{r_2}{a}\right)\exp\left(-\frac{r_2}{2a}\right)\frac{r_1}{a}\cos\theta\exp\left(-\frac{r_1}{2a}\right)\right)$$

$$= \frac{2}{a}\left(\frac{1}{2}\right)^{1/2}\cos\theta\exp\left(-\frac{(r_1+r_2)}{2a}\right)(r_2-r_1)$$

$$\boxed{\psi_-(1,2)_{(2s-2p_z)} = \left(\frac{1}{2}\right)^{1/2}\cdot\frac{2(r_2-r_1)}{a}\cos\theta\exp\left(-\frac{(r_1+r_2)}{2a}\right)}$$

2) Mixing between the 2s and $\langle 2p \rangle$ orbitals

In this case:

$$\psi_-(1,2) = \left(\frac{1}{2}\right)^{1/2}\left(\psi_{2s}(r_1)\psi_{\langle 2p\rangle}(r_2) - \psi_{2s}(r_2)\psi_{\langle 2p\rangle}(r_1)\right)$$

$$= \left(\frac{1}{2}\right)^{1/2}\left(\left(2-\frac{r_1}{a}\right)\exp\left(-\frac{r_1}{2a}\right)2\left(1-\frac{r_2}{a}\right)\exp\left(-\frac{r_2}{2a}\right)\right.$$
$$\left. - 2\left(2-\frac{r_2}{a}\right)\exp\left(-\frac{r_2}{2a}\right)\left(1-\frac{r_1}{a}\right)\exp\left(-\frac{r_1}{2a}\right)\right)$$

$$= 0$$

So the wavefunction is Na-zero only for mixing between 2s and individual 2p orbitals.

Summary of Na-Zero orbitals

1)
$$\psi_-(1,2)_{1s-2s} = \left(\frac{1}{2}\right)^{1/2}\left(\exp\left(-\left(\frac{r_2}{a}+\frac{r_1}{2a}\right)\right)\left(2-\frac{r_1}{a}\right) - \exp\left(-\left(\frac{r_1}{a}+\frac{r_2}{2a}\right)\right)\left(2-\frac{r_2}{a}\right)\right)$$

2)
$$\psi_1(1,2)_{2s-2p_z} = \frac{\sqrt{2}}{a}(r_2-r_1)\cos\theta\exp\left(-\frac{(r_1+r_2)}{a}\right)$$