

ATOMS, MOLECULES & REACTIONS

QUANTUM MECHANICS, SPRING 2006 - HW WEEK 2

Chapter 13

(34) Cd = Predict $[\text{Kr}] 5s^2 4d^{10}$ This is correct. no unpaired electrons.

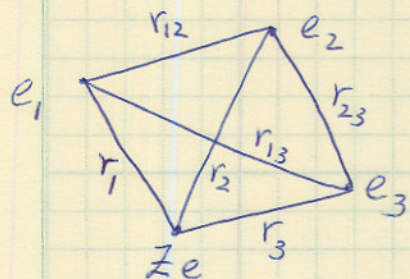
Br = Predict $[\text{Ar}] 4s^2 3d^{10} 4p^5$ ~~off~~ This is correct one unpaired \bar{e} .

W = Predict $[\text{Xe}] 6s^2 \text{ ~~5d} 4f^{14} 5d^4~~$ This is correct.
4 unpaired electrons

Nd = Predict $[\text{Xe}] 6s^2 5d^1 4f^3$ Table shows that the correct config. is $[\text{Xe}] 6s^2 4f^4$ 4 unpaired \bar{e} .

HW from assigned sheet

① Hamiltonian for the di atom



$$\hat{H} = \hat{T} + \hat{V}$$

$$\hat{H} = \underbrace{-\frac{\hbar^2}{2m_e} \nabla_1^2}_{\text{K.E. of electron 1}} - \underbrace{\frac{\hbar^2}{2m_e} \nabla_2^2}_{\text{K.E. of electron 2}} - \underbrace{\frac{\hbar^2}{2m_e} \nabla_3^2}_{\text{K.E. of electron 3}} - \underbrace{\frac{\hbar^2}{2m_N} \nabla_N^2}_{\text{K.E. of nucleus}} - \underbrace{\frac{Ze^2}{(4\pi\epsilon_0)r_1}}_{\text{e}_1\text{-nucleus attraction}}$$

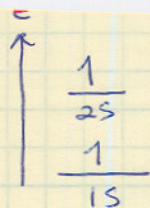
$$- \underbrace{\frac{Ze^2}{(4\pi\epsilon_0)r_2}}_{\text{e}_2\text{-nucleus attraction}} - \underbrace{\frac{Ze^2}{(4\pi\epsilon_0)r_3}}_{\text{e}_3\text{-nucleus attraction}} + \underbrace{\frac{e^2}{(4\pi\epsilon_0)r_{12}}}_{\text{e}_1\text{-e}_2\text{ repulsion}} + \underbrace{\frac{e^2}{(4\pi\epsilon_0)r_{13}}}_{\text{e}_1\text{-e}_3\text{ repulsion}} + \underbrace{\frac{e^2}{(4\pi\epsilon_0)r_{23}}}_{\text{e}_2\text{-e}_3\text{ repulsion}}$$

② $\psi_{\text{spatial}}(\text{He}) = 1s(1)1s(2)$ we did this in class

$$\hat{P}_{12} \psi_{\text{spatial}}(\text{He}) = 1s(2)1s(1) = \psi_{\text{spatial}}(\text{He})$$

$\therefore \psi_{\text{spatial}}(\text{He})$ is symmetric w.r.t. the permutation operator.

③



He in the first excited state.

$$\psi_{sp.} (\text{He } 1^{\text{st}} \text{ ex. state}) = 1s(1) 2s(2)$$

$$\hat{P}_{12} \psi_{sp.} 1s(1) 2s(2) = 1s(2) 2s(1)$$

neither symm. nor antisymm. w.r.t. \hat{P}_{12}

$$\text{try } \frac{1}{\sqrt{2}} [1s(1) 2s(2) + 1s(2) 2s(1)] = \psi_a \quad \text{and}$$

$$\frac{1}{\sqrt{2}} [1s(1) 2s(2) - 1s(2) 2s(1)] = \psi_b$$

$$\hat{P}_{12} \psi_a = \frac{1}{\sqrt{2}} [1s(2) 2s(1) + 1s(1) 2s(2)] \quad \text{symm. w.r.t. } \hat{P}_{12}$$

$$\hat{P}_{12} \psi_b = \frac{1}{\sqrt{2}} [1s(2) 2s(1) - 1s(1) 2s(2)] = -\psi_b$$

antisymm. w.r.t. to \hat{P}_{12}

\therefore Both ψ_a and ψ_b reflect the fact that the two electrons are indistinguishable. \therefore Both are acceptable spatial parts for the 1st excited state of He.