

Hi all,

In order to clear out the confusion that occurred close to the end of today's lesson and to compensate for the discomfort, I am writing this short message to clear the issue.

As we said in class, in the diatomic H_2^+ case we lose spherical symmetry and thus L^2 does not commute with the Hamiltonian of the system and thus l is not a good quantum number anymore. Nevertheless, the cylindrical symmetry is retained and thus L_z does commute with the Hamiltonian and m_l is a good quantum number by which we can characterize the molecular orbitals. This implies that when we transform from the Cartesian representation to any other coordinate system that includes the angle or rotation around the axis connecting the two nuclei (we'll define it as the Z axis) the Hamiltonian will be separable with respect to this coordinate and we'll obtain the following angular equation (similar to the case of the hydrogen atom and exactly the same equation obtained for a particle on a ring): $\frac{d^2\Phi(\varphi)}{d\varphi^2} = -\lambda^2\Phi(\varphi)$ where $\Phi(\varphi)$

is the angular part of the wave function and the full solution to the Schrödinger equation will be a product of this function and the function related to the other two variables. The solution of the above equation is

given by $\Phi_\lambda(\varphi) = \frac{1}{\sqrt{2\pi}} e^{i\lambda\varphi}$ **AND NOT** $\Phi_\lambda(\varphi) = \frac{1}{\sqrt{2\pi}} e^{i2\pi\lambda\varphi}$ as I mistakably

wrote in class. Now, the quantum number λ is quantized due to the requirement that the wave function is single valued, namely that $\Phi(\varphi) = \Phi(\varphi + 2\pi)$. Using the solution that we have we get

$\frac{1}{\sqrt{2\pi}} e^{i\lambda\varphi} = \frac{1}{\sqrt{2\pi}} e^{i\lambda(\varphi + 2\pi)}$, which gives $\frac{1}{\sqrt{2\pi}} e^{i\lambda 2\pi} = 1$. This condition is

satisfied by $\lambda = 0, \pm 1, \pm 2, \dots$. As the differential equation above implies, the energy will depend on λ^2 and thus all but the $\lambda = 0$ states are doubly degenerate. Molecular orbitals (MOs) with the quantum number $\lambda = 0$ are marked as σ orbitals, MOs with $\lambda = \pm 1$ are π orbitals, MOs with $\lambda = \pm 2$ are δ orbitals, and so on.

In order to learn about the spatial characteristics of the different orbitals we form real functions out of the degenerate complex $\Phi_\lambda(\varphi)$ functions,

such that $\tilde{\Phi}_{\lambda \neq 0}^+(\varphi) = N[\Phi_{\lambda}(\varphi) + \Phi_{-\lambda}(\varphi)] \propto \cos(\lambda\varphi)$ and $\tilde{\Phi}_{\lambda \neq 0}^-(\varphi) = N[\Phi_{\lambda}(\varphi) - \Phi_{-\lambda}(\varphi)] \propto \sin(\lambda\varphi)$. This allows us to check whether we have nodal planes by requiring that $\sin(\lambda\varphi) = 0$, which gives $\lambda\varphi = n\pi$; $n = 0, \pm 1, \pm 2, \dots$. Thus the angles at which nodal planes are obtained are ($\lambda \neq 0$) $\varphi = \frac{n\pi}{\lambda}$; $n = 0, \pm 1, \pm 2, \dots$. Distinguishable angles are given by the condition $n = 0, 1, \dots, \lambda - 1$ when $\lambda \neq 0$. Due to the symmetry of the system, these nodal planes include the inter-nuclear axis of the system, so that σ orbitals have 0 nodal planes which include the inter-nuclear axis, π orbitals have such a nodal plane at $\varphi = \frac{0\pi}{1} = 0$, δ orbitals have two such a nodal plane at $\varphi = \frac{0\pi}{2}, \frac{1\pi}{2}$, and so on. The same arguments hold for the cosine type functions but their nodal planes are located at different angles.

Due to my poor painting ability, I have posted on the website a java script that visualized the MOs of H_2^+ - feel free to play with it, it'll help you understand the different types of nodal planes.

We'll repeat this derivation one more time next week.

Have a wonderful new year's eve.

Oded