Project 1: Estimation of quantized molecules

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1 Determine the zero point energy of a methane molecule in a box having the dimension of 1m

To determine the energy of a methane molecule (CH_4) in a box, we employ the *particle-in-a-box quantum model*. In this case, the values of energy available for the particle are given by the formula for the *energy quantization of the molecule in an infinite potential well* :

$$E = \frac{h^2}{8ma^2}n^2 \tag{1}$$

where a represents the width of the potential well, h is Planck's constant, m represents the mass of the molecule considered and n dictates the energy level that we want to consider for the molecule.

In particular, for ZPE(*Zero Point Energy*), $n = 1$. Substituting in the formula both value of n and a sutable value for the molecule total mass ($m_{CH_4} = m_C + 4m_H$) ,we obtain an energy value equal to $E_{CH_4} = 2.06 \cdot 10^{-42} J = 1.28 \cdot 10^{-23} eV$

2 Determine the energy of the orbitals of atomic hydrogen, and the energy necessary for excitation between different orbitals.

From the theory on the hydrogen atom system, we know that the energy of the orbitals simply depends on the *n (Principal) Quantum Number*.

By solving the differential equation on the radial part of the wave function for the electron of the hydrogen atom, we obtain a law for the quantization of the atomic orbital energy as follows:

$$E = -\frac{m_e e^4}{8\epsilon_0^2 h^2 n^2} = -\frac{e^2}{8\pi\epsilon_0 a_0 n^2} = -\frac{E_0}{n^2} \tag{2}$$

with a_0 as Bohr's radius: $a_0 = \epsilon_0 h^2 / \pi m_e e^2$. The same *n quantum number* is used to *index* the orbitals: *Xs, Xp, Xd, Xf* , where X corresponds to the same value of n. The energy required to promote the electron of this system form one orbital to the other (excited state) is given as the difference of the *starting* and *landing orbital*'s energies:

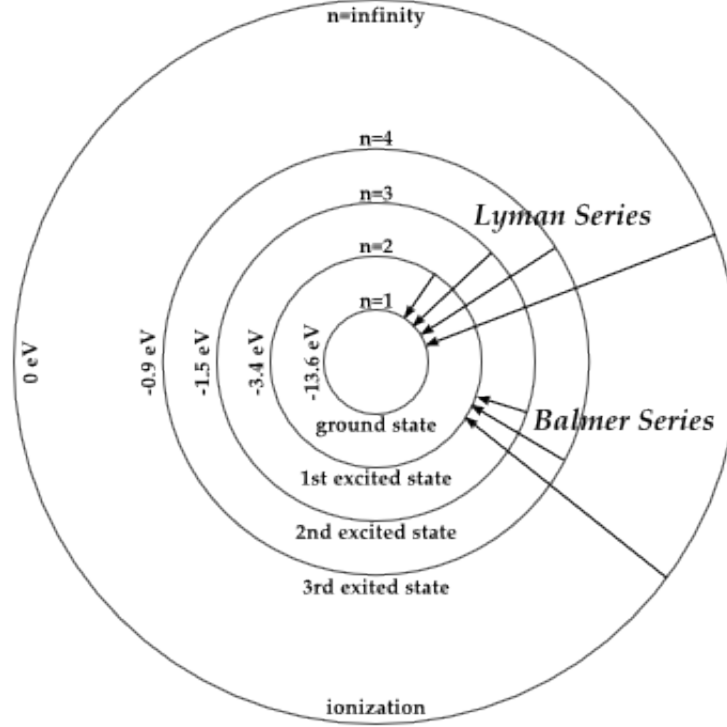$$\Delta E = E_f - E_i = E_0 \cdot (\frac{1}{n_i} - \frac{1}{n_f}) \tag{3}$$

Figure 1: hydrogen orbital's energy levels

where E_f and E_i represent respectively the final and initial orbital's energies The energetic values of the first levels are:

$$E_1 = -13.6eV; E_2 = -3.4eV; E_3 = -1.5eV; E_4 = -0.9eV \tag{4}$$

3 Draw the 1s, 2s, 2px, 2py, and 2pz orbitals on a xy plane

In general, the orbitals can be represented employing the probability distribution of finding the electron at a certain position away form the nucleus. This information is given by the squared absolute value of the complex wavefunction describing the system.

In spherical coordinates:

$$\Phi(r, \theta, \phi) \quad \rightarrow \quad P(r + dr, \theta + d\theta, \phi + d\phi) = |\Psi(r, \theta, \phi)|^2 dr\, d\theta\, d\phi \tag{5}$$

By solving the Shrödinger equation in a.u., employing the symmetry of the system and separation of variables, the wavefunction takes the general form:

$$\Phi_{nlm}(r, \theta, \phi) = \underbrace{R_{nl}(r)}_{\text{radial part}} \overbrace{Y_l^m(\theta, \phi)}^{\text{angular part}} \tag{6}$$
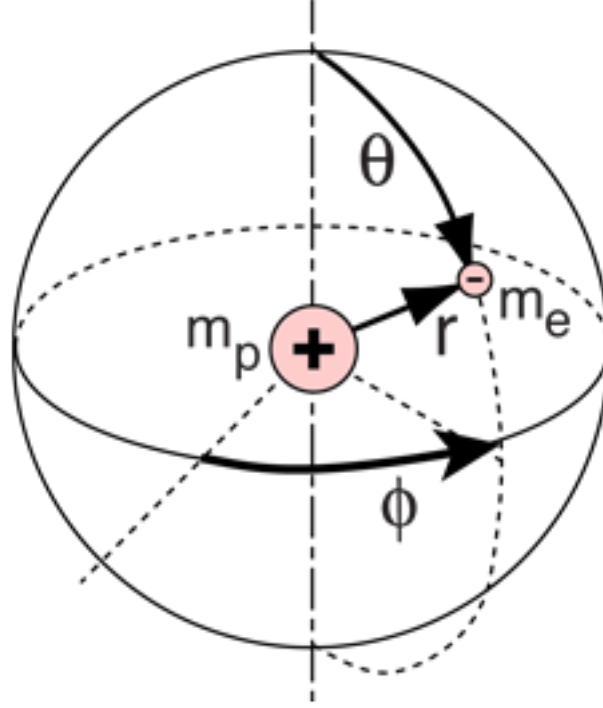
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Figure 2: hydrogen atom system

The exact form of this wavefunctions depends on the - available - quantum numbers:

- **n, principal quantum number** $\rightarrow$ energy, $n \in [1, 2, 3, ..]$

- **l, orbital quantum number** $\rightarrow$ angular momentum of the electron (absolute value), $l \in [0, 1, 2, ..., n-1]$

- **m, magnetic quantum number** $\rightarrow$ z-component of the angular momentum, $m \in [-l, -l+1, ..., 0, ..., l-1, l]$

In particular, for the *s* orbitals (i.e., those for which $l = 0$), spherical symmetry holds for the Ψ wavefunction, which does not depend on the θ and ϕ angles. For instance, for the *1s* orbital, radial wavefunction will have the following form, given by solving the corresponding radial differential equation:

$$R_{1s}(r) = \frac{2}{a_0^{3/2}} e^{-r/a0} \tag{7}$$

The *final wavefunction* describing *1s* will be given by multiplying R_{1s} with the angular (*polar* and *azimuth*) part, which, for $n = 1$, will be constant (for *1s*, $Y_0^0 = \frac{1}{\sqrt{4\pi}}$):

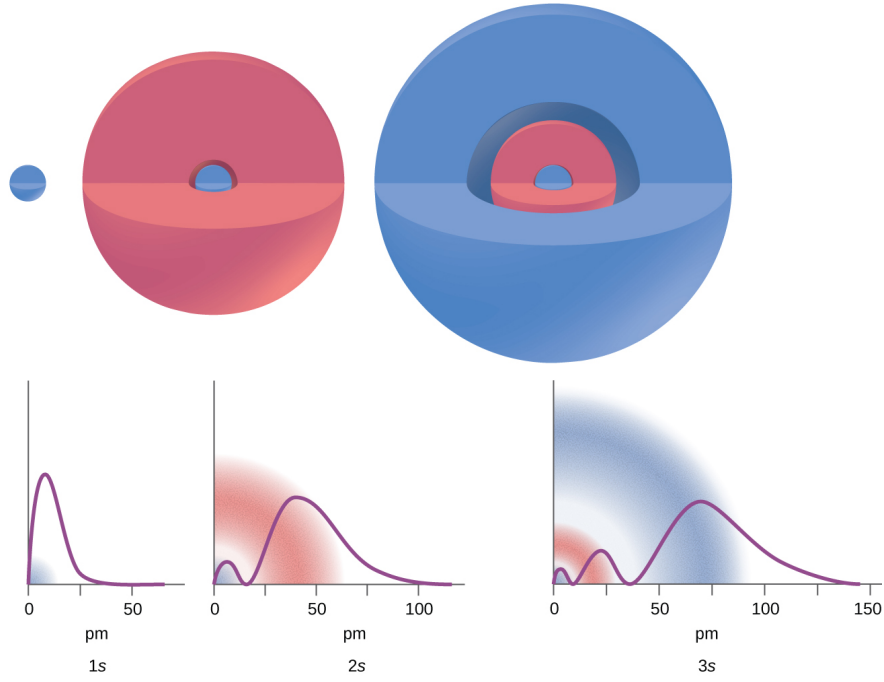$$\Psi_{1s}(r, \theta, \phi) = P_{10}(r)Y_0^0(\theta, \phi) = (\pi a_0^3)^{(} - 1/2)e^{-r/a0} \tag{8}$$

3

Figure 3: probability distributions for the 1s, 2s and 3s orbitals

Analogously, we can derive the *wavefunctions* for the orbitals *2s* and *2p*. Regarding this statement, while for *2s* Ψ is still a spherically symmetric function , this is not the case for the p orbitals, whose wavefunctions will also depend on θ and ϕ values. Solving the angular part of the Scrödinger equation, we can derive the corresponding part for the *wavefunction*. As a result, for $l = 1$ and $m = 0, \pm 1$ we will have:

$$Y_1^0(\theta, \phi) = \left(\frac{3}{4\pi}\right)^{1/2} cos\theta$$

$$Y_1^1(\theta, \phi) = \left(\frac{3}{8\pi}\right)^{1/2} sin\theta e^{i\phi} \tag{9}$$

$$Y_1^{-1}(\theta, \phi) = \left(\frac{3}{8\pi}\right)^{1/2} sin\theta e^{-i\phi}$$

While the p_z wavefunction is obtained by simply multiplying angular and radial parts as:

$$\Psi_{2p_0}(r, \theta, \phi) = R_{21}(r)Y_1^0(\theta, \phi) \tag{10}$$

the wavefunctions of p_x and p_y are obtained observing that, since Y_1^1 and Y_1^{-1} are degenerate solution of the angular d.e. (they give the same energy), any - normalized - linear combination of Y_1^1 e Y_1^{-1} will also be a solution for the eignevalue problem, with the same energy. This

trick is performed to get rid of the imaginary part of the solution.

$$p_x^{ang} = \frac{1}{\sqrt{2}}(Y_1^1 + Y_1^{-1}) = \left(\frac{3}{4\pi}\right)^{1/2} cos\phi \cdot sin\theta$$

$$p_y^{ang} = \frac{1}{\sqrt{2}}(Y_1^1 - Y_1^{-1}) = \left(\frac{3}{4\pi}\right)^{1/2} sin\phi \cdot sin\theta$$
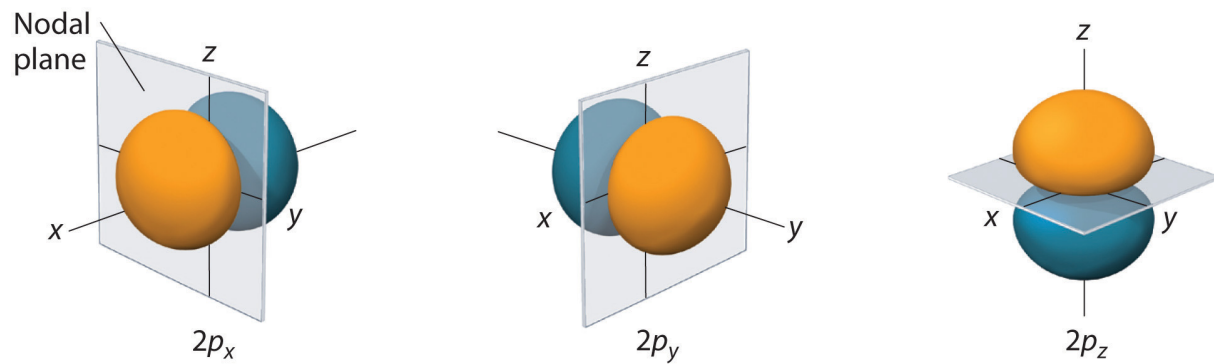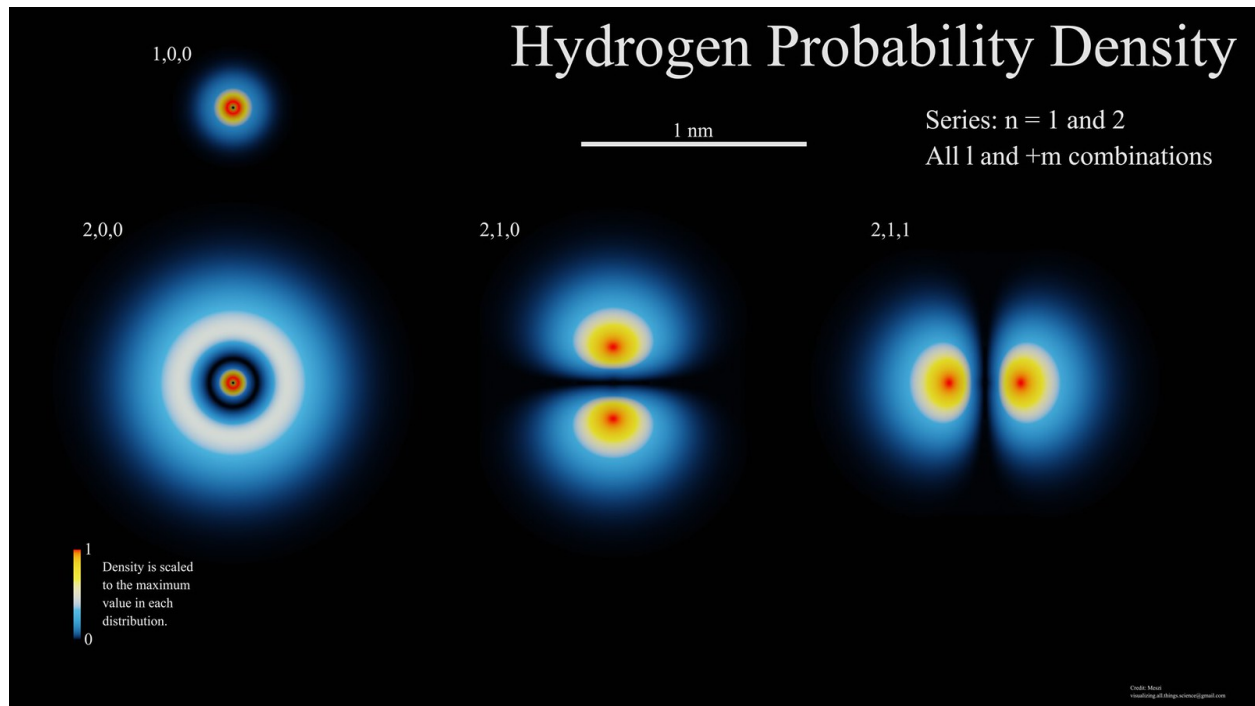
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Figure 4: 3d representation of p orbitals

4 Determine the average distance of an electron in a 1s, 2s, 2px, 2py, and 2pz orbital from the nuclei.

We exploit the definition of *expected value* for an observable in quantum mechanics:

$$\langle r \rangle = \langle \Psi | \, r \, | \Psi \rangle = \iiint \Psi(r, \theta, \phi)^* \; r \; \Psi(r, \theta, \phi) \; r^2 \sin\theta \, dr \, d\theta \, d\phi \tag{12}$$

together with the - pre-computed - *wavefunctions* for the different orbitals ($\sigma = \frac{Zr}{a_0}$, a_0 is Bohr's radius):

$$
\begin{array}{llll}
n = 1, & l = 0, & m = 0 & \psi_{1s} = \dfrac{1}{\sqrt{\pi}} \left(\dfrac{Z}{a_0}\right)^{3/2} e^{-\sigma} \\[3ex]
n = 2, & l = 0, & m = 0 & \psi_{2s} = \dfrac{1}{4\sqrt{2\pi}} \left(\dfrac{Z}{a_0}\right)^{3/2} (2 - \sigma) e^{-\sigma/2} \\[3ex]
 & l = 1, & m = 0 & \psi_{2p_z} = \dfrac{1}{4\sqrt{2\pi}} \left(\dfrac{Z}{a_0}\right)^{3/2} \sigma e^{-\sigma/2} \cos\theta \\[3ex]
 & l = 1, & m = \pm 1 & \psi_{2p_x} = \dfrac{1}{4\sqrt{2\pi}} \left(\dfrac{Z}{a_0}\right)^{3/2} \sigma e^{-\sigma/2} \sin\theta \cos\phi \\[3ex]
 & & & \psi_{2p_y} = \dfrac{1}{4\sqrt{2\pi}} \left(\dfrac{Z}{a_0}\right)^{3/2} \sigma e^{-\sigma/2} \sin\theta \sin\phi
\end{array}
$$

Chosen Z = 1 for the hydrogen atom and considering the 1s orbital wavefunction ($n = 1, l = 0, m = 0$), we can solve the integral by parts:

$$
\begin{aligned}
\langle r \rangle_{1s} &= \int_0^\infty \int_0^\pi \int_0^{2\pi} \Psi^* \, r \, \Psi \, r^2 \sin\theta \, dr \, d\theta \, d\phi \\[2ex]
&= \int_0^\infty \int_0^\pi \int_0^{2\pi} \frac{1}{\pi} \left(\frac{1}{a_0}\right)^3 e^{-2\frac{r}{a_0}} r^3 \sin\theta \, dr \, d\theta \, d\phi \\[2ex]
&= \frac{1}{\pi} \left(\frac{1}{a_0}\right)^3 \int_0^\infty r^3 e^{-2\frac{r}{a_0}} \, dr \int_0^\pi \sin\theta \, d\theta \int_0^{2\pi} d\phi \\[2ex]
&= \frac{1}{\pi} \left(\frac{1}{a_0}\right)^3 [\phi]_0^{2\pi} [-\cos\theta]_0^\pi \left[-\frac{a_0 \, r^3}{2} e^{-2\frac{r}{a_0}} + 3\frac{a_0^2 \, r^2}{4} e^{-2\frac{r}{a_0}} + \frac{3 \, a_0^3 \, r}{4} e^{-2\frac{r}{a_0}} + \frac{3 \, a_0^4}{8} e^{-2\frac{r}{a_0}} \right]_0^\infty \\[2ex]
&= \frac{1}{\pi} \left(\frac{1}{a_0}\right)^3 4\pi \frac{3 \, a_0^4}{8} = \frac{3}{2} a_0
\end{aligned}
\tag{13}
$$

Analogamente, per gli altri orbitali, otteniamo:

$$\langle r \rangle_{1s} = \frac{3}{2} \, a_0$$
$$\langle r \rangle_{2s} = 6 \, a_0$$
$$\langle r \rangle_{2p} = 5 \, a_0$$

(14)