

## 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 ( $\text{CH}_4$ ) 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* :

$$E = \frac{h^2}{8ma^2}n^2 \quad (1)$$

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 suitable value for the molecule total mass ( $m_{\text{CH}_4} = m_C + 4m_H$ ), we obtain an energy value equal to  $E_{\text{CH}_4} = 2.06 \cdot 10^{-42} \text{ J} = 1.28 \cdot 10^{-23} \text{ eV}$

### 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:

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

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 from one orbital to the other (excited state) is given as the difference of the *starting* and *landing orbital's* energies:

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

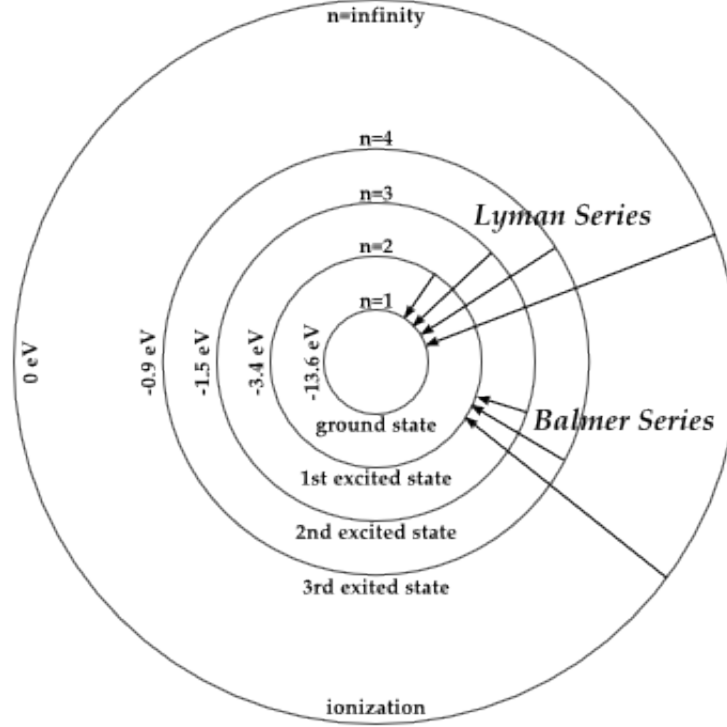


Figure 1: hydrogen orbital's energy levels

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

$$E_1 = -13.6\text{eV}; E_2 = -3.4\text{eV}; E_3 = -1.5\text{eV}; E_4 = -0.9\text{eV} \quad (4)$$

### 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 from the nucleus. This information is given by the squared absolute value of the complex wavefunction describing the system.

In spherical coordinates:

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

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

$$\Phi_{nlm}(r, \theta, \phi) = \underbrace{R_{nl}(r)}_{\text{radial part}} \underbrace{Y_l^m(\theta, \phi)}_{\text{angular part}} \quad (6)$$

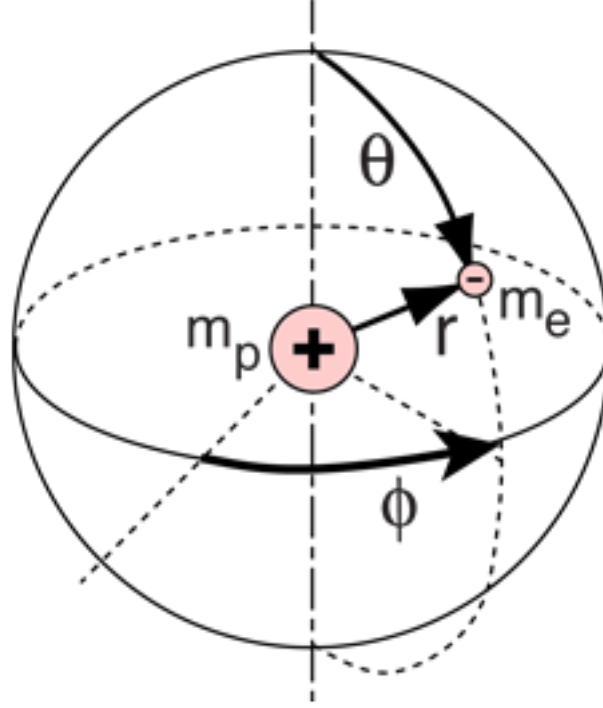


Figure 2: hydrogen atom system

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

- **n, principal quantum number**  $\rightarrow$  energy,  $n \in [1, 2, 3, \dots]$
- **l, orbital quantum number**  $\rightarrow$  angular momentum of the electron (absolute value),  $l \in [0, 1, 2, \dots, n - 1]$
- **m, magnetic quantum number**  $\rightarrow$  z-component of the angular momentum,  $m \in [-l, -l + 1, \dots, 0, \dots, l - 1, l]$

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

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

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  $1s$ ,  $Y_0^0 = \frac{1}{\sqrt{4\pi}}$ ):

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

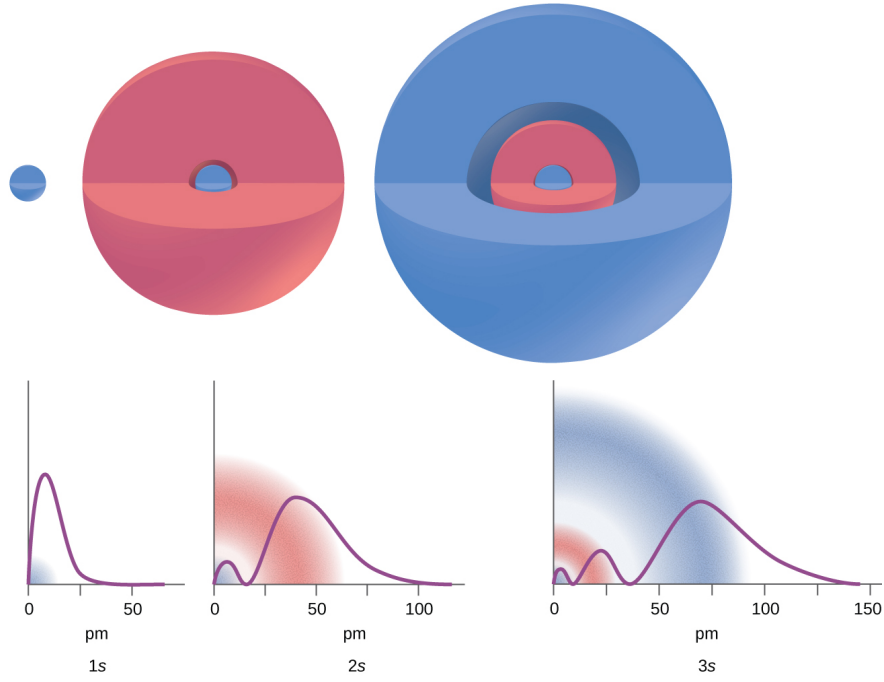


Figure 3: probability distributions for the 1s, 2s and 3s orbitals

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

$$\begin{aligned}
 Y_1^0(\theta, \phi) &= \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta \\
 Y_1^1(\theta, \phi) &= \left(\frac{3}{8\pi}\right)^{1/2} \sin\theta e^{i\phi} \\
 Y_1^{-1}(\theta, \phi) &= \left(\frac{3}{8\pi}\right)^{1/2} \sin\theta e^{-i\phi}
 \end{aligned} \tag{9}$$

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 solutions of the angular d.e. (they result in the same energy), any - normalized - linear combination of  $Y_1^1$  e  $Y_1^{-1}$  will also be a solution for the eigenvalue problem, with the same

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

$$\begin{aligned} p_x^{ang} &= \frac{1}{\sqrt{2}}(Y_1^1 + Y_1^{-1}) = \left(\frac{3}{4\pi}\right)^{1/2} \cos\phi \cdot \sin\theta \\ p_y^{ang} &= \frac{1}{\sqrt{2}}(Y_1^1 - Y_1^{-1}) = \left(\frac{3}{4\pi}\right)^{1/2} \sin\phi \cdot \sin\theta \end{aligned} \quad (11)$$

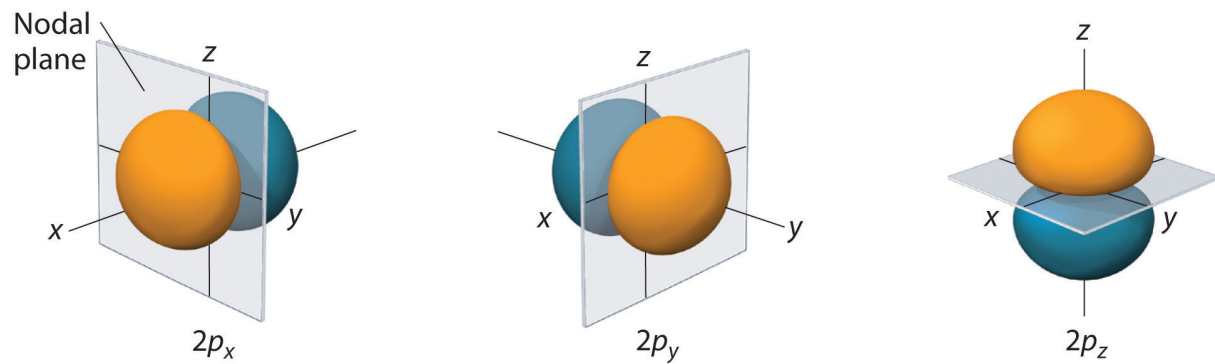
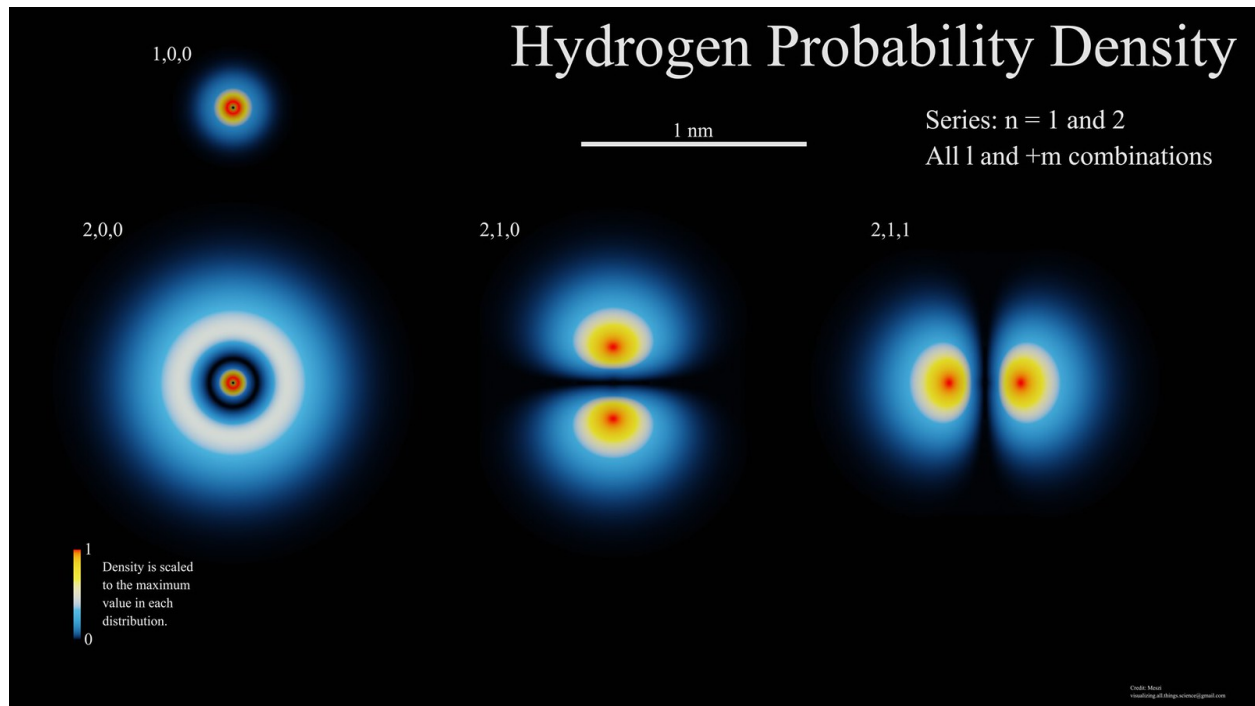


Figure 4: 3d representation of  $p$  orbitals



#### 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:

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

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

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

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:

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

Analogously for the other orbitals. we obtain:

$$\begin{aligned}\langle r \rangle_{1s} &= \frac{3}{2} a_0 \\ \langle r \rangle_{2s} &= 6 a_0 \\ \langle r \rangle_{2p} &= 5 a_0\end{aligned}\tag{14}$$