Chemistry in two-dimensional world

Jordi Llusar Camarelles

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Subject: Treball de Final de Grau (QU0943)   Supervisor: Juan Ignacio Climente Plasencia

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1) *Introduction: What are 2D materials?*

Ever since the discovery of graphene in 2004 (Novoselov, 2004), there has been increasing interest in 2D materials owing to their distinct electronic, photonic and mechanical properties. So far, graphene is still the most known 2D material. However, it faces some limitations for this use in applications which include a band gap, for example. This has triggered research on other 2D materials. Some 500 2D materials are already expected to be found.

Presently, known 2D materials include:

- Graphene – Xenes[1] (Dirac physics) (Ruijsenaars, 2006)
- TMDs (Nature, 2014)
- Semiconductors QWs (quantum wells) (Materials, 2017) (Bastard, 1988)

Graphene: properties and applications[2]

The properties of graphene are well known nowadays:
- It has a width of 3,5Å
- In photonics terms: when the light incides over a graphene layer, itself absorbs 2,3% of the white light.
- Its bandgap is between 0-0,25eV
- Experiments Kerr effect[3]
- There are transition metals dichalcogenides (TMDs) that may fills its gap

Some applications:

- It is used on optoelectronic devices (which is challenging, because of its lack or absence of natural GAP)
- On photonics (In spite of the graphene it is probably the best 2D materials on the photonics field, likewise the scientist must go further and try to find a better material on this field)

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[1] Xenes (Silicene, Germanene, Stanene, Phosphorene, Borophene, for instance)
[2] (Virendra Singha, 2011), (Photonics, 2016) (Rosei, 2017)
[3] Kerr effect: it is the change of the refraction index when it applies over a material an external electric field. Also called Non-linear electro-optic effect. (Δn= λ K E^2)

Xenes, semiconductors & TMDs the other familiars 2D of graphene

What are Xenes?

They are 2D structures of the correspondent 3D material. For instance, Silicon forms Silicene and this is arranged in a hexagonal way containing a crystalline atomically thin structure.

The Xenes share with graphene the same Dirac physics.

Semiconductors QWs[4]

In general a quantum well is a potential well with only discrete energy values.

The classic model used to demonstrate a quantum well is to confine particles, which were originally free to move in 3D, to 2D, by forcing them to occupy a planar region. The effects of quantum confinement take place when the quantum well thickness becomes comparable to the de Broglie wavelength of the electrons and holes, leading to energy levels called "energy subbands". As well the carriers may only have discrete energy values.
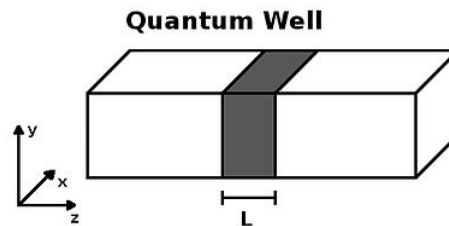
Figure 1. Quantum well geometry

The semiconductors utilised here are:

III-V: The famous III-V semiconductors are all those with relation to Gallium, for instance: GaAs, GaP, GaN and so on.

II-VI: The II-IV semiconductors comprise the compounds containing Zn, Cd, and Hg as the cations and O, S, Se, and Te as the anions.

Both sort of semiconductors turn into less covalent as it goes down in the periodic table.

Transition metal dichalcogenides (TMDs)

The TMDs are atomically thin semiconductors with a structure: MX_2[5]

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[4] (Emmanuel Lhuillier, 2015)

It is used as alternative to the absence of natural GAP problems that presents the graphene. However, detailed understanding of their optical and electronic behaviour lags behind their use in devices, and only now the effects of charge-carrier confinement in these 2D structures are being quantified.

With the TMDs it might be possible stack vertically various layers one above another, to create the so-called: Van der Waals heterostructure. First of all, you would put a MoSe$_2$, immediately you would introduce an h-BN dielectric, and finally another layer of MoSe$_2$. The h-BN dielectric is employed as a support for metal catalyst due to its chemical, thermal, acid-base stability and high thermal conductance.

To sum up where it is found in the electromagnetic spectrum each kind of material:

Figure 2. How some materials are distributed on the electromagnetic spectrum.

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[5] M: Mo, W; X: S, Se, Te and so on.
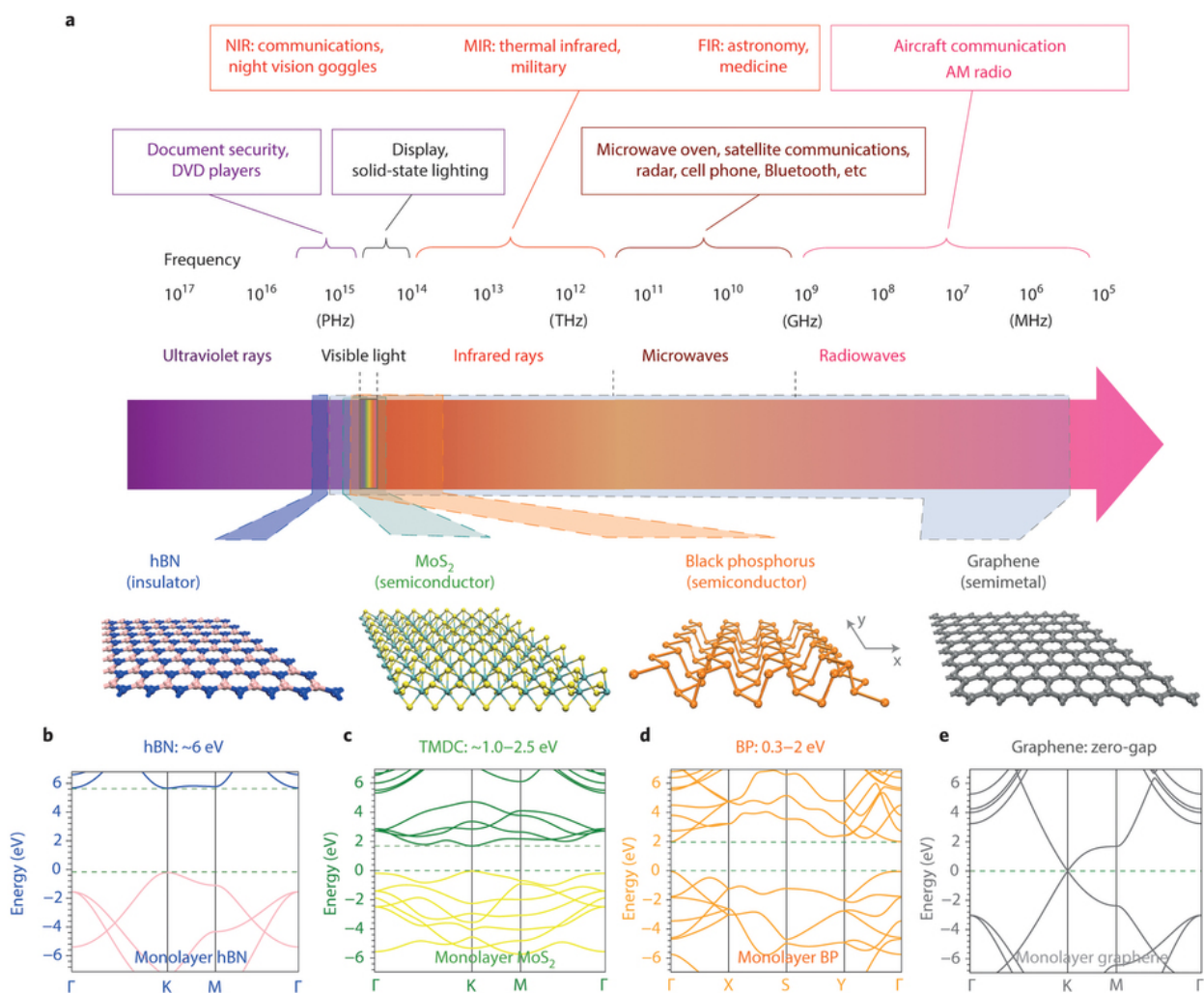
Beyond topological and spin-orbit properties which may arise in Xenes because of their Dirac physics, in general 2D materials present very different properties from their 3D counterparts. The next page table summarizes some of the most relevant ones.

3D	2D	Electron mobility (room T) (3D)(cm2/Vs)	Electron mobility (room T) (2D)(cm2/Vs)	Young's Modulus (TPa)(3D)	Young's Modulus (TPa)(2D)	Thermal conductivity (W/mK)(3D)	Thermal conductivity (W/mK)(2D)	Lattice constant (Å)(3D)	Lattice constant (Å)(2D)	Relative Permittivity (ε_r) (3D)	Relative Permittivity (ε_r) (2D)
Graphite[6]	Graphene[7]	20000	320000	0,0041-0,0276	1	8,7-114	3000-5000	3,567 (diamond)	a=2,461 / b=4,260	37,9	51
Si[8]	Silicene[9]	1500	257000	10^{-6}-5×10^{-5}	0,0617	0,2-2,55	150-200	5,431 (diamond)	a=3,880 / b=6,710	11,7	34,33
Ge[10]	Germanene[11]	3900	624000	0,103	0,0440	60,2	16,5	5,658 (diamond)	a=4,030 / b=6,970	16	~ 15
-	MoS$_2$[12]	-	200	-	0,33	-	34,5	-	a=3,1475	-	~ 15

Table 1. Comparison table between 2D & 3D materials and MoS$_2$ TMD

[6] (Xinghua Hong, 2015); (Smith)

[7] (Jin-Young Kim, 2014)
[8] (Fischetti, 1991)
[9] (Bohayra Mortazavi, 2017)
[10] (Ng, 1995)
[11] (Po-Hsin Shih, 2016)
[12] (Xiao Li, 2015); (Rusen Yan, 2014); (Young); (Bablu Mukherjee, 2015)

How it may appreciate on the previous table, certain values change drastically depending on its kind of dimensions, 3D or 2D. The question arises of why the physics and chemistry of 2D and 3D materials is so different. To this end, we will analyse the electronic properties of the most elementary of all atoms: the hydrogen atom. We will revisit the 3D resolution of the Schrödinger equation for this species. Next we will derive again solutions assuming the hydrogen atom is bound to live in a 2D universe.

We will study the implications that this has on the electronic properties, the optical spectrum, the formation of molecules and the interaction between electrons.

We would like to note that the interest of this study goes beyond an exceptionally interesting academic exercise. 2D hydrogen is currently being used to interpret the properties observed in 2D materials. (Alexey Chernikov, 2014) (S. Ithurria, 2011)

2) *Hydrogen atom in 3D*

The mechano-quantic study of the hydrogen atom is truly important because their wave functions work as base to an approximated quantum treatment on the rest of elements in the periodic table. Now, we will start by evaluating the most general case of the monoelectronics species with nuclear charge Ze following a similar derivation to that have been done on (Rajadell) (Levine, 2001). If m_N and m_e represents, respectively, the core and the electron masses, the Schrödinger equation follows as,

$$\left(-\frac{\hbar^2}{2m_N}\nabla_N{}^2 - \frac{\hbar^2}{2m_e}\nabla_e{}^2 + V(r)\right)\psi_{N,e} = E\psi_{N,e} \ (1)$$

where

$$\nabla_N{}^2 = \frac{\partial^2}{\partial x_N{}^2} + \frac{\partial^2}{\partial y_N{}^2} + \frac{\partial^2}{\partial z_N{}^2}$$

x_N, y_N, z_N are the core coordinates

$$\nabla_e{}^2 = \frac{\partial^2}{\partial x_e{}^2} + \frac{\partial^2}{\partial y_e{}^2} + \frac{\partial^2}{\partial z_e{}^2}$$

x_e, y_e, z_e are the electron coordinates

$$V(r) = -K\frac{(Ze)e}{r} \ (2)$$

$$r = \sqrt{(x_e - x_N)^2 + (y_e - y_N)^2 + (z_e - z_N)^2}$$

(The potential energy of the system depends only on the distance r between the core and the electron – it is central due to the force between both particles -)

$$\psi_{N,e} = \psi(x_e, y_e, z_e, x_N, y_N, z_N)$$
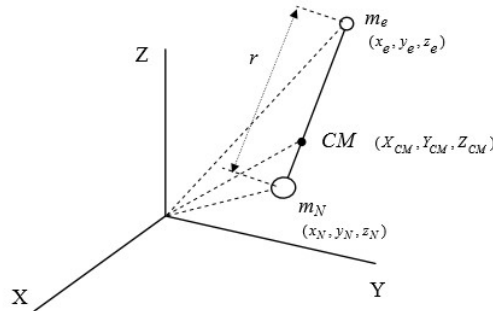
The coordinates of the system come defined by

Figure 3. Coordinates of 3D system

Where,

$$x = x_e + x_N \qquad\qquad X_{CM=} \frac{m_e x_e + m_N x_N}{M}$$

$$y = y_e + y_N \qquad\qquad Y_{CM=} \frac{m_e y_e + m_N y_N}{M}$$

$$z = z_e + z_N \qquad\qquad Z_{CM=} \frac{m_e z_e + m_N z_N}{M}$$

(Here $M = m_e + m_N$ is the total mass of the system, and x_{CM}, y_{CM}, z_{CM} the coordinates of the centre of mass)

Operating the two masses m_1 and m_2, we may get the next expression to the kinetic energy for the three dimensions:

$$T = \frac{M}{2}\left[\left(\frac{dX_{CM}}{dt}\right)^2 + \left(\frac{dY_{CM}}{dt}\right)^2 + \left(\frac{dZ_{CM}}{dt}\right)^2\right] + \frac{\mu}{2}\left[\left(\frac{dx_\mu}{dt}\right)^2 + \left(\frac{dy_\mu}{dt}\right)^2 + \left(\frac{dz_\mu}{dt}\right)^2\right]_{13,\ 14}$$

$$T = \frac{p^2_{CM}}{2M} + \frac{p^2_\mu}{2\mu} \quad (3)$$

The potential energy (2), only depends on the internal coordinates (x, y, z), therefore,

$$V(r) = -K\frac{(Ze)e}{\sqrt{x^2 + y^2 + z^2}}$$

$$r = \sqrt{(x_e - x_N)^2 + (y_e - y_N)^2 + (z_e - z_N)^2} = \sqrt{x^2 + y^2 + z^2}$$

The classical equations (2) & (3), allow us to write the Hamiltonian as follows,

$$\hat{\mathcal{H}} = -\frac{\hbar^2}{2M}\nabla_{CM}{}^2 - \left(\frac{\hbar^2}{2\mu}\nabla_\mu{}^2 + K\frac{(Ze)e}{r}\right) \quad (4)$$

The bracket term depends on the internal coordinates (x, y, z). So we can make the following variables separation,

$$\psi_{CM,\mu} = \psi(X_{CM}, Y_{CM}, Z_{CM}, x_\mu, y_\mu, z_\mu) = \psi_{CM}(X_{CM}, Y_{CM}, Z_{CM})\psi_\mu(x_\mu, y_\mu, z_\mu)$$

Then the Schrödinger equation for the term associated to the centre of mass and relative motion results, respectively,

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[13] We replace the subscript "N" by "CM" because $m_N >>> m_e$ and then $X_{CM} \cong x_N$, and the same logic for the replacing of the subscript "e" by "μ", since we have $\mu = m_e$.
[14] $\mu = \frac{m_1 m_2}{m_1 + m_2}$ in other words, μ is the reduced mass

$$-\frac{\hbar^2}{2M}\nabla_{CM}{}^2\psi_{CM} = E_{CM}\psi_{CM} \ (5)$$

$$-\left(\frac{\hbar^2}{2\mu}\nabla_\mu{}^2 + K\frac{(Ze)e}{r}\right)\psi_\mu = E_\mu\psi_\mu \ (6)$$

Now, equation (5) describes the free particle; on the other hand, the (6) equation describes the relative movement between core and electron. We just want the last equation (the (5) one leads to a constant value that it is not concerning us right now), then, removing every single subscript of the (6) equation we could rewrite

$$-\left(\frac{\hbar^2}{2\mu}\nabla^2 + K\frac{(Ze)e}{r}\right)\psi = E\psi \ (7)$$

At this point we cannot do any additional variable separation; however, if it uses spherical coordinates (suggested by the spherical symmetry of the potential -central force-) it is still possible this variable separation.

The Laplace's operator, in spherical coordinates, results from the expression,

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right) \ (8) \ (\text{Liston, 2013})$$

Keeping in mind the angular momentum equation in spherical coordinates and defining the operator $\widehat{D}$ as follows

$$\widehat{D} = \frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)$$

$$\widehat{L}^2 = -\hbar^2\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right)$$

The Laplacian operator (8) would remain as

$$\nabla^2 = \frac{1}{r^2}\left(\widehat{D} - \frac{\widehat{L}^2}{\hbar^2}\right) \ (9)$$

According to (9) & (7) equations we could write the Schrödinger equation

$$\widehat{D}\psi + \frac{2\mu r^2}{\hbar^2}\left(E + K\frac{(Ze)e}{r}\right)\psi = \frac{\widehat{L}^2}{\hbar^2}\psi \ (10)$$

Where the right term operator in the equation depends on the coordinates θ and φ, whereas the set of operators that appear on the other side just depend on the coordinate r. This permits us to do the following variable separation in the wave function ψ:

$$\psi(r, \theta, \varphi) = R(r)Y(\theta, \varphi) \ (11)$$

Replacing (11) in the Schrödinger equation (10) and immediately dividing on the resulting equality by (11), it results

$$\frac{1}{R(r)}\left[\widehat{D}R(r) + \frac{2\mu r^2}{\hbar^2}\left(E + K\frac{(Ze)e}{r}\right)R(r)\right] = \frac{1}{Y(\theta,\varphi)}\frac{\widehat{L}^2}{\hbar^2}Y(\theta,\varphi) \ (12)$$

Now, to get the previous equation (12) occur, both sides of the equality have to be the same constant value, then

$$\frac{1}{R}\left[\widehat{D}R + \frac{2\mu r^2}{\hbar^2}\left(E + K\frac{(Ze)e}{r}\right)R\right] = \gamma \ \rightarrow \ \widehat{D}R + \frac{2\mu r^2}{\hbar^2}\left(E + K\frac{(Ze)e}{r}\right)R = \gamma R \ (13)$$

$$\frac{1}{Y(\theta,\varphi)}\frac{\widehat{L}^2}{\hbar^2}Y = \gamma \ \rightarrow \ \widehat{L}^2 Y = \hbar^2 \gamma Y \ (14)$$

Where one may realise that equation (14) is similar to the spherical harmonics equation. So we can conclude

$$\widehat{L}^2 Y = l(l+1)\hbar^2 Y \rightarrow \gamma = l(l+1)(15)$$

So taking (15) and carrying it to (13) equation it obtains

$$\left[\widehat{D} + \frac{2\mu r^2}{\hbar^2}\left(E + K\frac{(Ze)e}{r}\right) - l(l+1)\right]R = 0 \ (16)$$

With the objective to transform the differential equation (16) to may identify it with any standard differential equation:

 i) We take into account the definition of the Laplace's operator:

$$\widehat{D} = \frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) = 2r\frac{\partial}{\partial r} + r^2\frac{\partial^2}{\partial r^2} \equiv 2r\frac{d}{dr} + r^2\frac{d^2}{dr^2} \ (17)^{15}$$

 ii) Afterwards, it does the constant replacing by the use of the Bohr's radius equation, a_0[16], on the r variable.

$$a_0 = \frac{\varepsilon_0 h^2}{\mu\pi e^2} \xrightarrow{\varepsilon_0 = \frac{1}{4\pi K}} a_0 = \frac{h^2}{4\pi^2 K\mu e^2} = \frac{\hbar^2}{K\mu e^2} \ (18)$$

With both expressions, (17) & (18) it could obtain

$$R'' + \frac{2}{r}R' + \left(\frac{2E}{Ke^2 a_0} + \frac{2Z}{a_0}\frac{1}{r} - \frac{l(l+1)}{r^2}\right)R = 0 \ (19)\ ^{17}$$

Once solved (19) differential equation by Laguerre polynomials it obtains the following expression

$$E = -\frac{Z^2 e^2 K}{2a_0}\frac{1}{n^2} \quad (with\ n = 1,2,3,\dots)\ (20)$$

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[15] We can turn into the partial derivatives in total derivatives, because those, it only applies on the r variable.

[16] The Bohr's radius is the first orbit to the hydrogen atom according to Bohr's model.

[17] R' (first "r" derivative) & R'' (second "r" derivative)

and

$$0 \le l \le n - 1 \ (21)$$

The R(r) functions, obtained as differential equation solutions (19), are the Associated Laguerre Polynomials,

For instance, to the 1s orbital (hydrogen atom); (n=1; l=0)

$$L_p(\rho) = e^\rho \frac{d}{d\rho}(\rho e^{-\rho}) = e^\rho(e^{-\rho} - \rho e^{-\rho}) = 1 - \rho \ (22.1)$$

$$L_{n+l}^{2l+1} = L_1^1 = \frac{\partial}{\partial \rho}\left(L_p(\rho)\right) = \frac{\partial}{\partial \rho}(1 - \rho) = -1 \ (22.2)$$

$$R_{n,l} = -\left(\left(\frac{2Z}{na_0}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}\right)^{\frac{1}{2}} e^{-\frac{\rho}{2}} \rho^l \, L_{n+l}^{2l+1} (22.3); \qquad \rho = \frac{2Zr}{n\, a_0} \ (22.4)$$

$$R_{1,0} = 2\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} e^{-\frac{Zr}{a_0}} \ (22)$$

Radial wave functions belonging to a different "n" value are orthogonal and, if they are normalized it may be performed as

$$\langle R_{n,l}|R_{n',l'}\rangle = \int_0^\infty R_{n,l}(r)R_{n',l'}(r)r^2 dr = \delta_{n,n'} \ (23)$$

On the next figures are drawn some radial wave functions for the hydrogen atom
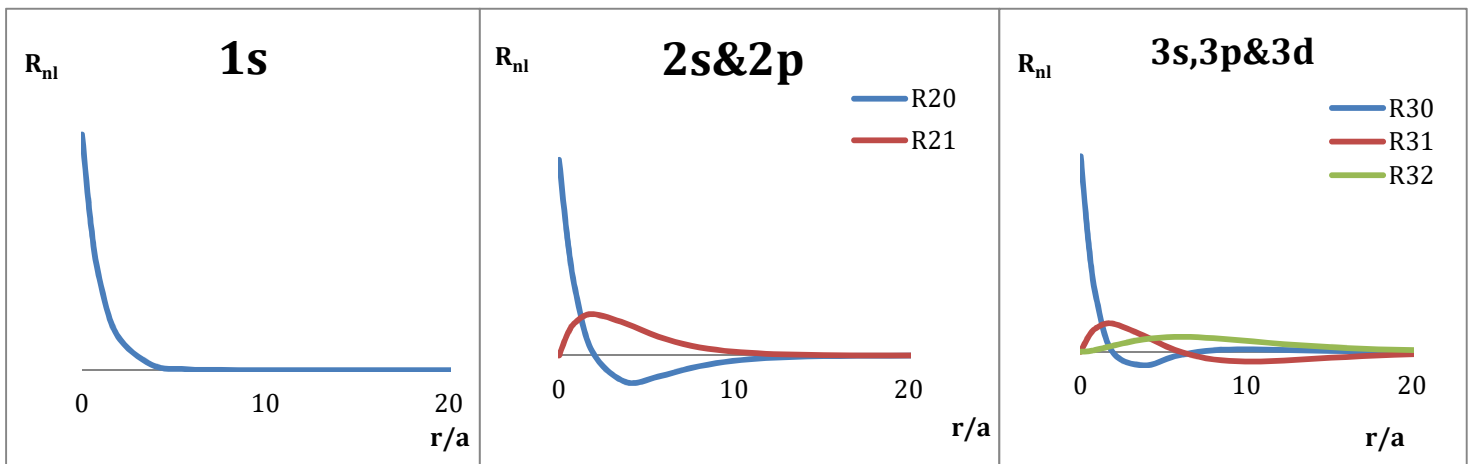
Figures 4, 5, 6. Hydrogen 3D orbitals from to 1s to 3d

Finally, the wave functions to monoelectronic atomic species might be written in the next form

$$\psi_{n,l,ml}(r,\theta,\varphi) = R_{n,l}(r)Y(\theta,\varphi) = R_{n,l}(r)\Theta_{l,ml}(\theta)\Phi(\varphi)$$

Orthonormality requirement

$$\langle \psi_{n,l,ml}(r,\theta,\varphi)|\psi_{n',l',ml}(r,\theta,\varphi)\rangle = \delta_{n,n'}\delta_{l,l'}\delta_{ml,ml'}$$

The probability to find an electron into a coordinates r,θ,φ comprised between r and r+dr, θ and θ+dθ, φ and φ+dφ, respectively, results from the expression

$$|\psi|^2 d\tau = |R_{n,l}(r)|^2 |Y_{l,ml}(\theta,\varphi)|^2 r^2 \sin\theta \, dr d\theta d\varphi$$

We ought to keep in mind that the spherical harmonics are normalized,

$$\int_0^\pi \int_0^{2\pi} |Y_{l,ml}(\theta,\varphi)|^2 \sin\theta \, d\theta d\varphi = 1$$

So finally, we can conclude that the radial distribution function is as follows

$$R_{n,l}(r)^2 r^2$$

Examples about representations of some orbitals
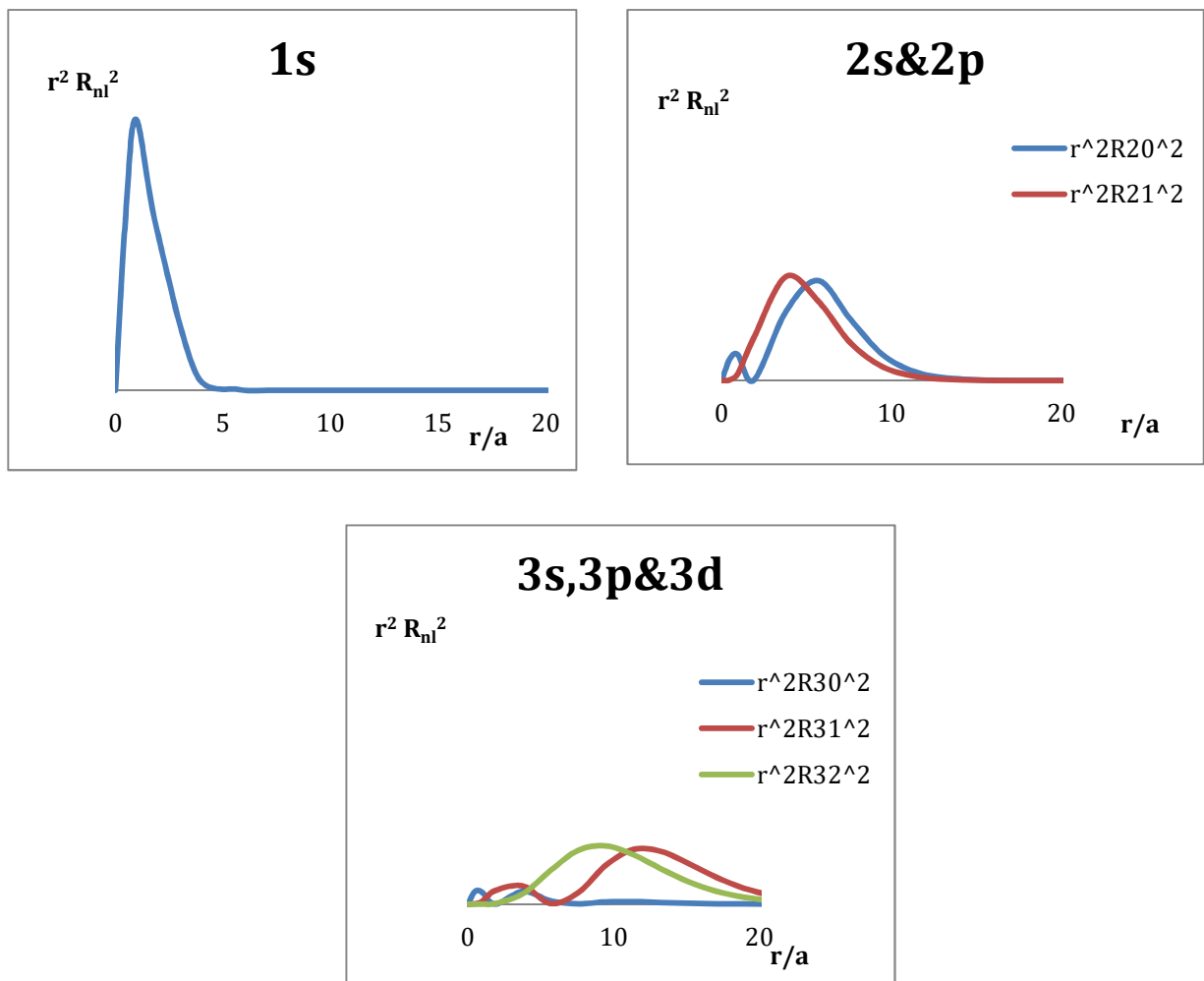
Figures 7, 8, 9. Hydrogen 3D Probability distribution from to 1s to 3d

Once seen most of the deduction about 3D hydrogen atom we could proceed to study the 2D hydrogen atom.

3) *Hydrogen atom in 2D*

We next derive equations for the 2D hydrogen atoms. The procedure we follow is largely based on analogies with the 3D case (Section 2). We begin by the Schrödinger equation,

$$\hat{H}\psi_{N,e} = E\,\psi_{N,e} \Longrightarrow \left(-\frac{\hbar^2}{2m_N}\nabla_N^{\,2} - \frac{\hbar^2}{2m_e}\nabla_e^{\,2} + V(r)\right)\psi_{N,e} = E\psi_{N,e} \ (24)$$

Where

$$\nabla_N^{\,2} = \frac{\partial^2}{\partial x_N^{\,2}} + \frac{\partial^2}{\partial y_N^{\,2}}$$

x_N & y_N are the coordinates of the core

$$\nabla_e^{\,2} = \frac{\partial^2}{\partial x_e^{\,2}} + \frac{\partial^2}{\partial y_e^{\,2}}$$

and x_e & y_e are the electron coordinates.

Now, the potential energy equation is the same as in 3D, just leaving out the z axis,

$$V(r) = -K\frac{(Ze)e}{\sqrt{x^2 + y^2}} = -K\frac{(Ze)e}{r}$$
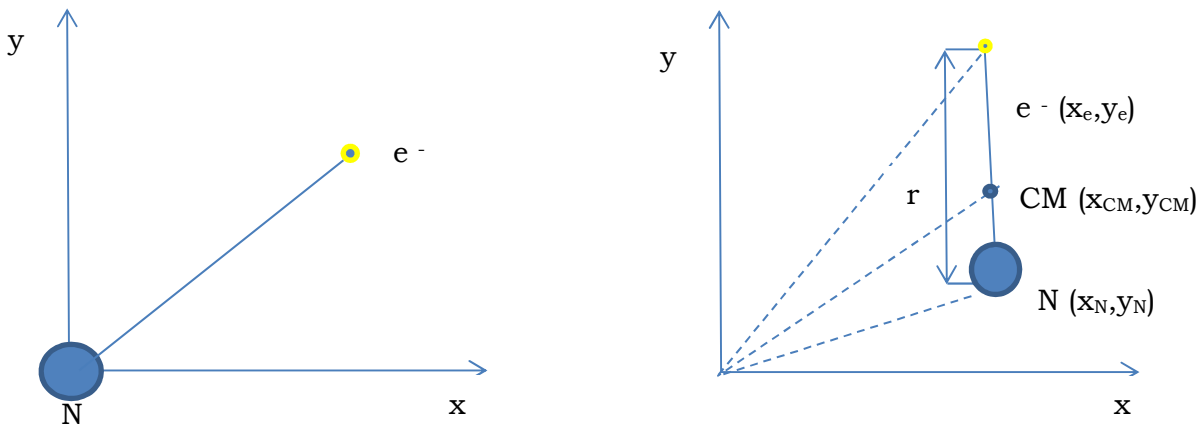
and

$$r = \sqrt{x^2 + y^2} = \sqrt{(x_e - x_N)^2 + (y_e - y_N)^2}$$

The potential energy of the system how it is known only depends on the distance r between core and electron.

$$\psi_{N,e} = \psi(x_e, y_e, x_N, y_N)$$

Once defined which elements there are into Hamiltonian, let us define the coordinates of our 2D system,

Figures 10, 11. Coordinates of the 2D system

Before continuing with the calculations, we need to first obtain the coordinates of the centre of mass to x and y.

We suppose x_1 and x_2 represents the momentary positions of the masses m_1 and m_2, respectively, respect the centre of mass. So we define the internal coordinates as

$$x = x_1 - x_2$$

$$x_{CM} = \frac{m_1 x_1 + m_2 x_2}{m_1 + m_2} \rightarrow M x_{CM} = m_1 x_1 + m_2 x_2 \quad (25.1)$$

where $M = m_1 + m_2$.

Next, we are going to obtain x_1 and x_2 values:

Obtaining of x_1

$$x_2 = x_1 - x \quad (25.2)$$

Taking (25.2) and carrying it to (25.1)

$$M x_{CM} = m_1 x_1 + m_2 x_1 - m_2 x \rightarrow M x_{CM} + m_2 x = (m_1 + m_2) x_1$$

Resulting

$$x_1 = x_{CM} + \frac{m_2}{M} x \quad (25.3)$$

And keeping on obtaining of x_2

$$x_1 = x_2 + x \quad (25.4)$$

Taking (25.4) and also carrying it to (25.1)

$$M x_{CM} = m_1 x_2 + m_1 x + m_2 x_2 \rightarrow M x_{CM} - m_1 x = (m_1 + m_2) x_2$$

Giving as result

$$x_2 = x_{CM} - \frac{m_1}{M} x \quad (25.5)$$

Taking into account that the kinetic energy is:

$$T = \frac{1}{2} m v^2 \quad (25.6)$$

Then, we are going to start operating on kinetic energy in a one-dimensional system

$$T = \frac{1}{2} m v^2 = \frac{1}{2} m_1 \left(\frac{\partial x_1}{\partial t} \right)^2 + \frac{1}{2} m_2 \left(\frac{\partial x_2}{\partial t} \right)^2 \quad (25.7)$$

Now, we may obtain the following expressions from (25.3) & (25.5) and carry them to (25.7) equation

$$\frac{\partial x_1}{\partial t} = \frac{\partial x_{CM}}{\partial t} + \frac{m_2}{M}\frac{\partial x}{\partial t} \rightarrow \left(\frac{\partial x_1}{\partial t}\right)^2 = \left(\frac{\partial x_{CM}}{\partial t}\right)^2 + \left(\frac{m_2}{M}\right)^2\left(\frac{\partial x}{\partial t}\right)^2$$

$$\frac{\partial x_2}{\partial t} = \frac{\partial x_{CM}}{\partial t} - \frac{m_1}{M}\frac{\partial x}{\partial t} \rightarrow \left(\frac{\partial x_2}{\partial t}\right)^2 = \left(\frac{\partial x_{CM}}{\partial t}\right)^2 - \left(\frac{m_1}{M}\right)^2\left(\frac{\partial x}{\partial t}\right)^2$$

$$T = \frac{1}{2}m_1\left[\left(\frac{\partial x_{CM}}{\partial t}\right)^2 + \left(\frac{m_2}{M}\right)^2\left(\frac{\partial x}{\partial t}\right)^2\right] + \frac{1}{2}m_2\left[\left(\frac{\partial x_{CM}}{\partial t}\right)^2 - \left(\frac{m_1}{M}\right)^2\left(\frac{\partial x}{\partial t}\right)^2\right]$$

Resulting the kinetic energy as,

$$T = \frac{1}{2}m_1\left(\frac{\partial x_{CM}}{\partial t}\right)^2 + \frac{m_1}{2}\left(\frac{m_2}{M}\right)^2\left(\frac{\partial x}{\partial t}\right)^2 + \frac{1}{2}m_2\left(\frac{\partial x_{CM}}{\partial t}\right)^2 - \frac{m_2}{2}\left(\frac{m_1}{M}\right)^2\left(\frac{\partial x}{\partial t}\right)^2$$

Since rearranging the previous expression we might obtain

$$T = \frac{1}{2}(m_1 + m_2)\left(\frac{\partial x_{CM}}{\partial t}\right)^2 + \frac{m_1}{2}\frac{m_2}{M^2}(m_1 + m_2)\left(\frac{\partial x}{\partial t}\right)^2$$

$$T = \frac{M}{2}\left(\frac{\partial x_{CM}}{\partial t}\right)^2 + \frac{\mu}{2}\left(\frac{\partial x}{\partial t}\right)^2 \equiv \frac{p_{CM}^2}{2M} + \frac{p_\mu^2}{2\mu} \quad (25)$$

So, making reference to kinetic energy part of equation (7) we can rewrite it as

$$T^{1D} = \frac{M}{2}\left(\frac{\partial x_{CM}}{\partial t}\right)^2 + \frac{\mu}{2}\left(\frac{\partial x}{\partial t}\right)^2$$

$$T^{1D} = \frac{p_{x_{CM}}^2}{2M} + \frac{p_x^2}{2\mu}$$

Where $\frac{p_{x_{CM}}^2}{2M}$ & $\frac{p_x^2}{2\mu}$ correspond to translation kinetic energy of the system centre of mass & relative motion, respectively

We can extrapolate toward a 2D equation,

$$T^{2D} = \frac{p_{x_{CM}}^2}{2M} + \frac{p_{y_{CM}}^2}{2M} + \frac{p_x^2}{2\mu} + \frac{p_y^2}{2\mu}$$

Next, we proceed to reconvert this classical equation in a quantum equation, taking into account that

$$p_q \rightarrow -i\hbar\frac{d}{dq}$$

$$p_q{}^2 \rightarrow -\hbar^2\frac{d^2}{dq^2}$$

We further add the potential energy we treat, the electrostatic energy. So we can write the Hamiltonian in 2D,

$$\hat{H} = \left(-\frac{\hbar^2}{2M}\nabla_{CM}^2 - \frac{\hbar^2}{2\mu}\nabla_\mu^2 - K\frac{(Ze)e}{r} \right)$$

Then, we can separate the internal coordinates from the centre of mass coordinates obtaining,

$$\hat{H} = -\frac{\hbar^2}{2M}\nabla_{CM}^2 - \left(\frac{\hbar^2}{2\mu}\nabla_\mu^2 + K\frac{(Ze)e}{r} \right) \quad (26)$$

Where the bracket term only depends on the internal coordinates (x,y)[18]. So we can make the following variables separation:

$$\psi_{CM,\mu} = \psi(x_{CM}, y_{CM}, x_\mu, y_\mu) = \psi_{CM}(x_{CM}, y_{CM})\psi_\mu(x_\mu, y_\mu)$$

After all, the Schrödinger equation for the associated terms to the centre of mass and relative movement result, respectively,

$$-\frac{\hbar^2}{2M}\nabla_{CM}^2\psi_{CM}(x_{CM}, y_{CM}) = E_{CM}\psi_{CM}(x_{CM}, y_{CM}) \quad (27)$$

$$-\left(\frac{\hbar^2}{2\mu}\nabla_\mu^2 + K\frac{(Ze)e}{r} \right)\psi_\mu(x_\mu, y_\mu) = E_\mu\psi_\mu(x_\mu, y_\mu) \quad (28)$$

Only is taken the second equation for the obtaining of the hydrogen atom energy.[19]

So, our Schrödinger equation is,

$$-\left(\frac{\hbar^2}{2\mu}\nabla^2 + K\frac{(Ze)e}{r} \right)\psi = E\psi \quad (29)$$

Once reached this point we cannot make more variables separation, unless we change our relative coordinates (x, y) by polar coordinates[20].

---

[18] Keeping our eyes on CM and μ subscripts, we could think: What about the previous subscripts N and e? What happened with them? The idea for both cases is clear enough. How it is known the core mass ($m_p = 1{,}672623x10^{-2} \ kg$) is larger than the electron mass($m_e = 9{,}10939x10^{-3} \ kg$) so the approximation is $m_p \gg m_e$. We conclude then, for x_{CM}:$x_{CM} = \frac{m_N x_N + m_e x_e}{m_N + m_e} \xrightarrow{m_N \gg m_e} x_{CM} \cong x_N$ and the same for μ:$\mu = \frac{m_N m_e}{m_N + m_e} \xrightarrow{m_N \gg m_e} \mu \cong m_e$

[19] Knowing that the Hamiltonian comes defined by $\hat{H} = \hat{H}_{CM} + \hat{H}_\mu$ we may disregard the $\hat{H}_{CM}$ term since in spectroscopy ΔE is used. In addition, the $\hat{H}_{CM}$ term is constant due it comes described by the free particle model. Finally, if we solve this Hamiltonian, we would obtain as eigenvalue $E_k = \frac{\hbar^2 k^2}{2M}$ where $k = \frac{2\pi}{L}$ (m=whole number) is a constant as the E_k is.

[20] Suggested by the spherical form of the potential in 3D and thus the circular form of the potential in 2D

Therefore we proceed with the obtaining of our 2D Laplacian in polar coordinates[21] to later make other variables separation.

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} = \frac{1}{r}\frac{\partial}{\partial r} + \frac{\partial^2}{\partial r^2} + \frac{1}{r^2}\frac{\partial^2}{\partial \varphi^2} \quad (30)$$

Keeping in mind that the (30) equation gives to us an operator with both terms, radial and angular, we can distinguish them defining $\hat{A}$ as follows:

$$\hat{A} = \frac{1}{r}\frac{\partial}{\partial r} + \frac{\partial^2}{\partial r^2} \quad (31)$$

where the Laplacian operator comes defined by

$$\nabla^2 = \hat{A} + \frac{1}{r^2}\frac{\partial^2}{\partial \varphi^2} \quad (32)$$

According to (32) equation we can write the Hamiltonian as

$$\hat{H} = -\frac{\hbar^2}{2\mu}\hat{A} - \frac{\hbar^2}{2\mu}\frac{1}{r^2}\frac{\partial^2}{\partial \varphi^2} - K\frac{(Ze)e}{r} \quad (33)$$

and the (29) equation as

$$-\frac{\hbar^2}{2\mu}\hat{A}\psi - \frac{\hbar^2}{2\mu}\frac{1}{r^2}\frac{\partial^2 \psi}{\partial \varphi^2} - K\frac{(Ze)e}{r}\psi = E\psi \quad (34)$$

Now, reordering and multiplying by $\left(-\frac{2\mu r^2}{\hbar^2}\right)$

$$r^2\hat{A}\psi + \frac{\partial^2 \psi}{\partial \varphi^2} + \frac{2\mu r^2}{\hbar^2}\left(K\frac{(Ze)e}{r} + E\right)\psi = 0 \quad (35)$$

we can observe that exists a radial and an angular part. Thus it proceeds to put the radial part (r) in a side and the angular part (φ) on the other side of the equation,

$$r^2\hat{A}\psi + \frac{2\mu r^2}{\hbar^2}\left(K\frac{(Ze)e}{r} + E\right)\psi = -\frac{\partial^2 \psi}{\partial \varphi^2} \quad (36)$$

Then knowing that $\psi = R(r)Y(\varphi)$ and leaving out the functions independents as much to the radial part as to the angular part we may arrive to the following equation:

$$Y(\varphi)\left[r^2\hat{A}R(r) + \frac{2\mu r^2}{\hbar^2}\left(K\frac{(Ze)e}{r} + E\right)R(r)\right] = -R(r)\frac{\partial^2 Y(\varphi)}{\partial \varphi^2} \quad (37)$$

Continuing with a multiplication of $\left(\frac{1}{R(r)Y(\varphi)}\right)$ on (37) equation. We obtain,

---

[21] Laplacian 2D obtaining it is found in annex (A.1)

$$\frac{1}{R(r)}\left[r^2\hat{A}R(r) + \frac{2\mu r^2}{\hbar^2}\left(K\frac{(Ze)e}{r} + E\right)R(r)\right] = -\frac{1}{Y(\varphi)}\frac{\partial^2 Y(\varphi)}{\partial\varphi^2}\,(38)$$

In order to (38) give meaning to the equation; both sides of the equality have to be constant. In other words, both sides are equal to the same constant. For instance:

$$\frac{1}{R}\left[r^2\hat{A}R + \frac{2\mu r^2}{\hbar^2}\left(K\frac{(Ze)e}{r} + E\right)R\right] = \Omega \;\rightarrow\; r^2\hat{A}R + \frac{2\mu r^2}{\hbar^2}\left(K\frac{(Ze)e}{r} + E\right)R = \Omega R\ (39)$$

$$-\frac{1}{Y}\frac{\partial^2 Y}{\partial\varphi^2} = \Omega \;\rightarrow\; \frac{\partial^2 Y}{\partial\varphi^2} = -\Omega Y\,(40)$$

Once reached this point we have a problem, we do not know what the Ω value is, so we are going to use symmetry to try to find that value focusing on the (40) equation.

First of all we need to check if we can use the symmetry to obtain Ω value. Knowing that the electron movement with respect to the core draws a circumference implies that exist an infinitesimal rotation axis (C_∞^ϕ):
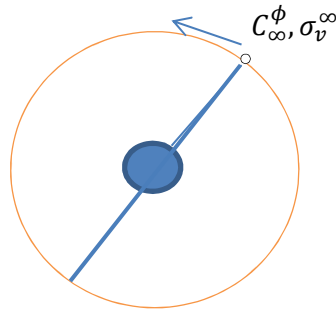

Figure 12. Electron movement respect to core

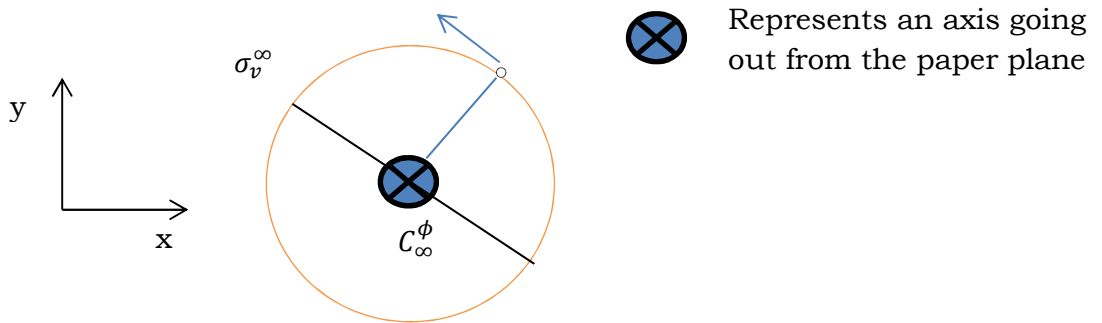Represents an axis going out from the paper plane

Figure 13. Symmetry elements

And if there are infinitesimal rotation axes, there also exists infinitesimal vertical planes. So we can conclude that our symmetry point group could be a $C_{\infty v}$. Next, we know that a rotation could be described by the following equation:

$$Y = e^{im\varphi} \ (41) \ [22]$$

With "m" as whole number. If we would apply our symmetry operation C_{∞}^{φ} to (41) we will obtain,

$$C_{\infty}^{\phi} e^{im\varphi} = e^{im\phi}e^{im\varphi} = e^{im(\varphi+\phi)} \ (42)$$

Function (42) represents,

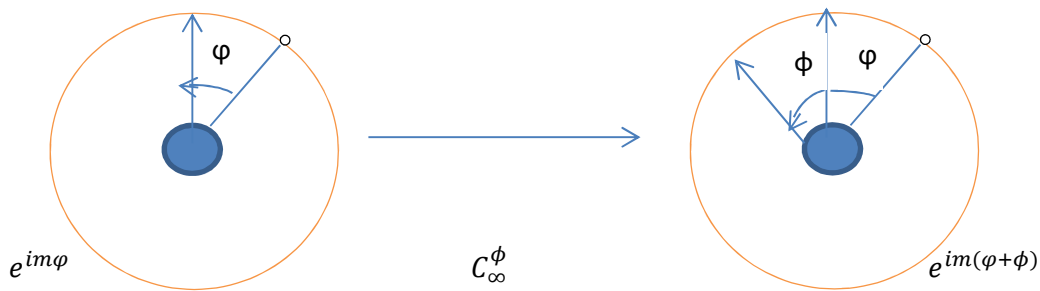$$e^{im\varphi} \qquad\qquad C_{\infty}^{\phi} \qquad\qquad e^{im(\varphi+\phi)}$$

Figure 14. How affects the rotation operator on $e^{im\varphi}$

Knowing how it is the behaviour of the rotation symmetry operation on the function mentioned before, we just need to verify if our rotation symmetry operation commutes with our Hamiltonian $\hat{H}_{\varphi} = \frac{\partial^2 Y}{\partial \varphi^2}$ to make possible that an eigenfunction from one operator be compatible with the other. Fortunately, it is like this,

$$[\hat{H}_{\varphi}, C_{\infty}^{\phi}]Y(\varphi) = 0 \ [23]$$

So, we can also affirm that $e^{im\varphi}$ is $C_{\infty v}$ base[24]and it is the general form of equation (40) eigenfunction Y as well. We have to point out that the orbital distribution is quite different in 2D respect to the orbital distribution in 3D, as one can see by comparing equation (41) with the spherical harmonics obtaining in the 3D case.

Now, making reference to equation (40) we can, right now, solve what the Ω value is,

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[22] It uses this kind of function because this functions describe the periodic movement of a rotation since is ranged between 0 and 2π. By means of Euler we have: $Y = e^{im\varphi} = \cos m\varphi + i\sin m\varphi$. In addition, m is always a whole number, that it is explained in the annex C.1)

[23] Deduction in the annex (B.1)

[24] Verification proof in annex (C.2)

$$\frac{\partial^2 Y}{\partial \varphi^2} = -(-m^2)Y \;\rightarrow\; \Omega = -m^2 \,(43)$$

Carrying Ω value to equation (39) it is obtained,

$$r^2 \hat{A} R + \frac{2\mu r^2}{\hbar^2}\left(K\frac{(Ze)e}{r} + E\right)R = m^2 R \;(44)$$

where reordering, we would have,

$$r^2 \hat{A} R + \frac{2\mu r^2}{\hbar^2}\left(K\frac{(Ze)e}{r} + E - m^2\right)R = 0 \;(45)$$

Regarding $\hat{A}$, we are going to replace it by its content (31), on (45):

$$r^2 \frac{1}{r}\frac{\partial R}{\partial r} + r^2 \frac{\partial^2 R}{\partial r^2} + \frac{2\mu r^2}{\hbar^2}\left(K\frac{(Ze)e}{r} + E - m^2\right)R = 0 \;(46)$$

Now, we are going to postulate that the solution of the 2D hydrogen 1s orbital it is quite similar to the 3D hydrogen, apart from the exponent. If in the 3D case we had equation (22), now we would have,

$$R = N_R e^{-\frac{br}{a_0}} \;(47)$$

Where N_R is the radial normalization, b is the 2D parameter and lastly a_0 is the Bohr's radius. Next, we take (47) to the equation (46),

$$r\frac{\partial\left(N_R e^{-\frac{br}{a_0}}\right)}{\partial r} + r^2 \frac{\partial^2\left(N_R e^{-\frac{br}{a_0}}\right)}{\partial r^2} + \frac{2\mu r^2}{\hbar^2}\left(K\frac{(Ze)e}{r} + E - m^2\right)\left(N_R e^{-\frac{br}{a_0}}\right) = 0 \;(48)$$

It is done the correspondents derivatives and this results on,

$$r\left(-\frac{b}{a_0}\right)N_R e^{-\frac{br}{a_0}} + r^2\left(\frac{b}{a_0}\right)^2 N_R e^{-\frac{br}{a_0}} + \frac{2\mu r^2}{\hbar^2}\left(K\frac{(Ze)e}{r} + E - m^2\right)N_R e^{-\frac{br}{a_0}} = 0$$

$$r\left(-\frac{b}{a_0}\right) + r^2\left(\frac{b}{a_0}\right)^2 + \frac{2\mu r^2}{\hbar^2}\left(K\frac{(Ze)e}{r} + E - m^2\right) = 0 \;(49)$$

Taking into account that we are dealing with a hydrogen atom 1s orbital we can make the "m" term equal to zero. Besides, terms are reordered according to "r" power, leading to,

$$\left[\left(\frac{b}{a_0}\right)^2 + \frac{2\mu E}{\hbar^2}\right]r^2 + \left[\frac{2\mu}{\hbar^2}K(Ze)e - \frac{b}{a_0}\right]r = 0 \;(50)$$

Because equation (50) must hold for any value of r, we can make both terms separately equal to zero, then obtaining b:

$$\frac{2\mu}{\hbar^2}K(Ze)e - \frac{b}{a_0} = 0 \rightarrow b = \frac{2\mu K Z e^2 a_0}{\hbar^2}$$

If we go further taking into account that $e'^2 = Ke^2$ and $a_0 = \hbar^2/\mu e'^2$, b results as,

$$b = \frac{2\mu K Z e^2 a_0}{\hbar^2} \xrightarrow{e'^2 = Ke^2} b = \frac{2\mu Z e'^2 a_0}{\hbar^2} \xrightarrow{a_0 = \hbar^2/\mu e'^2} \boxed{b = 2Z}. \,(51)$$

In order to obtain the Energy value, we use the same procedure as before. The first term of the (50) equation is solved, then obtaining E:

$$\left(\frac{b}{a_0}\right)^2 + \frac{2\mu E}{\hbar^2} = 0 \rightarrow E = -\left(\frac{b}{a_0}\right)^2 \frac{\hbar^2}{2\mu} \xrightarrow{a_0 = \hbar^2/\mu e'^2} E - \frac{b^2 e'^2}{2a_0} \xrightarrow{b=2Z} \boxed{E = -\frac{2Z^2 e'^2}{a_0}}. \,(52)$$

Next, to corroborate that (52) Energy equation is right; we verify its validity by means of virial theorem. Now, it is followed by the next series of operations:

1) $\langle T \rangle$ value

$$\int \psi^* \hat{T} \psi \, dA \xrightarrow{dA = r dr d\varphi} \int_0^{2\pi} \int_0^\infty \psi^* \hat{T} \psi \, r dr d\varphi \,(T.1)$$

To make the calculation more accurate, we proceed to calculate the $\hat{T}\psi$ term,

$$\hat{T}\psi = -\frac{\hbar^2}{2\mu} \nabla^2 \psi \xrightarrow{\psi = RY} -\frac{\hbar^2}{2\mu}\left[\frac{1}{r}\frac{\partial RY}{\partial r} + \frac{\partial^2 RY}{\partial r^2} + \frac{1}{r^2}\frac{\partial^2 RY}{\partial \varphi^2}\right] \,(T.2)$$

Knowing the functions definition $R = N_R e^{-\frac{br}{a_0}}$ and $Y = N_\varphi e^{im\varphi}$ we might reorder it (T.1) as

$$\nabla^2 \psi = \left[\frac{N_\varphi e^{im\varphi}}{r}\frac{\partial N_R e^{-\frac{br}{a_0}}}{\partial r} + N_\varphi e^{im\varphi}\frac{\partial^2 N_R e^{-\frac{br}{a_0}}}{\partial r^2} + \frac{N_R e^{-\frac{br}{a_0}}}{r^2}\frac{\partial^2 N_\varphi e^{im\varphi}}{\partial \varphi^2}\right]$$

Operating the derivatives and extracting the independent values, we get:

$$\nabla^2 \psi = N_\varphi N_R \left[\frac{e^{im\varphi}}{r}\left(-\frac{b}{a_0}\right)e^{-\frac{br}{a_0}} + e^{im\varphi}\left(\frac{b}{a_0}\right)^2 e^{-\frac{br}{a_0}} - \frac{e^{-\frac{br}{a_0}}}{r^2}m^2 e^{im\varphi}\right]$$

$$\nabla^2 \psi = N_\varphi N_R e^{im\varphi} e^{-\frac{br}{a_0}}\left[-\frac{b}{ra_0} + \left(\frac{b}{a_0}\right)^2 - \frac{m^2}{r^2}\right] \,(T.3)$$

Now it is multiplied by its conjugated function ψ^*,

$$\psi^* \nabla^2 \psi = N_\varphi{}^2 N_R{}^2 e^{im\varphi} e^{-im\varphi} e^{-\frac{2br}{a_0}}\left[-\frac{b}{ra_0} + \left(\frac{b}{a_0}\right)^2 - \frac{m^2}{r^2}\right]$$

Next, we make m equal to zero; according to we are on the 1s' orbital,

$$\psi^* \nabla^2 \psi = N_\varphi{}^2 N_R{}^2 \frac{b}{a_0}\left[-\frac{1}{r}+\frac{b}{a_0}\right]e^{-\frac{2br}{a_0}} \ (T.4)$$

Take (T.4) to (T.1) equation

$$\langle T \rangle = -\frac{\hbar^2}{2\mu}N_\varphi{}^2 N_R{}^2 \frac{b}{a_0}\left\{\int_0^{2\pi} d\varphi\left[-\int_0^\infty \left(\frac{r}{r}e^{-\frac{2br}{a_0}}dr\right)+\frac{b}{a_0}\int_0^\infty \left(re^{-\frac{2br}{a_0}}dr\right)\right]\right\}$$

It is integrated and it is obtained:

$$\langle T \rangle = -\frac{\hbar^2}{2\mu}N_\varphi{}^2 N_R{}^2 \frac{b}{a_0}\left\{2\pi\left[-\frac{a_0}{2b}+\frac{a_0}{4b}\right]\right\} \ (T.5)$$

Now, would be a perfect occasion to obtain both normalizations,

$$N_\varphi{}^2 \int_0^{2\pi} d\varphi = 1 \rightarrow N_\varphi{}^2\, 2\pi = 1 \rightarrow \boxed{N_\varphi = \frac{1}{\sqrt{2\pi}}}$$

$$N_R{}^2 \int_0^\infty re^{-\frac{2br}{a_0}}dr = 1 \rightarrow N_R{}^2 \left(\frac{a_0}{2b}\right)^2 = 1 \rightarrow N_R = \frac{2b}{a_0}\xrightarrow{b=2Z}\boxed{N_R = \frac{4Z}{a_0}}$$

Finally, the normalizations are replaced on (T.5) equation,

$$\langle T \rangle = -\frac{\hbar^2}{2\mu}\frac{1}{2\pi}\frac{4^2 Z^2}{a_0{}^2}\frac{b}{a_0}\left\{2\pi\left[-\frac{a_0}{2b}+\frac{a_0}{4b}\right]\right\} \rightarrow \langle T \rangle = -\frac{\hbar^2}{2\mu}\frac{1}{2\pi}\frac{4^2 Z^2}{a_0{}^2}\frac{b}{a_0}\frac{2\pi a_0}{b}\left[-\frac{1}{2}+\frac{1}{4}\right]$$

$$\langle T \rangle = -\frac{\hbar^2}{2\mu}\frac{4^2 Z^2}{a_0{}^2}\left[-\frac{1}{4}\right] \equiv 2\frac{\hbar^2}{\mu}\frac{Z^2}{a_0{}^2}\xrightarrow{a_0=\hbar^2/\mu e'^2}\boxed{\langle T \rangle = \frac{2Z^2 e'^2}{a_0}}$$

2) It is known that $\langle E \rangle = \langle T \rangle + \langle V \rangle$ where $\langle T \rangle$ and $\langle E \rangle$ come defined as,

$$\langle E \rangle = -\frac{2Z^2 e'^2}{a_0} \ ; \ \langle T \rangle = \frac{2Z^2 e'^2}{a_0}$$

So, the potential energy is,

$$\langle V \rangle = \langle E \rangle - \langle T \rangle = -\frac{2Z^2 e'^2}{a_0}-\frac{2Z^2 e'^2}{a_0}=-\frac{4Z^2 e'^2}{a_0}$$

3) In addition, it is also known that $2\langle T \rangle = n\langle V \rangle$ [25]where "n" is the order of the homogenous function representing the potential energy, in this case represented by the electrostatic potential, so

$$\langle V \rangle = \frac{2\langle T \rangle}{n}\xrightarrow[\langle T\rangle=\frac{2Z^2 e'^2}{a_0}]{n=-1}\langle V \rangle = \frac{2}{-1}\frac{2Z^2 e'^2}{a_0}\equiv -\frac{4Z^2 e'^2}{a_0}$$

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[25] The order of the homogenous function would be equal to minus zero, because:

$$V = K\frac{(Ze)e}{r^n}=K(Ze)e\,r^{-n}\xrightarrow{n=1}V=K(Ze)e\,r^{-1}$$

Therefore, our energies obey the virial theorem and according to it, we can make a series of calculations on a trustworthy way. Now, we find that we can make the following questions:

1) What is the probability to find an electron between core and the first Bohr radius in 2D?

$$\int |\psi|^2 dA = \int [R_n(r)]^2 [Y^m(\varphi)]^2 \, r dr d\varphi^{26}$$

As the polar harmonics are normalized we have then:

$$\int_0^{2\pi} [Y^m(\varphi)]^2 \, d\varphi = 1$$

Just remaining:

$$\int_0^{a_0} [R_n(r)]^2 \, r dr = \left(\frac{4Z}{a_0}\right)^2 \int_0^{a_0} r \, e^{-\frac{4Z}{a_0}} \, dr = \left(\frac{4Z}{a_0}\right)^2 \left[\frac{e^{-\frac{4Z}{a_0}}}{4^2 Z^2} a_0^2 \left(-\frac{4Zr}{a_0} - 1 \right) \right]\Bigg|_0^{a_0}$$

$$2D \ Probability = [e^{-4Z}(-4Z - 1) - e^0(-1)] \xrightarrow{Z=1} 2D \ Probability = 0{,}9084 \equiv 90{,}84\%$$

In 3D, the probability to find an electron is 0,3233 or 32,33%[27]. In the follow figure we may compare both probabilities as much in 2D as in 3D,
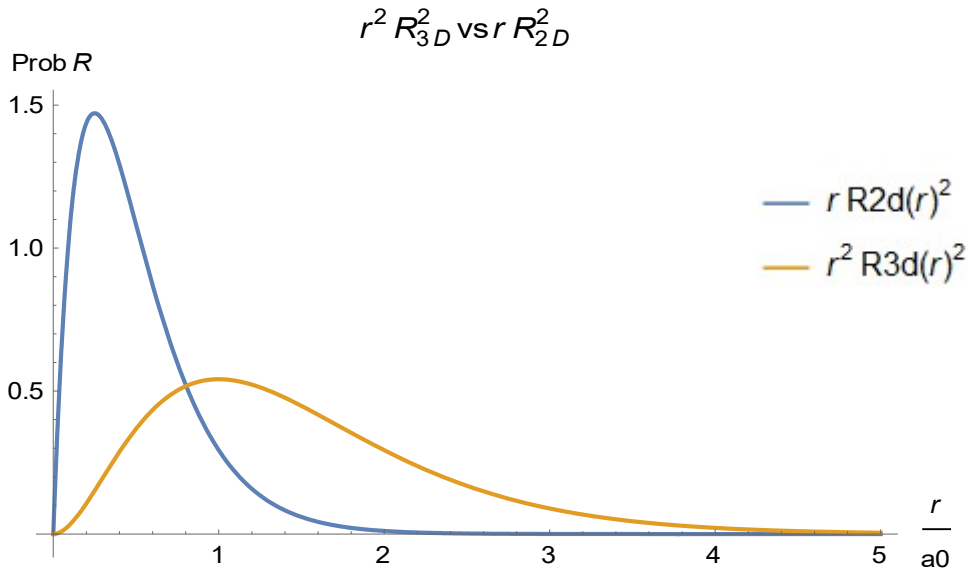

$$r^2 R_{3D}^2 \ vs \ r \, R_{2D}^2$$

Figure 15. Comparison of the probability to find an electron between 2D and 3D

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[26] Jacobian obtaining on annex A.2)
[27] Obtaining of 3D probability on annex D.1)

It is observed 2D probability is higher than 3D probability, this likely be due to the electron is more tightly bound to the nucleus than in 3D. In addition, the difference according to space is halved from 3D to 2D.[28]

Now the electron ground state energies as much in 2D as in 3D are,

$$E^{2D} = I.E.(2D) = -\frac{2Z^2 e'^2}{a_0} = -54{,}423 \; eV \; (53)^{[29]}$$

$$E^{3D} = I.E.(3D) = -\frac{Z^2 e'^2}{2a_0} = -13{,}606 \; eV \; (\text{Levine}, 2001)$$

It is observed that the 2D energy is higher than 3D energy. Therefore we would have to apply a 4 times greater energy to ionize the hydrogen atom or in other words, to pull out its electron.
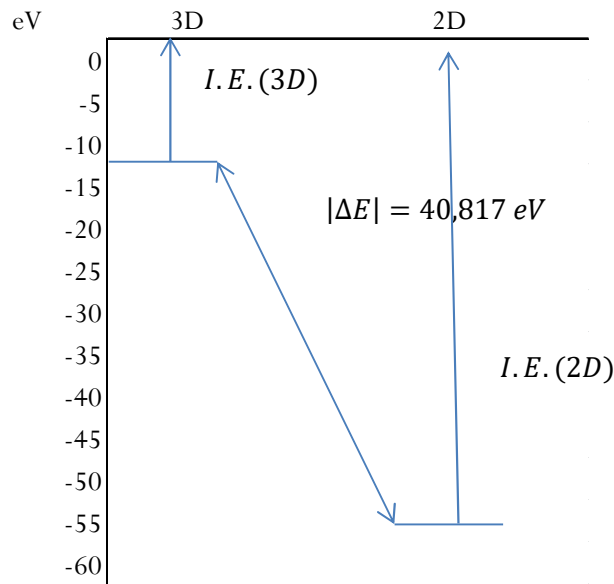
Figure16. Comparison between 1s orbital (3D) and 1s' orbital (2D)

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[28] In fact, as one can notice by comparing eq. (22) and eq. (47) (both without normalizations), the ground state wave function of the 2D hydrogen electron is like that of the 3D one but replacing the usual 3D Bohr radius, a_0 , by an effective 2D Bohr radius, a_0^* , which turns out to be simply $a_0^* = {a_0}/{2}$.

[29] $E^{3D} = -\frac{Z^2 e'^2}{n^2 2a_0}$ is the general equation for 3D ionization energy

Some differences between the 2D and 3D hydrogen atom

Similar procedure for other higher energy states where the series of energies and orbitals obtained differ systematically from the 3D case. The following table summarizes them[30]:

Constants values	Orbital	$Y(\varphi)$	$R(r)$	$\psi(r,\varphi) = R(r)Y(\varphi)$	Energies
$b = \dfrac{2Z}{a_0}$	1s	$\dfrac{1}{\sqrt{2\pi}}$	$\dfrac{4Z}{a_0} e^{-\frac{2Zr}{a_0}}$	$\dfrac{4Z}{a_0}\dfrac{1}{\sqrt{2\pi}} e^{-\frac{2Zr}{a_0}}$	$-\dfrac{2Z^2 e'^2}{a_0}$
$b = \dfrac{2Z}{3a_0}$	2s	$\dfrac{1}{\sqrt{2\pi}}$	$\dfrac{16\sqrt{5}}{45}\left(\dfrac{Z}{a_0}\right)^2\left(r - \dfrac{3a_0}{4Z}\right)e^{-\frac{2Zr}{3a_0}}$	$\dfrac{16\sqrt{5}}{45}\left(\dfrac{Z}{a_0}\right)^2\dfrac{1}{\sqrt{2\pi}}\left(r - \dfrac{3a_0}{4Z}\right)e^{-\frac{2Zr}{3a_0}}$	$-\dfrac{2}{9}\dfrac{Z^2 e'^2}{a_0}$
$c = \dfrac{3a_0}{4Z}$	2p	$\dfrac{1}{\sqrt{2\pi}}e^{i|1|\varphi}$	$\dfrac{8\sqrt{6}}{27}\left(\dfrac{Z}{a_0}\right)^2 r\, e^{-\frac{2Zr}{3a_0}}$	$\dfrac{8\sqrt{6}}{27}\left(\dfrac{Z}{a_0}\right)^2\dfrac{1}{\sqrt{2\pi}} r\, e^{-\frac{2Zr}{3a_0}} e^{i|1|\varphi}$	$-\dfrac{2}{9}\dfrac{Z^2 e'^2}{a_0}$
$b = \dfrac{2Z}{5a_0}$	3s	$\dfrac{1}{\sqrt{2\pi}}$	$\dfrac{64}{125\sqrt{111}}\left(\dfrac{Z}{a_0}\right)^3\left(r^2 - \dfrac{15a_0 r}{4Z} + \dfrac{75a_0^2}{16Z^2}\right)e^{-\frac{2Zr}{5a_0}}$	$\dfrac{64}{125\sqrt{111}}\left(\dfrac{Z}{a_0}\right)^3\dfrac{1}{\sqrt{2\pi}}\left(r^2 - \dfrac{15a_0 r}{4Z} + \dfrac{75a_0^2}{16Z^2}\right)e^{-\frac{2Zr}{5a_0}}$	$-\dfrac{2}{25}\dfrac{Z^2 e'^2}{a_0}$
$c = \dfrac{15a_0}{4Z}$	3p	$\dfrac{1}{\sqrt{2\pi}}e^{i|1|\varphi}$	$\dfrac{64}{125\sqrt{30}}\left(\dfrac{Z}{a_0}\right)^3\left(r - \dfrac{15a_0}{4Z}\right)r\, e^{-\frac{2Zr}{5a_0}}$	$\dfrac{64}{125\sqrt{30}}\left(\dfrac{Z}{a_0}\right)^3\dfrac{1}{\sqrt{2\pi}}\left(r - \dfrac{15a_0}{4Z}\right)r\, e^{-\frac{2Zr}{5a_0}} e^{i|1|\varphi}$	$-\dfrac{2}{25}\dfrac{Z^2 e'^2}{a_0}$
$d = \dfrac{75a_0^2}{16Z^2}$	3d	$\dfrac{1}{\sqrt{2\pi}}e^{i|2|\varphi}$	$\dfrac{32}{125\sqrt{30}}\left(\dfrac{Z}{a_0}\right)^3 r^2 e^{-\frac{2Zr}{5a_0}}$	$\dfrac{32}{125\sqrt{30}}\left(\dfrac{Z}{a_0}\right)^3\dfrac{1}{\sqrt{2\pi}} r^2 e^{-\frac{2Zr}{5a_0}} e^{i|2|\varphi}$	$-\dfrac{2}{25}\dfrac{Z^2 e'^2}{a_0}$

Table2. Different hydrogen 2D properties about energies and orbitals

By inspection of Table 2, one can infer a general expression for the energy of 2D hydrogenic atoms:

$$E^{2D} = -\frac{2Z^2 e'^2}{(2n-1)^2 a_0} \quad (54)$$

Where n is the quantum number ($n = 1,2,3,\dots$)
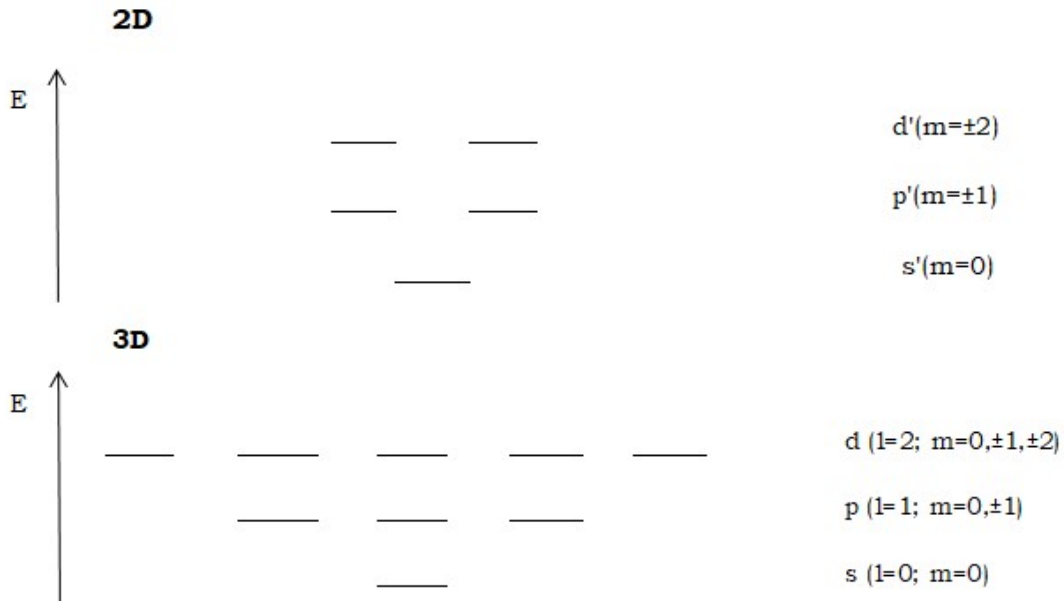

Figure 17. Comparison of energetic levels between 2D and 3D

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[30] All the calculations can be found in annex E.1)

The orbital symmetry regarding on their energies would be, for 2D and 3D respectively,
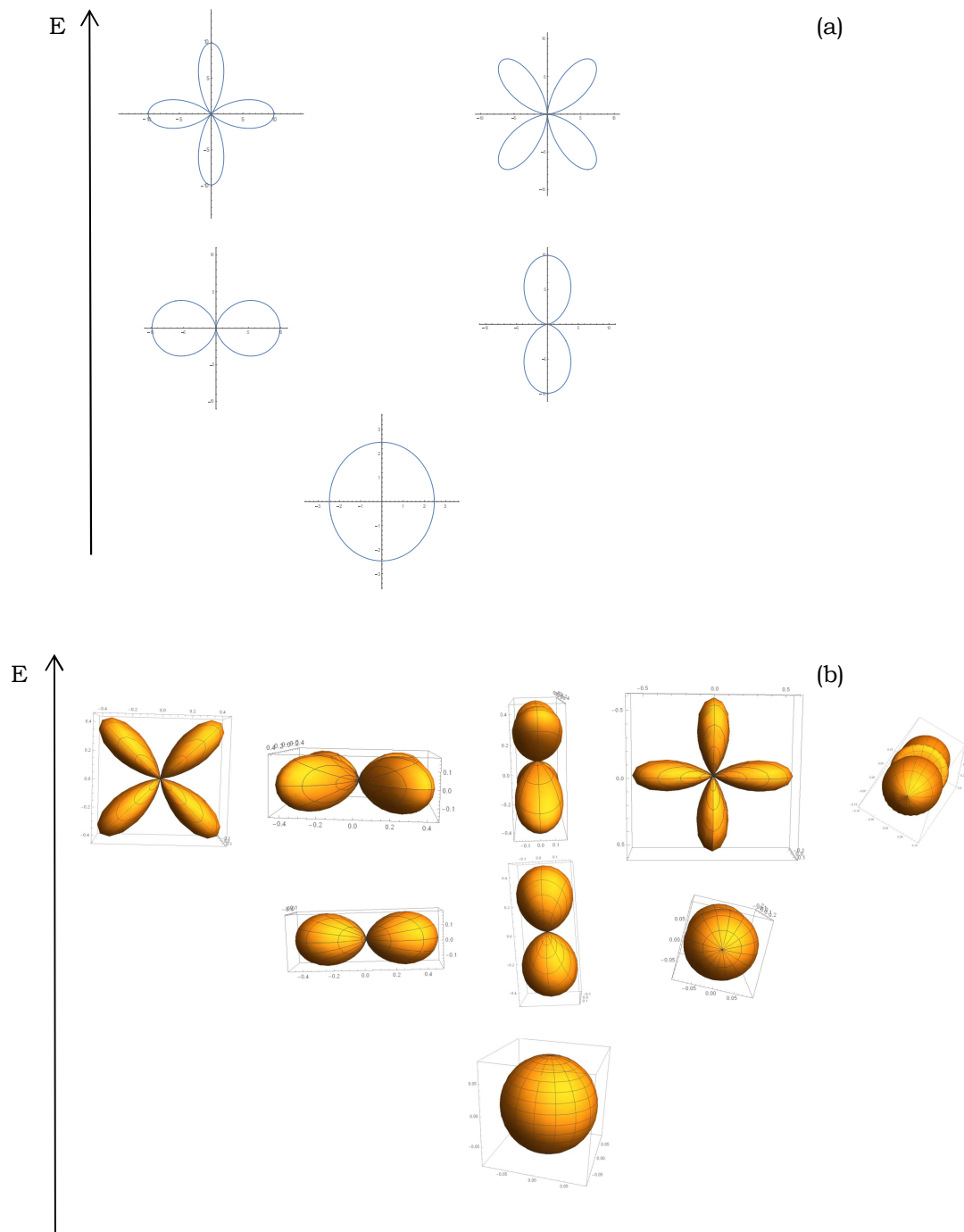

Figure 18. Comparison of orbitals between 2D and 3D. (a) 2D, (b) 3D

Further differences between the 2D and 3D hydrogen atom

In this section we illustrate further differences between the electronic properties of 3D and 2D hydrogenic atoms

-Energetic differences:
· Emission spectrum differences:
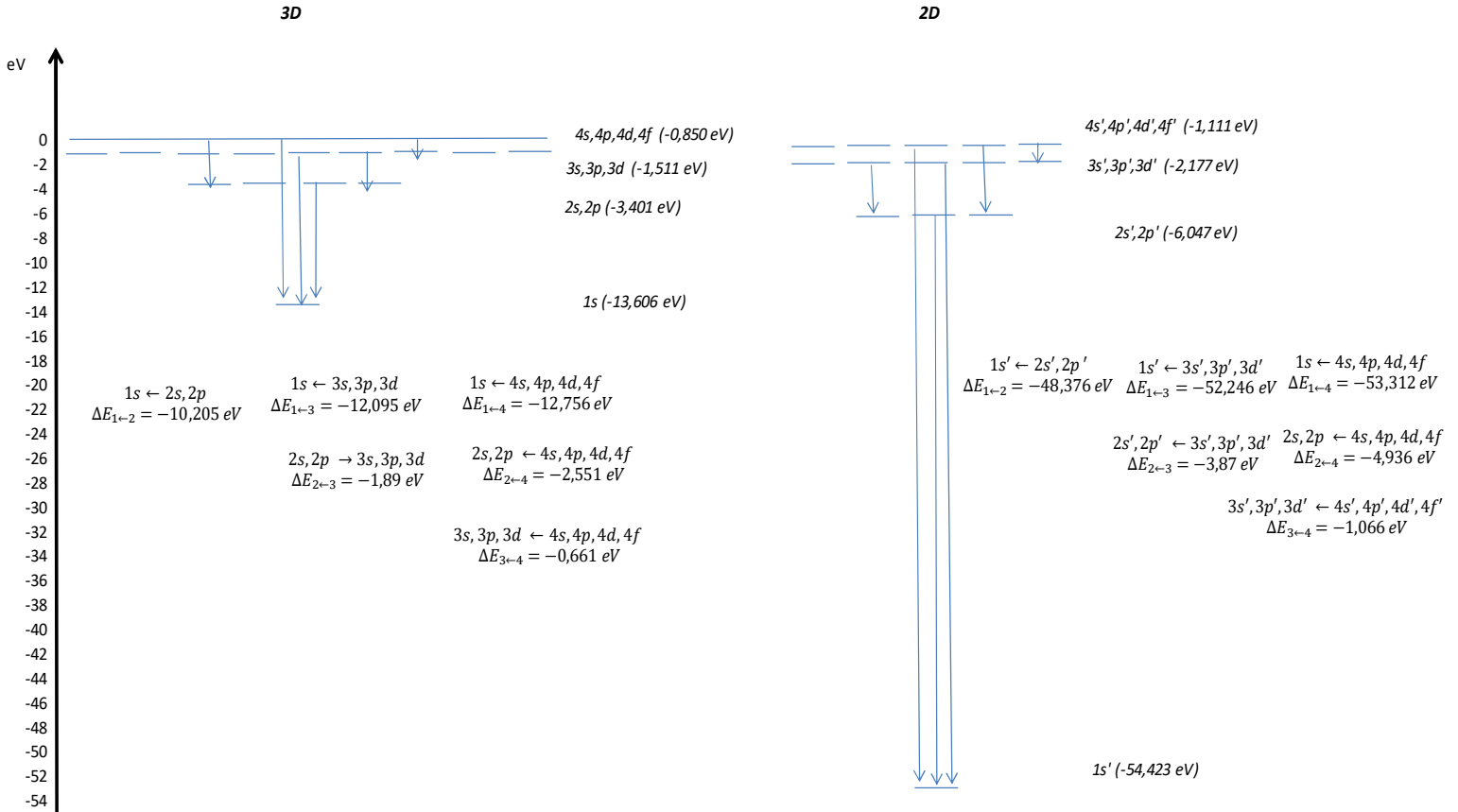
Figure 19. Emission spectrum comparison between 2D and 3D.

To obtain all this energies we only have to take into account the equation (54) for 2D energies and equation (ref.29) for 3D energies. Lastly, we would calculate the difference between states, to cover all the electron transitions.

For instance: *Electronic transition from 2s excited state to 1s ground state in 2D. (Emission process)*

First of all, we would obtain the single energies for 2s and 1s:

$$E_{1s} = -\frac{2Z^2 e'^2}{(2n-1)^2 a_0} \xrightarrow{n=1} E_{1s} = -2\,hartrees \equiv -54.423 eV \text{ [31]}$$

$$E_{2s} = -\frac{2Z^2 e'^2}{(2n-1)^2 a_0} \xrightarrow{n=2} E_{1s} = -\frac{2}{9}\,hartrees \equiv -6.047 eV \text{ [32]}$$

---

[31] $1 hartree = 27.212 eV$

Now, it is made the difference between these states obtaining,
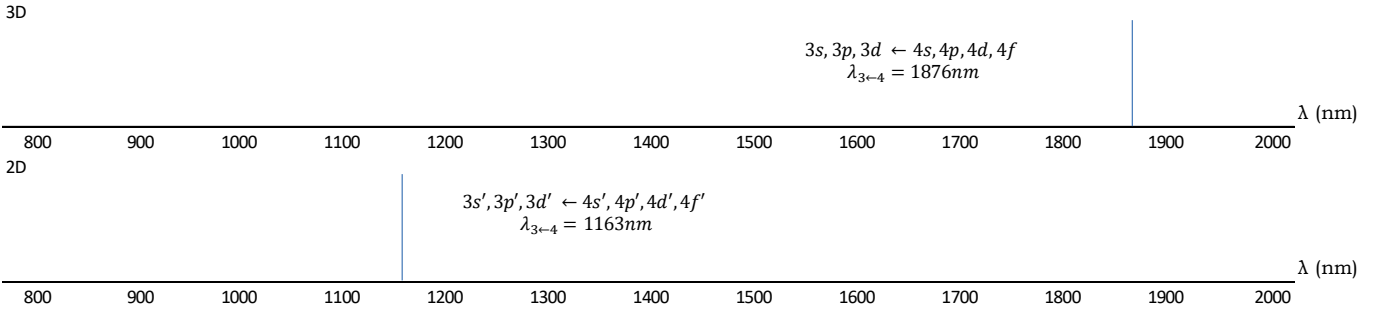
$$\Delta E_{0\leftarrow 1} = E_{1s} - E_{2s} = -\frac{16}{9}hartrees \equiv -48.376eV$$

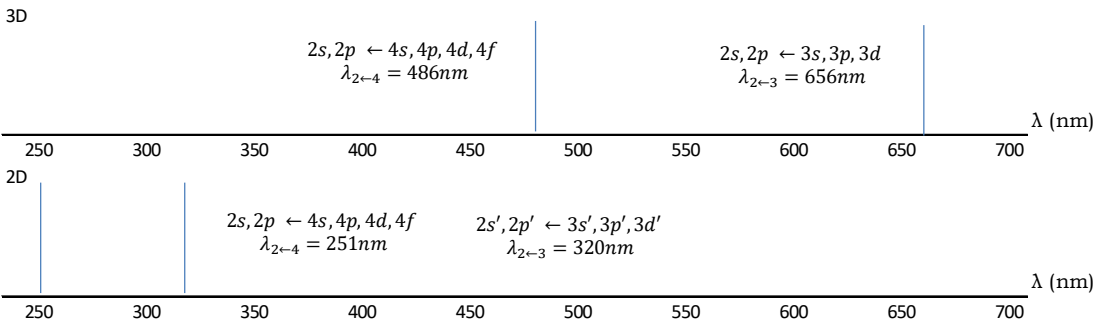So, in this way you could obtain all the electronic transitions for every single

Series de Paschen (IR)
3D

$3s, 3p, 3d \leftarrow 4s, 4p, 4d, 4f$
$\lambda_{3\leftarrow 4} = 1876nm$

2D

$3s', 3p', 3d' \leftarrow 4s', 4p', 4d', 4f'$
$\lambda_{3\leftarrow 4} = 1163nm$

orbital.

Series de Balmer (UV-Vis)
3D

$2s, 2p \leftarrow 4s, 4p, 4d, 4f$
$\lambda_{2\leftarrow 4} = 486nm$

$2s, 2p \leftarrow 3s, 3p, 3d$
$\lambda_{2\leftarrow 3} = 656nm$

2D

$2s, 2p \leftarrow 4s, 4p, 4d, 4f$
$\lambda_{2\leftarrow 4} = 251nm$

$2s', 2p' \leftarrow 3s', 3p', 3d'$
$\lambda_{2\leftarrow 3} = 320nm$

Series de Lyman (UV)
3D

$1s \leftarrow 3s, 3p, 3d$
$\Delta\lambda_{1\leftarrow 3} = 103nm$

$1s \leftarrow 4s, 4p, 4d, 4f$
$\Delta\lambda_{1\leftarrow 4} = 97nm$

$1s \leftarrow 2s, 2p$
$\Delta\lambda_{1\leftarrow 2} = 121nm$

2D

$1s' \leftarrow 2s', 2p'$
$\lambda_{1\leftarrow 2} = 25nm$

$1s' \leftarrow 3s', 3p', 3d'$
$\lambda_{1\leftarrow 3} = 24nm$

$1s \leftarrow 4s, 4p, 4d, 4f$
$\lambda_{1\leftarrow 4} = 23nm$

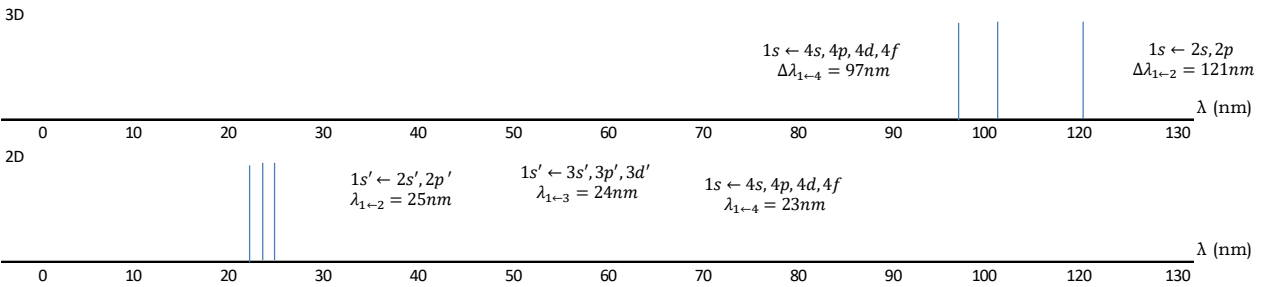*Figure 20, 21, 22. Comparison of the emission spectrum between 2D and 3D plotted as Paschen's, Balmer's & Lyman's series respectively.*

---

[32] Note as the 2s & 2p are degenerated, the energies would be the same and therefore the energy difference will be the same as well.

· *Periodic table differences (until Z=74)*

3D

	s		p						d										f														
1	H	He																															
2	Li	Be	B	C	N	O	F	Ne																									
3	Na	Mg	Al	Si	P	S	Cl	Ar	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn															
4	K	Ca	Ga	Ge	As	Se	Br	Kr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
5	Rb	Sr	In	Sn	Sb	Te	I	Xe	La	Hf	Ta	W	W	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
6	Cs	Ba	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

2D

	s		p				d				f		
1	H	He											
2	Li	Be	B	C	N	O							
3	F	Ne	Na	Mg	Al	Si	P	S	Cl	Ar			
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge
5	As	Se	Br	Kr	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd
6	Ag	Cd	In	Sn	Sb	Te	I	Xe	Cs	Ba	La	Ce	Pr	Nd
7	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	W

As can be observed on 2D periodic table, for simplicity we do not take into account with the Aufbau principle as it does on 3D periodic table.

4) The H_2^+ molecule[33]

We next study the formation of the simplest possible molecule in a 2D universe, the planar H_2^+ molecule. Again by comparison with the well-known case of 3D H_2^+, we will get a flavour of how different chemistry and reactivity would be in 2D.

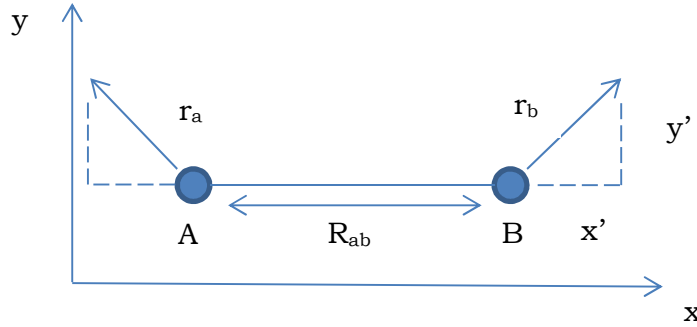First of all, we define the geometry of the system:

Figure 23. A & B are nuclei, r_a & r_b are the distance of the nuclei A & B with the electron and R_{ab} is the distance between nuclei.

$$r = \sqrt{x^2 + y^2}$$

$$r_a = \sqrt{(x' + \frac{R_{ab}}{2})^2 + y^2}; \; r_b = \sqrt{(x' - \frac{R_{ab}}{2})^2 + y^2}$$

Next, it does the following test to continue with the calculations:

$$S_{ab} = \langle \phi_a | \phi_b \rangle = 1 \qquad \qquad if \;\; a = b$$

Where $\phi_a = \frac{4}{\sqrt{2\pi}} e^{-2r_a}$ and $\phi_b = \frac{4}{\sqrt{2\pi}} e^{-2r_b}$. Note ϕ_a and ϕ_b have atomic units $(a_0 = 1 \; or \; a_0^* = 1/2)$.

To verify the previous equality it has to make R_{ab} equal to zero, so we have,

$$S_{ab} = \langle \phi_a | \phi_b \rangle = \langle Ne^{-2r_a} | Ne^{-2r_b} \rangle = N^2 \langle e^{-2r_a} | e^{-2r_a} \rangle^{34}$$

$$N^2 \int_{-\infty}^{\infty} e^{-2r_a} e^{-2r_a} \, dA \equiv N^2 \int_0^{\infty} \int_0^{2\pi} r_a \, e^{-2r_a} e^{-2r_a} \, dr_a d\varphi \; (55)$$

For simplicity, we may leave out the subscripts and (55) results such as

---

[33] Other way to treat H_2^+ molecule is reported in the annex F.3)
[34] Notice e^{-2r} is just the 2D hydrogen 1s wavefunction without their normalization.

$$S_{ab} \equiv N^2 \int\limits_0^\infty \int\limits_0^{2\pi} r e^{-4r} \, dr d\varphi \xrightarrow{N = 4/\sqrt{2\pi}} \boxed{S_{ab} = 1}^{35}$$

Then we can proceed changing the coordinates from polar to Cartesian obtaining the following expressions:

$$\phi_a = \frac{4}{\sqrt{2\pi}} e^{-2\sqrt{\left(x' + \frac{R_{ab}}{2}\right)^2 + y^2}}$$

$$\phi_b = \frac{4}{\sqrt{2\pi}} e^{-2\sqrt{\left(x' - \frac{R_{ab}}{2}\right)^2 + y^2}}$$

Now, it obtains the overlap integral between both nuclei in an infinite space,

$$S_{ab} \equiv \left(\frac{4}{\sqrt{2\pi}}\right)^2 \int\limits_{-\infty}^{\infty} \int\limits_{-\infty}^{\infty} \left(e^{-2\sqrt{\left(x' + \frac{R_{ab}}{2}\right)^2 + y^2}}\right)\left(e^{-2\sqrt{\left(x' - \frac{R_{ab}}{2}\right)^2 + y^2}}\right) dx dy = 1$$

Knowing that in 3D molecule H_2^+ the R_{eq} (equilibrium distance) is 2 Bohrs (Levine, 2001), we could extrapolate this information in order to obtain the 2D H_2^+ molecule R_{eq}. As we want to cover the whole space that occupies the 2D H_2^+ molecule, we are going to suppose, from the 2 Bohrs data, the whole space could be arbitrarily covered by 3 Bohrs where theoretically has to be similar to an infinite space.

$$S_{ab} \equiv \left(\frac{4}{\sqrt{2\pi}}\right)^2 \int\limits_{-3}^{3} \int\limits_{-3}^{3} \left(e^{-2\sqrt{\left(x' + \frac{R_{ab}}{2}\right)^2 + y^2}}\right)\left(e^{-2\sqrt{\left(x' - \frac{R_{ab}}{2}\right)^2 + y^2}}\right) dx dy = 0{,}999964 \approx 1$$

Once deduced the [-3, 3] limits are practically the same than $[-\infty, \infty]$ it may does all the calculations based on infinite limits. So the overlap integral has the next behaviour,
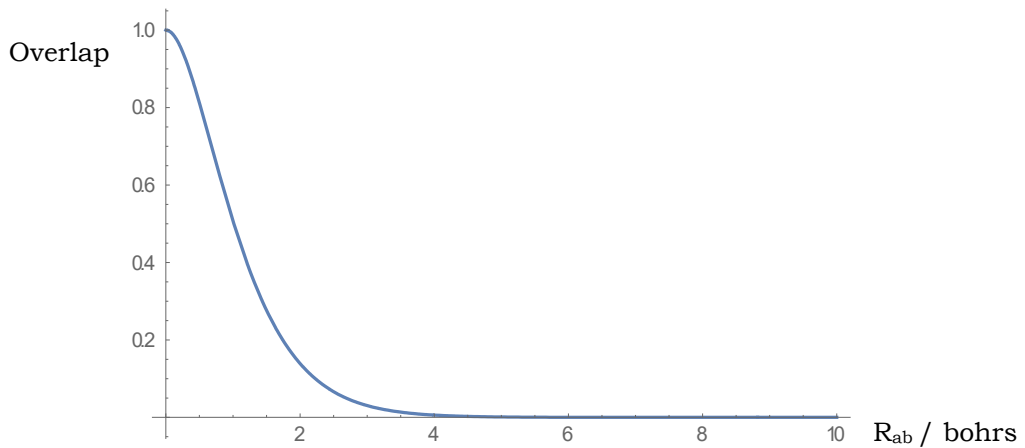
Where whenever it increases the R_{ab}, decreases the overlap. Therefore the function obtained has congruence because it is what was expected.

---

[35] The calculations have been done by Mathematica 10 and all the commands used are in the annex F.1)
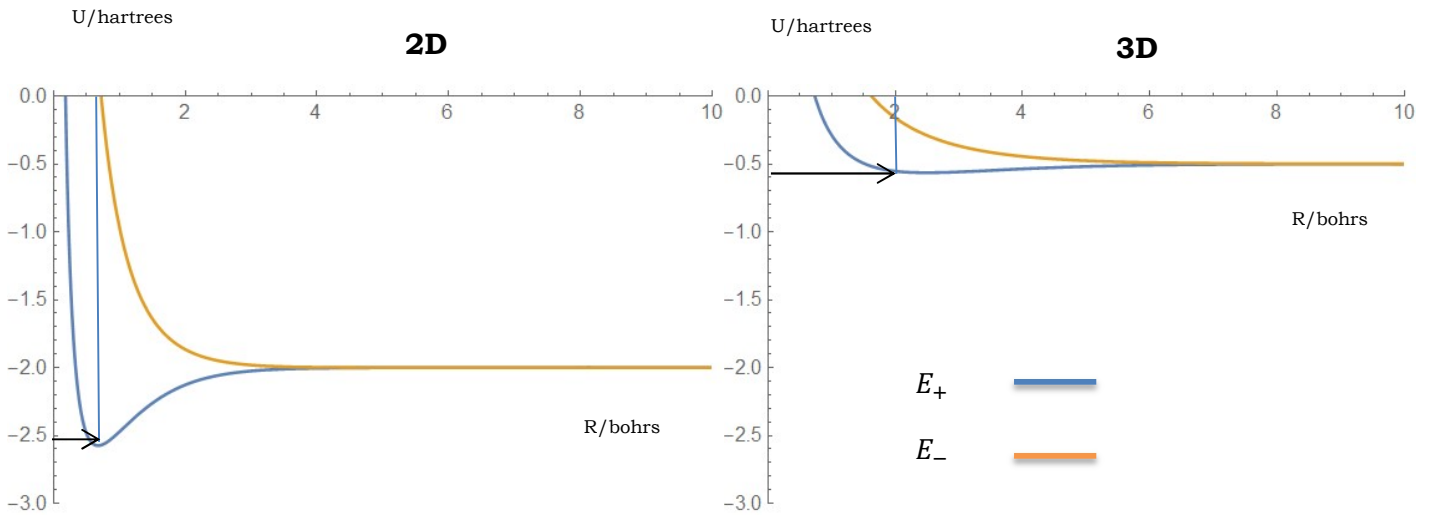
Next it is obtained the Haa & Hab[36]

$$H_{aa} = \langle \phi_a | \hat{H} | \phi_a \rangle = \int \phi_a^* \hat{H} \phi_a \, dA \quad (56)$$

$$H_{ab} = \langle \phi_a | \hat{H} | \phi_b \rangle = \int \phi_a^* \hat{H} \phi_b \, dA \quad (57)$$

Those integrals are carried to the bonding and antibonding energies equations which have been obtained and may be seen in the annex F.2).

$$E_+ = \frac{H_{aa} + H_{ab}}{1 + S_{ab}} + \frac{1}{R_{ab}}; \; E_- = \frac{H_{aa} - H_{ab}}{1 - S_{ab}} + \frac{1}{R_{ab}}$$

The U (R_{ab}) curves to 2D and 3D electronic state 1s of H_2^+ respectively are,

In those graphics it is observed the huge energy that has the 2D H_2^+ (-70,75eV) regarding to 3D H_2^+ (-16.32eV) and besides, the proximity of the electron to the hydrogen atoms leading to believe the great difference on the electrostatic energies between 2D and 3D. This is also a consequence of the enhanced e-nucleus interaction in 2D systems, and it implies 2D molecules should display much superior reactivity than 3D analogues.

On the other hand, 2D materials are expected to have higher melting point as well as stronger mechanical properties (compression, Young modulus and so on) than their 3D counterparts, since these properties often scale proportional to R_{eq}^{-2} . (Naumann, 2009)

---

[36] As we have a homonuclear molecule we can affirm that Haa=Hbb or Hab=Hba.

Difference about rotational constant between 3D and 2D

Let us start by the rotational constant definition,

$$B = \frac{h}{8\pi^2 I} \ (58)$$

Where h is just the Planck's constant and I the inertial moment what comes given by,

$$I = \mu R^2 \ (59)$$

Knowing μ is the reduced mass and that we are treating H_2^+, the reduced mass may be written as follows,

$$\mu = \frac{m_H m_H}{m_H + m_H} = \frac{m_H^{\ 2}}{2m_H} \rightarrow \boxed{\mu = \frac{m_H}{2}} \ (60)$$

Taking (60) to (59) and (59) to (58), it may obtains the next expression,

$$B = \frac{h}{4\pi^2 m_H R^2} \ (61)$$

So, once to this point we could obtain the rotational constant for both dimensions.

$$B^{3D} = 9{,}031x10^{11} s^{-1}{}^{37}$$

And if we go beyond we might obtain the $\Delta E_{0 \rightarrow 1}$, where by definition it is equal to 2B, then

$$\Delta E_{0 \rightarrow 1}^{3D} = v^{3D} = 2B^{3D} \longrightarrow \boxed{\Delta E_{0 \rightarrow 1}^{3D} = 1804{,}74 GHz}$$

And on the other hand we have,

$$\Delta E_{0 \rightarrow 1}^{2D} = v^{2D} = 2B^{2D} \longrightarrow \boxed{\Delta E_{0 \rightarrow 1}^{2D} = 20052 GHz}$$

Where $B^{2D} = 1{,}003x10^{13} s^{-1}$. So we could conclude with the following relation,

$$\boxed{10\Delta E_{0 \rightarrow 1}^{3D} \cong \Delta E_{0 \rightarrow 1}^{2D}} \ (62)$$

This implies that the rotational spectroscopy in 2D still in the microwave spectrum, but now, with a 10 times larger separation between lines than it was in 3D

---

[37] To calculate B, we need to turn into from the Bohr unit to I.S. (meters). So, if 1Bohr is 0,529177Å then 0,529177Å is 0,529177x10⁻¹⁰m

5) _2D helium atom_

We have seen in the previous section electron-nucleus interaction in 2D are stranger than usual, and this has important implications e.g. in the formation of molecules. The question arises whether the same is true for electron-electron interactions and if this has implications for polielectronic 2D atoms too. To this issue, in this address section we will study the helium atom.

The helium atom has two electrons and a nuclear charge +2e. We suppose that the core is stationary, and we will establish the coordinates system at the nucleus. The electron 1 & 2 coordinates are (x_1, y_1, z_1) and (x_2, y_2, z_2). If we take the nuclear charge as +Ze instead of +2e, we could treat ions with the helium configuration as H^-, Li^+, Be^{2+}. The Hamiltonian would be,

$$\hat{H} = -\frac{\hbar^2}{2\mu}\nabla_1^2 - \frac{\hbar^2}{2\mu}\nabla_2^2 - \frac{Ze'^2}{r_1} - \frac{Ze'^2}{r_2} + \frac{e'^2}{r_{12}} \ (63)$$

Where μ as we have already seen is like the electron mass and is independent use one terminology or another (electron mass or relative mass), r_1 and r_2 are the distance between electron 1 and 2 to the core, and r_{12} is just the distance between both electrons. The two first terms are the electrons kinetic energy. The third and fourth terms are the electron potential energy. Finally the last term is the Coulomb interaction between electrons.

The Schrödinger equation has four independent variables, one for each electron. In polar coordinates we have,

$$\psi = \psi(r_1, \varphi_1, r_2, \varphi_2)(64)$$

The 2D polar Laplacian comes given by (30), replacing r, φ by r_i, φ_i where i is the subscript of the electron on treatment. The r_{12} variable may be written as,

$$r_{12} = \sqrt{(x_1 - x_2)^2 + (y_1 - y_2)^2} \ (65)$$

Now, r_{12} is the responsible term that avoid we may separate on any coordinates system, so we only could use approximate methods. We shall study this problem with two different approaches of increasing complexity and accuracy: _1st order perturbational method[38] & variational method._

---

[38] By simplicity we will call it from here on out: Perturbational method

Perturbational method

First of all we need to know that the Hamiltonian might be divided in two terms,

$$\hat{H} = \hat{H}^0 + \hat{H}' \quad (66)$$

The first term will give us as eigenvalue the hydrogenoid atom energy in regard with both independent electrons. It may describes,

$$\hat{H}^0 = -\frac{\hbar^2}{2\mu}\nabla_1^2 - \frac{Ze'^2}{r_1} - \frac{\hbar^2}{2\mu}\nabla_2^2 - \frac{Ze'^2}{r_2} \quad (67)$$

It is observed that,

$$\hat{H}_1^0 = -\frac{\hbar^2}{2\mu}\nabla_1^2 - \frac{Ze'^2}{r_1}, \qquad \hat{H}_2^0 = -\frac{\hbar^2}{2\mu}\nabla_2^2 - \frac{Ze'^2}{r_2}$$

The second Hamiltonian is the perturbative term, what will correct the energy result.

$$\hat{H}' = \frac{e'^2}{r_{12}} \quad (68)$$

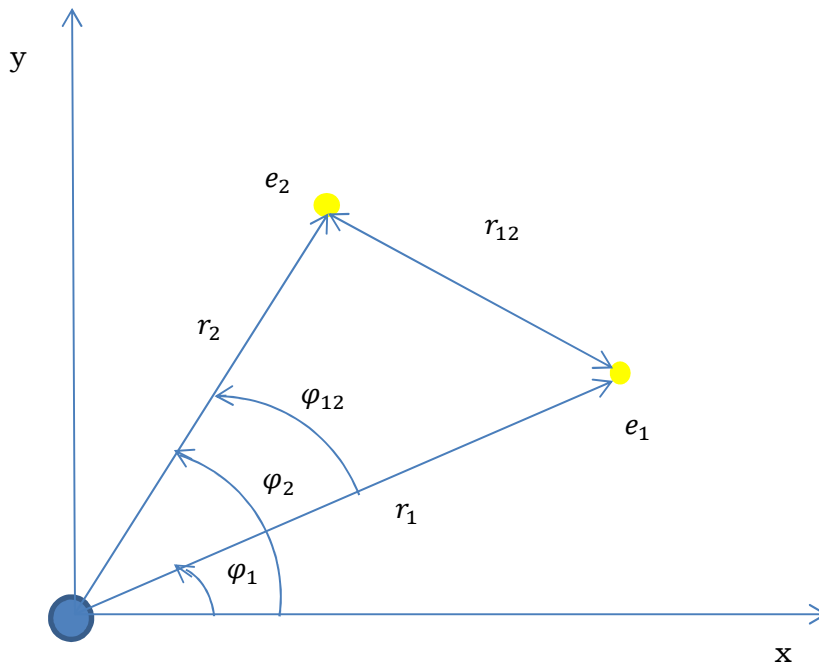We are going to start defining the system coordinates,

Figure 24. The nucleus is the blue circle, e_1 and e_2 are the yellow circles, r_1 and r_2 are the distance of electrons 1 & 2 with the nucleus and r_{12} is the distance between electrons.

Let us introduce about the wave function (64), we need to antisymmetrize it with the Slater determinant,

$$\psi_{ok} = \hat{A}\psi = \frac{1}{\sqrt{2}}\begin{vmatrix} \phi_1\alpha & \phi_1\beta \\ \phi_2\alpha & \phi_2\beta \end{vmatrix} = \frac{1}{\sqrt{2}}[\phi_1\phi_2(\alpha\beta - \beta\alpha)]^{39}$$

To check that the wave function ψ_{ok} is equal to $\phi_1\phi_2$, we are going to start by observe if is obeyed the ortonormality condition focusing mainly on the spin part,

$$\langle\psi_{ok}|\psi_{ok}\rangle = \left\langle \frac{1}{\sqrt{2}}[\phi_1\phi_2(\alpha\beta - \beta\alpha)]\middle|\frac{1}{\sqrt{2}}[\phi_1\phi_2(\alpha\beta - \beta\alpha)]\right\rangle$$

$$= \frac{\langle\phi_1\phi_2|\phi_1\phi_2\rangle}{2}[\langle\alpha\beta|\alpha\beta\rangle - \langle\alpha\beta|\beta\alpha\rangle - \langle\beta\alpha|\alpha\beta\rangle + \langle\beta\alpha|\beta\alpha\rangle] \xrightarrow{\langle i|i\rangle=1}$$

$$\xrightarrow{\langle i|j\rangle=0} \frac{\langle\phi_1\phi_2|\phi_1\phi_2\rangle}{2} 2 \xrightarrow{\langle\phi_1\phi_2|\phi_1\phi_2\rangle=1} \boxed{\langle\psi_{ok}|\psi_{ok}\rangle = 1}^{40}$$

How it is known, the equation (67) gives us as eigenvalue the hydrogenoid atom energy (54). To obtain (68), the expectation value, we use atomic units,

$$J_{12} = \left\langle\psi_{ok}\middle|\frac{e'^2}{r_{12}}\middle|\psi_{ok}\right\rangle \xrightarrow{e'^2=1\ (u.a.)} \left\langle\psi_{ok}\middle|\frac{1}{r_{12}}\middle|\psi_{ok}\right\rangle$$

$$\left\langle\psi_{ok}\middle|\frac{1}{r_{12}}\middle|\psi_{ok}\right\rangle = \int_0^{2\pi}\int_0^{2\pi}\int_0^{\infty}\int_0^{\infty} \psi_{ok}\,\psi_{ok}\,r_1r_2\frac{1}{r_{12}}\,dr_1dr_2d\varphi_1d\varphi_2 \quad (69)$$

By means of cosine theorem we can achieve the following,

$$r_{12} = \sqrt{r_1^2 + r_2^2 - 2r_1r_2\cos(\varphi_2 - \varphi_1)}$$

So (68) results as,

$$\left\langle\psi_{ok}\middle|\frac{1}{r_{12}}\middle|\psi_{ok}\right\rangle = \int_0^{2\pi}\int_0^{2\pi}\int_0^{\infty}\int_0^{\infty} \psi\,\psi\,r_1r_2\frac{1}{\sqrt{r_1^2 + r_2^2 - 2r_1r_2\cos(\varphi_2 - \varphi_1)}}\,dr_1dr_2d\varphi_1d\varphi_2 \quad (69)$$

Now, with the intention to reduce the dimensionality of this multiple integral we are going to make a variables change,

$$\varphi_+ = \varphi_2 + \varphi_1$$

$$\varphi_- = \varphi_2 - \varphi_1$$

Where $d\varphi_1 d\varphi_2 = \frac{1}{2}d\varphi_+ d\varphi_-$.[41] So (70) results as

---

[39] ψ_{ok} is the wave function antisymmetrized
[40] It is skipped this checking, but it is easily demonstrable
[41] It has taken account the following equalities,

$$\varphi_1 = \frac{\varphi_+ - \varphi_-}{2}; \quad \varphi_2 = \frac{\varphi_+ + \varphi_-}{2};$$

$$\left\langle \psi_{ok} \left| \frac{1}{r_{12}} \right| \psi_{ok} \right\rangle = \int_0^{4\pi} \int_0^{2\pi} \int_0^{\infty} \int_0^{\infty} \psi\, \psi\, r_1 r_2\, \frac{1}{2\,\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos(\varphi_-)}}\, d\,r_1 dr_2 d\varphi_+ d\varphi_- \quad (71)^{[42]}$$

Finally as an Ionization Potential we have,

$$I.P. = E_{1s^2} - E_{1s^1} = (E_1 + E_2 + J_{12}) - E_1$$

Where E_1 and E_2 are the monoelectronic energy already known and J_{12} is the Coulomb integral, so

$$I.P. = E_2 + J_{12} = -2Z^2 + \left\langle \psi_{ok} \left| \frac{1}{r_{12}} \right| \psi_{ok} \right\rangle = -8 + 4.71 = -3.29\, hartrees = -89.527eV$$

Variational method

This method consists on the addition of one term that is called α. The α term might be associated to the screening effect what will be responsible of the decreasing on the effective nuclear charge, α will be ranged from 0 to 1, where for the hydrogen atom (only one electron) α would be 1, and as soon as the electron amount increase, this parameter will go down.

It does the same calculations what we have done in the previous method, the difference how is already mentioned is α, then the wave function has the following form:

$$\psi(r, \varphi) = \frac{4Z}{\sqrt{2\pi}} e^{-2Z\alpha r}$$

To obtain the I.P. we would do the same what we have done on the perturbational method,

1- Antisymmetrize the wavefunction with the Slater determinant.
2- It would be obtained the hydrogenoid energy without the electronic repulsion energy. The hydrogenoid atom energy equation is,

$$E = 2Z^2\alpha^2 - 4Z^2\alpha$$

3- Next, just it is solved the Coulomb integral (J_{12}). Afterwards we would have to minimize the energy value and at this value of energy, take the α value($\alpha = 0.85$)[43].

$$E_{1s^2} = E_1 + E_2 + J_{12}{}^{[44]}$$

---

[42] It is observed the change on the integral range in regard with the angles. The explanation is left out of this study. Besides, this equation has been solved numerically using Mathematica. J_{12}=4.71hartrees. See annex G.1)

[43] Some curiosities about the α value on the annex G.3)

[44] Variational method J_{12} =4.37hartrees. See annex G.1)

4- To finish, it is obtained the Ionization Potential,

$$I.P. = E_2 + J_{12} = -2Z^2\alpha + \left\langle \psi_{ok} \left| \frac{1}{r_{12}} \right| \psi_{ok} \right\rangle = -3.63 \, hartrees = -98.780 eV$$

Lastly, we could say that the variational method improves the electrostatic repulsion energy from the perturbational method by 7,22%[45]

Having reached this point, we could compare the energies between hydrogen and helium atoms[46],
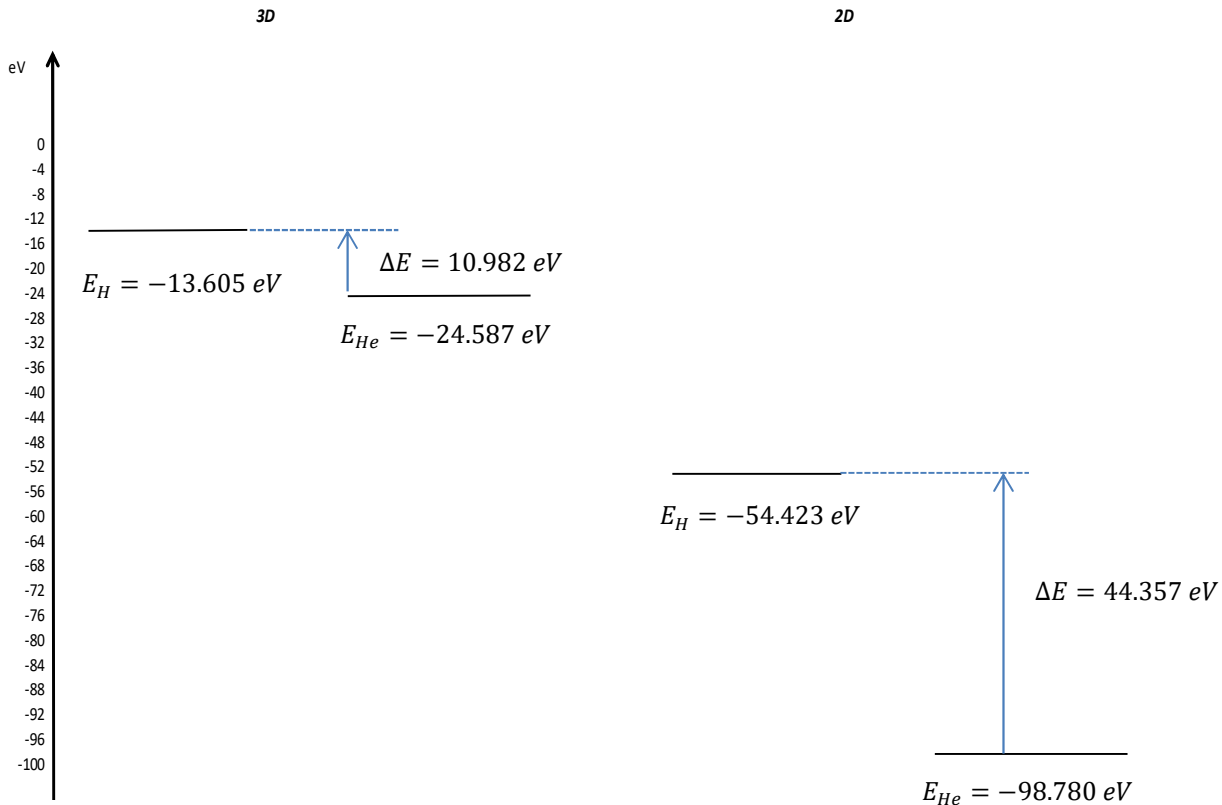
We realise that the energy differences in 2D & 3D between hydrogen & helium are proportional between them by approximately a 4 factor,

$$\frac{\Delta E^{2D}}{\Delta E^{3D}} = \frac{44.357 eV}{10.982 eV} \cong 4 \rightarrow \boxed{\Delta E^{2D} \cong 4 \, \Delta E^{3D}} \; (72)$$

So, if we would want to know 2D energies, just taking into account (72) we could know the 2D energy wished. (At least, in the case of hydrogen and helium)

---

[45] $\%improvement = \left(1 - \frac{J_{12}(var)}{J_{12}(per)}\right) x100 = 7.218\%$

[46] The energy used is the calculated by variational method, because it is the enhanced energy value.

Conclusions

The 2D science material is still in its infancy nowadays but, despite this, the scientists have already collected so much information about it. We have checked out e.g. Young modulus, thermal conductivity, electronic mobility, lattice constants, and relative permittivity (Table 1) finding an unbelievable properties on some 2D materials, which have really showed to be better than their 3D counterparts. From the study of this materials, arise the use of bidimensional models with the well-known simplest atom: the hydrogen atom.

We have seen the 2D hydrogen atom presents a strong interaction electron-nucleus. As a consequence of this, it generates more stability, taking place 4 times larger Ionization Energy, exactly: -54,423 eV, than 3D hydrogen atoms: -13,605 eV. In addition, it has been found a particular orbital distribution where the s orbitals are similar to the 3D, fitting as much 2 electrons. However, from the p orbital to next orbitals, just 4 electrons could be fit there, giving a periodic table more than unusual. Regarding with the hydrogen 2D emission spectrum, it has found that the transitions occur a lower wavelengths than in 3D hydrogen atom emission spectrum. Nevertheless, Paschen's, Balmer's and Lyman's series still similar to 3D.

With relation to the H_2^+ molecule, we have found out that the 2D energy and 3D energy at equilibrium distance differ, approximately, by a 4 factor. This huge energy belonging to 2D H_2^+ molecule results in large stability, causing an increasing on their mechanical properties as the Young modulus, compressivity and included as well, higher melting point. Besides, as far as rotational spectroscopy is concerned, it still is in the microwave spectrum, only differing with the 3D H_2^+ molecule that the difference between their rotational lines are 10 times larger than they are in 3D (eq. 62).

Finally, it has done two different treatments to obtain the helium 2D Ionization Energy: 1st order perturbational method & Variational method; where the variational method has improved the perturbational method by 7 points, approximately. Also, it is noticed that the energetic difference between hydrogen and helium atoms in 2D are 4 times, approximately, larger than they are in 3D (eq. 71).

Annex

A.1) Polar 2D Laplacian obtaining

First of all, it defines the system and the conversion from Cartesian coordinates to polar coordinates,

$$r = \sqrt{x^2 + y^2}\,;\; \varphi = arctg = \frac{y}{x}$$

$$x = rcos\varphi\,;\, y = rsin\varphi$$
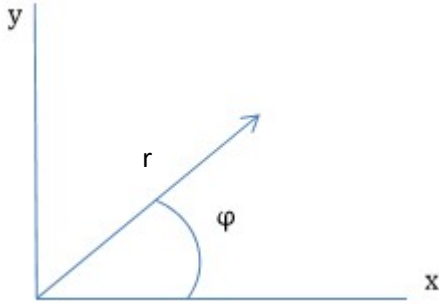
Now, it is prepared the equation for the variables changing regarding to x and to y:

$$\frac{\partial}{\partial x} = \frac{\partial}{\partial r}\frac{\partial r}{\partial x} + \frac{\partial}{\partial \varphi}\frac{\partial \varphi}{\partial x} \quad (a.1)$$

$$\frac{\partial}{\partial y} = \frac{\partial}{\partial r}\frac{\partial r}{\partial y} + \frac{\partial}{\partial \varphi}\frac{\partial \varphi}{\partial y} \quad (a.2)$$

$$\frac{\partial^2}{\partial x^2} = \frac{\partial^2}{\partial r^2}\frac{\partial r}{\partial x}\frac{\partial r}{\partial x} + \frac{\partial}{\partial r}\frac{\partial^2 r}{\partial x^2} + \frac{\partial^2}{\partial \varphi^2}\frac{\partial \varphi}{\partial x}\frac{\partial \varphi}{\partial x} + \frac{\partial}{\partial \varphi}\frac{\partial^2 \varphi}{\partial x^2} \quad (a.3)$$

$$\frac{\partial^2}{\partial y^2} = \frac{\partial^2}{\partial r^2}\frac{\partial r}{\partial y}\frac{\partial r}{\partial y} + \frac{\partial}{\partial r}\frac{\partial^2 r}{\partial y^2} + \frac{\partial^2}{\partial \varphi^2}\frac{\partial \varphi}{\partial y}\frac{\partial \varphi}{\partial y} + \frac{\partial}{\partial \varphi}\frac{\partial^2 \varphi}{\partial y^2} \quad (a.4)$$

With the chain rule is obtained the following derivative series for x:

$$\frac{\partial r}{\partial x} = 2x \cdot \frac{1}{2}(x^2 + y^2)^{-1/2} \equiv \frac{x}{\sqrt{x^2 + y^2}} \Longrightarrow \frac{\partial r}{\partial x} = \frac{x}{r}(a.3.1)$$

$$\frac{\partial^2 r}{\partial x^2} = \left((x^2 + y^2)^{-1/2}\right) + x\left[-\frac{2x}{2}(x^2 + y^2)^{-3/2}\right] = \frac{1}{r} - \frac{x^2}{r^3} = \frac{1}{r}\left[1 - \frac{x^2}{r^2}\right] (a.3.2)$$

$$\frac{\partial \varphi}{\partial x} = \frac{1}{1 + \frac{y^2}{x^2}} \cdot \left(-\frac{y}{x^2}\right) \equiv -y(x^2 + y^2)^{-1} \Longrightarrow \frac{\partial \varphi}{\partial x} = -\frac{y}{r^2} (a.3.3)$$

$$\frac{\partial^2 \varphi}{\partial x^2} = -y2x(-1)(x^2 + y^2)^{-2} = \frac{2xy}{r^4} (a.3.4)$$

And the same for y:

$$\frac{\partial r}{\partial y} = 2y \cdot \frac{1}{2}(x^2 + y^2)^{-1/2} \equiv \frac{y}{\sqrt{x^2 + y^2}} \implies \frac{\partial r}{\partial y} = \frac{y}{r} (a.4.1)$$

$$\frac{\partial^2 r}{\partial y^2} = \left((x^2 + y^2)^{-1/2}\right) + y\left[-\frac{2y}{2}(x^2 + y^2)^{-3/2}\right] = \frac{1}{r} - \frac{y^2}{r^3} = \frac{1}{r}\left[1 - \frac{y^2}{r^2}\right] (a.4.2)$$

$$\frac{\partial \varphi}{\partial y} = \frac{1}{1 + {y^2}/{x^2}} \cdot \left(-\frac{x}{x^2}\right) \equiv x(x^2 + y^2)^{-1} \implies \frac{\partial \varphi}{\partial x} = -\frac{x}{r^2} (a.4.3)$$

$$\frac{\partial^2 \varphi}{\partial x^2} = x2x(-1)(x^2 + y^2)^{-2} = \frac{2xy}{r^4} (a.4.4)$$

Now, knowing that $\frac{x}{r} = cos\varphi$; $\frac{y}{r} = sin\varphi$ may define (a.3.1) (a.3.2) (a.3.3) (a.3.4) & (a.4.1) (a.4.2) (a.4.3) (a.4.4) in the following way,

$$\frac{\partial r}{\partial x} = cos\varphi \ (a.3.1.1)$$

$$\frac{\partial^2 r}{\partial x^2} = \frac{1}{r}[1 - cos^2\varphi] = \frac{1}{r}sin^2\varphi (a.3.2.1)$$

$$\frac{\partial \varphi}{\partial x} = -\frac{sin\varphi}{r} \ (a.3.3.1)$$

$$\frac{\partial^2 \varphi}{\partial x^2} = \frac{2cos^2\varphi sin^2\varphi}{r^2} \ (a.3.4.1)$$

$$\frac{\partial r}{\partial y} = sin\varphi \ (a.4.1.1)$$

$$\frac{\partial^2 r}{\partial y^2} = \frac{1}{r}[1 - sin^2\varphi] = \frac{1}{r}cos^2\varphi \ (a.4.2.1)$$

$$\frac{\partial \varphi}{\partial y} = \frac{cos\varphi}{r} \ (a.4.3.1)$$

$$\frac{\partial^2 \varphi}{\partial y^2} = -\frac{2cos^2\varphi sin^2\varphi}{r^2} \ (a.4.4.1)$$

The Laplacian definition is,

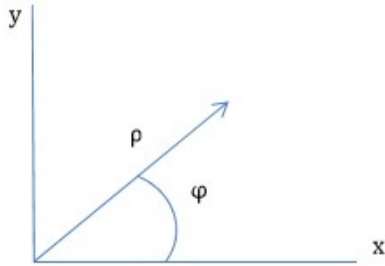$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \ (a.5)$$

Where (a.5), would result as,

$$\nabla^2 = \frac{\partial^2}{\partial \varphi^2}\left[\left(\frac{\partial \varphi}{\partial x}\right)^2 + \left(\frac{\partial \varphi}{\partial y}\right)^2\right] + \frac{\partial}{\partial \varphi}\left[\left(\frac{\partial^2 \varphi}{\partial x^2}\right) + \left(\frac{\partial^2 \varphi}{\partial y^2}\right)\right] + \frac{\partial^2}{\partial r^2}\left[\left(\frac{\partial r}{\partial x}\right)^2 + \left(\frac{\partial r}{\partial y}\right)^2\right] + \frac{\partial}{\partial r}\left[\left(\frac{\partial^2 r}{\partial x^2}\right) + \left(\frac{\partial^2 r}{\partial y^2}\right)\right] (a.5.1)$$

In order to obtain the final expression of the 2D Laplacian it just has to replace the previous expressions on (a.5.1) resulting,

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} = \frac{1}{r}\frac{\partial}{\partial r} + \frac{\partial^2}{\partial r^2} + \frac{1}{r^2}\frac{\partial^2}{\partial \varphi^2} \quad (a.6)$$

## A.2) Jacobian obtaining

$$x = rcos\varphi$$

$$y = rsin\varphi$$

Knowing that the area differential is: $dA = |J_p|drd\varphi$, we just have to obtain the Jacobian, then

$$|J_p| = \begin{vmatrix} \frac{\partial x}{\partial r} & \frac{\partial y}{\partial r} \\ \frac{\partial x}{\partial \varphi} & \frac{\partial y}{\partial \varphi} \end{vmatrix} = \begin{vmatrix} cos\varphi & sin\varphi \\ -rsin\varphi & rcos\varphi \end{vmatrix} = rcos^2\varphi - (-rsin^2\varphi) = r(cos^2\varphi + sin^2\varphi) \equiv r$$

So finally we have:

$$\boxed{dA = rdrd\varphi}$$

B.1) Deduction about if the Hamiltonian shares a set of eigenfunctions with symmetry operator C_∞^ϕ that represents a ϕ rotation into a circumference, ranged between 0 and 2π.
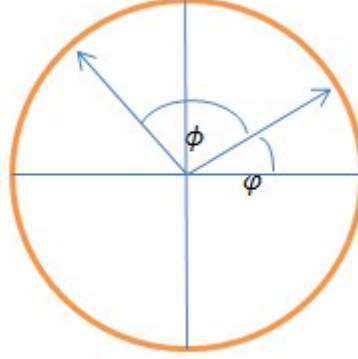
First of all, we define,

$$\hat{H}_\varphi = \frac{\partial^2}{\partial \varphi^2} \, (b.1) \qquad\qquad Y(\varphi) = e^{im\varphi} \, (b.2)$$

In other hand, we have the change produced by C_∞^ϕ over $Y(\varphi)$, since,

$$C_\infty^\phi \, Y(\varphi) = Y(\varphi + \phi) \, (b.3)$$

As $Y(\varphi + \phi)$ indeed, contain two variables, and it has an exponential form (b.2), the two variables function it may reconverts in two functions containing just one variable, therefore we have,

$$Y(\varphi + \phi) = Y(\varphi)Y(\phi) = e^{im\varphi} e^{im\phi}$$

So, the equality (b.3) would result as,

$$C_\infty^\phi \, Y(\varphi) = C_\infty^\phi \, e^{im\varphi} = e^{im\phi} e^{im\varphi} \, (b.3.1)$$

This equality (b.3.1) we will be taken into account later.

Now, we will verify if the operator that response in the presence of a rotation axis C_∞^ϕ commutes with the, so far defined, as Hamiltonian (b.1),

$$[\hat{H}_\varphi, C_\infty^\phi]Y(\varphi) = \frac{\partial^2}{\partial \varphi^2} C_\infty^\phi Y(\varphi) - C_\infty^\phi \frac{\partial^2}{\partial \varphi^2} Y(\varphi) = \frac{\partial^2}{\partial \varphi^2} C_\infty^\phi e^{im\varphi} - C_\infty^\phi \frac{\partial^2}{\partial \varphi^2} e^{im\varphi} \, (b.4)$$

It is observed that the first term in the equation (b.4) is equivalent to (b.3.1),

$$[\hat{H}_\varphi, C_\infty^\phi]Y(\varphi) = \frac{\partial^2}{\partial \varphi^2} e^{im\phi} e^{im\varphi} - C_\infty^\phi \frac{\partial^2}{\partial \varphi^2} e^{im\varphi} \, (b.4.1)$$

After it is left out from the derivatives, those independent terms to φ result in,

$$[\hat{H}_\varphi, C_\infty^\phi]Y(\varphi) = e^{im\phi}\frac{\partial^2}{\partial\varphi^2}e^{im\varphi} - C_\infty^\phi\frac{\partial^2}{\partial\varphi^2}e^{im\varphi} \quad (b.4.2)$$

Next the derivatives are operated

$$\frac{\partial e^{im\varphi}}{\partial\varphi} = ime^{im\varphi} \implies \frac{\partial^2 e^{im\varphi}}{\partial\varphi^2} = -m^2e^{im\varphi} \quad (b.5)$$

Now, it is carried the expression (b.5) to the expression (b.4.2) giving as a result,

$$[\hat{H}_\varphi, C_\infty^\phi]Y(\varphi) = -e^{im\phi}m^2e^{im\varphi} + C_\infty^\phi m^2e^{im\varphi} \quad (b.4.3)$$

Reordering (b.4.3) as follows,

$$[\hat{H}_\varphi, C_\infty^\phi]Y(\varphi) = -m^2e^{im\phi}e^{im\varphi} + m^2C_\infty^\phi e^{im\varphi} \quad (b.4.3.1)$$

It is observed the equivalence (b.3.1) in the equation (b.4.3.1), then, it is replaced resulting like this,

$$[\hat{H}_\varphi, C_\infty^\phi]Y(\varphi) = -m^2e^{im\phi}e^{im\varphi} + m^2C_\infty^\phi e^{im\varphi}e^{im\phi} = 0$$

Finally, we can affirm that both operators commute.

C.1) Why is "m" a whole number?

The explanation is simple, the exponential $e^{im\varphi}$ that represents the rotation, indeed is ranged between 0 and 2π, so

$$e^{im\varphi} \xrightarrow{[0,2\pi]} e^{im(\varphi+2\pi)} = e^{im\varphi}e^{im2\pi} = e^{im\varphi}$$

Therefore, to accomplish the previous equality, necessarily has to be $e^{im2\pi} = 1$. Next applying Euler we have,

$$e^{im2\pi} = \cos 2\pi m + i\sin 2\pi m = 1$$

The sinus function always is null in $0, \pi, 2\pi, 3\pi, \ldots m\pi$ and the cosines function always is the unity when it has an angle of $0, 2\pi, 4\pi, 6\pi, \ldots m\pi$

Finally it is concluded that m is a whole number that is ranged between 0 to infinity.

C.2) Proof that $e^{im\phi}$ it is $C_{\infty v}$ base

Study function: $(\phi) = e^{im\phi}$; $\phi = 0$; Symmetry elements: $\hat{E}, \hat{C}_2^1, \hat{C}_\infty^\phi, \hat{\sigma}_v$

1) How do the symmetry operators behave over the coordinates?

$$\hat{E}[\phi] = [\phi] \,; \hat{C}_2^1[\phi] = [\phi + \pi] \,; \hat{C}_\infty^\phi[\phi] = [\phi + \theta]; \hat{\sigma}_v[\phi] = [\phi + \theta]$$

2) How do the symmetry operators behave over the function?

m=0 $\rightarrow e^0 = 1$

$\sigma_{\hat{E}} f([\phi]) = f(\hat{E}^{-1}[\phi]) = f(\hat{E}[\phi]) = f([\phi]) = e^{i0\phi} = e^0 = 1 = \mathbf{1} \cdot f$

$\sigma_{\hat{C}_2^1} f([\phi]) = f(\hat{C}_2^{-1}[\phi]) = f(\hat{C}_2^1[\phi]) = f([\phi + \pi]) = e^{i0(\phi+\pi)} = e^0 = 1 = \mathbf{1} \cdot f$

$\sigma_{\hat{C}_\infty^\phi} f([\phi]) = f\left(\hat{C}_\infty^{-\phi}[\phi]\right) = f\left(\hat{C}_\infty^\phi[\phi]\right) = f([\phi + \theta]) = e^{i0(\phi+\theta)} = e^0 = 1 = \mathbf{1} \cdot f$

$\sigma_{\hat{\sigma}_v} f([\phi]) = 1$

$\sigma_{\hat{\sigma}_{v^*}} f([\phi]) = -1$

m=1 $\rightarrow e^{i1\phi}$

$\sigma_{\hat{E}} f([\phi]) = f(\hat{E}^{-1}[\phi]) = f(\hat{E}[\phi]) = f([\phi]) = e^{i1\phi} = \mathbf{1} \cdot f$

$\sigma_{\hat{C}_2^1} f([\phi]) = f(\hat{C}_2^{-1}[\phi]) = f(\hat{C}_2^1[\phi]) = f([\phi + \pi]) = e^{i1(\phi+\pi)} = e^{i\phi}e^{i\pi} = (\mathbf{-1}) \cdot f$

$\left(Euler \rightarrow e^{i\pi} = (\cos \pi + i\sin \pi) = -1\right)$

$\sigma_{\hat{C}_\infty^\phi} f([\phi]) = f\left(\hat{C}_\infty^{-\phi}[\phi]\right) = f\left(\hat{C}_\infty^\phi[\phi]\right) = f([\phi + \theta]) = e^{i1(\phi+\theta)} = e^{i\phi}e^{i\theta}$

$$= (\cos\theta + i\sin\theta) \cdot f$$

$\left(Euler \rightarrow e^{i\theta} = (\cos\theta + i\sin\theta)\right)$

<u>**m=-1 → $e^{i(-1)\phi}$**</u>

$\sigma_{\hat{E}} f([\phi]) = f(\hat{E}^{-1}[\phi]) = f(\hat{E}[\phi]) = f([\phi]) = e^{i(-1)\phi} = \mathbf{1} \cdot f$

$\sigma_{\hat{C}_2^1} f([\phi]) = f(\hat{C}_2^{-1}[\phi]) = f(\hat{C}_2^1[\phi]) = f([\phi + \pi]) = e^{i(-1)(\phi+\pi)} = e^{-i\phi}e^{-i\pi} = (\mathbf{-1}) \cdot f$

$\left(Euler \rightarrow e^{-i\pi} = (\cos \pi - i\sin \pi) = -1\right)$

$\sigma_{\hat{C}_\infty^\phi} f([\phi]) = f\left(\hat{C}_\infty^{-\phi}[\phi]\right) = f\left(\hat{C}_\infty^\phi[\phi]\right) = f([\phi + \theta]) = e^{i(-1)(\phi+\theta)} = e^{-i\phi}e^{-i}$

$\qquad\qquad = (\boldsymbol{\cos \theta - i\sin \theta}) \cdot f \left(Euler \rightarrow e^{-i} = (\cos \theta - i\sin \theta)\right)$

$m = |1| \longrightarrow e^{i|1|\phi}$

$\sigma_{\hat{E}} f([\phi]) = e^{i1\phi}e^{-i1\phi} = \cos \phi + i\sin \phi + \cos \phi - i\sin\phi = 2\cos\phi \xrightarrow{\phi=0} \sigma_{\hat{E}} f([\phi]) = \mathbf{2}$

$\sigma_{\hat{C}_2^1} f([\phi]) = e^{i\phi}e^{-i\phi}e^{i\pi}e^{-i} \xrightarrow{e^{i\phi}e^{-i\phi}=2} \cos \pi + i\sin \pi + \cos \pi - i\sin \pi = \mathbf{-2}$

$\sigma_{\hat{C}_\infty^\phi} f([\phi]) = e^{i\phi}e^{-i\phi}e^{i\theta}e^{-i\theta} \xrightarrow{e^{i\phi}e^{-i\phi}=2} \cos \theta + i\sin \theta + \cos \theta - i\sin \theta = \mathbf{2\cos \theta}$

$\sigma_{\hat{\sigma}_v} f([\phi]) = \mathbf{0}$

<u>**m=2 → $e^{i2\phi}$**</u>

$\sigma_{\hat{E}} f([\phi]) = f(\hat{E}^{-1}[\phi]) = f(\hat{E}[\phi]) = f([\phi]) = e^{i2\phi} = \mathbf{1} \cdot f$

$\sigma_{\hat{C}_2^1} f([\phi]) = f(\hat{C}_2^{-1}[\phi]) = f(\hat{C}_2^1[\phi]) = f([\phi + \pi]) = e^{i2(\phi+\pi)} = e^{i2\phi}e^{i2\pi} = \mathbf{1} \cdot f$

$\left(Euler \rightarrow e^{i2\pi} = (\cos 2\pi + i\sin 2\pi) = 1\right)$

$\sigma_{\hat{C}_\infty^\phi} f([\phi]) = f\left(\hat{C}_\infty^{-\phi}[\phi]\right) = f\left(\hat{C}_\infty^\phi[\phi]\right) = f([\phi + \theta]) = e^{i2(\phi+\theta)} = e^{i2\phi}e^{i2\theta}$

$\qquad\qquad = (\boldsymbol{\cos 2\theta + i\sin 2\theta}) \cdot f$

$\left(Euler \rightarrow e^{i2\theta} = (\cos 2\theta + i\sin 2\theta)\right)$

<u>**m=-2 → $e^{i(-2)\phi}$**</u>

$\sigma_{\hat{E}} f([\phi]) = f(\hat{E}^{-1}[\phi]) = f(\hat{E}[\phi]) = f([\phi]) = e^{i(-2)\phi} = \mathbf{1} \cdot f$

$\sigma_{\hat{C}_2^1} f([\phi]) = f(\hat{C}_2^{-1}[\phi]) = f(\hat{C}_2^1[\phi]) = f([\phi + \pi]) = e^{i(-2)(\phi+\pi)} = e^{-i2\phi}e^{-i2\pi} = (\mathbf{-1}) \cdot f$

$\left(Euler \rightarrow e^{-i\pi} = (\cos 2\pi - i\sin \pi) = 1\right)$

$\sigma_{\hat{C}_\infty^\phi} f([\phi]) = f\left(\hat{C}_\infty^{-\phi}[\phi]\right) = f\left(\hat{C}_\infty^\phi[\phi]\right) = f([\phi + \theta]) = e^{i(-2)(\phi+\theta)} = e^{-i2\phi}e^{-i2\theta}$

$\qquad\qquad = (\boldsymbol{\cos 2\theta - i\sin 2\theta}) \cdot f$

$\left(Euler \rightarrow e^{-i2\theta} = (\cos 2\theta - i\sin 2\theta)\right)$

$$m = |2| \longrightarrow e^{i|2|\phi}$$

$$\sigma_{\hat{E}} f([\phi]) = e^{i2\phi} e^{-i2\phi} = \cos 2\phi + i\sin 2\phi + \cos 2\phi - i\sin 2\phi$$

$$= 2\cos 2\phi \xrightarrow{\phi=0} \sigma_{\hat{E}} f([\phi]) = 2$$

$$\sigma_{\hat{C}_2^1} f([\phi]) = e^{i2\phi} e^{-i2\phi} e^{i2\pi} e^{-i2\pi} \xrightarrow{e^{i2\phi} e^{-i2\phi}=2} \cos 2\pi + i\sin 2\pi + \cos 2\pi - i\sin 2\pi = 2$$

$$\sigma_{\hat{C}_\infty^\phi} f([\phi]) = e^{i2\phi} e^{-i2\phi} e^{i2\theta} e^{-i2\theta} \xrightarrow{e^{i2\phi} e^{-i2\phi}=2} \cos 2\theta + i\sin 2\theta + \cos 2\theta - i\sin 2\theta$$

$$= 2\cos 2\theta$$

$$\sigma_{\hat{\sigma}_v} f([\phi]) = 0$$

Keeping in mind that $\hat{\sigma}_v$ has always a conjugated plane $\hat{\sigma}_{v^*}$ starting from the value $m = \pm 1, \pm 2, \pm 3, \ldots$ we may consider the planes equal to zero.

Character table of $C_{\infty v}$

$C_{\infty v}$	E	C_2	$2C_\infty^\phi$	$\cdots$	$\infty \sigma_v$
$A_1 \equiv \Sigma^+$	1	1	1	$\cdots$	1
$A_2 \equiv \Sigma^-$	1	1	1	$\cdots$	-1
$E_1 \equiv \Pi$	2	-2	$2\cos\phi$	$\cdots$	0
$E_2 \equiv \Delta$	2	2	$2\cos 2\phi$	$\cdots$	0
$E_3 \equiv \Phi$	2	-2	$2\cos 3\phi$	$\cdots$	0
$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$
$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$

D.1) Obtaining of 3D probability to find an electron

$$\int_0^{a_0} R_{10}^2 r^2 = \frac{4}{a_0^3} \int_0^{a_0} e^{-2r/a_0} r^2 dr = \frac{4}{a_0^3} e^{-2r/a_0} \left. -\frac{r^2 a_0}{2} - \frac{2r a_0^2}{4} - \frac{2a_0^3}{8} \right|_0^{a_0}$$

$$3D\ Probability = 4[e^{-2}(-5/4) - (-1/4)] = 0{,}3233 \equiv 32{,}33\%$$

E.1) Obtaining of radial functions and angular functions with its corresponding normalizations

The way to proceed in the obtaining of the radial functions is beginning by the last quantum number in the orbital which has no constant value out of the exponent, so finally carried out to the (46) equation. Let us start by 2s&2p,

$$2p\ orbital \rightarrow R(r) = re^{-br}\ and\ m = 1$$

The derivatives required are:

$$\frac{\partial R(r)}{\partial r} = e^{-br} - bre^{-br}; \frac{\partial^2 R(r)}{\partial r^2} = -2be^{-b} + b^2re^{-br}$$

Once the (46) equation replace the derivatives and is reordered by "r" it results as,

$$\left[b^2 + \frac{2E}{a_0 e'^2}\right]r^3 + \left[-3b + \frac{2Z}{a_0}\right]r^2 + [1 - m^2]r = 0$$

With the r^2 term is obtained b:

$$-3b + \frac{2Z}{a_0} = 0 \rightarrow \boxed{b = \frac{2Z}{3a_0}}$$

And now, with the r^3 term is obtained the Energy:

$$b^2 + \frac{2E}{a_0 e'^2} = 0 \xrightarrow{b = 2Z/3a_0} \boxed{E = -\frac{2}{9}\frac{Z^2 e'^2}{a_0}}$$

We continue with,

$$2s\ orbital \rightarrow R(r) = re^{-br} - ce^{-br}\ and\ m = 0$$

The derivatives required are:

$$\frac{\partial R(r)}{\partial r} = e^{-br} - bre^{-b} + cbe^{-br}; \frac{\partial^2 R(r)}{\partial r^2} = -2be^{-br} + br^2e^{-br} - cb^2e^{-b}$$

Once the (46) equation replace the derivatives and is reordered by "r" it results as,

$$\left[b^2 + \frac{2E}{a_0 e'^2}\right]r^3 + \left[-3b - cb^2 + \frac{2Z}{a_0} - \frac{2Ec}{a_0 e'^2}\right]r^2 + \left[1 + cb - \frac{2Zc}{a_0}\right]r = 0$$

Knowing that every constant value is the same to every single orbital we can deduce "c" taking into account the "r" term,

$$1 + cb - \frac{2Zc}{a_0} = 0 \xrightarrow{b = 2Z/3a_0} \boxed{c = \frac{3a_0}{4Z}}$$

In addition, as the energy is degenerated we would obtain again:

$$b^2 + \frac{2E}{a_0 e'^2} = 0 \xrightarrow{b = 2Z/3a_0} \boxed{E = -\frac{2}{9}\frac{Z^2 e'^2}{a_0}}$$

Once obtained the 2s&2p constants and energies, we carry on with the 3s, 3p & 3d orbitals constants and energies:

$$3d\ orbital \rightarrow R(r) = r^2e^{-b}\ and\ m = 2$$

The derivatives required are:

$$\frac{\partial R(r)}{\partial r} = 2re^{-br} - br^2 e^{-br}; \frac{\partial^2 R(r)}{\partial r^2} = 2e^{-b} - 4bre^{-br} + b^2 r^2 e^{-b}$$

The (46) equation once replaced the derivatives and reordered by "r" results as,

$$\left[b^2 + \frac{2E}{a_0 e'^2}\right]r^4 + \left[-5b + \frac{2Z}{a_0}\right]r^3 + [2 + 2 - m^2]r^2 = 0$$

With the r^3 term is obtained b:

$$-5b + \frac{2Z}{a_0} = 0 \rightarrow \boxed{b = \frac{2Z}{5a_0}}$$

And now, together with the r^4 term the energy obtained is:

$$b^2 + \frac{2E}{a_0 e'^2} = 0 \xrightarrow{b = 2Z/5a_0} \boxed{E = -\frac{2}{25}\frac{Z^2 e'^2}{a_0}}$$

Then, we may obtain the "d" constant value by 3p orbital, so

$$3p\ orbital \rightarrow R(r) = r^2 e^{-br} - rce^{-br}\ and\ m = 1$$

The derivatives required are:

$$\frac{\partial R(r)}{\partial r} = 2re^{-br} - br^2 e^{-br} - ce^{-br} + bcre^{-br};$$

$$\frac{\partial^2 R(r)}{\partial r^2} = 2e^{-br} - 4bre^{-b} + b^2 r^2 e^{-br} + 2bce^{-b} - b^2 cre^{-br}$$

The (46) equation once replaced the derivatives and reordered by "r" results as follows,

$$\left[b^2 + \frac{2E}{a_0 e'^2}\right]r^4 + \left[-5b - cb^2 + \frac{2Z}{a_0} - \frac{2Ec}{a_0 e'^2}\right]r^3 + \left[4 + 3bc - \frac{2Zc}{a_0} - m^2\right]r^2 + \left[-c - \frac{2Ec}{a_0 e'^2} - m^2 c\right]r = 0$$

With the r^2 term is obtained c:

$$4 + 3bc - \frac{2Zc}{a_0} - m^2 = 0 \xrightarrow{m=1} \xrightarrow{b=2Z/5a_0} \boxed{c = \frac{15a_0}{4Z}}$$

And the energy will be the same as the 3d orbital is,

$$-5b - cb^2 + \frac{2Z}{a_0} - \frac{2Ec}{a_0 e'^2} = 0 \xrightarrow{b=2Z/5a_0} \xrightarrow{c=15a_0/4Z} \boxed{E = -\frac{2}{25}\frac{Z^2 e'^2}{a_0}}$$

Finally with the 3s orbital we can obtain the constant that is left,

$$3s\ orbital \rightarrow R(r) = r^2 e^{-b} - rce^{-br} + de^{-br}\ and\ m = 0$$

The derivatives required are below:

$$\frac{\partial R(r)}{\partial r} = 2re^{-b} - br^2 e^{-b} - ce^{-br} + bcre^{-br} - dbe^{-br};$$

$$\frac{\partial^2 R(r)}{\partial r^2} = 2e^{-br} - 4bre^{-b} + b^2r^2e^{-br} + 2bce^{-br} - b^2cre^{-br} + db^2e^{-b}$$

The (46) equation once replaced the derivatives and reordered by "r" results as,

$$\left[b^2 + \frac{2E}{a_0 e'^2}\right]r^4 + \left[-5b + \frac{2Z}{a_0} - \frac{2Ec}{a_0 e'^2}\right]r^3 + \left[4 + 3bc - cb^2 + db^2 - \frac{2Zc}{a_0} + \frac{2Ed}{a_0 e'^2}\right]r^2 + \left[-c - db + \frac{2Ed}{a_0 e'^2}\right]r = 0$$

With the r term is obtained d:

$$-c - db + \frac{2Ed}{a_0 e'^2} = 0 \xrightarrow{b=2Z/5a_0} \xrightarrow{c=15\ ^0/4Z} \boxed{d = \frac{75a_0}{16Z^2}}$$

And the energy how it is known, is degenerated, so

$$4 + 3bc - cb^2 + db^2 - \frac{2Zc}{a_0} + \frac{2Ed}{a_0 e'^2} = 0 \xrightarrow{b=2Z/5a_0} \xrightarrow{c=15a_0/4Z} \xrightarrow{d=75a_0^2/16Z^2} \boxed{E = -\frac{2}{25}\frac{Z^2 e'^2}{a_0}}$$

E.2) Normalizations

-Radial part-

2s orbital

$$N_R^2\left[\int_0^\infty r^3 e^{-2br}dr - c^2\int_0^\infty re^{-2br}dr\right] = 1 \rightarrow N_R^2\left[\frac{3!}{2^4 b^4} - c^2\frac{1!}{2^2 b^2}\right] = 1 \xrightarrow{b=2Z/3a_0} \xrightarrow{c=3a_0/4Z} \boxed{N_R^{2s} = \frac{16\sqrt{5}}{45}\left(\frac{Z}{a_0}\right)^2}$$

2p orbital

$$N_R^2\left[\int_0^\infty r^3 e^{-2br}dr\right] = 1 \rightarrow N_R^2\left[\frac{3!}{2^4 b^4}\right] = 1 \xrightarrow{b=2Z/3a_0} \boxed{N_R^{2p} = \frac{2\sqrt{6}}{27}\left(\frac{Z}{a_0}\right)^2}$$

3s orbital

$$N_R^2\left[\int_0^\infty r^5 e^{-2br}dr - 2c^2\int_0^\infty r^4 e^{-2br}dr + 2d\int_0^\infty r^3 e^{-2br}dr + c^2\int_0^\infty r^3 e^{-2br}dr - 2cd\int_0^\infty r^2 e^{-2br}dr + d^2\int_0^\infty re^{-2br}dr\right] = 1$$

$$N_R^2\left[\frac{5!}{2^6 b^6} - 2c\frac{4!}{2^5 b^5} + 2d\frac{3!}{2^4 b^4} + c^2\frac{3!}{2^4 b^4} - 2cd\frac{2!}{2^3 b^3} + d^2\frac{1!}{2^2 b^2}\right] = 1 \xrightarrow{b=2Z/5a_0} \xrightarrow{c=15\ ^0/4Z} \xrightarrow{d=75\ ^0^2/16Z^2} \boxed{N_R^{3s} = \frac{64}{125\sqrt{111}}\left(\frac{Z}{a_0}\right)^3}$$

3p orbital

$$N_R^2\left[\int_0^\infty r^5 e^{-2br}dr + c^2\int_0^\infty r^3 e^{-2br}dr - 2c\int_0^\infty r^4 e^{-2br}dr\right] = 1 \rightarrow$$

$$N_R^2\left[\frac{5!}{2^6 b^6} + c^2\frac{3!}{2^4 b^4} - 2c\frac{4!}{2^5 b^5}\right] = 1 \xrightarrow{b=2Z/3a_0} \xrightarrow{c=3a_0/4Z} \boxed{N_R^{3p} = \frac{64}{125\sqrt{30}}\left(\frac{Z}{a_0}\right)^3}$$

3d orbital

$$N_R^2\left[\int_0^\infty r^5 e^{-2br}dr\right] = 1 \rightarrow N_R^2\left[\frac{5!}{2^6 b^6}\right] = 1 \xrightarrow{b=2Z/5a_0} \boxed{N_R^{2p} = \frac{32}{125\sqrt{30}}\left(\frac{Z}{a_0}\right)^3}$$

The angular part will be always the same in every single orbital because a single imaginary function multiplied by its conjugated will be 1, so we will always have the same result, then

$$N_\varphi^2 \int_0^{2\pi} e^{im\varphi} e^{-im\varphi} d\varphi = N_\varphi^2 \int_0^{2\pi} d\varphi = 1 \rightarrow N_\varphi^2 2\pi = 1 \rightarrow \boxed{N_\varphi = \frac{1}{\sqrt{2\pi}}}$$

F.1) Mathematica calculations

```
ClearAll["Global'*"]

fa[ra_] := 4/Sqrt[2*π] * Exp[-2*ra]; fb[rb_] := 4/Sqrt[2*π] * Exp[-2*rb]

NIntegrate[ra*fa[ra]^2, {ra, 0, ∞}, {φ, 0, 2*π}]

1.

(*The guideline it is accomplished*)

ClearAll["Global'*"]

fa[x_, y_] := 4/Sqrt[2*π] * Exp[-2*Sqrt[(x + Rab/2)^2 + y^2]]; Rab = 0; ra = Sqrt[(x + Rab/2)^2 + y^2];

SSab[Rab_] := NIntegrate[fa[x, y]^2, {x, -∞, ∞}, {y, -∞, ∞}]

SSab[Rab]

1.

Sab[Rab_] := NIntegrate[fa[x, y]^2, {x, -3, 3}, {y, -3, 3}]

Sab[Rab]

0.999964

(*Overlap values almost identical to the limits [-∞,∞] and to [-3,3]*)

ClearAll["Global'*"]

fa[x_, y_] := 4/Sqrt[2*π] * Exp[-2*Sqrt[(x + Rab/2)^2 + y^2]]; fb[x_, y_] := 4/Sqrt[2*π] * Exp[-2*Sqrt[(x - Rab/2)^2 + y^2]]

Plot[Sab[Rab], {Rab, 0, 10}, PlotRange -> Full]
```
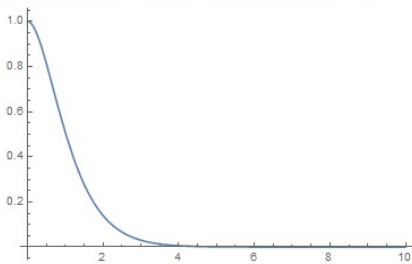
```
(*It is observed the overlap decrease whenever it is increased Rab, therefore the function has congruence*)

(*Haa & Hab Integrals*)

ClearAll["Global'*"]

fa[x_, y_] := 4/Sqrt[2*π] * Exp[-2*Sqrt[(x + Rab/2)^2 + y^2]]; fb[x_, y_] := 4/Sqrt[2*π] * Exp[-2*Sqrt[(x - Rab/2)^2 + y^2]]

Haa[Rab_] := NIntegrate[fa[x, y]*(-1/2*(D[fa[x, y], {x, 2}] + D[fa[x, y], {y, 2}]) - fa[x, y]/Sqrt[(x + Rab/2)^2 + y^2] - fa[x, y]/Sqrt[(x - Rab/2)^2 + y^2]), {x, -∞, ∞}, {y, -∞, ∞}]

Hab[Rab_] := NIntegrate[fa[x, y]*(-1/2*(D[fb[x, y], {x, 2}] + D[fb[x, y], {y, 2}]) - fb[x, y]/Sqrt[(x + Rab/2)^2 + y^2] - fb[x, y]/Sqrt[(x - Rab/2)^2 + y^2]), {x, -∞, ∞}, {y, -∞, ∞}]
```
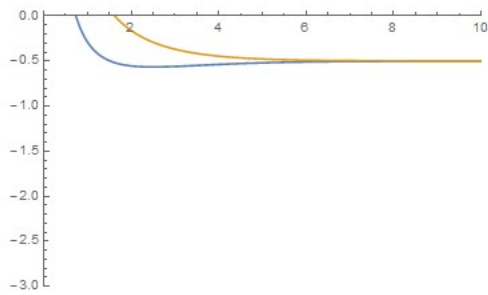
```
(*Bonding and antibonding energies*)
```

$$E_+[Rab\_] := \frac{Haa[Rab] + Hab[Rab]}{1 + Sab[Rab]} + \frac{1}{Rab} \; ; \; E_-[Rab\_] := \frac{Haa[Rab] - Hab[Rab]}{1 - Sab[Rab]} + \frac{1}{Rab} \; ;$$

```
Plot[{E₊[Rab], E₋[Rab]}, {Rab, 0, 10}, PlotRange → {{0, 10}, {-3, 0}}]
```
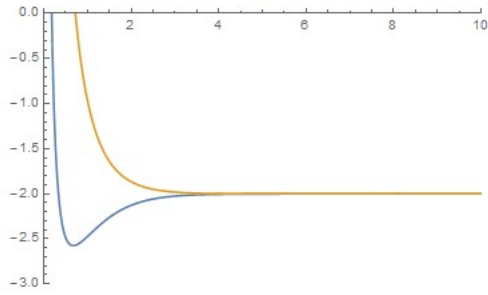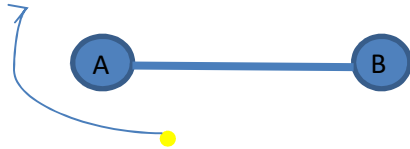


```
(*Energy minimum at 0.6 Bohrs approximately. E²ᴰ=-2 hartrees*)
```



```
(*This graphic is the correponding to the 3D at the same scale that the above graphic and the energy minimum
  it is at 2 Bohrs approximately. E³ᴰ=-½ hartrees*)
```

F.2) Secular equations

We have the following system,

Every single core has a particular behaviour (ϕ_a & ϕ_b), and the global behaviour comes given by the following LCAO,

$$\psi = c_a\phi_a + c_b\phi_b \quad (f.2.1)$$

Next, the energy can be obtained using the following expression,

$$E = \frac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle} \quad (f.2.2)$$

Now taking (f.2.1) to (f.2.2),

$$E = \frac{\langle c_a\phi_a + c_b\phi_b|c_a\hat{H}\phi_a + c_b\hat{H}\phi_b\rangle}{\langle c_a\phi_a + c_b\phi_b|c_a\phi_a + c_b\phi_b\rangle} = \frac{c_a^2\langle\phi_a|\hat{H}\phi_a\rangle + 2c_ac_b\langle\phi_a|\hat{H}\phi_b\rangle + c_b^2\langle\phi_b|\hat{H}\phi_b\rangle}{c_a^2 + 2c_ac_bS_{ab} + c_b^2}$$

$$\xrightarrow{\langle\phi_i|\hat{H}\phi_j\rangle = H_{ij}} \boxed{E = \frac{c_a^2 H_{aa} + 2c_ac_b H_{ab} + c_b^2 H_{bb}}{c_a^2 + 2c_ac_bS_{ab} + c_b^2}} \quad (f.2.3)$$

Now (f.2.3) is reordered obtaining the following expression,

$$c_a^2 E + 2c_a c_b S_{ab} E + c_b^2 E = c_a^2 H_{aa} + 2c_a c_b H_{ab} + c_b^2 H_{bb} \ (\kappa)$$

Next the energy is minimized in (κ),

$$\frac{\partial \kappa}{\partial c_a} = 0 = 2c_a E + 2c_b S_{ab} E = 2c_a H_{aa} + 2c_b H_{ab} \ (\kappa.1)$$

$$\boxed{E_{c_a} = \frac{c_a H_{aa} + c_b H_{ab}}{c_a + c_b S_{ab}}} \ (\xi.1)$$

$$\frac{\partial \kappa}{\partial c_b} = 0 = 2c_b E + 2c_a S_{ab} E = 2c_b H_{bb} + 2c_a H_{ab} \ (\kappa.2)$$

$$\boxed{E_{c_b} = \frac{c_b H_{bb} + c_a H_{ab}}{c_b + c_b S_{ab}}} \ (\xi.2)$$

Then we can order E_{c_a} & E_{c_b} respectively to solve the secular equations:

$$c_a H_{aa} + c_b H_{ab} - c_a E - c_b S_{ab} E = 0$$

$$c_b H_{bb} + c_a H_{ab} - c_b E + c_b S_{ab} E = 0$$

Continuing with the reordering according to c_a & c_b, we might obtain,

$$(H_{aa} - E)c_a + (H_{ab} - S_{ab}E)c_b = 0$$

$$(H_{ab} - S_{ab}E)c_a + (H_{bb} - E)c_b = 0$$

In addition to this, if we take into account H_2^+, which is a homonuclear molecule we can affirm $H_{aa} = H_{bb}$, so when we try to solve the previous equations all it turns easier to solve,

$$(H_{aa} - E)c_a + (H_{ab} - S_{ab}E)c_b = 0$$

$$(H_{ab} - S_{ab}E)c_a + (H_{aa} - E)c_b = 0$$

Next a determinant is prepared to obtain energy values:

$$\begin{vmatrix} H_{aa} - E & H_{ab} - S_{ab}E \\ H_{ab} - S_{ab}E & H_{aa} - E \end{vmatrix} = 0$$

$$[H_{aa} - E]^2 - [H_{ab} - S_{ab}E]^2 = 0 \rightarrow \boxed{[H_{aa} - E]^2 = \pm[H_{ab} - S_{ab}E]^2 (\alpha)}$$

If we make (α) positive we will obtain antibonding energy and if it makes (α) negative we will obtain bonding energy,

<u>(α) positive:</u>

$$\boxed{E_- = \frac{H_{aa} - H_{ab}}{1 - S_{ab}}}$$

(α) negative:

$$E_+ = \frac{H_{aa} + H_{ab}}{1 + S_{ab}}$$

ADDITIONAL

Now if we replace E_+ in the secular equations it may obtain,

$$\frac{c_a}{c_b} = 1 \rightarrow \boxed{c_a = c_b}$$

On the other hand, if we replace E_- in the secular equations it is obtained,

$$\frac{c_a}{c_b} = -1 \rightarrow \boxed{c_a = -c_b}$$

Knowing which is the relation regarding normalization constants, we are going to proceed on the obtaining of their values. Taking into account the normalization condition we will obtain them,

$$\langle \psi | \psi \rangle = c_a^2 + 2c_a c_b S_{ab} + c_b^2 = 1$$

If $c_a = c_b$:

$$2c_a^2 + 2c_a{}^2 S_{ab} = 1 \rightarrow \boxed{c_a = c_b = \frac{1}{\sqrt{2[1 + S_{ab}]}}}$$

If $c_a = -c_b$:

$$2c_b^2 - 2c_b{}^2 S_{ab} = 1 \rightarrow \boxed{c_b = \frac{1}{\sqrt{2[1 - S_{ab}]}} = -c_a = -\frac{1}{\sqrt{2[1 - S_{ab}]}}}$$

It concludes then,

$$E_+ \rightarrow \psi_+ = c_a \phi_a + c_a \phi_b = c_a(\phi_a + \phi_b) \rightarrow \boxed{\psi_+ = \frac{1}{\sqrt{2[1 + S_{ab}]}}(\phi_a + \phi_b)}$$

$$E_- \rightarrow \psi_- = c_a \phi_a - c_a \phi_b = c_a(\phi_a - \phi_b) \rightarrow \boxed{\psi_- = \frac{1}{\sqrt{2[1 - S_{ab}]}}(\phi_a - \phi_b)}$$

F.3) H_2^+ molecule (elliptical coordinates)

To start with, let me introduce the system,

$$r = \sqrt{x^2 + y^2}$$
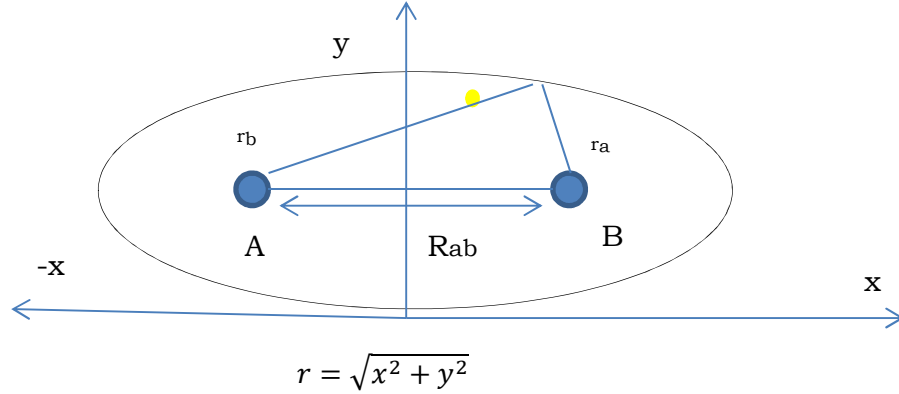
To make the variables change, we need to take into account the following equalities:

$$u = \frac{r_a + r_b}{R_{ab}}; \quad v = \frac{r_a - r_b}{R_{ab}}$$

Once known the previous equalities, it may obtain,

$$r_a = \frac{1}{2}R_{ab}(u + v) \ \& \ r_b = \frac{1}{2}R_{ab}(u - v) \quad (f.3.1) \ \& \ (f.3.2)$$

And now, making reference to 1s wave function for nuclei A & B,

$$\phi_a = \frac{4}{\sqrt{2\pi}}e^{-2r_a}; \ \phi_b = \frac{4}{\sqrt{2\pi}}e^{-2r_b}$$

We could carry (f.3.1) & (f.3.2) to the 1s wave functions, where we may obtain,

$$\phi_a = \frac{4}{\sqrt{2\pi}}e^{-R_{ab}(u+v)}; \ \phi_b = \frac{4}{\sqrt{2\pi}}e^{-R_{ab}(u-v)}$$

Next, we need to obtain the following parameters:[47]

1) 2D elliptical Laplacian,

$$\nabla^2 = \frac{4}{R_{ab}^2(u^2 - v^2)}\left[(u^2 - 1)\frac{\partial^2}{\partial u^2} + u\frac{\partial}{\partial u} + (1 - v^2)\frac{\partial^2}{\partial v^2} - v\frac{\partial}{\partial v}\right]$$

2) Area differential for an ellipse,

$$dA = dxdy = |J_p|dudv \equiv \left(\frac{R}{2}\right)^2\frac{u^2 - v^2}{[(u^2 - 1)(v^2 - 1)]^{1/2}}dudv$$

Now, it is obtained S_{ab}, H_{aa} and H_{ab},

---

[47] It will be detailled at the end of the section F.3)

$$S_{ab} = \langle \phi_a | \phi_b \rangle = \int \phi_a \phi_b \, dA \quad (f.3.3)$$

$$H_{aa} = \langle \phi_a | \widehat{H} | \phi_a \rangle = \int \phi_a^* \widehat{H} \phi_a \, dA \quad (f.3.4)$$

$$H_{ab} = \langle \phi_a | \widehat{H} | \phi_b \rangle = \int \phi_a^* \widehat{H} \phi_b \, dA \quad (f.3.5)$$

Note: The integration is done to x axis between $[1,\infty]$ and to y axis between $[-1,1]$. In addition, because of the x axis we will need to multiply by 2, because only it is considered in one side of the space. In other words, it is just taken into account the x positive values and so we need as many the positives as the negatives.

The calculations done by Mathematica 10 are:

```
ClearAll["Global'*"]

fa[u_, v_] := 4/√(2π) * e^(-R*(u+v)) ; fb[u_, v_] := 4/√(2π) * e^(-R*(u-v)) ;

Integrate[fa[u, v] * fb[u, v] * R²/4 * (u² - v²)/((u² - 1) * (1 - v²))^(1/2) , {u, 1, ∞}, {v, -1, 1}, Assumptions → {Re[R] ≥ 0, Im[R] == 0}]

ConditionalExpression[R² BesselK[2, 2 R], R > 0]

Sab[R_] := 2 R² BesselK[2, 2 R]

Plot[Sab[R], {R, 0, 10}, PlotRange → Full]
```
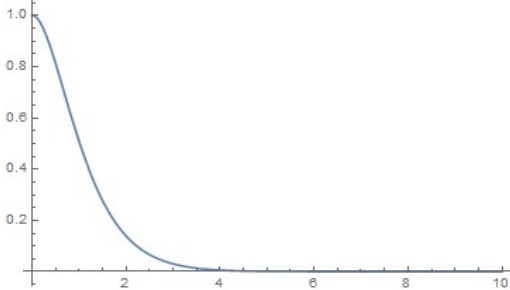

Here is observed the overlap behaviour what is congruent with the expected (y=overlap, x=internuclear distance).

Next we proceed with H_{aa} and H_{ab} obtaining,

```
Integrate[
fa[u, v] * (- 2/(R² * (u² - v²)) * (u² * D[fa[u, v], {u, 2}] - D[fa[u, v], {u, 2}] + u * D[fa[u, v], {u, 1}] + D[fa[u, v], {v, 2}] - v² * D[fa[u, v], {v, 2}] - v * D[fa[u, v], {v, 1}]) -

fa[u, v]/(1/2 * R * (u + v)) - fa[u, v]/(1/2 * R * (u - v))) * R²/4 * (u² - v²)/((u² - 1) * (1 - v²))^(1/2) , {u, 1, ∞}, {v, -1, 1}, Assumptions → {Re[R] ≥ 0, Im[R] == 0}]

ConditionalExpression[- (2 R (-π BesselI[1, 2 R] BesselK[0, 2 R] + 3 π BesselI[0, 2 R] BesselK[1, 2 R]))/π , R > 0]

Haa[R_] := - (4 R (-π BesselI[1, 2 R] BesselK[0, 2 R] + 3 π BesselI[0, 2 R] BesselK[1, 2 R]))/π
```

```
Integrate[

fb[u, v] * (- 2/(R^2 * (u^2 - v^2)) * (u^2 * D[fa[u, v], {u, 2}] - D[fa[u, v], {u, 2}] + u * D[fa[u, v], {u, 1}] + D[fa[u, v], {v, 2}] - v^2 * D[fa[u, v], {v, 2}] - v * D[fa[u, v], {v, 1}]) -

  fa[u, v]/(1/2 * R * (u + v)) - fa[u, v]/(1/2 * R * (u - v))) * R^2/4 * (u^2 - v^2)/((u^2 - 1) * (1 - v^2))^(1/2), {u, 1, ∞}, {v, -1, 1}, Assumptions → {Re[R] ≥ 0, Im[R] ∷ 0}]

ConditionalExpression[-2 R (R BesselK[0, 2 R] + 3 BesselK[1, 2 R]), R > 0]

Hab[R_] := -4 R (R BesselK[0, 2 R] + 3 BesselK[1, 2 R])
```
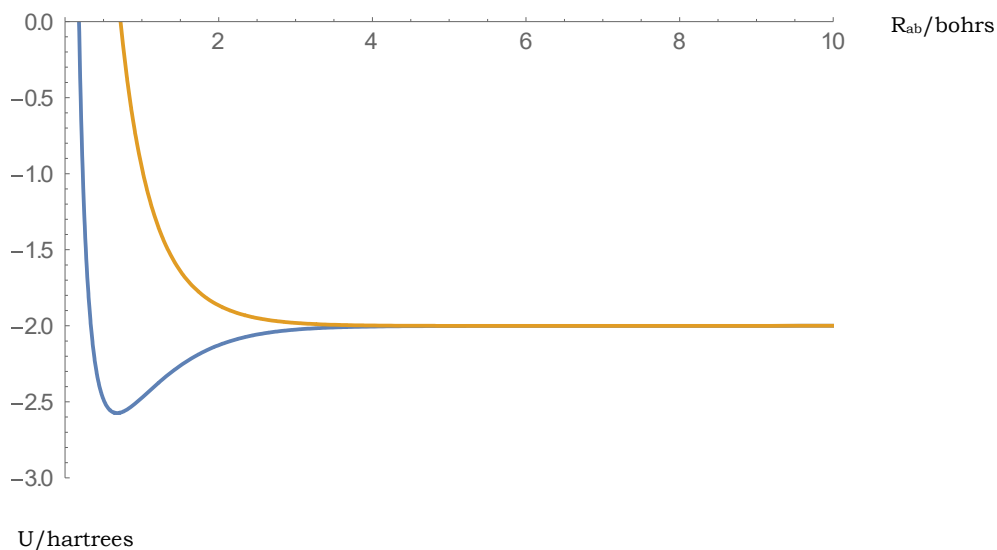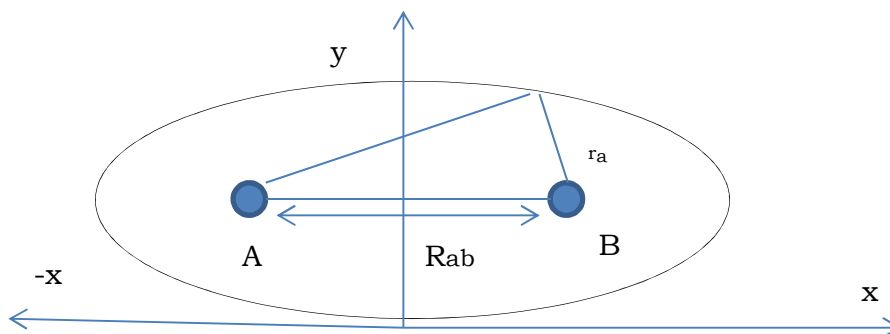
Now those integrals are carried to the next expressions,

$$E_+ = \frac{H_{aa} + H_{ab}}{1 + S_{ab}} + \frac{1}{R_{ab}}; \quad E_- = \frac{H_{aa} - H_{ab}}{1 - S_{ab}} + \frac{1}{R_{ab}}$$

Obtaining the following graphic,

U/hartrees

-*Differential area element for an ellipse*

$$x \rightarrow \frac{1}{2} R_{ab} u v$$

$$y \rightarrow \frac{1}{2} R_{ab} [(u^2 - 1)(1 - v^2)]^{1/2}$$

Knowing that the differential area element is: $dA = |J_p| du dv$, we just have to obtain the Jacobian, then

$$|J_p| = \begin{vmatrix} \dfrac{\partial x}{\partial u} & \dfrac{\partial y}{\partial u} \\ \dfrac{\partial x}{\partial v} & \dfrac{\partial y}{\partial v} \end{vmatrix} = \begin{vmatrix} \dfrac{1}{2}R_{ab}v & \dfrac{R_{ab}}{4}\dfrac{2u(1-v^2)}{[(u^2-1)(1-v^2)]^{\frac{1}{2}}} \\ \dfrac{1}{2}R_{ab}u & \dfrac{R_{ab}}{4}\dfrac{2v(1-u^2)}{[(u^2-1)(1-v^2)]^{\frac{1}{2}}} \end{vmatrix}$$

$$= \left(\dfrac{1}{2}R_{ab}u\right)\left(\dfrac{R_{ab}}{4}\dfrac{2u(1-v^2)}{[(u^2-1)(1-v^2)]^{\frac{1}{2}}}\right) - \left(\dfrac{1}{2}R_{ab}v\right)\left(\dfrac{R_{ab}}{4}\dfrac{2v(1-u^2)}{[(u^2-1)(1-v^2)]^{\frac{1}{2}}}\right)$$

$$= \dfrac{R^2}{2^2}\dfrac{u^2-v^2u^2}{[(u^2-1)(1-v^2)]^{\frac{1}{2}}} - \dfrac{R^2}{2^2}\dfrac{v^2-v^2u^2}{[(u^2-1)(1-v^2)]^{\frac{1}{2}}} \equiv \left(\dfrac{R}{2}\right)^2 \dfrac{u^2-v^2}{[(u^2-1)(v^2-1)]^{1/2}}$$

So finally we have:

$$\boxed{dA = \left(\dfrac{R}{2}\right)^2 \dfrac{u^2-v^2}{[(u^2-1)(v^2-1)]^{1/2}} du dv}$$

-Elliptical 2D Laplacian obtaining (Mathematica 10)

```
(*Laplacian*)

(*x part of the Laplacian*)
dx2 := (D[u[R], {x, 1}])^2 * cu2 + D[u[R], {x, 2}] * cu1 + (D[v[R], {x, 1}])^2 * cv2 + D[v[R], {x, 2}] * cv1

(*y part of the Laplacian*)
dy2 := (D[u[R], {y, 1}])^2 * cu2 + D[u[R], {y, 2}] * cu1 + (D[v[R], {y, 1}])^2 * cv2 + D[v[R], {y, 2}] * cv1

(*elliptical 2D Laplacian*)
Lap := dx2 + dy2

x = 1/2 * R * u * v; y = 1/2 * R * Sqrt[u^2 - u^2 * v^2 - 1 + v^2];

Lap
```

$$cv2\left(\partial_{\{\frac{Ruv}{2},1\}}\frac{1}{R}\left(-\sqrt{\left(-\frac{R}{2}+\frac{Ruv}{2}\right)^2+\frac{1}{4}R^2(-1+u^2+v^2-u^2v^2)}+\sqrt{\left(\frac{R}{2}+\frac{Ruv}{2}\right)^2+\frac{1}{4}R^2(-1+u^2+v^2-u^2v^2)}\right)\right)^2 +$$

$$cv1\,\partial_{\{\frac{Ruv}{2},2\}}\frac{1}{R}\left(-\sqrt{\left(-\frac{R}{2}+\frac{Ruv}{2}\right)^2+\frac{1}{4}R^2(-1+u^2+v^2-u^2v^2)}+\sqrt{\left(\frac{R}{2}+\frac{Ruv}{2}\right)^2+\frac{1}{4}R^2(-1+u^2+v^2-u^2v^2)}\right) +$$

$$cv2\left(\partial_{\{\frac{1}{2}R\sqrt{-1+u^2+v^2-u^2v^2},1\}}\frac{1}{R}\left(-\sqrt{\left(-\frac{R}{2}+\frac{Ruv}{2}\right)^2+\frac{1}{4}R^2(-1+u^2+v^2-u^2v^2)}+\sqrt{\left(\frac{R}{2}+\frac{Ruv}{2}\right)^2+\frac{1}{4}R^2(-1+u^2+v^2-u^2v^2)}\right)\right)^2 +$$

$$cv1\,\partial_{\{\frac{1}{2}R\sqrt{-1+u^2+v^2-u^2v^2},2\}}\frac{1}{R}\left(-\sqrt{\left(-\frac{R}{2}+\frac{Ruv}{2}\right)^2+\frac{1}{4}R^2(-1+u^2+v^2-u^2v^2)}+\sqrt{\left(\frac{R}{2}+\frac{Ruv}{2}\right)^2+\frac{1}{4}R^2(-1+u^2+v^2-u^2v^2)}\right) +$$

$$cu2\left(\partial_{\{\frac{Ruv}{2},1\}}\frac{1}{R}\left(\sqrt{\left(-\frac{R}{2}+\frac{Ruv}{2}\right)^2+\frac{1}{4}R^2(-1+u^2+v^2-u^2v^2)}+\sqrt{\left(\frac{R}{2}+\frac{Ruv}{2}\right)^2+\frac{1}{4}R^2(-1+u^2+v^2-u^2v^2)}\right)\right)^2 +$$

$$cu1\,\partial_{\{\frac{Ruv}{2},2\}}\frac{1}{R}\left(\sqrt{\left(-\frac{R}{2}+\frac{Ruv}{2}\right)^2+\frac{1}{4}R^2(-1+u^2+v^2-u^2v^2)}+\sqrt{\left(\frac{R}{2}+\frac{Ruv}{2}\right)^2+\frac{1}{4}R^2(-1+u^2+v^2-u^2v^2)}\right) +$$

$$cu2\left(\partial_{\{\frac{1}{2}R\sqrt{-1+u^2+v^2-u^2v^2},1\}}\frac{1}{R}\left(\sqrt{\left(-\frac{R}{2}+\frac{Ruv}{2}\right)^2+\frac{1}{4}R^2(-1+u^2+v^2-u^2v^2)}+\sqrt{\left(\frac{R}{2}+\frac{Ruv}{2}\right)^2+\frac{1}{4}R^2(-1+u^2+v^2-u^2v^2)}\right)\right)^2 +$$

$$cu1\,\partial_{\{\frac{1}{2}R\sqrt{-1+u^2+v^2-u^2v^2},2\}}\frac{1}{R}\left(\sqrt{\left(-\frac{R}{2}+\frac{Ruv}{2}\right)^2+\frac{1}{4}R^2(-1+u^2+v^2-u^2v^2)}+\sqrt{\left(\frac{R}{2}+\frac{Ruv}{2}\right)^2+\frac{1}{4}R^2(-1+u^2+v^2-u^2v^2)}\right)$$

```
FullSimplify[%45]
```

$$\left(2\left(R\left(\left(\sqrt{R^2(u-v)^2}+\sqrt{R^2(u+v)^2}\right)cu1+\left(\sqrt{R^2(u-v)^2}-\sqrt{R^2(u+v)^2}\right)cv1\right)+R^2(-2+u^2+v^2)(cu2-cv2)+\sqrt{R^2(u-v)^2}\sqrt{R^2(u+v)^2}(cu2+cv2)\right)\right)\Big/\left(R^2\sqrt{R^2(u-v)^2}\sqrt{R^2(u+v)^2}\right)$$

Where,

$$cu1 = \dfrac{\partial}{\partial u}; cu2 = \dfrac{\partial^2}{\partial u^2}; cv1 = \dfrac{\partial}{\partial v}; cv2 = \dfrac{\partial^2}{\partial v^2}$$

G.1) Perturbational & Variational method J_{12} obtaining

Perturbational method:

```
ee1 = NIntegrate[4 * π * r1 * r2 / 2 * fok * fok * 1 / r12, {r1, 0, ∞}, {r2, 0, ∞}, {φn, 0, 2 * π},
    MaxRecursion → 100, Method → {GlobalAdaptive, MaxErrorIncreases → 3530}]

4.71226
```

Variational method:

```
erep1[α_] := NIntegrate[4 * π * r1 * r2 / 2 * fok[r1, r2] * fok[r1, r2] * 1 / r12, {r1, 0, ∞}, {r2, 0, ∞}, {φn, 0, 2 * π}, MaxRecursion → 100, Method → {GlobalAdaptive, MaxErrorIncreases → 3530}]
```

```
enevar[α_] := e1[α] + e2[α] + erep1[α]
```
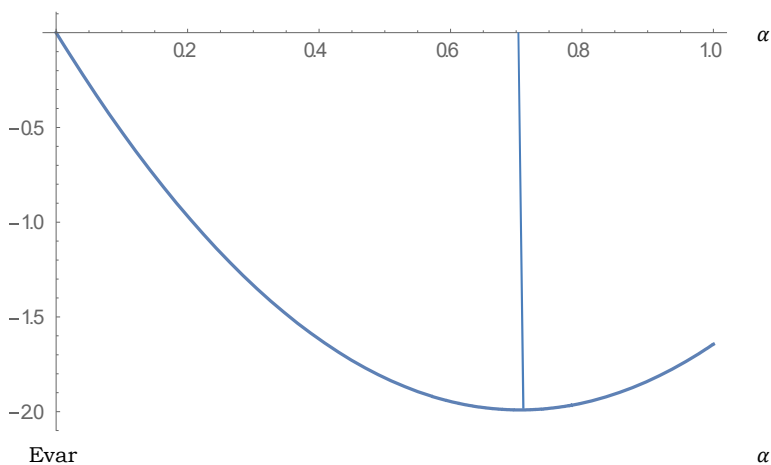
```
enevar[α] - (-8)
-3.63452
```

Therefore, if the I.P. is $-3.63452 hartrees$ and $E_1 + E_2 = -8 hartrees$, then
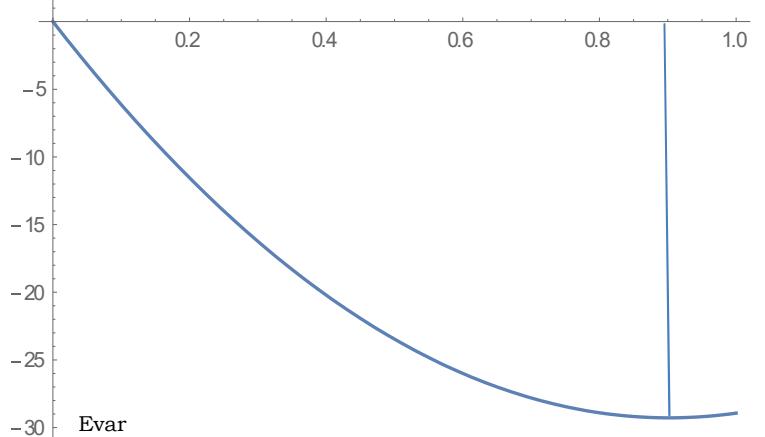$J_{12} = -3.63452 + 8 = 4.36548 hartrees$

G.2) Where do the Slater's rules come from?

We are going to put some examples to visualize better where the Slater's rules come from,

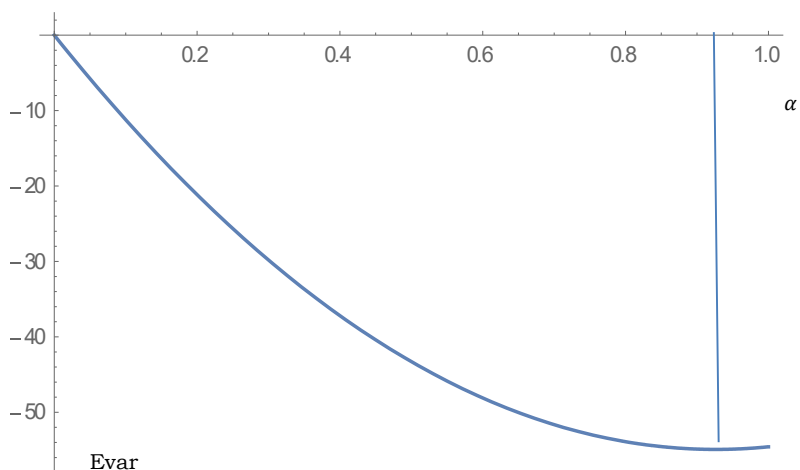
$$\boxed{H^-} \quad \alpha = 0.7; Z' = Z\alpha = 0.7$$

$$E = 0.009 \ hartrees$$

$$\boxed{Li^+} \quad \alpha = 0.9; Z' = Z\alpha = 2.7$$

$$E = -11.28 \ hartrees$$

$$\boxed{Be^{2+}} \alpha = 0.925; Z' = Z\alpha = 3.7$$

$$E = -22.92 \ hartrees$$

$$\boxed{H^- < He < Li^+ < Be^{2+}}$$

$$\alpha: 0.7 < 0.85 < 0.9 < 0.925$$

$$Z: 1 < 2 < 3 < 4$$

Alpha is given as a fraction of unity in relation with the effective nuclear charge that the electrons perceive with regard to the nucleus. We might call alpha as the non-shielding parameter according to: the largest it is the least shielding exists. It is observed that all the examples above obey the Slater's rules. $Z' = Z\alpha = Z - \sigma$. The Slater's rules say: for all the electrons that may be found in the 1s orbital of two-electron atom, the shielding will be $\sigma = 0.30$ and that is observed when we take into account the relation: $Z\alpha = Z - \sigma$.

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