A brief Study on Hydrogen MoleculAR Ion

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Declaration:

I affirm that I have identified all my sources and that no part of my dissertation paper uses acknowledged materials

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❖ <u>ABSTRACT:</u>

The **hydrogen molecular ion, dihydrogen cation**, or H_2^+, is the simplest molecular ion. It is composed of two positively charged protons and one negatively charged electron, and can be formed from ionization of a neutral hydrogen molecule. Here I have considered Born-Oppenheimer approximation and formulate the electronic Hamiltonian for H_2^+ in atomic units. Then considering the LCAO-MO (Linear Combination of Atomic Orbitals- Molecular Orbitals), my aim to make a short treatment on energy calculation. Then I shall plot energy for ground state and first excited state and formulated the wave functions, and probability density for it. Finally, I am continuing my project by plotting the probability density for the bonding and anti-bonding states.

❖ <u>INTRODUCTION :</u>

The Hydrogen molecular ion, the simplest molecular system, was studied in the earlier days of quantum mechanics. The demonstration that this species had, in agreement with experiment, a stable ground state corresponding to a bond between two atoms, was one of the earlier achievements of quantum theory. Classical mechanics could not predict a stable state for H_2^+.

The molecular orbital method, in the form of a linear combination of atomic orbitals (LCAO-MO method), was proposed at that time; its first application was to the Hydrogen molecular ion. Many other approximate treatments were then devised and applied to it.

*Burrau*showed that the confocal elliptic coordinate system allowed the complete separation of the hydrogen molecular ion Hamiltonian, thus paving the way towards an exact solution. This task was taken up by several investigators, including *Burrau* himself, *Teller, Jaffe*, and *Hylleraas*.

They showed that the energy of any state of the hydrogen molecular ion could be found by solving two coupled differential equations. Various method of solutions were proposed, all involving rather complicated expansions in series of associative Legendre functions. These led in turn to three term recurrence relations, from which intricate eigenvalue equations followed. In practice the energies could only be found numerically; formulas to compute the expansion coefficients were also given.

Hydrogen molecular ion is of great historical and theoretical interest because, having only one electron, the Schrödinger equation for the system can be solved in a relatively straight forward way due to the lack of electron – electron repulsion.

❖ THEORY:

I am starting my study of molecular quantum mechanics. Hydrogen Molecular Ion, the simplest diatomic molecule, is consists of two protons and one electron. This topic leads us to **Born-Oppenheimer Approximation** at first for a brief calculation. Let us, have a look on this approximation.

We have assumed the nuclei and the electrons to be point masses and neglected spin-orbit and other relativistic interactions. Then the molecular Hamiltonian is -------

$$\hat{H} = -\hbar^2/2 \sum_{\alpha} \frac{\nabla_{\alpha}^2}{m_{\alpha}} - \hbar^2/(2m_e) \sum_i \nabla_i^2 + \sum_{\alpha} \sum_{\beta > \alpha} (Z_{\alpha} Z_{\beta}\, e^2)/r_{\alpha\beta}$$

$$- \sum_{\alpha} \sum_i \frac{Z_{\alpha} e^2}{r_{i\alpha}} + \sum_i \sum_{i>j} e^2/r_{ij}$$

(1)

Here α and β refer to nuclei and i and j refer to electrons. The first term denotes the operator for kinetic energy of the nuclei. The second term denotes the operator for kinetic energy of electrons. The third term is the repulsive potential energy between the nuclei, where $r_{\alpha\beta}$ is the distance between the nuclei. The fourth term indicates attractive potential energy between electrons and nuclei. The last term is the repulsive potential energy between the electrons, where r_{ij} being the distance between the electrons i and j.

Now we can get the wave function and energies of a molecule from Schr$\ddot{O}$dinger equation:

$\hat{H}\Psi(q_i, q_\alpha) = E\Psi(q_i, q_\alpha)$, where q_i and q_α symbolize the electronic and nuclear coordinates, respectively. The key lies in the fact that the nuclei are much heavier than electrons: $m_\alpha \gg m_e$. Hence the electrons move much faster than the nuclei, so we can regard the nuclei to be fixed and electrons carry out their motions. Thus considering the nuclei as fixed, we eliminate the nuclear kinetic energy terms from eq (1) to obtain the Schr$\ddot{O}$dinger equation for electronic motion:

$$(\hat{H}_{el} + V_{NN})\Psi_{el} = U\ \Psi_{el} \tag{2}$$

Where the **purely electronic Hamiltonian** $\hat{H}_{el}$ is:

$$\hat{H}_{el} = \hbar^2/(2m_e) \sum_i \nabla_i^2 - \sum_\alpha \sum_i \frac{Z_\alpha e^2}{r_{i\alpha}} + \sum_i \sum_{i>j} e^2/r_{ij} \ \text{---} \tag{3}$$

The nuclear repulsive term is V_{NN} is given by

$$V_{NN} = \sum_\alpha \sum_{\beta>\alpha}(Z_\alpha Z_\beta\ e^2)/r_{\alpha\beta} \tag{4}$$

The energy U is the **electronic energy including inter-nuclear repulsion**.

The variables in the electronic Schr$\ddot{O}$dinger equation are the electronic coordinates. The quantity V_{NN} is independent of this coordinates and is constant for a given nuclear configuration. Now we can prove that the omission of a constant term from the Hamiltonian does not affect the wave function. This simply decreases each energy eigenvalue at a certain amount. Hence ,if V_{NN} is omitted from eq (2),we get

$$\hat{H}_{el}\Psi_{el} = E_{el}\Psi_{el} \tag{5}$$

Where $U = E_{el} + V_{NN}$. In this way purely electronic energy is related to the energy including inter-nuclear repulsion. Therefore, we can omit the inter-nuclear repulsion from the electronic Schrödinger equation. Then we can find E_{el} for a particular electronic configuration of the nuclei by solving eq (5). Then we calculate U ,where V_{NN} can be calculated from eq (4).

If we plot the electronic energy including nuclear repulsion for a bound state of a diatomic molecule against the nuclear distance R, we find a curve like Fig.1.At R=0, due to the inter-nuclear repulsion, U goes to infinity. The inter-nuclear separation at the minimum in this curve is called the **equilibrium inter-nuclear distance** R_e. The difference between the limiting value of U at infinite inter-nuclear separation and uts value at R_e is called the **equilibrium dissociation energy** D_e.

$$D_e \equiv U(\infty) - U(R_e) \tag{6}$$
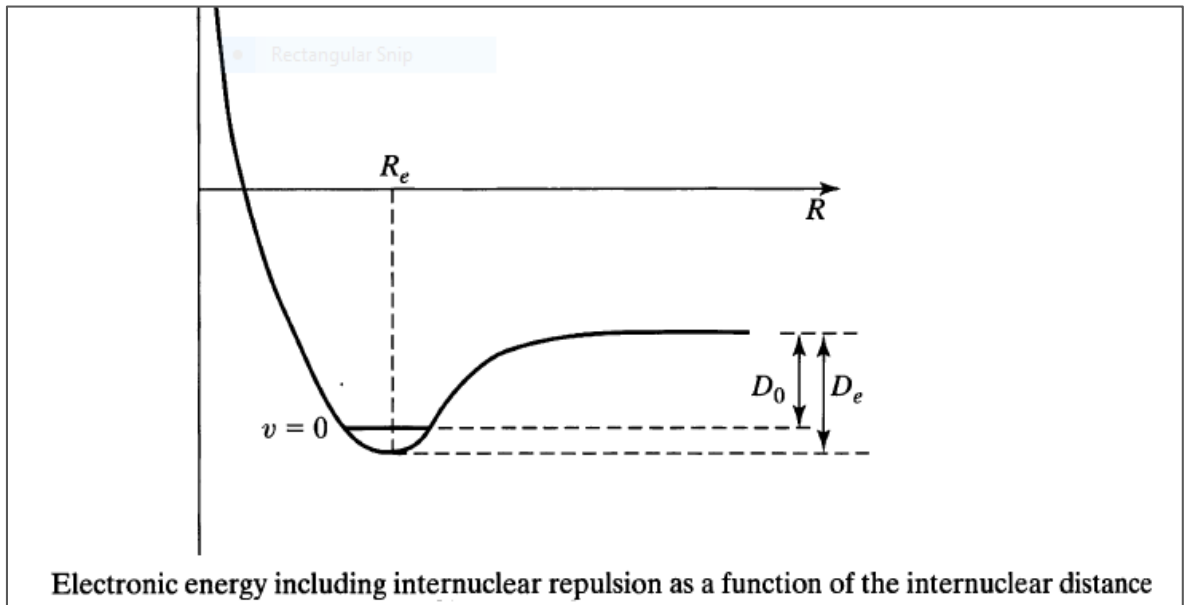
Electronic energy including internuclear repulsion as a function of the internuclear distance R for a diatomic molecule bound electronic state

Fig: 1

Here, in my report calculations are in **Atomic units**. In this case, the mass of electron m_e, $\hbar$, e' each have a numerical value 1.The ground state energy of the hydrogen atom is $(-e'^2/2a_0)$. Since $a_0 = \hbar^2/m_e e'^2$,the numerical value of a_0 in atomic unit is 1. Then the ground state energy of Hydrogen atom is (-1/2), if the nuclear motion is neglected. The atomic unit of energy,e'^2/a_0, is called the **Hartree** . 1 hartree= e'^2/a_0 = 27.2114 eV (e'=e/$\sqrt{4\pi\varepsilon_0}$)

THE HYDROGEN MOLECULAR ION:

We now begin our study of the electronic energy of molecules. We shall use the Born-Oppenheimer approximation, keeping the nuclei fixed. Now, we solve the Schr$\ddot{O}$dinger equation for the motion of electrons. We shall consider H_2^+ as an isolated molecule, ignoring the inter-molecular reactions. Let us investigate whether or not this molecule possesses a bound state: i.e, Whether or not it possesses a ground state whose energy is less than that of a hydrogen atom or a free proton. According to the variation principle, we can deduce that the H_2^+ion has a bound state if we can find out any trail wave function for which the total Hamiltonian of the system has an expectation value less than that of a hydrogen atom and a free proton.

Fig :2 shows H_2^+.The nuclei are at a and b; R is the inter-nuclear distance;r_a and r_b are the distances from the electron to nuclei a and b. Since, nuclei are fixed, we have a one particle problem whose purely electronic Hamiltonian is

$$\hat{H}_{el} = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e'^2}{r_a} - \frac{e'^2}{r_b}$$

(7)

The first term is the electronic kinetic energy operator; second and third term are the attractions between the electron and nuclei. In atomic unit the purely electronic Hamiltonian for H_2^+ is

$$\hat{H}_{el} = -\tfrac{1}{2}\nabla^2 - \frac{1}{r_a} - \frac{1}{r_b}$$

(8)

Fig:2   Inter-particle distance in H_2^+
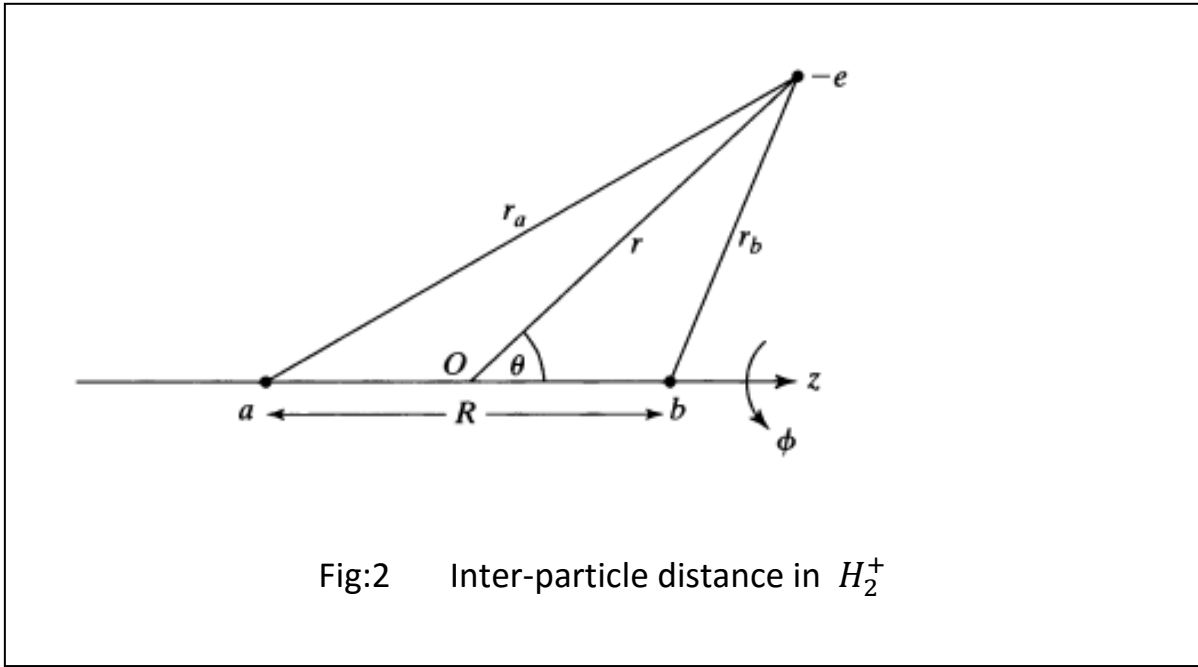
The coordinate origin is on the inter-nuclear axis, midway between the nuclei, with the z axis lying along the inter-nuclear axis. The H_2^+ electronic Schr$\ddot{O}$dinger equation is not separable in spherical coordinates. However, separation of variable is possible in *confocal elliptical coordinates* $\xi, \eta, and\ \phi$.The coordinate ϕ is the angle of rotation of the electron about the inter-nuclear(z) axis. The coordinates are defined by

$$\xi \equiv \frac{r_a + r_b}{R}, \qquad \eta \equiv \frac{r_a - r_b}{R}$$

(9)

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The range of the coordinates are

$$0 \leqslant \phi \leqslant 2\pi, \quad 1 \leqslant \xi \leqslant \infty, \quad -1 \leqslant \eta \leqslant 1$$

We put the Hamiltonian unto this coordinates. We have

$$r_a = \tfrac{1}{2}R(\xi + \eta), \qquad r_b = \tfrac{1}{2}R(\xi - \eta) \tag{10}$$

Now we will discuss it qualitatively. For the Hydrogen atom, Hamiltonian has spherical symmetry, the electronic angular momentum operators $\hat{L}^2$ and $\hat{L}_z$ both commute with $\hat{H}$ .The H_2^+ ion does not have a spherical symmetry. We can found that $[\hat{L}^2, \hat{H}_{el}] \neq 0$. However H_2^+ have axial symmetry, and we can found that $\hat{L}_z$ commutes with $\hat{H}_{el}$ of H_2^+. As we know that commutating operators have common eigen-functions so that electronic wave function will be the eigen-function of $\hat{L}_z$ .The eigen-function of $\hat{L}_z$ are

$$\text{constant} \cdot (2\pi)^{-1/2} e^{im\phi} , \qquad \text{where} \quad m = 0, \pm 1, \pm 2, \pm 3, \dots \tag{11}$$

The z component of electronic orbital angular momentum in H_2^+ is $m\hbar$. The total electronic orbital angular momentum is not a constant for H_2^+.

We now pick up a separation of variables:

$$\psi_{el} = L(\xi)M(\eta)(2\pi)^{-1/2}e^{im\phi}$$

<div align="right">(12)</div>

Now we substitute eq (12) into the eq: $\hat{H}_{el}\Psi_{el}=E_{el}\Psi_{el}$, in which variables are separable. Here we can get two differential equations, one for $L(\xi)$, and one for $M(\eta)$. Solving these equations we can find the condition for which Ψ_{el} will be well-behaved. For each fixed value of R, only certain values of E_{el} are allowed; this gives a set of different electronic states.

For the ground electronic state, the quantum no m is zero. At R=∞ the H_2^+ ground state is dissociated into a proton and a ground state hydrogen atom; hence $E_{el}(\infty)$=-1/2 hartree. At R=0, the two protons have come together to form the He^+ ion with ground state energy: $-\frac{1}{2}(2)^2$ hartrees = - 2 hartrees. Addition to the inter-nuclear repulsion 1/R (in atomic units) to $E_{el}(R)$ gives the U(R) potential energy curve for nuclear motion.

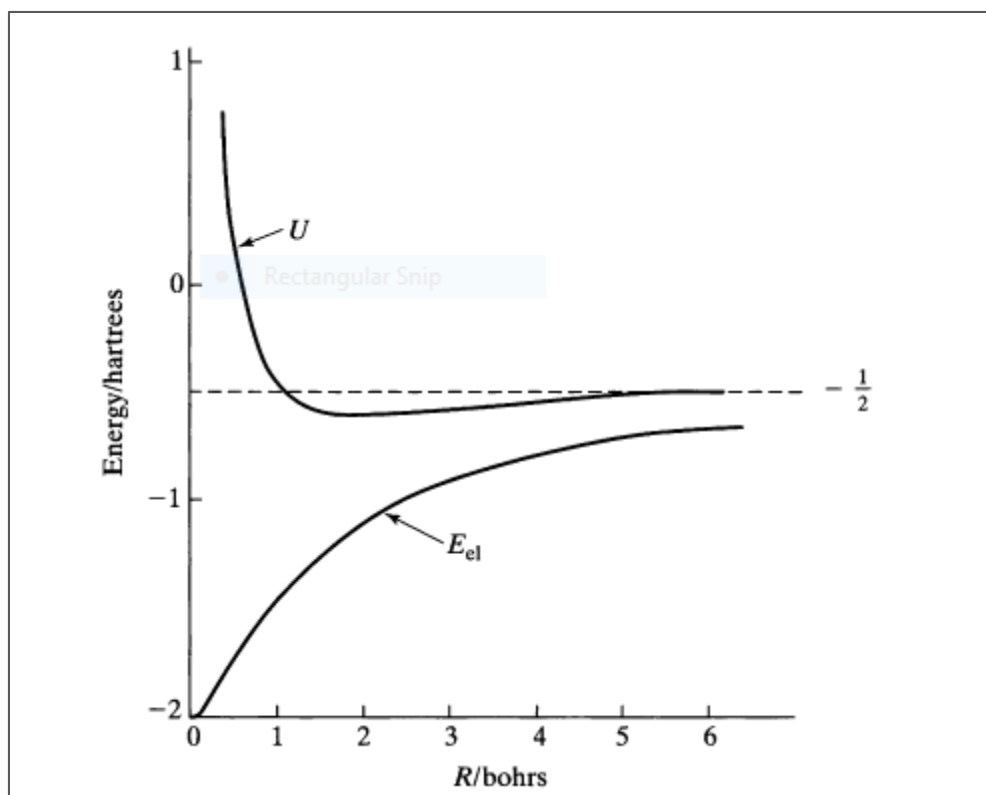We have plotted the (electronic energy /hartree) vs R and got the curve like this.

Fig : 3   Electronic energy U for the H_2^+ ground state

The U(R) curve is found to have minimum value at R_e= 1.9972 bohrs = 1.06 Å, which indicates

that H_2^+ ground electronic state is a stable bound state. The calculated value of E_{el} at 1.9972

bohrs is -1.1033 hartrees. Addition of the inter-nuclear repulsion (1/R) gives U(R) =-0.6026

hartrees. The ground state binding energy is thus D_e = 0.1026 hartree = 2.79 eV. Fig : 4 shows

the U(R) curves for the first several electronic energy levels of H_2^+ ,as found by solving the

electronic Schr$\ddot{O}$dinger equation.
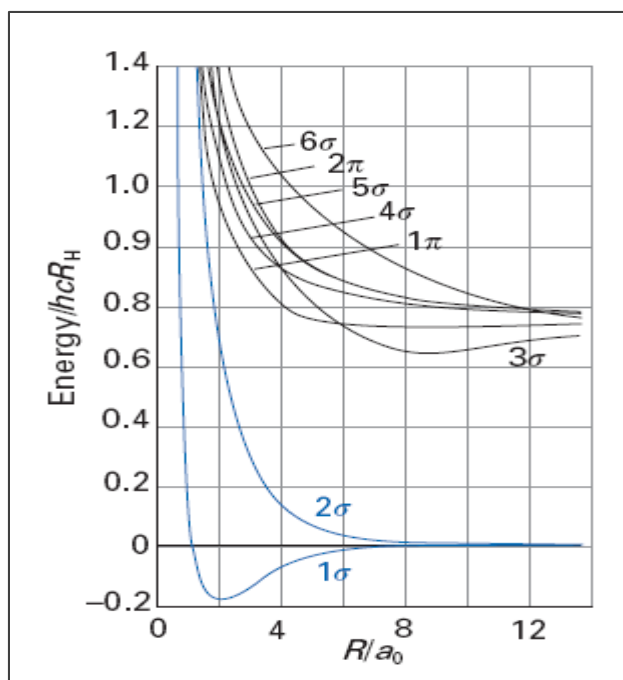
Fig:4   U(R) curves for several electronic states

The origin of the lower energy state can be discovered by examining the form of wave functions. Fig :5 shows that two molecular orbitals of lowest energy as contour diagrams for various values of R. The striking difference is that the higher energy orbitals (denoted as 2σ) has an inter-nuclear node whereas the lower energy orbital (denoted as 1σ) does not. There is greater probability of finding the electron in the inter-nuclear region if it is described by the wave function 1σ than if it is described by 2σ.
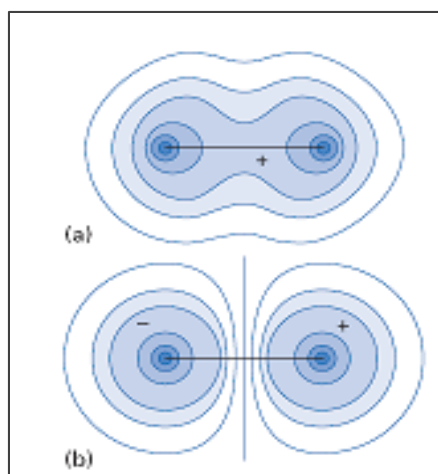
Fig: 5   contour diagram of the (a) bonding and (b) antibonding orbitals

CALCULATION OF ENERGY EXPRESSION:

The H_2^+ ground state has m=0.Now we shall use a more systematic approach based on the idea of a molecule as being formed from the interaction of atoms.

In Fig : 2 when the electron is near the nucleus a then nucleus b is so far away that we we have a hydrogen atom with origin at a. Thus when r_a is small ,for Z=1,and the Bohr radius has the numerical value 1 in atomic units, then the wave function will be like

$$\pi^{-1/2}e^{-r_a}$$

(13)

Similarly, when the electron is near the nucleus b then the ground state wave function will be like this

$$\pi^{-1/2}e^{-r_b}$$

(14)

Then the variation function will be

$$c_1\pi^{-1/2}e^{-r_a} + c_2\pi^{-1/2}e^{-r_b}$$

(15)

Where $c_1 \ and \ c_2$ are variational parameters. When the electron is near the nucleus a, the first term predominates and it looks like eq (13).

Now we will improve the trial function. If we consider the limiting behavior of the H_2^+ ground state electronic wave function as R goes to zero; then in this limit we get He^+ ion(Z=2), which has the ground state wave function

$$2^{3/2}\pi^{-1/2}e^{-2r}$$

(16)

In Fig : 2 we see that as R goes to zero, both r_a and r_b approaches to r. Hence the trial function goes to

$$(c_1 + c_2)\pi^{-1/2}e^{-r}.$$

(17)

Comparing with eq (16) we see that our trial function misbehaves at R=0; it should go to e^{-2r}, not e^{-r}. We can fix this by multiplying r_a and r_b in the exponentials by a variational parameter k, which will be some function of R; **k=k(R)** . For the correct limiting behavior at R=0 and R=∞,we have **k(0)=2** and **k(∞)=1** for the ground electronic state. We thus take the trial function

$$\phi = c_a 1s_a + c_b 1s_b$$

(18)

Where c's are the variational parameters and

$$1s_a = k^{3/2}\pi^{-1/2}e^{-kr_a}, \qquad 1s_b = k^{3/2}\pi^{-1/2}e^{-kr_b}$$

(19)

The factor $k^{3/2}$ normalizes $1s_a$ and $1s_b$. The molecular orbital function is a **linear combination of atomic orbitals**, an **LCMO-MO.** For the trial function the secular equation is

$$\begin{vmatrix} H_{aa} - WS_{aa} & H_{ab} - WS_{ab} \\ H_{ba} - WS_{ba} & H_{bb} - WS_{bb} \end{vmatrix} = 0$$

(20)

The integrals H_{aa} and H_{bb} are

$$H_{aa} = \int 1s_a^* \hat{H} 1s_a \, dv, \qquad H_{bb} = \int 1s_b^* \hat{H} 1s_b \, dv$$

(21)

Since, $\hat{H}$ is Hermitian and the functions in these are real, we conclude that $H_{ab} = H_{ba}$

Since, $1s_a$ and $1s_b$ are normalized and real, we have

$$S_{aa} = \int 1s_a^* 1s_a \, dv = 1 = S_{bb}$$

$$S_{ab} = \int 1s_a^* 1s_b \, dv = S_{ba}$$

(22)

S_{ab} is the **Overlap integral**.

The secular equation becomes

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

$$W_1 = \frac{H_{aa} + H_{ab}}{1 + S_{ab}} \quad W_2 = \frac{H_{aa} - H_{ab}}{1 - S_{ab}} \tag{23}$$

We now find the coefficients in eq (18) for each of the roots of the secular equation. We have

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

$$\tag{24}$$

Substituting in W_1 from eq (23), we get

$$c_a/c_b = 1$$
$$\phi_1 = c_a(1s_a + 1s_b)$$

$$\tag{25}$$

We fix c_a by normalization:

$$|c_a|^2 \int (1s_a^2 + 1s_b^2 + 2 \cdot 1s_a 1s_b)\, dv = 1$$

$$|c_a| = \frac{1}{(2 + 2S_{ab})^{1/2}}$$

$$\tag{26}$$

The normalized trial function corresponding to the energy W_1 is thus

$$\phi_1 = \frac{1s_a + 1s_b}{\sqrt{2}(1 + S_{ab})^{1/2}} \tag{27}$$

For the root W_2, we find $C_b = -C_a$

$$\phi_2 = \frac{1S_a - 1S_b}{\sqrt{2}(1-S_{ab})^{1/2}}$$ (28)

Equations (27) and (28) come as no surprise. Since the nuclei are identical, we expect $|\Phi|^2$ to

remain unchanged on interchanging a and b; on other words we expect no polarity in the bond.

Substituting the values of the integrals into eq (23), we get

$$W_{1,2} = -\frac{1}{2}k^2 + \frac{k^2 - k - R^{-1} + R^{-1}(1+kR)e^{-2kR} \pm k(k-2)(1+kR)e^{-kR}}{1 \pm e^{-kR}(1+kR+k^2R^2/3)}$$

(29)

Where the upper sign is for W_1. W_1 and W_2 are approximations to the purely electronic energy

E_{el}, and 1/R must be added to $W_{1,2}$ to get $U_{1,2}(R)$.

Our final task is to vary the parameter k at many fixed values of R to minimize first $U_1(R)$ and

then $U_2(R)$. We have done this numerically. We vary the k value from 1 to 2, and R value from

0.2 to 14. Then we got a minimum value of W_1 and W_2 for a particular k value where R is

constant. Then we have added (1/R)to W_1 and W_2 to get the value of U. After that, we have

plotted (U/hartree) vs R value; and got the following curve (which is exactly same as Fig :4 for

1σ *and* 2σ state).
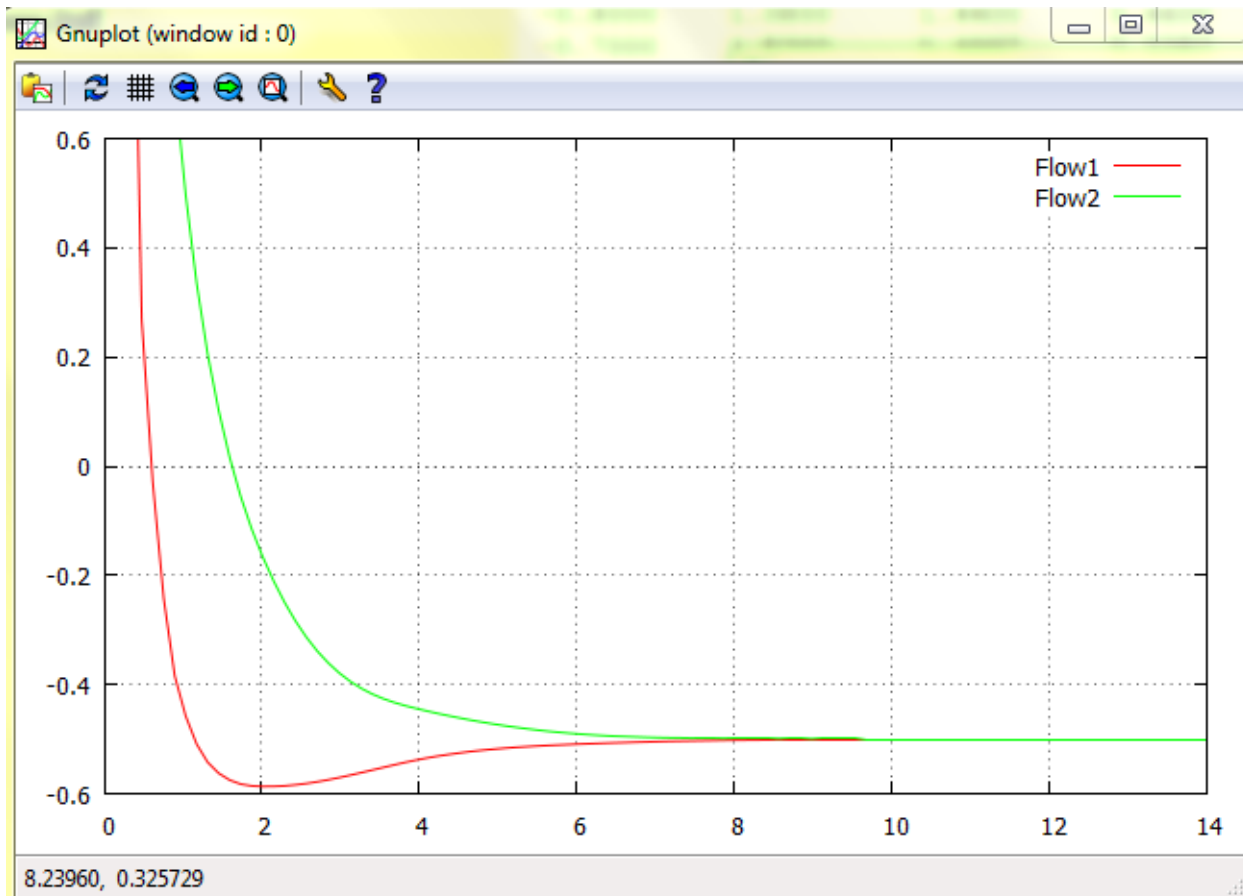
Here we have calculated the value of U(R)= 16.3402eV for R=2.00 bohr (True value 15.96eV)

and ground state binding energy D_e = 0.103 hartree = 2.8027 eV, where the exact value is D_e = 0.1026 hartree = 2.79 eV.

So,our estimation is almost same to the theoretical value.

The results are that, for the $1s_a + 1s_b$, k increases almost monotonically from 1 to 0.4 as R

decreases from ∞ to zero. For the $1S_a - 1S_b$,k decreases almost monotonically from 1 to

2,whereas R decreases from ∞ to zero.

AN EMPERICAL FORMULA:

Here, we are trying to introduce an empirical formula in terms of k and R , where k varies from

1 to 2, and R varies from ∞ to zero.

$$k(R) = 1+b*e^{-R/c} \tag{30}$$

Now we substitute this expression of k into eq (29). So, we have got the expression of $W_{1,2}$ in

terms of R only. Then added the (1/R) term to get the U value.

We have fitted the eq (30) with the following data set via column 1 and 2

k	R	U
1.95	0.2	3.07175
1.85	0.4	0.70131
1.75	0.6	0.00018
1.65	0.8	-0.29631
1.55	1.0	-0.44093
1.45	1.2	-0.51587

|		
1.40	1.4	-0.55530
1.35	1.6	-0.57516
1.30	1.8	-0.58400
1.25	2.0	-0.58643
1.05	4.0	-0.53706
1.0	6.0	-0.50906
1.0	8.0	-0.50173
1.0	10.0	-0.50030
1.0	12.0	-0.50000
1.0	14.0	-0.50000
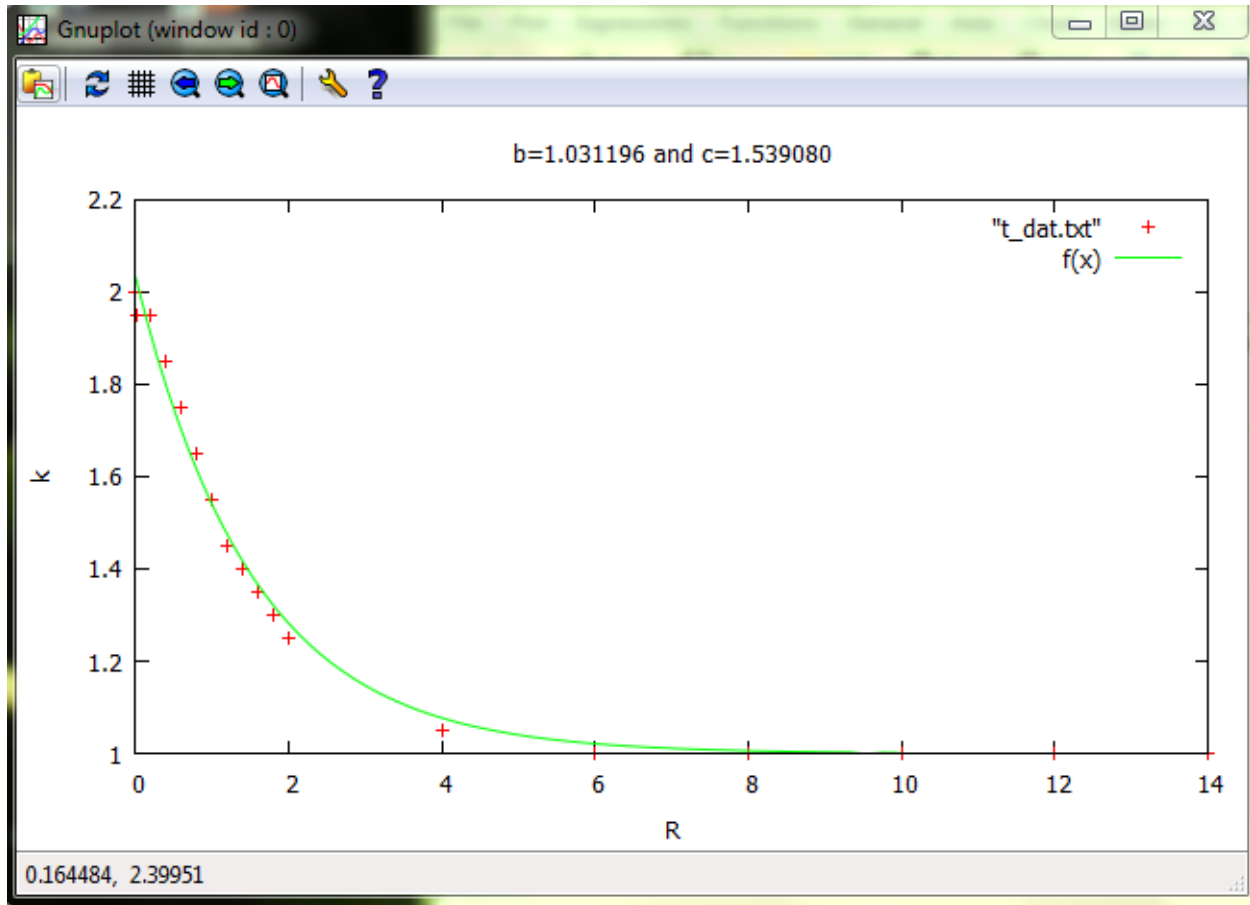
Where we have got **b=1.031196** and **c=1.539080**

At R= ∞ , k(R) = 1 and at R = 0 , k(R) =1+1.031196 = 2.031196 ~ 2.00

Now our task is to plot the probability density of the wave function. The H_2^+ ground state probability density is then

$$\phi_1^2 = \frac{(1s_a + 1s_b)^2}{2(1+S_{ab})} = \frac{k^3 \pi^{-1}(e^{-k|z-a|} + e^{-k|z-b|})^2}{2(1+S_{ab})} \tag{31}$$

(From eq (19))

Putting R=2.00 and k =1.24 , we find that S_{ab}= 0.46. At 2-D x=y=0 then if we plot ϕ_1^2 then it is like this (we have considered a=1 and b=2)
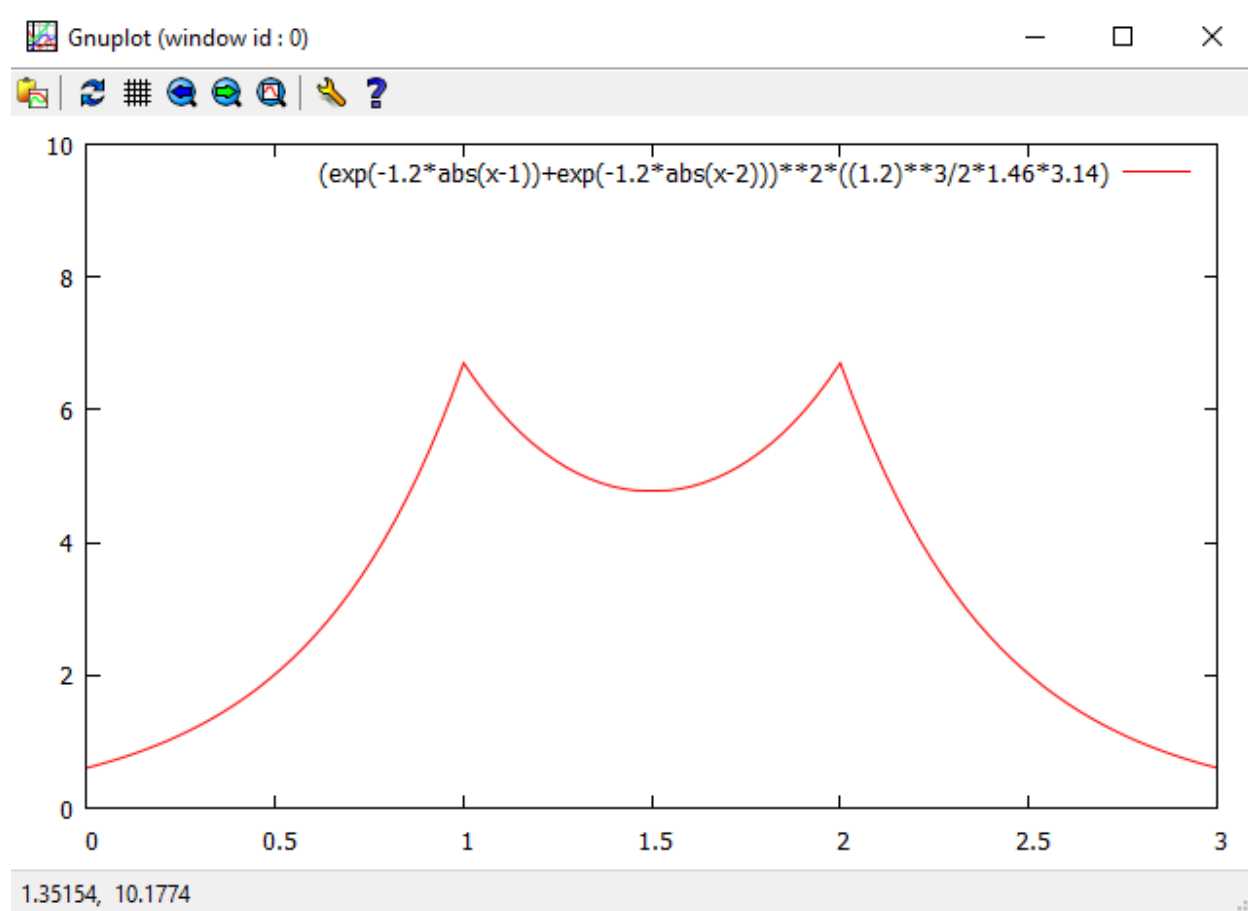
This is the plot for probability density along the inter-nuclear axis for the LCAO-MO function for N $(1s_a + 1s_b)$

The σ_u^*1strial function $1S_a - 1S_b$is proportional to $e^{-r_a} - e^{-r_b}$. On a plane perpendicular to the inter-nuclear axis and midway between the nuclei, we have$r_a = r_b$, so this plane is a nodal plane for the σ_u^*1sfunction. We do not build up a charge between the nuclei for this state, and

the U(R) curve has no minimum. We say that the $\sigma_g 1s$ orbital is **bonding** and $\sigma_u^* 1s$ orbital is

antibonding.
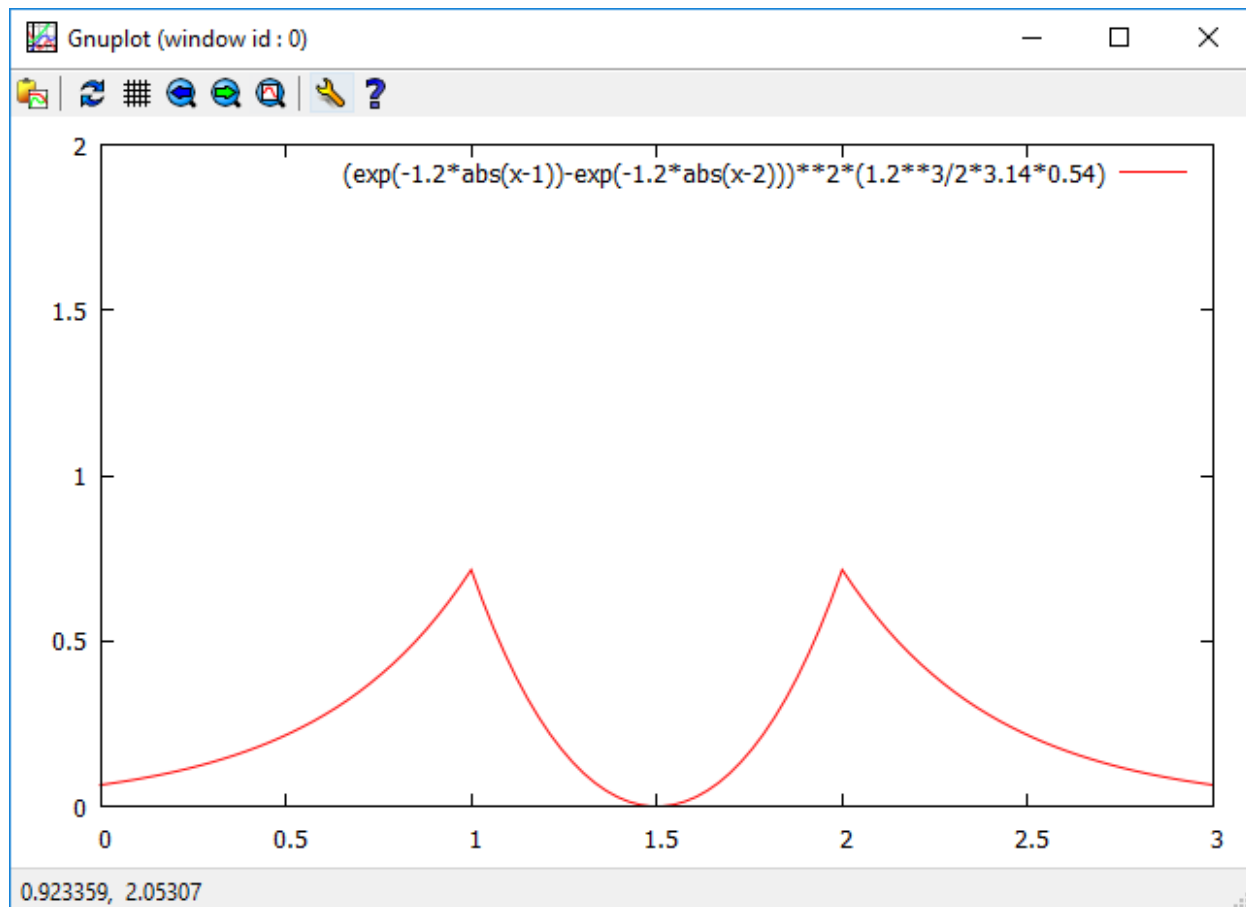
Probability density along the inter-nuclear axis for the LCAO-MO function

And that's all, what I have studied on hydrogen molecular ion till now.

❖ <u>CONCLUSION:</u>

Here, in my project report, I have plotted the electronic energy vs R for the ground states and first excited states. And it is almost same as we get it from the theoretical discussions.My calculated ground sate U(R) curve has a minimum at 2.00 bohrs, where the true value is also 2.00 bohrs and has U(R_e) = -15.96 eV . Our predicted value of dissociation energy D_e = 2.36 eV. Where the true value is 2.79 eV.

Then I have plotted the probability density for the two LCAO-MO functions and got the curves which almost satisfies my discussions.

And till now, that's it. Here I have learnt just an introduction about H_2^+ through this project and there is a vast amount of studyin front of me. I wish to continue this as far as possible.

❖ <u>ACKNOWLEDGEMENT :</u>

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