

Plots of the amplitude of the bonding and antibonding orbitals formed by the overlap of two H1s orbitals.

by

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Goal of these exercises:

To introduce students to the Molecular Orbital Theory by use of the simplest molecule, the one-electron hydrogen molecule ion "H₂⁺". The essential features of bonding of this molecule can be used as a guide to the structures of more complex molecules.

Audience: Students enrolled in Physical Chemistry at the junior or senior college level.

Prerequisites:

1. Basic knowledge of Mathcads functions; in particular the manipulation of equations and graphs.
2. Basic knowledge of the molecular orbital theory.

Objectives:

1. Gain familiarity with functions related to the linear combination of atomic orbitals and molecular orbitals.
2. Explain how variation in the distance between the hydrogen atoms affects the shape of the contour diagram, and the consequent bonding energy.

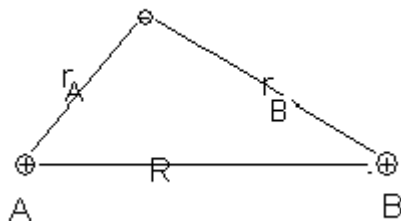
References:

1. Barrow, Gordon M. Physical Chemistry; 5th ed. New York: McGraw-Hill, (1988).
2. Atkins, P.W. Physical Chemistry; 5th ed. New York: W.H. Freeman and Company, (1994).
3. Karplus, Martin, and Porter, Richard N. Atoms & Molecules: An Introduction for Students of Physical Chemistry. New York: W.A. Benjamin, Inc., (1970).

Note: The use of units was avoided due to the complexities of Mathcad. All dimensions are related to picometers.

I. The trial molecular orbital wavefunction.

Figure 1 suggest that to construct a molecular orbital we should use the atomic 1s-orbital wavefunctions for both hydrogen atom A and hydrogen atom B. As the figure also suggest, we will define r_A and r_B as the distances of the single electron from atoms (protons) A and B. Rather than designating the wavefunction as $\Psi_{1s}(A)$ we have just used $1S_A$.



Therefore a good trial wavefunction for the bonding MO is $\Psi_b = 1/2(1S_A + 1S_B)$ and for the antibonding MO, $\Psi_a = 1/2(1S_A - 1S_B)$. However we must first normalize these functions to insure that they will behave properly.

II. Normalization of ϕ at the limit of $r_{AB} = \infty$.

$$1 \cdot S_A := \frac{1}{\sqrt{\pi}} \cdot \left(\frac{1}{a_0}\right)^{\frac{3}{2}} \cdot e^{-\frac{r_A}{a_0}} \quad 1 \cdot S_B = \frac{1}{\sqrt{\pi}} \cdot \left(\frac{1}{a_0}\right)^{\frac{3}{2}} \cdot e^{-\frac{r_B}{a_0}} \quad a_0 := 52.9 \text{ picometers}$$

With the atomic orbitals defined above we take the all-space integral of the bonding MO and set equal to 1 to normalize. N is the normalization constant.

$$N^2 \cdot \left(\int \Psi_b^2 d\tau \right) = 1$$

We use the symbolic "=" for these equations because we are not asking Mathcad to perform any computations. We are merely making declarations.

$$\int \Psi_b^2 d\tau = \int (1 \cdot S_A + 1 \cdot S_B)^2 d\tau$$

$$\int \Psi_b^2 d\tau = \int (1 \cdot S_A)^2 d\tau + \int (1 \cdot S_B)^2 d\tau + \int 1 \cdot S_A \cdot 1 \cdot S_B d\tau$$

The third term on the right above is the terrifying overlap integral, S. In the limit as R approaches infinity, there is no overlap so S is zero. Since the 1s atomic orbitals were normalized, the first two terms of the above equations are just one (1). Therefore,

$$\int \Psi_b^2 d\tau = 1 + 1 + 0 \quad \text{and} \quad N^2 = 1/2.$$

The normalized bonding MO is: $\Psi_b = \frac{1}{\sqrt{2}} \cdot (1 \cdot S_A + 1 \cdot S_B)$

Next, normalize Ψ_a for the negative linear combination (antibonding MO) to get:

$$\Psi_a = \frac{1}{\sqrt{2}} \cdot (1 \cdot S_A - 1 \cdot S_B)$$

At this point it is easy to determine that the normalization constants for the respective MOs at distances where overlap will occur are:

$$N_1(\text{bonding}) = \left[\frac{1}{2 \cdot (1 + S)} \right]^{\frac{1}{2}} \quad \text{and} \quad N_2(\text{antibonding}) = \left[\frac{1}{2 \cdot (1 - S)} \right]^{\frac{1}{2}}$$

III. Plot the amplitude function.

Plot of the amplitude function for H₂⁺: As a function of position along the x-axis, Atom-A is at zero and atom-B is at 106 pm. The index "i" runs 0 to 400 but in order to get negative values to plot on the x-axis, we used an offset of 253 (200 plus half of the bond distance) so that the zero point of the plot is midway between the atomic centers.

Bonding Molecular Orbital

$$i := 0..400 \quad a_0 := 52.9 \quad R := 106$$

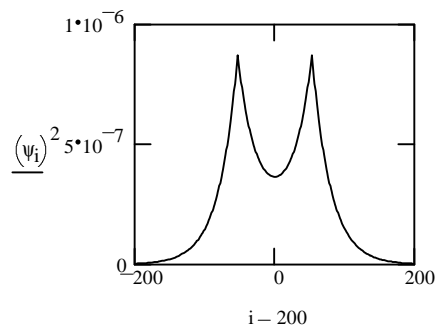
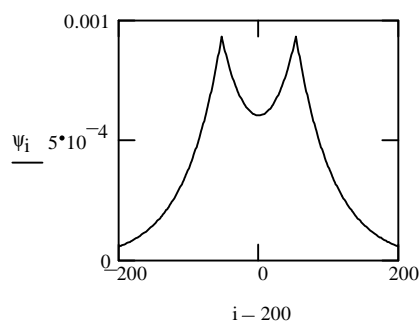
$$S := \left[1 + \frac{R}{a_0} + \frac{1}{3} \cdot \left(\frac{R}{a_0} \right)^2 \right] \cdot e^{-\frac{R}{a_0}} \quad \text{(The overlap integral see ref. 1)}$$

$$N_1 := \left[\frac{1}{2 \cdot (1 + S)} \right]^{\frac{1}{2}} \quad \text{The normalization constant}$$

$$\psi_{A_i} := \left(\frac{1}{\pi \cdot a_0^3} \right)^{\frac{1}{2}} \cdot e^{-\frac{|i-253|}{a_0}}$$

$$\psi_{B_i} := \left(\frac{1}{\pi \cdot a_0^3} \right)^{\frac{1}{2}} \cdot e^{-\frac{|i-253+R|}{a_0}}$$

$$\psi_i := N_1 \cdot (\psi_{A_i} + \psi_{B_i})$$



What area of the graph relates to the integration over $\{\psi_{1s}(A)\}^2$; $\{\psi_{1s}(B)\}^2$?

What area of the graph relates to the overlap integral (S), $2\psi_{1s}(A)\psi_{1s}(B)$?

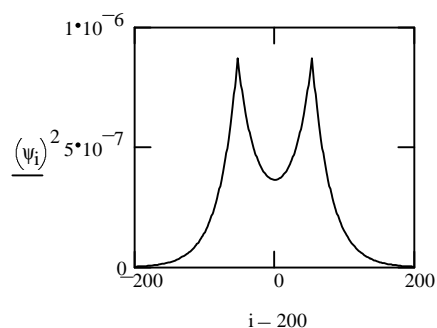
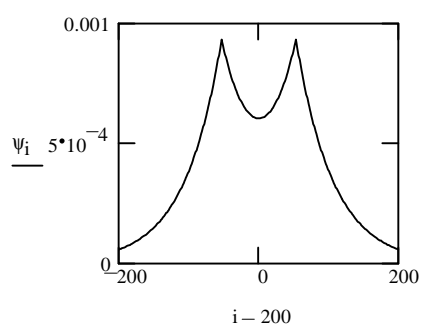
The overlap density represents the probability of finding an electron in the internuclear region above what it would be if it were confined to one of the atoms. The electron is free to move from one nucleus to the other.

How does the probability of finding an electron between the nuclei change at various values of R?

Manipulate the graphs below by changing the value of R.

$$R := 106 \quad S := \left[1 + \frac{R}{a_0} + \frac{1}{3} \cdot \left(\frac{R}{a_0} \right)^2 \right] \cdot e^{-\frac{R}{a_0}} \quad N_1 := \left[\frac{1}{2 \cdot (1 + S)} \right]^{\frac{1}{2}}$$

$$\psi_{A_i} := \left(\frac{1}{\pi a_0^3} \right)^{\frac{1}{2}} \cdot e^{-\frac{|i-253|}{a_0}} \quad \psi_{B_i} := \left(\frac{1}{\pi a_0^3} \right)^{\frac{1}{2}} \cdot e^{-\frac{|(i-253)+R|}{a_0}} \quad \psi_i := N_1 \cdot (\psi_{A_i} + \psi_{B_i})$$



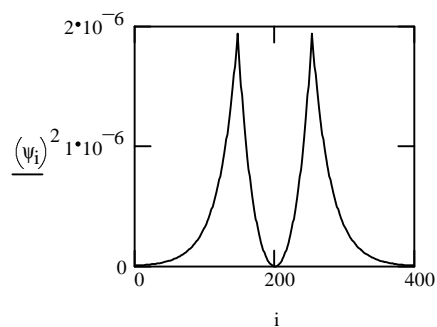
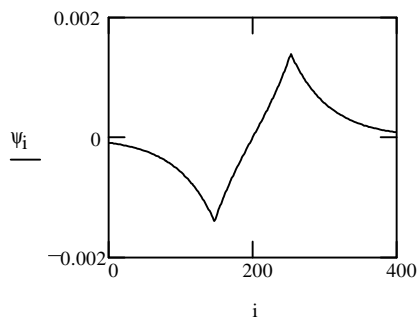
Antibonding Molecular Orbital

$$i := 0..400 \quad a_0 := 52.9 \quad R := 106$$

$$S := \left[1 + \frac{R}{a_0} + \frac{1}{3} \cdot \left(\frac{R}{a_0} \right)^2 \right] \cdot e^{-\frac{R}{a_0}} \quad N_2 := \left[\frac{1}{2 \cdot (1 - S)} \right]^{\frac{1}{2}}$$

$$\psi_{A_i} := \left(\frac{1}{\pi a_0^3} \right)^{\frac{1}{2}} \cdot e^{-\frac{|i-253|}{a_0}} \quad \psi_{B_i} := \left(\frac{1}{\pi a_0^3} \right)^{\frac{1}{2}} \cdot e^{-\frac{|(i-253)+R|}{a_0}}$$

$$\psi_i := N_2 \cdot (\psi_{A_i} - \psi_{B_i})$$



Does the energy of the σ_{1s}^* orbital increase or decrease as R decreases from large values?

How does the probability of finding an electron between the nuclei change at various values of R ?

Manipulate the graphs below by changing the value of R .

$$R := 106$$

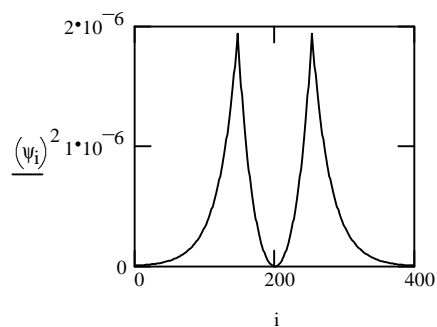
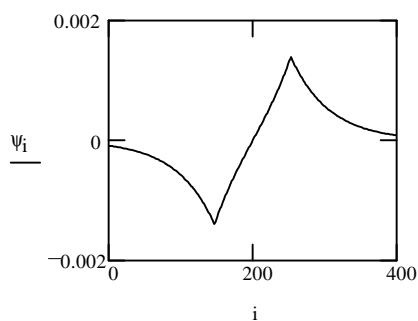
$$S := \left[1 + \frac{R}{a_0} + \frac{1}{3} \cdot \left(\frac{R}{a_0} \right)^2 \right] \cdot e^{-\frac{R}{a_0}}$$

$$N_2 := \left[\frac{1}{2 \cdot (1 - S)} \right]^{\frac{1}{2}}$$

$$\psi_{A_i} := \left(\frac{1}{\pi a_0^3} \right)^{\frac{1}{2}} \cdot e^{-\frac{|i - 253|}{a_0}}$$

$$\psi_{B_i} := \left(\frac{1}{\pi a_0^3} \right)^{\frac{1}{2}} \cdot e^{-\frac{|i - 253 + R|}{a_0}}$$

$$\psi_i := N_2 \cdot (\psi_{A_i} - \psi_{B_i})$$



Three dimensional plots of the amplitude functions:

$$pm := S \cdot 10^{\left[12 \cdot \frac{|R|}{a_0} + \frac{1}{3} \cdot \left(\frac{|R|}{a_0} \right)^2 \right]} \cdot e^{-\frac{|R|}{a_0}} \quad a_0 := 52.9 \quad i := 1..20 \quad j := 1..20$$

$$R := 2 \cdot \text{FRAME} + 100$$

$$n := 1 \quad Z := 1 \quad N := \left[\frac{1}{2 \cdot (1 + S)} \right]^{\frac{1}{2}}$$

$$r_{A_{i,j}} := \left[a_0 \cdot \left[(i - 10)^2 + \left(j - 5 + \frac{R - 100}{10} \right)^2 \right]^{\frac{1}{2}} \right]$$

$$r_{B_{i,j}} := \left[a_0 \cdot \left[(i - 10)^2 + \left(j - 15 - \frac{R - 100}{50} \right)^2 \right]^{\frac{1}{2}} \right]$$

$$\Psi_{1sA_{i,j}} := \left(\frac{1}{\pi \cdot a_0^3} \right)^{\frac{1}{2}} \cdot e^{-\frac{r_{A_{i,j}}}{a_0}}$$

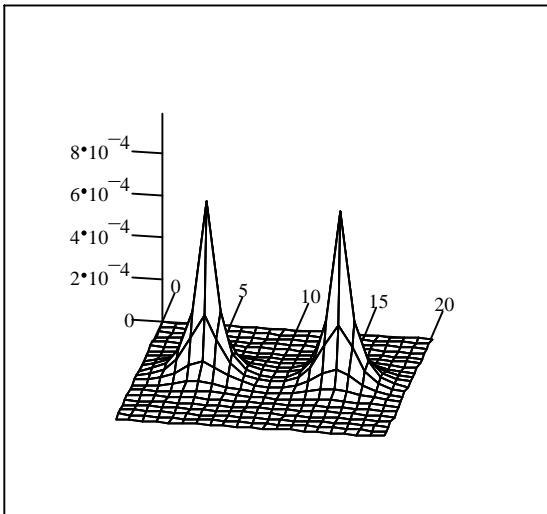
$$\Psi_{1sB_{i,j}} := \left(\frac{1}{\pi \cdot a_0^3} \right)^{\frac{1}{2}} \cdot e^{-\frac{r_{B_{i,j}}}{a_0}}$$

Bonding Molecular Orbital

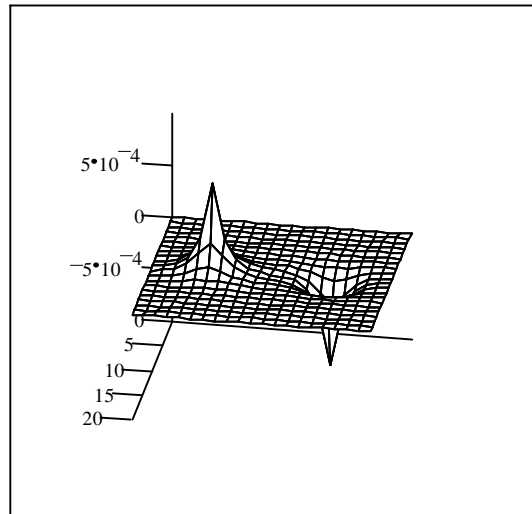
$$\Psi_{b_{i,j}} := N \cdot (\Psi_{1sA_{i,j}} + \Psi_{1sB_{i,j}})$$

$$\Psi_{a_{i,j}} := N \cdot (\Psi_{1sA_{i,j}} - \Psi_{1sB_{i,j}})$$

$$N := \left[\frac{1}{2 \cdot (1 - S)} \right]^{\frac{1}{2}}$$



Ψ_b



Ψ_a

III. Calculation of the Bonding Energy

$$a_0 := 5.29177 \cdot 10^{-11} \quad r := 2.30711 \cdot 10^{-28} \quad \frac{-e^2}{4 \pi \epsilon_0} = \text{repulsion} = r$$

$$\rho := 0.1, 0.2 \dots 10 \quad N := 6.023 \cdot 10^{23}$$

The V_{aa} term represents an integral that gives an energy contribution that is negative and its value depends on the coulombic attraction between an electron in the atomic orbital centered on A and the positive charge of nucleus A.

The V_{ab} term also represents an integral that gives an energy contribution that is negative and its value depends on the coulombic attraction between the positive charge of one nucleus and the electron distribution that is based on both the 1Sa and 1Sb atomic orbitals.

See reference 1 for further information concerning the terms V_{aa} and V_{ab} .

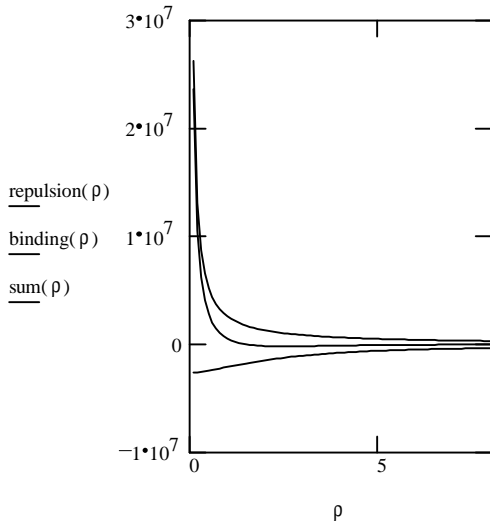
$$S(\rho) := e^{-\rho} \cdot \left(1 + \rho + \frac{\rho^2}{3} \right) \quad \text{repulsion}(\rho) := \frac{N \cdot r}{\rho \cdot a_0}$$

$$V_{aa}(\rho) := \frac{-N \cdot r}{a_0} \cdot \left[\frac{1}{\rho} - e^{-2 \cdot \rho} \cdot \left(1 + \frac{1}{\rho} \right) \right] \quad V_{ab}(\rho) := \frac{-N \cdot r}{a_0} \cdot \left[e^{-\rho} \cdot (1 + \rho) \right]$$

Bonding Orbital

$$\text{binding}(\rho) := \frac{V_{aa}(\rho) + V_{ab}(\rho)}{1 + S(\rho)}$$

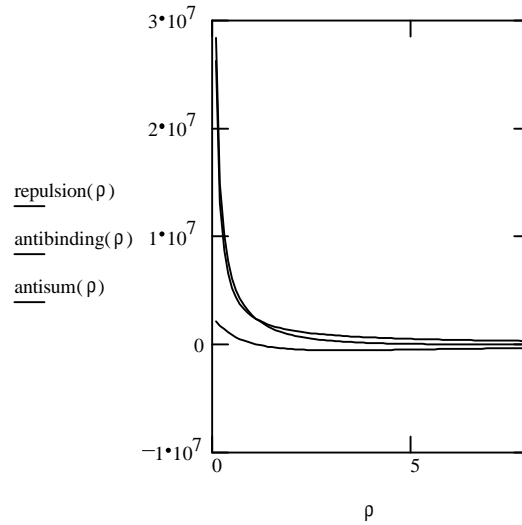
$$\text{sum}(\rho) := \text{repulsion}(\rho) + \text{binding}(\rho)$$



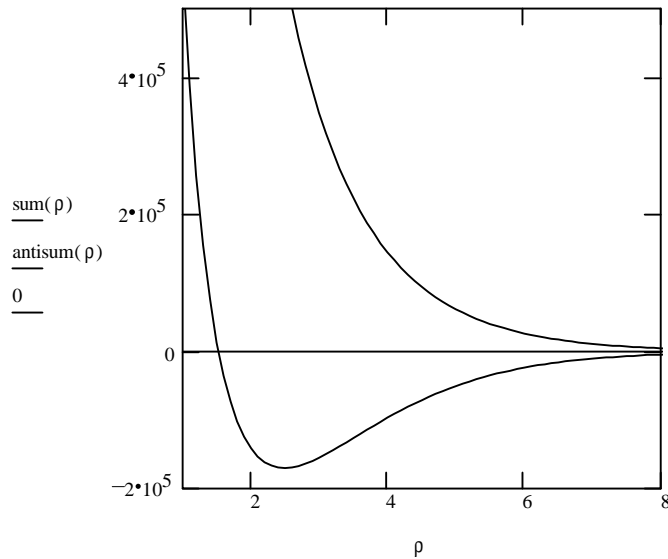
Antibonding Orbitals

$$\text{antibinding}(\rho) := \frac{V_{aa}(\rho) - V_{ab}(\rho)}{1 - S(\rho)}$$

$$\text{antisum}(\rho) := \text{repulsion}(\rho) + \text{antibinding}(\rho)$$



The following graph is focused on the sum of the binding and repulsion energies in the negative region of the binding energy "dip". The sum of the antibinding and repulsion has also been included.



Does the energy of the σ_{1s} orbital increase or decrease as R (the distance between nuclei) decreases from large values?

At very small values of R what happens to the energy of the σ_{1s} orbital?

Which expression of ψ is higher in energy the bonding or antibonding?

The V_{aa} term is negative lowering the energy. The V_{ab} term is also negative but occurs with a minus sign. How does this affect the stability of the molecule ion?