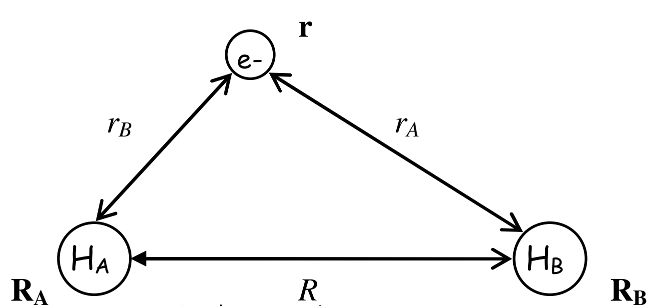
MOLECULAR ORBITAL THEORY- PART I

At this point, we have nearly completed our crash-course introduction to quantum mechanics and we're finally ready to deal with molecules. Hooray! To begin with, we are going to treat what is absolutely the simplest molecule we can imagine: H_2^+. This simple molecule will allow us to work out the basic ideas of what will become molecular orbital (MO) theory.

We set up our coordinate system as shown at right, with the electron positioned at $\mathbf{r}$, and the two nuclei positioned at points $\mathbf{R_A}$ and $\mathbf{R_B}$, at a distance R from one another. The Hamiltonian is easy to write down:



H_2^+ Coordinates

$$\hat{H} = \underbrace{-\frac{1}{2}\nabla_r^2}_{\substack{\text{Electron}\\ \text{Kinetic}\\ \text{Energy}}} \underbrace{-\frac{\nabla_A^2}{2M_A}}_{\substack{H_A\\ \text{Kinetic}\\ \text{Energy}}} \underbrace{-\frac{\nabla_B^2}{2M_B}}_{\substack{H_B\\ \text{Kinetic}\\ \text{Energy}}} \underbrace{-\frac{1}{\left|\hat{\mathbf{R}}_{\mathbf{A}}-\hat{\mathbf{r}}\right|}}_{\substack{e^--H_A\\ \text{Attraction}}} \underbrace{-\frac{1}{\left|\hat{\mathbf{R}}_{\mathbf{B}}-\hat{\mathbf{r}}\right|}}_{\substack{e^--H_B\\ \text{Attraction}}} \underbrace{+\frac{1}{\left|\hat{\mathbf{R}}_{\mathbf{A}}-\hat{\mathbf{R}}_{\mathbf{B}}\right|}}_{\substack{H_A-H_B\\ \text{Repulsion}}}$$

Now, just as was the case for atoms, we would like a picture where we can separate the electronic motion from the nuclear motion. For helium, we did this by noting that the nucleus was much heavier than the electrons and so we could approximate the center of mass coordinates of the system by placing the nucleus at the origin. For molecules, we will make a similar approximation, called the **Born-Oppenheimer approximation**. Here, we note again that the nuclei are much heavier than the electrons. As a result, they will move much more slowly than the light electrons. Thus, **from the point of view of the electrons, the nuclei are almost sitting still** and so *the moving electrons see a static field that arises from fixed nuclei*. A useful analogy here is that of gnats flying around on the back of an elephant. The elephant may be moving, but from the gnats' point of view, the elephant is always more or less sitting still. The electrons are like the gnats and the nucleus is like the elephant.

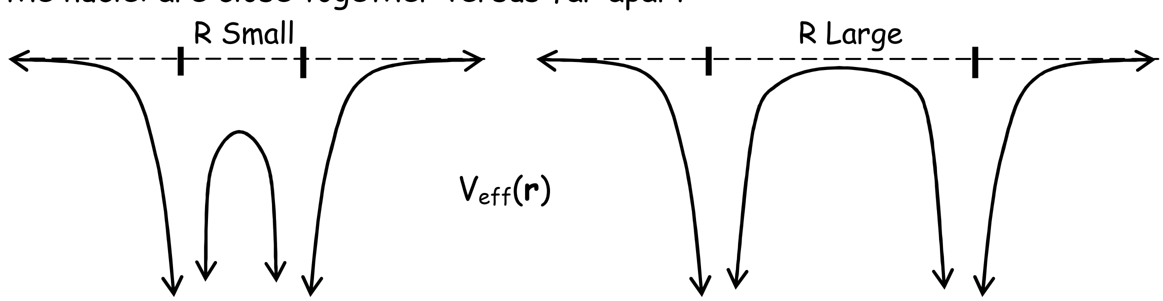
The result is that, if we are interested in the electrons, we can to a good approximation fix the nuclear positions – $\mathbf{R_A}$ and $\mathbf{R_B}$ – and just look at the motion of the electrons in a molecule. This is the B-Oppenheimer approximation, which is sometimes also called the clamped-nucleus approximation, for obvious reasons. Once the nuclei are clamped, we can make two simplifications of our Hamiltonian. First, we can neglect the kinetic energies of the nuclei because they are not moving. Second, because the nuclei are fixed, we can replace the operators $\hat{\mathbf{R}}_\mathbf{A}$ and $\hat{\mathbf{R}}_\mathbf{B}$ with the *numbers* $\mathbf{R_A}$ and $\mathbf{R_B}$. Thus, our Hamiltonian reduces to

$$\hat{H}_{el}\left(\mathbf{R_A},\mathbf{R_B}\right)=-\frac{\nabla_r^2}{2}-\frac{1}{\left|\mathbf{R_A}-\hat{\mathbf{r}}\right|}-\frac{1}{\left|\mathbf{R_B}-\hat{\mathbf{r}}\right|}+\frac{1}{\left|\mathbf{R_A}-\mathbf{R_B}\right|}$$

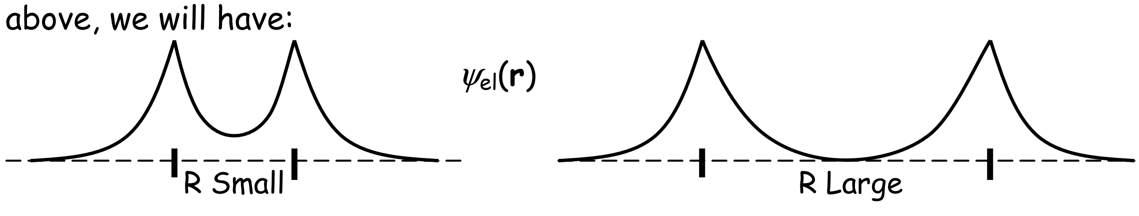
where the last term is now just a number – the electrostatic repulsion between two protons at a fixed separation. The second and third terms depends only on the position of the electron, $\mathbf{r}$, and not its momentum, so we immediately identify those as a potential and write:

$$\hat{H}_{el}\left(\mathbf{R_A},\mathbf{R_B}\right)=-\frac{\nabla_r^2}{2}+V_{eff}^{\mathbf{R_A},\mathbf{R_B}}\left(\hat{\mathbf{r}}\right)+\frac{1}{\left|\mathbf{R_A}-\mathbf{R_B}\right|}$$

This Hamiltonian now only contains operators for the electrons (hence the subscript "*el*"), but the eigenvalues of this Hamiltonian depend on the distance, R, between the two nuclei. For example, the figure below shows the difference between the effective potentials the electron "feels" when the nuclei are close together versus far apart:



Likewise, because the electron feels a different potential at each bond distance R, the wavefunction will also depend on R. In the same limits as above, we will have:



Finally, because the electron eigenfunction, ψ_{el}, depends on R then the eigenenergy of the electron, $E_{el}(R)$, will also depend on the bond length. Mechanically, then, what we have to do is solve for the electronic eigenstates, ψ_{el}, and their associated eigenvalues, $E_{el}(R)$, at many different fixed values of R. The way that these eigenvalues change with R will tell us about how the energy of the molecule changes as we stretch or shrink the bond. This is the central idea of the Born-Oppenheimer approximation, and it is really very fundamental to how chemists think about molecules. We think about classical point-like nuclei clamped at various different positions, with the quantum mechanical electrons whizzing about and gluing the nuclei together. When the nuclei move, the energy of the system changes because the energies of the electronic orbitals change as well. There are certain situations where this approximation breaks down, but for the most part the Born-Oppenheimer picture provides an extremely useful and accurate way to think about chemistry.

How are we going to solve for these eigenstates? It should be clear that looking for exact solutions is going to lead to problems in general. Even for H_2^+ the solutions are extremely complicated and for anything more complex than H_2^+exact solutions are impossible. So we have to resort to approximations again. The first thing we note is that if we look closely at our intuitive picture of the H_2^+ eigenstates above, we recognize that these molecular eigenstates look very much like the sum of the 1s atomic orbitals for the two hydrogen atoms. That is, we note that to a good approximation we should be able to write:

$$\psi_{el}\left(r\right) \approx c_1 1s_A\left(r\right) + c_2 1s_B\left(r\right)$$

where c_1 and c_2 are constants. In the common jargon, the function on the left is called a **molecular orbital** (MO), whereas the functions on the right are called atomic orbitals (AOs). If we write our MOs as sums of AOs, we are using what is called the linear combination of atomic orbitals (LCAO) approach. The challenge, in general, is to determine the "best" choices for c_1 and c_2 – for H_2^+ it looks like the best choice for the ground state will be c_1=c_2. But how can we be sure this is really the best we can do? And what about if we want something other than the ground state? Or if we want to describe a more complicated molecule like HeH^{+2}?

THE VARIATIONAL PRINCIPLE

In order to make further progress, we will use the **Variational Principle** to predict a better estimate of the ground state energy. This method is very general and its use in physical chemistry is widespread. Assume you have a Hamiltonian (such as the Helium atom) but you don't know the ground state energy E_0 and or ground state eigenfunction ϕ_0.

$$\hat{H}\phi_0 = E_0\phi_0 \quad \Rightarrow \quad \left\langle \hat{H} \right\rangle = \int \phi_0^* \hat{H}\phi_0 d\tau = \int \phi_0^* E_0 \phi_0 d\tau = E_0$$

Now, assume we have a guess, ψ, at the ground state wavefunction, which we will call the trial wavefunction. Compute the average value of the energy for the trial wavefunction:

$$E_{avg} = \frac{\int \psi^* \hat{H}\psi d\tau}{\int \psi^* \psi d\tau} \quad = \int \psi^* \hat{H}\psi d\tau \quad \text{(if } \psi \text{ normalized)}$$

the Variational Theorem tells us that $E_{avg} \geq E_0$ for any choice of the trial function ψ! This make physical sense, because the ground state energy is, by definition, the lowest possible energy, so it would be nonsense for the *average* energy to be lower.

SIDEBAR: PROOF OF VARIATIONAL THEOREM

Expand ψ (assumed normalized) as linear combination of the unknown eigenstates, ϕ_n, of the Hamiltonian:

$$\psi = \sum_n a_n \phi_n$$

Note that in practice you will not know these eigenstates. The important point is that no matter what function you choose you can always expand it in terms of the infinite set of orthonormal eigenstates of $\hat{H}$.

$$\int \psi^* \psi d\tau = \sum_{n,m} a_n^* a_m \int \phi_n^* \phi_m d\tau = \sum_{n,m} a_n^* a_m \delta_{mn} = \sum_n |a_n|^2 = 1$$

$$E_{avg} = \int \psi^* \hat{H}\psi d\tau = \sum_{n,m} a_n^* a_m \int \phi_n^* \hat{H}\phi_m d\tau = \sum_{n,m} a_n^* a_m \int \phi_n^* E_m \phi_m d\tau$$

$$= \sum_{n,m} a_n^* a_m E_m \delta_{mn} = \sum_n |a_n|^2 E_n$$

Now, subtracting the ground state energy from the average

$$E_0 = 1 \bullet E_0 = \sum_n |a_n|^2 E_0$$

$$\Rightarrow E_{avg} - E_0 = \sum_n |a_n|^2 E_n - \sum_n |a_n|^2 E_0 = \sum_n |a_n|^2 \left(E_n - E_0\right) \geq 0 \text{ since } E_n \geq E_0$$

Where, in the last line we have noted that the sum of terms that are non-negative must also be non-negative. It is important to note that the equals sign is only obtained if a_n=0 for all states that have E_n>E_0. In this situation, ψ actually is the ground state of the system (or at least one ground state, if the ground state is degenerate).

The variational method does two things for us. First, it gives us a means of comparing two different wavefunctions and telling which one is closer to the ground state – the one that has a lower average energy is the better approximation. Second, if we include parameters in our wavefunction variation gives us a means of optimizing the parameters in the following way. Assume that ψ depends on some parameters $\mathbf{c}$ – such as is the case for our LCAO wavefunction above. We'll put the parameters in brackets - $\psi[\mathbf{c}]$ – in order to differentiate them from things like positions that are inside of parenthesis - $\psi(r)$.Then the average energy will depend on these parameters:

$$E_{avg}(\mathbf{c}) = \frac{\int \psi[\mathbf{c}]^* \hat{H} \psi[\mathbf{c}]\, d\tau}{\int \psi[\mathbf{c}]^* \psi[\mathbf{c}]\, d\tau}$$

Note that, using the variational principle, **the best parameters will be the ones that minimize the energy**. Thus, the best parameters will satisfy

$$\frac{\partial E_{\text{ave}}(\mathbf{c})}{\partial c_i} = \frac{\partial}{\partial c_i} \frac{\int \psi[\mathbf{c}]^* \hat{H} \psi[\mathbf{c}]\, d\tau}{\int \psi[\mathbf{c}]^* \psi[\mathbf{c}]\, d\tau} = 0$$

Thus, we can solve for the optimal parameters without knowing anything about the exact eigenstates!

Let us apply this in the particular case of our LCAO-MO treatment of H_2^+. Our trial wavefunction is:

$$\psi_{el}[\mathbf{c}] = c_1 1s_A + c_2 1s_B$$

where $\mathbf{c}$=(c_1 c_2). We want to determine the best values of c_1 and c_2 and the variational theorem tells us we need to minimize the average energy to find the right values. First, we compute the average energy. The numerator gives:

$$\int \psi_{el}{}^* \hat{H}_{el} \psi_{el} d\tau = \int \left(c_1 1s_A + c_2 1s_B\right)^* \hat{H} \left(c_1 1s_A + c_2 1s_B\right) d\tau$$

$$= c_1{}^* c_1 \underbrace{\int 1s_A \hat{H}_{el} 1s_A d\tau}_{\equiv H_{11}} + c_1{}^* c_2 \underbrace{\int 1s_A \hat{H}_{el} 1s_B d\tau}_{\equiv H_{12}} + c_2{}^* c_1 \underbrace{\int 1s_B \hat{H}_{el} 1s_A d\tau}_{\equiv H_{21}} + c_2{}^* c_2 \underbrace{\int 1s_B \hat{H}_{el} 1s_B d\tau}_{\equiv H_{22}}$$

$$\equiv c_1{}^* H_{11} c_1 + c_1{}^* H_{12} c_2 + c_2{}^* H_{21} c_1 + c_2{}^* H_{22} c_2$$

while the normalization integral gives:

$$\int \psi_{el}{}^* \psi_{el} d\tau = \int \left(c_1 1s_A + c_2 1s_B\right)^* \left(c_1 1s_A + c_2 1s_B\right) d\tau$$

$$= c_1{}^* c_1 \underbrace{\int 1s_A 1s_A d\tau}_{\equiv S_{11}} + c_1{}^* c_2 \underbrace{\int 1s_A 1s_B d\tau}_{\equiv S_{12}} + c_2{}^* c_1 \underbrace{\int 1s_B 1s_A d\tau}_{\equiv S_{21}} + c_2{}^* c_2 \underbrace{\int 1s_B 1s_B d\tau}_{\equiv S_{22}}$$

$$\equiv c_1{}^* S_{11} c_1 + c_1{}^* S_{12} c_2 + c_2{}^* S_{21} c_1 + c_2{}^* S_{22} c_2$$

So that the average energy takes the form:

$$E_{avg}(\mathbf{c}) = \frac{c_1{}^* H_{11} c_1 + c_1{}^* H_{12} c_2 + c_2{}^* H_{21} c_1 + c_2{}^* H_{22} c_2}{c_1{}^* S_{11} c_1 + c_1{}^* S_{12} c_2 + c_2{}^* S_{21} c_1 + c_2{}^* S_{22} c_2}$$

We note that there are some simplifications we could have made to this formula: for example, since our 1s functions are normalized S_{11}=S_{22}=1. By not making these simplifications, our final expressions will be a little more general and that will help us use them in more situations.

Now, we want to minimize this average energy with respect to c_1 and c_2. Taking the derivative with respect to c_1 and setting it equal to zero [Note: when dealing with complex numbers and taking derivatives one must treat variables and their complex conjugates as independent variables. Thus d/dc_1 has no effect on c_1^*]:

$$\frac{\partial E_{avg}}{\partial c_1} = 0 = \frac{c_1{}^* H_{11} + c_2{}^* H_{21}}{c_1{}^* S_{11} c_1 + c_1{}^* S_{12} c_2 + c_2{}^* S_{21} c_1 + c_2{}^* S_{22} c_2}$$
$$- \frac{c_1{}^* H_{11} c_1 + c_1{}^* H_{12} c_2 + c_2{}^* H_{21} c_1 + c_2{}^* H_{22} c_2}{\left(c_1{}^* S_{11} c_1 + c_1{}^* S_{12} c_2 + c_2{}^* S_{21} c_1 + c_2{}^* S_{22} c_2\right)^2} \left(c_1{}^* S_{11} + c_2{}^* S_{21}\right)$$

$$\Rightarrow 0 = \left(c_1^* H_{11} + c_2^* H_{21}\right) - \frac{c_1^* H_{11} c_1 + c_1^* H_{12} c_2 + c_2^* H_{21} c_1 + c_2^* H_{22} c_2}{c_1^* S_{11} c_1 + c_1^* S_{12} c_2 + c_2^* S_{21} c_1 + c_2^* S_{22} c_2} \left(c_1^* S_{11} + c_2^* S_{21}\right)$$

$$\Rightarrow 0 = \left(c_1^* H_{11} + c_2^* H_{21}\right) - E_{avg}\left(c_1^* S_{11} + c_2^* S_{21}\right)$$

Applying the same procedure to c_2:

$$\frac{\partial E_{avg}}{\partial c_2} = 0 = \frac{c_1^* H_{12} + c_2^* H_{22}}{c_1^* S_{11} c_1 + c_1^* S_{12} c_2 + c_2^* S_{21} c_1 + c_2^* S_{22} c_2} - \frac{c_1^* H_{11} c_1 + c_1^* H_{12} c_2 + c_2^* H_{21} c_1 + c_2^* H_{22} c_2}{\left(c_1^* S_{11} c_1 + c_1^* S_{12} c_2 + c_2^* S_{21} c_1 + c_2^* S_{22} c_2\right)^2} \left(c_1^* S_{12} + c_2^* S_{22}\right)$$

$$\Rightarrow 0 = \left(c_1^* H_{12} + c_2^* H_{22}\right) - \frac{c_1^* H_{11} c_1 + c_1^* H_{12} c_2 + c_2^* H_{21} c_1 + c_2^* H_{22} c_2}{c_1^* S_{11} c_1 + c_1^* S_{12} c_2 + c_2^* S_{21} c_1 + c_2^* S_{22} c_2} \left(c_1^* S_{12} + c_2^* S_{22}\right)$$

$$\Rightarrow 0 = \left(c_1^* H_{12} + c_2^* H_{22}\right) - E_{avg}\left(c_1^* S_{12} + c_2^* S_{22}\right)$$

We notice that the expressions above look strikingly like matrix-vector operations. We can make this explicit if we define the **Hamiltonian matrix**:

$$\mathbf{H} \equiv \begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} \equiv \begin{pmatrix} \int 1s_A \hat{H}_{el} 1s_A d\tau & \int 1s_A \hat{H}_{el} 1s_B d\tau \\ \int 1s_B \hat{H}_{el} 1s_A d\tau & \int 1s_B \hat{H}_{el} 1s_B d\tau \end{pmatrix}$$

and the **Overlap matrix**:

$$\mathbf{S} \equiv \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix} \equiv \begin{pmatrix} \int 1s_A 1s_A d\tau & \int 1s_A 1s_B d\tau \\ \int 1s_B 1s_A d\tau & \int 1s_B 1s_B d\tau \end{pmatrix}$$

Then the best values of c_1 and c_2 satisfy the matrix eigenvalue equation:

$$\begin{pmatrix} c_1^* & c_2^* \end{pmatrix} \begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} = E_{avg} \begin{pmatrix} c_1^* & c_2^* \end{pmatrix} \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix}$$

Which means that:

$$\frac{\partial E_{avg}}{\partial \mathbf{c}} = 0 \Leftrightarrow \mathbf{c}^\dagger \bullet \mathbf{H} = E_{avg} \mathbf{c}^\dagger \bullet \mathbf{S} \qquad \textbf{Eq. 1}$$

This equation doesn't look so familiar yet, so we need to massage it a bit. First, it turns out that if we had taken the derivatives with respect to c_1^* and c_2^* instead of c_1 and c_2, we would have gotten a slightly different equation:

$$\begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = E_{avg} \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$$

or

$$\frac{\partial E_{avg}}{\partial \mathbf{c}^*} = 0 \Leftrightarrow \mathbf{H}\bullet\mathbf{c} = E_{avg}\mathbf{S}\bullet\mathbf{c} \qquad \textbf{Eq. 2}$$

Taking the derivatives with respect to c_1^* and c_2^* is mathematically equivalent to taking the derivatives with respect to c_1 and c_2 [because we can't change c_1 without changing its complex conjugate, and vice versa]. Thus, the two matrix equations (Eqs. 1&2) above are precisely equivalent, and the second version is a little more familiar. We can make it even more familiar if we think about the limit where $1s_A$ and $1s_B$ are orthogonal (e.g. when the atoms are very, very far apart). Then we would have for the Overlap matrix:

$$\mathbf{S} \equiv \begin{pmatrix} \int 1s_A 1s_A d\tau & \int 1s_A 1s_B d\tau \\ \int 1s_B 1s_A d\tau & \int 1s_B 1s_B d\tau \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \mathbf{1}$$

Thus, in an orthonormal basis the overlap matrix is just the identity matrix and we can write Eq. 2 as:

$$\frac{\partial E_{avg}}{\partial \mathbf{c}^*} = 0 \Leftrightarrow \mathbf{H}\bullet\mathbf{c} = E_{avg}\mathbf{c}$$

Now this equation is in a form where we certainly recognize it: this is an eigenvalue equation. Because of its close relationship with the standard eigenvalue equation, Eq. 2 is usually called a **Generalized Eigenvalue Equation**.

In any case, we see the quite powerful result that **the Variational theorem allows us to turn operator algebra into matrix algebra**. Looking for the lowest energy LCAO state is equivalent to looking for the lowest eigenvalue of the Hamiltonian matrix $\mathbf{H}$. Further, looking for the best c_1 and c_2 is equivalent to finding the lowest eigenvector of $\mathbf{H}$.

Let's go ahead and apply what we've learned to obtain the MO coefficients c_1 and c_2 for H_2^+. At this point we make use of several simplifications. The off-diagonal matrix elements of $\mathbf{H}$ are identical because the Hamiltonian is Hermitian and the orbitals are real:

$$\int 1s_A \hat{H}_{el} 1s_B d\tau = \left(\int 1s_B{}^* \hat{H}_{el} 1s_A d\tau\right)^* = \int 1s_B \hat{H}_{el} 1s_A d\tau \equiv V_{12}$$

Meanwhile, the diagonal elements are also equal, but for a different reason. The diagonal elements are the average energies of the states $1s_A$ and $1s_B$. If these energies were different, it would imply that having the electron on one side of H_2^+ was more energetically favorable than having it on the other, which would be very puzzling. So we conclude

$$\int 1s_A \hat{H}_{el} 1s_A d\tau = \int 1s_B \hat{H}_{el} 1s_B d\tau \equiv \varepsilon$$

Finally, we remember that $1s_A$ and $1s_B$ are normalized, so that

$$\int 1s_A 1s_A d\tau = \int 1s_B 1s_B d\tau = 1$$

and because the 1s orbitals are real, the off-diagonal elements of **S** are also the same:

$$S_{12} = \int 1s_A 1s_B d\tau = \int 1s_B 1s_A d\tau = S_{21}\,.$$

Incorporating all these simplifications gives us the generalized eigenvalue equation:

$$\begin{pmatrix} \varepsilon & V_{12} \\ V_{12} & \varepsilon \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = E_{avg} \begin{pmatrix} 1 & S_{12} \\ S_{21} & 1 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$$

All your favorite mathematical programs (Matlab, Mathematica, Maple, MathCad…) are capable of solving for the generalized eigenvalues and eigenvectors, and for more complicated cases we suggest you use them. However, this case is simple enough that we can solve it by guess-and test. Based on our physical intuition above, we guess that the correct eigenvector will have $c_1=c_2$. Plugging this in, we find:

$$\begin{pmatrix} \varepsilon & V_{12} \\ V_{12} & \varepsilon \end{pmatrix} \begin{pmatrix} c_1 \\ c_1 \end{pmatrix} = E_{avg} \begin{pmatrix} 1 & S_{12} \\ S_{21} & 1 \end{pmatrix} \begin{pmatrix} c_1 \\ c_1 \end{pmatrix}$$

$$\Rightarrow \begin{pmatrix} (\varepsilon + V_{12}) c_1 \\ (\varepsilon + V_{12}) c_1 \end{pmatrix} = E_{avg} \begin{pmatrix} (1 + S_{12}) c_1 \\ (1 + S_{12}) c_1 \end{pmatrix}$$

$$\Rightarrow E_{avg} = \frac{\varepsilon + V_{12}}{1 + S_{12}} \equiv E_\sigma$$

Thus, our guess is correct and one of the eigenvectors of this matrix has $c_1=c_2$. This eigenvector is the σ-bonding state of H_2^+, and we can write down the associated orbital as:

$$\psi_{el}^{\sigma} = c_1 1s_A + c_2 1s_B = c_1 1s_A + c_1 1s_B \propto 1s_A + 1s_B$$

where in the last expression we have noted that c_1 is just a normalization constant. In freshman chemistry, we taught you that the σ-bonding orbital existed, and this is where it comes from.

We can also get the σ^*-antibonding orbital from the variational procedure. Since the matrix is a 2x2 it has two unique eigenvalues: the lowest one (which we just found above) is bonding and the other is antibonding. We can again guess the form of the antibonding eigenvector, since we know it has the characteristic shape +/-, so that we guess the solution is $c_1=-c_2$:

$$\begin{pmatrix} \varepsilon & V_{12} \\ V_{12} & \varepsilon \end{pmatrix}\begin{pmatrix} c_1 \\ -c_1 \end{pmatrix} = E_{avg}\begin{pmatrix} 1 & S_{12} \\ S_{21} & 1 \end{pmatrix}\begin{pmatrix} c_1 \\ -c_1 \end{pmatrix}$$

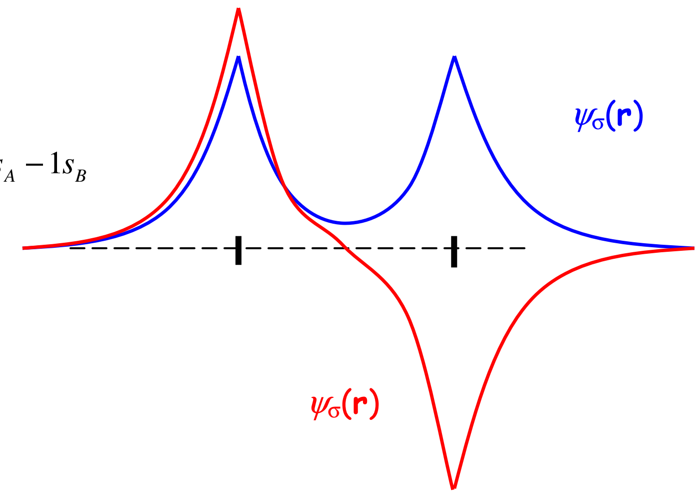
$$\Rightarrow \begin{pmatrix} (\varepsilon - V_{12})c_1 \\ -(\varepsilon - V_{12})c_1 \end{pmatrix} = E_{avg}\begin{pmatrix} (1-S_{12})c_1 \\ -(1-S_{12})c_1 \end{pmatrix}$$

$$\Rightarrow E_{avg} = \frac{\varepsilon - V_{12}}{1-S_{12}} = E_{\sigma*}$$

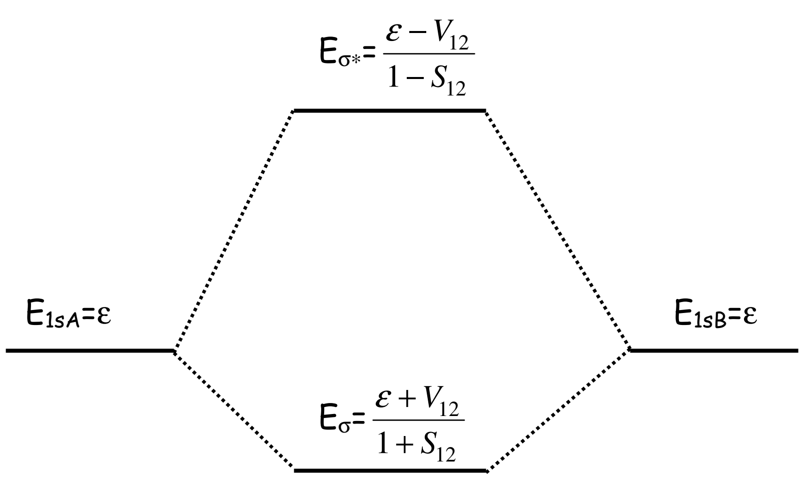
so, indeed the other eigenvector has $c_1=-c_2$. The corresponding antibonding orbital is given by:

$$\psi_{el}^{\sigma*} = c_1 1s_A + c_2 1s_B = c_1 1s_A - c_1 1s_B \propto 1s_A - 1s_B$$

where we note again that c_1 is just a normalization constant. Given these forms for the bonding and antibonding orbitals, we can draw a simple picture for the H_2^+ MOs (see right).



We can incorporate the energies obtained above into a simple MO diagram of H_2^+:



On the left and right, we draw the energies of the atomic orbitals (1sA and 1sB) that make up our molecular orbitals (σ and σ*) in the center. We note that when the atoms come together the energy of the bonding and antibonding orbitals are shifted by different amounts:

$$E_{\sigma*} - E_{1s} = \frac{\varepsilon - V_{12}}{1 - S_{12}} - \varepsilon = \frac{\varepsilon - V_{12}}{1 - S_{12}} - \frac{\varepsilon(1 - S_{12})}{1 - S_{12}} = \frac{\varepsilon S_{12} - V_{12}}{1 - S_{12}}$$

$$E_{1s} - E_{\sigma*} = \varepsilon - \frac{\varepsilon + V_{12}}{1 + S_{12}} = \frac{\varepsilon(1 + S_{12})}{1 + S_{12}} - \frac{\varepsilon + V_{12}}{1 + S_{12}} = \frac{\varepsilon S_{12} - V_{12}}{1 + S_{12}}$$

Now, S_{12} is the overlap between two 1s orbitals. Since these orbitals are never negative, S_{12} must be a positive number. Thus, the first denominator is greater than the second, from which we conclude

$$E_{\sigma*} - E_{1s} = \frac{\varepsilon S_{12} - V_{12}}{1 - S_{12}} > \frac{\varepsilon S_{12} - V_{12}}{1 + S_{12}} = E_{1s} - E_{\sigma*}$$

Thus, the antibonding orbital is destabilized more than the bonding orbital is stabilized. This conclusion need not hold for all diatomic molecules, but it is a good rule of thumb. This effect is called **overlap repulsion**. Note that in the special case where the overlap between the orbitals is negligible, S_{12} goes to zero and the two orbitals are shifted by equal amounts. However, when is S_{12} nonzero there are two effects that shift the energies: the physical interaction between the atoms and the fact that the 1sA and 1sB orbitals are not orthogonal. When we diagonalize $\mathbf{H}$, we account for both these effects, and the orthogonality constraint pushes the orbitals upwards in energy.