

Chapter 2: Molecules

Quantum mechanics can be used to calculate any property of a molecule. The energy E of a wavefunction Ψ evaluated for the Hamiltonian H is,

$$E = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle}. \quad (1)$$

At first this seems like just a way to calculate the energy. However, this formula is used to calculate quantities like the bond length, the bond strength and the bond angles of a molecule. To calculate a bond length, the length is first guessed and the Hamiltonian for that bond length is constructed, the lowest energy wavefunction for this Hamiltonian is determined and the energy of this state is evaluated using the formula above. Then the Hamiltonian is adjusted to have little longer bond length or a little shorter bond length and the process is repeated until the bond length with the lowest energy is found.

This is typically a computationally intensive process but it is remarkably accurate. Quantum mechanics is always correct. Discrepancies with experiment only appear when approximations are made to make the computation easier.

Many-particle Hamiltonian

The Hamiltonian that describes any molecule or solid is,

$$H_{\text{mp}} = - \sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_a \frac{\hbar^2}{2m_a} \nabla_a^2 - \sum_{a,i} \frac{Z_a e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_a|} + \sum_{i < j} \frac{e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_j|} + \sum_{a < b} \frac{Z_a Z_b e^2}{4\pi\epsilon_0 |\vec{r}_a - \vec{r}_b|}. \quad (2)$$

The first sum describes the kinetic energy of the electrons. The electrons are labeled with the subscript i . The second sum describes the kinetic energy of all of the atomic nuclei. The atoms are labeled with the subscript a . The third sum describes the attractive Coulomb interaction between the the positively charged nuclei and the negatively charge electrons. Z_a is the atomic number (the number of protons) of nucleus a . The fourth sum describes the repulsive electron-electron interactions. Notice the plus sign before the sum for repulsive interactions. The fifth sum describes the repulsive nuclei-nuclei interactions.

This Hamiltonian neglects some small details like the spin-orbit interaction and the hyperfine interaction. These effects will be ignored in this discussion. If they are relevant, they could be included as perturbations later. Remarkably, this Hamiltonian can tell us the shape of every molecule and the energy released (or absorbed) in a chemical reaction. Any observable quantity of any solid can also be calculated from this Hamiltonian. It turns

out, however, that solving the Schrödinger equation associated with this Hamiltonian is usually terribly difficult. Here we will present a standard approach to determine approximate solutions to the Schrödinger equation.

Born-Oppenheimer approximation

Since the nuclei are much heavier than the electrons, the electrons will move much faster than the nuclei. We may therefore fix the positions of the nuclei while solving for the electron states. The electron states are described by the electronic Hamiltonian H_{elec} .

$$H_{\text{elec}} = - \sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_{a,i} \frac{Z_a e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_a|} + \sum_{i<j} \frac{e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_j|} + \sum_{a<b} \frac{Z_a Z_b e^2}{4\pi\epsilon_0 |\vec{r}_a - \vec{r}_b|}. \quad (3)$$

Reduced electronic Hamiltonian

The kinetic energy of the nuclei do not appear in H_{elec} since the nuclei have been fixed. The last term in H_{elec} does not depend on the positions of the electrons so it just adds a constant to the energy. Since a constant can always be added to or subtracted from the energy, this term will be neglected as we solve for the motion of the electrons.

The electronic Hamiltonian cannot be solved analytically; it can only be solved numerically. To make further progress with an analytical solution, the electron-electron interaction term is neglected. This is not easily justified on physical grounds but this is the only known way to arrive at a reasonable analytic solution. When the electron-electron interactions are neglected, the reduced electronic Hamiltonian $H_{\text{elec.red}}$ can be written as a sum of molecular orbital Hamiltonians H_{mo} .

$$H_{\text{elec.red}} = - \sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_{a,i} \frac{Z_a e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_a|} = \sum_i H_{\text{mo}}. \quad (4)$$

The eigenfunctions of this Hamiltonian can be found by the separation of variables. The many-electron wavefunctions are antisymmetrized products of the solutions to the molecular orbital Hamiltonian.

Molecular orbital Hamiltonian

The molecular orbital Hamiltonian describes the motion of a single electron in the potential created by all of the positive nuclei.

$$H_{\text{mo}} = - \frac{\hbar^2}{2m_e} \nabla^2 - \sum_a \frac{Z_a e^2}{4\pi\epsilon_0 |\vec{r} - \vec{r}_a|}. \quad (5)$$

Note that while $H_{\text{elec.red}}$ is a sum of molecular orbital Hamiltonians, all of these Hamiltonians are the same. Instead of having to solve a many-electron Hamiltonian, it is only

necessary to solve a single one-electron Hamiltonian. This corresponds to a vast reduction in the computational effort required to solve the equations.

The molecular orbitals play a similar role in describing the many-electron wavefunctions of molecules as the atomic orbitals do in describing the many-electron wavefunctions of atoms. There are various way to solve the molecular orbital Hamiltonian. Let's postpone the discussion of how to find the solutions of the molecular orbital Hamiltonian and just assume that we have found a set of eigenfunctions,

$$H_{\text{mo}}\psi_n = E_n\psi_n. \quad (6)$$

A many-electron solution Ψ that is constructed as an antisymmetrized product of molecular orbitals is an exact solution to $H_{\text{elec.red}}$ and it is a good approximate solution to H_{elec} . It can be used to find the approximate energy of the many electron system using the equation,

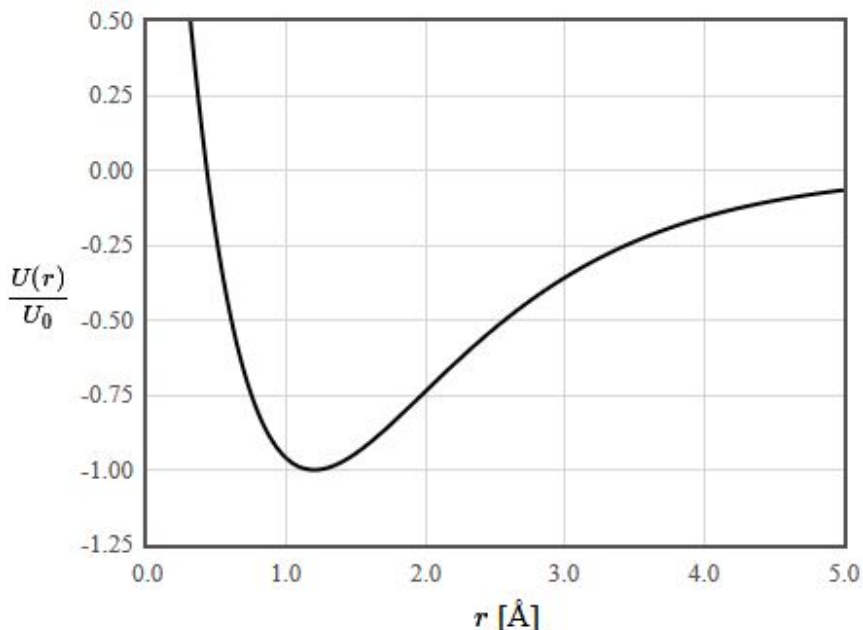
$$E = \frac{\langle \Psi | H_{\text{elec}} | \Psi \rangle}{\langle \Psi | \Psi \rangle}. \quad (7)$$

As stated above, the shape of a molecule in terms of bond lengths and bond angles is determined by finding the arrangement of the atoms that minimizes this energy.

Bond potential

To calculate the bond potential, fix the nuclei of the two atoms involved in the bond at a certain distance apart and calculate the energy of the electronic Hamiltonian evaluated with the ground state many-electron wave function.

Change the distance and recalculate the energy of the ground state. Repeat until the energy has been determined as a function of distance.



Bond length

The minimum of the bond potential gives the equilibrium bond length. Some books give tables of bond lengths for which provide an approximate value of the bond length. The bond length for a particular pair of atoms, like a carbon-carbon bond, is not always the same. It depends on the other atoms in the molecule.

Bond angle

Fix the nuclei at different bond angles and calculate the energy for each case. The bond angle with the lowest energy will be observed.

Shape of a molecule

The Schrödinger equation can tell us if a molecule is linear or forms a ring. It can tell us the shape of a complicated molecule like a protein or DNA.

To find the shape of a molecule, start with a guess for the shape and calculate the energy then make a small change in the shape and see if the energy decreases. The observed shape of the molecule will be at the energy minimum. There may be multiple energy minima resulting in different isomers of a molecule.

Rotational energy levels

The rotational levels of a diatomic molecule can be estimated by assuming that the atoms remain at their equilibrium spacing r_0 during rotation. In this case, the quantized energy levels of a rigid rotator can be used,

$$E_l = \frac{\hbar^2}{2I} l(l+1), \quad (8)$$

where I is the moment of inertia and l is orbital quantum number, $l = 0, 1, 2, \dots$. For a diatomic molecule with an equilibrium spacing of the atoms of r_0 and atomic masses m_a and m_b , the moment of inertia is $I = \frac{m_a m_b}{m_a + m_b} r_0^2$.

A molecule with N atoms has $3N$ degrees of freedom. There are always three translational degrees of freedom which describe the motion of the center of mass of the molecule. A linear molecule (all of the atoms are in a straight line) has two rotational degrees of freedom. If the atoms lie along the x-axis, there can be two different rotation speeds around the y- and z-axes. The atoms of a non-linear molecule do not all lie along a line and there are three rotational degrees of freedom.

Vibrational energy levels

For diatomic molecules, the bond potentials can be used to find the vibrational and rotational spectra of a molecule. Diatomic molecules only have one stretching mode where the

two atoms in a molecule vibrate with respect to each other.

In the simplest approximation, we imagine that the atoms are attached to each other by a linear spring. The spring constant can be determined from the bond potential. Near the minimum of the bond potential at r_0 , the potential can be approximated by a parabola. This is the same potential as for a harmonic oscillator where the effective spring constant is $k_{\text{eff}} = \left. \frac{d^2U}{dr^2} \right|_{r=r_0}$ and the reduced mass is $m_r = (1/m_a + 1/m_b)^{-1}$. Here m_a and m_b are the masses of the two atoms. The angular frequency of this vibration is $\omega = \sqrt{k_{\text{eff}}/m_r}$. The vibrational modes of the molecule have the same energy level spectrum as a harmonic oscillator,

$$E_\nu = \hbar\omega(\nu + 1/2) \quad \nu = 0, 1, 2, \dots \quad (9)$$

The number of vibrational normal modes for a molecule with N atoms is $3N - 5$ for a linear molecule and $3N - 6$ for a non-linear molecule.

Energy of a chemical reaction

Chemical reactions can be either exothermic (energy is released during the reaction) or endothermic (energy is absorbed during the reaction). To calculate how much energy is released or absorbed during a reaction, calculate the energies for all reactants and products. The change in energy during the reaction is the sum of the energies of the products minus the sum of energies of the reactants.

Speed of a chemical reaction

To calculate how long a chemical reaction takes, numerically integrate the time dependent Schrödinger equation for H_{total} starting with the reactants nearby each other. This is an exceedingly computationally intensive calculation.

More accurate calculations

Ignoring the electron-electron interactions is a fairly crude approximation. There are more sophisticated methods like Hartree-Fock or density functional theory. These methods are not exact but do include the electron-electron interactions in an approximate form. There are many commercial and public domain programs available for these types of calculations.

Molecular orbitals

The total quantum state of a molecule is described by a many-electron wavefunction. In the standard approximation, the many-electron wavefunction can be expressed as a product of single-electron wavefunctions called molecular orbitals. Molecular orbitals are used

very much like the hydrogen wavefunctions are used to construct the many-electron wavefunctions of atoms.

In the simplest approximation, the molecular orbitals are the wavefunction of a single electron moving in a potential created by all of the positively charged nuclei in a molecule. The molecular orbital Hamiltonian can be written,

$$H_{\text{mo}} = -\frac{\hbar^2}{2m_e} \nabla^2 - \sum_a \frac{Z_a e^2}{4\pi\epsilon_0 |\vec{r} - \vec{r}_a|}. \quad (10)$$

Here \vec{r}_a are the positions of the nuclei in the molecule, \vec{r} is the position of the single electron, and a sums over the atoms in the molecule.

The molecular orbital Hamiltonian is often solved by a method called the Linear Combination of Atomic Orbitals (LCAO). It is assumed that the wave function can be written in terms of hydrogen atomic orbitals that are centered around the nuclei,

$$\psi_{\text{mo}}(\vec{r}) = \sum_a \sum_{ao} c_{ao,a} \phi_{ao}^{Z_a}(\vec{r} - \vec{r}_a). \quad (11)$$

where ao labels the atomic orbitals ($ao = 1 : 1s, ao = 2 : 2s, ao = 3 : 2px, \dots$). The number of molecular orbitals that we calculate will be equal to the number of unknown coefficients. We call this number N .

We have to decide how many atomic orbitals should be included for each atom. A reasonable choice is to take all of the occupied atomic orbitals of the isolated atoms. For instance, for water one might use the 1s, 2s, and 2p orbitals of oxygen and the 1s orbitals of the two hydrogen atoms. In that case, there would be $N = 7$ terms in the wave function for the molecular orbital.

There is no strict rule as to which atomic orbitals to include. Including more atomic orbitals leads to a higher accuracy but makes the numerical calculation more difficult.

At this point it is convenient to relabel the atomic orbitals used in the wave function with integers $p = 1 \dots N$. For water we might choose $\phi_1 = \phi_{1s}^{Z=1}(\vec{r} - \vec{r}_{\text{H1}})$, $\phi_2 = \phi_{1s}^{Z=1}(\vec{r} - \vec{r}_{\text{H2}})$, $\phi_3 = \phi_{1s}^{Z=8}(\vec{r} - \vec{r}_{\text{O}})$, $\phi_4 = \phi_{2s}^{Z=8}(\vec{r} - \vec{r}_{\text{O}})$, etc. The trial wavefunction can then be written more compactly as,

$$\psi_{\text{mo}} = \sum_{p=1}^N c_p \phi_p. \quad (12)$$

The time independent Schrödinger equation is,

$$H_{\text{mo}} \psi_{\text{mo}} = E \psi_{\text{mo}}. \quad (13)$$

Multiply the Schrödinger equation from the left by each of the atomic orbitals and integrate over all space. This results in a set of N algebraic equations called the Roothaan equations.

$$\begin{aligned}
\langle \phi_1 | H_{\text{mo}} | \psi_{\text{mo}} \rangle &= E \langle \phi_1 | \psi_{\text{mo}} \rangle \\
\langle \phi_2 | H_{\text{mo}} | \psi_{\text{mo}} \rangle &= E \langle \phi_2 | \psi_{\text{mo}} \rangle \\
&\vdots \\
\langle \phi_N | H_{\text{mo}} | \psi_{\text{mo}} \rangle &= E \langle \phi_N | \psi_{\text{mo}} \rangle
\end{aligned} \tag{14}$$

By substituting in the form for ψ_{mo} from above, the Roothaan equations can be written in matrix form,

$$\begin{bmatrix} H_{11} & H_{12} & \cdots & H_{1N} \\ H_{21} & H_{22} & \cdots & H_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ H_{N1} & H_{N2} & \cdots & H_{NN} \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ \vdots \\ c_N \end{bmatrix} = E \begin{bmatrix} S_{11} & S_{12} & \cdots & S_{1N} \\ S_{21} & S_{22} & \cdots & S_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ S_{N1} & S_{N2} & \cdots & S_{NN} \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ \vdots \\ c_N \end{bmatrix}. \tag{15}$$

Here the elements of the Hamiltonian matrix and the overlap matrix are,

$$H_{pq} = \langle \phi_p | H_{\text{mo}} | \phi_q \rangle \quad \text{and} \quad S_{pq} = \langle \phi_p | \phi_q \rangle. \tag{16}$$

The Roothaan equations can be solved numerically to find N solutions for the energy E along with the corresponding coefficients that describe the N wave functions which are the molecular orbitals.

Hückel model

The Hückel model is an approximation that is often made to simplify the Roothaan equations. The overlap matrix is nearly the identity matrix. For normalized atomic orbitals, $S_{pp} = 1$ so all of the diagonal elements equal 1.

If two wavefunctions ϕ_p and ϕ_q are not the same but are centered on the same nucleus then $S_{pq} = 0$ because the hydrogen atomic orbitals are orthogonal to each other.

If two wavefunctions ϕ_p and ϕ_q are centered on different nuclei that are far apart in the molecule, then $S_{pq} \approx 0$. This only leaves off-diagonal elements of the matrix that correspond to two wavefunctions ϕ_p and ϕ_q that are centered on nearby atoms. Although these elements may not really be zero, they will be small compared to 1 and we make the approximation,

$$S_{pp} = 1 \quad \text{and} \quad S_{pq} = 0 \quad \text{for } p \neq q. \tag{17}$$

The equations that need to be solved reduce to an eigenvalue problem,

$$\begin{bmatrix} H_{11} & H_{12} & \cdots & H_{1N} \\ H_{21} & H_{22} & \cdots & H_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ H_{N1} & H_{N2} & \cdots & H_{NN} \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ \vdots \\ c_N \end{bmatrix} = E \begin{bmatrix} c_1 \\ c_2 \\ \vdots \\ c_N \end{bmatrix}. \tag{18}$$

Valence Bond Theory

Valence bond theory is similar to Molecular orbital theory but is mathematically simpler. The starting point is the many-particle Hamiltonian,

$$H_{\text{mp}} = -\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_a \frac{\hbar^2}{2m_a} \nabla_a^2 - \sum_{a,i} \frac{Z_a e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_a|} + \sum_{i<j} \frac{e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_j|} + \sum_{a<b} \frac{Z_a Z_b e^2}{4\pi\epsilon_0 |\vec{r}_a - \vec{r}_b|}. \quad (19)$$

As in molecule orbital theory, the Born-Oppenheimer approximation is used. Since the nuclei are much heavier than the electrons, the electrons will move much faster than the nuclei.

We may therefore fix the positions of the nuclei while solving for the electron states. The electron states are described by the electronic Hamiltonian H_{elec} .

$$H_{\text{elec}} = -\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_{a,i} \frac{Z_a e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_a|} + \sum_{i<j} \frac{e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_j|} + \sum_{a<b} \frac{Z_a Z_b e^2}{4\pi\epsilon_0 |\vec{r}_a - \vec{r}_b|}. \quad (20)$$

The kinetic energy of the nuclei do not appear in H_{elec} since the nuclei have been fixed. The last term in H_{elec} does not depend on the positions of the electrons so it just adds a constant to the energy. Since a constant can always be added to or subtracted from the energy, this term will be neglected as we solve for the motion of the electrons.

The electronic Hamiltonian cannot be solved analytically; it can only be solved numerically. To make further progress with an analytical solution in molecular orbital theory, we neglected the electron-electron interaction terms at this point. In valence bond theory we associate an each electron to an atom and neglect the electron-electron interactions and the interactions between an electron **and** the nuclei of other atoms that it is not associated with. The resulting Hamiltonian is a sum of atomic Hamiltonians.

$$H_{\text{vb}} = -\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_i \frac{Z_{ai} e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_{ai}|} = \sum_i H_{\text{atom}_i}. \quad (21)$$

Here Z_{ai} is the nuclear charge of the atom associated with electron i and \vec{r}_{ai} is the position of the atom associated with electron i . This Hamiltonian can be solved by the separation of variables. Since the solutions to the atomic Hamiltonians are the atomic orbitals, the solution to H_{vb} is an antisymmetrized product of atomic orbitals. This is an exact solution to H_{vb} and an approximate solution to H_{elec} . It can be used to find the approximate energy of the many electron system using the equation,

$$E = \frac{\langle \Psi | H_{\text{elec}} | \Psi \rangle}{\langle \Psi | \Psi \rangle}. \quad (22)$$

The shape of a molecule in terms of bond lengths and bond angles is determined by finding the arrangement of the atoms that minimizes this energy.

HeitlerLondon theory

The most famous application of valence bond theory is Heitler and London's description of the hydrogen molecule. This appeared in 1927, just two years after Schrodinger proposed his wave equation. For H_2 , all terms in the many-particle Hamiltonian are neglected except,

$$\begin{aligned}
 \Psi_{\uparrow\uparrow} &= \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_{1s}^H \uparrow(\vec{r}_1 - \vec{r}_a) & \phi_{1s}^H \uparrow(\vec{r}_1 - \vec{r}_b) \\ \phi_{1s}^H \uparrow(\vec{r}_2 - \vec{r}_a) & \phi_{1s}^H \uparrow(\vec{r}_2 - \vec{r}_b) \end{vmatrix} \\
 &= \frac{1}{\sqrt{2}} (\phi_{1s}^H(\vec{r}_1 - \vec{r}_a)\phi_{1s}^H(\vec{r}_2 - \vec{r}_b) - \phi_{1s}^H(\vec{r}_1 - \vec{r}_b)\phi_{1s}^H(\vec{r}_2 - \vec{r}_a)) \uparrow(\vec{r}_1) \uparrow(\vec{r}_2), \\
 \Psi_{\downarrow\downarrow} &= \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_{1s}^H \downarrow(\vec{r}_1 - \vec{r}_a) & \phi_{1s}^H \downarrow(\vec{r}_1 - \vec{r}_b) \\ \phi_{1s}^H \downarrow(\vec{r}_2 - \vec{r}_a) & \phi_{1s}^H \downarrow(\vec{r}_2 - \vec{r}_b) \end{vmatrix} \\
 &= \frac{1}{\sqrt{2}} (\phi_{1s}^H(\vec{r}_1 - \vec{r}_a)\phi_{1s}^H(\vec{r}_2 - \vec{r}_b) - \phi_{1s}^H(\vec{r}_1 - \vec{r}_b)\phi_{1s}^H(\vec{r}_2 - \vec{r}_a)) \downarrow(\vec{r}_1) \downarrow(\vec{r}_2), \\
 \Psi_{\uparrow\downarrow} &= \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_{1s}^H \uparrow(\vec{r}_1 - \vec{r}_a) & \phi_{1s}^H \downarrow(\vec{r}_1 - \vec{r}_b) \\ \phi_{1s}^H \uparrow(\vec{r}_2 - \vec{r}_a) & \phi_{1s}^H \downarrow(\vec{r}_2 - \vec{r}_b) \end{vmatrix} \\
 &= \frac{1}{\sqrt{2}} (\phi_{1s}^H(\vec{r}_1 - \vec{r}_a) \uparrow(\vec{r}_1)\phi_{1s}^H(\vec{r}_2 - \vec{r}_b) \downarrow(\vec{r}_2) - \phi_{1s}^H(\vec{r}_1 - \vec{r}_b) \downarrow(\vec{r}_1)\phi_{1s}^H(\vec{r}_2 - \vec{r}_a) \uparrow(\vec{r}_2)), \\
 \Psi_{\downarrow\uparrow} &= \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_{1s}^H \downarrow(\vec{r}_1 - \vec{r}_a) & \phi_{1s}^H \uparrow(\vec{r}_1 - \vec{r}_b) \\ \phi_{1s}^H \downarrow(\vec{r}_2 - \vec{r}_a) & \phi_{1s}^H \uparrow(\vec{r}_2 - \vec{r}_b) \end{vmatrix} \\
 &= \frac{1}{\sqrt{2}} (\phi_{1s}^H(\vec{r}_1 - \vec{r}_a) \downarrow(\vec{r}_1)\phi_{1s}^H(\vec{r}_2 - \vec{r}_b) \uparrow(\vec{r}_2) - \phi_{1s}^H(\vec{r}_1 - \vec{r}_b) \uparrow(\vec{r}_1)\phi_{1s}^H(\vec{r}_2 - \vec{r}_a) \downarrow(\vec{r}_2)).
 \end{aligned} \tag{23}$$

By constructing the linear combinations of the last two wave functions $\Psi_{\uparrow\downarrow+\downarrow\uparrow} = \Psi_{\uparrow\downarrow} + \Psi_{\downarrow\uparrow}$ and $\Psi_{\uparrow\downarrow-\downarrow\uparrow} = \Psi_{\uparrow\downarrow} - \Psi_{\downarrow\uparrow}$, the wave functions factor into an orbital part and a spin part,

$$\begin{aligned}
 & \Psi_{\uparrow\downarrow+\downarrow\uparrow}(\vec{r}_1, \vec{r}_2) \\
 &= \frac{1}{\sqrt{2}} (\phi_{1s}^H(\vec{r}_1 - \vec{r}_a)\phi_{1s}^H(\vec{r}_2 - \vec{r}_b) - \phi_{1s}^H(\vec{r}_2 - \vec{r}_a)\phi_{1s}^H(\vec{r}_1 - \vec{r}_b)) (\uparrow(\vec{r}_1) \downarrow(\vec{r}_2) + \downarrow(\vec{r}_1) \uparrow(\vec{r}_2)), \\
 & \Psi_{\uparrow\downarrow-\downarrow\uparrow}(\vec{r}_1, \vec{r}_2) \\
 &= \frac{1}{\sqrt{2}} (\phi_{1s}^H(\vec{r}_1 - \vec{r}_a)\phi_{1s}^H(\vec{r}_2 - \vec{r}_b) + \phi_{1s}^H(\vec{r}_2 - \vec{r}_a)\phi_{1s}^H(\vec{r}_1 - \vec{r}_b)) (\uparrow(\vec{r}_1) \downarrow(\vec{r}_2) - \downarrow(\vec{r}_1) \uparrow(\vec{r}_2)).
 \end{aligned}$$

The three wave functions with an antisymmetric orbital part, $\Psi_{\uparrow\uparrow}$, $\Psi_{\downarrow\downarrow}$, and $\Psi_{\uparrow\downarrow+\downarrow\uparrow}$ all have the same energy when evaluated with H_{elec} . This is the triplet state. The singlet state, $\Psi_{\uparrow\downarrow-\downarrow\uparrow}$ has a different energy when evaluated with H_{elec} . For H_2 , the singlet state has a lower energy than the triplet state so the singlet state is the molecular ground state. The bond potential for H_2 can be approximated by evaluating,

$$E = \frac{\langle \Psi_{\uparrow\downarrow-\downarrow\uparrow} | H_{\text{elec}} | \Psi_{\uparrow\downarrow-\downarrow\uparrow} \rangle}{\langle \Psi_{\uparrow\downarrow-\downarrow\uparrow} | \Psi_{\uparrow\downarrow-\downarrow\uparrow} \rangle}, \tag{24}$$

as a function of the distance between the atoms.

It is interesting to compare the ground state wave function found by Heitler and London to that found by molecular orbital theory:

$$\begin{aligned} & \Psi(\vec{r}_1, \vec{r}_2) \\ = & \frac{1}{2\sqrt{2}} (\phi_{1s}^H(\vec{r}_1 - \vec{r}_a) + \phi_{1s}^H(\vec{r}_1 - \vec{r}_b)) (\phi_{1s}^H(\vec{r}_2 - \vec{r}_a) + \phi_{1s}^H(\vec{r}_2 - \vec{r}_b)) (\uparrow(\vec{r}_1) \downarrow(\vec{r}_2) - \downarrow(\vec{r}_1) \uparrow(\vec{r}_2)). \end{aligned} \tag{25}$$

The ground state found by molecular orbital theory has two additional terms and evaluates to a lower energy with H_{elec} than the valence bond wave function. The molecular orbital wave function is closer to the true ground state.

Some molecular orbital calculations:

Molecular orbitals of the molecular ion H_2^+

The molecular ion H_2^+ consists of one electron and two protons. The molecular orbital Hamiltonian in this case is,

$$H_{\text{mo}}^{H_2^+} = -\frac{\hbar^2}{2m_e} \nabla^2 - \frac{e^2}{4\pi\epsilon_0|\vec{r} - \vec{r}_A|} - \frac{e^2}{4\pi\epsilon_0|\vec{r} - \vec{r}_B|}, \quad (1)$$

where \vec{r}_A and \vec{r}_B are the positions of the two protons. Consider a linear combination of the two 1s orbitals, $\psi_{\text{mo}} = c_1\phi_{1s}(\vec{r} - \vec{r}_A) + c_2\phi_{1s}(\vec{r} - \vec{r}_B)$. The time independent Schrödinger equation is,

$$H_{\text{mo}}\psi_{\text{mo}} = E\psi_{\text{mo}}. \quad (2)$$

Multiply the Schrödinger equation from the left by each of the atomic orbitals and integrate over all space. This results in a set of 2 algebraic equations called the Roothaan equations.

$$\begin{aligned} \langle \phi_{1s}(\vec{r} - \vec{r}_A) | H_{\text{mo}} | \psi_{\text{mo}} \rangle &= E \langle \phi_{1s}(\vec{r} - \vec{r}_A) | \psi_{\text{mo}} \rangle \\ \langle \phi_{1s}(\vec{r} - \vec{r}_B) | H_{\text{mo}} | \psi_{\text{mo}} \rangle &= E \langle \phi_{1s}(\vec{r} - \vec{r}_B) | \psi_{\text{mo}} \rangle \end{aligned} \quad (3)$$

By substituting in the form for ψ_{mo} from above, the Roothaan equations can be written in matrix form,

$$\begin{bmatrix} H_{11} & H_{12} \\ H_{12} & H_{11} \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = E \begin{bmatrix} S_{11} & S_{12} \\ S_{12} & S_{11} \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix}, \quad (4)$$

where

$$\begin{aligned} H_{11} &= \langle \phi_{1s}(\vec{r} - \vec{r}_A) | H_{\text{mo}} | \phi_{1s}(\vec{r} - \vec{r}_A) \rangle, \\ H_{12} &= \langle \phi_{1s}(\vec{r} - \vec{r}_A) | H_{\text{mo}} | \phi_{1s}(\vec{r} - \vec{r}_B) \rangle, \\ S_{11} &= \langle \phi_{1s}(\vec{r} - \vec{r}_A) | \phi_{1s}(\vec{r} - \vec{r}_A) \rangle = 1, \\ S_{12} &= \langle \phi_{1s}(\vec{r} - \vec{r}_A) | \phi_{1s}(\vec{r} - \vec{r}_B) \rangle. \end{aligned} \quad (5)$$

From experience with 2×2 matrices of this form, we know that the eigenvectors of both the Hamiltonian matrix and the overlap matrix are,

$$\begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = \begin{bmatrix} 1 \\ 1 \end{bmatrix}, \begin{bmatrix} 1 \\ -1 \end{bmatrix} \quad (6)$$

It is easy to check that these are the correct eigenvectors but letting \mathbf{H} and \mathbf{S} operate on them. The energies are,

$$E_+ = \frac{H_{11} + H_{12}}{1 + S_{12}}, \quad E_- = \frac{H_{11} - H_{12}}{1 - S_{12}}. \quad (7)$$

The normalized molecular orbitals are,

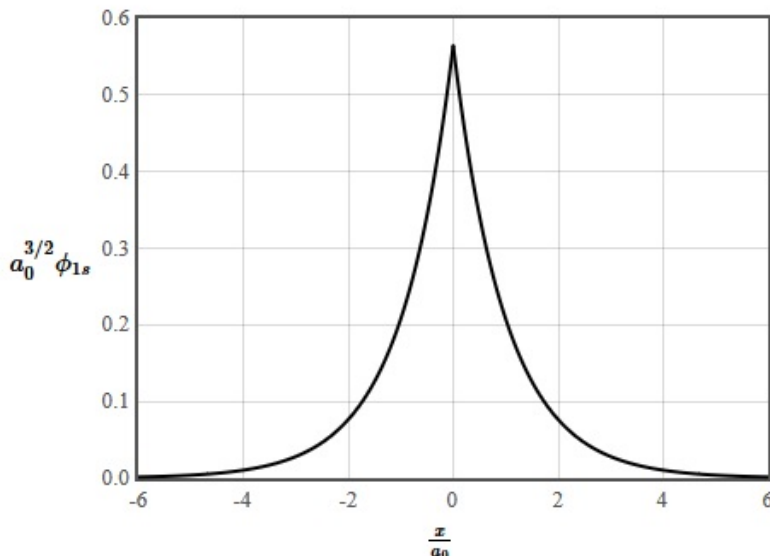
$$\psi_{\pm} = \frac{1}{\sqrt{2}} (\phi_{1s}(\vec{r} - \vec{r}_A) \pm \phi_{1s}(\vec{r} - \vec{r}_B)) \quad (8)$$

Both H_{11} and H_{12} will turn out to be negative so the bonding orbital ψ_+ , has a lower energy than the antibonding orbital ψ_- .

Determining the matrix elements H_{11} , H_{12} , S_{11} , and S_{12}

The 1s atomic orbital has the form,

$$\phi_{1s} = \frac{1}{\sqrt{\pi a_0^3}} \exp\left(-\frac{r}{a_0}\right). \quad (9)$$

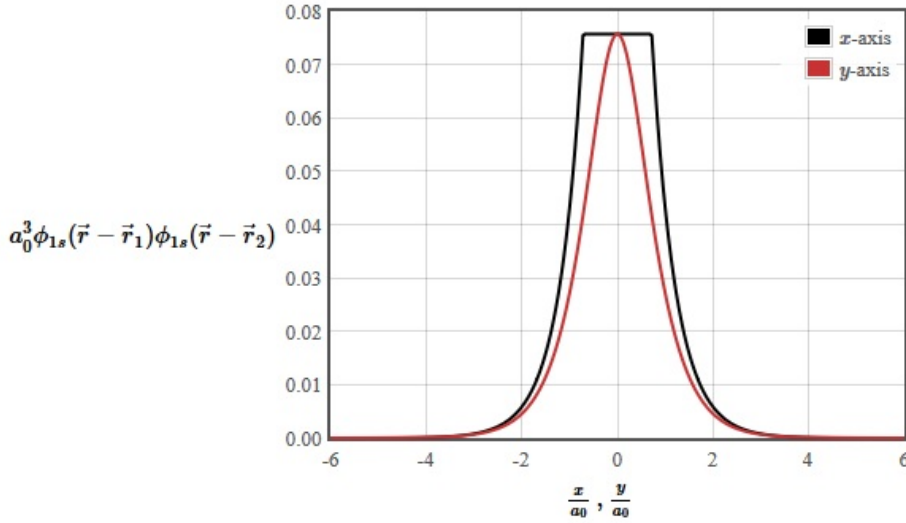


For normalized wavefunctions, the diagonal elements of the overlap matrix are equal to 1, $S_{11} = \langle \phi_{1s}(\vec{r} - \vec{r}_A) | \phi_{1s}(\vec{r} - \vec{r}_A) \rangle = 1$.

The overlap integral S_{12} of two 1s orbitals located at positions \vec{r}_1 and \vec{r}_2 is,

$$S_{12} = \langle \phi_{1s}(\vec{r} - \vec{r}_1) | \phi_{1s}(\vec{r} - \vec{r}_2) \rangle. \quad (10)$$

For a hydrogen molecule, $\vec{r}_1 = -0.38 \hat{x}$ and $\vec{r}_2 = 0.38 \hat{x}$. Below $\phi_{1s}(\vec{r} - \vec{r}_1)\phi_{1s}(\vec{r} - \vec{r}_2)$ is plotted along the x-axis and along the y-axis.



The diagonal Hamiltonian matrix element with two 1s orbitals located at position \vec{r}_1 is,

$$H_{11} = \left\langle \phi_{1s}(\vec{r} - \vec{r}_1) \left| -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0|\vec{r} - \vec{r}_1|} - \frac{e^2}{4\pi\epsilon_0|\vec{r} - \vec{r}_2|} \right| \phi_{1s}(\vec{r} - \vec{r}_1) \right\rangle. \quad (11)$$

This can be broken into two terms,

$$H_{11} = \left\langle \phi_{1s}(\vec{r} - \vec{r}_1) \left| -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0|\vec{r} - \vec{r}_1|} \right| \phi_{1s}(\vec{r} - \vec{r}_1) \right\rangle + \left\langle \phi_{1s}(\vec{r} - \vec{r}_1) \left| -\frac{e^2}{4\pi\epsilon_0|\vec{r} - \vec{r}_2|} \right| \phi_{1s}(\vec{r} - \vec{r}_1) \right\rangle. \quad (12)$$

The wave function $\phi_{1s}(\vec{r} - \vec{r}_1)$ is an eigenfunction of the atomic orbital Hamiltonian in the first term $H\phi_{1s}(\vec{r} - \vec{r}_1) = E_1\phi_{1s}(\vec{r} - \vec{r}_1)$, so the first term is easily evaluated,

$$H_{11} = E_1 - \left\langle \phi_{1s}(\vec{r} - \vec{r}_1) \left| \frac{e^2}{4\pi\epsilon_0|\vec{r} - \vec{r}_2|} \right| \phi_{1s}(\vec{r} - \vec{r}_1) \right\rangle. \quad (13)$$

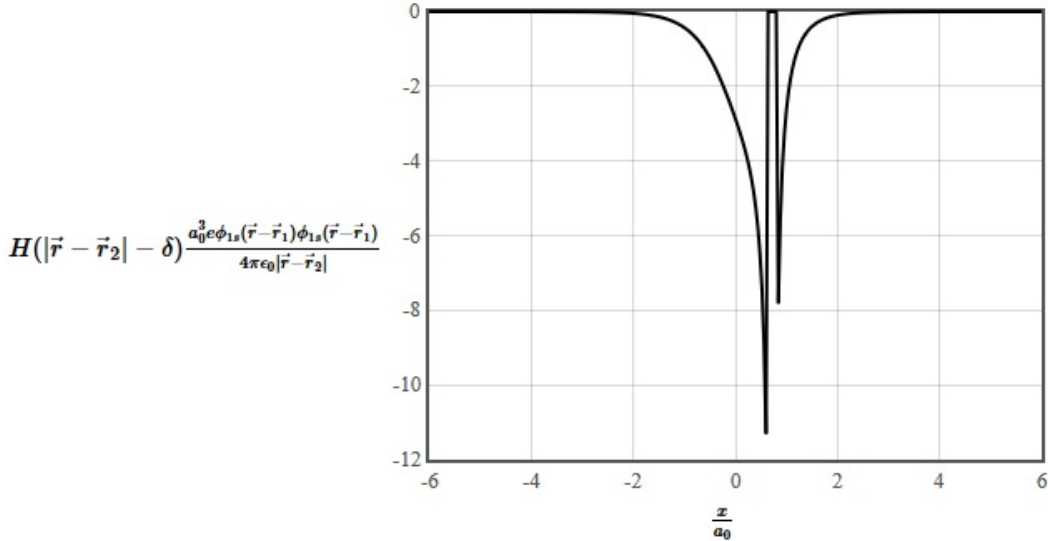
The second term has a singularity at \vec{r}_2 which makes it difficult to evaluate numerically. We break the second term into an integral over a spherical volume of radius δ centered around \vec{r}_2 and a second integral outside that volume.

$$H_{11} = E_1 - \int_{|\vec{r} - \vec{r}_2| < \delta} \phi_{1s}(\vec{r} - \vec{r}_1) \frac{e^2}{4\pi\epsilon_0|\vec{r} - \vec{r}_2|} \phi_{1s}(\vec{r} - \vec{r}_1) d^3r - \int_{|\vec{r} - \vec{r}_2| > \delta} \phi_{1s}(\vec{r} - \vec{r}_1) \frac{e^2}{4\pi\epsilon_0|\vec{r} - \vec{r}_2|} \phi_{1s}(\vec{r} - \vec{r}_1) d^3r. \quad (14)$$

Close to \vec{r}_2 , $\exp\left(\frac{-|\vec{r}-\vec{r}_1|}{a_0}\right) \approx \exp\left(\frac{-|\vec{r}_2-\vec{r}_1|}{a_0}\right)$. Using this approximation, the first integral which includes the singularity can be performed analytically for small δ .

$$H_{11} = E_1 - \frac{e^2 \delta^2}{2\pi\epsilon_0 a_0^3} \exp(-2|\vec{r}_1 - \vec{r}_2|/a_0) - \int H(|\vec{r} - \vec{r}_2| - \delta) \phi_{1s}(\vec{r} - \vec{r}_1) \frac{e^2}{4\pi\epsilon_0 |\vec{r} - \vec{r}_2|} \phi_{1s}(\vec{r} - \vec{r}_1) d^3r, \quad (15)$$

The second integral integrates over all space but a Heaviside step function has been introduced. $H(|\vec{r} - \vec{r}_2| - \delta) = 0$ for $|\vec{r} - \vec{r}_2| < \delta$ and is 1 otherwise. The second integral contains no singularity and can be evaluated numerically.



The integrand of the matrix element plotted along the x-axis for $\delta = a_0/10$.

Similarly, the off-diagonal Hamiltonian matrix element with two 1s orbitals located at positions \vec{r}_1 and \vec{r}_2 is,

$$H_{12} = \left\langle \phi_{1s}(\vec{r} - \vec{r}_1) \left| -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 |\vec{r} - \vec{r}_1|} - \frac{e^2}{4\pi\epsilon_0 |\vec{r} - \vec{r}_2|} \right| \phi_{1s}(\vec{r} - \vec{r}_2) \right\rangle. \quad (16)$$

This can be broken into two terms,

$$H_{12} = \left\langle \phi_{1s}(\vec{r} - \vec{r}_1) \left| -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 |\vec{r} - \vec{r}_2|} \right| \phi_{1s}(\vec{r} - \vec{r}_2) \right\rangle + \left\langle \phi_{1s}(\vec{r} - \vec{r}_1) \left| -\frac{e^2}{4\pi\epsilon_0 |\vec{r} - \vec{r}_1|} \right| \phi_{1s}(\vec{r} - \vec{r}_2) \right\rangle. \quad (17)$$

The wave function $\phi_{1s}(\vec{r} - \vec{r}_2)$ is an eigenfunction of the atomic orbital Hamiltonian in the first term $H\phi_{1s}(\vec{r} - \vec{r}_2) = E_1\phi_{1s}(\vec{r} - \vec{r}_2)$, so the first term is easily evaluated,

$$H_{12} = E_1 S_{12} - \left\langle \phi_{1s}(\vec{r} - \vec{r}_1) \left| \frac{e^2}{4\pi\epsilon_0 |\vec{r} - \vec{r}_1|} \right| \phi_{1s}(\vec{r} - \vec{r}_2) \right\rangle. \quad (18)$$

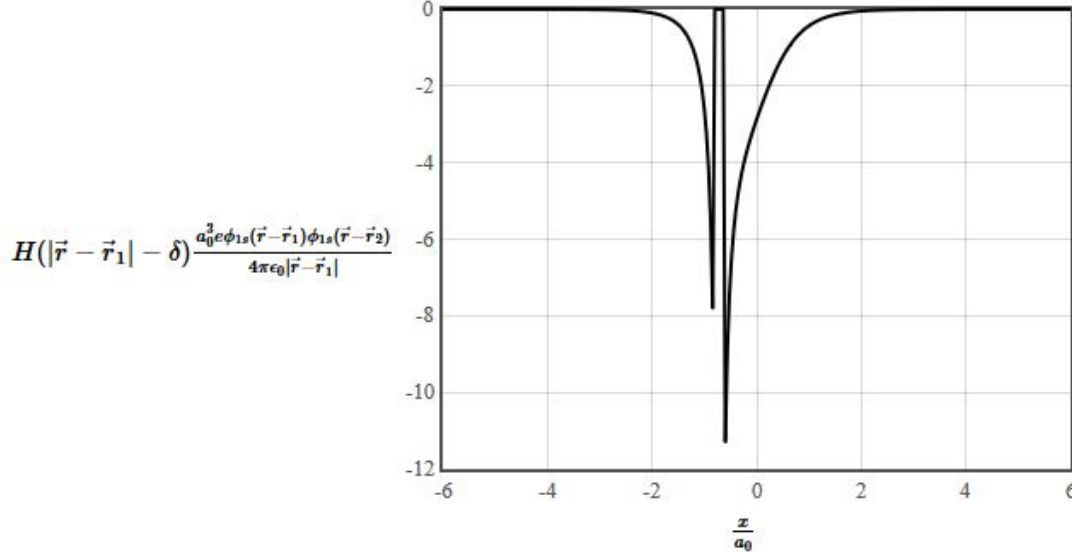
The second term has a singularity at \vec{r}_1 which makes it difficult to evaluate numerically. We break the second term into an integral over a spherical volume of radius δ centered around \vec{r}_1 and a second integral outside that volume.

$$H_{12} = E_1 S_{12} - \int_{|\vec{r}-\vec{r}_1|<\delta} \phi_{1s}(\vec{r}-\vec{r}_1) \frac{e^2}{4\pi\epsilon_0|\vec{r}-\vec{r}_1|} \phi_{1s}(\vec{r}-\vec{r}_2) d^3r - \int_{|\vec{r}-\vec{r}_1|>\delta} \phi_{1s}(\vec{r}-\vec{r}_1) \frac{e^2}{4\pi\epsilon_0|\vec{r}-\vec{r}_1|} \phi_{1s}(\vec{r}-\vec{r}_2) d^3r. \quad (19)$$

Close to \vec{r}_1 , $\exp\left(\frac{-Z|\vec{r}-\vec{r}_2|}{a_0}\right) \approx \exp\left(\frac{-Z|\vec{r}_1-\vec{r}_2|}{a_0}\right)$. Using this approximation, the first integral which includes the singularity can be performed analytically for small δ .

$$H_{12} = E_1 S_{12} - \frac{Z^4 e^2}{\pi a_0^2 \epsilon_0} (a_0 - \exp(-\delta Z/a_0)(a_0 + \delta Z)) \exp(-Z|\vec{r}_1 - \vec{r}_2|/a_0) - \int H(|\vec{r} - \vec{r}_1| - \delta) \phi_{1s}(\vec{r} - \vec{r}_1) \frac{e^2}{4\pi\epsilon_0|\vec{r} - \vec{r}_1|} \phi_{1s}(\vec{r} - \vec{r}_2) d^3r, \quad (20)$$

The second integral integrates over all space but a Heaviside step function has been introduced. $H(|\vec{r} - \vec{r}_1| - \delta) = 0$ for $|\vec{r} - \vec{r}_1| < \delta$ and is 1 otherwise. The second integral contains no singularity and can be evaluated numerically.



The integrand of the matrix element plotted along the x-axis for $\delta = a_0/10$.

To calculate the bond potential, the energy of the ground-state wavefunction is evaluated with the Hamiltonian that includes the proton-proton interaction energy.

$$H^{H_2^+} = -\frac{\hbar^2}{2m_e} \nabla^2 - \frac{e^2}{4\pi\epsilon_0|\vec{r}-\vec{r}_A|} - \frac{e^2}{4\pi\epsilon_0|\vec{r}-\vec{r}_B|} + \frac{e^2}{4\pi\epsilon_0|\vec{r}_A-\vec{r}_B|}. \quad (21)$$

For a given distance between the protons, $|\vec{r}_A - \vec{r}_B|$, the energy is evaluated by calculating,

$$E = \frac{\langle \psi_+ | H^{H_2^+} | \psi_+ \rangle}{\langle \psi_+ | \psi_+ \rangle}. \quad (22)$$

Molecular orbitals of H_2

The simplest neutral molecule is molecular hydrogen, H_2 , which consists of two electrons and two protons. The molecular orbital Hamiltonian in this case is the same as it is for the molecular hydrogen ion and the molecular orbitals are the same as for the molecular ion.

$$H_{\text{mo}}^{H_2} = -\frac{\hbar^2}{2m_e} \nabla^2 - \frac{e^2}{4\pi\epsilon_0|\vec{r} - \vec{r}_A|} - \frac{e^2}{4\pi\epsilon_0|\vec{r} - \vec{r}_B|}, \quad (23)$$

where \vec{r}_A and \vec{r}_B are the positions of the two protons. Consider a linear combination of the two 1s orbitals, $\psi_{\text{mo}} = c_1\phi_{1s}(\vec{r} - \vec{r}_A) + c_2\phi_{1s}(\vec{r} - \vec{r}_B)$. The time independent Schrödinger equation is,

$$H_{\text{mo}}\psi_{\text{mo}} = E\psi_{\text{mo}}. \quad (24)$$

Multiply the Schrödinger equation from the left by each of the atomic orbitals and integrate over all space. This results in a set of 2 algebraic equations called the Roothaan equations.

$$\begin{aligned} \langle \phi_{1s}(\vec{r} - \vec{r}_A) | H_{\text{mo}} | \psi_{\text{mo}} \rangle &= E \langle \phi_{1s}(\vec{r} - \vec{r}_A) | \psi_{\text{mo}} \rangle \\ \langle \phi_{1s}(\vec{r} - \vec{r}_B) | H_{\text{mo}} | \psi_{\text{mo}} \rangle &= E \langle \phi_{1s}(\vec{r} - \vec{r}_B) | \psi_{\text{mo}} \rangle \end{aligned} \quad (25)$$

By substituting in the form for ψ_{mo} from above, the Roothaan equations can be written in matrix form,

$$\begin{bmatrix} H_{11} & H_{12} \\ H_{12} & H_{11} \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = E \begin{bmatrix} S_{11} & S_{12} \\ S_{12} & S_{11} \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix}, \quad (26)$$

where

$$\begin{aligned} H_{11} &= \langle \phi_{1s}(\vec{r} - \vec{r}_A) | H_{\text{mo}}^{H_2} | \phi_{1s}(\vec{r} - \vec{r}_A) \rangle, \\ H_{12} &= \langle \phi_{1s}(\vec{r} - \vec{r}_A) | H_{\text{mo}}^{H_2} | \phi_{1s}(\vec{r} - \vec{r}_B) \rangle, \\ S_{11} &= \langle \phi_{1s}(\vec{r} - \vec{r}_A) | \phi_{1s}(\vec{r} - \vec{r}_A) \rangle = 1, \\ S_{12} &= \langle \phi_{1s}(\vec{r} - \vec{r}_A) | \phi_{1s}(\vec{r} - \vec{r}_B) \rangle. \end{aligned} \quad (27)$$

From experience with 2×2 matrices of this form, we know that the eigenvectors of both the Hamiltonian matrix and the overlap matrix are,

$$\begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = \begin{bmatrix} 1 \\ 1 \end{bmatrix}, \begin{bmatrix} 1 \\ -1 \end{bmatrix} \quad (28)$$

It is easy to check that these are the correct eigenvectors but letting \mathbf{H} and \mathbf{S} operate on them. The energies are,

$$E_+ = \frac{H_{11} + H_{12}}{1 + S_{12}}, \quad E_- = \frac{H_{11} - H_{12}}{1 - S_{12}}. \quad (29)$$

The normalized molecular orbitals are,

$$\psi_{\pm} = \frac{1}{\sqrt{2}} (\phi_{1s}(\vec{r} - \vec{r}_A) \pm \phi_{1s}(\vec{r} - \vec{r}_B)) \quad (30)$$

The calculation of the matrix elements H_{11} , H_{12} , S_{11} , and S_{12} , is discussed on the page for the molecular hydrogen ion. The calculations are identical in this case. Both H_{11} and H_{12} are negative so the bonding orbital ψ_+ , has a lower energy than the antibonding orbital ψ_- . The difference in the bond potentials for H_2 and H_2^+ comes from how the ground state energy is evaluated.

For H_2^+ , there is only one electron so there are no electron-electron interactions. For H_2 , we must use a properly antisymmetrized two-electron wavefunction and include the electron-electron interactions. The two-electron ground state wavefunction for molecular hydrogen is,

$$\begin{aligned} \Psi(\vec{r}_1, \vec{r}_2) &= \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_+ \uparrow(\vec{r}_1) & \psi_+ \downarrow(\vec{r}_1) \\ \psi_+ \uparrow(\vec{r}_2) & \psi_+ \downarrow(\vec{r}_2) \end{vmatrix} \\ &= \frac{1}{2\sqrt{2}} (\phi_{1s}(\vec{r}_1 - \vec{r}_A) + \phi_{1s}(\vec{r}_1 - \vec{r}_B)) (\phi_{1s}(\vec{r}_2 - \vec{r}_A) + \phi_{1s}(\vec{r}_2 - \vec{r}_B)) (\uparrow\downarrow - \downarrow\uparrow). \end{aligned} \quad (31)$$

To calculate the bond potential, the energy of the two-electron wavefunction is evaluated with the electronic Hamiltonian that includes the electron-electron interactions and the proton-proton interactions.

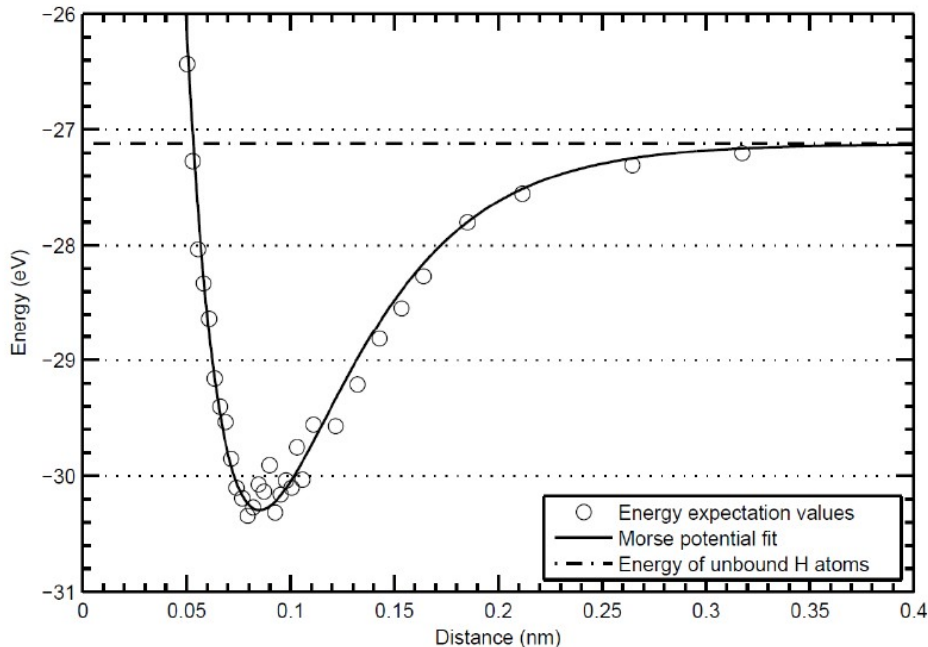
$$\begin{aligned} H_{\text{elec}}^{H_2} &= -\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{\hbar^2}{2m_e} \nabla_2^2 - \frac{e^2}{4\pi\epsilon_0|\vec{r}_1 - \vec{r}_A|} - \frac{e^2}{4\pi\epsilon_0|\vec{r}_1 - \vec{r}_B|} \\ &\quad - \frac{e^2}{4\pi\epsilon_0|\vec{r}_2 - \vec{r}_A|} - \frac{e^2}{4\pi\epsilon_0|\vec{r}_2 - \vec{r}_B|} + \frac{e^2}{4\pi\epsilon_0|\vec{r}_1 - \vec{r}_2|} + \frac{e^2}{4\pi\epsilon_0|\vec{r}_A - \vec{r}_B|}. \end{aligned} \quad (32)$$

For a given distance between the protons, $|\vec{r}_A - \vec{r}_B|$, the energy is evaluated by calculating,

$$E = \frac{\langle \Psi | H_{\text{elec}}^{H_2} | \Psi \rangle}{\langle \Psi | \Psi \rangle}. \quad (33)$$

This is a six-dimensional integral because it is necessary to integrate over the x, y, and z components of \vec{r}_1 and \vec{r}_2 . The integral is difficult because of the singularities that occur when $\vec{r}_1 = \vec{r}_A$, $\vec{r}_1 = \vec{r}_B$, $\vec{r}_2 = \vec{r}_A$, $\vec{r}_2 = \vec{r}_B$, or $\vec{r}_1 = \vec{r}_2$.

The energy is calculated as a function of the distance $|\vec{r}_A - \vec{r}_B|$ which results in a plot of the bond potential like the one below.



Electronic excitations

The first excited state of an H_2 molecule has one electron in the bonding ψ_+ orbital and one in the antibonding ψ_- orbital. This state will be split into a spin singlet and a spin triplet. There are four possible spin states: $\uparrow\uparrow$, $\downarrow\downarrow$, $\downarrow\uparrow$, $\uparrow\downarrow$. Four Slater determinants can be constructed for the four spin possibilities. These four two-electron wavefunctions span a certain function space.

The functions with spin $\uparrow\uparrow$ and $\downarrow\downarrow$ have an antisymmetric orbital part of the wavefunction. Make a transformation of the wavefunctions with spin $\downarrow\uparrow$ and $\uparrow\downarrow$ to wavefunctions with spin $(\downarrow\uparrow + \uparrow\downarrow)/\sqrt{2}$ and $(\downarrow\uparrow - \uparrow\downarrow)/\sqrt{2}$. The wavefunction with spin $(\downarrow\uparrow + \uparrow\downarrow)/\sqrt{2}$ has an antisymmetric orbital part while the wavefunction with spin $(\downarrow\uparrow - \uparrow\downarrow)/\sqrt{2}$ has a symmetric orbital part.

When the energies of these four wavefunctions are evaluated using the $H_{\text{elec}}^{H_2}$ Hamiltonian, the three wavefunctions with the antisymmetric orbital part will have the same energy; this is the spin triplet. The one wavefunction with the symmetric orbital part will have a different energy and is the spin singlet. If a magnetic field is applied, it will couple to the spin and split the spin triplet state into three energy levels.

Vibrational states

The quantum calculations of the bond potential yields a bond length of $r_0 = 0.74 \text{ \AA}$ and a dissociation energy $U_0 = 4.52 \text{ eV}$. These parameters can be used with the Morse potential to calculate the vibrational states of the H_2 molecule. Since there are two atoms in this

molecule there are six degrees of freedom corresponding to the x, y, and z motion of the two atoms.

There are 3 translational degrees of freedom. Since is a linear molecule, there are two rotational degrees of freedom. This means there is just one vibration degree of freedom ($3N - 5 = 1$).

Rotational states

The rotational energy levels can be estimated using a rigid rotator model where the energies are given by,

$$E_l = \frac{\hbar^2}{2I} l(l+1) \quad l = 0, 1, 2, \dots, \quad (34)$$

where I is the moment of inertia. The quantum calculations of the bond potential yields a bond length of $r_0 = 0.74 \text{ \AA}$. This can be used to calculate the moment of inertia,

$$I = 2m_H(r_0/2)^2 = 4.58 \times 10^{-48} \text{ kg m}^2, \quad (35)$$

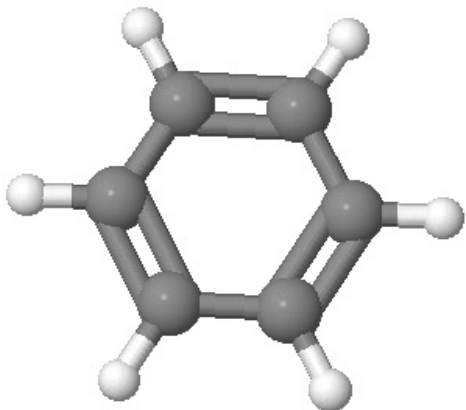
where m_H is the mass of a hydrogen atom. The energy between the $l = 0$ and $l = 1$ levels is,

$$\Delta E = \frac{\hbar^2}{I} = 2.4 \times 10^{-21} \text{ J} = 15 \text{ meV}. \quad (36)$$

This agrees with the value calculated from the spectroscopic constants.

Molecular orbitals of benzene

Benzene (C_6H_6) consists of 6 carbon atoms in a ring. A hydrogen atom is attached to each carbon atom. The carbon-carbon bond length is 1.40 \AA and the carbon-hydrogen bond length is 1.10 \AA .



The molecular orbital Hamiltonian is,

$$H_{\text{mo}} = -\frac{\hbar^2}{2m_e} \nabla^2 - \sum_{a=1}^A \frac{Z_a e^2}{4\pi\epsilon_0 |\vec{r} - \vec{r}_a|}. \quad (37)$$

Here a sums over all of the atoms in the molecule. For bezene there is one Coulomb term for each carbon atom with $Z = 6$ and one Coulomb term for each hydrogen atom with $Z = 1$.

Carbon has 6 electrons. Two electrons occupy the 1s orbital. Three electrons participate in sp^2 bonds with the neighboring carbon atoms or with a hydrogen atom. The sixth electron occupies the $2p_z$ orbital which is half filled. The valence orbitals are the 6 carbon $2p_z$ orbitals. Using the LCAO method, we guess that a good solution to the molecular orbital Hamiltonian can be found in terms of a linear combination of the valence orbitals.

$$\begin{aligned} \psi_{\text{mo}} = & c_1 \phi_{2p_z}^C(\vec{r} - \vec{r}_1) + c_2 \phi_{2p_z}^C(\vec{r} - \vec{r}_2) + c_3 \phi_{2p_z}^C(\vec{r} - \vec{r}_3) \\ & + c_4 \phi_{2p_z}^C(\vec{r} - \vec{r}_4) + c_5 \phi_{2p_z}^C(\vec{r} - \vec{r}_5) + c_6 \phi_{2p_z}^C(\vec{r} - \vec{r}_6). \end{aligned} \quad (38)$$

Here c_i are constants that need to be determined and $\phi_{2p_z}^C(\vec{r})$ is the $2p_z$ atomic orbital with $Z = 6$. This wavefunction is inserted into the time-independent Schrödinger equation,

$$H_{\text{mo}} \psi_{\text{mo}} = E \psi_{\text{mo}}. \quad (39)$$

Multiplying the Schrödinger equation from the left by each of the atomic orbitals results in a set of N algebraic equations called the Roothaan equations.

$$\begin{aligned} \langle \phi_{2p_z}^C(\vec{r} - \vec{r}_1) | H_{\text{mo}} | \psi_{\text{mo}} \rangle &= E \langle \phi_{2p_z}^C(\vec{r} - \vec{r}_1) | \psi_{\text{mo}} \rangle \\ \langle \phi_{2p_z}^C(\vec{r} - \vec{r}_2) | H_{\text{mo}} | \psi_{\text{mo}} \rangle &= E \langle \phi_{2p_z}^C(\vec{r} - \vec{r}_2) | \psi_{\text{mo}} \rangle \\ \langle \phi_{2p_z}^C(\vec{r} - \vec{r}_3) | H_{\text{mo}} | \psi_{\text{mo}} \rangle &= E \langle \phi_{2p_z}^C(\vec{r} - \vec{r}_3) | \psi_{\text{mo}} \rangle \\ \langle \phi_{2p_z}^C(\vec{r} - \vec{r}_4) | H_{\text{mo}} | \psi_{\text{mo}} \rangle &= E \langle \phi_{2p_z}^C(\vec{r} - \vec{r}_4) | \psi_{\text{mo}} \rangle \\ \langle \phi_{2p_z}^C(\vec{r} - \vec{r}_5) | H_{\text{mo}} | \psi_{\text{mo}} \rangle &= E \langle \phi_{2p_z}^C(\vec{r} - \vec{r}_5) | \psi_{\text{mo}} \rangle \\ \langle \phi_{2p_z}^C(\vec{r} - \vec{r}_6) | H_{\text{mo}} | \psi_{\text{mo}} \rangle &= E \langle \phi_{2p_z}^C(\vec{r} - \vec{r}_6) | \psi_{\text{mo}} \rangle \end{aligned} \quad (40)$$

The Roothaan equations can be written in matrix form,

$$\begin{bmatrix} H_{11} & H_{12} & H_{13} & H_{14} & H_{15} & H_{16} \\ H_{21} & H_{22} & H_{23} & H_{24} & H_{25} & H_{26} \\ H_{31} & H_{32} & H_{33} & H_{34} & H_{35} & H_{36} \\ H_{41} & H_{42} & H_{43} & H_{44} & H_{45} & H_{46} \\ H_{51} & H_{52} & H_{53} & H_{54} & H_{55} & H_{56} \\ H_{61} & H_{62} & H_{63} & H_{64} & H_{65} & H_{66} \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \\ c_5 \\ c_6 \end{bmatrix} = E \begin{bmatrix} S_{11} & S_{12} & S_{13} & S_{14} & S_{15} & S_{16} \\ S_{21} & S_{22} & S_{23} & S_{24} & S_{25} & S_{26} \\ S_{31} & S_{32} & S_{33} & S_{34} & S_{35} & S_{36} \\ S_{41} & S_{42} & S_{43} & S_{44} & S_{45} & S_{46} \\ S_{51} & S_{52} & S_{53} & S_{54} & S_{55} & S_{56} \\ S_{61} & S_{62} & S_{63} & S_{64} & S_{65} & S_{66} \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \\ c_5 \\ c_6 \end{bmatrix}. \quad (41)$$

Here the elements of the Hamiltonian matrix and the overlap matrix are,

$$\begin{aligned}
H_{ij} &= \langle \phi_{2p_z}^C(\vec{r} - \vec{r}_i) | H_{\text{mo}} | \phi_{2p_z}^C(\vec{r} - \vec{r}_j) \rangle \quad \text{and} \\
S_{ij} &= \langle \phi_{2p_z}^C(\vec{r} - \vec{r}_i) | \phi_{2p_z}^C(\vec{r} - \vec{r}_j) \rangle.
\end{aligned} \tag{42}$$

In general, the Roothaan equations must be solved numerically.

A common approximation that is made is to assume that the overlap matrix equals the identity matrix $\mathbf{S} = \mathbf{I}$. In that case, the Roothaan equations reduce to an eigenvalue problem $\mathbf{H}\vec{c} = E\vec{c}$ which can easily be solved by a program like Matlab or Mathematica.

There are six eigen energies E and six sets of coefficients c_i that describe the molecular orbitals. The molecular orbitals can each be occupied by two electrons, one with spin up and one with spin down. In the ground state, the 6 electrons will occupy the 3 molecular orbitals with the lowest energies.

Benzene is a special case where some progress can be made analytically. Elements of the Hamiltonian matrix and the overlap matrix corresponding to orbitals that are not on the same atom or on neighboring atoms are negligibly small and are set to zero.

Because of the symmetry of the molecule all of the diagonal elements are the same and the elements corresponding to orbitals on neighboring sites are the same. The only integrals that need to be calculated are S_{11} , S_{12} , H_{11} , and H_{12} . Assuming that $\vec{r}_1 = 0$,

$$S_{11} = \langle \phi_{2p_z}^C(\vec{r}) | \phi_{2p_z}^C(\vec{r}) \rangle, \tag{43}$$

where,

$$\phi_{2p_z}^C = \frac{1}{4} \sqrt{\frac{6^3}{2\pi a_0^3}} \frac{6r}{a_0} \exp\left(-\frac{3r}{a_0}\right) \cos\theta. \tag{44}$$

$$S_{11} = \int_0^{2\pi} \int_0^\pi \int_0^\infty \frac{1}{16} \frac{216}{2\pi a_0^3} \frac{36r^2}{a_0^2} \exp\left(-\frac{6r}{a_0}\right) \cos^2\theta r^2 \sin\theta dr d\theta d\varphi. \tag{45}$$

The three integrals can be evaluated,

$$\begin{aligned}
\int_0^{2\pi} d\varphi &= 2\pi, & \int_0^\pi \cos^2\theta \sin\theta d\theta &= \frac{2}{3}, \\
\int_0^\infty \frac{1}{16} \frac{216}{2\pi a_0^3} \frac{36r^2}{a_0^2} \exp\left(-\frac{6r}{a_0}\right) r^2 dr &= \frac{3}{4\pi}.
\end{aligned} \tag{46}$$

Thus,

$$S_{11} = 1. \tag{47}$$

To calculate S_{12} it is convenient to use Cartesian coordinates where $z = r \cos\theta$,

$$\phi_{2p_z}^C = \frac{1}{4} \sqrt{\frac{6^3}{2\pi a_0^3}} \frac{6z}{a_0} \exp\left(-\frac{3\sqrt{x^2 + y^2 + z^2}}{a_0}\right). \tag{48}$$

The Roothaan equations take the form,

$$\begin{bmatrix} H_{11} & H_{12} & 0 & 0 & 0 & H_{12} \\ H_{12} & H_{11} & H_{12} & 0 & 0 & 0 \\ 0 & H_{12} & H_{11} & H_{12} & 0 & 0 \\ 0 & 0 & H_{12} & H_{11} & H_{12} & 0 \\ 0 & 0 & 0 & H_{12} & H_{11} & H_{12} \\ H_{12} & 0 & 0 & 0 & H_{12} & H_{11} \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \\ c_5 \\ c_6 \end{bmatrix} = E \begin{bmatrix} 1 & S_{12} & 0 & 0 & 0 & S_{12} \\ S_{12} & 1 & S_{12} & 0 & 0 & 0 \\ 0 & S_{12} & 1 & S_{12} & 0 & 0 \\ 0 & 0 & S_{12} & 1 & S_{12} & 0 \\ 0 & 0 & 0 & S_{12} & 1 & S_{12} \\ S_{12} & 0 & 0 & 0 & S_{12} & 1 \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \\ c_5 \\ c_6 \end{bmatrix}. \quad (49)$$

The matrix on each side of this equation can be written in terms of the identity matrix \mathbf{I} , the translation operator \mathbf{T} , and the inverse of the translation operator \mathbf{T}^{-1} .

$$H = H_{11}\mathbf{I} + H_{12}\mathbf{T} + H_{12}\mathbf{T}^{-1} \quad S = \mathbf{I} + S_{12}\mathbf{T} + S_{12}\mathbf{T}^{-1} \quad (50)$$

The eigenvectors of these matrices are also eigenvectors of the translation operator,

$$\begin{bmatrix} e^{i\pi/3} \\ e^{i2\pi/3} \\ -1 \\ e^{i4\pi/3} \\ e^{i5\pi/3} \\ 1 \end{bmatrix}, \begin{bmatrix} e^{i2\pi/3} \\ e^{i4\pi/3} \\ 1 \\ e^{i8\pi/3} \\ e^{i10\pi/3} \\ 1 \end{bmatrix}, \begin{bmatrix} -1 \\ 1 \\ -1 \\ 1 \\ -1 \\ 1 \end{bmatrix}, \begin{bmatrix} e^{i4\pi/3} \\ e^{i8\pi/3} \\ 1 \\ e^{i16\pi/3} \\ e^{i20\pi/3} \\ 1 \end{bmatrix}, \begin{bmatrix} e^{i5\pi/3} \\ e^{i10\pi/3} \\ -1 \\ e^{i20\pi/3} \\ e^{i25\pi/3} \\ 1 \end{bmatrix}, \begin{bmatrix} 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \end{bmatrix}. \quad (51)$$

The eigen energies are,

$$E_{\text{mo},j} = \frac{H_{11} + 2H_{12} \cos\left(\frac{\pi j}{3}\right)}{1 + 2S_{12} \cos\left(\frac{\pi j}{3}\right)} \quad j = 1, 2, \dots, 6. \quad (52)$$

The molecular orbitals are,

$$\psi_{\text{mo},j} = \frac{1}{\sqrt{6}} \sum_{n=1}^6 \exp\left(\frac{i\pi n j}{3}\right) \phi_{2pz}^C(\vec{r} - \vec{r}_n) \quad j = 1, 2, \dots, 6. \quad (53)$$

There are 6 valence electrons and we have calculated 6 molecular orbitals. In the ground state, the 6 electrons will occupy the 3 molecular orbitals with the lowest energies. Because $H_{12} < 0$, the occupied orbitals are $\psi_{\text{mo},6}$, $\psi_{\text{mo},1}$ and $\psi_{\text{mo},5}$. $\psi_{\text{mo},6}$ has the lowest energy and $\psi_{\text{mo},1}$ and $\psi_{\text{mo},5}$ have the same energy.

Molecular orbitals of a conjugated ring

The Roothaan equations for a conjugated ring of N atoms have the form,

$$\begin{bmatrix} H_{11} & H_{12} & 0 & \cdots & 0 & H_{12} \\ H_{12} & H_{11} & H_{12} & 0 & & 0 \\ 0 & H_{12} & H_{11} & H_{12} & \ddots & \vdots \\ \vdots & \ddots & \ddots & \ddots & \ddots & 0 \\ 0 & & 0 & H_{12} & H_{11} & H_{12} \\ H_{12} & 0 & \cdots & 0 & H_{12} & H_{11} \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \\ \vdots \\ c_N \end{bmatrix} = E \begin{bmatrix} 1 & S_{12} & 0 & \cdots & 0 & S_{12} \\ S_{12} & 1 & S_{12} & 0 & & 0 \\ 0 & S_{12} & 1 & S_{12} & \ddots & \vdots \\ \vdots & \ddots & \ddots & \ddots & \ddots & 0 \\ 0 & & 0 & S_{12} & 1 & S_{12} \\ S_{12} & 0 & \cdots & 0 & S_{12} & 1 \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \\ \vdots \\ c_N \end{bmatrix}. \quad (54)$$

In general, the Roothaan equations must be solved numerically. A common approximation that is made is to assume that the overlap matrix equals the identity matrix $\mathbf{S} = \mathbf{I}$. In that case, the Roothaan equations reduce to an eigenvalue problem $\mathbf{H}\vec{c} = E\vec{c}$ which can easily be solved by a program like Matlab or Mathematica.

The conjugated ring is a special case where some progress can be made analytically. The eigen vectors of the Hamiltonian matrix and the overlap matrix are also the eigen vectors of the translation operator. The energies of the molecular orbitals are,

$$E_{\text{mo},j} = \frac{H_{11} + 2H_{12} \cos\left(\frac{2\pi j}{N}\right)}{1 + 2S_{12} \cos\left(\frac{2\pi j}{N}\right)} \quad j = 1, 2, \dots, N. \quad (55)$$

The molecular orbitals are,

$$\psi_{\text{mo},j} = \frac{1}{\sqrt{N}} \sum_{n=1}^N \exp\left(\frac{i2\pi nj}{N}\right) \phi_{2pz}^C(\vec{r} - \vec{r}_n) \quad j = 1, 2, \dots, N. \quad (56)$$

There are valence electrons will occupy the molecular orbitals with the lowest energies. Because $H_{12} < 0$, the molecular orbital with the lowest energy is $\psi_{\text{mo},N}$.

Molecular orbitals of a conjugated chain

The Roothaan equations for a conjugated chain of N atoms have the form,

$$\begin{bmatrix} H_{11} & H_{12} & 0 & \cdots & 0 & 0 \\ H_{12} & H_{11} & H_{12} & 0 & & 0 \\ 0 & H_{12} & H_{11} & H_{12} & \ddots & \vdots \\ \vdots & \ddots & \ddots & \ddots & \ddots & 0 \\ 0 & & 0 & H_{12} & H_{11} & H_{12} \\ 0 & 0 & \cdots & 0 & H_{12} & H_{11} \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \\ \vdots \\ c_N \end{bmatrix} = E \begin{bmatrix} 1 & S_{12} & 0 & \cdots & 0 & 0 \\ S_{12} & 1 & S_{12} & 0 & & 0 \\ 0 & S_{12} & 1 & S_{12} & \ddots & \vdots \\ \vdots & \ddots & \ddots & \ddots & \ddots & 0 \\ 0 & & 0 & S_{12} & 1 & S_{12} \\ 0 & 0 & \cdots & 0 & S_{12} & 1 \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \\ \vdots \\ c_N \end{bmatrix}. \quad (57)$$

In general, the Roothaan equations must be solved numerically. A common approximation that is made is to assume that the overlap matrix equals the identity matrix $\mathbf{S} = \mathbf{I}$. In that case, the Roothaan equations reduce to an eigenvalue problem $\mathbf{H}\vec{c} = E\vec{c}$ which can easily be solved by a program like Matlab or Mathematica.

The conjugated chain is a special case where some progress can be made analytically. We know from experience that the eigenvectors of matrices like those in the Roothaan equations have the form,

$$\begin{bmatrix} \sin\left(\frac{\pi j}{N+1}\right) \\ \sin\left(\frac{2\pi j}{N+1}\right) \\ \sin\left(\frac{3\pi j}{N+1}\right) \\ \vdots \\ \sin\left(\frac{N\pi j}{N+1}\right) \end{bmatrix} \quad j = 1, 2, \dots, N. \quad (58)$$

This can be checked by substituting the eigenvectors into the Roothaan equations,

$$\begin{aligned} & \begin{bmatrix} H_{11} \sin\left(\frac{\pi j}{N+1}\right) + H_{12} \sin\left(\frac{2\pi j}{N+1}\right) \\ H_{12} \sin\left(\frac{\pi j}{N+1}\right) + H_{11} \sin\left(\frac{2\pi j}{N+1}\right) + H_{12} \sin\left(\frac{3\pi j}{N+1}\right) \\ H_{12} \sin\left(\frac{2\pi j}{N+1}\right) + H_{11} \sin\left(\frac{3\pi j}{N+1}\right) + H_{12} \sin\left(\frac{4\pi j}{N+1}\right) \\ \vdots \\ H_{12} \sin\left(\frac{(N-1)\pi j}{N+1}\right) + H_{11} \sin\left(\frac{N\pi j}{N+1}\right) \end{bmatrix} \\ &= E \begin{bmatrix} \sin\left(\frac{\pi j}{N+1}\right) + S_{12} \sin\left(\frac{2\pi j}{N+1}\right) \\ S_{12} \sin\left(\frac{\pi j}{N+1}\right) + \sin\left(\frac{2\pi j}{N+1}\right) + S_{12} \sin\left(\frac{3\pi j}{N+1}\right) \\ S_{12} \sin\left(\frac{2\pi j}{N+1}\right) + \sin\left(\frac{3\pi j}{N+1}\right) + S_{12} \sin\left(\frac{4\pi j}{N+1}\right) \\ \vdots \\ S_{12} \sin\left(\frac{(N-1)\pi j}{N+1}\right) + \sin\left(\frac{N\pi j}{N+1}\right) \end{bmatrix}. \end{aligned} \quad (59)$$

Using the trigonometric relations $\sin a + \sin b = 2 \sin\left(\frac{a+b}{2}\right) \cos\left(\frac{a-b}{2}\right)$, $\sin a \cos b = \frac{\sin(a+b)}{2} + \frac{\sin(a-b)}{2}$, and $\sin 2a = 2 \sin a \cos a$,

$$\left(H_{11} + 2H_{12} \cos\left(\frac{\pi j}{N+1}\right) \right) \begin{bmatrix} \sin\left(\frac{\pi j}{N+1}\right) \\ \sin\left(\frac{2\pi j}{N+1}\right) \\ \sin\left(\frac{3\pi j}{N+1}\right) \\ \vdots \\ \sin\left(\frac{N\pi j}{N+1}\right) \end{bmatrix} = E \left(1 + 2S_{12} \cos\left(\frac{\pi j}{N+1}\right) \right) \begin{bmatrix} \sin\left(\frac{\pi j}{N+1}\right) \\ \sin\left(\frac{2\pi j}{N+1}\right) \\ \sin\left(\frac{3\pi j}{N+1}\right) \\ \vdots \\ \sin\left(\frac{N\pi j}{N+1}\right) \end{bmatrix} \quad j = 1, 2, \dots, N. \quad (60)$$

The energies of the molecular orbitals are,

$$E_{\text{mo},j} = \frac{H_{11} + 2H_{12} \cos\left(\frac{\pi j}{N+1}\right)}{1 + 2S_{12} \cos\left(\frac{\pi j}{N+1}\right)} \quad j = 1, 2, \dots, N. \quad (61)$$

The normalized molecular orbitals are,

$$\psi_{\text{mo},j} = \sqrt{\frac{2}{N+1}} \sum_{n=1}^N \sin\left(\frac{\pi n j}{N+1}\right) \phi_{pz,n} \quad j = 1, 2, \dots, N. \quad (62)$$

There are valence electrons will occupy the molecular orbitals with the lowest energies. Because $H_{12} < 0$, the molecular orbital with the lowest energy is $\psi_{\text{mo},1}$ and the molecular orbital with the highest energy is $\psi_{\text{mo},N}$.