The Hydrogen Molecular Ion H_2^+ with Overlap: Symmetric and Antisymmetric States via the LCAO Method

Diego Valenzuela Castro

June 2026 (v1.1)

Abstract

In this note, we present a derivation of the symmetric and antisymmetric states of the hydrogen molecular ion H_2^+ with overlap. Employing the Born-Oppenheimer approximation and the LCAO method, we construct the generalized eigenvalue problem. In addition, we provide a physical interpretation of the hopping term, a parameter that couples the time evolution of the atomic orbitals. Finally, we determine the eigenenergies and the eigenstates of the system.

1 Physical System and Theoretical Framework

We analyze the system composed of two hydrogen nuclei and one electron. Since the nuclei are much heavier than the electron, we can fix the nuclear positions and solve the Schrödinger equation for the single electron. This approach is known as the *Born-Oppenheimer approximation*.

Our objective is to calculate the eigenergies of the system, and once they are determined, derive their corresponding eigenstates.

1.1 Hamiltonian of the Molecular Ion

To write the Hamiltonian, we consider the kinetic energy of the electron and the potential energies due to the nuclei. Thus, the Hamiltonian of the system can be expressed as follows:

$$H = T + V_1(\mathbf{r}) + V_2(\mathbf{r}) \,,$$

where T is the kinetic energy operator of the electron, and $V_1(\mathbf{r})$ and $V_2(\mathbf{r})$ are the Coulomb potential energies between the nuclei and the electron, given by:

$$V_i(\mathbf{r}) = -\frac{e^2}{4\pi\epsilon_0|\mathbf{r} - \mathbf{R}_i|} \,,$$

with $\mathbf{R}_i$ denoting the position of the nucleus i (with $i = 1, 2$), which is fixed.

Note that since the nuclei are fixed, the potential due to the interaction between the nuclei is constant and we can ignore it in the Hamiltonian.

DOI: https://doi.org/10.5281/zenodo.20656086
ORCID: https://orcid.org/0009-0006-9386-0692
Contact: diegovc.phys@gmail.com
Project: *Domina la Física* — https://dominalafisica.com

1.2 The LCAO Method

Instead of solving the Schrödinger equation directly to obtain an exact solution, which is quite a complex procedure, we will derive an approximate solution by proposing the following trial state vector:

$$|\psi\rangle = c_1 |1\rangle + c_2 |2\rangle \ , \tag{1}$$

where c_1 and c_2 are complex coefficients, and the kets $|1\rangle$ and $|2\rangle$ are called *atomic orbitals* or *tight-binding orbitals*.

This approach is known as the *Linear Combination of Atomic Orbitals (LCAO)*, which can be improved by adding more orbitals with their respective coefficients.

The states $|1\rangle$ and $|2\rangle$ that we use here represent the ground-state solution of the Schrödinger equation when there is only one nucleus present. Due to the nature of the system, the behavior of the electron is well captured by the ground states; therefore, to obtain a good approximation it is not necessary to consider excited states in our ansatz.

Thus, we have the following eigenvalue equations:

$$H_1 |1\rangle = E_f |1\rangle \tag{2}$$

$$H_2 |2\rangle = E_f |2\rangle \ , \tag{3}$$

where $H_i = T + V_i$, with $i = 1, 2$. E_f represents the energy of the ground state of the hydrogen atom without the presence of the other nucleus. Specifically, $|1\rangle$ represents the ground state of an electron bound to the nucleus 1, and $|2\rangle$ denotes the ground state of an electron bound to the nucleus 2.

1.3 Relation between the Atomic Orbitals

We consider both ground states normalized, i.e., $\langle 1|1\rangle$=$\langle 2|2\rangle = 1$. At this point, we introduce a condition that changes the manner in which we usually treat the problems where the inner product is involved. Due to the overlap between the orbitals, we have that $\langle 1|2\rangle$=$\langle 2|1\rangle = S$, where for normalized ground states, S is a real number and bounded within the range of $0 < S < 1$.

A simple physical interpretation of the overlap is that the orbitals of both nuclei share a common region of space. This means that $S = 0$ (the orthogonal case) represents the situation where the nuclei are infinitely far from each other, so the orbitals do not share any region of space. Conversely, $S = 1$ represents the case where the nuclei are sharing the same region of space, which is not physically possible.

2 Derivation of the Symmetric and Antisymmetric States

When we approach a problem with the LCAO method, we must determine the coefficients of the trial state vector. To accomplish this, we can use the variational principle, which involves minimizing the expectation value of the Hamiltonian by taking partial derivatives with respect to the coefficients. This results in a system of equations that allows us to determine the coefficients.

However, we will use another method, which consists of substituting the trial state vector into the time-independent Schrödinger equation by exploiting the fact that the basis chosen $\{|1\rangle , |2\rangle\}$ is composed of the respective stationary ground states of each hydrogen atom.

2.1 The Generalized Eigenvalue Problem

We invoke the time-independent Schrödinger equation:

$$H |\psi\rangle = E |\psi\rangle \ , \tag{4}$$

where E is the energy eigenvalue associated with the state vector $|\psi\rangle$.

Substituting the trial state from Eq. (1) into the Schrödinger equation yields:

$$H(c_1 |1\rangle + c_2 |2\rangle) = E(c_1 |1\rangle + c_2 |2\rangle) . \tag{5}$$

In order to derive a system of equations for the coefficients c_1 and c_2, we project Eq. (4) onto each of the basis states. We will follow a general treatment to exhibit the structure of the problem, and subsequently, we will evaluate each matrix element of the Hamiltonian separately.

If we project Eq. (5) onto the orbital $|1\rangle$, we get:

$$c_1 \underbrace{\langle 1|H|1\rangle}_{H_{11}} + c_2 \underbrace{\langle 1|H|2\rangle}_{H_{12}} = E(c_1 \underbrace{\langle 1|1\rangle}_{1} + c_2 \underbrace{\langle 1|2\rangle}_{S})$$

$$\therefore \quad H_{11}\, c_1 + H_{12}\, c_2 = E(c_1 + S c_2) . \tag{6}$$

Similarly, projecting onto the orbital $|2\rangle$ gives:

$$c_1 \underbrace{\langle 2|H|1\rangle}_{H_{21}} + c_2 \underbrace{\langle 2|H|2\rangle}_{H_{22}} = E(c_1 \underbrace{\langle 2|1\rangle}_{S} + c_2 \underbrace{\langle 2|2\rangle}_{1})$$

$$\therefore \quad H_{21}\, c_1 + H_{22}\, c_2 = E(S c_1 + c_2) . \tag{7}$$

Combining Eq. (6) and Eq. (7), we obtain the following system of equations:

$$\begin{cases} H_{11}\, c_1 + H_{12}\, c_2 = E(c_1 + S c_2) \\ H_{21}\, c_1 + H_{22}\, c_2 = E(S c_1 + c_2) . \end{cases}$$

We can rewrite the system of equations in matrix form as follows:

$$\begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = E \begin{pmatrix} c_1 + S c_2 \\ S c_1 + c_2 \end{pmatrix} . \tag{8}$$

Expressing the right-hand side of Eq. (8) as a matrix product allows us to identify the structure of the problem.

$$\begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = E \begin{pmatrix} 1 & S \\ S & 1 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} . \tag{9}$$

We have constructed a *generalized eigenvalue problem*:

$$\mathbf{Hc} = E\mathbf{Sc} ,$$

where $\mathbf{H}$ is the Hamiltonian operator represented in the basis $\{|1\rangle , |2\rangle\}$, known as the *Hamiltonian matrix*, and $\mathbf{S}$ is called the *overlap matrix*.

Note that the Hamiltonian matrix is not diagonal, even though we are representing H in the basis of the eigenstates of the hydrogen atom Hamiltonian. This is because H, as established earlier in Eqs. (2) and (3), is the Hamiltonian of the H_2^+ ion. Consequently, $|1\rangle$ and $|2\rangle$ are not eigenstates of H, but rather of H_1 and H_2 respectively.

2.2 The Hamiltonian Matrix Elements

Now, we will evaluate each term of the Hamiltonian matrix. We start with the diagonal terms, due to the similarity of their structure.

$$\begin{aligned} H_{11} = \langle 1|H|1\rangle &= \langle 1|T + V_1 + V_2|1\rangle \\ &= \langle 1|T + V_1|1\rangle + \langle 1|V_2|1\rangle \\ &= \langle 1|H_1|1\rangle + \langle 1|V_2|1\rangle . \end{aligned}$$

Recalling Eq. (2), we obtain that $\langle 1|H_1|1\rangle = E_f$.

$$\therefore \quad H_{11} = E_f + \langle 1|V_2|1\rangle \ . \tag{10}$$

We do the same for the other diagonal term:

$$\begin{aligned} H_{22} = \langle 2|H|2\rangle &= \langle 2|T + V_1 + V_2|2\rangle \\ &= \langle 2|T + V_2|2\rangle + \langle 2|V_1|2\rangle \\ &= \langle 2|H_2|2\rangle + \langle 2|V_1|2\rangle \ . \end{aligned}$$

Eq. (3) implies that $\langle 2|H_2|2\rangle = E_f$.

$$\therefore \quad H_{22} = E_f + \langle 2|V_1|2\rangle \ . \tag{11}$$

From Eqs. (10) and (11), the diagonal terms of the Hamiltonian matrix are:

$$\begin{cases} H_{11} = E_f + \langle 1|V_2|1\rangle \\ H_{22} = E_f + \langle 2|V_1|2\rangle \ . \end{cases}$$

Due to the symmetry of the system, we introduce the following notation:

$$\langle 1|V_2|1\rangle = \langle 2|V_1|2\rangle = V_{cross} \ .$$

These terms are the same, because $\langle 1|V_2|1\rangle$ is the Coulomb potential energy of the orbital $|1\rangle$ due to the nucleus 2, and $\langle 2|V_1|2\rangle$ is the Coulomb potential energy of the orbital $|2\rangle$ due to the nucleus 1. Since both are hydrogen nuclei, both values must be equal. We denote this value as V_{cross}.

For the off-diagonal terms H_{12} and H_{21}, we exploit that H is a Hermitian operator. Therefore, we can use the relation:

$$H_{12} = H_{21}^* \ .$$

We define $H_{12} = \langle 1|H|2\rangle = \beta$, thus $H_{21} = \beta^*$. Given that we are dealing with ground-state orbitals ($1s$), these are real, so the Hamiltonian matrix elements must be real. Consequently, $\beta = \beta^*$.

Substituting the above value of the off-diagonal terms along with the value of the diagonal ones into Eq. (9) yields:

$$\begin{pmatrix} E_f + V_{cross} & \beta \\ \beta & E_f + V_{cross} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = E \begin{pmatrix} 1 & S \\ S & 1 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} \ . \tag{12}$$

2.3 The Hopping Term

The physical interpretation of Eq. (12) is, for the diagonal terms, that the orbitals $|1\rangle$ and $|2\rangle$ have energies E_f, which are shifted by V_{cross}, due to the presence of the other nucleus. Then, to simplify the notation, we denote the sum $E_f + V_{cross}$ as E_0.

Furthermore, the most interesting physics is contained in the off-diagonal matrix elements, i.e., in β. This term is known as the *hopping*, because it represents the process of the electron hopping from one nucleus to the other. This establishes an interaction that couples the time evolution between the atomic orbitals.

In order to visualize this phenomenon, we provide a time evolution analysis. For simplicity, to isolate the effect of the hopping, we assume for this particular discussion that $S = 0$. We invoke the time-dependent Schrödinger equation:

$$i\hbar \frac{d}{dt} |\psi(t)\rangle = H |\psi(t)\rangle \ . \tag{13}$$

We recall Eq. (1):

$$|\psi\rangle = c_1 |1\rangle + c_2 |2\rangle \ .$$

By using the $\{|1\rangle, |2\rangle\}$ basis, we can express the time evolution of the state vector as:

$$|\psi(t)\rangle = c_1(t)\,|1\rangle + c_2(t)\,|2\rangle \ ,$$

Since the kets $|1\rangle$ and $|2\rangle$ are eigenstates of their respective time-independent Hamiltonians, all the time dependence is contained within $c_1(t)$ and $c_2(t)$.

Therefore, in this basis, we have the following representation of the time-dependent Schrödinger equation:

$$i\hbar \frac{d}{dt}\begin{pmatrix} c_1(t) \\ c_2(t) \end{pmatrix} = \mathbf{H}\begin{pmatrix} c_1(t) \\ c_2(t) \end{pmatrix} , \tag{14}$$

where $\mathbf{H}$ is given by:

$$\mathbf{H} = \begin{pmatrix} E_0 & \beta \\ \beta & E_0 \end{pmatrix} .$$

Consequently, Eq. (14) can be written as:

$$i\hbar \frac{d}{dt}\begin{pmatrix} c_1(t) \\ c_2(t) \end{pmatrix} = \begin{pmatrix} E_0 & \beta \\ \beta & E_0 \end{pmatrix}\begin{pmatrix} c_1(t) \\ c_2(t) \end{pmatrix} . \tag{15}$$

Expressing Eq. (15) as a system of linear equations yields:

$$\begin{cases} \dfrac{d}{dt}c_1(t) = -\dfrac{i}{\hbar}\left[E_0 c_1(t) + \beta c_2(t)\right] \\ \dfrac{d}{dt}c_2(t) = -\dfrac{i}{\hbar}\left[\beta c_1(t) + E_0 c_2(t)\right] . \end{cases}$$

Therefore, the time evolution of $c_1(t)$ depends on $c_2(t)$, and vice versa, i.e., they are coupled.

If the hopping term $\beta = 0$, we obtain:

$$\begin{cases} \dfrac{d}{dt}c_1(t) = -\dfrac{i}{\hbar}E_0 c_1(t) \\ \dfrac{d}{dt}c_2(t) = -\dfrac{i}{\hbar}E_0 c_2(t) . \end{cases}$$

This means that without hopping the two orbitals evolve independently of each other, in consequence, there is no bond between them.

We can construct an analogy with a classical coupled oscillator. Consider two pendulums connected by a spring. In this system, the motion of one pendulum influences the other due to the action of the spring. If the spring is removed, the two pendulums oscillate as if the other were not present. Similarly, in the quantum system under consideration, the hopping term represents the interaction that couples the two orbitals.

2.4 Eigenenergies of the System

Once we have explained the physical interpretation of the hopping term, we continue with the eigenvalue problem. We recall Eq. (12), and substituting the notation introduced earlier, $E_0 = E_f + V_{cross}$, yields:

$$\begin{pmatrix} E_0 & \beta \\ \beta & E_0 \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = E\begin{pmatrix} 1 & S \\ S & 1 \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} .$$

We rewrite the eigenvalue equation in homogeneous form:

$$\left[\begin{pmatrix} E_0 & \beta \\ \beta & E_0 \end{pmatrix} - E\begin{pmatrix} 1 & S \\ S & 1 \end{pmatrix}\right]\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} .$$

By simplifying the equation, we obtain:

$$\begin{pmatrix} E_0 - E & \beta - ES \\ \beta - ES & E_0 - E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} . \tag{16}$$

Note that contrary to usual eigenvalue problems, the eigenvalues are not only in the diagonal but also in the off-diagonal as a consequence of the overlap matrix.

In order to get non-trivial solutions for c_1 and c_2, we must impose the following condition:

$$\begin{vmatrix} E_0 - E & \beta - ES \\ \beta - ES & E_0 - E \end{vmatrix} = 0 .$$

Evaluating the determinant yields:

$$(E - E_0)^2 - (\beta - ES)^2 = 0 .$$

Recognizing a difference of squares, we obtain:

$$[(E - E_0) + (\beta - ES)][(E - E_0) - (\beta - ES)] = 0$$

$$[E(1 - S) - E_0 + \beta][E(1 + S) - E_0 - \beta] = 0 ,$$

which results in:

$$\begin{cases} E_+ = \dfrac{E_0 + \beta}{1 + S} \\ E_- = \dfrac{E_0 - \beta}{1 - S} \end{cases}$$

$$\therefore \quad E_\pm = \frac{E_0 \pm \beta}{1 \pm S} . \tag{17}$$

Depending on which of the eigenenergies is lower, E_+ or E_-, its corresponding eigenstate is called the *bonding state*, and the other is known as the *antibonding state*.

2.5 Coefficients of the Eigenstates

We substitute the eigenvalues $E_\pm$ from Eq. (17) into Eq. (16).

$$\begin{pmatrix} E_0 - E_\pm & \beta - E_\pm S \\ \beta - E_\pm S & E_0 - E_\pm \end{pmatrix} \begin{pmatrix} c_{1_\pm} \\ c_{2_\pm} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} .$$

It is convenient to express the above equation as a system of linear equations.

$$\begin{cases} (E_0 - E_\pm)c_{1_\pm} + (\beta - E_\pm S)c_{2_\pm} = 0 \\ (\beta - E_\pm S)c_{1_\pm} + (E_0 - E_\pm)c_{2_\pm} = 0 . \end{cases}$$

Exploiting the linear dependence of the equations (a direct consequence of the zero-determinant condition), we can deduce the relation between the coefficients $c_{1_\pm}$ and $c_{2_\pm}$ just from one of the above equations. Taking the first equation yields:

$$(E_0 - E_\pm)c_{1_\pm} + (\beta - E_\pm S)c_{2_\pm} = 0$$

$$c_{2_\pm} = \frac{E_\pm - E_0}{\beta - E_\pm S} c_{1_\pm} . \tag{18}$$

Substitution of E_+ Recalling the value of E_+ from Eq. (17), we substitute it into Eq. (18).

$$c_{2_+} = \frac{\frac{E_0+\beta}{1+S} - E_0}{\beta - \frac{E_0+\beta}{1+S} S} c_{1_+}$$

$$c_{2_+} = \frac{\frac{E_0+\beta-E_0-E_0S}{1+S}}{\frac{\beta+\beta S-E_0S-\beta S}{1+S}} c_{1_+} .$$

After simplification, we obtain:

$$c_{2_+} = \frac{\beta - E_0S}{\beta - E_0S} c_{1_+}$$

$$\therefore \quad c_{2_+} = c_{1_+} . \tag{19}$$

Substitution of E_- Similar to the previous case, we substitute the value of E_- from Eq. (17) into Eq. (18).

$$c_{2_-} = \frac{\frac{E_0-\beta}{1-S} - E_0}{\beta - \frac{E_0-\beta}{1-S} S} c_{1_-}$$

$$c_{2_-} = \frac{\frac{E_0-\beta-E_0+E_0S}{1-S}}{\frac{\beta-\beta S-E_0S+\beta S}{1-S}} c_{1_-} ,$$

which, after simplification, yields:

$$c_{2_-} = \frac{-\beta + E_0S}{\beta - E_0S} c_{1_-}$$

$$\therefore \quad c_{2_-} = -c_{1_-} . \tag{20}$$

Recalling our analogy of the coupled oscillator, the results of Eqs. (19) and (20) represent the relation between the amplitudes of the two oscillators in their symmetric and antisymmetric normal modes, respectively. In addition, these normal modes are analogous to the eigenstates we are looking for.

2.6 The $|\psi_+\rangle$ and $|\psi_-\rangle$ Eigenstates

We shall denote the symmetric state as $|\psi_+\rangle$ and the antisymmetric state as $|\psi_-\rangle$. Given the results of Eqs. (19) and (20), it is straightforward to derive these eigenstates.

We recall the trial state vector of the system:

$$|\psi\rangle = c_1 |1\rangle + c_2 |2\rangle ,$$

which, considering the symmetric and antisymmetric states, can be written as:

$$|\psi_\pm\rangle = c_{1_\pm} |1\rangle + c_{2_\pm} |2\rangle .$$

Recalling that $c_{2_+} = c_{1_+}$ and $c_{2_-} = -c_{1_-}$, we have that:

$$\begin{cases} |\psi_+\rangle = c_{1_+}(|1\rangle + |2\rangle) \\ |\psi_-\rangle = c_{1_-}(|1\rangle - |2\rangle) . \end{cases}$$

To simplify the notation, we denote c_{1_+} as c_+ and c_{1_-} as c_-.

$$\begin{cases} |\psi_+\rangle = c_+(|1\rangle + |2\rangle) \\ |\psi_-\rangle = c_-(|1\rangle - |2\rangle) . \end{cases}$$

Furthermore, we can determine the values of c_+ and c_- by normalizing the eigenstates, i.e., applying the following condition:

$$\langle \psi_\pm | \psi_\pm \rangle = 1 \, .$$

Note that the normalization constant is not the typical $\frac{1}{\sqrt{2}}$ because the basis $\{|1\rangle, |2\rangle\}$ is not orthogonal.

Symmetric State

$$\begin{aligned} \langle \psi_+ | \psi_+ \rangle &= |c_+|^2 \left(\langle 1| + \langle 2| \right) \left(|1\rangle + |2\rangle \right) \\ &= |c_+|^2 [\underbrace{\langle 1|1\rangle}_{1} + \underbrace{\langle 1|2\rangle}_{S} + \underbrace{\langle 2|1\rangle}_{S} + \underbrace{\langle 2|2\rangle}_{1}] \, . \end{aligned}$$

Thus, we have that:

$$2|c_+|^2 (1 + S) = 1 \, ,$$

and by taking $c_+ \in \mathbb{R}$, we obtain:

$$\begin{aligned} c_+ &= \frac{1}{\sqrt{2(1+S)}} \\ \therefore \quad |\psi_+\rangle &= \frac{1}{\sqrt{2(1+S)}} (|1\rangle + |2\rangle) \, . \end{aligned} \tag{21}$$

Antisymmetric State Similarly, we can derive the antisymmetric state:

$$\begin{aligned} \langle \psi_- | \psi_- \rangle &= |c_-|^2 \left(\langle 1| - \langle 2| \right) \left(|1\rangle - |2\rangle \right) \\ &= |c_-|^2 [\underbrace{\langle 1|1\rangle}_{1} - \underbrace{\langle 1|2\rangle}_{S} - \underbrace{\langle 2|1\rangle}_{S} + \underbrace{\langle 2|2\rangle}_{1}] \, . \end{aligned}$$

Consequently, this yields:

$$2|c_-|^2 (1 - S) = 1 \, .$$

By taking $c_- \in \mathbb{R}$, we get:

$$\begin{aligned} c_- &= \frac{1}{\sqrt{2(1-S)}} \\ \therefore \quad |\psi_-\rangle &= \frac{1}{\sqrt{2(1-S)}} (|1\rangle - |2\rangle) \, . \end{aligned} \tag{22}$$

To express the symmetric and antisymmetric states as a single equation, we can combine Eqs. (21) and (22) as follows:

$$|\psi_\pm\rangle = \frac{1}{\sqrt{2(1 \pm S)}} (|1\rangle \pm |2\rangle) \tag{23}$$

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Version History

1.1 (June 2026): Typesetting adjustements. No changes to results or methodology.
1.0 (June 2026): Original release.