Molecular Orbital Theory Description of $\mathrm{H_2}^+$

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1 An Approach to the Exact Solution

Solving the problem of the monoelectronic H_2^+ molecule is equivalent to solving the monoelectronic part of the problem of the H_2 molecule with its two electrons based on the independent electrons approximation.

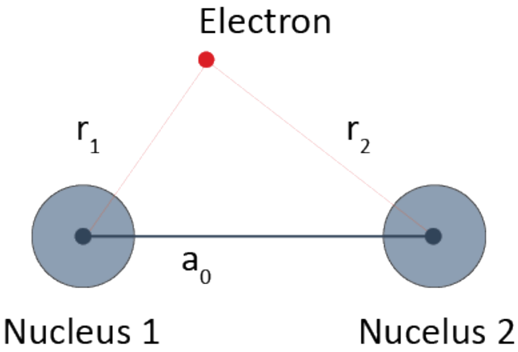

Figure 1: Schematic representation of the H_2^+ ion problem

The Born-Oppenheimer approximation states that one can decouple nuclear motion from electronic motion due to the large mass difference between the nuclei and electrons. Under this approximation, one can write the time-independent Schrödinger equation as follows:

$$(\hat{H}_{el} + \hat{V}_{NN})\Psi = E\Psi \tag{1}$$

with

$$\hat{H}_{el} = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\epsilon_0}(\frac{1}{r_A} + \frac{1}{r_B})$$

and

$$\hat{V}_{NN} = \frac{e^2}{4\pi\epsilon_0 a_0}$$

Here, $\hat{V}_{NN}$ is a constant relative to the electron position.

$$(1) \Leftrightarrow \hat{H}_{el}\Psi = E_{el}\Psi \tag{2}$$

with $E_{el} = E - V_{NN}$ which is a purely electronic energy.

One can solve the monoelectronic Schrödinger equation and then add the internuclear repulsion energy to determine to total energy of the system E, by utilizing an elliptical coordinate system. However, calculating the Laplace operator in these coordinates is complex and the resolution must be done numerically for every value of a_0. Two energetic functions are obtained. This means that for each value of a_0 there are two possible states.

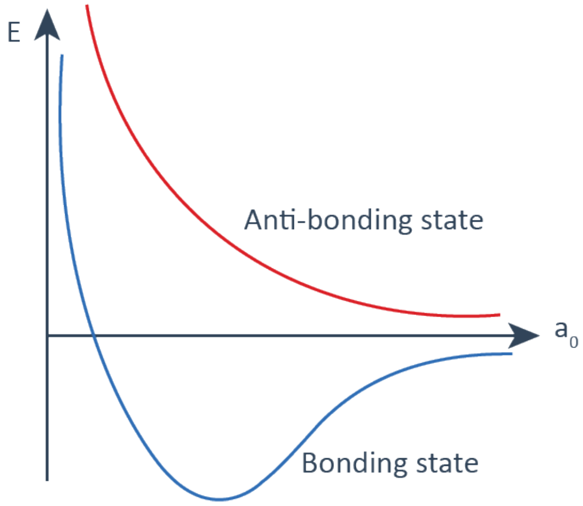

Figure 2: Different energy levels obtained for the H_2^+ ion as a function of internuclear distance

2 Molecular Orbital Theory Description

Molecular Orbital Theory (MOT) provides an approximated solution to the Schrödinger equation in the case of a polyatomic quantum system. In addition to the Born-Oppenheimer and the independent electrons approximationa, the approach uses the further approximation that the monoelectronic molecular wavefunctions Ψ can be described as a linear combination of monoelectronic atomic orbitals ψ (LCAO).

$$\Psi_j = \sum_{i=1}^{n} c_{ij}\psi_i \tag{3}$$

with $j \in [1 \ldots \mathrm{n}]$.

The coefficients are determined by substituting this equation in the Schrödinger equation and by applying the variational principle which minimizes the energy of the system. In the case of H_2^+, the wavefunctions have the form:

$$\Psi_{H_2^+} = c_1\Psi_{1s_A} + c_2\Psi_{1s_B} \tag{4}$$

with $(c_1, c_2 \in \mathbb{R})$.

We are thus looking for two sets of c_1 and c_2 as there will be the same number of molecular wavefunctions as there are atomic wavefunctions.

The Schrödinger equation gives:

$$\hat{H}\left|\Psi_{H_2^+}\right\rangle = E\left|\Psi_{H_2^+}\right\rangle \tag{5}$$

and thus by projecting on each orbital we have

$$\begin{cases} \left\langle \Psi_{1s_A} \middle| \hat{H} \middle| \Psi_{H_2^+} \right\rangle = E \left\langle \Psi_{1s_A} \middle| \Psi_{H_2^+} \right\rangle \\ \left\langle \Psi_{1s_B} \middle| \hat{H} \middle| \Psi_{H_2^+} \right\rangle = E \left\langle \Psi_{1s_B} \middle| \Psi_{H_2^+} \right\rangle \end{cases} \tag{6}$$

which is equivalent to

$$\begin{cases} \int \Psi_{1s_A} \hat{H} \Psi_{H_2^+} d\tau = E \int \Psi_{1s_A} \Psi_{H_2^+} d\tau \\ \int \Psi_{1s_B} \hat{H} \Psi_{H_2^+} d\tau = E \int \Psi_{1s_B} \Psi_{H_2^+} d\tau \end{cases}$$

By injecting (4) into (6) we obtain

$$\begin{cases} \langle \Psi_{1s_A} | \hat{H} | c_1 \Psi_{1s_A} + c_2 \Psi_{1s_B} \rangle = E \langle \Psi_{1s_A} | c_1 \Psi_{1s_A} + c_2 \Psi_{1s_B} \rangle \\ \langle \Psi_{1s_B} | \hat{H} | c_1 \Psi_{1s_A} + c_2 \Psi_{1s_B} \rangle = E \langle \Psi_{1s_B} | c_1 \Psi_{1s_A} + c_2 \Psi_{1s_B} \rangle \end{cases} \tag{7}$$

By distributing we obtain:

$$\begin{cases} c_1 \langle \Psi_{1s_A} | \hat{H} | \Psi_{1s_A} \rangle + c_2 \langle \Psi_{1s_A} | \hat{H} | \Psi_{1s_B} \rangle = E(c_1 \langle \Psi_{1s_A} | \Psi_{1s_A} \rangle + c_2 \langle \Psi_{1s_A} | \Psi_{1s_B} \rangle) \\ c_1 \langle \Psi_{1s_B} | \hat{H} | \Psi_{1s_A} \rangle + c_2 \langle \Psi_{1s_B} | \hat{H} | \Psi_{1s_B} \rangle = E(c_1 \langle \Psi_{1s_B} | \Psi_{1s_A} \rangle + c_2 \langle \Psi_{1s_B} | \Psi_{1s_B} \rangle) \end{cases} \tag{8}$$

From this form we can note the following:

$$\langle \Psi_{1s_A} | \hat{H} | \Psi_{1s_A} \rangle = \langle \Psi_{1s_B} | \hat{H} | \Psi_{1s_B} \rangle = \alpha \tag{9}$$

$$\langle \Psi_{1s_A} | \hat{H} | \Psi_{1s_B} \rangle = \langle \Psi_{1s_B} | \hat{H} | \Psi_{1s_A} \rangle = \beta \tag{10}$$

α and β are both called Hamiltonian integrals.

$$\langle \Psi_{1s_A} | \Psi_{1s_B} \rangle = \langle \Psi_{1s_B} | \Psi_{1s_A} \rangle = S \tag{11}$$

S corresponds to the overlap integral between both orbitals of each atom.

Furthermore

$$\langle \Psi_{1s_A} | \Psi_{1s_A} \rangle = \langle \Psi_{1s_B} | \Psi_{1s_B} \rangle = 1 \tag{12}$$

due to the fact that this integral corresponds to the probability of finding an electron in the entire space, which must be equal to 1.

By simplifying (8) with all of these abbreviations, we obtain

$$\begin{cases} c_1\alpha + c_2\beta = Ec_1 + Ec_2S \\ c_1\beta + c_2\alpha = Ec_1S + Ec_2 \end{cases} \tag{13}$$

which is equivalent to

$$\begin{cases} c_1(\alpha - E) + c_2(\beta - ES) = 0 \\ c_1(\beta - ES) + c_2(\alpha - E) = 0 \end{cases} \tag{14}$$

Therefore, we have obtained a system of two equations and three unknowns (c_1, c_2 and E). There only exist solutions different from the trivial solution (c_1^0=c_2^0=0) if the following secular determinant is not equal to zero

$$\begin{vmatrix} \alpha - E & \beta - ES \\ \beta - ES & \alpha - E \end{vmatrix} = 0 \tag{15}$$

$$\Leftrightarrow \quad (\alpha - E)^2 - (\beta - ES)^2 = 0 \tag{16}$$

$$\Leftrightarrow \quad \alpha - E = \beta - ES \;\text{ or }\; \alpha - E = -\beta - ES \tag{17}$$

$$\Leftrightarrow \quad E_- = \frac{\alpha - \beta}{1 - S} \;\text{ or }\; E_+ = \frac{\alpha + \beta}{1 + S} \tag{18}$$

Both of these solutions correspond to the energy levels of the two newly formed molecular orbitals.

By substituting these energy values back into (14) we obtain with E_-:

$$\begin{cases} c_1(\frac{\beta-\alpha S}{1-S}) + c_2(\frac{\beta-\alpha S}{1-S}) = 0 \\ c_1(\frac{\beta-\alpha S}{1-S}) + c_2(\frac{\beta-\alpha S}{1-S}) = 0 \end{cases} \tag{19}$$

$$\Leftrightarrow \quad c_1 + c_2 = 0 \tag{20}$$

$$\Leftrightarrow \quad c_1 = -c_2 \tag{21}$$

Proceeding in the same manner for E_+ we obtain

$$c_1 = c_2 \tag{22}$$

We have thus found the two wavefunctions we have been looking for

$$\Psi_{H_2^+,+} = c_0(\Psi_{1s_A} + \Psi_{1s_B}) \tag{23}$$

associated with E_+ and

$$\Psi_{H_2^+,-} = c_0^{'}(\Psi_{1s_A} - \Psi_{1s_B}) \tag{24}$$

associated with E_-.

By normalizing these function under the condition that $\langle\Psi|\Psi\rangle = 1$, we obtain for $\Psi_{H_2^+,+}$:

$$2c_0^2 + 2c_0^2 S = 1 \tag{25}$$

$$\Leftrightarrow \quad 2(1+S)c_0^2 = 1 \tag{26}$$

$$\Leftrightarrow \quad c_0 = \pm\frac{1}{\sqrt{2(1+S)}} \tag{27}$$

And similarly for $\Psi_{H_2^+,-}$, we find

$$c_0^{'} = \pm\frac{1}{\sqrt{2(1-S)}} \tag{28}$$

In both cases, the positive and negative coefficients describe the same wavefunction, we can only take positive values. Our final wavefunctions are thus

$$\Psi_{H_2^+,+} = \frac{1}{\sqrt{2(1+S)}}(\Psi_{1s_A} + \Psi_{1s_B}) \tag{29}$$

and

$$\Psi_{H_2^+,-} = \frac{1}{\sqrt{2(1-S)}}(\Psi_{1s_A} - \Psi_{1s_B}) \tag{30}$$

Now, let's have a closer look at α and β. Remember that in this problem

$$\hat{H} = \hat{H}_{el} + \hat{V}_{NN} = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\epsilon_0}(\frac{1}{r_A} + \frac{1}{r_B}) + \frac{e^2}{4\pi\epsilon_0 a_0} \tag{31}$$

Therefore we have

$$\alpha = \langle\Psi_{1s_i}|-\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_i}|\Psi_{1s_i}\rangle + \frac{e^2}{4\pi\epsilon_0 a_0}\langle\Psi_{1s_i}|\Psi_{1s_i}\rangle - \langle\Psi_{1s_i}|\frac{e^2}{4\pi\epsilon_0 r_j}|\Psi_{1s_i}\rangle \tag{32}$$

$$\beta = \langle\Psi_{1s_i}|-\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_j}|\Psi_{1s_j}\rangle + \frac{e^2}{4\pi\epsilon_0 a_0}\langle\Psi_{1s_i}|\Psi_{1s_j}\rangle - \langle\Psi_{1s_i}|\frac{e^2}{4\pi\epsilon_0 r_i}|\Psi_{1s_j}\rangle \tag{33}$$

with i ≡ A or B and j ≠ i ≡ A or B

In α, the first term corresponds to the energy of an orbital 1s in a hydrogen atom E_H. The second term corresponds to the Coulomb repulsion of the two nuclei. The third term, including the minus sign, is noted J and called the Coulomb integral.

In β, Ψ_{1SJ} is an eigenvector of the operator in the first term with the eigenvalue E_H. As E_H is a constant it factors out the integral which becomes the overlap integral S. Then, the first term corresponds to $E_H S$. The second term correspond to the product of the Coulomb repulsion of the two nuclei and the overlap integral. The third term, including the minus sign, is noted K and called the exchange integral.

Then we have

$$\alpha = E_H + \frac{e^2}{4\pi\epsilon_0 a_0} + J \tag{34}$$

and

$$\beta = E_H S + \frac{e^2}{4\pi\epsilon_0 a_0}S + K \tag{35}$$

By substituting α and β expressions in E_+ and E_- we found

$$E_- = \frac{1}{1-S}[(E_H + \frac{e^2}{4\pi\epsilon_0 a_0})(1-S) + J - K] = E_H + \frac{e^2}{4\pi\epsilon_0 a_0} + \frac{J-K}{1-S} \tag{36}$$

and

$$E_+ = \frac{1}{1+S}[(E_H + \frac{e^2}{4\pi\epsilon_0 a_0})(1+S) + J + K] = E_H + \frac{e^2}{4\pi\epsilon_0 a_0} + \frac{J+K}{1+S} \tag{37}$$

With further more exact considerations of the integrals J, K and S, and the study of the terms involving them as a function of the inter-atomic distance a_0, that will not be developed here, it is possible to establish that

$$E_+ < E_H < E_- \tag{38}$$

These levels correspond to those in Figure 2 at equilibrium.