

The Hydrogen Molecular Ion in the Simplest Atomic Basis Set

Consider a quantum mechanical description of the hydrogen molecular ion in its simplest version. Let us use the molecular orbital theory with the atomic basis set composed of only two Slater Type Orbitals (STOs): $1s_a$ and $1s_b$ centered on the nuclei a and b . The mean value of the Hamiltonian computed with the bonding (+) and antibonding (−) orbital (see p. 439 and Appendix D available at booksite.elsevier.com/978-0-444-59436-5) reads as

$$E_{\pm} = \frac{H_{aa} \pm H_{ab}}{1 \pm S},$$

where the Hamiltonian (in atomic units)¹ $\hat{H} = -\frac{1}{2}\Delta - \frac{1}{r_a} - \frac{1}{r_b} + \frac{1}{R}$ and S stands for the overlap integral of the two atomic orbitals. Thus, we have

$$\begin{aligned} E_{\pm} &= \frac{1}{R} + \frac{H_{aa} \pm H_{ab}}{1 \pm S} = \frac{1}{R} + \frac{\left(-\frac{1}{2}\Delta - \frac{1}{r_a} - \frac{1}{r_b}\right)_{aa} \pm \left(-\frac{1}{2}\Delta - \frac{1}{r_a} - \frac{1}{r_b}\right)_{ab}}{1 \pm S} \\ &= \frac{1}{R} + \frac{E_H + V_{aa,b} \pm E_H S \pm V_{ab,b}}{1 \pm S} = E_H + \frac{1}{R} + \frac{V_{aa,b} \pm V_{ab,b}}{1 \pm S}, \end{aligned}$$

where E_H means the energy of the hydrogen atom, while the nuclear attraction integrals are as follows:

$$\begin{aligned} V_{aa,b} &= -\left(a \left| \frac{1}{r_b} \right| a\right), \\ V_{ab,b} &= -\left(a \left| \frac{1}{r_b} \right| b\right). \end{aligned}$$

The energy E_{\pm} is a function of the internuclear distance R , which is hidden in the dependence of the integrals on R . We want to have this function explicitly. To this end, we have to compute the integrals S , $V_{aa,b}$ and $V_{ab,b}$. We use the elliptic coordinates (Fig. R.1):

$$\mu = \frac{r_a + r_b}{R},$$

¹ See Fig. R.1 for explanations of the symbols.

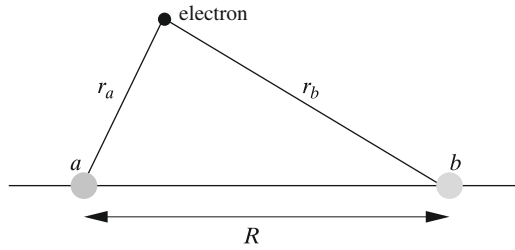


Fig. R.1. The elliptic coordinates $\mu = \frac{r_a+r_b}{R}$, $\nu = \frac{r_a-r_b}{R}$ are built using the distances r_a and r_b from the two foci (the location of the nuclei, and their distance is R) of the ellipse. The angle ϕ measures the rotation of the plane defined by ab and the corresponding electron about the ab axis.

$$\nu = \frac{r_a - r_b}{R},$$

$$\phi = \arctan\left(\frac{y}{x}\right).$$

The volume element in the elliptic coordinates is $dV = R^3/8(\mu^2 - \nu^2)d\mu d\nu d\phi$, where $1 \leq \mu < \infty$, $-1 \leq \nu \leq 1$, $0 \leq \phi \leq 2\pi$.

We will need two auxiliary integrals:

$$A_n(\sigma, \alpha) = \int_{\sigma}^{\infty} x^n \exp(-\alpha x) dx = \exp(-\alpha\sigma) \sum_{k=0}^n \frac{n!}{(n-k)!} \frac{\sigma^{n-k}}{\alpha^{k+1}},$$

$$B_n(\alpha) = \int_{-1}^{+1} x^n \exp(-\alpha x) dx = A_n(-1, \alpha) - A_n(1, \alpha).$$

The integrals $A_n(\sigma, \alpha)$ satisfy the following recurrence relation:

$$A_n(\sigma, \alpha) = \sigma^n A_0(\sigma, \alpha) + \frac{n}{\alpha} A_{n-1}(\sigma, \alpha)$$

$$A_0(\sigma, \alpha) = \frac{1}{\alpha} \exp(-\sigma\alpha).$$

These are some simplest auxiliary integrals (which we will need in a moment):

$$A_1(\sigma, \alpha) = \sigma \frac{1}{\alpha} \exp(-\sigma\alpha) + \frac{1}{\alpha} \frac{1}{\alpha} \exp(-\sigma\alpha) = \frac{1}{\alpha} \left(\sigma + \frac{1}{\alpha} \right) \exp(-\sigma\alpha)$$

$$A_2(\sigma, \alpha) = \sigma^2 \frac{1}{\alpha} \exp(-\sigma\alpha) + \frac{2}{\alpha} \left(\frac{1}{\alpha} \left(\sigma + \frac{1}{\alpha} \right) \exp(-\sigma\alpha) \right)$$

$$= \frac{1}{\alpha} \exp(-\sigma\alpha) \left[\sigma^2 + \frac{2}{\alpha} \left(\sigma + \frac{1}{\alpha} \right) \right]$$

$$B_0(\alpha) = \frac{1}{\alpha} \exp(\alpha) - \frac{1}{\alpha} \exp(-\alpha) = \frac{1}{\alpha} [\exp(\alpha) - \exp(-\alpha)]$$

$$\begin{aligned}
 B_1(\alpha) &= \frac{1}{\alpha} \left(-1 + \frac{1}{\alpha} \right) \exp(\alpha) - \frac{1}{\alpha} \left(1 + \frac{1}{\alpha} \right) \exp(-\alpha) \\
 &= \frac{1}{\alpha} \left[\left(\frac{1}{\alpha} - 1 \right) \exp(\alpha) - \left(\frac{1}{\alpha} + 1 \right) \exp(-\alpha) \right].
 \end{aligned}$$

Thus, the overlap integral S is calculated in the following way:

$$\begin{aligned}
 S &= \frac{R^3}{8\pi} \int_1^\infty d\mu \exp(-R\mu) \int_{-1}^{+1} dv (\mu^2 - v^2) \int_0^{2\pi} d\phi \\
 &= \frac{R^3}{2} \left[\int_1^\infty d\mu \mu^2 \exp(-R\mu) - \frac{1}{3} \int_1^\infty d\mu \exp(-R\mu) \right] \\
 &= \frac{R^3}{2} \left[A_2(1, \alpha) - \frac{1}{3} A_0(1, \alpha) \right] \\
 &= \frac{R^3}{2} \left[\frac{1}{R} \exp(-R) \left(1 + \frac{2}{R} + \frac{2}{R^2} \right) - \frac{1}{3} \frac{1}{R} \exp(-R) \right] = \exp(-R) \left(\frac{R^2}{3} + R + 1 \right).
 \end{aligned}$$

Thus we have the explicit dependence on R . The formula for S satisfies correctly the following limiting cases: $\lim_{R \rightarrow \infty} S(R) = 0$ and $\lim_{R \rightarrow 0} S(R) = 1$ (normalization of the $1s$ orbital). In addition, $\frac{dS}{dR} = -\exp(-R) \left(\frac{R^2}{3} + R + 1 \right) + \exp(-R) \left(\frac{2}{3} R + 1 \right) = -\exp(-R) \left(\frac{R^2 + R}{3} \right) < 0$; i.e., the overlap integral of the $1s$ functions decreases from 1 to 0, if $R \rightarrow \infty$ (see Fig. R.2a).

It is seen that for small R , the function S decreases gently, while for larger R , its decreasing happens more quickly.²

Using the elliptic coordinates and the formulas for the integrals $A_n(\sigma, \alpha)$ and $B_n(\alpha)$, we obtain

$$\begin{aligned}
 -V_{aa,b} &= \left(a \left| \frac{1}{r_b} \right| a \right) = \frac{1}{\pi} \int \exp(-2r_a) \frac{1}{r_b} d\tau \\
 &= \frac{R^3}{8\pi} \frac{2}{R} \int_1^\infty d\mu \exp[-R(\mu + v)] \int_{-1}^{+1} dv \frac{(\mu^2 - v^2)}{\mu - v} \int_0^{2\pi} d\phi \\
 &= \frac{R^2}{4\pi} 2\pi \int_1^\infty d\mu \int_{-1}^{+1} dv \exp(-R\mu) \exp(-Rv) (\mu + v) \\
 &= \frac{R^2}{2} \left[\int_1^\infty d\mu \mu \exp(-R\mu) \int_{-1}^{+1} dv \exp(-Rv) \right. \\
 &\quad \left. + \int_1^\infty d\mu \exp(-R\mu) \int_{-1}^{+1} dv v \exp(-Rv) \right] \\
 &= \frac{R^2}{2} [A_1(1, R) B_0(R) + A_0(1, R) B_1(R)] = \frac{1}{R} - \exp(-2R) \left(1 + \frac{1}{R} \right).
 \end{aligned}$$

² Just to get an idea: at $R = 5$ a.u. (quite typical for van der Waals complexes), the value of the overlap integral is of the order of 0.1.

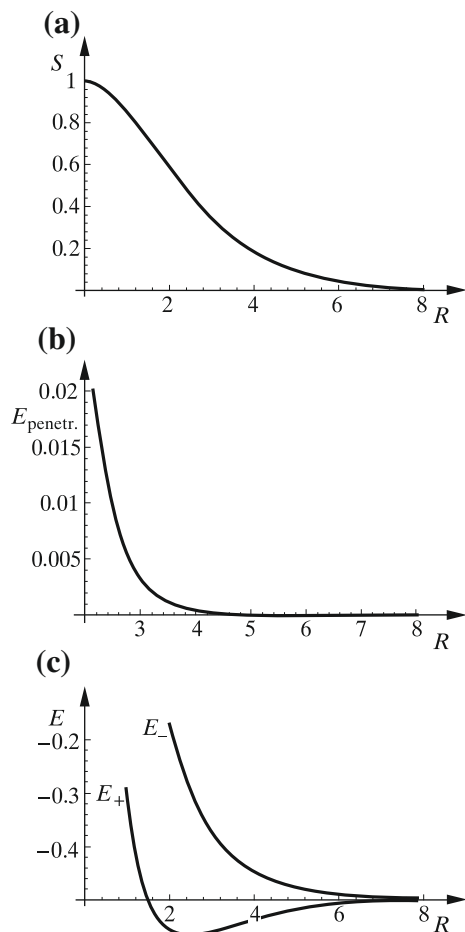


Fig. R.2. The hydrogen molecule in the simplest basis set of two $1s$ STOs. (a) The overlap integral S as a function of the internuclear distance R ; (b) the penetration energy represents the difference between the electron-proton interaction calculated assuming the electronic charge distribution and the same energy calculated assuming the point charges (the electron is located on the nucleus a); (c) the energies E_+ and E_- of the bonding (lower curve) and of the antibonding (upper curve) orbitals, respectively.

This is an interesting result. The integral $-V_{aa,b}$ means $(a|\frac{1}{r_b}|a)$, where at large R should give the Coulombic interaction of the two unit point charges; i.e., $\frac{1}{R}$. This is the first term. The second term, $E_{\text{penetr}} = -\exp(-2R)(1 + \frac{1}{R})$, represents what is known as *penetration energy* resulting from the non-pointlike character of one of the interacting charges.³

From Fig. R.2b, it is seen that the penetration energy vanishes much faster than the overlap integral. This is not a surprise because it vanishes as $\exp(-2R)$, while the overlap integral vanishes only as $\exp(-R)$.

³ The electron cloud with the electronic density distribution a^2 .

It is seen that

the diffuse charges interact more weakly.

On the one hand, diffuse charges offer a chance to be close together in space (this increases the interaction). On the other hand, some charges become more distant. The second effect prevails, and therefore the penetration energy makes the Coulombic interaction weaker.

What will happen if $R \rightarrow 0$?

Let us expand the exponential function in the Taylor series. We obtain

$$\begin{aligned} \lim_{R \rightarrow 0} [V_{aa,b}(R)] &= - \lim_{R \rightarrow 0} \left[\frac{1}{R} - \left[1 - 2R + \frac{1}{2}R^2 + \dots \right] \left(1 + \frac{1}{R} \right) \right] \\ &= - \lim_{R \rightarrow 0} \left(\frac{1}{R} - 1 + 2R - \frac{1}{2}R^2 - \frac{1}{R} + 2 + \frac{1}{2}R + \dots \right) = -1. \end{aligned}$$

This is exactly what we get for the hydrogen atom when computing: $V_{aa,a} = - \int dv \frac{1}{r} (1s)^2 = -\frac{1}{\pi} \int \exp(-2r) \frac{1}{r} r^2 \sin \theta dr d\theta d\phi = -4 \int_0^\infty r \exp(-2r) dr = -4 \times 2^{-2} = -1$. Thus, everything is all right.

Similarly, we compute

$$\begin{aligned} -V_{ab,b} &= \left(a \left| \frac{1}{r_b} \right| b \right) = \frac{1}{\pi} \int \exp(-(r_a + r_b)) \frac{1}{r_b} dv \\ &= \frac{1}{\pi} \frac{2}{R} \int \exp(-R\mu) \frac{1}{(\mu - \nu)} \frac{R^3}{8} (\mu^2 - \nu^2) d\mu d\nu d\phi \\ &= \frac{R^2}{2} \int_1^\infty \int_{-1}^{+1} d\mu d\nu [\mu \exp(-R\mu) + \nu \exp(-R\mu)] \\ &= \frac{R^2}{2} 2A_1(1, R) + 0 = (1 + R) \exp(-R). \end{aligned}$$

If $R \rightarrow \infty$, and then $-V_{ab,b} \rightarrow 0$, which is the correct behavior. Do we get $V_{aa,a} = -1$, if $R \rightarrow 0$? Again, let us expand the exponential function:

$$\begin{aligned} V_{aa,a} &= - \lim_{R \rightarrow 0} (1 + R) \exp(-R) = - \lim_{R \rightarrow 0} (1 + R) \left(1 - R + \frac{R^2}{2} + \dots \right) \\ &= - \lim_{R \rightarrow 0} \left[1 + R - R - R^2 + \frac{R^2}{2} + \dots \right] = -1. \end{aligned}$$

This is what we have expected.

Bonding and Antibonding Orbital Energy

If we insert the results obtained into the formula for the energy of the bonding and antibonding orbitals, then we obtain the most important formulas for the problem under consideration:

$$\begin{aligned}
 E_{\pm} &= E_H + \frac{1}{R} + \frac{V_{aa,b} \pm V_{ab,b}}{1 \pm S} \\
 &= E_H + \frac{1}{R} + \frac{-\frac{1}{R} + \exp(-2R) \left(1 + \frac{1}{R}\right) \pm (-1 - R) \exp(-R)}{1 \pm \left[\exp(-R) \left(\frac{R^2}{3} + R + 1\right)\right]}.
 \end{aligned}$$

The plots of E_{\pm} are shown in Fig. R.2c. It is seen that in the quite primitive LCAO MO approximation, the bonding energy is lower than the energy of the hydrogen atom E_H for all sufficiently large R (a single minimum), while the energy of the antibonding orbital is higher than E_H for all R (no minimum). This simple theory predicts the position of the energy minimum for the ground state as $R_e = 2.5$ a.u., while the experimental value is equal⁴ to ca. 2.0 a.u.

⁴ These two quantities are not directly comparable because the experimental value does not correspond exactly to the position of the minimum (because of anharmonicity).