R. THE HYDROGEN MOLECULAR ION IN THE SIMPLEST ATOMIC BASIS SET

Consider the quantum mechanical description of the hydrogen molecular ion in its simplest version. Let us use molecular orbital theory with the atomic basis set composed of only two Slater Type Orbitals (STO): $1s_a$ and $1s_b$ centred on the nuclei a and b. The mean value of the Hamiltonian calculated with the bonding $(+)$ and antibonding $(-)$ orbital (see Chapter 8 and Appendix D) reads as

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

where the Hamiltonian (in a.u.)[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

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

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):

$$\mu = \frac{r_a + r_b}{R}, \qquad \nu = \frac{r_a - r_b}{R}, \qquad \phi = \arctan\left(\frac{y}{x}\right).$$

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

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[1] See Fig. R.1 for explaining symbols.
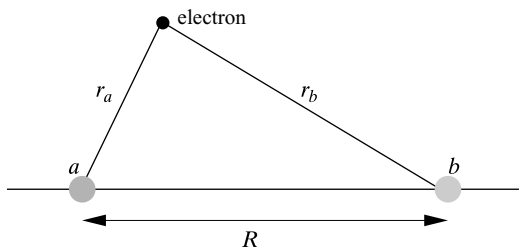
electron

r_a

r_b

a

b

R

Fig. R.1. The elliptic coordinates $\mu = \frac{r_a + r_b}{R}$, $\nu = \frac{r_a - r_b}{R}$ built using distances r_a and r_b from the two foci (where the nuclei are, 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.

We will need two auxiliary integrals:

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

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

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 simple auxiliary integrals (we will need them in a moment):

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

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

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

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

$$B_1(\alpha) = \frac{1}{\alpha}\left(-1 + \frac{1}{\alpha}\right) \exp(\alpha) - \frac{1}{\alpha}\left(1 + \frac{1}{\alpha}\right) \exp(-\alpha)$$

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

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

$$S = \frac{R^3}{8\pi} \int_1^\infty \mathrm{d}\mu \, \exp(-R\mu) \int_{-1}^{+1} \mathrm{d}\nu \, (\mu^2 - \nu^2) \int_0^{2\pi} \mathrm{d}\phi$$

$$= \frac{R^3}{2}\left[\int_1^\infty d\mu\, \mu^2 \exp(-R\mu) - \frac{1}{3}\int_1^\infty d\mu \exp(-R\mu)\right]$$

$$= \frac{R^3}{2}\left[A_2(1,\alpha) - \frac{1}{3}A_0(1,\alpha)\right]$$

$$= \frac{R^3}{2}\left[\frac{1}{R}\exp(-R)\left(1+\frac{2}{R}+\frac{2}{R^2}\right) - \frac{1}{3}\frac{1}{R}\exp(-R)\right]$$

$$= \exp(-R)\left(\frac{R^2}{3}+R+1\right).$$

Thus we have explicit dependence on R. The formula for S satisfies correctly the limiting cases: $\lim_{R\to\infty} S(R) = 0$ and $\lim_{R\to 0} S(R) = 1$ (normalization of the $1s$ orbital). Besides

$$\frac{dS}{dR} = -\exp(-R)\left(\frac{R^2}{3}+R+1\right) + \exp(-R)\left(\frac{2}{3}R+1\right)$$

$$= -\exp(-R)\left(\frac{R^2+R}{3}\right) < 0,$$

i.e. the overlap integral of the $1s$ functions decreases from 1 to 0, if $R \to \infty$ (see Fig. R.2.a).

We see that for small R the function S decreases gently, while for larger R it decreases fast.[2]

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

$$-V_{aa,b} = \left(a\left|\frac{1}{r_b}\right|a\right) = \frac{1}{\pi}\int \exp(-2r_a)\frac{1}{r_b}\,d\tau$$

$$= \frac{R^3}{8\pi}\frac{2}{R}\int_1^\infty d\mu \exp[-R(\mu+\nu)]\int_{-1}^{+1} d\nu\,\frac{(\mu^2-\nu^2)}{\mu-\nu}\int_0^{2\pi} d\phi$$

$$= \frac{R^2}{4\pi}2\pi\int_1^\infty d\mu \int_{-1}^{+1} d\nu \exp(-R\mu)\exp(-R\nu)(\mu+\nu)$$

$$= \frac{R^2}{2}\left[\int_1^\infty d\mu\, \mu\exp(-R\mu)\int_{-1}^{+1} d\nu \exp(-R\nu)\right.$$

$$\left.+\int_1^\infty d\mu \exp(-R\mu)\int_{-1}^{+1} d\nu\, \nu\exp(-R\nu)\right]$$

$$= \frac{R^2}{2}\left[A_1(1,R)B_0(R) + A_0(1,R)B_1(R)\right] = \frac{1}{R}-\exp(-2R)\left(1+\frac{1}{R}\right).$$

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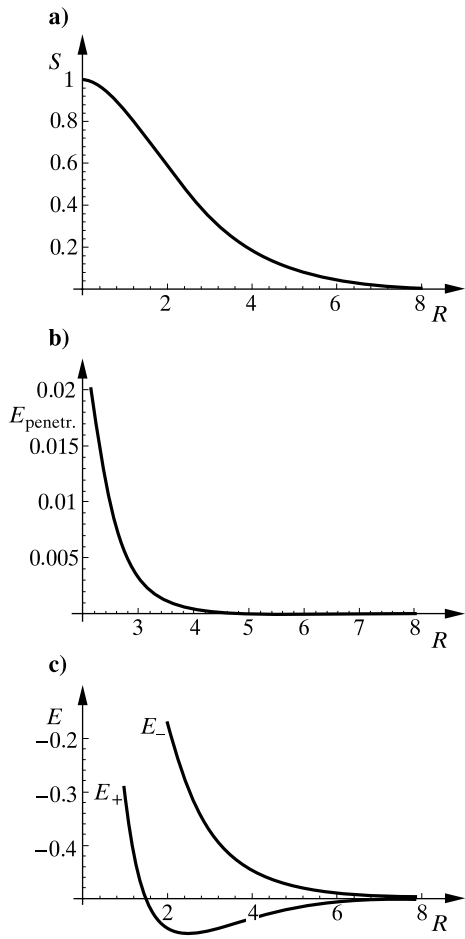
Fig. R.2. The hydrogen molecule in the simplest basis set of two $1s$ Slater type orbitals (STO). (a) The overlap integral S as a function of the internuclear distance R. (b) The penetration energy represents the difference between the electron–proton interaction calculated assuming the electronic charge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

This is an interesting result. The integral $-V_{aa,b}$ means $(a|\frac{1}{r_b}|a)$, which at large R should give the Coulombic interaction of the two unit point charges, i.e. $\frac{1}{R}$. This is what we have as the first term. The second term: $E_{\text{penetr}} = -\exp(-2R)(1+\frac{1}{R})$

penetration
energy

represents what is known as *penetration energy* resulting from the non-point-like character of one of the interacting charges.[3]

From Fig. R.2.b we see that the penetration energy vanishes much faster that the overlap integral. No wonder it vanishes as $\exp(-2R)$, while the overlap integral vanishes only as $\exp(-R)$.

It is seen that

> the diffuse charges interact more weakly.

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[3]The electron cloud of electronic density a^2.

On the one hand diffuse charges offer the chance to be close 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 $R \to 0$?

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

$$\lim_{R \to 0} \left[V_{aa,b}(R) \right] = - \lim_{R \to 0} \left[\frac{1}{R} - \left[1 - 2R + \frac{1}{2} R^2 + \cdots \right] \left(1 + \frac{1}{R} \right) \right]$$

$$= - \lim_{R \to 0} \left(\frac{1}{R} - 1 + 2R - \frac{1}{2} R^2 - \frac{1}{R} + 2 + \frac{1}{2} R + \cdots \right) = -1.$$

This is exactly what we get for the hydrogen atom when calculating:

$$V_{aa,a} = - \int dv \frac{1}{r} (1s)^2 = - \frac{1}{\pi} \int \exp(-2r) \frac{1}{r} r^2 \sin \theta \, dr \, d\theta \, d\phi$$

$$= -4 \int_0^\infty r \exp(-2r) \, dr = -4 \times 2^{-2} = -1.$$

Thus everything is all right.

Similarly we calculate

$$-V_{ab,b} = \left(a \left| \frac{1}{r_b} \right| b \right) = \frac{1}{\pi} \int \exp\left(-(r_a + r_b) \right) \frac{1}{r_b} \, dv$$

$$= \frac{1}{\pi} \frac{2}{R} \int \exp(-R\mu) \frac{1}{(\mu - \nu)} \frac{R^3}{8} (\mu^2 - \nu^2) \, d\mu \, d\nu \, d\phi$$

$$= \frac{R^2}{2} \int_1^\infty \int_{-1}^{+1} d\mu \, d\nu \left[\mu \exp(-R\mu) + \nu \exp(-R\mu) \right]$$

$$= \frac{R^2}{2} 2 A_1(1, R) + 0 = (1 + R) \exp(-R).$$

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

$$V_{aa,a} = - \lim_{R \to 0} (1 + R) \exp(-R) = - \lim_{R \to 0} (1 + R) \left(1 - R + \frac{R^2}{2} + \cdots \right)$$

$$= - \lim_{R \to 0} \left[1 + R - R - R^2 + \frac{R^2}{2} + \cdots \right] = -1.$$

This is what we expected.

Bonding and antibonding orbital energy

If we insert the results into the formula for the energy of the bonding and antibonding orbitals, we obtain the most important formulae for the problem being considered:

$$E_\pm = E_H + \frac{1}{R} + \frac{V_{aa,b} \pm V_{ab,b}}{1 \pm S}$$

$$= E_H + \frac{1}{R} + \frac{-\frac{1}{R} + \exp(-2R)\left(1 + \frac{1}{R}\right) \pm (-1 - R)\exp(-R)}{1 \pm \left[\exp(-R)\left(\frac{R^2}{3} + R + 1\right)\right]}.$$

The plots of $E_\pm$ are shown in Fig. R.2.c. 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). 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 equal[4] ca. 2.0 a.u.

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[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).