

I. AN EXAMPLE OF THE VARIATIONAL THEORY: THE H_2^+ MOLECULE ION

The H_2^+ molecule ion is the simplest example of a chemical bond. It is a particularly important example to study because it is an analytically solvable problem, therefore, any approximation method applied to it can be assessed against the exact solution.

The geometry and coordinate system we will adopt are shown in the figure below:

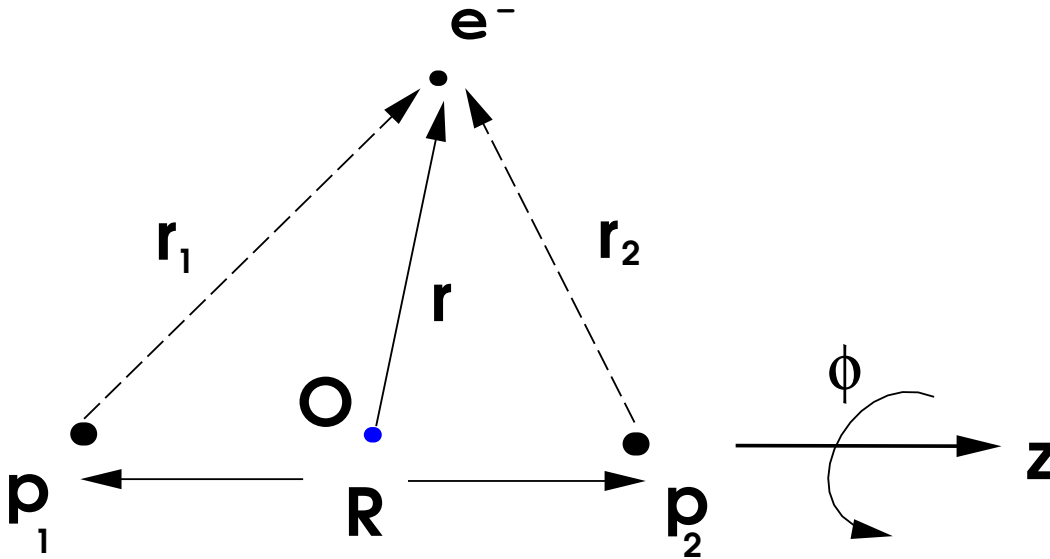


FIG. 1.

The origin, which lies midway between the two protons on the z axis, is shown as the blue dot. The position vector of the electron is \mathbf{r} . Denoting the positions of the two protons p_1 and p_2 as \mathbf{R}_1 and \mathbf{R}_2 , respectively, we see that these vectors are simply:

$$\mathbf{R}_1 = \left(0, 0, -\frac{R}{2}\right)$$

$$\mathbf{R}_2 = \left(0, 0, \frac{R}{2}\right)$$

since the line joining the two protons is assumed to lie along the z -axis.

The Hamiltonian for the H_2^+ molecule ion, assuming the two protons are fixed in space, is

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{|\mathbf{r} - \mathbf{R}_1|} - \frac{e^2}{|\mathbf{r} - \mathbf{R}_2|} + \frac{e^2}{R}$$

$$= -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{|\mathbf{r} + \frac{R}{2}\hat{\mathbf{z}}|} - \frac{e^2}{|\mathbf{r} - \frac{R}{2}\hat{\mathbf{z}}|} + \frac{e^2}{R}$$

Also, using the vectors \mathbf{r}_1 and \mathbf{r}_2 for the position of the electron with respect to the two protons, respectively, the Hamiltonian can be written in shorthand form as

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{r_1} - \frac{e^2}{r_2} + \frac{e^2}{R}$$

where it should be kept in mind that r_1 and r_2 are functions of \mathbf{r} , the coordinates of the electron with respect to our chosen coordinate system. Note that the term e^2/R is just a constant, representing the Coulomb repulsion between the two protons. We can, therefore, define the electronic Hamiltonian, H_{el} as

$$H = H_{\text{el}} + \frac{e^2}{R}$$

A. The trial wavefunction: a linear combination of atomic orbitals

Physically, when the two protons are far apart, and the electron is close to one or the other proton, the ground state wavefunction of the system should resemble that of a $1s$ orbital of hydrogen centered on one of the protons. When the electron is proton p_1 , its wavefunction should approximately be

$$\psi_0(\mathbf{r}) = \left(\frac{1}{\pi a_0^3}\right)^{1/2} e^{-r_1/a_0} = \left(\frac{1}{\pi a_0^3}\right)^{1/2} e^{-|\mathbf{r} + \frac{R}{2}\hat{\mathbf{z}}|/a_0} \equiv \psi_1(\mathbf{r}) = \langle \mathbf{r} | \psi_1 \rangle$$

Similarly, when it is on proton p_2 , it should be

$$\psi_0(\mathbf{r}) = \left(\frac{1}{\pi a_0^3}\right)^{1/2} e^{-r_2/a_0} = \left(\frac{1}{\pi a_0^3}\right)^{1/2} e^{-|\mathbf{r} - \frac{R}{2}\hat{\mathbf{z}}|/a_0} \equiv \psi_2(\mathbf{r}) = \langle \mathbf{r} | \psi_2 \rangle$$

This suggests that we might construct a trial wavefunction from an arbitrary linear combination of these two atomic orbitals according to

$$\begin{aligned} |\psi\rangle &= C_1|\psi_1\rangle + C_2|\psi_2\rangle \\ \psi(\mathbf{r}; C_1, C_2) &= C_1\psi_1(\mathbf{r}) + C_2\psi_2(\mathbf{r}) \end{aligned}$$

and treat the coefficients C_1 and C_2 as variational parameters. Such a trial wave function is called a *linear combination of atomic orbitals* or LCAO wave function. Notice that $|\psi_1\rangle$ and $|\psi_2\rangle$ are *not* orthogonal.

In accordance with the variational procedure, we construct the function

$$E(C_1, C_2) = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle}$$

Then,

$$\begin{aligned} \langle \psi | \psi \rangle &= [C_1^* \langle \psi_1 | + C_2^* \langle \psi_2 |] [C_1 |\psi_1\rangle + C_2 |\psi_2\rangle] \\ &= |C_1|^2 + |C_2|^2 + C_1 C_2^* \langle \psi_2 | \psi_1 \rangle + C_1^* C_2 \langle \psi_1 | \psi_2 \rangle \end{aligned}$$

Define the overlap between $|\psi_1\rangle$ and $|\psi_2\rangle$ by

$$\begin{aligned} S_{12} &= \langle \psi_1 | \psi_2 \rangle \\ S_{21} &= S_{12}^* \end{aligned}$$

Then,

$$\langle \psi | \psi \rangle = |C_1|^2 + |C_2|^2 + C_1 C_2^* S_{21} C_1^* C_2 S_{12}$$

Similarly,

$$\langle \psi | H | \psi \rangle = |C_1|^2 \langle \psi_1 | H | \psi_1 \rangle + |C_2|^2 \langle \psi_2 | H | \psi_2 \rangle + C_1 C_2^* \langle \psi_2 | H | \psi_1 \rangle + C_1^* C_2 \langle \psi_1 | H | \psi_2 \rangle$$

Define the matrix elements of H by

$$H_{ij} = \langle \psi_i | H | \psi_j \rangle$$

we find

$$\langle \psi | H | \psi \rangle = |C_1|^2 \langle H_{11} \rangle + |C_2|^2 \langle H_{22} \rangle + C_1 C_2^* H_{21} + C_1^* C_2 H_{12}$$

so that the energy becomes

$$E(C_1, C_2) = \frac{|C_1|^2 \langle H_{11} \rangle + |C_2|^2 \langle H_{22} \rangle + C_1 C_2^* H_{21} + C_1^* C_2 H_{12}}{|C_1|^2 + |C_2|^2 + C_1 C_2^* S_{21} C_1^* C_2 S_{12}}$$

Now we perform the variation $\partial E / \partial \langle \psi |$, which is equivalent to the conditions:

$$\frac{\partial E}{\partial C_1^*} = 0 \qquad \frac{\partial E}{\partial C_2^*} = 0$$

Defining the denominator as D

$$D = |C_1|^2 + |C_2|^2 + C_1 C_2^* S_{21} C_1^* C_2 S_{12}$$

these conditions yield two equations for C_1 and C_2 :

$$\begin{aligned} \frac{\partial E}{\partial C_1^*} &= \frac{C_1 H_{11} + C_2 H_{12}}{D} - \frac{E(C_1, C_2)}{D} (C_1 + C_2 S_{12}) = 0 \\ \frac{\partial E}{\partial C_2^*} &= \frac{C_2 H_{22} + C_1 H_{21}}{D} - \frac{E(C_1, C_2)}{D} (C_2 + C_1 S_{21}) = 0 \end{aligned}$$

or, since $D \neq 0$,

$$\begin{aligned} (H_{11} - E(C_1, C_2)) C_1 + (H_{12} - E(C_1, C_2) S_{12}) C_2 &= 0 \\ (H_{22} - E(C_1, C_2)) C_2 + (H_{21} - E(C_1, C_2) S_{21}) C_1 &= 0 \end{aligned}$$

These may be written as a matrix equation:

$$\begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \end{pmatrix} = E(C_1, C_2) \begin{pmatrix} 1 & S_{12} \\ S_{21} & 1 \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \end{pmatrix}$$

which is called a *generalized eigenvalue equation*. In matrix notation it becomes

$$\mathbf{HC} = E\mathbf{SC}$$

where \mathbf{H} and \mathbf{S} are the *Hamiltonian* and *overlap* matrices, respectively.

We may, therefore, regard E as an eigenvalue and solve the above eigenvalue equation. This requires that we solve the determinant:

$$\begin{vmatrix} H_{11} - E & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - E \end{vmatrix} = 0$$

Recognizing that $\langle \mathbf{r} | \psi_1 \rangle$ and $\langle \mathbf{r} | \psi_2 \rangle$ are both real, it is clear that $S_{12} = S_{21} \equiv S$. Similarly, by symmetry $H_{11} = H_{22} \equiv H_{11}$ and $H_{12} = H_{21} \equiv H_{12}$. Thus, the determinant simplifies to

$$\begin{vmatrix} H_{11} - E & H_{12} - ES \\ H_{12} - ES & H_{11} - E \end{vmatrix} = 0$$

which yields the condition

$$(H_{11} - E)^2 = (H_{12} - ES)^2$$

or

$$(H_{11} - E) = \pm (H_{12} - ES)$$

which yields two solutions. For the case of $+$, we have

$$E_+ = \frac{H_{11} - H_{12}}{1 - S}$$

and for $-$,

$$E_- = \frac{H_{11} + H_{12}}{1 + S}$$

The overlap, S , and Hamiltonian matrix elements will now be computed explicitly. For the overlap, S , the integral that needs to be performed is

$$\begin{aligned} S = \langle \psi_1 | \psi_2 \rangle &= \int d\mathbf{r} \psi_1(\mathbf{r}) \psi_2(\mathbf{r}) = \frac{1}{\pi a_0^3} \int d\mathbf{r} e^{-|\mathbf{r} + \frac{R}{2}\hat{\mathbf{z}}|/a_0} e^{-|\mathbf{r} - \frac{R}{2}\hat{\mathbf{z}}|/a_0} \\ &= \frac{1}{\pi a_0^3} \int d\mathbf{r} e^{-(|\mathbf{r} + \frac{R}{2}\hat{\mathbf{z}}| + |\mathbf{r} - \frac{R}{2}\hat{\mathbf{z}}|)/a_0} \end{aligned}$$

This integral is most easily performed in the confocal elliptic coordinate system using

$$\begin{aligned} \mu &= \frac{|\mathbf{r} + \frac{R}{2}\hat{\mathbf{z}}| + |\mathbf{r} - \frac{R}{2}\hat{\mathbf{z}}|}{R} \\ \nu &= \frac{|\mathbf{r} + \frac{R}{2}\hat{\mathbf{z}}| - |\mathbf{r} - \frac{R}{2}\hat{\mathbf{z}}|}{R} \\ J &= \frac{\partial(x, y, z)}{\partial(\mu, \nu, \phi)} = \frac{R^3}{8}(\mu^2 - \nu^2) \end{aligned}$$

Note that the range of μ is $[1, \infty]$, while that of ν is $[-1, 1]$. In addition, there is the integral over ϕ from $[0, 2\pi]$. Thus, transforming the integral, one obtains

$$S = \frac{1}{\pi a_0^3} \int_1^\infty d\mu \int_{-1}^1 d\nu \int_0^{2\pi} d\phi \frac{R^3}{8} (\mu^2 - \nu^2) e^{-\mu\rho}$$

where $\rho = R/a_0$. The integral can be performed straightforwardly yielding

$$S = e^{-\rho} \left[1 + \rho + \frac{1}{3}\rho^2 \right]$$

In order to evaluate the Hamiltonian matrix elements, let us look at the structure of H_{11} :

$$\begin{aligned} H &= \frac{P^2}{2m} - \frac{e^2}{r_1} - \frac{e^2}{r_2} + \frac{e^2}{R} \\ H_{11} &= \langle \psi_1 | H | \psi_1 \rangle = \left\langle \psi_1 \left| \frac{P^2}{2m} - \frac{e^2}{r_1} - \frac{e^2}{r_2} + \frac{e^2}{R} \right| \psi_2 \right\rangle \end{aligned}$$

Noting that $|\psi_1\rangle$ is an eigenvector of the operator $P^2/2m - e^2/r_1$ with eigenvalue $-e^2/2a_0$:

$$\left(\frac{P^2}{2m} - \frac{e^2}{r_1} \right) |\psi_1\rangle = -\frac{e^2}{2a_0} |\psi_1\rangle$$

it can be seen that H_{11} becomes

$$\begin{aligned} H_{11} &= -\frac{e^2}{2a_0} + \frac{e^2}{R} - \left\langle \psi_1 \left| \frac{e^2}{r_2} \right| \psi_2 \right\rangle \\ H_{11} &= -\frac{e^2}{2a_0} + \frac{e^2}{R} - C \end{aligned}$$

where the last term, C , is called the *Coulomb integral* and is given by

$$C = \left\langle \psi_1 \left| \frac{e^2}{r_2} \right| \psi_2 \right\rangle = \int d\mathbf{r} \psi_1^2(\mathbf{r}) \frac{e^2}{r_2}$$

Explicitly, the Coulomb integral is

$$C = \frac{e^2}{\pi a_0^3} \int d\mathbf{r} e^{-2|\mathbf{r} + \frac{R}{2}\hat{\mathbf{z}}|/a_0} \frac{1}{|\mathbf{r} - \frac{R}{2}\hat{\mathbf{z}}|}$$

which, again, is most easily evaluated using the confocal elliptic coordinates. Transforming into this coordinate system gives

$$\begin{aligned} C &= \frac{e^2}{\pi a_0^3} \frac{R^3}{8} \int_1^\infty d\mu \int_{-1}^1 d\nu \int_0^{2\pi} d\phi e^{-(\mu+\nu)\rho} \frac{2}{R(\mu-\nu)} (\mu^2 - \nu^2) \\ &= \frac{2e^2}{a_0^3} \frac{R^3}{8} \frac{2}{R} \int_1^\infty d\mu \int_{-1}^1 d\nu e^{-(\mu+\nu)\rho} (\mu + \nu) \end{aligned}$$

where the fact that $(\mu^2 - \nu^2) = (\mu + \nu)(\mu - \nu)$ has been used. Thus, the integral can be performed straightforwardly, to yield:

$$H_{11} = -\frac{e^2}{2a_0} + \frac{e^2}{R} - \frac{e^2}{2a_0} \frac{2}{\rho} [1 - e^{-2\rho}(1 + \rho)]$$

Note that

$$\lim_{R \rightarrow \infty} H_{11} = -\frac{e^2}{2a_0}$$

as expected.

The off-diagonal matrix element H_{12} can be evaluated in a similar manner.

$$\begin{aligned} H_{12} &= \left\langle \psi_1 \left| \frac{P^2}{2m} - \frac{e^2}{r_1} - \frac{e^2}{r_2} + \frac{e^2}{R} \right| \psi_2 \right\rangle \\ &= \left\langle \psi_1 \left| \frac{P^2}{2m} - \frac{e^2}{r_1} \right| \psi_2 \right\rangle + \frac{e^2}{R} \langle \psi_1 | \psi_2 \rangle - \left\langle \psi_1 \left| \frac{e^2}{r_1} \right| \psi_2 \right\rangle \\ &= -\frac{e^2}{2a_0} \langle \psi_1 | \psi_2 \rangle + \frac{e^2}{R} \langle \psi_1 | \psi_2 \rangle - \left\langle \psi_1 \left| \frac{e^2}{r_1} \right| \psi_2 \right\rangle \\ &= \left(-\frac{e^2}{2a_0} + \frac{e^2}{R} \right) S - \left\langle \psi_1 \left| \frac{e^2}{r_1} \right| \psi_2 \right\rangle \end{aligned}$$

Where the fact that $|\psi_2\rangle$ is an eigenvector of the operator $P^2/2m - e^2/r_2$ with eigenvalue $-e^2/2a_0$ has been used. The last term

$$\left\langle \psi_1 \left| \frac{e^2}{r_1} \right| \psi_2 \right\rangle \equiv A = \int d\mathbf{r} \psi_1(\mathbf{r}) \frac{e^2}{r_1} \psi_2(\mathbf{r})$$

is called the *exchange* or *resonance* integral. Substituting in the atomic wave functions, the integral becomes

$$A = \left(\frac{e^2}{\pi a_0^3} \right) \int d\mathbf{r} \frac{1}{|\mathbf{r} + \frac{R}{2}\hat{\mathbf{z}}|} e^{-|\mathbf{r} + \frac{R}{2}\hat{\mathbf{z}}|/a_0} e^{-|\mathbf{r} - \frac{R}{2}\hat{\mathbf{z}}|/a_0} = \left(\frac{e^2}{\pi a_0^3} \right) \int d\mathbf{r} \frac{1}{|\mathbf{r} + \frac{R}{2}\hat{\mathbf{z}}|} e^{-(|\mathbf{r} + \frac{R}{2}\hat{\mathbf{z}}| + |\mathbf{r} - \frac{R}{2}\hat{\mathbf{z}}|)/a_0}$$

Transforming to confocal elliptic coordinates, the integral becomes

$$\begin{aligned} A &= \left(\frac{e^2}{\pi a_0^3} \right) \frac{R^3}{8} \int_1^\infty d\mu \int_{-1}^1 d\nu \int_0^{2\pi} d\phi (\mu^2 - \nu^2) \frac{2e^{-\mu\rho}}{(\mu + \nu)} \\ &= 2\pi \left(\frac{e^2}{\pi a_0^3} \right) \frac{R^3}{8} \frac{2}{R} \int_1^\infty d\mu \int_{-1}^1 d\nu e^{-\mu\rho} (\mu - \nu) \end{aligned}$$

which can be integrated straightforwardly. Thus, the off-diagonal matrix element becomes

$$H_{12} = \left(-\frac{e^2}{2a_0} + \frac{e^2}{R} \right) S - \frac{e^2}{2a_0} 2e^{-\rho}(1 + \rho)$$

Using these expressions, the energies

$$E_+ = \frac{H_{11} - H_{12}}{1 - S} \qquad E_- = \frac{H_{11} + H_{12}}{1 + S}$$

can be determined. It is useful, however, to define ΔE_{\pm} relative to the energy at $R = \infty$, namely $-e^2/2a_0$. This will be given by

$$\Delta E_{\pm} = E_{\pm} + \frac{e^2}{2a_0} = -\frac{e^2}{2a_0} \left[\frac{2}{\rho} \pm \frac{2e^{-\rho}(1 + \rho) \mp [1 - e^{-2\rho}(1 + \rho)]}{1 \mp e^{-\rho} \left(1 + \rho + \frac{\rho^2}{3}\right)} \right]$$

A plot of $\Delta E_{\pm}(\rho)$ is sketched below.

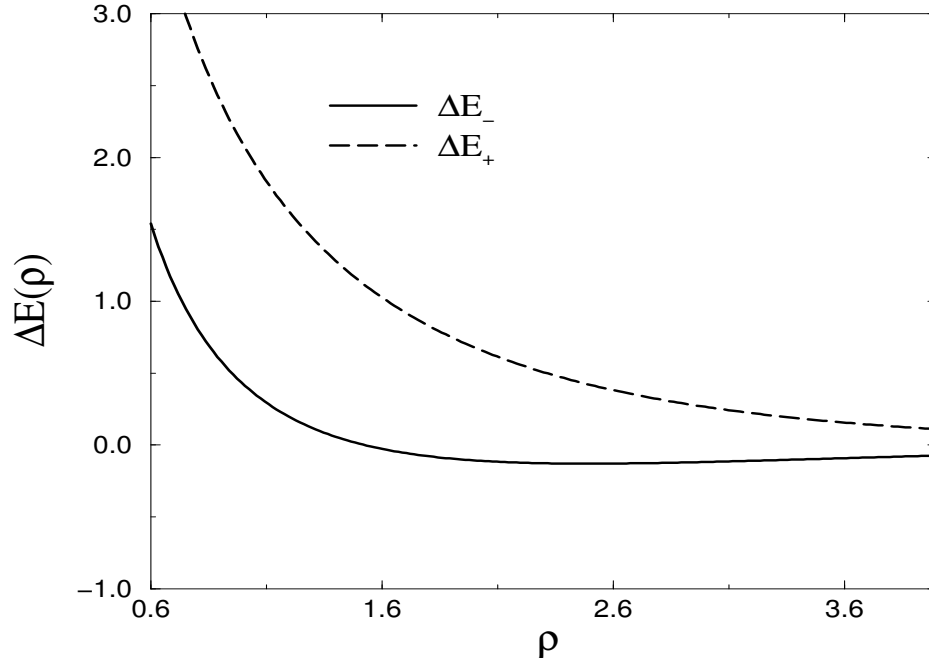


FIG. 2.

It can be seen that $\Delta E_+(\rho) > \Delta E_-(\rho)$ for all ρ . Also, $\Delta E_-(\rho)$ has a minimum at a particular value of ρ , which corresponds to the equilibrium bond length while $\Delta E_+(\rho)$ exhibits no such minimum. The location of the minimum and depth of the well will be the prediction of the equilibrium bond length and binding energy within this approximation, respectively. Before reporting these values, however, a few points are worth noting.

First, the presence of the minimum in ΔE_- is due primarily to the contribution of H_{12} , the off-diagonal matrix element of H . The reason for this is evident. In order for a chemical bond to form, there needs to be a significant overlap between the two atomic orbitals, which can only happen if the distance R between the two protons is not too large.

Second, the fact that ΔE_+ has no minimum means that in the state corresponding to this energy, the molecule will be likely to dissociate and not form a stable H_2^+ molecule.

The values obtained at this level of approximation from the location of the minimum of ΔE_- and the depth of the minimum are:

$$\begin{aligned} \text{bond length} &= 2.50a_0 \\ \text{binding energy} &= 1.76 \text{ eV} \end{aligned}$$

The exact values are $2.0a_0$ and 2.76 eV , respectively. Therefore, the result is only qualitatively correct. We will explore the problem of how to improve the current approximation by adding more variational parameters to the trial wave function, however, let us first see what other physical insights can be gained from the simple LCAO picture.

B. Bonding and anti-bonding orbitals

We look, first, at the form of the orbitals that correspond to the energies ΔE_{\pm} , respectively. These can be obtained by solving for the variational coefficients, C_1 and C_2 . These will be given by the matrix equation:

$$\begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \end{pmatrix} = E_{\pm} \begin{pmatrix} 1 & S_{12} \\ S_{21} & 1 \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \end{pmatrix}$$

For example, using $E_+ = (H_{11} - H_{12})/(1 - S)$, the following equations for the coefficients are obtained:

$$\begin{aligned} H_{11}C_1 + H_{12}C_2 &= \frac{H_{11} - H_{12}}{1 - S}(C_1 + SC_2) \\ H_{12}C_1 + H_{11}C_2 &= \frac{H_{11} - H_{12}}{1 - S}(SC_1 + C_2) \end{aligned}$$

which are not independent but are satisfied if $C_1 = -C_2 \equiv C_+$. Similarly, for $E = E_-$, we obtain the two equations:

$$\begin{aligned} (H_{11}C_1 + H_{12}C_2) &= \frac{H_{11} + H_{12}}{1 + S}(C_1 + SC_2) \\ (H_{12}C_1 + H_{11}C_2) &= \frac{H_{11} + H_{12}}{1 + S}(SC_1 + C_2) \end{aligned}$$

which are satisfied if $C_1 = C_2 \equiv C_-$. Thus, the two states corresponding to E_{\pm} are

$$\begin{aligned} |\psi_{-}\rangle &= C_{-} (|\psi_1\rangle + |\psi_2\rangle) \\ |\psi_{+}\rangle &= C_{+} (|\psi_1\rangle - |\psi_2\rangle) \end{aligned}$$

The overall constants C_{\pm} are determined by requiring that $|\psi_{\pm}\rangle$ both be normalized. For C_- , for example, we find

$$\begin{aligned} \langle \psi_{-} | \psi_{-} \rangle &= |C_{-}|^2 (\langle \psi_1 | + \langle \psi_2 |) (|\psi_1\rangle + |\psi_2\rangle) \\ &= |C_{-}|^2 (1 + 1 + \langle \psi_1 | \psi_2 \rangle + \langle \psi_2 | \psi_1 \rangle) \\ &= 2|C_{-}|^2(1 + S) \\ &= 1 \end{aligned}$$

which requires that

$$C_{-} = \frac{1}{2\sqrt{1+S}}$$

Similarly, it can be shown that

$$C_{+} = \frac{1}{2\sqrt{1-S}}$$

Thus, the two states become

$$\begin{aligned} |\psi_{-}\rangle &= \frac{1}{2\sqrt{1+S}} (|\psi_1\rangle + |\psi_2\rangle) \\ |\psi_{+}\rangle &= \frac{1}{2\sqrt{1-S}} (|\psi_1\rangle - |\psi_2\rangle) \end{aligned}$$

Notice that these are orthogonal:

$$\langle \psi_{+} | \psi_{-} \rangle = 0$$

Projecting onto a coordinate basis, we have

$$\begin{aligned} \psi_{-}(\mathbf{r}) &= \frac{1}{2\sqrt{1+S}} (\psi_1(\mathbf{r}) + \psi_2(\mathbf{r})) \\ \psi_{+}(\mathbf{r}) &= \frac{1}{2\sqrt{1-S}} (\psi_1(\mathbf{r}) - \psi_2(\mathbf{r})) \end{aligned}$$

The state ψ_- , which corresponds to the energy E_- admits a chemical bond and is, therefore, called a *bonding state*. The state ψ_+ , which corresponds to the energy E_+ does not admit a chemical bond and is, therefore, called an *anti-bonding state*. $\psi_+(\mathbf{r})$ and $\psi_-(\mathbf{r})$ are examples of what are called *molecular orbitals*. In this case, they are constructed from linear combinations of atomic orbitals.

The functional form of the two molecular orbitals for H_2^+ within the current approximation scheme is

$$\begin{aligned}\langle \mathbf{r} | \psi_- \rangle = \psi_-(\mathbf{r}) &= \frac{1}{2\sqrt{1+S}} \left(\frac{1}{\pi a_0^3} \right) \left[e^{-|\mathbf{r} + \frac{R}{2}\hat{\mathbf{z}}|/a_0} + e^{-|\mathbf{r} - \frac{R}{2}\hat{\mathbf{z}}|/a_0} \right] \\ \langle \mathbf{r} | \psi_+ \rangle = \psi_+(\mathbf{r}) &= \frac{1}{2\sqrt{1-S}} \left(\frac{1}{\pi a_0^3} \right) \left[e^{-|\mathbf{r} + \frac{R}{2}\hat{\mathbf{z}}|/a_0} - e^{-|\mathbf{r} - \frac{R}{2}\hat{\mathbf{z}}|/a_0} \right]\end{aligned}$$

The contours of these functions are sketched below (the top plot shows the two individual two atomic orbitals, while the middle and bottom show the linear combinations $\psi_-(\mathbf{r})$ and $\psi_+(\mathbf{r})$, respectively):

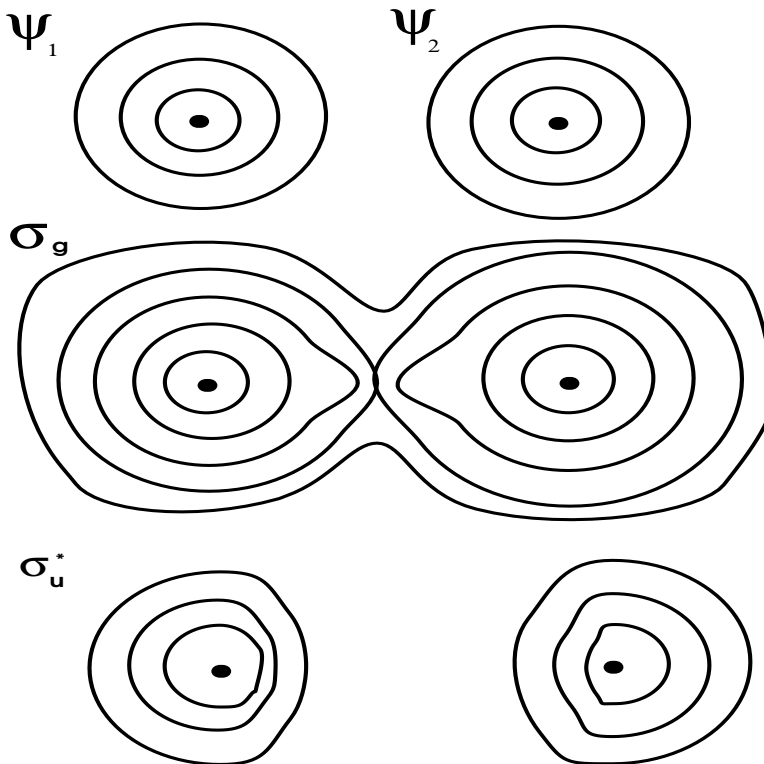


FIG. 3.

Since $\psi_1(\mathbf{r})$ and $\psi_2(\mathbf{r})$ have the same value at the origin and very similarly values near the origin, it is clear that the electron probability density in this region will intensify for $\psi_-(\mathbf{r})$ which is the sum of $\psi_1(\mathbf{r})$ and $\psi_2(\mathbf{r})$. This clearly corresponds to a chemical bonding situation. In contrast, for $\psi_+(\mathbf{r})$, which is the difference between $\psi_1(\mathbf{r})$ and $\psi_2(\mathbf{r})$, there will be a deficit of electron density in the region between the two protons, which is indicative of a non-bonding situation.

C. Improvements on the approximation

The LCAO approximation employed above leads to only a qualitatively correct description of chemical bonding in the H_2^+ molecule ion. The bond length and binding energy are quantitatively off from the exact values. In order to see how to improve the approximation, let us look at some of the limits of the LCAO approximation.

First in the limit $R \rightarrow 0$, the two protons are in approximately the same spatial location (exactly, strictly speaking, but this is unphysical), so that the wave function should have the same spatial dependence as that of a He^+ wave function (the neutrons in an actual He nucleus have no significant effect on the electronic wave function). The ground

state energy of He^+ should be $E_0 = -Z^2 e^2 / 2a_0 = -2e^2 / a_0$. However, in the LCAO approximation employed above, the energy $E_- - e^2/R$ (the nuclear repulsion term must be subtracted off because it becomes both infinite and unphysical if we fuse the two protons together into a single “nucleus”) becomes

$$E_- - \frac{e^2}{R} \longrightarrow -\frac{3e^2}{2a_0}$$

Thus, this limit is not properly represented in the current LCAO scheme. In addition, the form of the wave function $\psi_-(\mathbf{r})$ does not reduce to a He^+ wave function when $R \rightarrow 0$ but rather reduces to

$$\psi_-(\mathbf{r}) \longrightarrow \left(\frac{1}{\pi a_0^3}\right)^{1/2} e^{-r/a_0}$$

i.e., just a $1s$ orbital of hydrogen. In order to remedy this situation, one might imagine introducing Z , the atomic number, as a variational parameter into the LCAO approximation. That is, one could introduce atomic orbitals of the form

$$\begin{aligned} \langle \mathbf{r} | \psi_1(Z) \rangle = \psi_1(\mathbf{r}; Z) &= \left(\frac{Z^3}{\pi a_0^3}\right)^{1/2} e^{-Z|\mathbf{r} + \frac{R}{2}\hat{\mathbf{z}}|/a_0} \\ \langle \mathbf{r} | \psi_2(Z) \rangle = \psi_2(\mathbf{r}; Z) &= \left(\frac{Z^3}{\pi a_0^3}\right)^{1/2} e^{-Z|\mathbf{r} - \frac{R}{2}\hat{\mathbf{z}}|/a_0} \end{aligned}$$

and then construct a modified LCAO scheme with a trial wave function of the form

$$|\psi\rangle = C_1|\psi_1(Z)\rangle + C_2|\psi_2(Z)\rangle$$

The bond length and binding energy obtained in this case are $2.00 a_0$ and 2.35 eV , respectively. While the bond length is now correct, the energy is still off from the exact value, which illustrates that the geometry tends to converge faster than the energy.

In the limit of R large but not infinite, the approximation of spherical atomic orbitals is also not entirely correct. The reason for this can be seen by the fact that a positive charge in the vicinity of a hydrogen atom will produce an electric field that causes a distortion of the electronic charge distribution about the hydrogen nucleus, as the figure below illustrates:

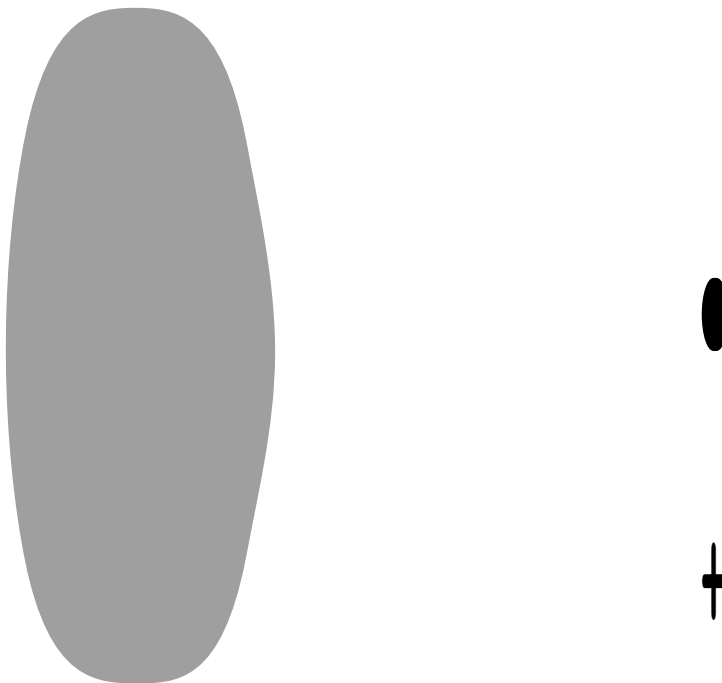


FIG. 4.

This *polarization* effect can be included in the trial wavefunction by mixing in a little bit of a p -orbital. For example, if we constructed a trial wavefunction of the form

$$|\psi\rangle = C_1|\chi_1\rangle + C_2|\chi_2\rangle$$

where

$$\langle \mathbf{r}|\chi_1\rangle = \chi_1(\mathbf{r}) = \psi_{1s}^2(\mathbf{r}_1) + \sigma\psi_{2p}^2(\mathbf{r}_1)$$

where σ is a mixing coefficient that is treated as a variational parameter, then, with a similar definition for $|\chi_2\rangle$, a variational scheme that includes the polarization effect is obtained.

In order to include *both* limits, one would then introduce the Z dependence into the χ orbitals above and use as a trial wavefunction

$$|\psi\rangle = C_1|\chi_1(Z)\rangle + C_2|\chi_2(Z')\rangle$$

which allows for an asymmetry due to the presence of Z and Z' . Thus, treating C_1 , C_2 , Z , Z' , and σ as variational parameters, a bond length of $2.00 a_0$ and binding energy of $2.73 eV$ are obtained, which are in very good agreement with the exact results.

D. Other molecular orbitals

As noted above, L_z commutes with the total Hamiltonian for H_2^+ , i.e.,

$$[L_z, H] = 0$$

Thus, the eigenvalue m can be used to characterize molecular orbitals. The following nomenclature has been adopted for designating molecular orbitals from the m value:

$$|m| = 0 \longrightarrow \sigma \text{ orbital.}$$

$$|m| = 1 \longrightarrow \pi \text{ orbital.}$$

$$|m| = 2 \longrightarrow \delta \text{ orbital.}$$

which are clearly analogous to s , p and d atomic orbitals.

In addition, molecular orbitals are given another designation based on how they transform under a parity transformation. The parity transformation operator, Π or P , produces a spatial reflection $\mathbf{r} \longrightarrow -\mathbf{r}$. Possible eigenvalues of Π are 1 or -1, and an orbital with a parity eigenvalue of 1 is said to be a state of even parity, while an orbital with a parity eigenvalue of -1 is said to be a state of odd parity. Even and odd parity states are designated by a g or a u , which derive from the German words *gerade* and *ungerade* for “even” and “odd”, respectively. Thus, a σ orbital of even parity would be denoted as σ_g .

To see how to designate the molecular orbitals $\psi_-(\mathbf{r})$ and $\psi_+(\mathbf{r})$, let us look at how they transform under the parity operation:

$$\begin{aligned} \Pi\psi_-(\mathbf{r}) &= \psi_-(-\mathbf{r}) = C_- \left[e^{-|\mathbf{r} + \frac{R}{2}\hat{\mathbf{z}}|/a_0} + e^{-mpt/a_0} \right] \\ &= C_- \left[e^{-pt/a_0} + e^{-|\mathbf{r} + \frac{R}{2}\hat{\mathbf{z}}|/a_0} \right] = \psi_-(\mathbf{r}) \\ \Pi\psi_+(\mathbf{r}) &= \psi_+(-\mathbf{r}) = C_+ \left[e^{-|\mathbf{r} + \frac{R}{2}\hat{\mathbf{z}}|/a_0} - e^{-mpt/a_0} \right] \\ &= C_+ \left[e^{-pt/a_0} - e^{-|\mathbf{r} + \frac{R}{2}\hat{\mathbf{z}}|/a_0} \right] = -\psi_+(\mathbf{r}) \end{aligned}$$

Thus, we see that $\psi_-(\mathbf{r})$ is an even parity state while $\psi_+(\mathbf{r})$ is an odd parity state. Thus, these molecular orbitals should be designated as

$$\begin{aligned} |\psi_-\rangle &\equiv |\sigma_g(1s)\rangle \\ |\psi_+\rangle &\equiv |\sigma_u(1s)\rangle \end{aligned}$$

or simply $\sigma_g(1s)$ and $\sigma_u(1s)$, respectively. The $1s$ is also shown explicitly to indicate that these are constructed from $1s$ orbitals of hydrogen. Finally, in order to distinguish the bonding from the anti-bonding state, an asterisk (*) is added to the anti-bonding state, so that its full designation is $\sigma_u^*(1s)$. Note that both orbitals are eigenfunctions of L_z although they are not exact eigenfunctions of H , as expected.

In a similar manner, molecular orbitals can be constructed from $2s$ orbitals of hydrogen. These will correspond qualitatively to excited states of H_2^+ although their accuracy will be relatively low compared to the exact excited state wave functions. Nevertheless, they can be useful in understanding qualitatively what the electronic distribution will be in such an excited state. It is clear that there will be analogous $|\psi_-\rangle$ and $|\psi_+\rangle$ states which will correspond to bonding and anti-bonding molecular orbitals, $\sigma_g(2s)$ and $\sigma_u^*(2s)$, respectively. Again, they will be eigenfunctions of L_z but not of H .

Orbitals can also be constructed from $2p_z$ atomic orbitals. These will clearly have $m = 0$ and hence be σ orbitals. The even and odd parity combinations will therefore be

$$\begin{aligned} |\sigma_g(2p_z)\rangle &\propto |\psi_{2p_z}^{(1)}\rangle + |\psi_{2p_z}^{(2)}\rangle \\ |\sigma_u^*(2p_z)\rangle &\propto |\psi_{2p_z}^{(1)}\rangle - |\psi_{2p_z}^{(2)}\rangle \end{aligned}$$

These are both eigenfunctions of L_z with $m = 0$ as required for a σ orbital. The contours of these orbitals are shown in the figure below (again, the top plot shows the individual contours of the two $2p_z$ orbitals and the middle and bottom show the g and u combinations):

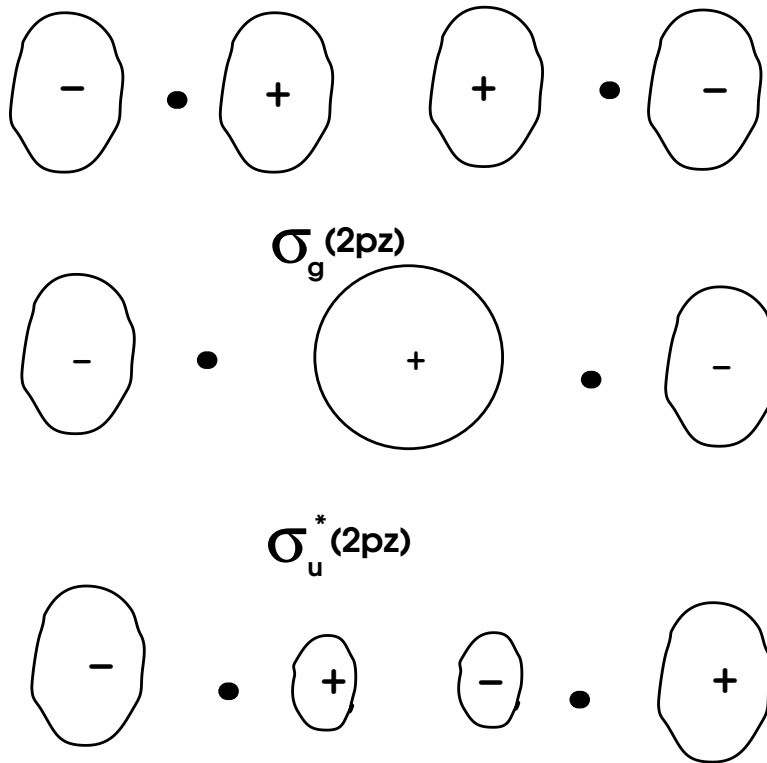


FIG. 5.

From the figure it is clear that $\sigma_g(2p_z)$ must be a bonding state while $\sigma_u^*(2p_z)$ must be anti-bonding.

Finally, we can construct molecular orbitals from $2p_x$ or $2p_y$ orbitals. Since these will be similar in shape and have the same energy, we only need to consider one case. Let us look at the $2p_x$ orbitals. Since the $2p_x$ orbitals have $m = 1$, the molecular orbitals will be π orbitals. In this case, the even and odd parity states will be:

$$|\pi_u(2p_x)\rangle \propto |\psi_{2p_x}^{(1)}\rangle + |\psi_{2p_x}^{(2)}\rangle$$

$$|\pi_g^*(2p_x)\rangle \propto |\psi_{2p_x}^{(1)}\rangle - |\psi_{2p_x}^{(2)}\rangle$$

as can be easily checked. Again, these are both eigenfunctions of L_z with $m = 1$ as required for a π orbital. The contours of these molecular orbitals are shown in the figure below:

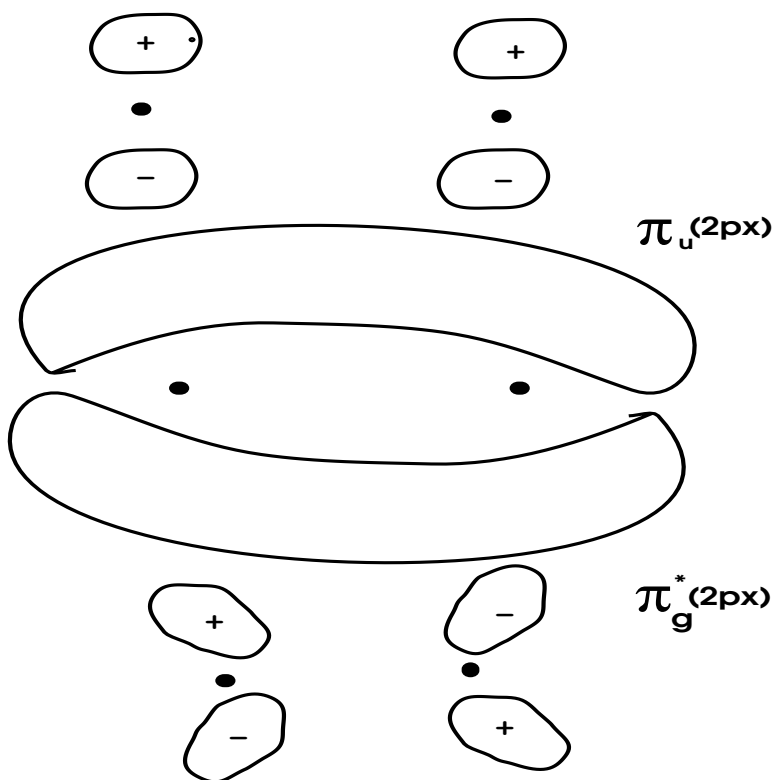


FIG. 6.

In the bonding state, the electron becomes highly delocalized over the entire molecule in a banana shaped orbital, while in the anti-bonding state, the lobes are more well localized.

The energies of these various molecular orbitals are ordered according to the figure below:

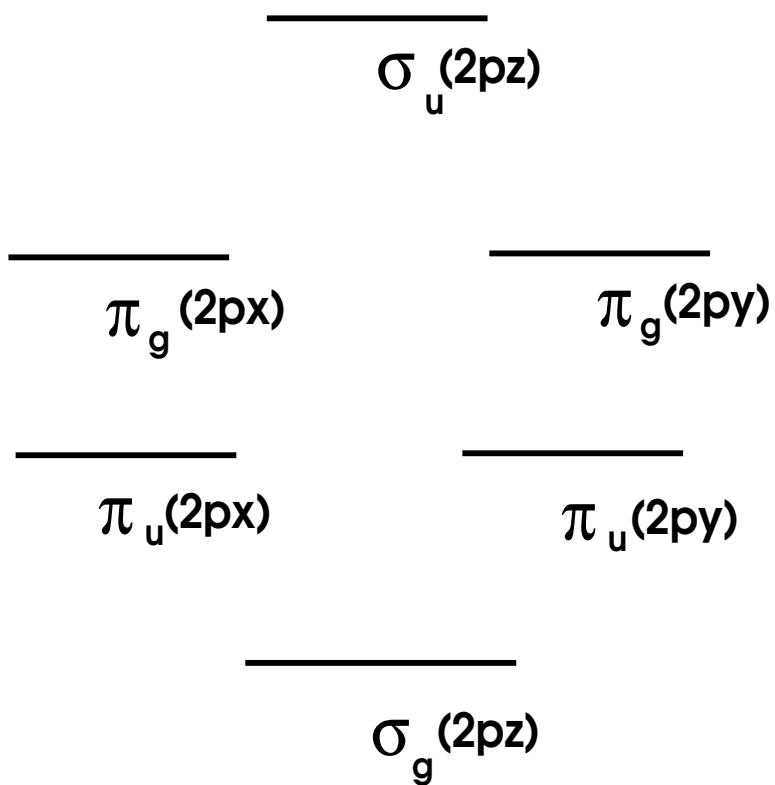


FIG. 7.

The figure shows that the bonding orbitals all have lower energies than the anti-bonding orbital as expected.