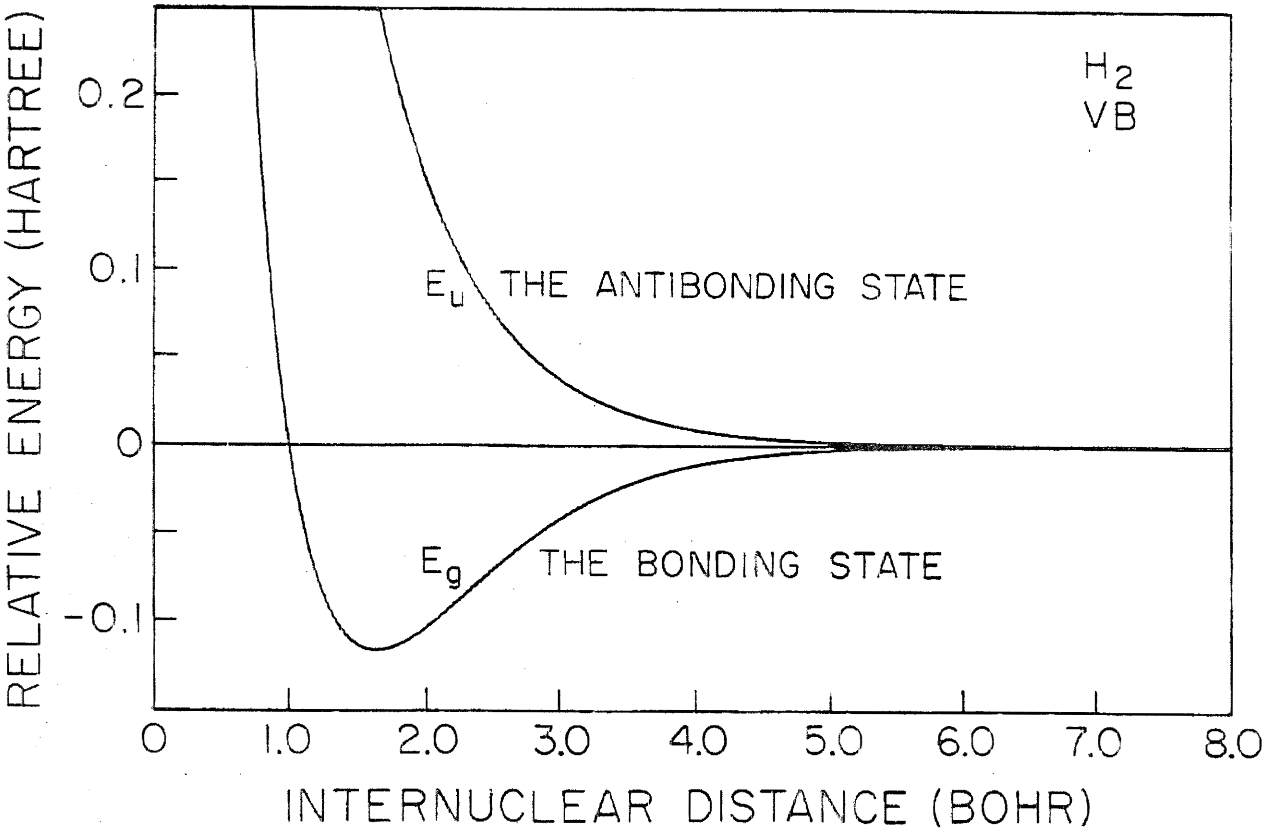
NATURE OF THE CHEMICAL BOND

CHEMISTRY 120
CALIFORNIA INSTITUTE OF TECHNOLOGY

VOLUME I

Chapter 1: **The Concepts of Quantum Mechanics**
Chapter 2: The Chemical Bond: H_2^+ and H_2
Chapter 3: More Exact Wavefunctions for One- and Two-Electron Systems



Acknowledgments

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General Comments

Chapters are divided into **sections,** for example §1.3, which are usually partitioned into **subsections,** §1.3.2, which are, in turn, occasionally divided into further subsections, §1.3.2b. **Tables** and **Figures** are numbered sequentially through each **chapter** as Fig. 1-1, Fig. 1-2,...; however, within a chapter the chapter number is suppressed, e.g., Fig. 1, Fig. 2,.... **Equations** are numbered sequentially through each **sections,** e.g., (1), (2),...; however, when referring to an equation in another section, the section number is included, e.g., (1.3-1), (1.3-2),.... **Pages** are numbered sequentially for each **chapter.** Most chapters and some sections start with a summary of the major points.

Ch 120a

Chapter 1. The Concepts of Quantum Mechanics.

Contents:

Appendices:

Summary:

It is assumed that all students reading this material have had some course (e.g., the traditional semester of a junior-level physical chemistry course) presenting the basic elements of quantum mechanics with some treatment of the hydrogen atom, the harmonic oscillator, and angular momentum. This course will concentrate on the explanation of the structure and reactivity of molecules using quantum mechanical ideas. The explanations will stress qualitative and semi-quantitative considerations with the emphasis on developing ***principles*** (based on quantum mechanics) that can be used to make reliable ***predictions on new systems*** (rather than merely rationalize known results).

Chapter 1 is a review of materals that all students should have had previously, but with an emphasis on those points that will be important later in the course.

The basic principles of quantum mechanics are summarized in § 1.1. A key idea here is that ***in the classical description of an atom, the electron would collapse into the nucleus***. The critical difference with the quantum description is that the kinetic energy is proportional to the average value of the square of the gradient of the wavefunction, $T = \frac{1}{2} \langle |\nabla\varphi|^2 \rangle$. Consequently, for an electron sitting on the nucleus, the kinetic energy is infinite (since $\nabla\varphi$ is infinite). This forces the electron to remain distributed over a ***finite*** region surrounding the nucleus and prevents the collapse of the electron into the nucleus. Thus ***the quantum description is essential for stability of atoms***. We will find in later chapters that modifications in the kinetic energy (due to superposition of orbitals) also plays the key role in the formation of chemical bonds.

Throughout this course we will be searching for qualitative ideas concerning the sizes and shapes of wavefunctions and for simple ways of predicting the energy ordering of the states of a system. A useful concept here is the ***nodal*** theorem described in §1.3. Basically, this theorem tells us that the ground state of a system is everywhere positive [no nodal planes (zeros) interior to the boundaries of the system].

§1.1 BASIC PRINCIPLES OF QUANTUM MECHANICS

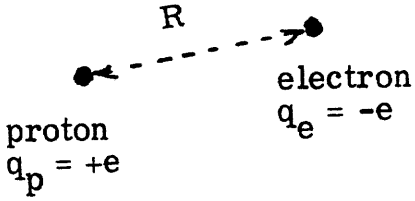
In the following section we highlight the basic concepts of quantum mechanics relevant for this course. All of these ideas should be familiar to you; good references for reviewing these topics and for outside reading during the first part of Ch 120a are:

I. N. Levine, *Quantum Chemistry* (Allyn and Bacon, Boston, 1974), Second Edition.

H. Eyring, J. Walter, and G. W. Kimball (EWK), *Quantum Chemistry* (Wiley and Sons, New York, 1944).

§1.1.1 The Need for Quantum Mechanics

In order to see why quantum mechanics is so important to chemistry, let's examine the classical mechanical description of the hydrogen atom



The total energy is given by

$$E = T + V \tag{1}$$

where the kinetic energy is*

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* Actually, the total kinetic energy of the hydrogen atom has *two* terms,

$$T = \frac{1}{2} m_p v_p^2 + \frac{1}{2} m_e v_e^2 = \frac{1}{2m_p} (p_p)^2 + \frac{1}{2m_e} (p_e)^2 . \tag{3}$$

However, considering the case where there is no net motion (i.e., no net inertia or momentum) leads to

$$p_p + p_e = 0$$

and hence $(p_p)^2 = (p_e)^2$, so that (3) becomes

$$T = \frac{1}{2}mv^2 = \frac{1}{2m}p^2 , \tag{2}$$

where m, v, and p are the mass, velocity, and momentum of the electron, and the potential energy is

$$V = \frac{q_p q_e}{r} = -\frac{e^2}{r} . \tag{6}$$

where $q_e = -e$ and $q_p = +e$ and the charge of the electron and proton and r is the distance between them.

The ***ground state*** is when the system has its ***lowest possible*** total ***energy***. Any other state (higher energy) is referred to as an ***excited state***. Generally, systems in excited states will eventually decay to lower energy states,[†] and we will be interested in the stable (ground) states. The lowest kinetic energy occurs for p = 0, leading to T = 0, while the lowest potential energy occurs for r = 0, leading to V = -∞. Thus, in the classical description, the ground state of the hydrogen atom has the electron standing (or sitting) on the nucleus, leading to

$$E = -\infty .$$

Since the charges cancel and the atom has a radius of zero, these atoms would not combine to form molecules. Thus, **in classical mechanics the atom is not stable!** If classical mechanics provided the proper

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$$T = \frac{1}{2\mu}(p_e)^2 , \tag{4}$$

where

$$\frac{1}{\mu} = \frac{1}{m_p} + \frac{1}{m_e} \quad \text{or} \quad \mu = \frac{m_p m_e}{m_p + m_e} = \frac{m_e}{1 + \frac{m_e}{m_p}} . \tag{5}$$

Since $m_p = 1836\ m_e$, then $\mu = 0.9995\ m_e$, and for our purposes we can consider just the kinetic energy of the electron as in (2).

[†] For systems containing charges, this is accompanied by emission of light.

description of atoms, and we would not be here pondering the universe.

The solution to this problem is provided by quantum mechanics, as will be discussed below. Essentially the conclusion is that electrons must be described in terms of wavefunctions $\varphi(\mathbf{r})$, where the shape of the wavefunction *simultaneously* determines both the kinetic energy and the potential energy. [In classical mechanics we can independently adjust r and p.] The result is that the state of the system with lowest potential energy (r = 0) has an infinite kinetic energy preventing the atoms from collapse.

§1.1.2 INTERFERENCE AND DIFFRACTION OF LIGHT

Before proceeding to a discussion of quantum mechanics, we will review some relevant features concerning the properties of light.

The early controversy upon the nature of light between Newton, who considered light as corpuscles, and Huygens, who considered light as waves, was settled partly on the basis of the fact that (coherent) light waves interfere, a property difficult to explain except on the basis of waves. Basically, the idea is that

(i) light is described by a *wavefunction*

$$\psi(x,t)$$

that depends upon x and t, for example,

$$\psi(x,t) = \cos\left[\frac{2\pi}{\lambda}x - 2\pi\nu t\right]$$

(where λ is the wavelength and ν is the frequency),

(ii) *detection* of the light is proportional to the square of the wavefunction (called the *intensity*) averaged over a time long compared with the frequency

$$I(x) = <[\psi(x,t)]^2>_t$$

where the brackets indicate an average and the subscript t indicates that the average is over t,

(iii) superimposition of two wavefunctions leads to a new wavefunction

$$\psi^{new} = \psi_1^{old} + \psi_2^{old},$$

where the ***amplitudes add***, and

(iv) the intensity for two superimposed waves is [from (ii)]

$$I^{new}(x) = <[\psi_1^{old} + \psi_2^{old}]^2>_t$$

$$= <[\psi_1^{old}]^2>_t + <[\psi_2^{old}]^2>_t + 2 <\psi_1^{old}\,\psi_2^{old}>_t$$

$$= I_1^{old} + I_2^{old} + I_{int} \;,$$

where the I_1^{old} and I_2^{old} are the intensities of the component waves and I_{int} is a new *interference* term present only when the component waves are present simultaneously.

The interference term in (iv) may be nonzero and can lead to complete cancellation of the other terms. Particularly impressive interference phenomena are the diffraction effects found for such uniformly spaced scatterers as diffraction gratings as illustrated in Fig. 1.

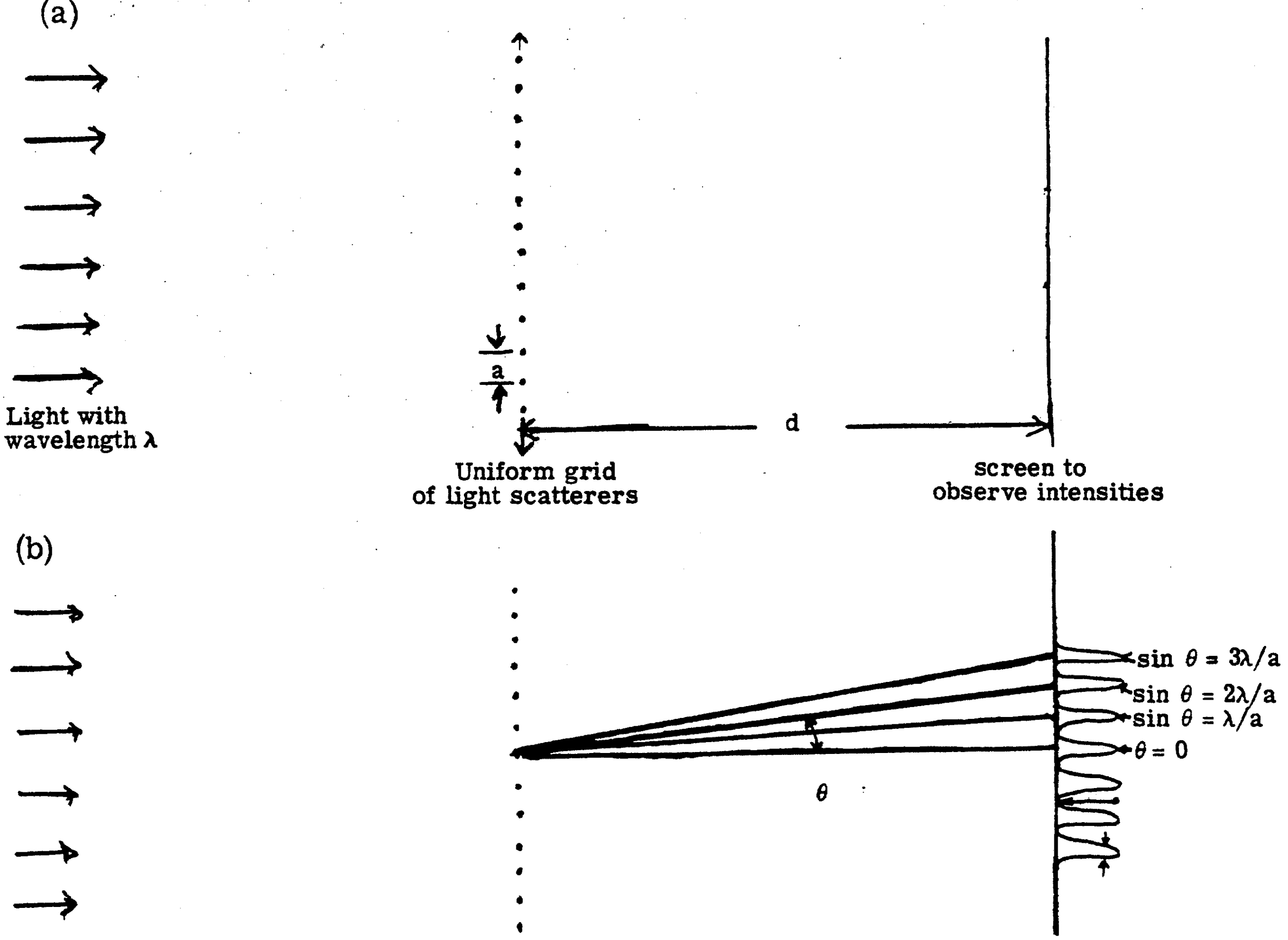

Figure 1-1.

With a set of uniformly spaced scatterers, the observed intensities are sharp spikes at particular angles ϑ_n, where* $\sin \vartheta_n = n\frac{\lambda}{a}$. From measurements of $\sin \vartheta_{obs}$ one can calculate $\frac{\lambda}{a}$. Therefore, knowing the λ of light, we can determine the spacing **a** or vice versa, knowledge of the spacing **a** can be used with $\sin \vartheta_{obs}$ to determine λ. A comparison of the observed intensity with that expected if light did not interfere is given in Fig. 2.

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* To have maxima for $\vartheta_n \neq 0$, we must have $n\lambda < a$; the wavelength must be smaller that the spacing of the scattering.

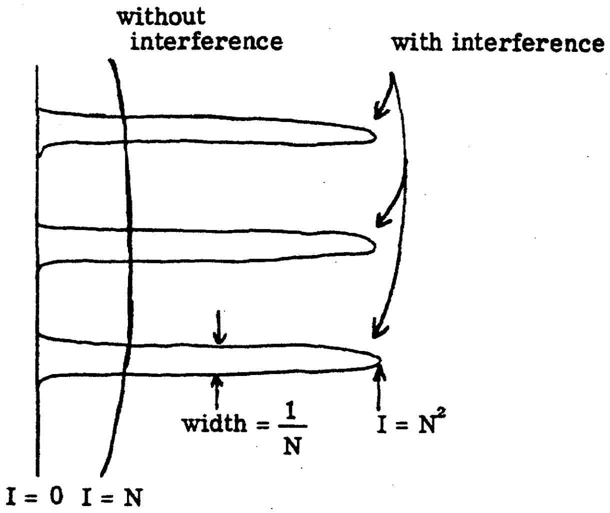

Figure 2-2.

A particularly exciting application of these ideas occurred around 1912. By that time a number of scientists believed that x-rays were electromagnetic waves like light but with very short wavelengths, $\lambda \sim 1$ Å. If so, they should exhibit diffraction, if a grating could be found having equally spaced scatterers with uniform separations of ~1 Å . In addition, by 1912 a number of scientists were convinced that atoms do exist (rather than being just theoretical constructs) and that crystals might consist of uniformly spaced atoms having separations of a few angstroms. F. von Lave, an expert on diffraction theory, suggested the experiment of exposing a crystal to a beam of x-rays and looking for diffraction spikes. After a couple of years of work the experiments were successful, proving both the wave nature of x-rays and the existence of ordered atoms in crystals. Since then, such x-ray diffraction studies have led to enormous advances in our atomic-level understanding of matter.

§1.1.3 Electrons

The critical experiment* establishing the wave nature of the electrons is that a crystal **diffracts a beam of electrons in exactly the same**

was as it diffracts a beam of x-rays, as illustrated in Fig. 3. Thus, **electrons must be described as waves.**

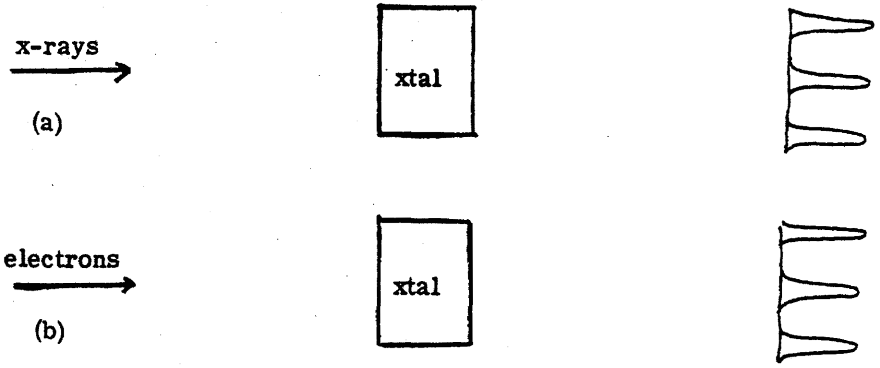

Figure 1-3.

Indeed, from these observations one can determine the relation between the wave properties and particle properties of the electrons, namely,

$$p = \frac{h}{\lambda} , \qquad (1')$$

where $p = \sqrt{2mE}$ is the momentum of the electron and E is the kinetic energy of the electron, h is a constant (Planck's), and λ is the wavelength of the electrons (obtained from the spacing of the diffraction peaks).

Based on this and other experiments, we now know that electrons should be described as wavefunctions,

$$\psi(x,t)$$

where the probability, P, of observing the electrons at some point x is proportional to the square of the wavefunction,

$$P(x) = <[\psi(x,t)]^2>_t \ .$$

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* This experiment was carried out in 1928 as a test of the ideas arising from the theorists developing quantum mechanics. Earlier experiments had, in fact, observed what is now recognized as diffraction; however, the experiments were not properly interpreted.

The consequences of this will be pondered in the next section.

§1.1.4 **The Schrödinger Equation**

In the 1920's, a number of experiments, such as electron diffraction, showed that matter exhibits interference phenomena just as does light. This led to the idea that matter, like light, should be described by an amplitude function,

$$\psi(\mathbf{r},t) \ ,$$

called a **wavefunction,** such that superposition of two systems ψ_1 and ψ_2 leads to superposition of the amplitudes

$$\psi = \psi_1 + \psi_2 \ . \tag{1}$$

but such that the probability of finding the total system with particular coordinates **r** and t is given by the (absolute) square of this amplitude.

$$P(\mathbf{r},t) = |\psi(\mathbf{r},t)|^2 = \psi^*(\mathbf{r},t)\psi(\mathbf{r},t) \ . \tag{2}$$

Combining (1) and (2) leads to

$$P(r,t) = \psi_1{}^*\psi_1 + \psi_2{}^*\psi_2 + \psi_1{}^*\psi_2 + \psi_2{}^*\psi_1 \ ,$$

and hence interference effects--as observed.

Putting these ideas together leads to the **basic postulate of quantum mechanics:** *Every physical system is described in terms of a wavefunction ψ containing all observable information about the system.* This wavefunction is probability amplitude, meaning that a superposition of states of the system leads to a superposition of the amplitudes,

$$\psi = \sum_i \psi_i \ . \tag{3}$$

As part of this basic postulate, we assume that if ψ_1 and ψ_2 are two acceptable wavefunctions of a system, then

$$\psi = c_1\psi_1 + c_2\psi_2 \ , \tag{4}$$

(where c_1 and c_2 are constants) is also an acceptable wavefunction (this is called the **principle of superposition).**

As part of this basic postulate, the probability of the system having particular coordinates at a particular time is taken as the absolute square of the wavefunction $|\psi|^2$ as in (2). Since the total probability of the system being somewhere is 1, we have the **normalization condition:**

$$1 = \int P(\mathbf{r},t)d\tau = \int \psi^*\psi d\tau \equiv \langle\psi|\psi\rangle \tag{5}$$

(dτ is the incremental volume element and this integration goes over all regions of space). The normalization of the wavefunction ψ is independent of time (being always unity).

The above postulate implies that anything we can know about the system must be extracted from the wavefunction. Thus the wavefunction at some future time, $t_0 + \delta t$, is completely determined by the form of the wavefunction at time t_0. In other words, there must be some rule or formula relating $\psi(\mathbf{r},t_0 + \delta t) \equiv \varphi_1(\mathbf{r})$ to $\psi(\mathbf{r},t_0) \equiv \varphi_0(\mathbf{r})$. Such an association of functions is generally called a **transformation** and is denoted as

$$\varphi_1(\mathbf{r}) = \hat{A}_{10}\,\varphi_0(\mathbf{r}) \ ,$$

where $\hat{A}_{10}$ is referred to as the operator effecting the particular transformation from state φ_0 to state φ_1. Similarly, the time derivative of the wavefunction at time t_0, $\frac{\partial\psi}{\partial t}$, must be determined by the form of the wavefunction at time t_0, and hence we can write

$$\left(\frac{\partial\psi}{\partial t}\right)_{t_0} = \hat{B}\,\psi(\mathbf{r},t_0) \ , \tag{6}$$

where $\hat{B}$ is called the **time evolution operator.** For convenience we replace $\hat{B}$ with $\hat{H} \equiv i\hbar\hat{B}$, where H is referred to as the **Hamiltonian.** Thus (6) becomes

$$\boxed{i\hbar \frac{\partial\psi}{\partial t} = \hat{H}\,\psi \,,} \tag{7}$$

which is known as the **time-dependent Schrödinger equation.** In (7), i = $\sqrt{-1}$, $\hbar$ is Planck's constant* (1.054589 10^{-27} erg sec), and H has the dimensions of energy. Since (7) must also apply to any superposition of wavefunctions (3), H must be a ***linear*** operator,†

$$H(\psi_1 + \psi_2) = H\psi_1 + H\psi_2 \,. \tag{8}$$

We find that the operator $\hat{H}$ depends upon the nature of the system and that it is, in general, a function of both position **r** and time t.

If the Hamiltonian $\hat{H}$ is ***independent of time***, then the solutions of (7) have the form

$$\psi(\mathbf{r},t) = \varphi(\mathbf{r})T(t) \,, \tag{9}$$

where

$$\frac{\partial T}{\partial t} = -i\omega\, T(t) \tag{10}$$

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* Actually, the original Planck's constant $\hbar$ is

$$h = 2\pi\hbar \,.$$

However, we will use only $\hbar$ and refer to it as Planck's constant.

† From (4)

$$i\hbar\frac{\partial}{\partial t}\psi = c_1\left[i\hbar\frac{\partial\psi_1}{\partial t}\right] + c_2\left[i\hbar\frac{\partial\psi_2}{\partial t}\right] = c_1H\psi_1 + c_2H\psi_2 \,,$$

where (7) was applied to ψ_1 and ψ_2, respectively. Applying (7) directly to ψ leads to

$$i\hbar\frac{\partial}{\partial t}\psi = \dot{H}(c_1\psi_1 + c_2\psi_2)$$

and hence (8).

and

$$\hat{H}(\mathbf{r})\varphi(\mathbf{r}) = \hbar\omega\varphi(\mathbf{r}) \; . \tag{11}$$

Equation (10) has the solution

$$T(t) = e^{-i\omega t} \; , \tag{12}$$

so that (9) becomes

$$\psi(\mathbf{r},t) = \varphi(\mathbf{r})e^{-i\omega t} \; , \tag{13}$$

where $\varphi(\mathbf{r})$ is yet to be determined from (11).

At this point we recall the quantum mechanical interpretation of two experiments. In the photoelectric experiment, light behaves as a stream of particles (called photons), each having a quantum of energy

$$E = \hbar\omega \; , \tag{14}$$

where

$$\omega = 2\pi\nu = 2\pi c/\lambda$$

is the angular frequency of the light. This suggests that the $\hbar\omega$ in (11) be considered as the energy in (14). In electron diffraction, the diffraction pattern for electrons with momentum p and energy E is equivalent to the diffraction pattern for light with wave vector

$$k = 2\pi/\lambda \tag{15}$$

and angular frequency ω, where ω is given by (12) and k is given by

$$p = \hbar k \; . \tag{16}$$

Thus we postulate that the energy and frequency are always related by (14), leading to

$$\psi(\mathbf{r},t) = \varphi(\mathbf{r})\, e^{-iEt/\hbar} \tag{17}$$

$$\boxed{\hat{H}(\mathbf{r})\varphi(\mathbf{r}) = E\,\varphi(\mathbf{r})\ .} \qquad (18)$$

The latter equation is known as the **time-independent Schrödinger equation and is the fundamental equation determining chemical bonding.**

§1.1.5 The Form of the Hamiltonian

In (18) we see that there is a relationship between the operator $\hat{H}$ and the total energy of the system, E. In classical mechanics, the operator associated with the total energy of the system is the Hamiltonian, H^{cl}, which is given by

$$H^{\mathrm{cl}} = T^{\mathrm{cl}} + V^{\mathrm{cl}}$$

(for nondissipative systems), where T^{cl} and V^{cl} are the kinetic and potential energies. We will postulate that there are quantum mechanical operators $\hat{T}$ and $\hat{V}$, corresponding to the classical quantities T and V, such that the quantum mechanical operator $\hat{H}$ is given by

$$\hat{H} = \hat{T} + \hat{V}\ ,$$

and we will refer to $\hat{H}$ as the **Hamiltonian** operator. For a system in which the classical potential V^{cl} is velocity-independent [that is, a function of the coordinates of the particle only], we will postulate that the quantum mechanical operator corresponding to $V(\mathbf{r})$ is just the classical function

$$\hat{V}(\mathbf{r}) = V(\mathbf{r})^{\mathrm{cl}}\ . \qquad (19)$$

Thus for the hydrogen atom,

$$\hat{V}(r) = -\frac{e^2}{r}\ .$$

For a particle moving in a potential $V(\mathbf{r})^{\mathrm{cl}}$, the kinetic energy (classically) is

$$T^{cl} = \frac{1}{2m}p^2 , \tag{20}$$

where $\mathbf{p} = m\mathbf{v}$ is the momentum of the particle. We will postulate that the quantum mechanical Hamiltonian operator corresponding to (20) is

$$\hat{T} = \frac{1}{2m}\hat{p}^2 , \tag{21}$$

where $\hat{\mathbf{p}}$ is the quantum mechanical operator corresponding to the momentum.

Now we need the form of the quantum mechanical momentum operator, $\hat{\mathbf{p}}$. A plane wave of wave vector k and angular frequency ω has the form

$$\varphi(x,t) = e^{i(kx - \omega t)} , \tag{22}$$

and hence the wave vector is given by

$$k = \frac{1}{\varphi}\left(\frac{1}{i}\frac{d\varphi}{dx}\right) .$$

From the diffraction experiments it was found that p = ħk, leading to

$$p = \frac{1}{\varphi}\left(\frac{\hbar}{i}\frac{d\varphi}{dx}\right) .$$

Thus we postulate that the momentum operator $\hat{p}_x$ corresponding to momentum in the x direction is given by

$$\hat{p}_x = \frac{\hbar}{i}\frac{\partial}{\partial x} \tag{23a}$$

and similarly for the other directions

$$\hat{p}_y = \frac{\hbar}{i}\frac{\partial}{\partial y} \tag{23b}$$

$$\hat{p}_z = \frac{\hbar}{i}\frac{\partial}{\partial z} . \tag{23c}$$

Just as the classical momentum is a vector quantity, the three quantities in (23) are considered as the three components of a **vector operator**

$$\boxed{\hat{\mathbf{p}} = \frac{\hbar}{i}\nabla} \tag{24}$$

where ∇ is the gradient operator.

Now we construct the kinetic energy operator. Since

$$\nabla^2 = \nabla \cdot \nabla = \left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right] , \tag{25}$$

we obtain

$$\hat{p}^2 = \hat{\mathbf{p}} \cdot \hat{\mathbf{p}} = \left[\frac{\hbar}{i}\nabla\right] \cdot \left[\frac{\hbar}{i}\nabla\right]$$

$$= -\hbar^2\nabla^2 = -\hbar^2\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right] ,$$

and hence

$$\hat{T} = \frac{1}{2m}\hat{p}^2 = -\frac{\hbar^2}{2m}\nabla^2 . \tag{26}$$

From (18), (19), and (26) we obtain

$$\boxed{\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})} \tag{27}$$

as the explicit form of the Hamiltonian for a particle of mass m moving in a potential $V(\mathbf{r})$.

Basically, the Schrödinger equation (8) arises from considering the time evolution of a system, and the Hamiltonian $\hat{H}$ describes how the system changes with time. If we change the system, say, by applying an electric or magnetic field, this change is manifested by a change in the Hamiltonian $\hat{H}$. Such changes in $\hat{H}$ lead to changes in ψ. With suitably ingenious experiments, it is often possible to determine something about how ψ changes in response to the field and thereby something about the form of ψ before changing $\hat{H}$. In this way we can determine various properties of ψ. Ultimately each physical property can be related somehow to some type of change in the Hamiltonian of the system and hence to some (Hermitian) operator,

$$\hat{O}_p = \Delta \hat{H} \ .$$

§1.1.6 More on the Schrödinger Equation

§1.1.6a *The Hilbert Space*

Given any two functions ψ_1 and ψ_2, we can generate from (3) an infinite number of wavefunctions

$$\psi = C_1\psi_1 + C_2\psi_2$$

by using various C_1 and C_2. In addition, there is an infinite number of choices for the functions ψ_1 and ψ_2. Even so, the postulates of quantum mechanics lead to constraints on the functions, and hence we need not consider every wavefunction. For example, from (5) we need consider only wavefunctions for which the integral of the square of the wavefunction is unity $<\psi|\psi> = 1$. Of course, given some wavefunction $\bar{\psi}$ with

$$<\bar{\psi}|\bar{\psi}> = \int d\tau \, |\psi|^2 = a$$

with finite (nonzero) a, we can always define a new function*

$$\psi = \bar{\psi}/\sqrt{a}$$

that is normalized, i.e.,

$$<\psi|\psi> = 1 \ .$$

On the other hand, we need *not* consider any wavefunctions ψ for which

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* Note that a can never be negative.

the integral $\int d\tau\ |\psi|^2$ does *not* converge. That is, we need deal only with square-integrable functions. The set of all possible such functions (satisfying whatever boundary conditions are being imposed) is referred to as the **Hilbert space** (for systems having this particular set of boundary conditions). Thus the Hilbert space is merely ***the collection of all possible wavefunctions for our system.***

§1.1.6b *Hermitian Operators*

In Appendix A we consider the implications of requiring that the norm of the wavefunction be unity,

$$<\psi|\psi> = 1$$

and hence independent of time for any superposition of wavefunctions,

$$\psi = \psi_i + \psi_j \ .$$

The conclusion is that for all possible functions φ_i and φ_j the Hamiltonian operator H must satisfy the condition

$$\int d\tau(\hat{H}\psi_i)^*\psi_j = \int d\tau\, \psi_i{}^*(\hat{H}\psi_j) \ ,$$

which we denote as

$$<(\hat{H}\psi_i)|\psi_j> = <\psi_i|\hat{H}|\psi_j> \ .$$

Such an operator is called **Hermitian.**

The expectation value

$$\frac{<\psi|\hat{H}|\psi>}{<\psi|\psi>}$$

of a Hermitian operator is always real (see Appendix A). Hence the energy

$$E = \frac{<\psi|\hat{H}|\psi>}{<\psi|\psi>}$$

in the Schrödinger equation must be real.

In Appendix A we show that the momentum operator, $\mathbf{p} = (\hbar/i)\nabla$, and the kinetic energy operator, $\hat{T} = (1/2m)\hat{p}^2$, are hermitian. Similarly, any function of coordinates, V(r), is hermitian, so that the Hamiltonian in (27) is also hermitian.

§1.1.7 **Analysis of Kinetic Energy and Potential Energy**

In the above sections we have established the Schrödinger equation

$$\hat{H}\varphi = E\varphi \ , \tag{18}$$

where

$$\hat{H} = \hat{T} + \hat{V}$$

$$\hat{T} = -\frac{\hbar^2}{2m}\nabla^2$$

$$\hat{V} = V(r) \ .$$

Multiplying both sides of (18) by φ^* and integrating leads to

$$<\varphi|\hat{H}|\varphi> = E<\varphi|\varphi> = E \ ,$$

where

$$<\varphi|\hat{H}|\varphi> = \int d\tau\, \varphi^*\hat{H}\varphi$$

and

$$<\varphi|\varphi> = 1 \ .$$

Defining the *numbers* $\overline{T}$ and $\overline{V}$ as

$$\overline{T} = <\varphi|\hat{T}|\varphi> = \int d\,\tau\, \varphi^*(r)\left[-\frac{\hbar^2}{2m}\nabla^2\right]\varphi(r) \tag{28}$$

$$\overline{V} = <\varphi|\hat{V}|\varphi> = \int d\,\tau\, \varphi^*(r)V(r)\varphi(r) \ , \tag{29}$$

we see that the total quantum mechanical energy E can be written as a sum of quantities

$$E = \bar{T} + \bar{V} \tag{30}$$

interpreted as a kinetic energy ($\bar{T}$) and potential energy ($\bar{V}$).

The quantity (29) can be rewritten as

$$V = \int d\tau\, \rho(r) V(r) \ ,$$

where

$$\rho(r) = \varphi^{*}(r)\varphi(r)$$

is the probability of finding the system in the volume element $d\tau$ near configuration $\mathbf{r}$. Thus $\bar{V}$ corresponds to the average of the classical potential energy, weighted by the probability of the electron being at any particular position.

As written in (6), $\bar{T}$ does not seem to bear much relation to the classical kinetic energy. However, in Appendix B we show that

$$\langle\varphi| -\nabla^2 |\varphi\rangle = \langle |\nabla\varphi|^2 \rangle \ , \tag{31}$$

so that (28) becomes

$$\boxed{\bar{T} = \frac{\hbar^2}{2m}\langle |\nabla\varphi|^2 \rangle} = \frac{1}{2m}\left\langle \left| \frac{\hbar}{i}\nabla\varphi \right|^2 \right\rangle . \tag{32}$$

Since $\hat{p} = (\hbar/i)\nabla$, we see that

$$\bar{T} = \frac{1}{2m}\langle |\hat{p}\varphi|^2 \rangle \ ,$$

which can be compared with the classical kinetic energy, $T^{cl} = \frac{1}{2m}p^2$, suggesting that $\langle |\hat{p}\varphi|^2 \rangle$ corresponds to the square of the classical momentum. Throughout this course we will find (32) to be a useful way to think about kinetic energy. This expression says that big gradients or slopes lead to large kinetic energy, and hence the ***best kinetic energy occurs for the smoothest functions***. Thus, comparing the wavefunctions in Fig. 4 (all normalized), we see immediately that φ_c has the highest $\bar{T}$, while φ_a has the lowest.*

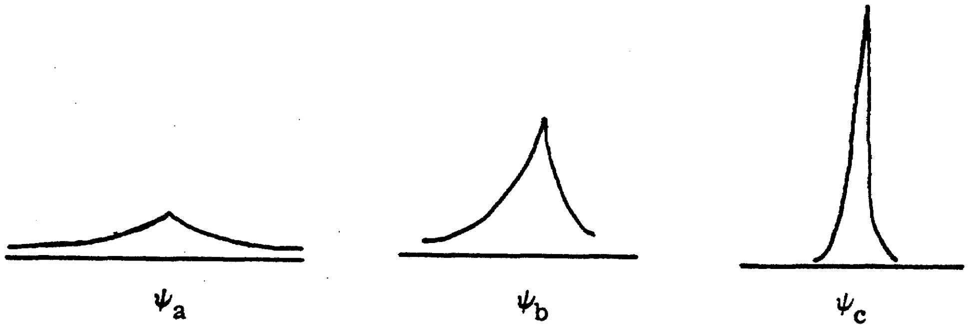


Figure 1-4.

The essential difference between classical mechanics and quantum mechanics is that in classical mechanics the kinetic energy and the potential energy are independent (one is determined by momentum, the other by position), whereas in quantum mechanics ***$\bar{T}$ and $\bar{V}$ are simultaneously determined by the wavefunction***, with the kinetic energy proportional to the average square of the gradient of the amplitude function. It is the balance of trying to find a wavefunction leading to both the lowest $\bar{T}$ and the lowest $\bar{V}$ that is responsible for the stability of quantum mechanical atoms.

---

* Of course, (32) assumes that $\langle\varphi\,|\,\varphi\rangle = 1$.

§1.2 The Ground State of Hydrogen Atom

In this section we consider the ground state of the hydrogen atom, that is, an electron with mass m and charge -e interacting with a nucleus of infinite mass and charge +Ze. Classically, the energy is given by

$$E = \frac{p^2}{2m} - \frac{Ze^2}{r} ,$$

where r is the distance of the electron from the nucleus. Thus the ground state (lowest energy) is for r = 0 and p = 0, leading to E = -∞. That is, the classical H atom collapses to a point.

Quantum mechanically, the Hamiltonian is

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{r} , \tag{1}$$

and the energy is obtained by solving the Schrödinger equation,

$$\hat{H}\varphi(\mathbf{r}) = E\varphi(\mathbf{r}) . \tag{2}$$

We will find that the quantum mechanical form of the kinetic energy keeps the electron from collapsing into the nucleus.

In these sections we will obtain the wavefunction $\varphi(r)$ for the ground state of H atom. The result is that

$$\varphi(r,\vartheta,\varphi) = N_0 e^{-\zeta r} ,$$

where

$$N_0 = \sqrt{\zeta^3/\pi}$$

$$\zeta = \frac{Z}{a_0}$$

$$E = -\tfrac{1}{2} Z^2 \left(\frac{e^2}{a_0}\right)$$

$$a_0 = \hbar^2/me^2 \ .$$

In §1.2.3 we define atomic units where

$$\hbar = 1 \ , \qquad m = 1 \ , \qquad |e| = 1 \ .$$

In these units, the unit of length is

$$1 \text{ bohr} = 1 a_0 = \hbar^2/me^2 = 0.529177 \text{ Å} \ ,$$

and the unit of energy is

$$1 \text{ hartree} = 1 h_0 = e^2/a_0 = me^4/\hbar^2 = 27.2116 \text{ eV} = 627.510 \text{ kcal/mol.}$$

In these units, the Hamiltonian for H atom becomes

$$\hat{H} = -\tfrac{1}{2}\nabla^2 - \frac{Z}{r} \ ,$$

the energy becomes

$$E = -\tfrac{1}{2}Z^2 \ ,$$

and the scale parameter becomes

$$\zeta = Z \ .$$

Before going into the details of the wavefunctions of the hydrogen atom, we will consider why such an atom can exist.

§1.2.1 **Atoms Exist!**

In §1.1.1, we found that the classical description of the atom leads to collapse,

$$T = \frac{1}{2m}p^2 \to 0 \quad \text{as} \quad p \to 0$$

$$V = -\frac{e^2}{r} \to -\infty \quad \text{as} \quad r \to 0 \ .$$

Therefore, the lowest energy state is for the electron sitting on the nucleus. Since the charges cancel, this is like not having an atom. Now we will look at this problem with quantum mechanics. A major difference in quantum mechanics is that both $\bar{T}$ and $\bar{V}$ are determined by the *same quantity*, the wavefunction, whereas in classical mechanics, T and V involved independent quantities p and r. Thus,

$$\begin{aligned} \bar{V} &= \left\langle \Phi \left| -\frac{e^2}{r} \right| \Phi \right\rangle \\ \bar{T} &= \frac{\hbar^2}{2m} \langle [\nabla \Phi]^2 \rangle \ . \end{aligned} \tag{3}$$

Consider now the sequence of similar wavefunctions in Fig. 5.*

---

* To be specific, consider the normalized function

$$\Phi = N\, e^{-r/\bar{R}} \ , \tag{4}$$

where** $N = 1/\sqrt{\pi \bar{R}^3}$. Thus, if $\bar{R}$ is very large, Φ decreases very slowly with r, leading to the delocalized function a in Fig. 5a, while with very small $\bar{R}$, φ decreases rapidly to zero for small r, leading to the localized function in Fig. 5c.

**

$$\langle \Phi^2 \rangle = \int_0^{\pi} \sin \vartheta d\vartheta \int_{-\pi}^{\pi} d\vartheta \int_0^{\infty} \Phi^2 r^2 dr = 4\pi N^2 \int_0^{\infty} r^2 dr\, e^{-2(r/\bar{R})}$$

$$= 4\pi N^2 \left[\frac{\bar{R}}{2} \right]^3 \int_0^{\infty} \rho^2 d\rho\, e^{-\rho} = \pi N^2 \bar{R}^3 = 1 \ ,$$

where we used $\int_0^{\infty} e^{-\rho} \rho^m \, d\rho = m!$

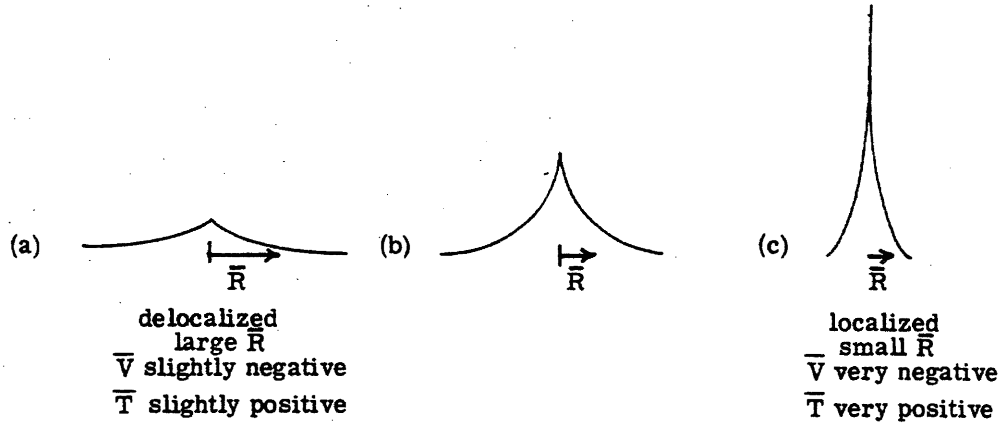


Figure 1-5.

Clearly, $\bar{V}$ becomes more and more negative (lower energy) as the electron is localized closer and closer to the nucleus (just as in classical mechanics), and in the limit the wavefunction leading to the best $\bar{V}$ is localized at the nucleus ($\bar{R} = 0$). However, this localization of the electron near the nucleus now leads to a very large and positive $\bar{T}$. Since $\bar{V}$ and $\bar{T}$ have opposite effects as the electron is concentrated near the nucleus, we need to be a little more quantitative in the analysis.

First we define an average radius $\bar{R}$ as

$$\left\langle\Phi\left|\frac{1}{r}\right|\Phi\right\rangle = \frac{1}{R},$$

leading to

$$\bar{V} = -\frac{e^2}{R}, \tag{5}$$

Consider now some wavefunction, say b, in Figure 5 as the reference wavefunction (with $\bar{R} = 1$ in some units) and let

$$\bar{V}_1 \text{ and } \bar{T}_1$$

be the energies for this wavefunction. Using this reference point, we will examine how $\bar{V}$ and $\bar{T}$ change as the wavefunction is squeezed or expanded.*

From (5) we see that

$$\bar{V}_R = \left\langle \Phi_R \left| \frac{1}{r} \right| \Phi_R \right\rangle = \frac{1}{\bar{R}} V_1 . \tag{6}$$

In order to see how kinetic energy changes, note that each term has the form

$$\left\langle \left(\frac{\partial \Phi}{\partial x} \right)^2 \right\rangle ,$$

so that[†]

$$\bar{T}_R = \left(\frac{1}{\bar{R}} \right)^2 T_1 . \tag{7}$$

Thus, $\bar{T}$ becomes small for delocalized smooth functions (large $\bar{R}$), and $\bar{T}$ becomes large (and positive) for localized functions (small $\bar{R}$). From (6) and (7) we see that

$$\frac{\bar{T}_R}{\bar{V}_R} = \left(\frac{1}{\bar{R}} \right) \frac{\bar{T}_1}{\bar{V}_1} \tag{8}$$

(note that $\bar{T}$ is always positive and $\bar{V}$ is always negative).

Consider first the case as $\bar{R} \rightarrow \infty$, then from (6) and (7)

$$\begin{aligned} \bar{T} &\rightarrow 0 \\ \bar{V} &\rightarrow 0 \end{aligned}$$

and

$$\bar{E} = \bar{T} + \bar{V} \rightarrow 0 ,$$

---

* The technical term is **scaled.**

[†] Basically, the gradient is proportional to $\frac{1}{\bar{R}}$ and hence the gradient squared is proportional to $\left(\frac{1}{\bar{R}} \right)^2$.

as expected. For sufficiently large $\bar{R}$ (that is, $\bar{R} \gg |\bar{T}_1/\bar{V}_1|$), we see from (8) that

$$|\bar{V}| \gg |\bar{T}| \ ,$$

and hence the total energy

$$E = \bar{T} + \bar{V}$$

must be ***negative***. However, for very small $\bar{R}$ (that is, $\bar{R} \ll |\bar{T}_1/\bar{V}_1|$), we see from (8) that

$$|\bar{T}| \gg |\bar{V}| \ ,$$

and hence the total energy must be ***positive***. Thus, the energy of the wavefunctions in Fig. 5 must behave as in Fig. 6 as a function of $\bar{R}$ (i.e., as a function of the size of the wavefunction). That is, the lowest energy (corresponding to the ground state of the atom) occurs at a ***finite size***, $\bar{R} = \bar{R}_{OPT}$. *In quantum mechanics* **the hydrogen atom is stable!**

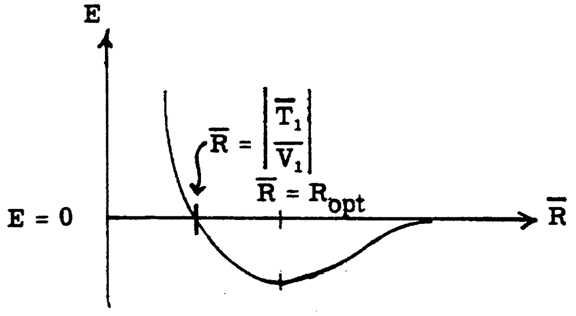


Figure 1-6.

In the above example, we considered just the stretching and compression of the one function considered in Fig. 5. However, the same result is obtained independent of the shape (namely, the optimum energy occurs for finite $\bar{R}$), and hence trying all possible shapes we will eventually find the optimum wavefunction and its optimum $\bar{R}$. This optimum wavefunction is discussed in the next section.

Summarizing the above discussion, we find that: The potential energy wants the wavefunction to be localized at the nucleus. Thus, starting with a delocalized wavefunction (Fig. 5a), the total energy drops as the wavefunction is localized closer to the nucleus. This localization that aids the potential energy leads concomitantly to a more repulsive kinetic energy; however, for sufficiently diffuse wavefunctions, potential energy always wins.* On the other hand, the kinetic energy increases quadratically as the wavefunction is compressed, while the potential energy only drops linearly, so that eventually the increase in kinetic energy will prevent any further contraction of the wavefunction. For the optimum wavefunction there is a balance in these potential energy and kinetic energy terms. One might say that ***kinetic energy provides a pressure that keeps the atom from collapsing***.

§1.2.2 The Ground State Wavefunction

Now we wish to obtain the wavefunction $\varphi(r)$ of the ground state of H atom,

$$H\varphi(\mathbf{r}) = E\varphi(r) \ , \tag{2}$$

where

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{r} \ . \tag{1}$$

The Hamiltonian in (1) is independent of orientation of the atom in space, and hence the eigenfunctions will have the form

$$f(r)Z(\vartheta,\varphi) \ , \tag{9}$$

where f is a function of r only and $Z(\vartheta,\varphi)$ is a function of angular coordi-

---

* We are assuming here Coulombic attractions.

nates only. Since kinetic energy favors having smooth wavefunctions, the ground state wavefunction should be as devoid of wiggles as possible. Thus we will take $Z(\vartheta,\varphi)$ as a constant leading to

$$-\frac{\hbar^2}{2m}\nabla^2 f(r) - \frac{Ze^2}{r} f(r) = E f(r) \tag{10}$$

for the Schrödinger equation.

There are straightforward mathematical techniques for solving (9); for example, see Appendix D. Here we will use a physically oriented approach to examine some features of the solutions. At $r = \infty$, the potential in (1) is zero; thus the bound states of (2) have negative energy,

$$E < 0 .$$

Now consider a very large r so that the Coulomb term is negligible,

$$\frac{Ze^2}{r} \ll |E| . \tag{11}$$

In this case the Schrödinger equation reduces to

$$-\frac{\hbar^2}{2m}\nabla^2 f(r) = E f(r)$$

or

$$\nabla^2 f(r) = +\zeta^2 f(r) , \tag{12}$$

where

$$\zeta^2 \equiv -\frac{2m}{\hbar^2} E \tag{13}$$

(note that E is negative and hence ζ is real). Consider a point along the positive x axis. Since r is very large, $(\partial f / \partial y) \approx 0$ and $(\partial f / \partial z) \approx 0$. Thus (12) becomes

$$+\frac{\partial^2 f}{\partial x^2} = \zeta^2 f .$$

Consequently,

$$f = e^{-\zeta x}$$

($f = e^{+\zeta x}$ is also a solution, but this function is not normalizable). Since f is spherically symmetric, the wavefunction at very large r is of the form

$$f(r) = e^{-\zeta r} . \tag{14}$$

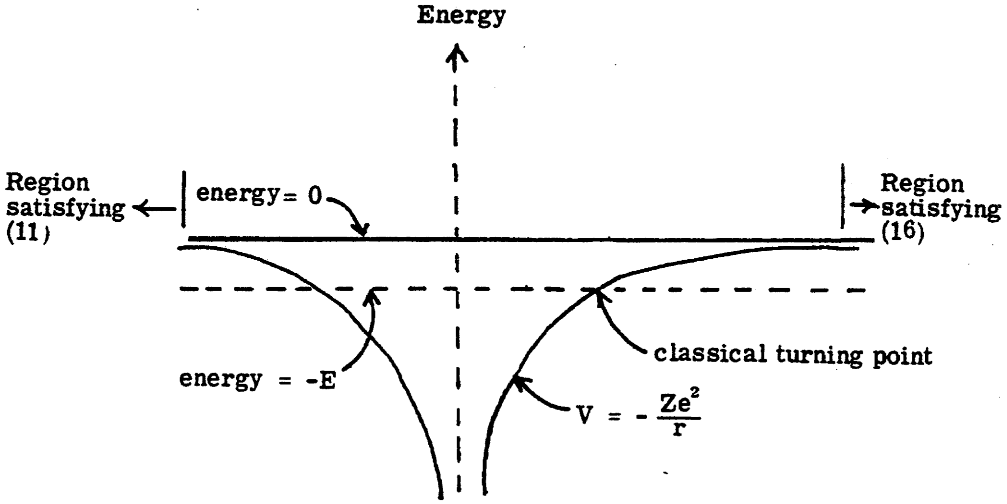


Figure 1-7.

In Appendix D we show that the wavefunction (14) is an eigenfunction of (10) for all r if ζ is chosen so that

$$\boxed{\zeta = \frac{Z}{a_0} ,} \tag{15}$$

where

$$a_0 = \hbar^2/me^2 . \tag{16}$$

From (13) and (15) we have

$$E = -\frac{\hbar^2}{2m}\zeta^2 = -\frac{\hbar^2}{2m}\frac{Z^2}{a_0} = -\frac{1}{2}\frac{Z^2e^2}{a_0} ,$$

and hence

$$\boxed{E = -\tfrac{1}{2} Z^2 \left[\frac{e^2}{a_0} \right] .} \tag{17a}$$

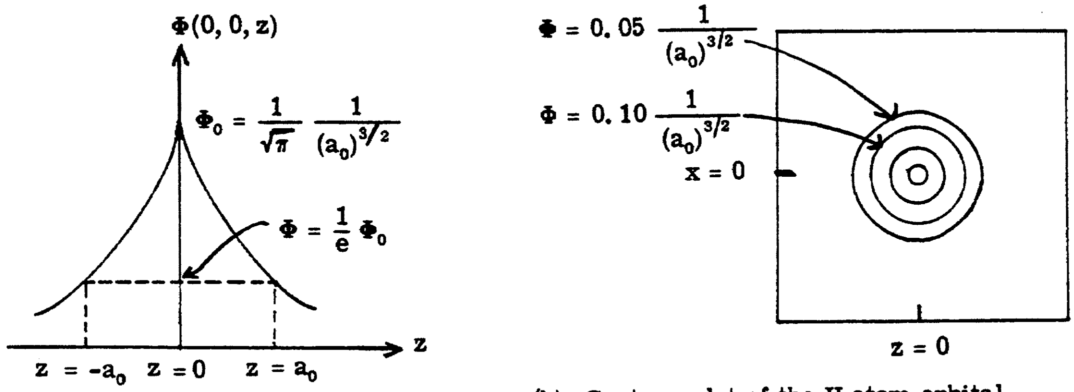
Normalizing the wavefunction (14) leads to (see Appendix D)

$$\boxed{\psi(r,\vartheta,\varphi) = N_0 \, e^{-Zr/a_0} ,} \tag{17b}$$

where

$$N_0 = \sqrt{Z^3/\pi a_0^3} . \tag{18}$$

This wavefunction is plotted in Fig. 8.



(a) Line plot of the H atom orbital.

(b) Contour plot of the H atom orbital. Adjacent contours differ by 0.05 a.u.

Figure 1-8.

The average radius of the wavefunction (16) is

$$\frac{1}{\bar{R}} = \left\langle \psi \middle| \frac{1}{r} \middle| \psi \right\rangle = \frac{Z}{a_0} ,$$

so that

$$\bar{R} = \frac{a_0}{Z} , \tag{19}$$

where $a_0 = \hbar^2/me^2$ is referred to as the Bohr radius (or, more simply, the Bohr) in honor of Niels Bohr. Substituting into (15) leads to

$$E = -\tfrac{1}{2} \frac{Ze^2}{\bar{R}} , \tag{20}$$

which can be compared with

$$\bar{V} = \left\langle\psi\left| -\frac{Ze^2}{r} \right|\psi\right\rangle = \frac{Ze^2}{\bar{R}} .$$

Thus

$$E = \tfrac{1}{2}\bar{V}$$

and

$$\bar{T} = E - \bar{V} = -\tfrac{1}{2}\bar{V} = \tfrac{1}{2}\frac{Ze^2}{\bar{R}} .$$

Equation (20) provides an easy way to remember the proper energy expression (it is just half the total potential energy).

For the hydrogen atom (Z = 1), the above equations become

$$E = -\tfrac{1}{2}\frac{e^2}{a_0} \qquad (21)$$

$$\bar{V} = -\frac{e^2}{a_0} \qquad (22)$$

$$\bar{T} = +\tfrac{1}{2}\frac{e^2}{a_0} = +\frac{\hbar^2}{2m}\frac{1}{a_0^2} ,$$

where

$$\langle 1/r \rangle = \frac{1}{a_0}$$

$$\langle [\nabla\varphi]^2 \rangle = \frac{1}{a_0^2} .$$

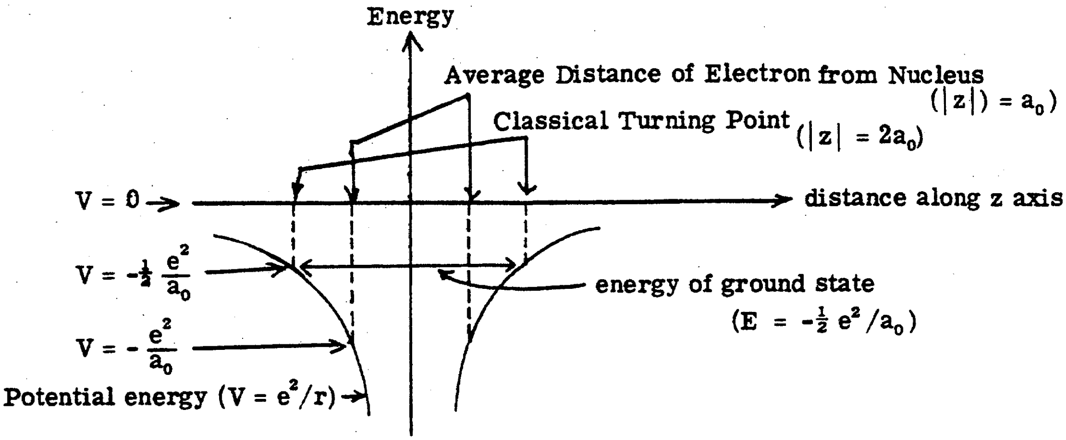


Figure 1-9.

In Fig. 9 we show the potential energy as a function of distance. Imagining a classical particle with this same energy E moving in the potential $V(r) = -(e^2/r)$, we would find the particle bouncing back and forth from $z = -2a_0$ to $z = +2a_0$. The kinetic energy is $T = E - V = E + \frac{e^2}{r} = -\frac{e^2}{2a_0} + \frac{e^2}{r}$. For $r > 2a_0$, we would have $T < 0$, but this is not possible classically since $T = \frac{1}{2}mv^2$ must be positive. Thus the classical limit for the motion of the electron is $|z| = 2a_0$, at which point the velocity has reduced to zero. In the quantum description there is a finite probability (but not large) of the electron being farther than $2a_0$ from the nucleus.

Note that the wavefunction (17a) is positive for all finite x, y, z. Since it is never zero for finite distances, we say that the wavefunction is *nodeless*.

§1.2.3 Atomic Units

As mentioned above, the "size" of the atom is $\bar{R} = \frac{a_0}{Z}$; thus a natural unit of length for atomic problems is the bohr radius

$$a_0 = \frac{\hbar^2}{me^2}. \tag{23}$$

The quantity ($e^2/a_0 = me^2/\hbar^2$) in the energy expression (17b) has units of energy. It is referred to as the **hartree** (in honor of D. R. Hartree who first suggested the atomic system of units in 1927)* and is denoted as h_0,

$$h_0 = \frac{e^2}{a_0} = \frac{me^4}{\hbar^2},$$

so that the energy of the hydrogen atom (17b) becomes

$$E = -\tfrac{1}{2} Z^2 h_0 . \tag{25}$$

Throughout this course will encounter quantities such as $a_0 = \hbar^2/me^2$ corresponding to a length, $h_0 = e^2/a_0 = me^4/\hbar^2$ corresponding to an energy, and dimensionless quantities such as

$$\alpha = \frac{e^2}{\hbar c} = \frac{1}{137.03604} \tag{26}$$

(the fine structure constant).

We will find it convenient to use a particular set of units, called **atomic units,**** where

$$\begin{aligned} \hbar &= 1 \\ m_e &= 1 \\ |e| &= 1 . \end{aligned} \tag{27}$$

We use these units because they simplify many of the equations of quantum mechanics and give a reasonable order of magnitude (near unity) for the properties of molecular systems. Some useful conversion constants

---

* D. R. Hartree, *Proc. Cambridge Phil. Soc.*, **24,** 89 (1927).

** Sometimes called hartree atomic units t0 distinguish from other occasionally used atomic units; see Appendix E.

are included in Appendix F.

With atomic units, the Hamiltonian for the hydrogen atom becomes

$$H = -\tfrac{1}{2}\nabla^2 - \frac{Z}{r} \tag{1'}$$

and the ground state wavefunction become

$$\psi(r,\vartheta,\varphi) = N_0 e^{-Zr} \ , \tag{17}$$

where

$$\mathrm{N}_0 = \sqrt{Z^3/\pi} \tag{28}$$

and the ground state energy becomes

$$E = -\tfrac{1}{2} Z^2 \ . \tag{17'}$$

§1.2.3a *Conversion Factors*

In order to compare the results of quantum mechanics (expressed in atomic units) with those of experiment (expressed in cgs units), it is necessary to become facile at converting between those units. To do this most simply it is sufficient to remember a few basic conversions (e.g., energy and distance) and to rewrite the expressions involving other quantities in terms of these basic units before converting. Thus, from (17) the ionization potential of the ground state of hydrogen atom is

$$\mathrm{IP_H} = \tfrac{1}{2}\left(\frac{e^2}{a_0}\right) .$$

In atomic units this quantity is

$$\mathrm{IP_H} = 0.5\, h_0 \ ,$$

and experimentally it is known that*

---

* The numbers in parentheses indicate the estimated limits of error in the last digit quoted, the standard deviation.

$$\mathrm{IP_H} = 13.605805(37)\ \mathrm{eV}\ ^{**}$$

Thus,[†]

$$1\,h_0 = \frac{e^2}{a_0} = 27.21161\ \mathrm{eV}\ . \tag{29}$$

Similarly, using the known values of ħ, m, and e

$$\hbar = 1.0545887(56) \times 10^{-27}\ \mathrm{gm\ cm^2\ sec^{-1}}$$

$$m_e = 9.109534(47) \times 10^{-28}\ \mathrm{gm} \tag{30}$$

$$e = 4.803242(14) \times 10^{-10}\ \mathrm{gm^{1/2}\ cm^{3/2}\ sec^{-1}}\ ,$$

we find that the atomic unit of length is

$$1\,a_0 = \frac{\hbar^2}{me^2} = 0.52917704(44)\ \mathrm{A}\ . \tag{31}$$

Another useful relation is the fine structure constant

$$\alpha = \frac{e^2}{\hbar c} = \frac{1}{137.03604(11)}\ ,$$

a dimensionless constant. In atomic units, e = 1 and ħ = 1, and hence the speed of light is

$$c = 137.03604\ \mathrm{a.u.} \tag{32}$$

in atomic units. From the cgs value of c,

$$c = 2.99792458(1) \times 10^{10}\ \mathrm{cm/sec}\ ,$$

we find the atomic unit of time (denoted τ_0)

$$t_0 = 2.41888 \times 10^{-17}\ \mathrm{sec}\ . \tag{33}$$

** This is corrected to correspond to a nucleus of infinite mass.

[†] An underline indicates that there is uncertainty in the underlined number.

The biggest disadvantage in using atomic units is that the various quantities such as $\hbar$, e, and m_e will be missing from the equations, making it difficult to convert to cgs units. The best way to convert is to rewrite the quantity of interest in terms of energy, length, and velocity quantities and then to use the above conversions. For example, what if we want to evaluate the Coulomb interaction between Na^+ and Cl^- at 10 Å? We convert R to bohr

$$R = \frac{10}{0.529177} = 18.897\, a_0 \ .$$

Since $|e| = 1$, the energy of interaction in atomic units is

$$E = -\frac{1}{R} = -0.052918\, h_0 \ .$$

We can now convert back to electron volts,

$$E = -0.052917 \times 27.2116 = -1.43998 \text{ eV} \ .$$

In general, then

$$E(\text{eV}) = \frac{-14.3998}{R(\text{A})} \ . \qquad (34)$$

It would be instructive to calculate other quantities in terms of atomic units, e.g., what is the average momentum of the electron in the ground state of H? In Bohr's model, how long does it take the electron to orbit the atom?

§1.3 THE NODAL THEOREM

Even without carrying out detailed calculations of the eigenfunctions for a system, it is often possible to make some general conclusions concerning the ordering of the states by considering their nodal structures (i.e., the loci of points for which $\psi = 0$). Here we will develop some of the general considerations for such analyses.

First we consider a *one- dimensional*, one-particle system with Hamiltonian

$$H = -\frac{1}{2M}\frac{d^2}{dx^2} + V(x) \ , \tag{1}$$

where $M \equiv m/\hbar^2$ and V(x) is some function of x depending only upon the spatial coordinates.* If this potential contains bound states, then we can prove the **nodal theorem:**

i) *The ground state wavefunction* does not change sign (i.e., *has no nodes);*

ii) The bound state with n sign changes (n nodes) has a lower energy than the state with n + 1 sign changes (n + 1 nodes).

That is,

$$\begin{aligned} E_0 &< E_n \\ E_n &< E_{n+1} \ , \end{aligned} \tag{2}$$

where n is the number of nodal points (internal to the boundaries). In the case of a sufficiently singular potential, some inequalities in (2) may be equalities.

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* [V(x) is independent of momentum and spin and is not an integral operator].

The nodal theorem is proved in Appendix C. Here we will provide some intuitive reasoning concerning this theorem.

§1.3.1 The Ground State is Nodeless

Consider first ψ_1, the lowest eigenstate of the Hamiltonian

$$\hat{H}\psi_1 = E_1\psi_2$$

having *one* sign change as in Fig. 10a.

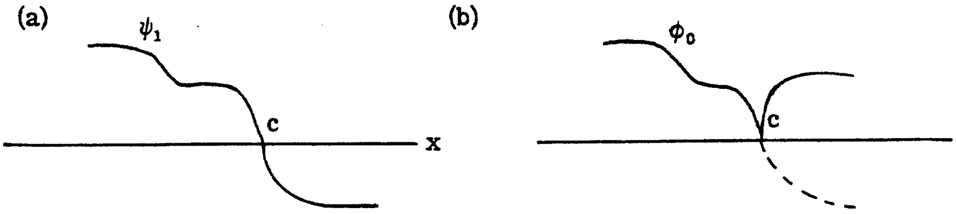


Figure 1-10. Illustration for the Nodal Theorem.

From ψ_1 we can form a wavefunction $\varphi_0 = |\psi_1|$ (not necessarily an eigenfunction of $\hat{H}$) that has *no* sign changes, as in Fig. 10b. Since ψ_1 is normalized, then φ_0 is also normalized,

$$<\varphi_0|\varphi_0> = \int dx\, |\varphi_0(x)|^2 = \int dx\, |\psi_1(x)|^2 = 1 \ ,$$

and the energy of φ_0 becomes

$$\varepsilon_0 = <\varphi_0|H|\varphi_0> = \left\langle \varphi_0 \left| -\frac{1}{2M}\frac{d^2}{dx^2} \right| \varphi_0 \right\rangle + <\varphi_0|V|\varphi_0> \ .$$

The potential energy of φ_0 is the same as that of ψ_1,

$$<\varphi_0|V|\varphi_0> = \int dx\ V(x)|\varphi_0(x)|^2 = \int dx\ V(x)|\psi_1(x)|^2 = <\psi_1|V|\psi_1> \ . \quad (3)$$

From Appendix B the kinetic energy of ψ_1 can be expressed as

$$\left\langle \psi_1 \left| -\frac{1}{2m}\frac{d^2}{dx^2} \right| \psi_1 \right\rangle = \frac{1}{2M}<|\nabla\psi_1|^2>$$

$$= \frac{1}{2M} \int_{-\infty}^{+\infty} dx \left| \frac{d\psi_1}{dx} \right|^2 .$$

But

$$\tfrac{1}{2} \int_{-\infty}^{+\infty} dx \left| \frac{d\psi_1}{dx} \right|^2 = \tfrac{1}{2} \int_{-\infty}^{+\infty} dx \left| \frac{d\varphi_0}{dx} \right|^2$$

since the integrands are equal except at one point (x_0). Thus the kinetic energies of φ_0 and ψ_1 are equal,

$$\left\langle \psi_1 \left| -\frac{1}{2M}\frac{d^2}{dx^2} \right| \psi_1 \right\rangle = \left\langle \varphi_0 \left| -\frac{1}{2M}\frac{d^2}{dx^2} \right| \varphi_0 \right\rangle , \tag{4}$$

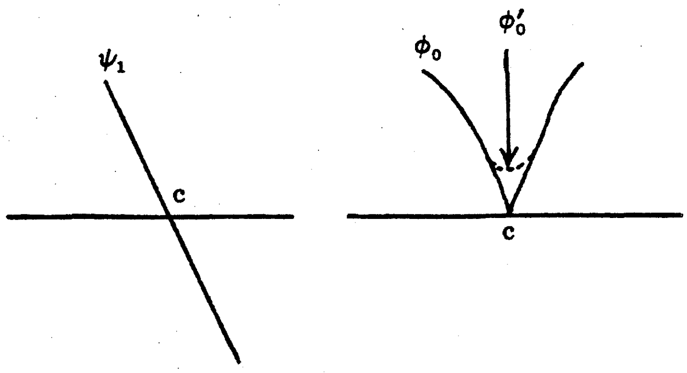
and consequently from (3) and (4) the total energies of ψ_1 and φ_0 are equal,

$$\varepsilon_0 = \langle\varphi_0|H|\varphi_0\rangle = \langle\psi_1|H|\psi_1\rangle = E_1 .$$

That is, given ***any*** eigenfunction ψ_1 of $\hat{H}$ that changes sign, we can construct a function φ_0 which does not change sign and yet has the same energy.

Now consider a new function $\bar{\varphi}_0$ identical to φ_0 except that it is smoothed in the region very close to the position of the node c. If the potential is not singular at this point, the function $\bar{\varphi}_0$ can be chosen to have the same potential energy (and normalization) as φ_0,

$$\langle\bar{\varphi}_0|H|\bar{\varphi}_0\rangle = \langle\varphi_0|V|\varphi_0\rangle .$$



(a) (b)

Figure 1-11.

However, since

$$\left|\frac{d\bar{\varphi}_0}{dx}\right| \ll \left|\frac{d\varphi_0}{dx}\right|$$

in the region near c, φ_0' will have a smaller kinetic energy than φ_0,

$$\frac{1}{2M}\left\langle\left|\frac{d\bar{\varphi}_0}{dx}\right|^2\right\rangle < \frac{1}{2m}\left\langle\left|\frac{d\varphi_0}{dx}\right|^2\right\rangle . \tag{5}$$

Consequently, the energy of $\bar{\varphi}_0$ is lower than that of φ_0

$$\bar{\varepsilon}_0 < \varepsilon_0 = E_1 .$$

The best (i.e., lowest energy) nodeless (i.e., non-negative) wavefunction has an energy, E_0, no higher than $\bar{\varepsilon}_0$ and hence

$$E_0 < E_1 . \tag{6}$$

Similar arguments can be used to derive the other relations. Thus, for a general potential we expect the bound solutions to increase in the number of nodes as E increases, as in Fig. 12.

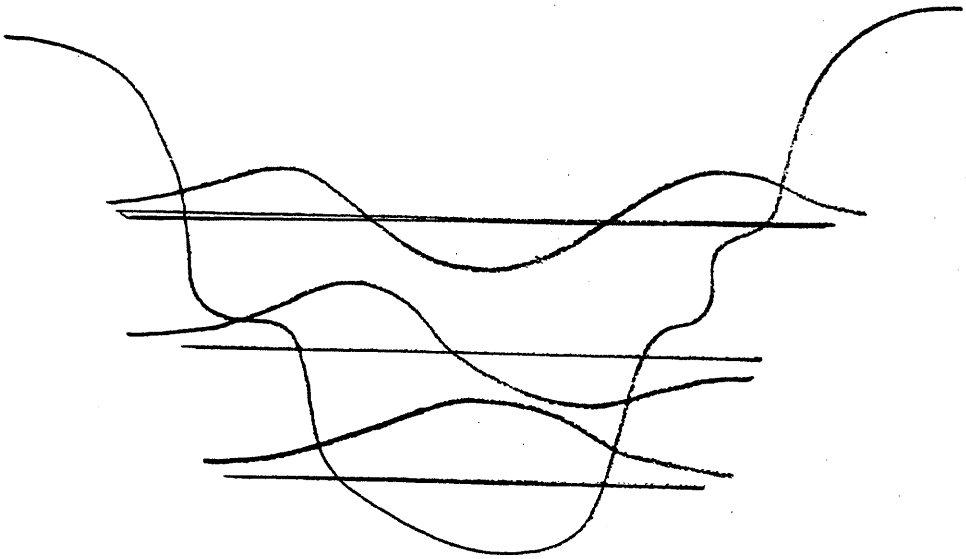


Figure 1-12. Illustration of the nodal patterns of successive states of a general (one-dimensional) potential.

§1.3.2 Multidimensions

In two dimensions, a wavefunction that changes sign will have a line of points with $\psi = 0$ (a nodal line), and for three dimensions there will be a surface of points with $\psi = 0$ (a nodal surface). Just as in one dimension, the ground state will always be nodeless. However, for multidimensions one can no longer use the nodal theorem to order all states. Thus, in two dimensions we can construct three orthogonal wavefunctions (all orthogonal to the ground nodeless state), each with one nodal surface, as illustrated in Fig. 13.*

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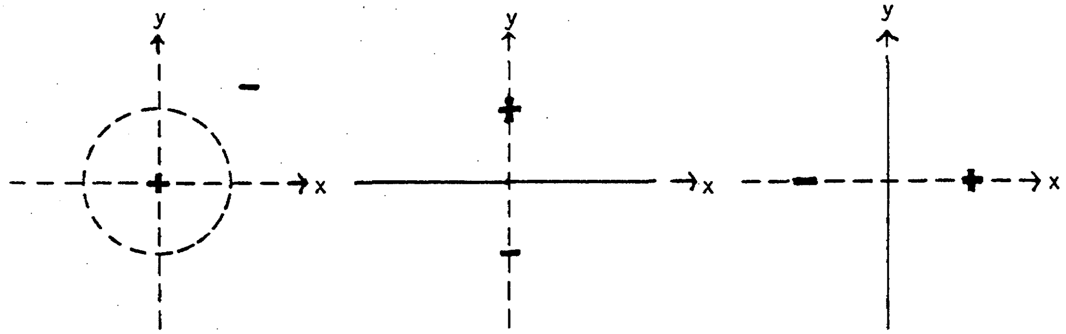
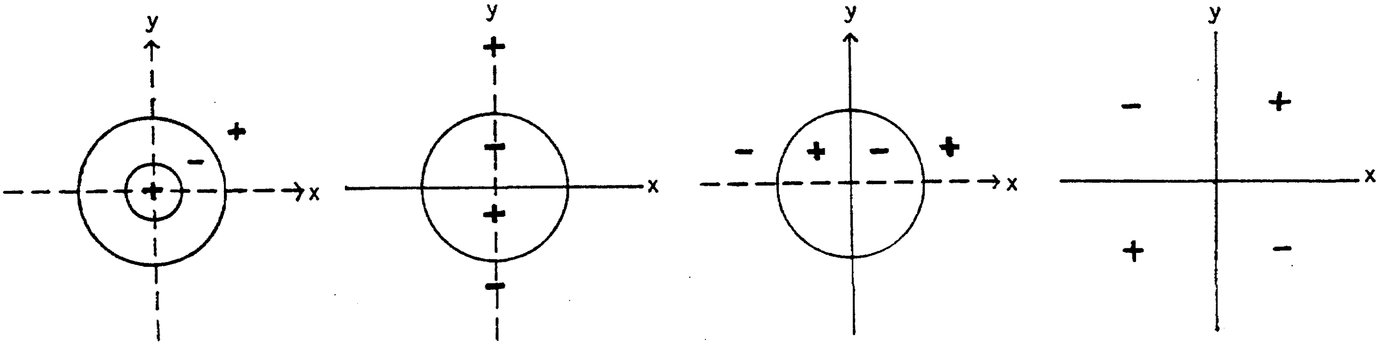
* We will, in this section, use the same notation nl as for states of the three-dimensional H atom.



(a) 2s function (b) $2p_y$ function (c) $2p_x$ function

Figure 1-13. Two-Dimensional States with One Nodal Line.

If the potential energy is independent of angle, the wavefunctions in Fig. 13b and 13c will have the same energy; however, the wavefunction in Fig. 13a may be higher or lower than the other two, depending on the exact form of the potential. Even worse, we cannot use the nodal theorem to determine whether the 3s function in Fig. 14a is above or below the 2p functions of Fig. 13b and 13c.



(a) 3s function (b) $3p_y$ (c) $3p_x$ (d) $3d_{xy}$

Figure 1-14. Two-Dimensional States with Two Nodal Lines.

The clue to which comparisons can be made and which cannot is apparent from the way that the one-dimensional theorem was proved in the previous section. Start with the optimum wavefunction of some nodal structure, say Fig. 14b, and change the sign on opposite sides of a *single* nodal surface to obtain either Fig. 15a or 15b, each of which has exactly the same energy as Fig. 14c.

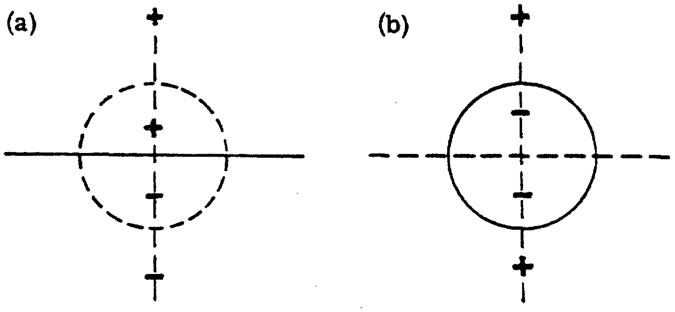


Figure 1-15.

The wavefunction in Fig. 15a is an upper bound on the $2p_y$ wavefunction of Fig. 13b, and the wavefunction in Fig. 15b is an upper bound on the 2s wavefunction of Fig. 13a.

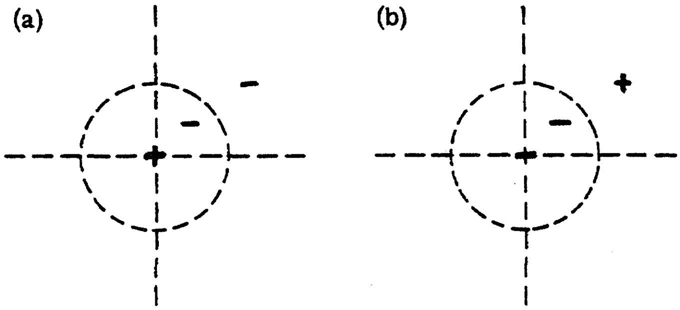


Figure 1-16.

Similarly, starting with the 3s wavefunction of Fig. 14a, we see that the wavefunctions in Fig. 16 have the same energy and are upper bounds to the 2s wavefunctions of Fig. 13a. However, there is no wavefunction to compare the energy of the 3s wavefunctions with those of the 2p wavefunctions. Continuing in this way, we can derive the following relations:

$$1s < 2s < 3s < 4s \ldots$$

$$1s < 2p < 3p < 4p \ldots$$

$$2s < 3p \ldots$$

$$3s < 4p \ldots$$

$$2p < 3d < 4d \ldots$$

$$3p < 4d \ldots,$$

etc.

§1.4 VIBRATION AND ROTATION

Throughout this course we will focus upon the **electronic wavefunctions** for molecules. Thus for an N electronic wavefunction, we determine

$$\Psi^{el}(1,2,\ldots,N) \ ,$$

with energy

$$E = \frac{\langle\Psi^{el}|H|\Psi^{el}\rangle}{\langle\Psi^{el}|\Psi^{el}\rangle} \ ,$$

where $\hat{H}$ is the Hamiltonian for the system. The electronic wavefunction and its energy will depend upon the geometry of the molecule. For each geometry, we solve for the optimum wavefunction and energy at that geometry. For a diatomic molecule the result is a total energy that is a function of R (internuclear distance), as indicated in Fig. 17.

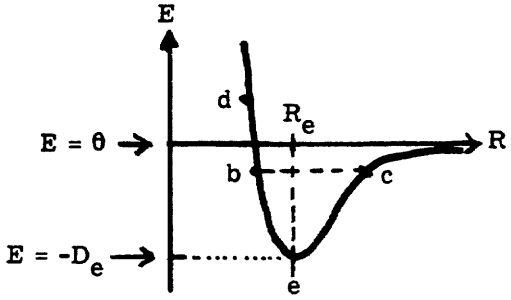


Figure 1-17.

As the nuclei move together or move apart, we imagine the electrons readjusting at each instant to reoptimize for that particular R. For a classical system, if we started at some particular R, say point b, the nuclei would move apart until they reached point c and would then come together till point b and would continue oscillating between these points (assuming no friction). Starting at point d, the R would continue increasing until R = ∞. On the other hand, if we started at point e, the system would stay still. Thus point e is called the **equilibrium** bond distance

(R_e). Starting with the molecule at equilibrium, R_e, the energy to pull it apart (to break the bond) is called the **bond energy,** D_e.

For energies below the limit at infinity, we can think of the system in terms of two masses (each corresponding to a proton) connected by a spring of length R_e. However, in quantum mechanics, this spring can never be completely at rest. The nuclear motions are described in terms of wavefunctions, just as are the electrons, and the kinetic energy of the nuclear motions depends on how localized the wavefunctions are. To localize the nuclei at exactly $R = R_e$ would imply an infinite kinetic energy. The result is that for the ground state the nuclear wavefunction has the form

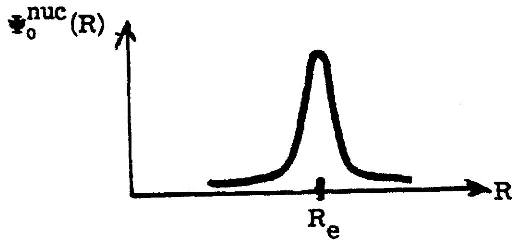


Figure 1-18.

That is, the most likely R is R_e, but the nuclei have a finite probability of being found at other R near R_e. The result is that the energy of the molecule is higher than the absolute minimum ($E = -D_e$) in the energy curve by an amount referred to as the **zero-point energy.** This lowest state, Fig. 18, is referred to as the ground vibrational state (Φ^{vib}, with v = 0), and one thinks of the molecule as vibrating back and forth with a frequency ν_0.

At the bottom of a potential curve, the slope of the energy curve is zero and the curvature is positive, so we can write

$$E(R) = E(R_e) + \tfrac{1}{2}k(R - R_e)^2 , \qquad (1)$$

where k, the curvature* at the bottom of the well, is called the force constant. In this approximation (called the **harmonic oscillator** approximation), the vibrational frequency is given by

$$\nu_0 = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}\,, \tag{2}$$

where μ is the reduced mass

$$\mu = \frac{M_1 M_2}{M_1 + M_2} \tag{3}$$

and M_1 and M_2 are the masses of the two nuclei. In this case, the zero-point energy is given by

$$\tfrac{1}{2}\mathrm{h}\nu_0 \tag{4}$$

(where h is Planck's constant). Thus the energy of the ground vibrational state is

$$E = -D_0\,,$$

where

$$D_0 = D_e - \tfrac{1}{2}\mathrm{h}\,\nu_0\,. \tag{5}$$

The quantity D_0 is the actual energy to break the bond starting with the molecule is in the ground vibrational state, and it is the quantity that would be measured experimentally.

In QM, the excited vibrational wavefunctions must be orthogonal to the ground wavefunction, leading to the form in Fig. 19,

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*

$$k = \left(\frac{\partial^2 E}{\partial R^2}\right)_{R_e}.$$

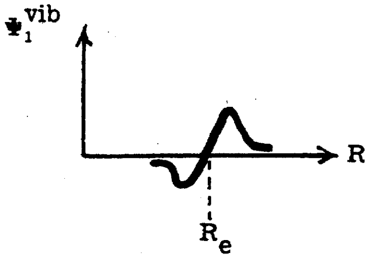

Figure 1-19.

for the first excited vibrational state (v = 1). The excitation energy is

$$E_1 - E_0 = h\nu_0 \; . \tag{6}$$

(in the harmonic approximation). The separations between vibrational states, as in (6), can be determined experimentally, thereby providing experimental values for the zero-point energy (4) and for the force constant k.

So far we have considered the molecule to lie along the z axis. In fact, the axis of the molecule can be oriented along any direction in space. Generally, the molecule will be rotating, but the ground rotational state is the one for which all orientations are equally likely. This is analogous to the L = 0 or s state for electrons and is denoted as the J = 0 rotational state. Excited rotational states have energies of

$$E_{rot} = \frac{\hbar^2}{2I} J(J+1) \; ,$$

where $I = \mu R_e^2$ is called the moment of inertia. This is analogous to the classical rotational energy

$$E_{rot}^{class} = \frac{1}{2I} L^2 \; ,$$

where L is the rotational angular momentum. Experimentally, the bond distance of molecules is often obtained by measuring the rotational energies and thereby deriving I and hence R_e.

For H_2 and H_2^+, the vibrational energies are

$$h\,\nu_0 = 4401\ \text{cm}^{-1} = 0.546\ \text{eV} = 12.58\ \text{kcal for } H_2$$

$$h\,\nu_0 = 2322\ \text{cm}^{-1} = 0.288\ \text{eV} = 6.64\ \text{kcal for } H_2^+$$

and the rotational energies are

$$E_J = BJ(J+1) \ ,$$

where

$$B = 60.85\ \text{cm}^{-1} \quad \text{for } H_2$$

$$B = 30.21\ \text{cm}^{-1} \quad \text{for } H_2^+ \ .$$

In these systems, the total bond energies are

$$D_0 = 36117\ \text{cm}^{-1} = 4.478\ \text{eV} = 103.3\ \text{kcal} \quad \text{for } H_2$$

$$D_0 = 21382\ \text{cm}^{-1} = 2.651\ \text{eV} = 61.1\ \text{kcal} \quad \text{for } H_2^+ \ .$$

Appendix 1-A. Hermitian Operators

In §1.1, we found that the basic postulate of quantum mechanics implies that the wavefunction ψ is normalized,

$$<\psi|\psi> = 1 , \tag{1}$$

and that the time derivative of the wavefunction is determined by the relation

$$i \hbar \frac{\partial\psi}{\partial t} = H\psi . \tag{2}$$

Here we will show that these conditions imply that H is a Hermitian operator

$$<\psi_j|H^\dagger|\psi_k> = <(H\psi_j)|\psi_k> = <\psi_j|H|\psi_k$$

for all (allowed) functions ψ_j and ψ_k. This roperty results from the requirement that the total integrated probability (1) not change with time for any superposition of (allowed) functions.

1-A.1 Notation

First we must establish some notation. For any operator $\hat{B}$ and any functions ψ_j and ψ_k, we define the jk matrix element of $\hat{B}$ as

$$B_{jk} \equiv <\psi_j|\hat{B}|\psi_k> \equiv \int d\tau \psi_j^*(\hat{B}\psi_k) . \tag{3}$$

The ***Hermitian conjugate*** of $\hat{B}$ is defined as the operator $\hat{B}^\dagger$

$$(B^\dagger)_{jk} = <\psi_j|\hat{B}^\dagger|\psi_k> = \int d\tau(\hat{B}\psi_j)^* \psi_k = <(\hat{B}\psi_j)|(\psi_k> \tag{4}$$

for all ψ_j and ψ_k (of the Hilbert space). From (3) we see that

$$<(\hat{B}\psi_j)|\psi_k> = <\psi_k|\hat{B}\psi_j>^* = B^*_{kj} , \tag{5}$$

and hence (4) can be written

$$(B^\dagger)_{jk} = B^*_{kj} . \tag{6}$$

If $\hat{B}$ is equal to its Hermtian conjugate,

$$<\psi_j|B^\dagger|\psi_k> \; = \; <\psi_i|B|\psi_k> \; , \tag{7}$$

we say that $\hat{B}$ is **Hermitian** and write

$$\hat{B}^\dagger = \hat{B} \; . \tag{8}$$

1-A.2 Hermitivity of *H*

From (1) the total probability of finding the particle somewhere,

$$<\psi|\psi> \; = \; 1 \; ,$$

is independent of time. Thus, taking the derivative with respect to time, we have

$$0 = \left\langle \frac{\partial\psi}{\partial t} \middle| \psi \right\rangle + \left\langle \psi \middle| \frac{\partial\psi}{\partial t} \right\rangle = \int d\tau \left[\frac{\partial\psi^*}{\partial t}\psi + \psi^* \frac{\partial\psi}{\partial t} \right] .$$

Substituting the Schrödinger equation (2) here leads to

$$0 = (i\hbar)^{-1} \int d\tau[-(H\psi)^*\psi + \psi^*(H\psi)]$$

or

$$0 = \{-<\psi|H|\psi>^* + <\psi|H|\psi>\} \; , \tag{9a}$$

which implies that the quantity

$$E \equiv <\psi|H|\psi>$$

(referred to as the energy) is real.

Consider now the superposition

$$\psi = C_j\psi_j + C_k\psi_k$$

(where C_j and C_k are numbers, possibly complex) of two states ψ_j and ψ_k that are orthogonal

$$<\psi_j|\psi_k> \; = \; 0$$

at some time t_0. Then, since $<\psi|\psi>$, $<\psi_j|\psi_j>$, and $<\psi_k|\psi_k>$ are all unity and independent of time, it must be that

$$C^*_k\, C_j <\psi_k|\psi_j> \;+\; C^*_j\, C_k <\psi_j|\psi_k> \tag{10a}$$

$$= \;<\psi|\psi> - C^*_j\, C_j <\psi_j|\psi_j> - C^*_k\, C_k <\psi_k|\psi_k>$$

is also independent of time. Similarly, considering

$$\psi' \;=\; i\, C_j \psi_j + C_k \psi_k$$

(where $i = \sqrt{-1}$), we find that for $<\psi'|\psi'>$ to be independent of time requires that

$$i\, C^*_k C_j <\psi_k|\psi_j> \;-\; i\, C^*_j C_k <\psi_j|\psi_k> \tag{10b}$$

also be independent of time. Combining (10a) and (10b) leads to the condition that

$$<\psi_j|\psi_k> \;=\; 0$$

is independent of time. This leads to

$$0 \;=\; \left< \frac{\partial \psi_j}{\partial t} \middle| \psi_k \right> + \left< \psi_j \middle| \frac{\partial \psi_k}{\partial t} \right>$$

$$= i\hbar\,[\, - <\psi_j|\hat{H}^\dagger|\psi_k> \;+\; <\psi_j|\hat{H}|\psi_j>] \;.$$

and hence

$$<\psi_j|\hat{H}|\psi_k> \;=\; <\psi_j|\hat{H}^\dagger|\psi_k> \tag{9b}$$

(which also applies to j = k). This relation (9b) must apply to all possible pairs of functions ψ_j and ψ_k, and hence *the Hamiltonian operator, H, must be a Hermitian operator*. From this derivation we see that *the Hermitian property of $\hat{H}$ results from the assumption that the total integrated probability of any superposition of functions is independent of time* (conservation of normalization).

1-A.3 The Momentum Operator

An example is appropriate here. Consider a one-dimensional system with coordinates in the range

$$0 \leq x \leq a .$$

Is the operator

$$\hat{p} = \frac{\hbar}{i}\frac{d}{dx}$$

Hermitian? To find out we consider

$$<\psi_j|\hat{p}^\dagger|\psi_k> \equiv \int_0^a dx(\hat{p}\,\psi_j)^*\psi_k = -\frac{\hbar}{i}\int_0^a dx\,\frac{d\psi_j{}^*}{dx}\psi_k .$$

Integrating by parts, this becomes

$$<\psi_j|\hat{p}^\dagger|\psi_k = -\frac{\hbar}{i}\{\psi_j{}^*(a)\psi_k(a) - \psi_j{}^*(0)\psi_k(0)\} + \frac{\hbar}{i}\int_0^a dx\,\psi_j{}^*\,\frac{d\psi_k}{dx}$$

or

$$<\psi_j|\hat{p}^\dagger|\psi_k> = -\frac{\hbar}{i}[\psi^*_j(a)\psi_k(a) - \psi^*_j(0)\psi_k(0)] + <\psi_j|\hat{p}|\psi_k> . \tag{11}$$

Thus, the operator $\hat{p}$ is Hermitian if and only if the boundary conditions are such that

$$\psi^*_j(a)\psi_k(a) = \psi^*_j(0)\psi_k(0) \tag{12}$$

for ***all*** allowed functions ψ_j and ψ_k. Thus, it is nonsense to say that $\hat{p} = \frac{\hbar}{i}\frac{d}{dx}$ is an Hermitian operator; rather, one must say that the operator is Hermitian given such and such boundary conditions. Some acceptable boundary conditions for the above case are

(i) $\psi(a) = 0$, $\psi(0) = 0$ (this is the case of a particle in a box),

(ii) $\psi(a) = \psi(0)$ (this corresponds to periodic boundary conditions where the point $x = a$ is physically equivalent to the point $x = 0$; a common example is for angular coordinates φ where $a = 2\pi$ is identically the same point as $x = 0$), and

(iii) for systems of infinite range $-\infty < x < +\infty$, then for φ to be normalized, $<\varphi|\varphi> = 1$, it must be that $\varphi \to 0$ as $x \to \pm\infty$, leading hence to

$$\varphi_j{}^*(a)\varphi_k(a) \to \infty \quad \text{as} \quad a \to \pm\infty .$$

If the boundary conditions are such that $\hat{p}$ is Hermitian, then the kinetic energy operator

$$T = \frac{1}{2m}\hat{p}^2$$

is necessarily Hermitian. This follows by applying the Hermitian properties of p sequentially,

$$<(\hat{p}_x\hat{p}_x\psi_j)|\psi_k> = <(\hat{p}_x\psi_j)|\hat{p}_x|\psi_k> = <\psi_j|\hat{p}_x\hat{p}_x\psi_k> .$$

Appendix 1-B. The Kinetic Energy

Summary: We will show in this section that the matrix element

$$t_{ab} = \langle \varphi_a | -\tfrac{1}{2}\nabla^2 | \varphi_b \rangle \tag{1}$$

can be written as

$$t_{ab} = \tfrac{1}{2}\langle \nabla \varphi_a \cdot \nabla \varphi_b \rangle \ , \tag{2}$$

where the dot product is indicated. Thus the kinetic energy of an orbital becomes

$$t_{aa} = \tfrac{1}{2}\langle | \nabla \varphi_a |^2 \rangle \tag{3a}$$

in atomic units or

$$t_{aa} = \frac{\hbar^2}{2m}\langle | \nabla \varphi_a |^2 \rangle \tag{3b}$$

in other units.

* * *

Consider first the integral

$$\left\langle \varphi_a \left| \frac{\partial^2}{\partial x^2} \right| \varphi_b \right\rangle = \int \int \int_{-\infty}^{+\infty} dx\, dy\, dz\, \varphi^*_a \frac{\partial^2 \varphi_b}{\partial x^2} .$$

Integrating by parts, this becomes

$$Q(x = +\infty) - Q(x = -\infty) - \int \int \int_{-\infty}^{+\infty} dx\, dy\, dz\, \frac{\partial \varphi^*_a}{\partial x} \frac{\partial \varphi_b}{\partial x} \ , \tag{4}$$

where

$$Q = \int \int_{-\infty}^{+\infty} dy\, dz\, \varphi^*_a \frac{\partial \varphi_b}{\partial x}$$

(this is referred to as Green's theorem). However, for φ_a and φ_b to satisfy the basic postulates of QM, we must have

$$\langle \varphi_a | \varphi_a \rangle = 1$$

$$\langle \varphi_b | \varphi_b \rangle = 1 \; ,$$

and hence

$$\varphi_a \rightarrow 0 \qquad \text{as} \qquad x \rightarrow \pm\infty \; .$$

Thus

$$Q(x = +\infty) = 0$$

$$Q(x = -\infty) = 0$$

and we obtain

$$\left\langle \varphi_a \left| \frac{\partial^2}{\partial x^2} \right| \varphi_b \right\rangle = - \left\langle \frac{\partial \varphi_a}{\partial x} \middle| \frac{\partial \varphi_b}{\partial x} \right\rangle . \tag{5}$$

Proceeding similarly for the other terms of (1), we obtain

$$t_{ab} = \tfrac{1}{2} \int d\tau \, [\nabla \varphi^*_a \cdot \nabla \varphi_b] \equiv \tfrac{1}{2} \langle \nabla \varphi_a \cdot \nabla \varphi_b \rangle \; , \tag{6}$$

and letting $\varphi_a = \varphi_b$ leads to (3).

Appendix 1-C. The Nodal Theorem

In this section we consider the eigenfunctions φ_n for a general one-dimensional system,

$$H\varphi_n = E_n\varphi_n ,$$

where

$$H = -\frac{1}{2M}\frac{d^2}{dx^2} + V(x)$$

is real (so that the eigenfunctions are real) and

$$M = m/\hbar^2 .$$

Letting n denote the number of nodes (internal to the boundaries), we will show that

$$\boxed{\begin{aligned} E_0 &< E_n \qquad (1) \\ \text{and} \quad E_n &< E_{n+1} . \qquad (2) \end{aligned}}$$

That is, the ground state of the system is nodeless and the state with n nodes has a lower energy than the state with n+1 nodes. For sufficiently singular potentials, the inequalities in (1) and (2) become equalities.

1-C.1. The Inequalities

Consider first the functions φ_0 and φ_1, which are the eigenstates of $\hat{H}$,

$$\begin{aligned} \hat{H}\varphi_0 &= (\hat{T} + V)\varphi_0 = E_0\varphi_0 \\ \hat{H}\varphi_1 &= (\hat{T} + V)\varphi_1 = E_1\varphi_1 , \end{aligned} \qquad (3)$$

with zero and one node, respectively, as in Figure 20. Here a and b are the boundaries of the system (they may be at ± ∞) and zeroes at the boundaries are not counted.

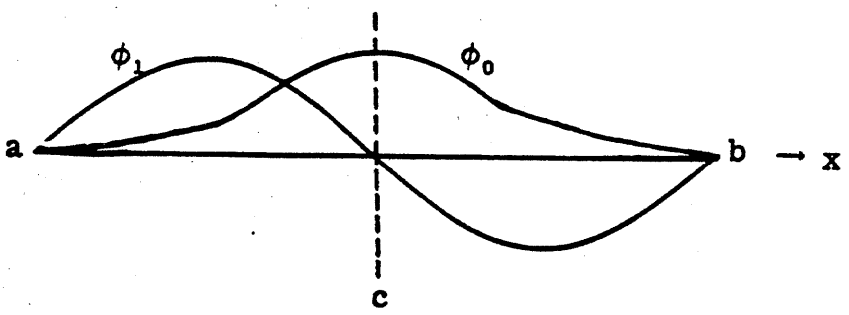

Figure 1-20. φ_0 and φ_1 for the proof of the Nodal Theorem.

First we will show that

$$E_1 \geq E_0 \ .$$

Letting c be the location of the node in φ_1, we consider the region

$$a < x < c \tag{4}$$

so that both φ_1 and φ_0 are positive. Then from (3) we have

$$\begin{aligned} E_0 &= V + \frac{1}{\varphi_0}\hat{T}\,\varphi_0 \\ E_1 &= V + \frac{1}{\varphi_1}\hat{T}\,\varphi_1 \end{aligned} \tag{5}$$

for all points in region (4). Thus the energy difference is given by

$$E_1 - E_0 = \frac{1}{\varphi_1}\hat{T}\,\varphi_1 - \frac{1}{\varphi_0}\hat{T}\,\varphi_0 = \frac{1}{\varphi_1\varphi_0}[\varphi_0(\hat{T}\,\varphi_1) - \varphi_1(\hat{T}\varphi_0)] \ . \tag{6}$$

The integral over all space of the term in brackets is zero since T is Hermitian,*

$$\int_a^b dx[\varphi_0(\hat{T}\,\varphi_1) - \varphi_1(\hat{T}\,\varphi_0)] = \langle\varphi_0|\hat{T}|\varphi_1\rangle - \langle\hat{T}\,\varphi_0|\varphi_1\rangle = 0 \ ;$$

however, the integrand is generally *not* zero.

---

* For a one-dimensional system, the orbitals can always be taken as real.

To estimate the sign of (6), we multiply by $\varphi_1\varphi_0$, then integrate from a to c, and then divide appropriately to obtain

$$(E_1 - E_0) = \frac{B}{A}\,, \tag{7}$$

where

$$B = \int_a^c dx\, \varphi_0\, \hat{T}\, \varphi_1 - \int_a^c dx\, \varphi_1\, \hat{T}\, \varphi_0 \tag{8}$$

$$A = \int_a^c dx\, \varphi_1\varphi_0\ . \tag{9}$$

Integrating by parts, the first term of (8) becomes

$$\int_a^c dx\, \varphi_0\, \hat{T}\, \varphi_1 = -\frac{1}{2M}\int_a^c dx\, \varphi_0 \left(\frac{\partial^2\varphi_1}{\partial x^2}\right)$$

$$= \left\{+\frac{1}{2M}\int_a^c dx \left(\frac{\partial\varphi_0}{\partial x}\right)\left(\frac{\partial\varphi_1}{\partial x}\right)\right\} - \left\{\left[\frac{1}{2M}\varphi_0\left(\frac{\partial\varphi_1}{\partial x}\right)\right]_a^c\right\}$$

$$= \left\{-\frac{1}{2M}\int_a^c dx\, \frac{\partial^2\varphi_0}{\partial x^2}\varphi_1\right\} + \frac{1}{2M}\left\{\left[\left(\frac{\partial\varphi_C}{\partial x}\right)\varphi_1 - \varphi_0\left(\frac{\partial\varphi_1}{\partial x}\right)\right]_a^c\right\}\ . \tag{10}$$

Combining (7)-(10) together, we obtain

$$(E_1 - E_0) = \frac{1}{2A}\left[\varphi_1\left(\frac{\partial\varphi_0}{\partial x}\right) - \left(\frac{\partial\varphi_1}{\partial x}\right)\varphi_0\right]_a^c\ .$$

Since

$$\varphi_1(c) = 0$$

$$\varphi_0(c) > 0$$

$$\left(\frac{\partial\varphi_1}{\partial x}\right)_{x=c} < 0$$

and

$$A = \int_a^c dx\, \varphi_1{}^* \varphi_0 > 0 ,$$

we obtain

$$E_1 - E_0 = -\frac{1}{2A}\varphi_0(c)\left(\frac{\partial \varphi_1}{\partial x}\right)_{x=c} > 0 , \tag{11}$$

that is,

$$E_1 - E_0 > 0 . \tag{12}$$

Thus the nodeless wavefunction has a lower energy than the wavefunction with one node. The same proof shows that φ_0 has a lower energy than any wavefunction with more than one node. Hence, ***the ground state of the system has no nodal points*** (inside the boundaries).

Similarly, the above proof can be applied to the comparison of E_n and E_{n+1}, that is, the energies for wavefunctions having n and n+1 nodes, respectively. The result is that

$$E_{n+1} > E_n , \tag{13}$$

and hence the eigenstates of a system have energies increasing in the same sequence as the number of nodes.

1-C.2. Singular Potentials

To obtain (12) we assumed in (11) that

$$\varphi_0(c) \neq 0 \tag{14a}$$

and that

$$\left(\frac{\partial \varphi_1}{\partial x}\right)_{x=c} \neq 0 . \tag{14b}$$

Usually these conditions (14) are satisfied; however, there can be cases where the potential is such that one of the quantities in (14) is zero. In this case we have

$$E_1 - E_0 = 0 \ ,$$

and hence the general condition (12) should be

$$E_1 \geq E_0 \ , \tag{15a}$$

and (13) should be

$$E_{n+1} \geq E_n \ . \tag{15b}$$

For example, consider the case wherein the potential V(x) is so strongly repulsive at some point c that *all solutions* of finite energy must have a node at c. In this case, the functions φ_0 and φ_1 in Figure 20 will have the shapes in Figure 21.

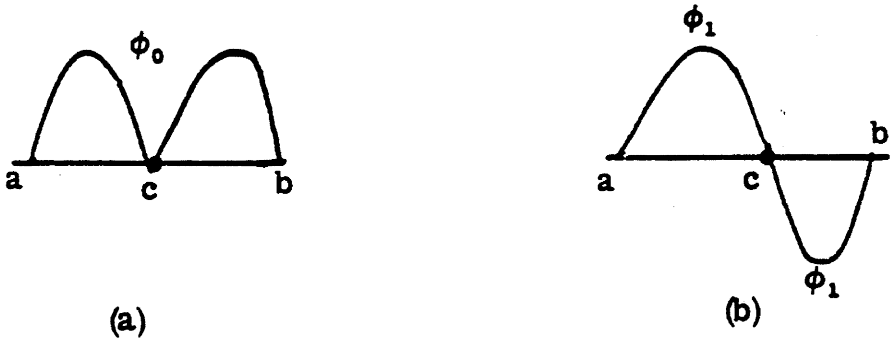

Figure 1-21. The first two solutions for a potential sufficiently singular at point c.

From (11) this leads to

$$E_1 - E_0 = 0 \ ,$$

so that E_0 and E_1 are degenerate. In this case, the functions φ_0 and φ_1 will have the same shape in each region. At x = c, one of them changes sign but since both must be zero there, they have the same energy.

If the potential is not singular at c, the function φ_0 can generally lead to a lower energy by being positive near c (thereby obtaining a smaller kinetic energy).

The presence of cases such as in Figure 9a complicated our notation for the states (in referring to the number of nodes). To keep things simple, n refers to the number of points at which the wavefunction changes sign.

Singularities in the potential would also lead to equalities in the energies for some excited states,

$$E_{n+1} = E_n \ .$$

1-C.3. A Singular Example

As discussed above, the equal sign in (1) would occur when the potential V(x) is sufficiently singular that the best non-negative wavefunction φ_0 has a node at some point. For example, if

$$V(x) = \frac{1}{|x - x_0|} \ ,$$

the potential energy is

$$<\varphi(x)\,|V(x)|\,\varphi(x)> = \int_{-\infty}^{x_0} dx \, \frac{|\varphi(x)|^2}{|x - x_0|} + \int_{x_0}^{\infty} dx \, \frac{|\varphi(x)|^2}{|x - x_0|} \ .$$

Expanding

$$\varphi(x) = \varphi(x_0) + (x - x_0)\,\varphi'(x_0) + \cdots \ ,$$

we see that the dominant term in the integral

$$\int^{x_0} dx \, \frac{\varphi(x)^2}{|x - x_0|}$$

is

$$\varphi(x_0)^2 \int^{x_0} \frac{dx}{|x - x_0|} = \varphi(x_0)^2 \ln 0$$

and hence the energy diverges if $\varphi(x_0) \neq 0$.

Thus, for φ to yield an $E < \infty$ (and hence to describe the ground state) it must be that

$$\varphi(x) \to 0 \qquad \text{as} \qquad x \to x_0 .$$

In this case,

$$E_0 = E_1$$

[assuming no other singularities in $V(x)$].

Appendix 1-D. The Ground State of Hydrogen Atom

Summary

The ground state of the hydrogen-like atom (with nuclear charge Z) has the wavefunction

$$\psi(r,\vartheta,\varphi) = N_0 e^{-Zr/a_0} , \tag{19}$$

where

$$N_0 = \sqrt{\frac{Z^3}{\pi a_0^3}} \tag{23}$$

and

$$a_0 = \frac{\hbar}{me^2} \tag{16}$$

is defined as the Bohr. The energy of this wavefunction is

$$E = -\tfrac{1}{2} Z^2 \left[\frac{e^2}{a_0}\right] = -\tfrac{1}{2} \frac{Ze^2}{\bar{R}} , \tag{18}$$

where

$$\bar{R} = \frac{a_0}{Z}$$

is the average size of the atom, where a_0 is denoted as the Bohr radius.

1-D.1. Solution of the Schrödinger Equation

We will solve for the ground state of the hydrogen atom, that is, the lowest solution of

$$\left[-\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{r} \right] \psi(r,\vartheta,\varphi) = E\psi(r,\vartheta,\varphi) . \tag{1}$$

Since the potential term is independent of angle, the wavefunction has the form (see §1.1.1)

$$\psi(r,\vartheta,\varphi) = f(r)Z(\vartheta,\varphi) , \tag{2}$$

where the angular function $Z(\vartheta,\varphi)$ is a constant for the ground state,*

$$Z(\vartheta,\varphi) = 1/\sqrt{4\pi} \ . \tag{3}$$

Thus, our chore is to solve

$$-\frac{\hbar^2}{2m}\nabla^2 f(r) - \frac{Ze^2}{r} f(r) = Ef(r) \ . \tag{4}$$

First we must express $\nabla^2 f(r)$ in terms of spherical coordinates,

$$\begin{aligned} z &= r\cos\vartheta \\ x &= r\sin\vartheta\cos\varphi \\ y &= r\sin\vartheta\sin\varphi \\ r^2 &= x^2+y^2+z^2 \ . \end{aligned} \tag{5}$$

Since

$$\left(\frac{\partial r}{\partial z}\right)_{x,y} = \frac{\partial}{\partial z}\sqrt{x^2+y^2+z^2} = \frac{z}{r}$$

(where the subscript x,y indicates that x and y are fixed), we see that

$$\left[\frac{\partial}{\partial z} f(r)\right]_{x,y} = \left(\frac{\partial r}{\partial z}\right)_{x,y}\left(\frac{\partial f}{\partial r}\right) = \frac{z}{r} f'(r) \ .$$

Thus, letting

$$\begin{aligned} f''(r) &= \frac{d^2f}{dr^2} \\ f'(r) &= \frac{df}{dr} \ , \end{aligned} \tag{6}$$

---

*The normalization condition is

$$\int_0^{2\pi} d\varphi \int_0^{\pi} \sin\vartheta \, d\vartheta [Z(\vartheta,\varphi)]^2 = 1 \ ,$$

leading to (3).

we obtain

$$\frac{\partial^2}{\partial z^2} f(r) = \frac{\partial}{\partial z}\left[\frac{z}{r} f'(r)\right] = \frac{1}{r} f'(r) + z\,\frac{\partial z}{\partial r}\,\frac{\partial}{\partial r}\left[\frac{1}{r} f'(r)\right]$$

$$= \frac{1}{r} f'(r) + \frac{z^2}{r}\left[\frac{1}{r} f''(r) - \frac{1}{r^2} f'(r)\right]$$

$$= \left(\frac{1}{r} - \frac{z^2}{r^3}\right) f'(r) + \frac{z^2}{r^2} f''(r) .$$

Combinding with $\frac{\partial^2}{\partial x^2} f(r)$ and $\frac{\partial^2}{\partial y^2} f(r)$ leads then to

$$\nabla^2 f(r) = f''(r) + \frac{2}{f} f'(r) . \tag{7}$$

Substituting (7) into (4) leads to

$$\boxed{-\frac{\hbar^2}{2m}\left[\frac{d^2f}{dr^2} + \frac{2}{r}\frac{df}{df}\right] - \frac{Ze^2}{r} f(r) = Ef(r)} \tag{8}$$

as the Schrödinger equation. Since the potential in (1) goes to zero as $r \to \infty$, only the states with $E < 0$ are bound, and hence we take

$$E < 0 . \tag{9}$$

Consider now a sufficiently large r that

$$\left|\frac{Ze^2}{r}\right| \ll |E|$$

(10)

and

$$\frac{2}{r}\left|\frac{df}{dr}\right| \ll \left|\frac{d^2f}{dr^2}\right| .$$

In this case, (8) reduces to

$$\frac{d^2f}{\partial r^2} = \zeta^2 f(r) , \tag{11}$$

where

$$\zeta^2 \equiv -\frac{2mE}{\hbar^2} \geq 0 \ . \tag{12}$$

The solution of (11) is

$$f(r) = e^{-\zeta r} \ . \tag{13}$$

Thus all bound state solutions of (8) must necessarily go to zero exponentially.*

Consider now the substitution of the exponential function (13) into the Schrödinger equation (8),

$$\frac{d^2f}{dr^2} + \frac{2}{r}\frac{df}{dr} = \zeta^2 f(r) - \frac{2mZe^2}{\hbar^2}\frac{1}{r}f(r) \ . \tag{14}$$

From (11) the first term of each side (the long-range terms) cancel at all r, leaving

$$\frac{2}{r}\frac{df}{dr} = -\frac{2\zeta}{r}f(r) = -\frac{2mZe^2}{\hbar^2}\frac{1}{r}f(r) \ .$$

Thus the exponential function (13) is an eigenfunction of the Schrödinger equation if

$$\zeta = \frac{mZe^2}{\hbar^2} \ . \tag{15}$$

Since ζ has the units of inverse length [e.g., see (12)], it is convenient to consider the length quantity

$$a_0 = \hbar^2 / me^2 \tag{16}$$

(referred to as the **Bohr** radius or simply the Bohr) as the fundamental

---

* Note that in the limit of very large r, the function

$$r^n e^{-\zeta r}$$

would also satisfy (8).

atomic length leading to

$$\boxed{\zeta = Z/a_0 .} \tag{17}$$

From (12) the value of ζ is related also to the energy,

$$E = -\frac{\hbar^2}{2m}\zeta^2 .$$

Thus,

$$\begin{aligned} E &= -\left(\frac{\hbar^2}{2m}\right)\frac{Z^2}{a_0^2} \\ &= -\tfrac{1}{2}Z^2\left(\frac{e^2}{a_0}\right) . \end{aligned} \tag{18}$$

Summarizing, we find that the wavefunction

$$\boxed{\psi_0(r,\vartheta,\varphi) = f(r) = N_0\,e^{-Zr/a_0} ,} \tag{19}$$

is an eigenfunction of the Schrödinger equation with an energy of

$$\boxed{E_0 = -\tfrac{1}{2}Z^2\left(\frac{e^2}{a_0}\right) ,} \tag{18}$$

where

$$\boxed{a_0 = \hbar^2/me^2 .} \tag{16}$$

Since the wavefunction (19) is nodeless, we know from the nodal theorem that this eigenfunction of $\hat{H}$ is the ***ground state*** of the hydrogen atom. For the wavefunction (19), the average value of $\frac{1}{r}$ is

$$\frac{1}{\bar{R}} = \left\langle\psi\left|\frac{1}{r}\right|\psi\right\rangle = \frac{Z}{a_0} . \tag{20}$$

Thus, the average potential energy is

$$\bar{V} = \left\langle\psi\left|-\frac{Ze^2}{r}\right|\psi\right\rangle = -\frac{Ze^2}{\bar{r}} = -\frac{Z^2e^2}{a_0} \tag{21}$$

and the total energy can be written as

$$E = \tfrac{1}{2}\bar{V} = -\tfrac{1}{2}\frac{Ze^2}{\bar{R}} = -\tfrac{1}{2}\frac{Z^2e^2}{a_0} . \tag{22}$$

In order to normalize the wavefunction (19), note that

$$<\psi|\psi> = \int_0^\infty r^2 dr \int_0^\pi \sin\vartheta\, d\vartheta \int_0^{2\pi} d\varphi [f(r)]^2 = 4\pi \int_z^\infty r^2 dr f(r)^2 ,$$

where the angular integral is

$$\int d\Omega = \int_0^\pi \sin\vartheta\, d\vartheta \int_0^{2\pi} d\varphi = 4\pi .$$

Since

$$\int_0^\infty r^2 dr\, f(r)^2 = N_0^2 \int_0^\infty r^2 dr\, e^{-2\zeta r} = \frac{N_0^2}{(2\zeta)^3}\int_0^\infty \rho^2\, d\rho\, e^{-\rho} = \frac{N_0^2}{(2\zeta)^3} 2! ,$$

we see that

$$N_0 = \sqrt{\frac{\zeta^3}{\pi}} = \sqrt{\frac{Z^3}{\pi a_0^3}} . \tag{23}$$

1-D.2. Analysis of the Wavefunction

A plot of the orbital along the z axis is given in Figure 22. Note that the slope in the wavefunction is discontinuous at z = 0. This singular behavior is referred to as a *cusp* and results from the singular behavior in the potential energy at this point.

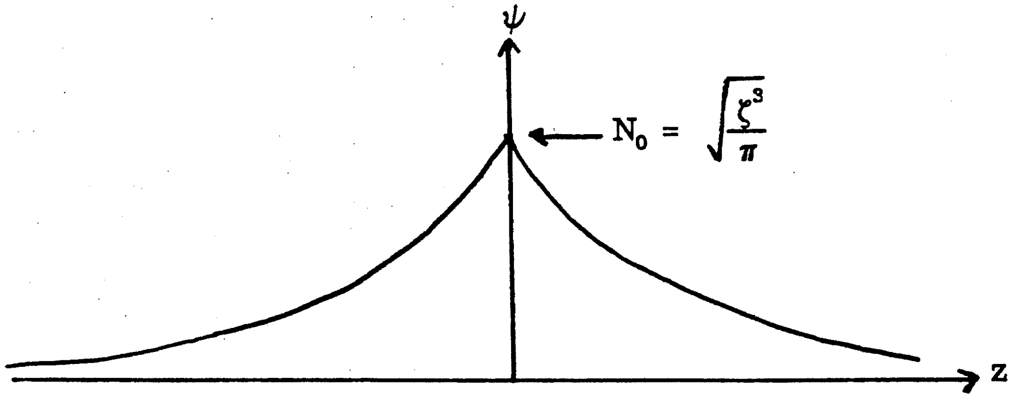

Figure 1-22. The ground state wavefunction, ψ_0, for the H atom (plotted along the z axis).

The Schrödinger equation (3) says that

$$Ef(r)$$

is equal to

$$-\frac{\hbar^2}{2m}\nabla^2 f(r) - \frac{Ze^2}{r}f(r)$$

for every point r. But, as r → 0, the term

$$-\frac{Ze^2}{r}f(r)$$

goes to $-\infty$. Thus, since Ef(r) is finite, the Schrödinger equation requires that

$$-\frac{\hbar^2}{2m}\nabla^2 f(r)$$

goes to $+\infty$ as r → 0. The cusp in the wavefunction leads to a $\nabla^2 f(r)$ that goes to $+\infty$ as r → 0 and exactly cancels the negative singularity in the potential term.

Appendix 1-E. Rydberg Atomic Units

Another set of atomic units used occasionally employs as the unit of energy the ionization potential of the hydrogen atom,

$$R_\infty = \frac{me^4}{2\hbar^2} . \qquad (1)$$

This quantity is called a **Rydberg** and is related to the hartree by

$$1 \text{ Rydberg} = \tfrac{1}{2} \text{ hartree}.$$

With this choice for the unit of energy ($me^4/2\hbar^2 = 1$), we cannot use the convenient sets of units in §1.2-23. If the unit of length is still taken as the Bohr ($\hbar^2/me^2 = 1$), then Rydberg units lead to

$$me^4 = 2\hbar^2 = 2me^2 ,$$

and hence we *must* choose

$$|e| = \sqrt{2}$$

and

$$\hbar^2 = 2m .$$

If we take $m = 1$, then

$$\hbar = \sqrt{2} .$$

These units are sometimes used by scattering theorists since the kinetic energy of a plane wave, $(\hbar^2/2m)k^2$, becomes simply k^2. Also, some workers reporting band calculations on solids use Rydberg units. The series of books by Slater also uses these units. However, the regular atomic units (or hartree atomic units), as described in §1.2.3, are more convenient and more common, and we will always use them.

Appendix 1-F. Units and Conversion Factors

1-F.1. SI Units

In an effort to bring some order to the proliferation of units that continues to occur in the sciences, and international group adopted (in 1960) what is referred to (in English) as the International System of Units, or more commonly as SI units.

In this system there are seven fundamental units:

Unit	Abbreviation	Physical Quantity
meter	m	length
kilogram	kg	mass
second	s (or sec)	time
ampere*	A	electric current
kelvin*	K	thermodynamic temperature
mole	mol	amount of substance
candela	cd	luminous intensity

* Note that these units are *not* capitalized even though they are derived from the names of people.

From these fundamental units can be derived a number of combined units that prove quite useful. Thus, from Newton's Law, F = ma, we know that force has units of $\frac{\text{mass} \times \text{length}}{(\text{time})^2}$; and it is convenient to define the unit of force (newton*) as

$$1 \text{ newton} = 1 \text{ kg m sec}^{-2}.$$

Similarly, a constant force F exerted over a distance l does an amount of work W, so that the unit of energy (joule) is

$$1 \text{ joule} = 1 \text{ newton meter} = 1 \text{ kg m}^2 \text{ sec}^{-2}.$$

Some common derived units in SI are

Unit	Abbreviation	Definition in Terms of Fundamental Units	Physical Quantity
liter	l	10^{-3} m^3	volume
newton	N	m kg sec^{-2}	force
joule	J	Nm = m^2 kg sec^{-2}	energy
watt	W	J sec^{-1} = m^2 kg sec^{-2}	power
pascal	Pa	Nm^{-2} = m^{-1} kg sec^{-2}	pressure
coulomb	C	A sec	electric charge
volt	V	W A^{-1} = m^2 kg sec^{-3} A^{-1}	electric potential
ohm	Ω	V A^{-1} = m^2 kg sec^{-3}A^{-2}	electric resistance
hertz	Hz	sec^{-1}	frequency

The acceptable multiples or fractions to be used for the basic SI units are designated by the following prefixes:

Fraction	Prefix	Symbol
10^{-18}	atto	a
10^{-15}	femto	f
10^{-12}	pico	p
10^{-9}	nano	n
10^{-6}	micro	μ
10^{-3}	milli	m
10^{-2}	centi	c
10^{-1}	deci	d
10	deka	da
10^{2}	hecto	h
10^{3}	kilo	k
10^{6}	mega	M
10^{9}	giga	G
10^{12}	tera	T

Although the above fundamental units are convenient for a number of quantities, they are quite inconvenient for others. Examples include

Physical Quantity	Abbreviation	Definition in Terms of SI Units
Charge on an Electron	e	1.602189×10^{-19} C
Atmospheric Pressure (at sea level)	atm	101.325 Pa

Other units are not necessarily superior to the SI quantities, but their use is so widespread that scientists must be facile with their use. Examples include:

Unit	Abbreviation	Definition	Relation to Fundamental Units
Kilocalorie	kcal	original definition was: energy to heat 1 kg of H_2O by a temperature of 1°K (at 15°C)	1 kcal = 4.184 kJ (defined to be exact)
Angstrom	Å	--	1 Å = 10^{-10} m = 10^{-8} cm
Electron Volt	eV	energy change upon moving a charge of 1 electron through an electric potential of 1 volt	1 eV = 96.483 kJ mol^{-1}

1-F.2. Units for Coulombs Law

Conversion between units can sometimes get confusing for coulomb interactions. Coulombs law states that the force between two charges Q_1 and Q_2, separated by a distance R is

$$\text{Total Force} = \frac{Q_1 Q_2}{R^2} .$$

and hence the enegy of interaction is

$$E = \int_{-\infty}^{R} F \cdot dr = \frac{Q_1 Q_2}{R} .$$

In cgs units, we define the electrostatic unit of charge (esu) as that charge which leads to a force of 1 dyne when the charges are separated by 1 cm. Thus

$$\text{Force (dynes)} = \frac{[Q(esu)]^2}{[R(cm)]^2}$$

and

$$\text{Energy (ergs)} = \frac{[Q(esu)]^2}{R(cm)} . \qquad (1)$$

In SI units, the unit of charge (the Coulomb) is defined in terms of a current (1 ampere = 1 Coulomb/sec), and the units of current are related to force and distance through a different force law (magnetic induction). The relationship between Coulombs and esu turns out to be

$$1 \text{ Coulomb} = \frac{1\ esu}{(2.998\ 10^9)} ,$$

where the 2.998 comes from the speed of light (2.998 10^8 m/sec). Since

$$\text{Force (newtons)} = 10^{-5} \text{ force (dynes)}$$

$$R \text{ (meters)} = 10^{-2} R \text{ (cm)} ,$$

the Coulomb law becomes

$$\text{Force (newtons)} = [8.988\ 10^9] \frac{[Q \text{ (coulomb)}]^2}{[R\ (m)]^2} . \qquad (2)$$

and

$$\text{Energy (joules)} = [8.988\ 10^9] \frac{[Q\text{(coulomb)}]^2}{R\text{(cm)}} .$$

In SI units, the constant in this expression is generally written as

$$8.988 \times 10^9 = \frac{1}{4\pi\varepsilon_0} ,$$

where

$$\varepsilon_0 \equiv 8.854\ 10^{-12}\ C^2 N^{-1} m^{-2} \qquad (3)$$

is called the **permittivity of a vacuum.** This leads to

$$\text{Energy } (N) = \frac{Q_1(C) Q_2(C)}{4\pi\varepsilon_0 R(M)} \qquad (4)$$

for the coulomb energy.

In this course the Q_1 and Q_2 are always some multiple of the fundamental charge on a proton (or electron),

$$\begin{aligned} 1e &= 1.602\ 10^{-19}\ C \\ &= 4.803\ 10^{-10}\ esu\ . \end{aligned}$$

Thus we will write

$$Q_1 = q_1 e \qquad \text{and} \qquad Q_2 = q_2 e\ , \tag{5}$$

where q_1 and q_2 have no units. In addition, we will often write R in terms of Bohr radii, e.g.,

$$R = r\, a_0\ , \tag{6}$$

where r has no units. In this case the coulomb energy becomes

$$\text{Energy} = \frac{q_1 q_2}{r}\left(\frac{e^2}{a_0}\right)\ . \tag{7}$$

where **no** $4\pi\varepsilon_0$ factor is included. In (7) the unit of energy is

$$\begin{aligned} 1\ h_0 &= 1\ \text{hartree} = \frac{e^2}{a_0} \\ &= 27.2116\ eV = 2625.5\ \text{kJ/mol} = 627.51\ \text{kcal/mol}\ . \end{aligned} \tag{8}$$

The fast way to calculate atomic level coulomb energies in various units is to first express all distances and charges in atomic units, as in (5) and (6), calculate the energy using (7), and then to convert from atomic units to SI units using (8).

Example: Calculate the interaction of two protons at a distance of R = 5 Å.

Answer:

$$R = 5\,\text{Å} = \frac{5}{0.529}\,a_0 = 9.45\,a_0$$

$$E(h_0) = \frac{1}{R(a_0)} = \frac{1}{9.45} = 0.1058\,h_0$$

$$= 2.88 \text{ eV} = 278 \text{ kJ/mole} = 66.4 \text{ kcal}.$$

Useful conversion factors here are

$$e^2 = 14.3998 \text{ eV Å} = 332.059 \text{ (kcal/mol) Å}$$

1-F.3. Units for Mass

In atomic units, the mass of the *electron* is unity; however, this is not to be confused with the atomic mass unit (amu) which is the standard for relating the masses of *atoms*. The modern convention is to define the dominant isotope of C (i.e.,^{12}C) as having a mass of 12.0000. In these units, the mass of the hydrogen atom is

$$1.00783 \text{ amu},$$

the mass of a proton is

$$1.00728 \text{ amu},$$

and the mass of an electron is

$$\frac{1}{1822.89} \text{ amu}.$$

Thus, in (hartree) atomic units, the mass of the proton is

$$1.00728 \times 1822.89 = 1836.16$$

The conversion to SI units is

$$1 \text{ amu} = 1.660566 \times 10^{-27} \text{ kg}.$$

1-F.4. Energy Quantities for Photons

The wavelength (λ) and frequency (ν) of light are related by the speed of light (c)

$$\lambda\nu = c \ .$$

Thus, since c = 2.99792458 × 10^{10} cm/sec, the frequency for yellow light (λ = 600 nm) is

$$\nu = \frac{3 \times 10^{10}}{6 \times 10^{-7}} = 5 \times 10^{16} \text{ Hz}$$

(1 Hz = 1 cycle per sec), and the wavelength for KZLA (ν = 94 MHz) is

$$\lambda = \frac{3 \times 10^{10}}{94 \times 10^{6}} = 319 \text{ cm} = 3.19 \text{ m} \ .$$

In the quantum description of light, the energy of a photon is given by

$$E = h\nu$$

(where $h = 2\pi\hbar$ is the original Planck's constant); thus the energy of a photon of light can be expressed as

$$E = h\nu = \frac{hc}{\lambda} = hc\bar{\nu} \ ,$$

where $\bar{\nu} = \frac{1}{\lambda}$ is called the ***wavenumber*** (and denoted as cm^{-1}). Substitution for the known values of h and c leads to

$$E(\text{eV}) = \frac{1239.85}{\lambda(\text{nm})} = 8065.48 \ \bar{\nu} \ (\text{cm}^{-1})$$

$$\bar{\nu}(\text{cm}^{-1}) = \frac{10^{7}}{\lambda(\text{nm})}$$

Thus, when an electron decreases its energy by 1 eV (dropping into a lower energy state), it may emit this energy as a single photon with wavelength λ = 1240 nm = 1.24 microns or wavenumber $\bar{\nu}$ = 8065 cm^{-1}.

1-F.5. Other Energy Relations

Chemists often use the energy quantity kilocalories per mole which we will abbreviate as kcal,

$$1 \text{ eV} = 23.06036(14) \text{ kcal.}$$

Recently, emphasis has been placed on SI units in which the kilojoule per mole (denoted as kJpm) is the energy unit,

$$1 \text{ kcal} = 4.18400 \text{ kJpm.}$$

The atomic unit of energy, the hartree, is kind of large for convenient use and we will often use the millihartree, denoted as mh. Relations between these units are

$$1 \text{ eV} = 36.7490 \text{ mn} = 23.0604 \text{ kcal} = 96.4847 \text{ kJpm} = 8065.48 \text{ cm}^{-1}$$

$$1 \text{ mh} = 0.27212 \text{ eV} = 0.627511 \text{ kcal} = 2.62550 \text{ kJpm} = 219.475 \text{ cm}^{-1}.$$

The average thermal energy of an oscillator at room temperature is

$$kT = \frac{1}{40} \text{eV} = 1 \text{ mh} = 0.6 \text{ kcal} = 200 \text{ cm}^{-1} = 2.4 \text{ kJpm.}$$

The strength of the H_2^+ bond is

$$2.5 \text{ eV} = 92 \text{ mn} = 58 \text{ kcal} = 241 \text{ kJpm.}$$

The vibrational energy $\hbar\omega_e$ of H_2^+ is

$$3000 \text{ cm}^{-1} = 14 \text{ mh} = 8.6 \text{ kcal} = 0.37 \text{ eV} = 36 \text{ kJpm.}$$

1-F.6 Examples

The fundamental constants are experimentally determined and hence the best values for them change with time. For aid in calculating these constants in the future, we summarize the procedure.

$$1 \text{ (eV/atom)} \times 1.6021892 \times 10^{-22} \text{ (kJ/eV)} \times \frac{1\text{kcal}}{4.184 \text{ kJ}} \times 6.022045$$

$$\times\ 10^{23} \text{ (atoms/mol)} = 23.06036 \text{ kcal mol}^{-1}.$$

Therefore, 1 eV/atom = 23.06036 kcal mol^{-1}. For force constants we use

$$k = M\omega^2 = \frac{\text{mass}}{(\text{Time})^2} = \frac{\text{Energy}}{(\text{Length})^2}$$

$$1 \text{ au} = \frac{h}{a_0^2} = \frac{27.21161 * 1.6021892 * 10^{-12} \text{ erg}}{(0.52917706 * 10^{-8} \text{ cm})^2}$$

$$= 1.556919 * 10^6 \text{ dyne/cm}$$

$$= 15.56919 \text{ mdyne/A} .$$

1-F.7. Conversion Factors

Included herein are the fundamental constants as of 1973. The reference is E. R. Cohen and B. N. Taylor, *J. Phys. Chem. Ref. Data*, **2**, 717 (1973), and some tables from this reference are included on the following pages.

Commonly used constants are:*

1. 1 bohr = 0.5291771 (4) Å
2. 1 hartree = 27.21161 (7) eV

   1 hartree = 627.5096 (4) kcal/mol = 219474.7 cm^{-1}
3. 1 eV = 23.06036 (14) kcal/mol = 96.483 kJ/mol

   1 eV = 8065.48 (2) cm^{-1}

   $1 \text{ eV} = \frac{1239.852(3)}{\lambda(\text{nm})}$
4. 1 kcal = 4.18400 kJ = 349.755 cm^{-1}

---

* A number in parentheses indicates the standard deviation in the error for the last quoted digit.

5. Atomic Masses: 1 amu = 1822.887 (1) m_e

   This is used to convert atomic masses (mass ^{12}C = 12.000) to hartree atomic units

6. Force Constant: 1 au = 15.56919 mdyne/Å

7. Gas Constant: $R = 1.98719$ (7) cal mol^{-1} K^{-1}

   Gas Constant: $R = 82.0568$ cc atm mol^{-1} K^{-1}

8. Avogadro's Constant = 6.022045 (31)* 10^{23} molecules/mol

9. Fine Structure Constant: $1/\alpha = \hbar c/e^2 = 137.03604$ (11)

10. Dipole Moment: 1 au = 2.541765 (8) Debye

    Dipole Moment: 1 au = 2.541765 (8) * (10^{-18} esu*cm)

11. Quadrupole Moment: 1 au = 1.345044 * 10^{-26} esu cm^2

    Quadrupole Moment: 1 au = 1.345044 Buckingham

12. Electric Field Gradient: 1 au = 3.241391 * 10^{15} esu cm^{-3}

13. Coulomb Energies: $\frac{e^2}{R}(\text{eV}) = \frac{14.3998}{R(\text{Å})}$, $\frac{e^2}{R}(\text{kcal}) = \frac{332.059}{R(\text{Å})}$

Table 1-F.I. Current Values for Selected Fundamental Constants.[a]

Quantity	Symbol	Value	Uncertainty (ppm)	Units	
				SI	cgs[b]
Elementary charge	e	1.6021892(46) 4.803242(14)	2.9 2.9	10^{-19} C	10^{-20} emu 10^{-10} esu
Planck constant	h $\hbar = h/2\pi$	6.626176(36) 1.0545887(57)	5.4 5.4	10^{-34} J·s 10^{-34} J·s	10^{-27} erg·s 10^{-27} erg·s
Speed of light in vacuum	c	299792458(1.2)	0.004	10^{8} m·s^{-1}	10^{10}cm·s^{-1}
Fine-structure constant, $[\mu_0 c^2/4\pi](e^2/\hbar c)$	α α^{-1}	7.2973506(60) 137.03604(11)	0.82 0.82	10^{-3}	10^{-3}
Electron rest mass	m_e	9.109534(47) 5.4858026(21)	5.1 0.38	10^{-31} kg 10^{-4} u	10^{-28} g 10^{-4} u
Proton rest mass	m_p	1.6726485(86) 1.007276470(11)	5.1 0.011	10^{-27} kg u	10^{-24} g u
Ratio of proton to electron mass	m_p/m_e	1836.15152(70)	0.38		
Atomic mass unit, 10^{-3} kg·mol^{-1} N_A^{-1}	u	1.6605655(86)	5.1	10^{-27} kg	10^{-24} g
Ratio amu to m_e	u/m_e	= 1822.887(1)m_e			
Bohr radius, $[\mu_0 c^2/4\pi]^{-1}(\hbar^2/m_e e^2) = \alpha/4\pi R_\infty$	a_0	5.2917706(44)	0.82	10^{-11} m	10^{-9} cm
Rydberg constant, $[\mu_0 c^2/4\pi]^2(m_e e^4/4\pi\hbar^3 c)$	R_∞	1.097373177(83)	0.075	10^{7}m^{-1}	10^{5} cm^{-1}
Avogadro constant	N_A	6.022045(31)	5.1	10^{23} mol^{-1}	10^{23} mol^{-1}
Faraday constant, $N_A e$	F	9.648456(27) 2.8925342(82)	2.8 2.8	10^{4} C·mol^{-1}	10^{3} emu·mol^{-1} 10^{14} esu·mol^{-1}
Bohr magneton, [c] $(e\hbar/2m_e c)$	μ_B	9.274078(36)	3.9	10^{-24} J·T^{-1}	10^{-21} erg·G^{-1}
Nuclear magneton, [c] $(e\hbar/2m_p c)$	μ_N	5.050824(20)	3.9	10^{-27} J·T^{-1}	10^{-24} erg·G^{-1}
Molar volume of ideal gas at s.t.p.	V_m	22.41383(70)	31	10^{-3}m^3·mol^{-1}	10^{3}cm^3·mol^{-1}
Molar gas constant, p_0V_m/T_0 (T_0 = 273.15 K; p_0 = 101325 Pa = 1 atm)	R	8.31441(26) 8.20568(26) = 1.98719(7) kcal/mol K	31 31	J·mol^{-1}·K^{-1} 10^{-5}m^3·atm·mol^{-1}·K^{-1}	10^{7}erg·mol^{-1}·K^{-1} 10 cm^3·atm·mol^{-1}·K^{-1}
Boltzmann constant, R/N_A	k	1.380662(44)	32	10^{-23} J·K^{-1}	10^{-16} erg·K^{-1}

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[a] Note that the numbers in parentheses are the one standard-deviation uncertainties in the last digits of the quoted value computed on the basis of internal consistency, that the unified atomic mass scale ^{12}C = 12 has been used throughout, that u = atomic mass unit, C = coulomb, F = farad, G = gauss, H = henry, Hz = hertz = cycles/s, J = joule, K = kelvin (degree Kelvin), Pa = pascal = N·m^{-2}, T = tesla (10^4 G), V = volt, Wb = weber = T·m^2, and W = watt. In cases where formulas for constants are given (e.g., R_∞), the relations are written as the product of two factors. The second factor, in parentheses, is the expression to be used when all quantities are expressed in cgs units, with the electron charge in electrostatic units.

[b] In order to avoid separate columns for "electromagnetic" and "electrostatic" units, both are given under the single heading "cgs Units." When using these units, the elementary charge e in the second column should be understood to be replaced by e_m or e_e, respectively.

Ch 120a

CHAPTER 2: *The Chemical Bond:* H_2^+ *and* H_2

Chapter 2. The Chemical Bond: H_1^+ and H_2

Summary:

In this chapter we consider the two states of H_2^+

$$\varphi_g = \chi_l + \chi_r$$
$$\varphi_u = \chi_l - \chi_r$$

(the LCAO wavefunctions) arising from bringing a proton up to the ground state of hydrogen, and we consider the two states of H_2

$$\Phi_g = \chi_l \chi_r + \chi_r \chi_l$$
$$\Phi_u = \chi_l \chi_r - \chi_r \chi_l$$

(the VB wavefunctions) arising from bringing together two hydrogen atoms each in the ground state. As expected from the nodal theorem, the g state (symmetric) is the ground state for both systems. Indeed, in each case we find that the g state leads to bonding, while the u state leads to a repulsive potential curve. The g state of H_2^+ leads to an increase of the electron density in the bond region; however (contrary to popular belief), this leads to an *increase* in the electrostatic interactions, thus opposing bond formation. A bond is formed because of a very large decrease in the kinetic energy due to the molecular orbital having a significantly decreased gradient in the bond region. The bonding of the g state of H_2 arises from the same term (modified by an additional overlap factor due to the second electron).

The potential curves for both states of both molecules are dominated by exchange terms of the form

$$\varepsilon_g^x = \frac{\tau}{1 + S}$$
$$\varepsilon_u^x = -\frac{\tau}{1 - S}$$

for H_2^+ and

$$E_g^x = \frac{2S\tau}{1 + S^2}$$

$$E_u^x = -\frac{2S\tau}{1 - S^2}$$

for H_2, where S is the overlap of the atomic orbitals. The quantity τ is the quantitative manifestation of the decreased kinetic energy (and increased potential energy) arising from interference of the χ_l and χ_r orbitals. It has the form

$$\tau \approx -\frac{2}{R}S$$

for large R. Thus, at large R the bonding of H_2^+ is proportional to S, while the bonding of H_2 is proportional to S^2. Consequently, for large R the bond energy of H_2^+ **exceeds** that of H_2. For small R , where S ≈ 1, the bond energy of H_2 is approximately twice that of H_2^+. The u states are far more repulsive than the g states are attractive (due to the $1 \pm S$ and $1 \pm S^2$ terms in the denominators of ε^x and E^x).

We also examine the molecular orbital (MO) wavefunction for H_2

$$\Phi_g^{MO}(1,2) = \varphi_g(1)\varphi_g(2) ,$$

which provides a simple description of the ground and excited states for small R. For large distances, the ionic terms implicit in the MO wavefunction lead to an improper description.

2.0 The Chemical Bond in H_2^+ and H_2

Many atoms will combine with other atoms to form a strongly bound molecule. The point of this chapter will be to establish the origin of the chemical bond for the simplest one- and two-electron systems.

We will observe the following conventions on notation in this and following chapters: *Lower-case letters* will be used for *one-particle* wavefunctions (φ) and energies (ε), while *upper-case letters* will be used for *many-particle* wavefunctions (Φ) and energies (E).

2.1 Origin of the Bond in H_2^+

We first consider the smallest possible molecule, H_2^+, consisting of one electron plus two protons separated by a distance R. This system is sketched in Figure 1, where the two protons are denoted as a and b.

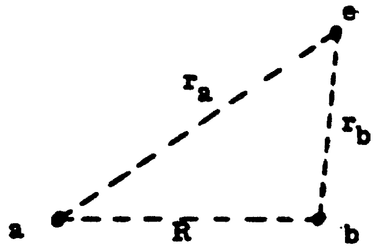


Figure 2-1. Coordinates for H_2^+.

2.1.1 LCAO Description

Consider first the case with R = ∞. With the two protons infinitely far apart, the ground state is obtained by placing the electron in the 1s orbital of one of the other of the two protons. This leads to the two states,

$$\text{H} \qquad \text{H}^+ \tag{1a}$$

and

$$\text{H}^+ \qquad \text{H} \tag{1b}$$

which are described by the wavefunctions,*

$$\varphi = \chi_l = N e^{-r_a} \tag{2a}$$

and

$$\varphi = \chi_r = N e^{-r_b} \,, \tag{2b}$$

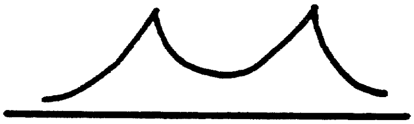
respectively, where χ_l and χ_r denote hydrogen 1s orbitals centered on the left and right protons.

For finite R, the exact wavefunctions no longer have the atomic form, but useful approximate wavefunctions can be obtained by allowing the wavefunction to be a (linear) combination of the atomic orbitals in (2),

$$\varphi = C_l \chi_l + C_r \chi_r \ . \tag{3}$$

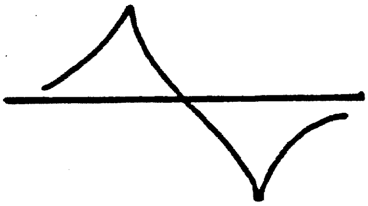
This simple type of wavefunction is often referred to as LCAO for a **linear combination of atomic orbitals.** We will find that the optimum LCAO wavefunction is the symmetric combination,

$$\varphi_g = (\chi_l + \chi_r)/\,D_g \tag{4}$$



(where D_g is a normalization factor). The other combination of the orbitals (5.3) is the antisymmetric combination,

$$\varphi_u = (\chi_l - \chi_r)/\,D_u \tag{5}$$



(D_u is the normalization factor).

The energies for the wavefunctions φ_g and φ_u in (4) and (5) are shown as a function of R in Figure 2. Here we see that the g state is strongly

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* N is the normalization factor.

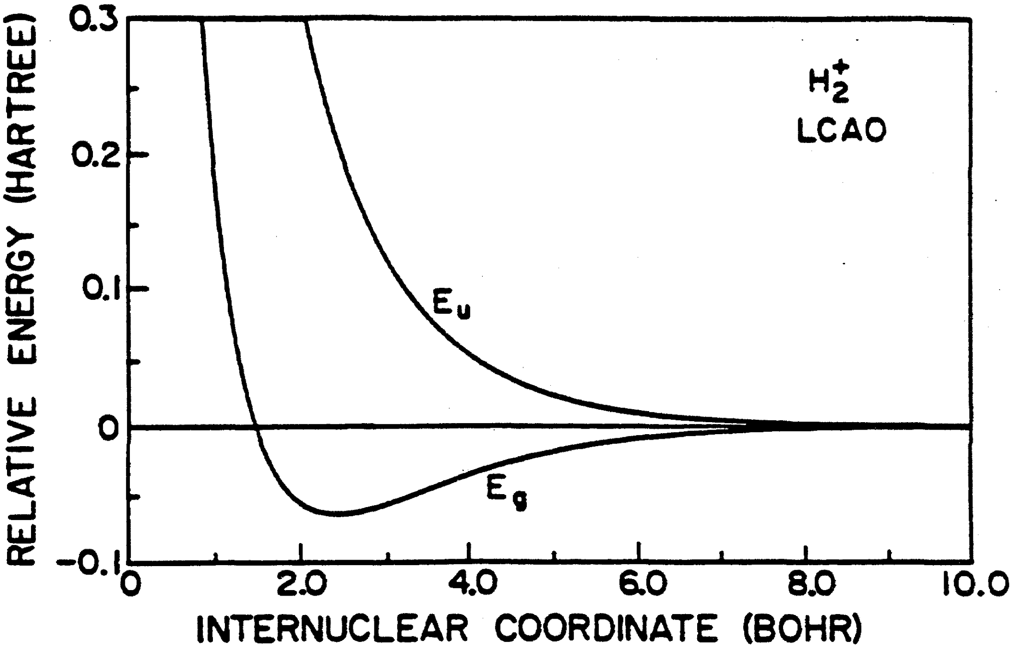

Figure 2-2. The energies of the LCAO wavefunctions for H_2^+.

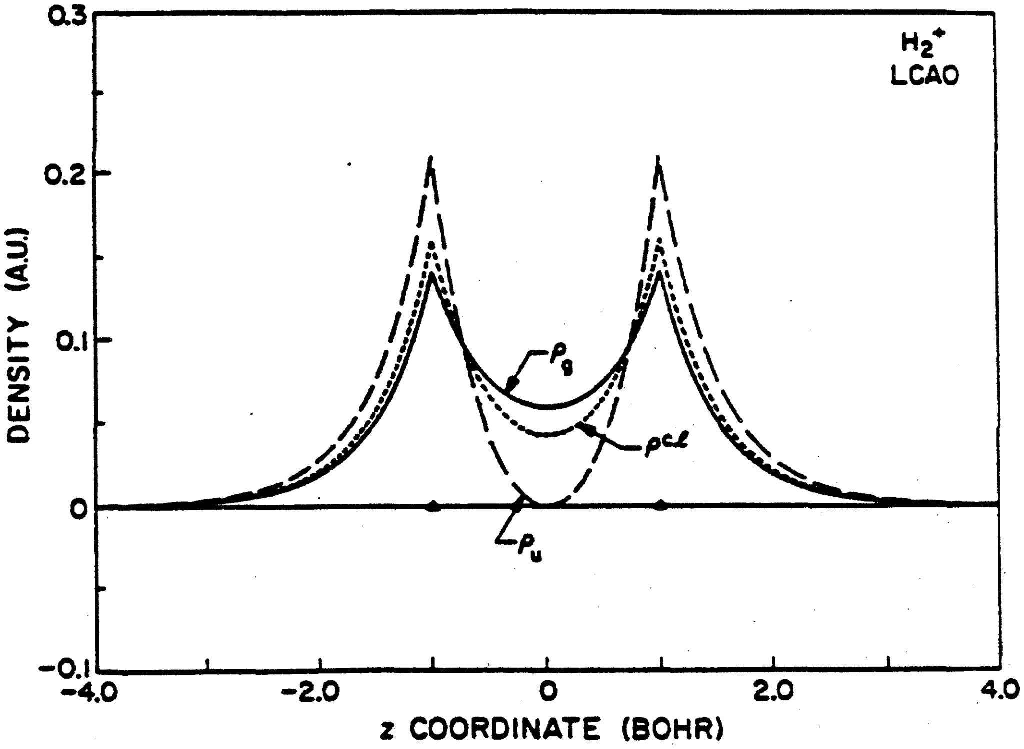

Figure 2-3. The densities ρ_g and ρ_u for the LCAO wavefunctions of H_2^+ compared with the superposition of atomic densities, ρ^{cl}.

bonding (that is, the energy drops as the nuclei are brought together), while the u state is strongly **antibonding** (the energy increases as the nuclei are brought together). The objective of this section will be to understand the ***origin*** of the bonding and antibonding charactered exhibited by the φ_g and φ_u states.

2.1.1a Electrostatic Energy

First we consider the electron density,

$$\rho_g = \varphi_g^2 = \frac{1}{D_g^2}(\chi_l + \chi_r)^2 = (\chi_l^2 + \chi_r^2 + 2\,\chi_l\chi_r)/\,D_g^2 \; . \tag{6}$$

Integrating φ_g^2 over all space must give one electron

$$\langle\varphi_g^2\rangle = 1 \tag{7}$$

and similarly

$$\langle\chi_l^2\rangle = 1$$
$$\langle\chi_r^2\rangle = 1$$

(recall that these are just the 1s orbitals of H atom). Thus (6) leads to

$$1 = \frac{1 + 1 + 2S}{D_g^2} \; ,$$

where

$$S = \langle\chi_l\chi_r\rangle \tag{8}$$

is called the ***overlap*** of the two atomic orbitals. Consequently, the normalization condition in (4) is

$$D_g = \sqrt{2(1+S)} \; . \tag{9}$$

If there were no interference terms in (6), the density would be*

$$\rho^{cl} = \tfrac{1}{2}\,(\chi_l^2 + \chi_r^2) \tag{10}$$

---

* The factor of ½ leads to the required condition $\langle\rho^{cl}\rangle = 1$.

but because of the interference terms ***the density near the bond midpoint is increased***, as shown in Figure 3. This result has given rise to the prevalent idea that the ***chemical bond arises from the increase in the electron charge density in the bond region***. The idea is that an electron in between the nuclei attracts both nuclei, holding them together to form the chemical bond,

$$p^+ \quad e^- \quad p^+ \tag{11}$$

This reasoning is false as will now be demonstrated. The total potential energy is given by

$$V(\mathbf{r}) = -\frac{e^2}{r_a} - \frac{e^2}{r_b} + \frac{e^2}{R}\,, \tag{12}$$

as sketched in Figure 4.

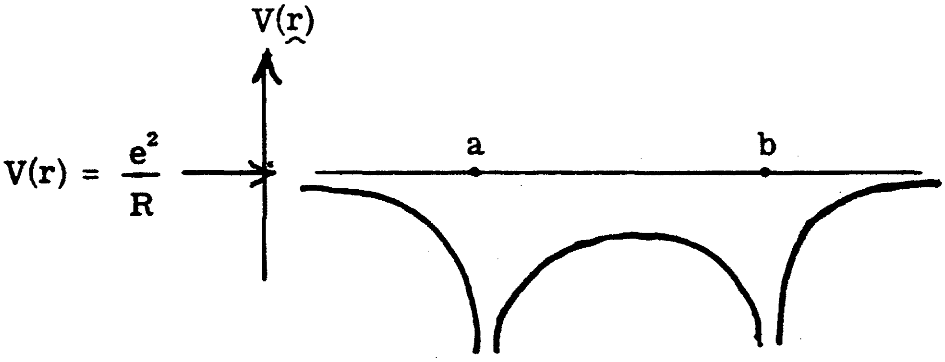

Figure 2-4. The nuclear attraction potential V(r) for H_2^+.

as sketched in Figure 4. Here we see that the best place for the electron (i.e., lowest energy) is at a nucleus ($r_a = 0$ or $r_b = 0$), ***not*** at the bond midpoint. From Figure 3 we observe that the increase in charge at the bond midpoint is at the expense of charge near the nucleus. Thus, in forming a bond, the charge is transferred from a low energy region (near the nucleus) to a high energy region (the bond midpoint), an effect that should operate ***against*** bond formation. Indeed, this is the case, as shown in Figure 5, where

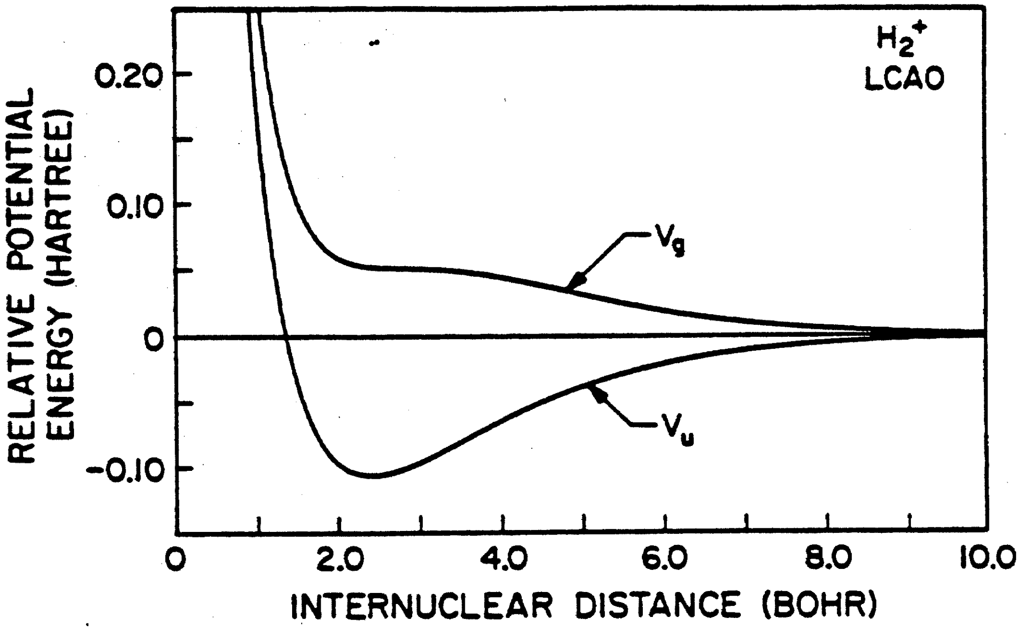

Figure 2-5. The relative potential energies, $\mathbf{V}_g$ and $\mathbf{V}_u$, for the LCAO wavefunctions of H_2^+. The absolute values are obtained by noting that $\mathbf{V}_g = \mathbf{V}_u = -1.0$ at $R = \infty$.

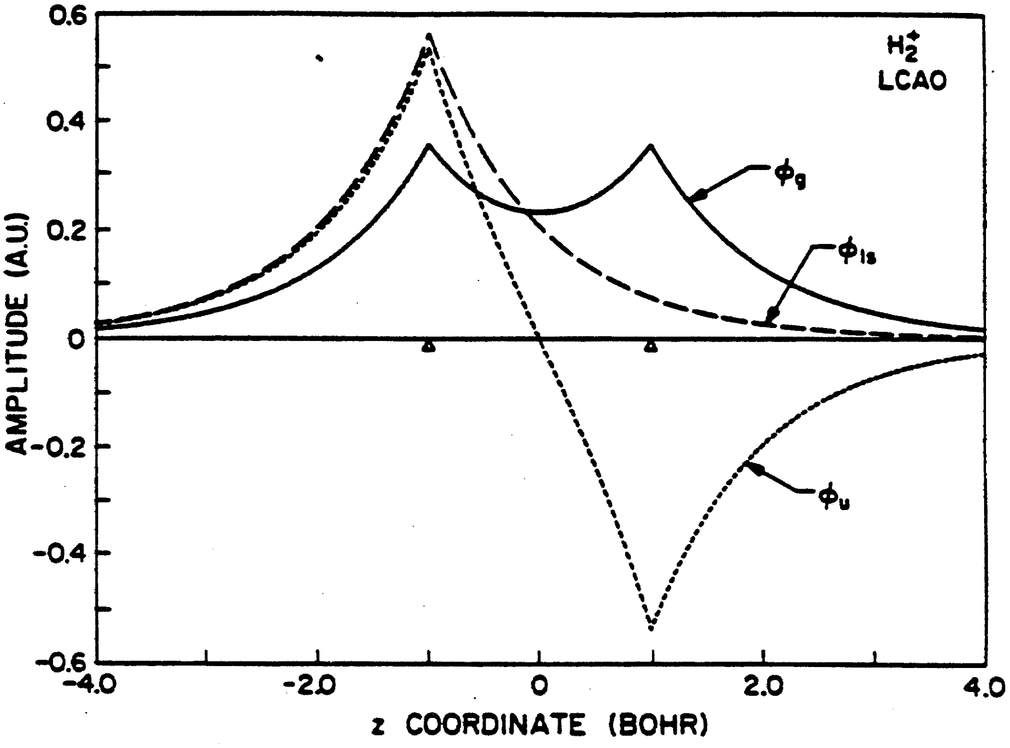

Figure 2-6. Comparison of the φ_g and φ_u LCAO's of H_2^+ with the hydrogen atom orbital, φ_{1s}. All wavefunctions have been normalized.

$$V_g = \langle \varphi_g^2 V(\mathbf{r}) \rangle$$

is the total potential energy for the φ_g wavefunction.

Our conclusion then is that ***transfer of electron charge into the bond region leads to repulsive electrostatic interactions***. The fact that the bonding state leads to such a transfer indicates that the ***origin of the bond lies in*** the other contribution to the energy, ***the kinetic energy***, as will be discussed next.

2.1.1b Kinetic Energy

A qualitative prediction of changes in kinetic energy upon bond formation is easy. The kinetic energy is the (average) square of the gradient of the wavefunction, $T = (\hbar^2/2m) \langle |\nabla\psi|^2 \rangle$. Superimposing two atomic orbitals symmetrically as in φ_g leads to a large ***decrease*** in the slope in the bond region (see Fig. 6), and hence a large decrease in the kinetic energy (see T_g of Fig. 7),

$$T_g = (\hbar^2/2m) \langle (\nabla\varphi_g)^2 \rangle$$

resulting in a strong bond. On the other hand, the antisymmetric combination in φ_u leads to a large ***increase*** in the slope in the bond region (see Fig. 6) and hence the kinetic energy opposes bond formation (see T_u of Fig. 7).

The resulting total energies are given in Fig. 2, where we see that φ_g is strongly bonding while φ_u is strongly antibonding.

2.1.2 Bonding to p Orbitals

Above we found that it is the ***change*** in the kinetic energy that dominates the energy changes in the LCAO description. Basically, if two atomic orbitals are superimposed so that no new nodal planes are created, as in Fig. 8a, then the kinetic energy drops significantly due to

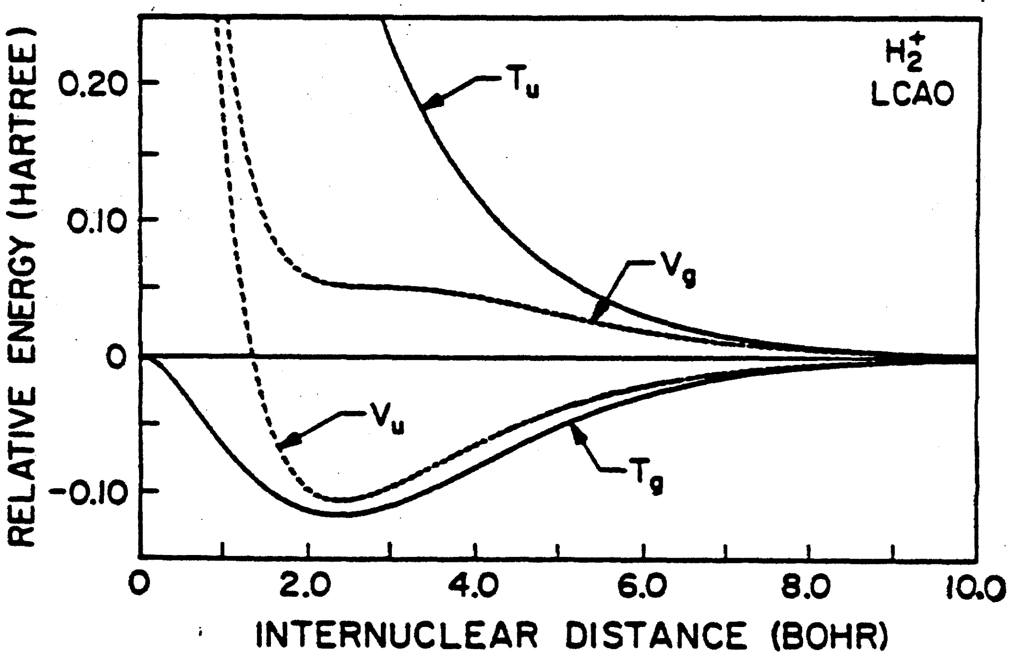

Figure 2-7. The changes in the total kinetic and potential energies for the g and u LCAO wavefunctions of H_2^+. The actual values at $R = \infty$ are $T_u(\infty) = T_g(\infty) = +\frac{1}{2}$ and $V_u(\infty) = V_g(\infty) = -1$.

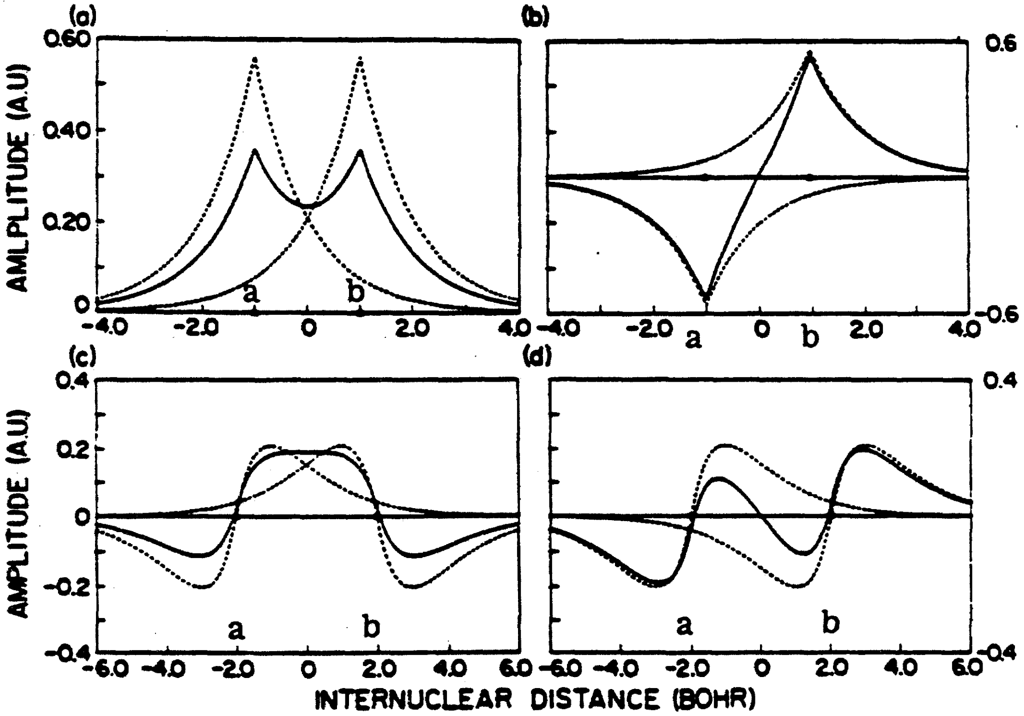

Figure 2-8. (a,b) Symmetric and antisymmetric superposition of 1s atomic orbitals. (c,d) Symmetric and antisymmetric superposition of $2p_x$ orbitals (oriented along the axis).

the decrease in the gradient of the orbital in the internuclear region. This is a general phenomenon and depends only on the fact that in the bond region the gradients of the atomic orbitals are in opposite directions **(contragradient)** so that (symmetric) superposition of the orbitals leads to a decrease in the gradients.

Conversely, superposition of orbitals so as to lead to a new nodal plane, as in Fig. 8b, gives rise to much steeper gradients and a much larger kinetic energy, leading to antibonding potential curves.

These results are not limited to superimposing 1s orbitals. Consider, for example, a bond between p_z orbitals on two atoms (assuming z to be the internuclear axis), as in Figure 9. The plus combination leads to a new nodal plane (higher gradients) and antibonding (see Fig. 8d), while the minus combination leads to lower grandients and bonding (see Fig. 8c). Similarly, bonding of the p_x orbitals leads to Figure 10. Now the minus combination leads to a new nodal plane and antibonding, while the plus combination leads to bonding.

2.1.3 The Optimum Distance for Bonds

There is a natural optimum range for the effects that dominate bonding:

i) If R is very large (near ∞), there is a large region in which the gradient is decreased; however, at each point, one or the other of the two orbitals has a very small gradient, so that the decrease in the gradient is very small (and goes to zero as $R \rightarrow \infty$). The result is a small bonding contribution for large R.

ii) If R is very small (near 0), there is a large decrease in the gradient; however, the region of this large decrease is only the small region between the nuclei (which goes to zero as $R \rightarrow 0$). [The latter effect is

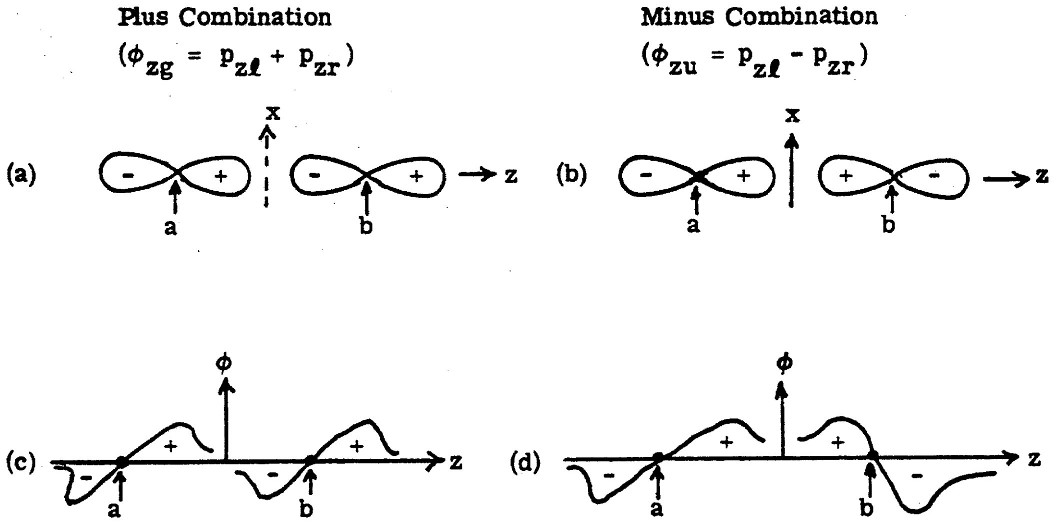

Figure 2-9. Bonding between p_z orbitals. (a) and (b) are schematic diagrams of the shape of the orbitals in the xz plane. (c) and (c) are plots of the orbitals along the z axis.

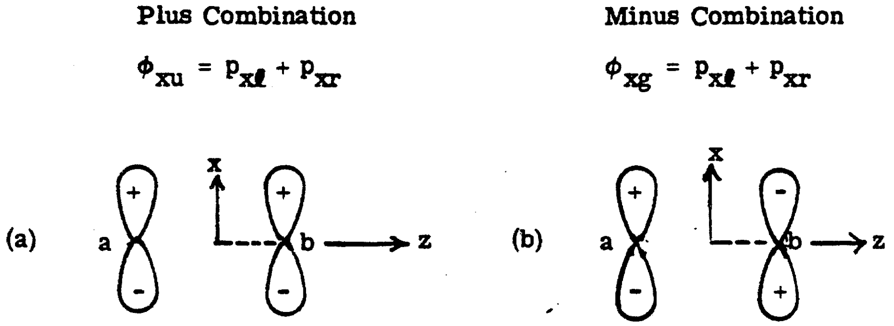

Figure 2-10. Bonding between p_x orbitals.

illustrated in Figure 11, where the left side is for R near optimum and the right side is for small R.]

Thus the optimum bond is formed at an intermediate distance where the gradients are large and opposite (contragradient) for a large region. For the hydrogen 1s orbital, the optimum distance is about $2a_0$, which is just the sum of the atomic radii. For a p orbital, the optimum decrease in the gradient occurs when the outer lobes are separated significantly, as illustrated in Fig. 11c.

2.1.4 Symmetry Considerations

The H_2^+ molecule has a great deal of symmetry. In quantum mechanics, symmetry in the molecule generally leads to symmetry in the wavefunction, and knowledge of these symmetries can aid us both in solving for the wavefunctions and in reasoning qualitatively about them. For the time being we will concern ourselves with only one of the symmetries in H_2^+, namely, the inversion symmetry.

2.1.4a The Hamiltonian

First we need to consider the form of the Hamiltonian for H_2^+. Using the coordinate system of Figure 1, the full Hamiltonian for H_2^+ is

$$\hat{H}(H_2^+) = -\frac{\hbar^2}{2M_a}\nabla_a^2 - \frac{\hbar^2}{2M_b}\nabla_b^2 - \frac{\hbar^2}{2m}\nabla_1^2 - \frac{Z_a e^2}{r_a} - \frac{Z_b e^2}{r_b} + \frac{Z_a Z_b e^2}{R} . \qquad (13)$$

We will simplify (13) by assuming the nuclear masses to be infinitely heavy ($M_a = M_b = \infty$), by taking the nuclear charges as unity (as appropriate for H_2^+) and by using atomic units ($\hbar = m = e = 1$). This reduces (13) to

$$\hat{H}(H_2^+) = -\tfrac{1}{2}\nabla_1^2 - \frac{1}{r_a} - \frac{1}{r_b} + \frac{1}{R} . \qquad (14)$$

We will group together all the terms depending upon the coordinates of

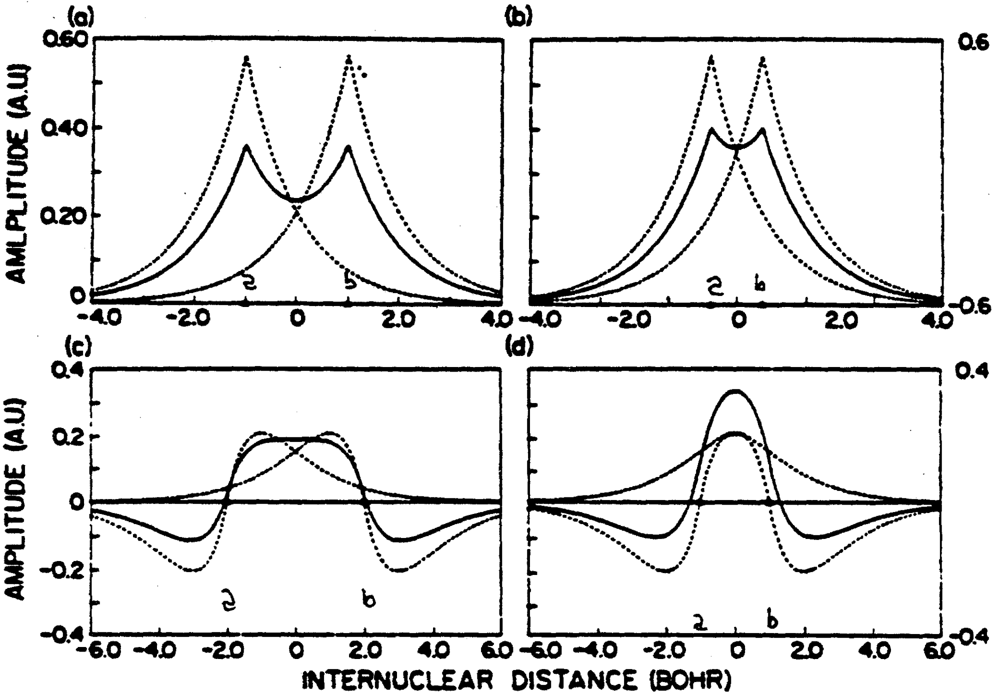

Figure 2-11. Illustration of the effect of R on the contragradience of orbitals. In each case the R for the left case is near optimum, while the R for the right case is too small.

one (and only one) electron as

$$h(1) = -\tfrac{1}{2}\nabla_1^2 + v(1) \tag{15}$$

(referred to as the **one-electron Hamiltonian**), where

$$v(1) = -\frac{1}{r_a} - \frac{1}{r_b} \tag{16}$$

is the **nuclear attraction term** (arising from the attractive electron-nuclear interactions). This leads to

$$\boxed{\hat{H}(H_2^+) = h(1) + \frac{1}{R}\,.} \tag{17}$$

The exact (electronic) wavefunction of H_2^+ is obtained by solving

$$\hat{H}\,\varphi(1) = E\,\varphi(1)\ , \tag{18}$$

where H is given by (17). Substituting (17) into (18) and rearranging, we obtain

$$h\varphi = \varepsilon\varphi\ , \tag{19}$$

where

$$\varepsilon = E - \frac{1}{R} \tag{20}$$

is referred to as the **electronic energy.** Although (19) may appear to involve only the electronic coordinates **r**, the internuclear coordinate R is involved implicitly since it determines the spacing of the attractive terms in v, (16). In solving for the wavefunction of H_2^+, we choose an R and solve (19) to obtain the electronic wavefunction $\varphi(\mathbf{r})$ and the electronic energy ε. We then choose a new R and again solve (17), obtaining a new $\varphi(\mathbf{r})$ and a new ε. The result is an electronic wavefunction $\varphi(\mathbf{r})$ and an electronic energy ε, each of which is parametrically dependent upon R. (This procedure is referred to as the **Born-Oppenheimer approximation.)**

2.1.4b *Inversion Symmetry*

The operation of **inversion** through the origin of a coordinate system leads to the changes

$$\begin{aligned} x &\rightarrow -x \\ y &\rightarrow -y \\ z &\rightarrow -z \end{aligned} \tag{21}$$

in the coordinates, and will be denoted as $\hat{I}$.

Taking the origin of the coordinate systems as the bond midpoint in Fig. 1, the inversion of the coordinates of the electron leads to Figure 12.

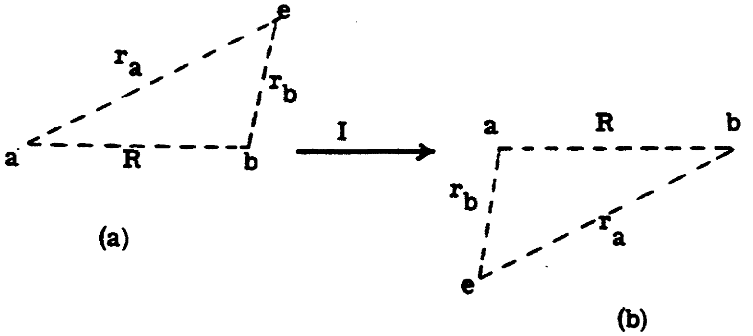

Figure 2-12. The effect of inverting the coordinates of the electron.

The electron is now r_a from the right nucleus (b) and r_b from the left nucleus (a). However, since the nuclear charges are the same, the potential terms in the Hamiltonian are the same.

Upon inversion, the kinetic energy terms in $\hat{H}$ are also unchanged

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \rightarrow \frac{\partial^2}{\partial (-x)^2} + \frac{\partial^2}{\partial (-y)^2} + \frac{\partial^2}{\partial (-z)^2} = \nabla^2 ,$$

and hence the Hamiltonian is invariant upon inversion of the electronic coordinate (through the bond midpoint).

Now consider that we have solved (18) to obtain eigenstates of H_2^+,

$$\hat{H}\varphi = E\varphi , \tag{22}$$

and apply $\hat{I}$ to both sides of (22). The result is

$$\hat{I}(\hat{H}\Phi) = E(\hat{I}\varphi) \ , \tag{23}$$

which we could write as

$$\hat{H}(-\mathbf{r})\,\varphi(-\mathbf{r}) = E\varphi(-\mathbf{r}) \ , \tag{24}$$

indicating the result of inversion. But $\hat{H}$ is invariant under $\hat{I}$

$$\hat{H}(-\mathbf{r}) = H(\mathbf{r}) \tag{25}$$

so that (24) becomes

$$\hat{H}(\mathbf{r})\varphi(-\mathbf{r}) = E\,\varphi(-\mathbf{r})$$

or

$$\hat{H}(\mathbf{r})\,(\hat{I}\varphi) = E(\hat{I}\varphi) \ . \tag{26}$$

Equations (22) and (26) state that φ and $\hat{I}\varphi$ are each eigenfunctions of exactly the same Hamiltonian with exactly the same energy. There are two possibilities here:

(i) The state is nondegenerate, in which case $I\varphi$ and φ must be proportional to each other, or

(ii) the state is degenerate, in which case $I\varphi$ and φ may be linearly independent* functions.

First we consider that the state is nondegenerate. In this case

$$\hat{I}\varphi = \lambda\varphi \ , \tag{27}$$

where λ is some constant. But, applying $\hat{I}$ twice leads to

$$\begin{aligned} x &\to x \\ y &\to y \\ z &\to z \ , \end{aligned}$$

---

* i.e., not proportional.

and thus must return the original function

$$\hat{I}^2\varphi(\mathbf{r}) = \hat{I}\varphi(-\mathbf{r}) = \varphi(\mathbf{r}) \ , \tag{28}$$

whereas applying $\hat{I}$ to (27) leads to

$$\hat{I}^2\varphi = \lambda\hat{I}\varphi$$

and using (27) on the right side leads to

$$\hat{I}^2\varphi = \lambda^2\varphi \ . \tag{29}$$

Combining (28) and (29) leads to

$$\varphi(r) = \lambda^2\varphi(r)$$

or

$$\lambda^2 = 1$$

leading to

$$\lambda = \pm 1 \ .$$

That is, nondegenerate states of H_2^+ *must be* either *symmetric* under inversion ($\lambda = +1$) or *antisymmetric* ($\lambda = -1$). Wavefunctions with these symmetries are denoted with g (for *gerade* or even in German) or u (for *ungerade* or uneven), as in φ_g or φ_u.

Consider now the case (ii) of a degenerate state with $\hat{I}\varphi$ *not* proportional to φ. We can form two new functions,

$$\varphi_g \equiv \varphi + \hat{I}\varphi$$

$$\varphi_u \equiv \varphi - \hat{I}\varphi$$

such that each function is still an eigenfunction of H (with the same energy) $H\varphi_g = E\varphi_g$, $H\varphi_u = E\varphi_u$ but such that one function is gerade

$$\hat{I}\varphi_g = \varphi_g \ ,$$

while the other is ungerade

$$\hat{I}\varphi_u = -\varphi_u \ .$$

Thus, in this case also the eigenfunctions of *H* are g or u.[†]

The same procedure can be used for higher degeneracies, and hence the conclusion is that for any $\hat{H}$ ***invariant under inversion, each eigenstate can be taken as either g or u.*** Examples are given in Figures 8, 9, and 10.

2.1.4c The Nodal Theorem

An ungerade wavefunction for H_2^+ necessarily must change sign at the plane passing through the bond midpoint. Consequently, from the nodal theorem we know that ***the ground state of*** H_2^+ ***will be a g state.***[*]

2.1.5 The Exchange Energy

There is a direct relationship between the bonding observed in φ_g and the antibonding observed in φ_u, both being dominated by changes in kinetic energy as the bond is formed. We will now obtain an explicit form for this relationship.

2.1.5a The Classical Energy

Consider first the wavefunction for H_2^+ with no superimposition of atomic orbitals,

$$\varphi^{cl} = \chi_l \ . \tag{30}$$

We refer to this as the **classical** wavefunction because it does not have

---

[†] If a certain state is doubly-degenerate with wavefunctions φ_a and φ_b, then starting with just one function, say φ_a, we generate both a g function and a u function, $\varphi_{ga} = \varphi_a + I\varphi_a$ and $\varphi_{ua} = \varphi_a - I\varphi_a$. If these functions are both nonzero, then φ_b will be a linear combination of φ_{ga} and φ_{ua}, and nothing need be done with it. However, if φ_a were already g or u, then φ_b is needed to generate the second function.

[*] Since there is no singularity at the nodal point, the inequality in the nodal theory applies, resulting in $E_g < E_u$. However, for $R = \infty$, even the u wavefunction is zero at the midpoint, and hence the lowest g and u states are degenerate.

interference effects arising from superposition of atomic orbitals. The energy of this wavefunction,

$$\varepsilon^{cl} ,$$

is nonbonding, as shown in Figure 13. Using (17) we obtain

$$\varepsilon^{cl} = \langle\chi_l\,|H|\,\chi_l\rangle = \left\langle \chi_l \left| -\tfrac{1}{2}\nabla^2 - \frac{1}{r_a} - \frac{1}{r_b} \right| \chi_l \right\rangle \tag{31}$$

$$= \varepsilon_{\text{atom}} + \left\langle \chi_l \left| -\frac{1}{r_b} \right| \chi_l \right\rangle ,$$

where

$$\varepsilon_{\text{atom}} = \left\langle \chi_l \left| -\tfrac{1}{2}\nabla^2 - \frac{1}{r_a} \right| \chi_l \right\rangle = -\tfrac{1}{2}(e^2/a_0) . \tag{32}$$

Thus

$$\varepsilon^{cl} = \varepsilon_{\text{atom}} + \delta\bar{V}^{cl} , \tag{33}$$

where

$$\delta\bar{V}^{cl} = \left[\left\langle \chi_l^2 \left(-\frac{e^2}{r_b} \right) \right\rangle + \frac{e^2}{R} \right] \tag{34}$$

is repulsive.

2.1.5b *The Exchange Energy*

Now we consider the wavefunction φ_g with energy

$$\varepsilon_g = \frac{\langle l + r|H|l + r\rangle}{\langle l + r|l + r\rangle}$$

$$= \frac{\langle l\,|H|\,l + r\rangle}{\langle l\,|\,l + r\rangle} . \tag{35}$$

Since

$$\langle l\,|\hat{H}|\,l + r\rangle = \langle l\,|\hat{H}|\,l\rangle + \langle l\,|\hat{H}|\,r\rangle$$

$$= \varepsilon^{cl} + \langle l\,|\hat{H}|\,r\rangle$$

$$\langle l\,|\,l + r\rangle = \langle l\,|\,l\rangle + \langle l\,|\,r\rangle = 1 + S ,$$

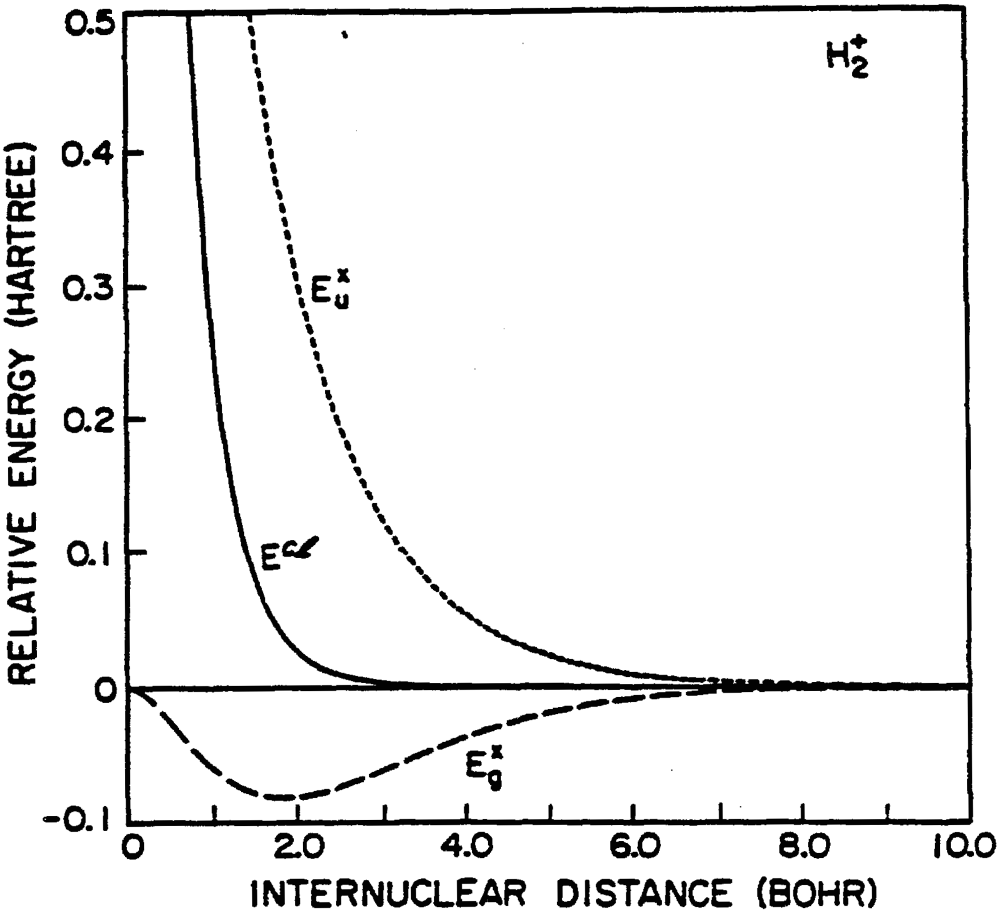

Figure 2-13. The classical energy and the exchange energies for the LCAO wavefunctions H_2^+.

we obtain

$$\varepsilon_g = \frac{\varepsilon^{cl} + \langle l|\hat{H}|r\rangle}{1+S} = \varepsilon^{cl} + \frac{\langle l|\hat{H}|r\rangle - \varepsilon^{cl}S}{1+S}$$

$$\boxed{\varepsilon_g = \varepsilon^{cl} + \frac{\tau}{1+S} ,} \qquad (36)$$

where

$$\tau = \langle l|H|r\rangle - S\varepsilon^{cl}$$

$$= \left[h_{lr} + S\frac{1}{R}\right] - S\left[h_{ll} + \frac{1}{R}\right]$$

or

$$\boxed{\tau = h_{lr} - S\,h_{ll} \ .} \qquad (37)$$

Similarly,

$$\varepsilon_u = \frac{\langle l-r|H|l-r\rangle}{\langle l-r|l-r\rangle} = \frac{\langle l|H|l-r\rangle}{\langle l|l-r\rangle}$$

$$= \frac{\varepsilon^{cl} - \langle l|H|r\rangle}{1-S}$$

or

$$\boxed{\varepsilon_u = \varepsilon^{cl} - \frac{\tau}{1-S} ,} \qquad (38)$$

where τ is again given by (37). Thus the interference resulting from superimposing the χ_l and χ_r wavefunctions can be viewed as corrections upon the classical energy,

$$\boxed{\begin{aligned} \varepsilon_g &= \varepsilon^{cl} + \varepsilon_g^x \\ \varepsilon_u &= \varepsilon^{cl} + \varepsilon_u^x \ , \end{aligned}} \qquad (39)$$

where the correction terms

$$\varepsilon_g^x = \frac{\tau}{1+S} \qquad (40)$$

$$\boxed{\varepsilon_u^x = \frac{-\tau}{1-S}}$$

are referred to as interference, *exchange*, or resonance terms. These energies are shown in Figure 13, where we see that ε_g^x favors bond formation, while ε_u^x opposes bond formation.

The *classical energy*, as defined above, is *the total energy of the system if the wavefunction is forced to remain an atomic orbital as R is decreased.* The *exchange part* of the energy *is the change in the energy due to the interference* of χ_l and χ_r, that is, due to exchange of the electron between the left and right centers. As shown in Figure 12, ε^{cl} is weakly antibonding, and hence bonding in the g state of H_2^+ results from the exchange energy ε_g^x. On the other hand, the exchange term ε_u^X for the u state is strongly repulsive, resulting in a strongly antibonding potential curve.

These quantities ε_g^x and ε_u^x constitute a quantitative representation of the effects discussed qualitatively in §2.1.1. Thus, the decrease in *kinetic energy* for the g states resulting from the decrease in the average gradient in the wavefunction yields a large *negative contribution* to τ. The increase in the *potential energy* for the g state arising from the shift of charge from the nuclear to the bond region yields a *positive contribution* to τ. The net result is a *negative* τ, leading to a negative value for

$$\varepsilon_g^x = \tau / (1 + s)$$

and a positive value for

$$\varepsilon_u^x = -\tau / (1 - S) .$$

2.1.5c Comparison of g and u States

For *large R*, where the overlap S is nearly zero, we see that (40) leads to

$$\begin{aligned} \varepsilon_g^x &= \tau \\ \varepsilon_u^x &= -\tau \ , \end{aligned}$$

so that the bonding in the g state and the antibonding in the u state are equal.

However, for *small R* the (1 + S) and (1 - S) terms lead to asymmetry, where the antibonding state is several times more antibonding than the bonding state is bonding. Thus, at $R = 2.5a_0 = 1.32$ Å , we have

$$\begin{aligned} S &= 0.4583 \\ \tau &= -0.1083 \ (e^2/a_0) \ , \end{aligned}$$

leading to

$$\begin{aligned} \varepsilon_g^x &= -0.0743 \ (e^2/a_0) \\ \varepsilon_u^x &= +0.20939 \ (e^2/a_0) \ , \end{aligned}$$

whereas

$$\varepsilon^{cl} = 0.00943 \ (e^2/a_0) \ .$$

2.1.5d Analytic Results

Explicit evaluation of the various quantities involved in the energy of H_2^+ is carried out in Appendix A, leading to

$$S = [1 + R + \frac{1}{3}R^2] \, e^{-R} \tag{41}$$

$$\varepsilon^{cl} = -\tfrac{1}{2} + (1 + \frac{1}{R}) \, e^{-2R}$$

$$\begin{aligned} \tau &= -\left[\frac{2}{3}R - \frac{1}{R}\right] e^{-R} - (1 + \frac{1}{r})(1 + R + \frac{1}{3}R^2) \, e^{-3R} \\ &\cong -\left[\frac{2}{3}R - \frac{1}{R}\right] e^{-R} \ , \end{aligned}$$

where terms of order e^{-3R} are neglected. Thus for large R

$$\tau \approx -\frac{2}{R} S \ . \tag{42}$$

That is, *the quantity* τ *dominating the bond in* H_2^+ *is proportional to the overlap between the orbitals*. At large R, this leads to a bond strength of the form

$$\tau \approx -\frac{2}{3} R\, e^{-R} \ ; \tag{43}$$

thus the bond energy decreases exponentially with internuclear distance.

This simple relation between bonding does *not* hold for small R. We saw above that τ is a minimum (most negative) at $R = 2a_0$, and the total energy is also a minimum (bonding a maximum) around $R = 2a_0$. On the other hand, the overlap continues to increase as R is decreased until $S = 1$ at $R = 0$.

2.1.5e *Contragradience*

The above discussions indicate that the interference or exchange part of the kinetic energy dominates the bonding in H_2^+. This term is dominated by

$$t^x = \tfrac{1}{2}[<(\nabla\chi_l) + (\nabla\chi_r)> - S<(\nabla\chi_l)^2>] \ , \tag{44}$$

which is large and negative in between the atoms. The region of space leading to negative $\nabla\chi_l \cdot \nabla\chi_r$ (and hence dominating the bond) is indicated for H_2 in Figure 14.

2.1.5f *Historical Development*

H. Hellmann [after escaping from Hitler Germany into Russia in ~1934 and before suddenly vanishing into Stalin Russia around 1937] was the first[*Z. Physik*, **85**, 180 (1933)] to suggest that bonding arises essentially from a decrease in kinetic energy. He suggested that the bond in H_2^+ results basically because the electron is allowed to delocalize over the

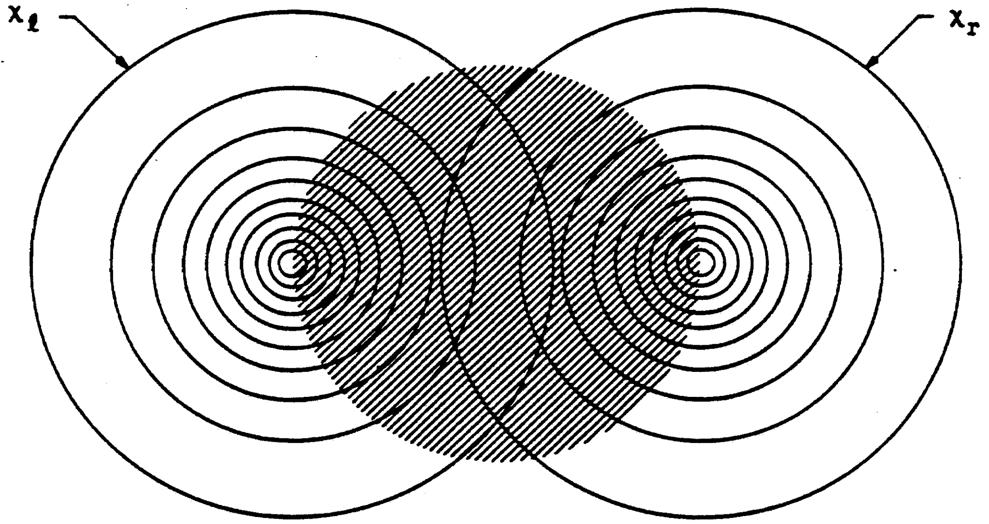

Figure 2-14. Contour plots of two hydrogen atomic orbitals for $R = 2a_0$ (contour increment 0.05 a.u.). The shaded region leads to negative values of $\nabla\chi_l \cdot \nabla\chi_r$ and hence to large contragradience. As a result, this region dominates the bonding.

region spanning two protons rather than just one. Using the uncertainty principle, he reasoned that a bigger "box" for the electron leads to a lower kinetic energy. Essentially the idea is as illustrated in Figure 15, where we see that for the φ_g state the electron is distributed over a larger volume in H_2^+ than in H atom. From the study of a particle-in-a-box, we know that the kinetic energy decreases as the box is made larger. Hence, because of a decrease in kinetic energy, the φ_g state is expected to be stabilized with respect to H atoms.

On the other hand, since the φ_u state has a node in the middle, the energy is just the same as if we had put the electron in either of two boxes, each of which is smaller than for H atom. This leads to an increase in the kinetic energy.

Hellmann presented only very simple qualitative ideas and his view of bonding was largely ignored until Klaus Ruedenberg [*Rev. Mod. Phys.*, **34,** 326 (1962)] provided a more quantitative framework, showing (for specific cases) that interference terms resulting from the superposition of amplitudes leads to a significant decrease in the kinetic energy. Indeed, most workers before Ruedenberg argued that the bonding results from electrostatic interactions arising from increasing the density in the bond region. The development in this chapter is derived from a series of papers by C. W. Wilson, Jr., and W. A. Goddard III [*Chem. Phys. Lett.*, **5,** 45 (1970); *Theor. Chim. Acta*, **26,** 195, 211 (1972)]. Other somewhat related viewpoints have also been proposed: M. J. Feinberg and K. Ruedenberg, *J. Chem. Phys.*, **54,** 1495 (1971); M. J. Feinberg, K. Ruedenberg, and E. L. Mehler, *Advan. Quant. Chem.*, **5,** 28 (1970); R. F. Bader and A. D. Baudraut, *J. Chem. Phys.*, **49,** 1653 (1968).

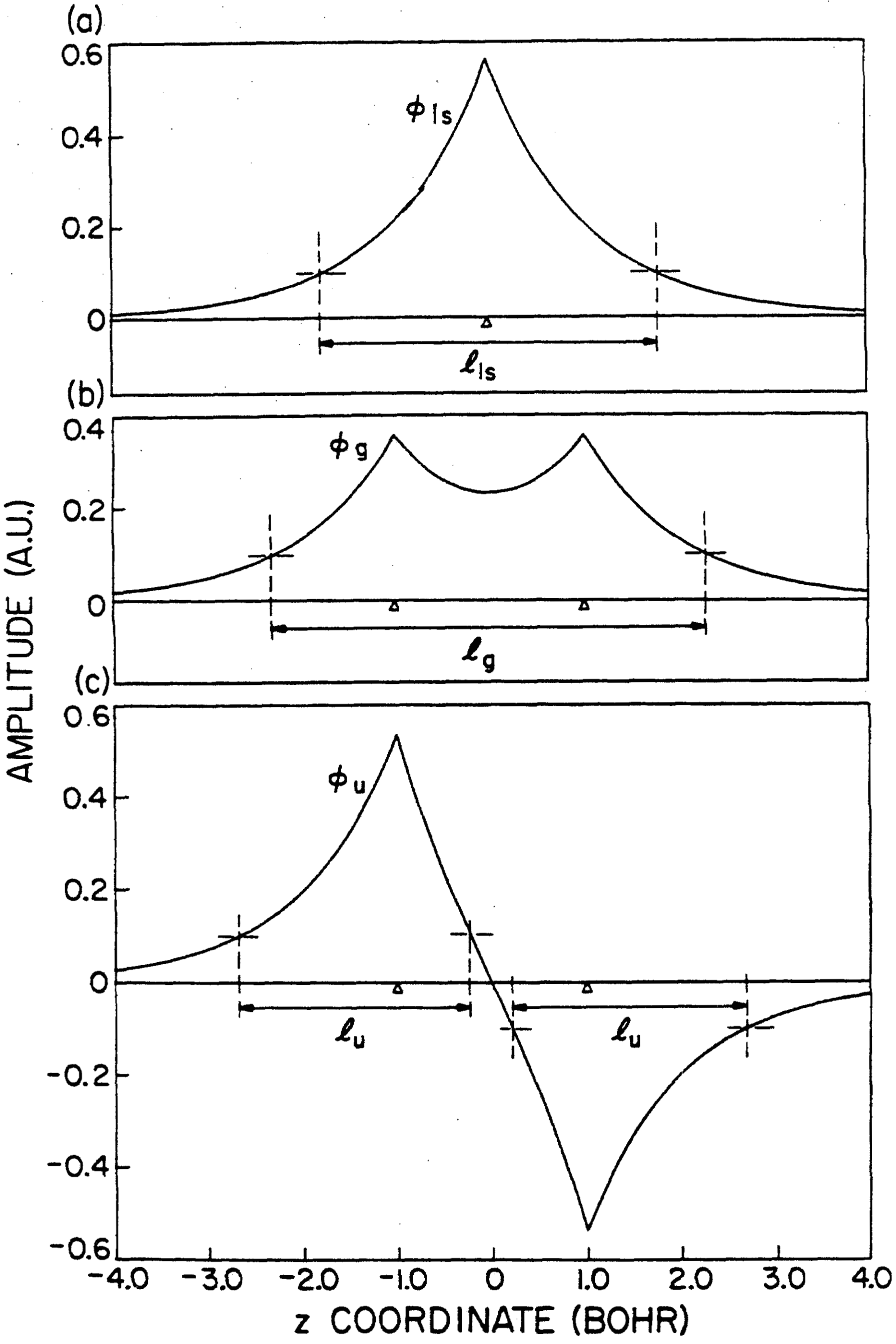

Figure 2-15. Illustration of the differences in the effective size of the box for the electron in the hydrogen atom and in the g and u states of H_2^+.

2.2 The Molecular Orbital Description of H_2

We will now add a second electron to H_2^+ to obtain the H_2 molecule. The simplest wavefunction for H_2 is to start with an electron in the best molecular orbital of H_2^+ and to place a second electron in this φ_g orbital. This leads to the **molecular orbital** (MO) wavefunction for H_2,

$$\Phi_{gg}^{MO}(\mathbf{r}_1,\mathbf{r}_2) = \varphi_g(\mathbf{r}_1)\varphi_g(\mathbf{r}_2) \tag{1}$$

where

$$\varphi_g = (\chi_l + \chi_r)/D_g \ , \tag{2a}$$

and

$$D_g = \sqrt{2(1+S)} \ . \tag{2b}$$

With two electrons, the total wavefunction $\Phi(\mathbf{r}_1,\mathbf{r}_2)$ must specify the probability amplitude for electron 1 to have each possible value of its three coordinates (x_1, y_1, and z_1, symbolized collectively as $\mathbf{r}_1$), and for electron 2 to have each possible value of its three coordinates (x_2, y_2, and z_2, symbolized collectively as $\mathbf{r}_2$). Thus, the wavefunction must be specified for all six simultaneous components of $\mathbf{r}_1$ and $\mathbf{r}_2$ as in (1).

First we will examine the meaning of the wavefunction (1). The total probability for electron 1 to be at some position $\mathbf{r}_1$, while electron 2 is simultaneously at some position $\mathbf{r}_2$ is

$$P(\mathbf{r}_1,\mathbf{r}_2) = |\Phi^{MO}(\mathbf{r}_1,\mathbf{r}_2)|^2 = |\varphi_g(\mathbf{r}_1)|^2\,|\varphi_g(\mathbf{r}_2)|^2 = P_g(\mathbf{r}_1)P_g(\mathbf{r}_2) \ . \tag{3}$$

This is just the product of the independent probabilities for electron 1 to be at position $\mathbf{r}_1$ and electron 2 to be at position $\mathbf{r}_2$. Thus, the probability distribution for electron 1 is independent of electron 2.* Summarizing, *a product wavefunction* as in (1) implies that the *electrons move independently* of each other (no correlations in their motions) and vice versa.

---

* Consider the analogous case of a red die (electron 1) and a green die (electron

In addition to using the φ_g MO as in (2), we can construct wavefunctions of H_2 using the φ_u MO,

$$\varphi_u = (\chi_l - \chi_r) / \sqrt{2(1-S)} \ . \tag{4}$$

This leads to wavefunctions of the form

$$\Phi_{ug}(1,2) = \varphi_u(1)\varphi_g(2) \tag{5}$$

$$\Phi_{gu}(1,2) = \varphi_g(1)\varphi_u(2) \tag{6}$$

$$\Phi_{uu}(1,2) = \varphi_u(1)\varphi_u(2) \ . \tag{7}$$

Since the φ_u orbital is antibonding, the above wavefunctions of H_2 lead to much higher energies than (1) (except at large R), and we expect an energy level diagram as in Figure 16.

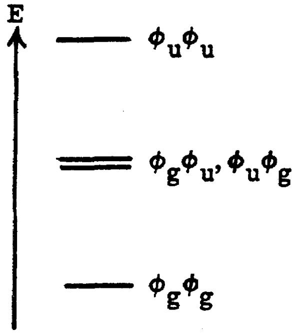

Figure 2-16. Simple energy diagram for MO wavefunctions of H_2.

2.2.1 Energies

For H_2 we use the coordinate system of Figure 17.

---

2). The probability of rolling a red 3 is 1/6 and the probability of rolling a green 5 is 1/6 so that the total probability of getting both a red 3 *and* a green 5 is $\frac{1}{6} \times \frac{1}{6} = \frac{1}{36}$. The dice are independent so that the probabilities multiply.

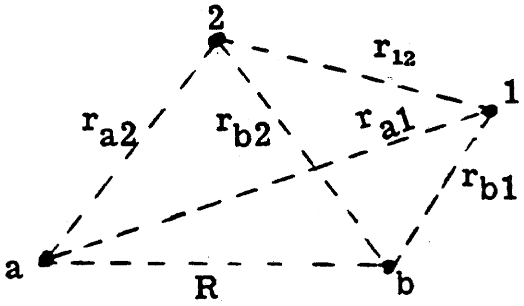

Figure 2-17. Coordinates for H_2.

Using the same conventions and assumptions as for H_2^+ leads to the Hamiltonian

$$\hat{H}(H_2) = h(1) + h(2) + \frac{1}{r_{12}} + \frac{1}{R}, \qquad (8)$$

where $\frac{1}{r_{12}}$ is the Coulomb interaction between the two electrons, and where

$$h(i) = -\tfrac{1}{2}\nabla_i^2 - \frac{1}{r_{ai}} - \frac{1}{r_{bi}} \qquad (9)$$

contains all terms depending only upon the coordinates of electron i.

Consider now the energy of a product wavefunction

$$\Phi_{ab}(1,2) = \varphi_a(1)\varphi_b(2) \qquad (10)$$

and note that many two-electron integrals factor into products of one-electron integrals, e.g.,*

$$\begin{aligned} \langle\Phi_{ab}(1,2)|h(2)|\Phi_{ab}(1,2)\rangle &= \int\int d^3r_1 d^3r_2 \varphi_a{}^*(1)\varphi_b{}^*(2)h(2)\varphi_a(1)\varphi_b(2) \\ &= [\int d^3r_1\varphi_a{}^*(1)\varphi_a(1)]\,[\int d^3r_2\varphi_b{}^*(2)h(2)\varphi_b(2)] \\ &= \langle\varphi_a|\varphi_a\rangle\,\langle\varphi_b|h|\varphi_b\rangle \qquad (11) \end{aligned}$$

---

* Note that the < > notation implies integration over however many electrons are in the wavefunction.

$$= \langle \varphi_b | h | \varphi_b \rangle$$

since $\langle \varphi_a | \varphi_a \rangle = 1$. In order to simplify the energy expressions, we will define

$$h_{ij} \equiv \langle \varphi_i | h | \varphi_j \rangle \ . \tag{12}$$

The integral that does not factor is the one arising from the $1/r_{12}$ terms in the Hamiltonian, which we will denote as

$$J_{ij} = \left\langle \Phi_{ij}(1,2) \left| \frac{1}{r_{12}} \right| \Phi_{ij}(1,2) \right\rangle = \iint d^3r_1 d^3r_2 \, \frac{\varphi_i^*(1)\varphi_i(1)\varphi_j^*(2)\varphi_j(2)}{r_{12}} \ . \tag{13}$$

Note that

$$\rho_i(1) = \varphi_i^*(1)\varphi_i(1) \tag{14a}$$

is the probablity density for finding the electron in orbital i at position $\mathbf{r}_1$, and

$$\rho_j(2) = \varphi_j^*(2)\varphi_j(2) \tag{14b}$$

is the probability density for finding the electron in orbital j at position $\mathbf{r}_2$. Thus we can rewrite (13) as

$$J_{ij} = \iint d^3r_1 d^3r_2 \, \frac{\rho_i(1)\rho_j(2)}{r_{12}} \ . \tag{15}$$

But (15) is just the classical electrostatic interaction energy (the Coulomb energy) between the two charge distributions ρ_i and ρ_j. Thus we refer to J_{ij} as the **Coulomb integral** between orbitals φ_i and φ_j. This term cannot be factored into a product of one-electron terms because of the

$$r_{12} = \sqrt{(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2}$$

term.

Since ρ_i, ρ_j, and $\frac{1}{r_{ij}}$ are always positive, we see that the Coulomb integral is always positive

$$J_{ij} \geq 0 \ . \tag{16}$$

Using the above results we can write

$$E_{gg} = 2h_{gg} + J_{gg} + \frac{1}{R} \tag{17}$$

$$E_{gu} = h_{uu} + h_{gg} + J_{gu} + \frac{1}{R} \tag{18}$$

$$E_{ug} = E_{gu} \tag{19}$$

$$E_{uu} = 2h_{uu} + J_{uu} + \frac{1}{R} \ . \tag{20}$$

For $R = 2a_0 = 1.06$ Å (the R_e for H_2^+), the MO wavefunctions lead to

$h_{gg} =$

(21)

$h_{uu} =$

$J_{gu} =$

$J_{uu} =$ (22)

$J_{uu} =$

$\frac{1}{r} =$

resulting in

$E_{gg} =$

$E_{ug} = E_{gu} =$ (23)

$E_{uu} =$

Thus the MO states are ordered as in Fig. 16. Note here that the Coulomb interactions are not negligible, but nonetheless, overall ordering of states can be predicted solely from considering the one-electron terms.

2.2.2 Symmetries

Before proceeding further in the discussion of H_2, we will examine how symmetry can help us in sorting out the states.

2.2.2a Inversion

Starting with the configuration of particles in Figure 17 and inverting* the coordinates of electron 1 leads to Figure 18a,

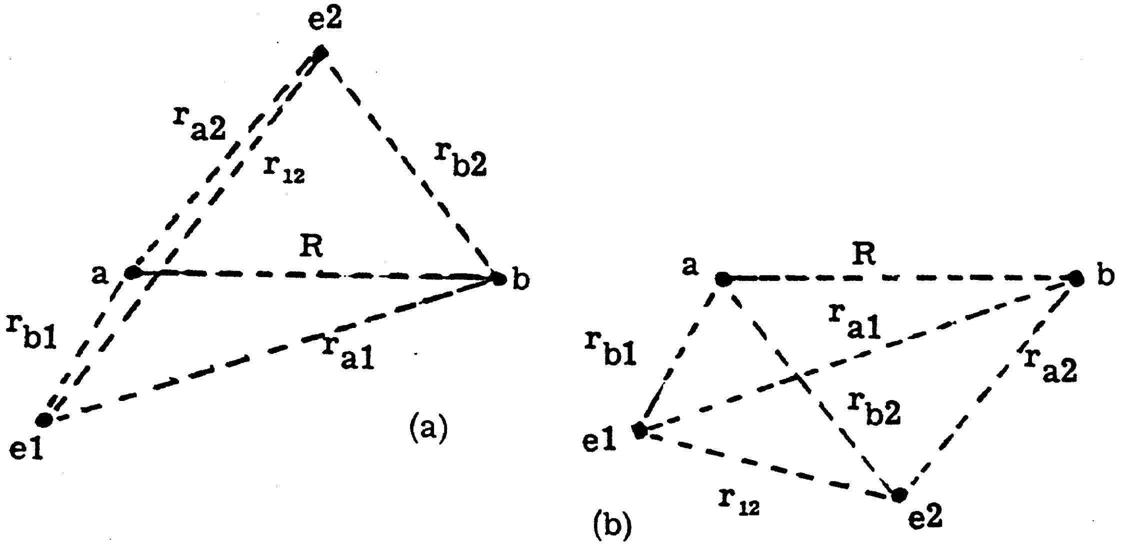

Figure 2-18.

with electron 1 at a distance of r_{b1} from nucleus a and r_{a1} from b). Just as for H_2^+, this does not change the nuclear attraction terms if the nuclei have identical charges. Even so, the total potential energy is changed since the distance between electrons 1 and 2 is changed. Thus, in order to preserve the same potential energy, we must **simultaneously invert** the coordinates of **both electrons,** leading to Figure 18. Thus we define the **inversion operator,** $\hat{I}$, for H_2 as

---

* Recall that the center of inversion is the bond midpoint.

$$\begin{array}{ccc} x_1 \rightarrow -x_1 & & x_2 \rightarrow -x_2 \\ y_1 \rightarrow -y_1 & \text{and} & y_2 \rightarrow -y_2 \\ z_1 \rightarrow -z_1 & & z_2 \rightarrow -z_2 \end{array} \tag{24a}$$

or

$$\mathbf{r}_1 \rightarrow -\mathbf{r}_1 \quad \text{and} \quad \mathbf{r}_2 \rightarrow -\mathbf{r}_2 \ , \tag{24b}$$

and the total Hamiltonian is invariant under this inversion,

$$\hat{I}\hat{H}(\mathbf{r}_1,\mathbf{r}_2) = \hat{H}(-\mathbf{r}_1, -\mathbf{r}_2) = \hat{H}(\mathbf{r}_1, \mathbf{r}_2) \ . \tag{25}$$

The exact wavefunction for H_2 is obtained by solving

$$\hat{H}(1,2)\Phi(1,2) = E\,\Phi(1,2) \tag{26}$$

(don't panic; we won't try this yet). Since $\hat{H}(1,2)$ is invariant under the inversion $\hat{I}$ (25), we find that (26) implies

$$\hat{H}(I\Phi) = E(I\Phi) \tag{27}$$

and hence (just as for H_2^+), the exact eigenstates of H_2 are either g or u,

$$\begin{aligned} \hat{I}\Phi_g(1,2) &= +\,\Phi_g(1,2) \\ \hat{I}\Phi_u(1,2) &= -\,\Phi_u(1,2) \ . \end{aligned} \tag{28}$$

Applying the $\hat{I}$ operator to the MO wavefunctions (1), (5)-(7) leads to the conclusion that

$$\begin{gathered} \Phi_{gg} \text{ and } \Phi_{uu} \text{ are g states} \\ \text{and} \\ \Phi_{gu} \text{ and } \Phi_{ug} \text{ are u states.} \end{gathered} \tag{29}$$

Since a u wavefunction must always have a nodal plane, somewhere we expect the ground state of H_2 to be g, just as indicated by Figure 16.

2.2.2b Permutational Symmetry

The Hamiltonian for H_2 is unchanged if we renumber the electrons so that electron 1 becomes electron 2 and vice versa, that is,

$$\hat{H}(2,1) = \hat{H}(1,2) \ . \tag{30}$$

To discuss such symmetries we define the **transposition** operator τ_{12} as

$$\mathbf{r}_1 \rightarrow \mathbf{r}_2 \qquad \text{and} \qquad \mathbf{r}_2 \rightarrow \mathbf{r}_1 \ . \tag{31}$$

Thus, starting with the exact wavefunction (26), applying τ_{12} to both sides, and using (30), we find that

$$\hat{H}(\tau_{12}\Phi) = \mathrm{E}(\tau_{12}\Phi) \ . \tag{32}$$

Since $(\tau_{12})^2$ transposes the electrons twice, taking us back to the original starting point,

$$(\tau_{12})^{12} = \tau_{12}\tau_{12} = \mathrm{e} \tag{33}$$

[where e signifies doing nothing, i.e., the unity or einheit (German) operator], we can show (just as for inversion) that the exact eigenstates have the behavior

$$\begin{aligned} &\tau_{12}\Phi^{s}(1,2) = \Phi^{s}(2,1) = +\,\Phi^{s}(1,2) \\ &\text{or} \\ &\tau_{12}\Phi^{a}(1,2) = \Phi^{a}(2,1) = -\,\Phi^{a}(1,2) \end{aligned} \tag{33}$$

under transposition. Examining the wavefunctions (1), (5)-(7), we see that

$$\tau_{12}[\varphi_g(1)\varphi_g(2)] = [\varphi_g(1)\varphi_g(2)] \qquad \text{symmetric} \tag{35a}$$

$$\left.\begin{aligned} \tau_{12}[\varphi_g(1)\varphi_u(2)] &= [\varphi_u(1)\varphi_g(2)] \\ \tau_{12}[\varphi_u(1)\Phi_g(2)] &= [\varphi_g(1)\varphi_u(2)] \end{aligned}\right\} \quad \text{no symmetry}$$

$$\tau_{12}[\varphi_u(1)\varphi_u(2)] = [\varphi_u(1)\varphi_u(2)] \qquad \text{symmetric} \ . \tag{35b}$$

Thus the g states, Φ_{gg} and Φ_{uu}, have the proper permutational symmetry, but the u states, Φ_{gu} and Φ_{ug}, do not. In the next section we will fix up this problem with the u states.

2.2.2c The u States

Combining the u wavefunctions as follows*

$$^3\Phi_u = (\varphi_g\varphi_u - \varphi_u\varphi_g) \tag{36}$$

$$^1\Phi_u = (\varphi_g\varphi_u + \varphi_u\varphi_g) \tag{37}$$

leads to

$$\tau_{12}\,{}^3\Phi_u = (\varphi_u\varphi_g - \varphi_g\varphi_u) = -\,{}^3\Phi_u \tag{35c}$$

$$\tau_{12}\,{}^1\Phi_u = (\varphi_u\varphi_g + \varphi_g\varphi_u) = +\,\Phi_u \tag{35d}$$

so that the combinations (36) and (37) have proper permutational symmetry.

Now we must examine the physics ***behind*** the combinations (36) and (37). Aside from mathematical analyses indicating that the wavefunctions ***should*** have permutational symmetry, we also want to determine ***why*** one combination is favored in terms of achieving a lower energy.

In order to carry out such an analysis, we will plot the two-electron wavefunction for the case where both electrons 1 and 2 are along the bond axis (z). In order to show the relative locations of both electrons, we will let the z coordinate of electron 1 be the ordinate (z_1) and the z coordinate of electron 2 be the abscissa (z_2). This is indicated in Figure 19 where some special points are indicated.

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* The notation will become clear when we discuss spin in Chapter 4.

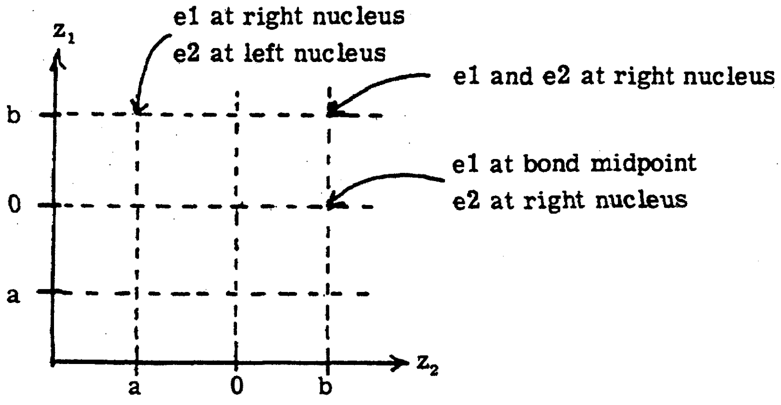
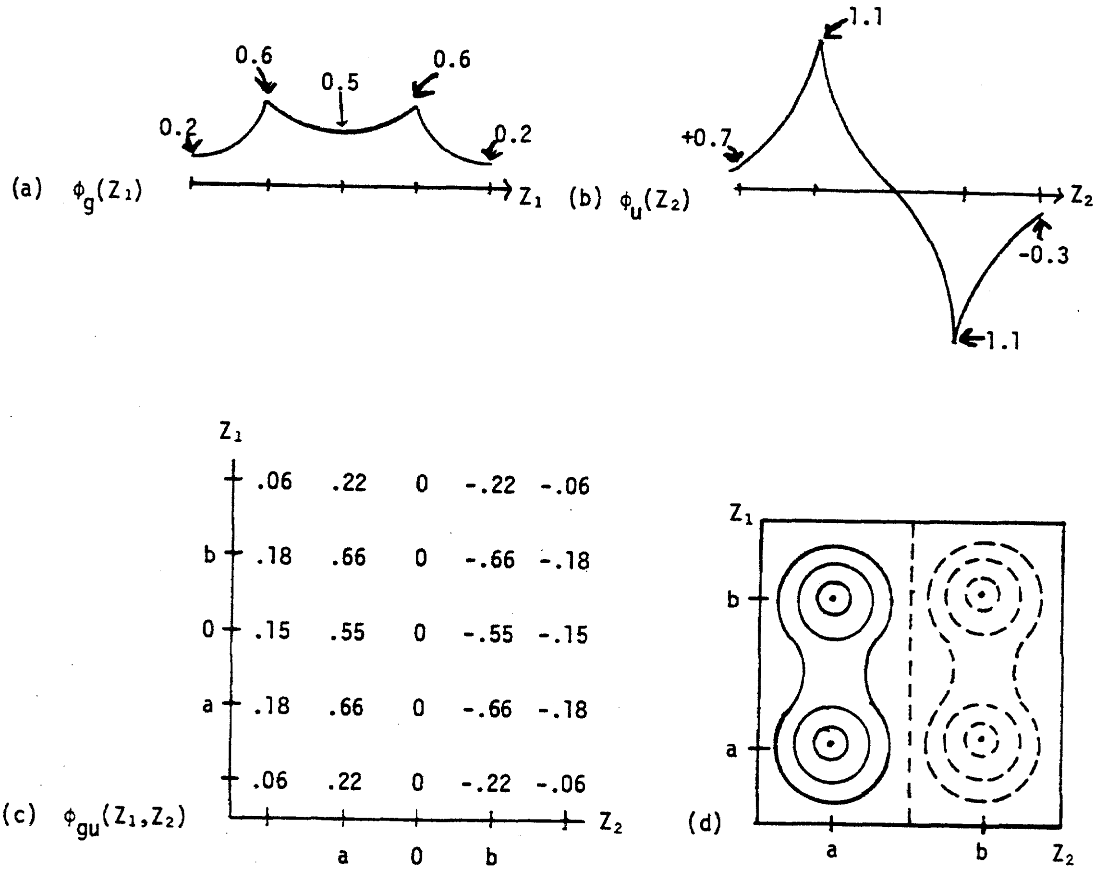


Figure 2-19. Coordinates showing simultaneous positions for z_1 and Z_1.

In order to see how to plot the wavefunction on Figure 19, consider the orbitals $\varphi_g(z_1)$ and $\varphi_u(z_2)$ in Figure 20ab.



		a	0	b	
	.06	.22	0	-.22	-.06
b	.18	.66	0	-.66	-.18
0	.15	.55	0	-.55	-.15
a	.18	.66	0	-.66	-.18
	.06	.22	0	-.22	-.06

Figure 2-20.

Multiplying these orbitals leads to the wavefunction $\Phi_{gu}(z_1, z_2)$ with amplitudes at various points, as given in Figure 20c. Rather than listing numbers as in Figure 20c, we will draw contours of equal amplitude as indicated in Figure 20d, where solid lines indicate positive amplitude, dotted lines indicate negative amplitude, and long dashes indicate zero amplitude. Here one sees that the maximum positive amplitudes occur for $z_2 = a$ and $z_1 = a$ or b, while the amplitude remains large or positive between the above two points. The maximum negative amplitude occurs for $z_2 = b$ and $z_1 = a$ or b and remains large between the above two points. For $z_2 = 0$, the total wavefunction is zero, independent of z_1. The reader should practice constructing fig. 20d directly from Figures 20a and 20b (without going through Fig. 20c).

In Figure 21 we compare the two-electron wavefunctions of Φ_{gu}, Φ_{ug}, ${}^3\Phi_u$, and ${}^1\Phi_u$. All cases involve a single nodal plane, and if there were no electron-electron interactions, all these wavefunctions would have the same total energy.* The difference lies in the electron-electron interactions. In Figure 21 e we see that the ${}^3\Phi_u$ wavefunction is zero along the line with $z_1 = z_2$, whereas in Figure 21f we see that the largest values (positive and negative) of ${}^1\Phi_u$ occur for $z_1 = z_2$. Since the electron repulsion term

$$\frac{e^2}{r_{12}}$$

is large and repulsive when the electrons are close, we see that ${}^3\Phi_u$ is favored and ${}^1\Phi_u$ is disfavored. Indeed, considering all possible combinations of Φ_{gu} and Φ_{ug}, the one with the lowest electron repulsion is just ${}^3\Phi_u$.

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* Note from (18) that both u states have the same total energy and that any combination of these states leads to the same one-electron energy, $h_{uu} + h_{gg}$.

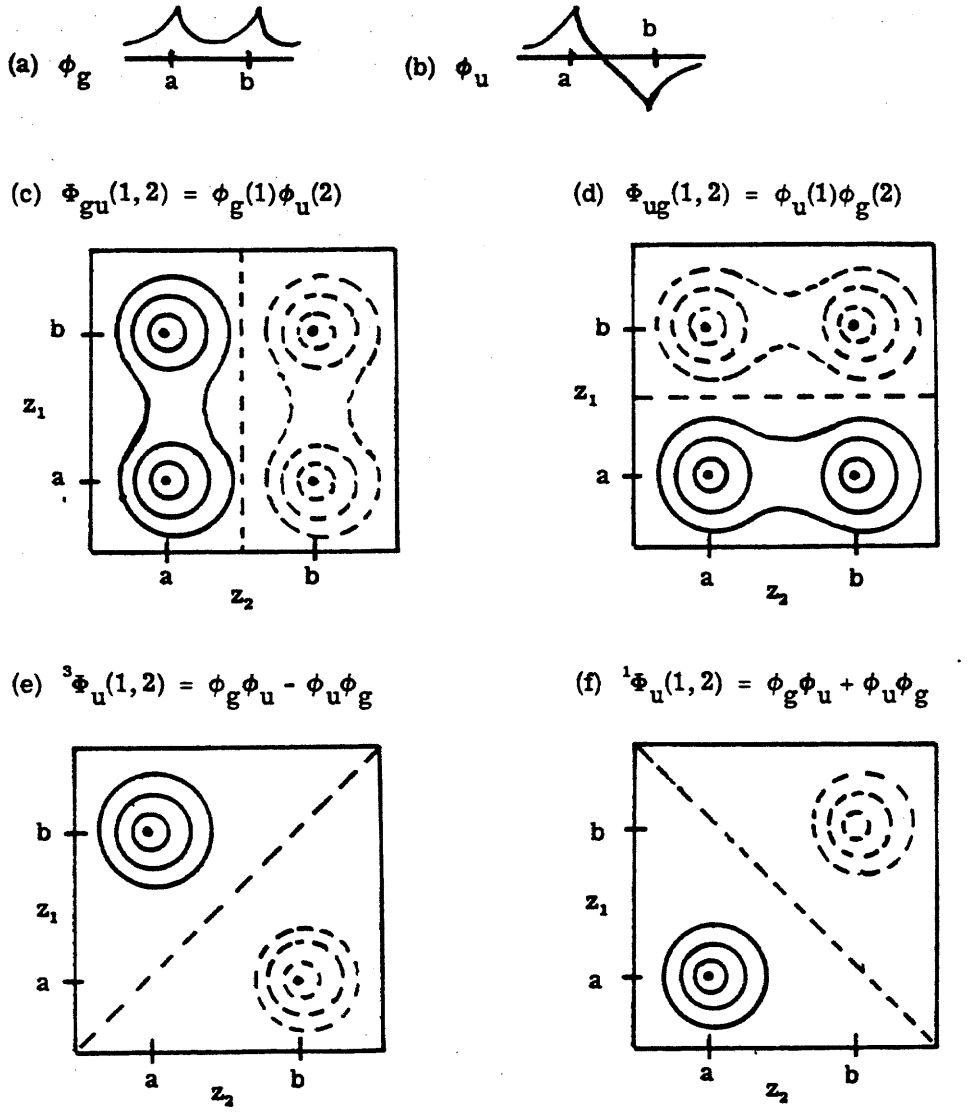
(a) ϕ_g
a
b
(b) ϕ_u
a
b
(c) $\Phi_{gu}(1,2) = \phi_g(1)\phi_u(2)$
(d) $\Phi_{ug}(1,2) = \phi_u(1)\phi_g(2)$
(e) ${}^3\Phi_u(1,2) = \phi_g\phi_u - \phi_u\phi_g$
(f) ${}^1\Phi_u(1,2) = \phi_g\phi_u + \phi_u\phi_g$
z_1
z_2
a
b

Figure 2-21.

Thus the energy diagram for the MO wavefunctions of H_2 becomes as in Figure 22.

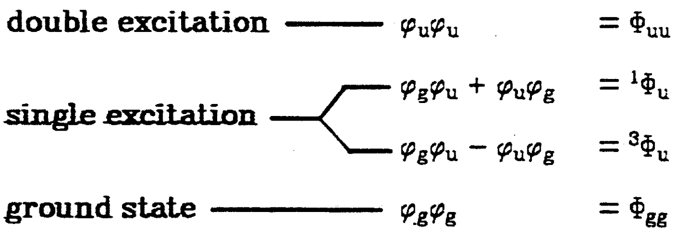

Figure 2-22.

2.2.2d Quantitative Aspects of the Energies for the u States

Now that we see the physics behind why the ${}^3\Phi_u$ wavefunction (36) is the best u state, we will examine the quantitative energy expression.

$$E({}^3\Phi_u) = \frac{\langle {}^3\Phi_u | H | {}^3\Phi_u \rangle}{\langle {}^3\Phi_u | H | {}^3\Phi_u \rangle} = \frac{\langle gu - ug | H | gu - ug \rangle}{\langle gu - ug | gu - ug \rangle}$$

$$= \frac{2\langle gu | H | gu - ug \rangle}{2\langle gu | gu - ug \rangle} = \frac{\langle gu | H | gu \rangle - \langle gu | H | ug \rangle}{\langle gu | gu \rangle - \langle gu | ug \rangle} \tag{38}$$

Since

$$\langle gu | ug \rangle = \langle g | u \rangle \langle u | g \rangle = 0$$

$$\langle gu | h(1) | ug \rangle = \langle g | h | u \rangle \langle u | g \rangle = 0$$

$$\langle gu | h(2) | ug \rangle = \langle g | u \rangle \langle u | h | g \rangle = 0 \ ,$$

we are left with

$$E({}^3\Phi_u) = E_{gu} - \langle gu | H | ug \rangle \ , \tag{39}$$

where

$$\langle gu | H | ug \rangle = \left\langle gu \middle| \frac{1}{r_{12}} \middle| ug \right\rangle$$

$$= \iint d^3r_1 d^3r_2 \, \frac{\varphi_g{}^*(1)\varphi_u(1)\varphi_u{}^*(2)\varphi_g(2)}{r_{12}} \equiv K_{gu} \ , \tag{40}$$

where this two-electron term is called the **exchange integral** between orbitals φ_g and φ_u. The net result is

$$\begin{aligned} E(^3\Phi_u) &= E_{gu} - K_{gu} \\ E(^1\Phi_u) &= E_{gu} + K_{gu} \; . \end{aligned} \tag{41}$$

Since the previous section showed that

$$E(^1\Phi_u) > E(^3\Phi_u) \; ,$$

we see that the exchange integral must be positive,

$$K_{gu} \geq 0 \; . \tag{42}$$

What is the physical significance of K_{gu}? It tells us how much the two-electron energy changes when we go from the wavefunctions in Figure 21 c or 21d to the wavefunctions in Figure 21e or 21f. Thus the K_{gu} is the quantitative representation of our earlier argument that $^3\Phi_u$ has a better two-electron energy than $^1\Phi_u$. It is better by precisely $2K_{gu}$.

Another way to look at this is to substitute (17) into (40), leading to

$$\begin{aligned} E(^3\Phi_u) &= [h_{gg} + h_{uu} + \frac{1}{R}] + [J_{gu} - K_{gu}] \\ E(^1\Phi_u) &= [h_{gg} + h_{uu} + \frac{1}{R}] + [J_{gu} + K_{gu}] \; . \end{aligned} \tag{43}$$

Here $J_{gu} - K_{gu}$ is the total two-electron energy of Figure 21f, while $J_{gu} + K_{gu}$ is the total two-electron energy of Figure 21e, and J_{gu} is the two-electron energy of Figure 21c and 21d. The two-electron energy of $^3\Phi_u$ can also be written as

$$J_{gu} - K_{gu} = \frac{\left\langle ^3\Phi_u \middle| \frac{1}{r_{12}} \middle| ^3\Phi_u \right\rangle}{\langle ^3\Phi_u | ^3\Phi_u \rangle} = \iint d^3r_1 d^3r_2 \, \frac{^3P_u(1,2)}{r_{12}} \; , \tag{44}$$

where*

---

* The $\frac{1}{2}$ comes from $\langle ^3\Phi_u | ^3\Phi_u \rangle = 2$.

$$^3P_u(1,2) = \frac{1}{2} {}^3\Phi_u{}^*(1,2)\, {}^3\Phi_u(1,2) .$$

Since ^3P_u is the absolute square of $^3\Phi_u$, it is positive for all possible values of r_1 and r_2. Since the integral in (44) is always positive, we see that the total two-electron energy of the $^3\Phi_u$ state must be positive

$$J_{gu} - K_{gu} \geq 0 , \tag{45}$$

and hence

$$J_{gu} \geq K_{gu} \tag{46}$$

the exchange integral is always less than the Coulomb integral. Combining (46) with (16) leads then to*

$$J_{gu} \geq K_{gu} \geq 0 . \tag{47}$$

2.2.3 Potential Curves

So far we have discussed the MO wavefunction assuming that the bonding orbital φ_g is much better than the antibonding orbital φ_u. This is true for shorter internuclear distances R but does not remain true as the bond is broken. Thus, in Figure 23 we compare the energy of the MO wavefunction Φ_{gg} with the exact energy for the ground state of H_2. This MO wavefunction leads to a good value for the bond length but a very bad description of the processes of breaking the bond.

The origin of this problem can be seen by substituting the atomic orbital describtion of the MO (2) into the MO wavefunction (1), leading to

$$\begin{aligned} \Phi_{gg}^{MO}(1,2) &= N[\chi_l\chi_l + \chi_r\chi_r + \chi_l\chi_r + \chi_r\chi_l] \\ &= \Phi_{covalent} + \Phi_{ionic} , \end{aligned} \tag{48}$$

where $N = [2(1 + S)]^{-1}$ and

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* This relation is true for any pairs of orbitals, as shown in Appendix 2-C.

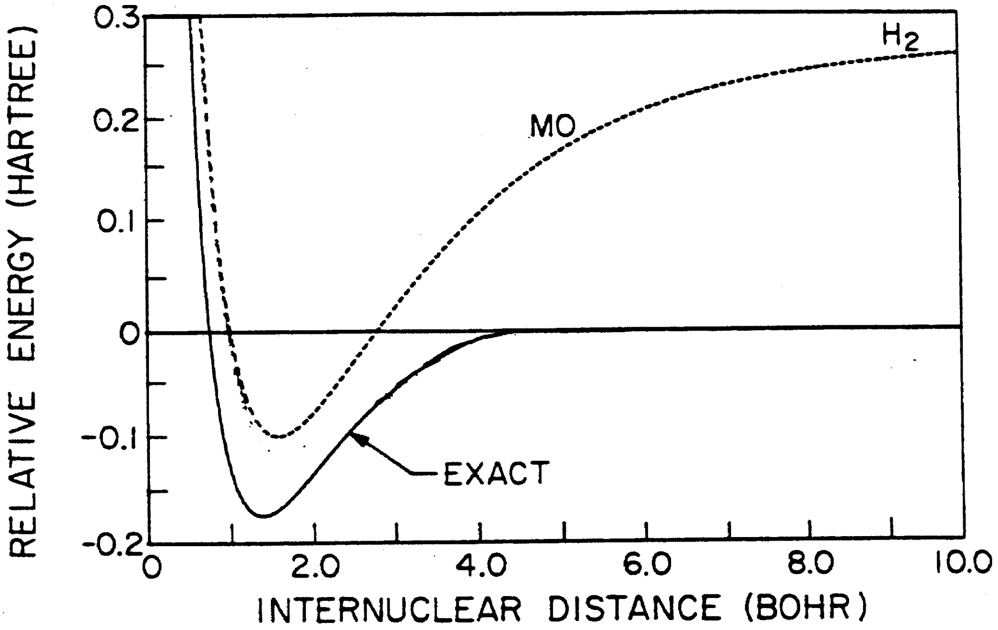


Figure 2-23. The energy of the MO wavefunction for the ground state of H_2 with comparison to the VB and exact energies.

$$\Phi_{\text{covalent}} = N(\chi_l \chi_r + \chi_r \chi_l) \qquad (49)$$

$$\Phi_{\text{ionic}} = N(\chi_l \chi_l + \chi_r \chi_r) \; . \qquad (50)$$

At very large R, the exact wavefunction will have one electron near the left proton and one at the right, as in (49), which we will refer to as the **covalent** part of the wavefunction. The other terms of (48) have both electrons near one proton and none near the other, thus an **ionic** wavefunction. At R = ∞, these ionic terms lead to the energy of H^- and H^+ rather than the energy of two hydrogen atoms. Since the MO wavefunction must have equal covalent and ionic contributions, it yields terrible energies for large R.

The basic problem with the MO wavefunction is that both electrons are in the same φ_g orbital and hence each electron has an equal probability of being on either center, regardless of the instantaneous location of the *other* electron. In the exact wavefunction, the motions of the electrons tend to be correlated so that if one electron is on the left, the other tends to be on the right. This correlation is necessarily ignored in the MO wavefunction, and the resulting error is often referred to as the **correlation error**. For small R, the two centers are close to each other and this neglect of correlation is not so important. At R = ∞, however, the correlation of electrons is of paramount importance and neglect of correlation leads to ludicrously poor wavefunctions.

In the next section we will discuss a simple wavefunction, the **valence bond** wavefunction, that eliminates this problem of describing large R.

2.3 The Valence Bond Description of H_2

2.3.1 The Covalent States

We will now reexamine the ground state of H_2 molecule. However, rather than the approach of the above section (plopping electrons one by one into the orbitals of H_2^+), we will instead start with the exact wavefunction at $R = \infty$. This, of course, consists of two hydrogen atoms infinitely far apart, say electron 1 on the left and electron 2 on the right as in Figure 24.

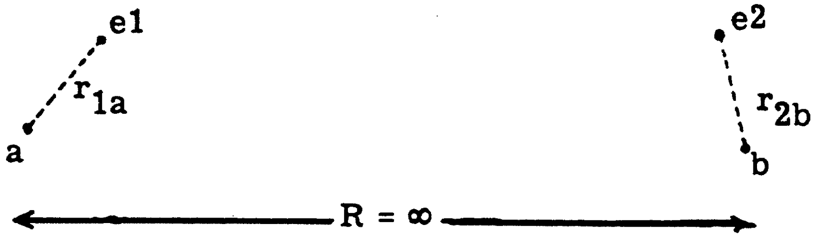


Figure 2-24.

The wavefunction for Figure 24 is

$$\Phi_a(\mathbf{r}_1,\mathbf{r}_2) = \chi_l(\mathbf{r}_1)\chi_r(\mathbf{r}_2) \ , \tag{1}$$

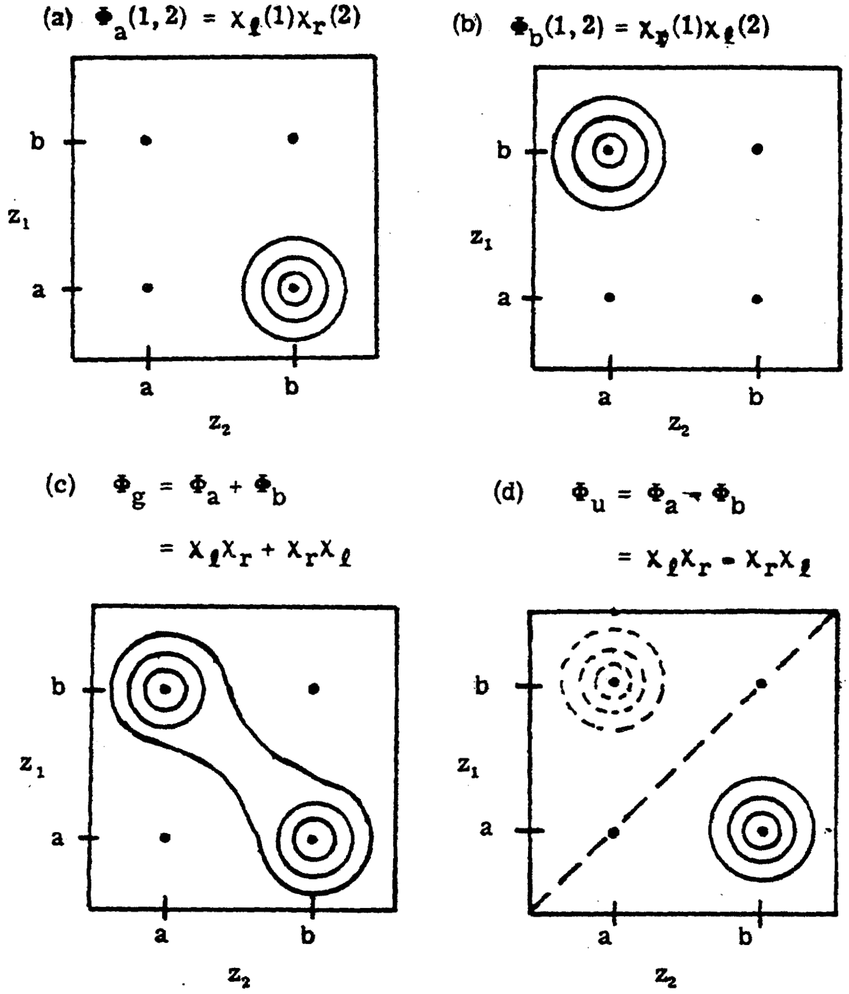
where

$$\begin{aligned} \chi_l(\mathbf{r}_1) &= N\, e^{-r_{a1}} \\ \chi_r(\mathbf{r}_2) &= \mathrm{N}\, e^{-r_{b2}} \end{aligned} \tag{2}$$

(and N is the normalization factor).

This wavefunction Φ_a says that the probability of electron 1 being at a particular position is independent of where electron 2 is and vice versa (since the atoms are infinitely far apart, the electrons should not be influenced by each other).

There is a second wavefunction that is just as good (or as bad) as Φ_a in (1), namely,



(a) $\Phi_a(1,2) = \chi_\ell(1)\chi_r(2)$

(b) $\Phi_b(1,2) = \chi_r(1)\chi_\ell(2)$

(c) $\Phi_g = \Phi_a + \Phi_b = \chi_\ell\chi_r + \chi_r\chi_\ell$

(d) $\Phi_u = \Phi_a - \Phi_b = \chi_\ell\chi_r - \chi_r\chi_\ell$

Figure 2-25.

$$\Phi_b(\mathbf{r}_1,\mathbf{r}_2) = \chi_r(\mathbf{r}_1)\chi_l(\mathbf{r}_2) \; , \tag{3}$$

where the electrons have been interchanged. This wavefunction Φ_b is different from Φ_a since electron 1 is on the opposite sides of the universe; however, the energies of Φ_b and Φ_a must be the same (since electrons 1 and 2 have the same properties).

We will find it useful to combine Φ_a and Φ_b into two new wavefunctions,

$$\Phi_g(1,2) = \Phi_a(1,2) + \Phi_b(1,2) = \chi_l(1)\chi_r(2) + \chi_r(1)\chi_l(2) \tag{4a}$$

$$\Phi_u(1,2) = \Phi_a(1,2) - \Phi_b(1,2) = \chi_l(1)\chi_r(2) - \chi_r(1)\chi_l(2) \tag{4b}$$

(unnormalized) because at finite R these are the optimum wavefunctions. Before examining the energies, we need to understand how to think about the relative locations of the electrons in these wavefunctions.

In Figure 25, we plot the four wavefunctions, Φ_a, Φ_b, Φ_g, and Φ_u. Here we see that Φ_u has a nodal plane (coresponding to $z_1 = z_2$) while Φ_g does not. Indeed, along the line between the two peaks in Figure 25c, we see that the gradient of the Φ_g wavefunction is smaller than that of Φ_a or Φ_b, while the gradient of the Φ_u wavefunction is larger. This decrease in the gradient of Φ_g (and increase for Φ_u) depends upon R with a bigger effect for smaller R; thus, based on kinetic energy, we would expect that Φ_g is bonding and Φ_u is antibonding, and indeed this is the case, as shown in Figure 26.

2.3.2 Symmetry

Inversion of the coordinates of the electrons $r_{a1} \leftrightarrow r_{b1}$ and $r_{a2} \leftrightarrow r_{b2}$ leads to [see (2)]

$$\chi_l(\mathbf{r}_i) \leftrightarrow \chi_r(\mathbf{r}_i) \; .$$

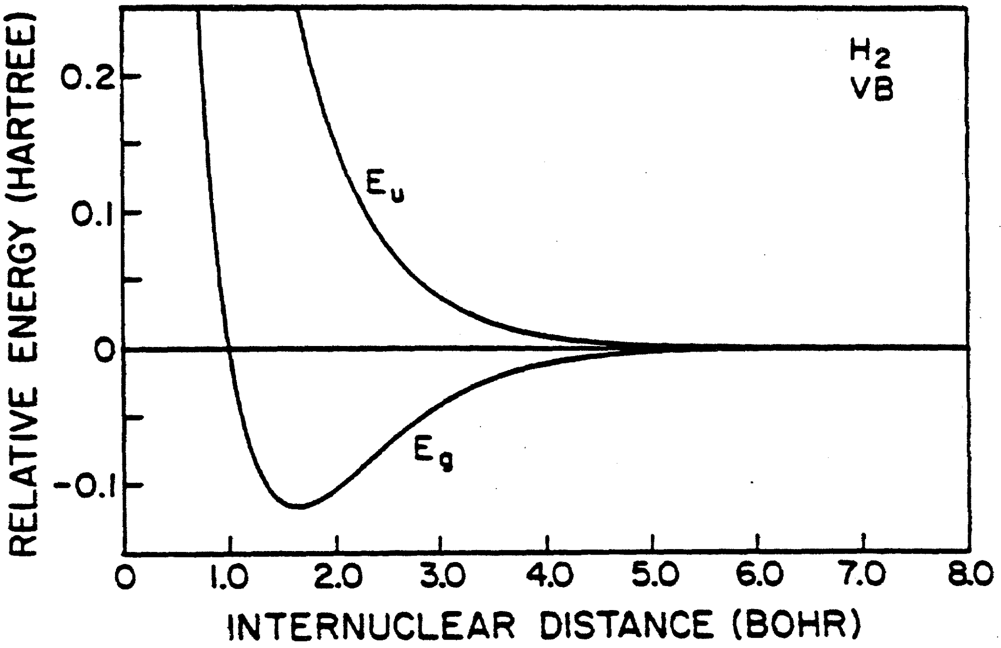


Figure 2-26. The energies E_g and E_u for the valence bond wavefunctions of H_2.

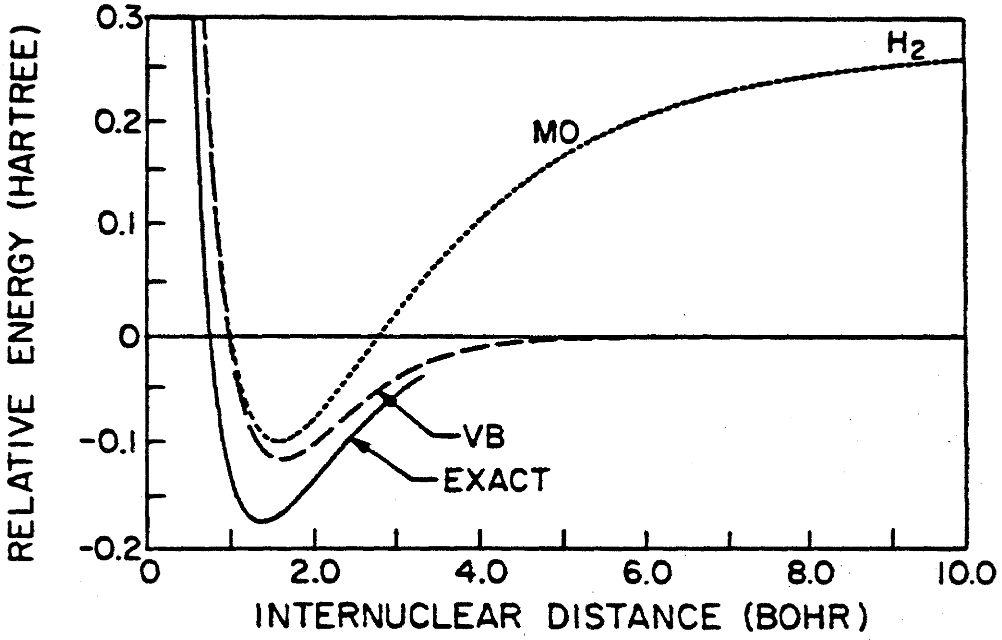


Figure 2-27. The energy of the MO wavefunction for the ground state of H_2 with comparison to the VB and exact energies.

Consequently,

$$\hat{I}\Phi_a(\mathbf{r}_1,\mathbf{r}_2) = \chi_r(\mathbf{r}_1)\chi_l(\mathbf{r}_2) = \Phi_b(\mathbf{r}_1,\mathbf{r}_2)$$

or

$$\hat{I}\Phi_b = \Phi_a \ .$$

As a result,

$$\begin{aligned} \hat{I}\,\Phi_g &= I(\Phi_a + \Phi_b) = (\Phi_b + \Phi_a) = \Phi_g \\ \hat{I}\,\Phi_u &= I(\Phi_a - \Phi_b) = \Phi_b - \Phi_a = -\Phi_u \ , \end{aligned} \qquad (5)$$

and we see that Φ_g and Φ_u are indeed gerade and ungerade, respectively.

2.3.3 Comparison of VB and MO Wavefunctions

2.3.3a Ground State

The MO wavefunction is (ignoring normalization)

$$\Phi^{\mathrm{MO}}_{gg}(1,2) = \varphi_g(1)\varphi_g(2) = [\chi_l\chi_r + \chi_r\chi_l] + [\chi_l\chi_l + \chi_r\chi_r] \ ,$$

whereas the VB wavefunction is

$$\Phi^{\mathrm{VB}}(1,2) = [\chi_l\chi_r + \chi_r\chi_l] \ .$$

The energies for these wavefunctions are compared in Figure 27 where we see that the VB is always better but that the difference becomes negligible for small R.

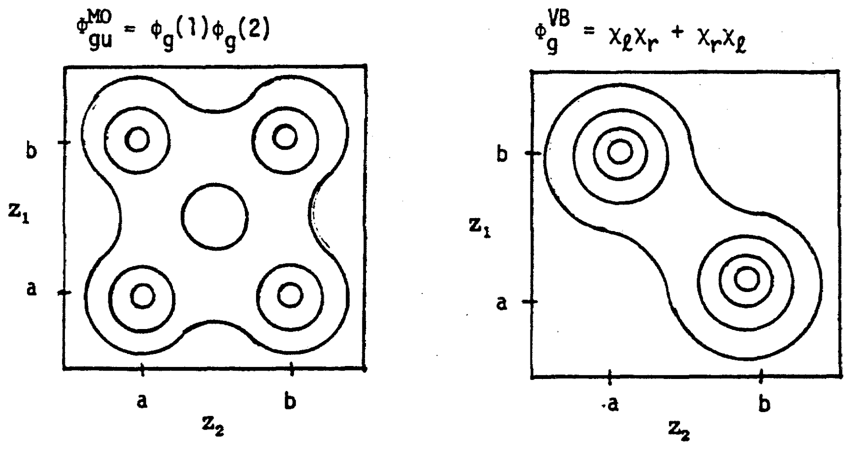


Figure 2-28.

The wavefunctions are compared in Figure 28, showing graphically how the VB wavefunction has smaller probability of having $z_1 = z_2$, leading to lower electron repulsion energies. On the other hand, the MO wavefunction is smoother, leading to smaller kinetic energies. For normal bond distances, the electron repulsion effects dominate so that the VB wavefunction is better. However, for very short R, the kinetic energy becomes dominant so that the MO and VB wavefunctions lead to nearly identical total energies.

2.3.3b *The u States*

Expanding the MO's in terms of AO's (and ignoring normalization) leads to

$$\Phi_{gu} = (\ell + r)(\ell - r) = \ell\ell + r\ell - \ell r - rr$$

$$\Phi_{ug} = (\ell - r)(\ell + r) = \ell\ell - r\ell + \ell r - rr \ .$$

Thus

$$^3\Phi_u = \Phi_{gu} - \Phi_{ug} = 2(r\ell - \ell r) = \Phi_u^{VB} \qquad (6)$$

$$ {}^1\Phi_u = gu + ug = 2(ll - rr) = \Phi_u^{ION} \; . \qquad (7) $$

That is, the first excited state in the MO description, ${}^3\Phi_u$, *is identical* to the first excited state in the VB description. Both describe a covalent repulsive state that separates to two free H atoms, as indicated in Figure 29.

The second state, ${}^1\Phi_u$, leads for $R = \infty$ to the wavefunctions $\chi_l\chi_l$ corresponding to

$$ H^- \qquad H^+ $$

and $\chi_r\chi_r$ corresponding to

$$ H^+ \qquad H^- \; . $$

Thus we refer to this state as the **ionic state.** The energy curve is shown in Figure 29.

2.3.3c The Second g State

In the MO description*

$$ \begin{aligned} \Phi_{uu}^{MO} &= (l - r)(l - r) = [(ll + rr) - (lr + rl)] / 2(1 - S) \\ \Phi_{gg}^{MO} &= (l + r)(l + r) = [(ll + rr) + (lr + rl)] / 2(1 + S) \; . \end{aligned} \qquad (8) $$

In contrast, the VB description leads to*

$$ \Phi_g^{VB} = (lr + rl) / \sqrt{2(1 + S^2)} \qquad (9) $$

and

$$ \Phi_g^{ION} = (ll + rr) / \sqrt{2(1 + S^2)} $$

for the covalent and ionic g states.

The connections between these states are

$$ \Phi_g^{VB} = \frac{1}{\sqrt{2(1 + S^2)}} \left[(1 + S)\, \Phi_{gg}^{MO} - (1 - S)\, \Phi_{uu}^{MO} \right] $$

---

* Now we include normalization factors.

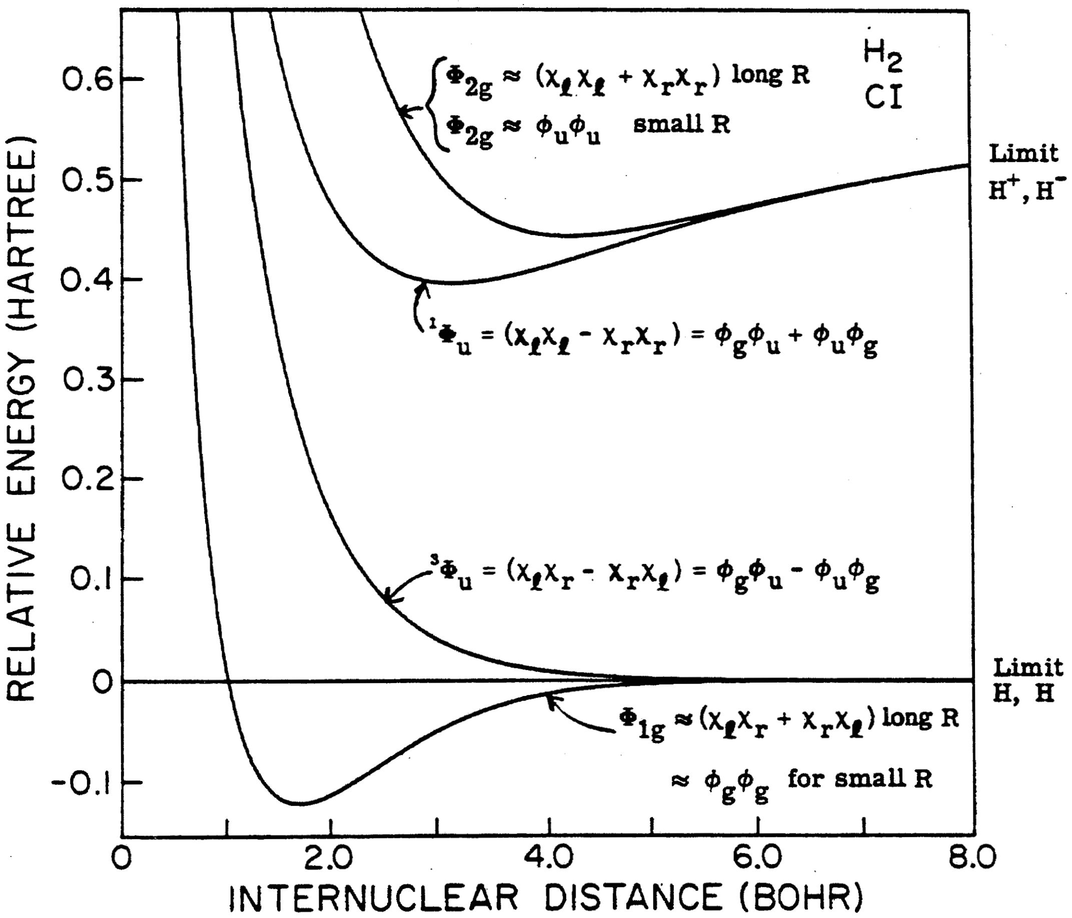


Figure 2-29. Energies for the states of H_2, using atomic orbitals ($\zeta = 1.0$).

$$= \frac{(1 + S)}{\sqrt{2(1 + S^2)}} \left[\Phi_{gg}^{MO} - \lambda \, \Phi_{uu}^{MO} \right] , \tag{10}$$

where

$$\lambda = \frac{1 - S}{1 + S} . \tag{11}$$

Thus we can fix up the MO wavefunction so that it behaves like the VB wavefunction by mixing together the Φ_{gg}^{MO} and Φ_{uu}^{MO} wavefunctions. This is related to the configuration interaction (CI) wavefunction, as discussed below. For large R, S = 0 so that $\lambda = 1$, whereas for R = 1.6a_0 = 0.8 Å , S = 0.7, leading to $\lambda = 0.18$. Thus the CI is most important at larger R.

For a more general description of these states, we would consider the wavefunction to have the form

$$\Phi_{1g}^{CI} = C_1 \, \Phi_{gg}^{MO} + C_2 \, \Phi_{uu}^{MO} \tag{12a}$$

or*

$$\Phi_{1g}^{CI} = D_1 \, \Phi_g^{COV} + D_2 \, \Phi_g^{ION} , \tag{12b}$$

and choose the coefficients that lead to the best energy. This is called the configuration interaction or CI wavefunction and leads to the results shown in Figure 29. The excited g state, Φ_{2g}^{CI}, can also be taken to have the form (12); however, it must be orthogonal to Φ_{1g}^{CI}, leading to

$$<\Phi_{2g}^{CI} | \Phi_{1g}^{CI}> = 0 .$$

The overlap between the covalent and ionic g states is

$$<\Phi_g^{ION} | \Phi_g^{COV}> = \frac{< \ell\ell + rr | \ell r + r\ell >}{2(1 + S^2)} \tag{13}$$

$$= \frac{2S}{1 + S^2} .$$

---

* Equations (12a) and (12b) lead to an equivalent total wavefunction, as can be seen by comparing (8) and (9).

Thus, for S = 0.7 (R = $1.6a_0$ = 0.8 Å) this overlap is 0.95, demonstrating just how similar are the ionic and covalent wavefunctions for small R. This creates a problem in describing the excited g state. The VB wavefunction is a close approximation to the Φ_{1g}^{CI} wavefunction; however, except for S ≈ 0, the Φ_g^{ION} wavefunction is *not* a good approximation to the excited state, Φ_{2g}^{CI}. Instead, we must orthogonalize Φ_g^{ION} to Φ_g^{COV}, leading to new nodal planes and a much higher energy. This explains why the Φ_{2g}^{CI} state is always above the Φ_u^{ION} state. Based on the nodal theorem, we would expect that Φ_g^{ION} (which has no nodal planes) would have a lower energy than Φ_u^{ION}, and it does. However, the only nodeless state is the ground state Φ_{1g} which mixes whatever combination of Φ_g^{COV} and Φ_g^{ION} gives the best energy. The excited g state, Φ_{2g}^{CI}, necessarily has nodal surfaces since it must be orthogonal to the ground state. The result is that the ionic g state, Φ_{2g}^{CI}, is always above the ionic u state.

2.3.4 Quantitative Analysis of Bonding in H_2

We will analyze the energies of the VB wavefunctions for the g and u states of H_2 in a manner very similar to that used for the LCAO wavefunction of the g and u states of H_2^+.

First we consider the energy of the simple product wavefunction

$$\Phi^{cl}(1,2) = \chi_l(1)\chi_r(2) = \chi_l\chi_r \ , \tag{14}$$

which is just part of the wavefunction for the g and u states, (4a) and (4b). We will refer to this wavefunction as the **classical wavefunction** and the energy

$$\begin{aligned} E^{cl} &= \frac{\langle\Phi^{cl}|H|\Phi^{cl}\rangle}{\langle\Phi^{cl}|\Phi^{cl}\rangle} \\ &= h_{ll} + h_{rr} + J_{lr} + \frac{1}{R} \end{aligned} \tag{15}$$

as the **classical energy.**

The total energy of H_2 differs from the classical energy due to the presence of a second term in the wavefunctions (4a) and (4b). The second term has the electrons interchanged (exchanged) and hence is called the **exchange term.**

The effect of the exchange term in the wavefunction, say (4a), is to change the energy from E^{cl} to E_g. We will refer to this change in energy as the exchange energy E_g^x, so that

$$\boxed{\begin{aligned} E_g &\equiv E^{cl} + E_g^x \\ E &\equiv E^{cl} + E_u^x \end{aligned}} \tag{16}$$

In Figure 30 we show the behavior of these quantities with R. Just as for H_2^+, we see that it is ***the exchange term*** that ***dominates the bonding*** energy. Indeed, we will find that it is the one-electron part of the exchange terms that provides the dominant interaction, just as for H_2^+. First we consider the detailed form of the various energy quantities.

2.3.4a *Analysis of E^{cl}*

At large R, the one-electron term

$$h_{ll} = \underbrace{\left\langle \chi_l \left| -\tfrac{1}{2}\nabla^2 - \frac{1}{r_z} \right| \chi_l \right\rangle}_{\text{atomic energy}} + \underbrace{\left\langle \chi_l \left| -\frac{1}{r_b} \right| \chi_l \right\rangle}_{\text{penetration term}} ,$$

has the form

$$h_{ll} \approx \varepsilon_{1s} - \frac{1}{R} . \tag{17}$$

Neglecting terms of order e^{-2R}, and the Coulomb term has the form

$$J_{lr} \sim \frac{1}{R}$$

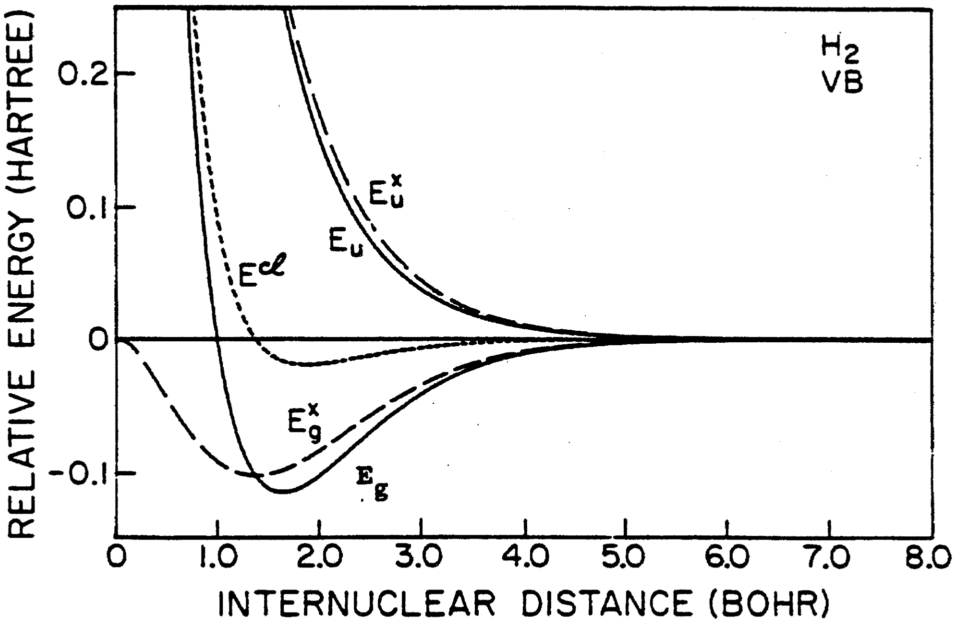


Figure 2-30. The classical (E^{cl}), exchange (E^x), and total (E) energies for the VB wavefunctions of H_2. Note that each energy is references to the value for R = ∞, that is, $E^{cl}(\infty) = E_g(\infty) = E_u(\infty) = -1.0$ and $E_g^x(\infty) = E_u^x(\infty) = 0.0$.

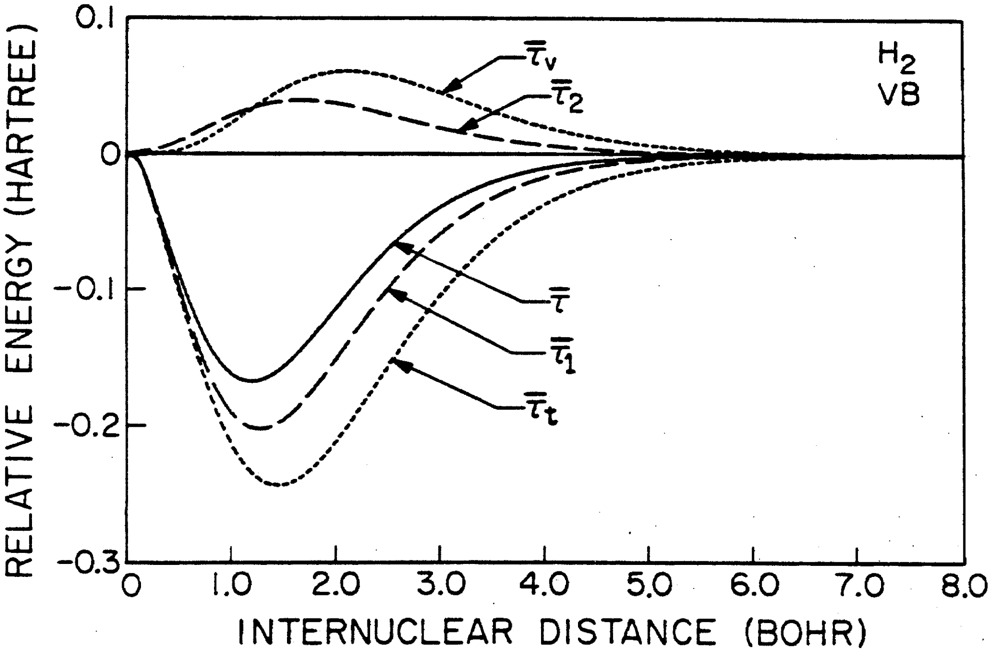


Figure 2-31. The total exchange term ($\bar{\tau}$) and the one-electron ($\bar{\tau}_1$) and two-electron ($\bar{\tau}_2$) parts. The potential ($\bar{\tau}_v$) and kinetic ($\bar{\tau}_t$) parts of $\bar{\tau}_1$ are also shown. All results are for H_2.

(neglecting terms of order e^{-2R}). Thus the classical term is just twice the energy of an H atom (ε_{1s}),

$$E^{cl} \approx 2\varepsilon_{1s}$$

(neglecting terms of order e^{-2R}), with no net Coulomb terms. Including the additional penetration terms leads to

$$E^{cl} = 2\varepsilon_{1s} + \left(\frac{1}{R} + \frac{5}{8} + \frac{3}{4}R - \frac{1}{6}R^2\right)e^{-2R} , \qquad (18)$$

corresponding to the interpenetration of the two atomic electron clouds. Although negative for $R > 1.4a_0$, this quantity is small, as shown in Figure 30. Thus the bonding of H_2 cannot be explained as due to penetration of the charge clouds of two hydrogen atoms.

2.3.4b *The Exchange Terms*

Now we consider the energy of Φ_g^{cov}, (4a),

$$E_g = <\Phi_g|\hat{H}|\Phi_g> / <\Phi_g|\Phi_g> .$$

By symmetry

$$\begin{aligned} <\Phi_g|\Phi_g> &= <\chi_l\chi_r|\Phi_g> + <\chi_r\chi_l|\Phi_g> \\ &= 2<\chi_l\chi_r|\Phi_g> \end{aligned}$$

and

$$\begin{aligned} <\Phi_g|\hat{H}|\Phi_g> &= <\chi_l\chi_r|\hat{H}|\Phi_g> + <\chi_r\chi_l|\hat{H}|\Phi_g> \\ &= 2<\chi_l\chi_r|\hat{H}|\Phi_g> . \end{aligned}$$

Hence

$$E_g = \frac{<\chi_l\chi_g|\hat{H}|\Phi_g>}{<\chi_l\chi_r|\Phi_g>} .$$

Evaluating the individual terms, we find

$$<\chi_l\chi_r|\Phi_g> \;=\; 1 + <\chi_l|\chi_r><\chi_r|\chi_l>$$

$$= 1 + S^2$$

and

$$<\chi_l\chi_r|\hat{H}|\Phi_g> \;=\; <\chi_l\chi_r|\hat{H}|\chi_l\chi_r> + <\chi_l\chi_r|\hat{H}|\chi_r\chi_l> \;=\; E^{cl} + \mathcal{E}\ ,$$

where

$$\mathcal{E} \equiv <\chi_l\chi_r|\hat{H}|\chi_r\chi_l> \tag{19}$$

is referred to as the **VB exchange term.** Thus

$$E_g \;=\; \frac{E^{cl} + \mathcal{E}}{1 + S^2} \;=\; E^{cl} + E_g^x\ , \tag{20}$$

where the **exchange energy** is

$$E_g^x \;\equiv\; \frac{(\mathcal{E} - S^2 E^{cl})}{(1 + S^2)}\ . \tag{21}$$

The same analysis for the Φ_u^{VB} wavefunction (4b) leads to

$$E_u \;=\; \frac{E^{cl} - \mathcal{E}}{1 - S^2} \;=\; E^{cl} + E_u^x\ , \tag{22}$$

where

$$E_u^x \;=\; -\ \frac{(\mathcal{E} - S^2 E^{cl})}{(1 - S^2)}\ . \tag{23}$$

The close relationship between E_g^x and E_u^x is emphasized by defining*

$$\mathcal{T} \;\equiv\; (\mathcal{E} - S^2 E^{cl}) \tag{24}$$

so that

$$E_g^x \;=\; \frac{\mathcal{T}}{(1 + S^2)} \tag{25}$$

$$E_u^x \;=\; \frac{-\mathcal{T}}{(1 - S^2)}\ . \tag{26}$$

From (25) and (26) the energy separation between the g and u states is

$$E_g - E_u = \frac{2\bar{\tau}}{1 - S^4} . \tag{27}$$

From the nodal theorem, $E_g < E_u$, and hence

$$\bar{\tau} < 0$$

since $S < 1$.

These results for H_2 are quite analogous to the case of H_2^+ where the φ_g and φ_u state have energies

$$\varepsilon_g = \varepsilon^{cl} + \left[\frac{1}{1 + S}\right]\tau \tag{28}$$

$$\varepsilon_u = \varepsilon^{cl} - \left[\frac{1}{1 - S}\right]\tau \tag{29}$$

$$\varepsilon_g - \varepsilon_u = \frac{2\tau}{(1 - S^2)} , \tag{30}$$

with

$$\varepsilon^{cl} = h_{\ell\ell} + \frac{1}{R} \tag{31}$$

$$\tau = h_{\ell r} - S h_{\ell\ell} . \tag{32}$$

2.3.4c Analysis of $\mathcal{E}$

The components of $\mathcal{E}$ (19) are

$$\begin{aligned} \langle \chi_\ell \chi_r | h(1) | \chi_r \chi_\ell \rangle &= \langle \chi_\ell | h | \chi_r \rangle \langle \chi_r | \chi_\ell \rangle \\ &= h_{\ell r} S \\ \langle \chi_\ell \chi_r | h(2) | \chi_r \chi_\ell \rangle &= \langle \chi_\ell | \chi_r \rangle \langle \chi_r | h | \chi_\ell \rangle \end{aligned} \tag{33}$$

---

* We use $\bar{\tau}$ here in order to distinguish this quantity for H_2 from the τ of H_2^+.

$$= Sh_{r\ell}$$

$$\langle \chi_\ell \chi_r | \frac{1}{r_{12}} | \chi_r \chi_\ell \rangle = \int d\tau \chi_\ell{}^*(1)\chi_r(1) \int d\tau_2 \frac{1}{r_{12}} \chi_r{}^*(2)\chi_\ell(2)$$

$$\equiv K_{\ell r}$$

$$\langle \chi_\ell \chi_r | \frac{1}{R} | \chi_r \chi_\ell \rangle = \frac{S^2}{R} \, .$$

where S is the overlap and $K_{\ell r}$ is referred to as an **exchange integral.** (Note the distinction between $\mathscr{E}$, the VB exchange *term*, and $K_{\ell r}$, the exchange *integral*.) Thus,

$$\boxed{\mathscr{E} = 2Sh_{\ell r} + K_{\ell r} + \frac{S^2}{R} \, .} \tag{34}$$

2.3.4d *Analysis of $\bar{\tau}$*

Using E^{cl} from (15) in (24), we find that

$$\bar{\tau} = \bar{\tau}_1 + \bar{\tau}_2 \, , \tag{35}$$

where

$$\bar{\tau}_1 = [2Sh_{\ell r} - S^2(h_{\ell\ell} + h_{rr})] = 2S[h_{\ell r} - Sh_{\ell\ell}] = 2S\tau \tag{36}$$

$$\bar{\tau}_2 = [K_{\ell r} - S^2 J_{\ell r}] \tag{37}$$

are the one- and two-electron parts, respectively.* These quantities are plotted in Figure 31 where we see that $\bar{\tau}_2$ has a smaller magnitude that $\bar{\tau}_1$. Thus we can write

$$\bar{\tau} \approx \bar{\tau}_1 \, . \tag{38}$$

Comparing (27) and (31a) we see that

$$\bar{\tau}_1 = 2S\tau \, , \tag{39}$$

---

* The $\frac{1}{R}$ terms cancel.

that is, *the one- electron part of* $\bar{\tau}$ *for* H_2 *is related directly to the* τ *of* H_2^+, leading to

$$\boxed{\bar{\tau} \cong \bar{\tau}_1 = 2S\tau ,} \tag{40}$$

where τ is the quantity for H_2^+. Thus, for H_2 the bonding energy is determined by

$$E_g^x \approx \frac{2S\tau}{1 + S^2} \equiv \bar{E}_g^x \tag{41}$$

$$E_u^x \approx -\frac{2S\tau}{1 - S^2} \equiv \bar{E}_u^x , \tag{42}$$

whereas for H_2^+ it is determined by

$$\varepsilon_g^x = \frac{\tau}{1 + S} \tag{43}$$

$$\varepsilon_u^x = -\frac{\tau}{1 - S} . \tag{44}$$

These quantities are compared in Figure 32.

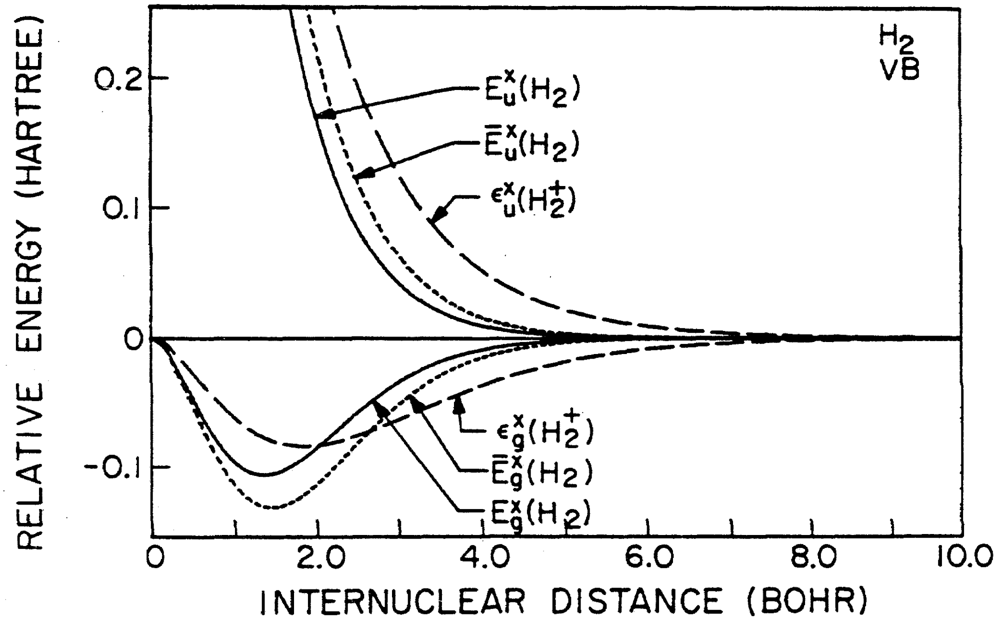


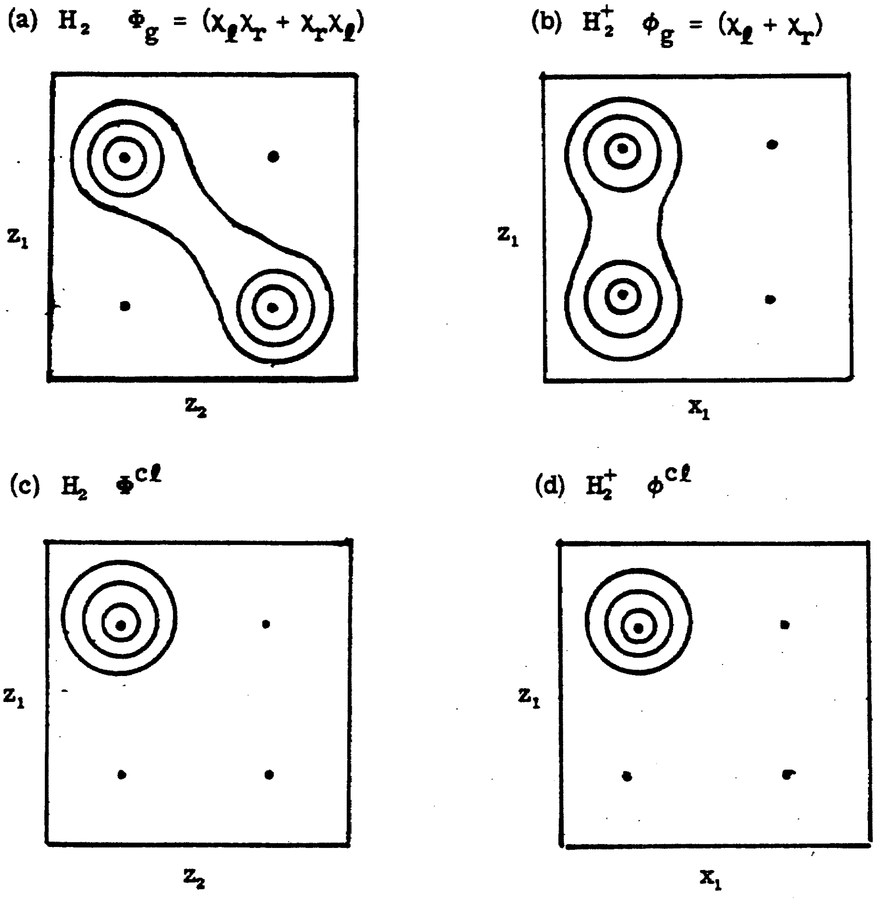
Figure 2-32. The exchange energies (E_g^x and E_u^x) for H_2^+ and H_2. In addition, the one-electron approximation $\bar{E}^x$ to the E^x for H_2 is shown for each state.

2.3.4e *Analysis of* $\bar{\tau}_1 = 2S\tau$

Since the quantities $\bar{\tau}_1$ and τ dominating the bonding in H_2 and H_2^+ are related,

$$\bar{\tau}_1 = 2S\tau$$

it is well to examine the reasons for these relations. The wavefunctions for the bonding states of H_2 and H_2^+ are sketched in Figure 33ab. In both cases the kinetic energy is decreased from that in the classical wavefunctions, Figure 33cd. The decrease in the kinetic energy for electron 1 is obtained by examining the gradients in the vertical direction (ordinate) of Figure 33abcd. Here we see that H_2^+ leads to a larger decrease that H_2. Thus the contribution is $S\tau$ for H_2 but τ for H_2^+. However, for H_2 there is a second electron (number 2) that has a similar decrease. Thus, for H_2 the net is $2S\tau$ as compared to τ for H_2^+.



(a) H_2 $\Phi_g = (\chi_\ell\chi_r + \chi_r\chi_\ell)$

(b) H_2^+ $\phi_g = (\chi_\ell + \chi_r)$

(c) H_2 $\Phi^{c\ell}$

(d) H_2^+ $\phi^{c\ell}$

Figure 2-33.

2.3.4f *Comparison of Bonding in* H_2 *and* H_2^+

Although the bonding energies of H_2 and H_2^+ are both determined by τ, we see from (41)-(44) that the value of the overlap S also plays an important role. From 2.1 the form of τ at large R is

$$\tau \approx -(2/R)S \ ,$$

hence

$$\tau_1 = 2S\tau \approx -(4/R)S^2 \ . \qquad (45)$$

Thus the bonding in H_2^+ is proportional to S, but the bonding in H_2 is proportional to the ***square*** of S.

At $R = 1.6a_0$, the value of S is

$$S = 0.7,$$

and hence

$$\begin{array}{ll} H_2: & E_g^x = 0.94\,\tau \\ & E_u^x = -2.75\,\tau \\ H_2^+: & \varepsilon_g^x = 0.67\,\tau \\ & \varepsilon_u^x = -3.33\,\tau \ . \end{array} \qquad (46)$$

Thus the g state of H_2 should have a bond energy about 50% larger than the g state of H_2^+, while the u state of H_2 should be 17% less repulsive than the u state of H_2^+. In addition, we see that the u state of H_2 should be about three times as repulsive as the g state is attractive.

At $R = 3a_0$, the overlap is $S = 0.1$ and hence we obtain

$$\begin{aligned} H_2: \quad & E_g^x = 0.20\,\tau \\ & E_u^x = -0.20\,\tau \\ H_2^+: \quad & \varepsilon_g^x = 0.91\,\tau \\ & \varepsilon_u^x = -1.11\,\tau\ . \end{aligned} \qquad (47)$$

Thus, at this large R, the g and u states of H_2^+ are five times as attractive or repulsive as the g and u states of H_2. That is, ***at large R, the one-electron bond is much stronger than the two-electron bond!*** This difference in relative bond strengths of H_2 and H_2^+ for small and large R just results from the overlap term S that automatically arises in the exchange of a two-electron wavefunction.

In the limit that S = 1, we have*

$$\begin{aligned} H_2: \quad & E_g^x = \tau \\ H_2^+: \quad & \varepsilon_g^x = \tfrac{1}{2}\tau\ , \end{aligned}$$

leading to an H_2 bond twice that of H_2^+, the commonly expected result.

PROBLEM: Experimentally (and theoretically), the molecules Li_2^+, Na_2^+, K_2^+, with one-electron bonds, are found to have ***stronger*** bonds than the corresponding molecules Li_2, Na_2, K_2 having two-electron bonds. Explain the origin of this effect.

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* Actually, S = 1 implies R = 0, which in turn implies $\tau = 0$.

APPENDIX 2-A: ENERGY QUANTITIES FOR H_2^+

We will consider an atomic orbital of the form

$$\chi = \sqrt{\zeta^3/\pi}\ \ e^{-\zeta r} \tag{1}$$

centered at each of the two nuclei of H_2^+. The coordinates are indicated in Figure 34.

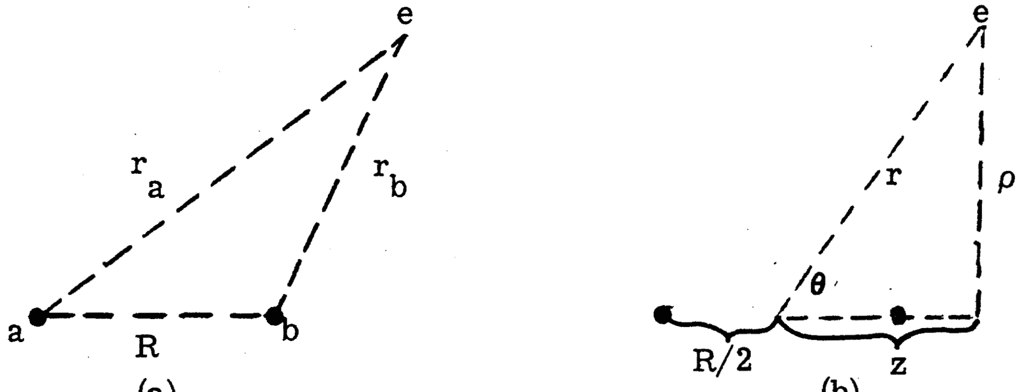


Figure 2-34.

With $\zeta = 1$ the orbitals (1) correspond to hydrogen 1s orbitals on each center. First we evaluate the atomic integrals for general ζ, then the new energy quantities occurring in H_2^+.

2-A.1 Atomic Energy Quantities

The norm of χ is

$$\begin{aligned}\langle\chi\,|\,\chi\rangle &= (\zeta^3/\pi)\underbrace{\int_0^{\pi}\sin\Theta\, d\Theta\int_0^{2\pi} d\varphi}_{4\pi}\int_0^{\infty} r^2\, dr\, e^{-2\zeta r}\\ &= 4\zeta^3\int_0^{\infty} r^2\, dr\, e^{-2\zeta r}\\ &= \tfrac{1}{2}\int_0^{\infty} p^2\, e^{-p}\, dp\\ &= 1,\end{aligned}$$

where we set $p = 2\zeta r$ and used

$$\int_0^{\infty} p^m\, e^{-p}\, dp = m!\ .$$

Similarly the atomic potential energy is

$$\langle\chi|-\frac{1}{r}|\chi\rangle = -4\zeta^3 \int_0^\infty r^2 dr\, e^{-2\zeta r} = -\zeta . \tag{2}$$

and the kinetic energy is

$$\langle\chi|-\tfrac{1}{2}\nabla^2|\chi\rangle = \tfrac{1}{2}\langle|\nabla\chi|^2\rangle = \tfrac{1}{2}\zeta^2\langle\chi|\chi\rangle = \tfrac{1}{2}\zeta^2 . \tag{3}$$

2-A.2 Elliptic Coordinates

In evaluating the energy quantities for diatomic molecules, it is convenient to use elliptic coordinates

$$\xi = (r_a + r_b)/R$$

$$\eta = (r_a - r_b)/R \tag{4}$$

φ = azimuthal angle about the z axis (measured from the xz plane)

in place of the cylindrical polar coordinates ρ, φ, z (see Fig. 34b) or spherical coordinates r, θ, φ. (See Fig. 34b.) The geometric condition defining an ellipse is that the sum of the distances to the two foci is a constant, and hence each curve of constant ξ corresponds to an ellipse. Similarly from the defining condition for a hyperbola, each surface of constant η correspon
to a hyperbola. The range of the elliptic coordinates is

$$0 \le \xi < \infty$$

$$-1 \le \eta \le +1 \tag{5}$$

$$0 \le \varphi < 2\pi$$

The volume increments in the various coordinate systems are

$$\begin{aligned} d\tau &= dx\, dy\, dz \\ d\tau &= \rho\, d\rho\, d\varphi\, dz \\ d\tau &= r^2 \sin\theta\, dr\, d\theta\, d\varphi \\ d\tau &= \tfrac{1}{8} R^3 (\xi^2 - \eta^2)\, d\xi\, d\eta\, d\varphi \end{aligned} \tag{6}$$

The latter relationship can be derived from

$$\begin{aligned} x &= \tfrac{1}{2} R \sqrt{(\xi^2 - 1)(1 - \eta^2)} \quad \cos\varphi \\ y &= \tfrac{1}{2} R \sqrt{(\xi^2 - 1)(1 - \eta^2)} \quad \sin\varphi \\ z &= \tfrac{1}{2} R \xi \eta \end{aligned} \tag{7}$$

since the Jacobian $\frac{1}{8}R^3 (\xi^2 - \eta^2)$ is just the determinant of the derivative matrix.

From Fig. 34b we see that

$$\begin{aligned} r_b^2 &= \rho^2 + (z - \frac{R}{2})^2 \\ r_a^2 &= \rho^2 + (z + \frac{R}{2})^2 \\ r^2 &= \rho^2 + z^2 , \end{aligned}$$

and hence

$$\tfrac{1}{2}(r_a^2 + r_b^2) = r^2 + (\frac{R}{2})^2$$

and

$$r_a^2 - r_b^2 = 2zR .$$

From (4) we find

$$\begin{aligned} \tfrac{1}{2}(\xi^2 + \eta^2) &= (r_a^2 + r_b^2)/R^2 \\ \xi\eta &= (r_a^2 - r_b^2)/R^2 \\ \xi^2 - \eta^2 &= 4 r_a r_b / R^2 , \end{aligned} \tag{9}$$

and hence

$$r^2 = \tfrac{1}{4}R^2[\,\xi^2 + \eta^2 - 1\,] \,. \qquad (8)$$

These relations will be useful in the next section.

In evaluating integrals over ξ the following integral will be useful

$$\int_{x_0}^{\infty} x^m e^{-\alpha x} dx = \frac{m!\,e^{-\alpha x_0}}{\alpha^{m+1}} \sum_{k=0}^{m} \frac{(\alpha x_0)^k}{k!} \equiv A_m(\alpha x_0) \qquad (10)$$

For $x_0 = 1$ and $m = 0, 1,$ and 2 this becomes

$$A_0(\alpha) = \frac{1}{\alpha}\, e^{-\alpha} \qquad (11)$$

$$A_1(\alpha) = \frac{1}{\alpha^2}\, e^{-\alpha}[\,1 + \alpha\,] \qquad (12)$$

$$A_2(\alpha) = \frac{2}{\alpha^3}\, e^{-\alpha}[\,1 + \alpha + \tfrac{1}{2}\alpha^2\,] \qquad (13)$$

2-A.3 Diatomic Energy Quantities

2-A.3a Overlap Integral

First we evaluate the overlap integral,

$$S = \langle \chi_\ell | \chi_r \rangle \,.$$

Using (1), (6), (11) and (13), this becomes

$$S = \int d\tau\, \chi_\ell\, \chi_r = \left(\frac{\zeta^3}{\pi}\right)\left(\frac{R^3}{8}\right)(2\pi) \int_1^{\infty} d\xi \int_{-1}^{+1} d\eta\, (\xi^2 - \eta^2) e^{-2\zeta R\xi}$$

$$= e^{-\zeta R}\,[\,1 + (\zeta R) + \tfrac{1}{3}(\zeta R)^2\,] \qquad (14)$$

2-A.3b The Exchange Potential Energy Term

There are two terms involved in evaluating the potential energy of H_2^+, the exchange terms

$$V_{\ell r} \equiv \langle \chi_\ell | \hat{v} | \chi_r \rangle \ , \tag{15}$$

where

$$\hat{v} = -\frac{1}{r_a} - \frac{1}{r_b} \tag{16}$$

and

$$V_{\ell\ell} \equiv \langle \chi_\ell | \hat{v} | \chi_\ell \rangle \ . \tag{17}$$

In this section we evaluate $V_{\ell r}$.

First we convert $\hat{v}$ to elliptic coordinates

$$\hat{v} = -\frac{(r_a + r_b)}{r_a r_b} = -\frac{4\xi}{R(\xi^2 - \eta^2)} \tag{18}$$

using (4) and (9). Combining (18) with (6) leads to

$$\hat{v} d\tau = -\tfrac{1}{2} R^2 \xi \, d\xi \, d\eta \, d\varphi \ ,$$

and integrating over φ we obtain

$$\begin{aligned} V_{\ell r} &= \left(-\frac{R^2}{2}\right)\left(\frac{\zeta^3}{\pi}\right)(2\pi) \int_1^\infty \xi d\, \xi e^{-\zeta R \xi} \int_{-1}^{+1} d\eta \\ &= -2\zeta e^{-\zeta R}(1 + \zeta R) \ . \end{aligned} \tag{19}$$

A.3c The Penetration Term

The other potential energy term $V_{\ell\ell}$ has two parts

$$V_{\ell\ell} \equiv \langle \chi_\ell | -\frac{1}{r_a} | \chi_\ell \rangle + \langle \chi_\ell | -\frac{1}{r_b} | \chi_\ell \rangle \ ; \tag{20}$$

the first of which

$$V_{\ell\ell}^{(1)} \equiv \langle \chi_\ell | -\frac{1}{r_a} | \chi_\ell \rangle \tag{21}$$

is a one center integral (involving only the left nucleus) and the other of which

$$V_{\ell\ell}^{(2)} \equiv \langle \chi_\ell | -\frac{1}{r_b} | \chi_\ell \rangle \tag{22}$$

involves two centers. This second term is the Coulomb interaction between the spherically symmetric charge distribution $\rho_\ell = |\chi_\ell|^2$ centered on the left nucleus with the charge centered at the right nucleus and is referred to as the penetration integral.

As shown in equation 8 of Appendix B

$$V_{\ell\ell}^{(2)} = A + B ,$$

where

$$B = -4\pi \left(\frac{\zeta^3}{\pi}\right) \int_R^\infty r_a dr_a \, e^{-2\zeta r_a}$$

$$A = -\frac{Q}{R}$$

and

$$Q = 4\pi \left(\frac{\zeta^3}{\pi}\right) \int_0^R r_a^2 \, dr_a e^{-2\zeta r_a} .$$

Using

$$\int_0^R r^2 dr e^{-\alpha r} = \frac{2}{\alpha^3} \left[1 - (1 + \alpha R + \tfrac{1}{2}\alpha^2 R^2) e^{-\alpha R} \right] , \tag{23}$$

we obtain

$$Q = \left[1 - (1 + 2\zeta R + 2\zeta^2 R^2) e^{-2\zeta R} \right] . \tag{24}$$

Using (10) we obtain

$$B = -\zeta e^{-2\zeta R} (1 + 2\zeta R) ,$$

and hence

$$V^{(2)}_{\ell\ell} = -\frac{1}{R}(1 - e^{-2\zeta R}) + \zeta e^{-2\zeta R} \quad . \tag{25}$$

2-A.3d The Kinetic Energy Term

The two-center kinetic energy integral is

$$t_{\ell r} \equiv \langle \chi_\ell | -\tfrac{1}{2}\nabla^2 | \chi_r \rangle \ ,$$

which from Appendix 1-A becomes

$$\begin{aligned} t_{\ell r} &= \tfrac{1}{2}\langle \nabla \chi_\ell \cdot \nabla \chi_r \rangle \\ &= \tfrac{1}{2}\int d\tau\, (\nabla\chi_\ell \cdot \nabla\chi_r) . \end{aligned} \tag{26}$$

Since

$$\begin{aligned} r_b &= \sqrt{x^2 + y^2 + (z - R/2)^2} \\ r_a &= \sqrt{x^2 + y^2 + (z + R/2)^2} \quad , \end{aligned}$$

we obtain

$$\hat{\underset{\wedge}{\nabla}} e^{-\zeta r_a} = -\frac{\zeta}{r_a}\, e^{-\zeta r_a}\,[x\hat{e}_x + y\hat{e}_y + (z + \tfrac{1}{2}R)\hat{e}_z]$$

$$\underset{\wedge}{\nabla}\, e^{-\zeta r_b} = -\frac{\zeta}{r_b}\, e^{-\zeta r_b}[x\hat{e}_x + y\hat{e}_y + (z - \tfrac{1}{2}R)\hat{e}_z\,]$$

(where $\hat{e}_x$ denotes a unit vector in the x direction).

Hence

$$(\underset{\sim}{\nabla} e^{-\zeta r_a}) \cdot (\underset{\sim}{\nabla} e^{-\zeta r_b}) = (\zeta^2/r_a r_b)e^{-\zeta R\xi}[x^2 + y^2 + (z^2 - \tfrac{1}{4}R^2)] \tag{27}$$

Using (6), (8), and (9) we obtain

$$d\tau(\nabla\chi_\ell \cdot \nabla\chi_r) = (\frac{R^3}{8})(\frac{4\zeta^2}{R^2})(\frac{\zeta^3}{\pi})(\frac{R^2}{4})e^{-\zeta R\xi}(\xi^2 + \eta^2 - 2)d\xi d\eta d\varphi .$$

Integrating over φ and substituting into (26) leads to

$$t_{\ell r} = \tfrac{1}{8}R^3\zeta^5 \int_1^\infty d\xi e^{-\zeta R\xi} \int_{-1}^{+1} d\eta\, (\xi^2 + \eta^2 - 2)$$

$$= \tfrac{1}{4}R^3\zeta^5 \int_1^\infty (\xi^2 - \tfrac{5}{3})\, e^{-\zeta R\xi} d\xi$$

$$= \tfrac{1}{2}\zeta^2 e^{-\zeta R}[1 + \zeta R - \tfrac{1}{3}(\zeta R)^2] \,. \qquad (28)$$

2-A.4 Summary

Collecting together the quantities of the previous sections we have

$$\chi = \sqrt{\zeta^3/\pi} \quad e^{-\zeta r} \qquad (1)$$

$$t_{\ell\ell} = \langle \chi_\ell | \hat{t} | \chi_\ell \rangle = \tfrac{1}{2}\zeta^2 \qquad (2)$$

$$V_{\ell\ell}^{(1)} = \langle \chi_\ell | -\frac{1}{r_a} | \chi_\ell \rangle = -\zeta \qquad (3)$$

$$S = \langle \chi_\ell | \chi_r \rangle = e^{-\zeta R}[1 + \zeta R + \tfrac{1}{3}(\zeta R)^2] \qquad (14)$$

$$t_{\ell r} = \langle \chi_\ell | t | \chi_r \rangle = \tfrac{1}{2}\zeta^2 e^{-\zeta R}[1 + \zeta R - \tfrac{1}{3}(\zeta R)^2] \qquad (28)$$

$$V_{\ell r} = \langle \chi_\ell | (-\frac{1}{r_a} - \frac{1}{r_b}) | \chi_r \rangle = -2\zeta e^{-\zeta R}(1 + \zeta R) \qquad (19)$$

$$V_{\ell\ell}^{(2)} = -\frac{1}{R}[1 - (1 + \zeta R)e^{-2\zeta R}] \qquad (25)$$

2-A.5 Qualitative Examination of Diatomic Quantities

The amplitude of χ_r evaluated at the left nucleus is

$$\chi_r (R) = \sqrt{\zeta^3/\pi} \quad e^{-\zeta R}$$

while the amplitude of χ_ℓ at the left nucleus is

$$\chi_\ell (0) = \sqrt{\zeta^3/\pi}$$

Thus

$$\chi_r (R) = e^{-\zeta R} \chi_\ell(0) \tag{29}$$

If χ_ℓ were highly concentrated about the left nucleus the overlap would be given by

$$S = e^{-\zeta R} \tag{30}$$

Comparing with the correct formula (14) we see that the approximate form (30) has the correct exponential behavior on R but the numerical coefficient in (30) is correct only for R = 0. Using $R = 2.0a_0$ and $\zeta = 1.0$ in (14) leads to a coefficient of 3.33 and using $R = 6.0a_0$ leads to a coefficient of 19.0, many times the value obtained with (30).

APPENDIX 2-B. THE LEGENDRE EXPANSION

Consider a system such as in Fig. 34. It is often necessary to convert expressions involving say the distance of the electron from nucleus b over to a new expression involving the distance of the electron from nucleus a, as indicated in Fig. 35.

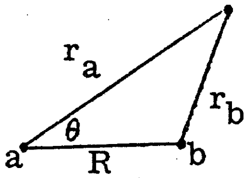


Figure 2-35.

The relation between these coordinates is

$$r_b^2 = r_a^2 + R^2 - 2 r_a R \cos\theta \tag{1}$$

A case of particular importance is to convert $1/r_b$ over to the new coordinates. This leads to

$$\frac{1}{r_b} = \frac{1}{r_a \sqrt{1 + \rho^2 - 2\rho\cos\theta}} \tag{2}$$

where $\rho = R/r_a$. If $\rho < 1$ the radical in (2) can be expanded as

$$\frac{1}{\sqrt{1 + \rho^2 - 2\rho\cos\theta}} = \sum_{\ell=0}^{\infty} \rho^{\ell} P_{\ell}(\cos\theta) , \tag{3}$$

where the $P_\ell(\cos\theta)$ are the Legendre polynomials

$$\begin{aligned} P_0(\cos\theta) &= 1 \\ P_1(\cos\theta) &= \sin\theta \\ P_2(\cos\theta) &= \tfrac{1}{2}(3\cos^2\theta - 1) \\ &\vdots \end{aligned} \tag{4}$$

Thus (2) becomes

$$\frac{1}{r_b} = \sum_{\ell=0}^{\infty} \frac{(r_\langle)^\ell}{(r_\rangle)^{\ell+1}} P_\ell(\cos\theta), \tag{5}$$

where $r_\langle$ and $r_\rangle$ denote the lesser and greater, respectively, of r_a and R.

If there is a spherically symmetric charge distribution $\rho_a(r_a)$ centered at a, then the total electrostatic interaction with a charge centered at b is

$$\begin{aligned} V &= \int d\tau\, \rho_a(r_a) \frac{1}{r_b} \\ &= 2\pi \sum_{\ell=0}^{\infty} \int_0^\infty r_a^2\, dr_a\, \rho_a(r_a) \left[\frac{r_\langle^\ell}{r_\rangle^{\ell+1}}\right] \int_0^\pi \sin\theta\, d\theta\, P_\ell(\cos\theta), \end{aligned} \tag{6}$$

where we integrated over the φ coordinate. The Legendre polynomials have the property that

$$\int_0^\pi \sin\theta\, d\theta\, P_\ell(\cos\theta) = 2\,\delta_{\ell 0}, \tag{7}$$

so that (6) becomes

$$\begin{aligned} V &= 4\pi \int_0^\infty r_a^2\, dr_a\, \rho(r_a) \frac{1}{r_\rangle} \\ &= 4\pi \{ \frac{1}{R} \int_0^R r_a^2\, dr_a\, \rho_a(r_a) + \int_R^\infty r_a\, dr_a\, \rho_a(r_a) \}. \end{aligned} \tag{8}$$

The quantity

$$Q = 4\pi \int_0^R r_a^2\, dr_a\, \rho_a(r_a) \tag{9}$$

is the amount of charge within the sphere centered at a and passing through b. The contribution of this charge to V is just the same as if all this charge were concentrated at a.

The quantity

$$\delta Q = 4\pi r_a^2 \rho_a(r_a)\, \delta r_a \qquad (10)$$

is the amount of charge on a sphere of radius r_a and thickness δr_a. The potential within such a uniformly charged sphere is constant and equal to $\frac{1}{r_a}\,\delta Q$ as implied by the second term of (8).

Appendix 2-C Coulomb and Exchange Integrals

In §2.4 we indicated that

$$J_{ij} \geqslant K_{ij} \geqslant 0 .$$

These relationships are derived below

(a) $J_{ij} \geqslant 0.$

The Coulomb integral is

$$\begin{aligned} J_{ij} &= \int d\tau_1\, \phi_i^*(1)\, \phi_i(1) \int d\tau_2 \frac{1}{r_{12}}\, \phi_j^*(2)\, \phi_j(2) \\ &= \int d\tau_1\, d\tau_2 \frac{\phi_i^*(1)\, \phi_i(1)\, \phi_j^*(2)\, \phi_j(2)}{r_{12}} \quad . \end{aligned}$$

Since the integrand is positive for all values of $\underset{\sim}{r}_1$ and $\underset{\sim}{r}_2$, the integral must be positive. This integral is also denoted as

$$J_{ij} = [\phi_i^*\, \phi_i \,|\, \phi_j^*\, \phi_j] \ ,$$

where the orbitals on the left are for electron 1 and those on the right are for electron 2.

(b) $K_{ij} \geqslant 0.$

The exchange integral is

$$\begin{aligned} K_{ij} &= \int d\tau_1\, \phi_i^*(1)\, \phi_j(1) \int d\tau_2 \frac{1}{r_{12}}\, \phi_j^*(2)\, \phi_i(2) \\ &= [\phi_i^*\, \phi_j \,|\, \phi_j^*\, \phi_i] \ . \end{aligned}$$

To prove that $K_{ij} \geqslant 0$ we set

$$\phi_i = \xi_i + i\eta_i$$

$$\phi_j = \xi_j + i\eta_j$$

where ξ_i, η_i, ξ_j , and η_j are real. This substitution leads to

$$K_{ij} = [\{\xi_i(1) - i\eta_i(1)\}\{\xi_j(1) + i\eta_j(1)\}|\{\xi_i(2) + i\eta_i(2)\}\{\xi_j(2) - i\eta_j(2)\}]$$

$$= [\ \xi_i\xi_j + \eta_i\eta_j + i(\xi_i\eta_j - \eta_i\xi_i)|\xi_i\xi_j + \eta_i\eta_j - i(\xi_i\eta_j - \eta_i\xi_j)]\ .$$

We now define the charge distributions ρ_1 and ρ_2 as

$$\rho_1 = \xi_i\xi_j + \eta_i\eta_j$$

$$\rho_2 = \xi_i\eta_j - \eta_i\xi_j\ .$$

This leads to

$$K_{ij} = [\rho_1 + i\rho_2|\rho_1 - i\rho_2]$$

$$= \underbrace{[\rho_1|\rho_1]}_{\geqslant 0} + i\underbrace{\{[\rho_2|\rho_1] - [\rho_1|\rho_2]\}}_{= 0} + \underbrace{[\rho_2|\rho_2]}_{\geqslant 0}\ ,$$

and hence

$$K_{ij} \geqslant 0\ .$$

<u>(c) $J_{ij} \geqslant K_{ij}$.</u>

To show that $J_{ij} \geqslant K_{ij}$ we consider the wavefunction

$$\Psi(1,2) = \phi_i\phi_j - \phi_j\phi_i \qquad (1)$$

The electron-electron interaction energy for this state is

$$\langle\Psi|\frac{1}{r_{12}}|\Psi\rangle = \int\int d\tau_1\, d\tau_2\ \frac{1}{r_{12}}\ |\psi(1,2)|^2 \geqslant 0,$$

since the integrand is positive everywhere. Substituting the wavefunction (1) leads to

$$\langle \Psi | \frac{1}{r_{12}} | \Psi \rangle = 2(J_{ij} - K_{ij}) \tag{2}$$

and hence

$$J_{ij} \geqslant K_{ij} .$$

Expression (2) provides the physical significance of K_{ij}. It is the change in electron repulsion energy upon superimposing both products of orthogonal orbitals $\phi_i\phi_j$. That is, the wavefunctions $\frac{1}{\sqrt{2}}[\phi_i\phi_j \pm \phi_j\phi_i]$ lead to Coulomb repulsion energies of

$$J_{ij} \pm K_{ij} .$$

Appendix 2-D. Two-Electron Integrals for H_2

2-D.1 The Coulomb integral, $J_{\ell r}$

The Coulomb integral, $J_{\ell r}$ has the form

$$J_{\ell r} = \langle \chi_\ell(1)\, \chi_\ell(1) | \frac{1}{r_{12}} | \chi_r(2)\, \chi_r(2) \rangle \tag{1}$$

$$= \int d\tau_2 \left[\int d\tau_2\, \chi_\ell^*(1)\, \chi_\ell(1) \frac{1}{r_{12}} \right] \chi_r^*(2)\, \chi_r(2)$$

where χ_ℓ and χ_r are 1s atomic orbitals centered on the left and right protons. Letting

$$J_\ell(2) = \int d\tau_1\, \chi_\ell^*(1)\, \chi_\ell(1) \frac{1}{r_{12}} \ , \tag{2}$$

we have

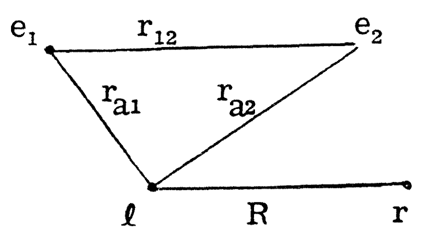
$$J_{\ell r} = \int d\tau_2\, J_\ell(2)\, \chi_r^*(2)\, \chi_r(2) \ . \tag{3}$$

In the remainder of this section we will assume χ_ℓ and χ_r are real.

First we evaluate J_ℓ by expanding $\frac{1}{r_{12}}$ as

$$\frac{1}{r_{12}} = \sum_{k=0}^{\infty} \sum_{m=-k}^{k} \frac{(k-|m|)!\, r_<^k}{(k+|m|)!\, r_>^{k+1}} P_k^{|m|}(\cos\theta_1)\, P_k^{|m|}(\cos\theta_2)\, e^{im(\varphi_1-\varphi_2)} \tag{4}$$

(the Laplace expansion) where r_{12} is the distance between the points with spherical coordinates $(r_1, \theta_1, \varphi_1)$ and $(r_2, \theta_2, \varphi_2)$.



Note that both r_1 and r_2 are with respect to the left-hand center.

Since χ_ℓ is spherically symmetric (about center ℓ) the integrals over θ_1 and ϕ_1 will be nonzero only when $k = m = 0$

$$J_\ell = 4\pi \int_0^\infty r_{a1}^2 \, dr_{a1} \, \chi_\ell^2(r_{a1}) \frac{1}{r_>} \quad . \tag{5}$$

Breaking the interval of integration to remove the $r_>$ yields,

$$J_\ell(2) = \frac{1}{r_{a2}} 4\pi \left[\int_0^{r_{a2}} \chi_\ell^2 (r_{a1}) r_{a1}^2 \, dr_{a1} + \int_{r_{a2}}^\infty \chi_\ell^2 (r_{a1}) r_{a1} r_{a2} \, dr_{a1} \right] \tag{6}$$

Letting

$$\chi_\ell(1) = \sqrt{\frac{\zeta^3}{\pi}} \, e^{-\zeta r_{a1}} \, , \tag{7}$$

we find

$$J_\ell(r_{a2}) = \frac{1}{r_{a2}} \left[1 - e^{-2\zeta r_{a2}} (1 + \zeta r_{a2}) \right] . \tag{8}$$

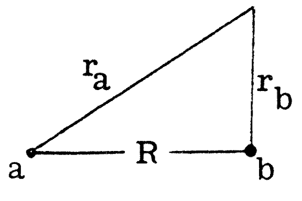
Now we must change to elliptic coordinates in order to evaluate the integral over the coordinates of electron 2.

Using elliptical coordinates ξ and η (see Appendix 2-A)

$$\xi = (r_a + r_b)/R$$

$$\eta = (r_a - r_b)/R$$

$$d\tau = \frac{R^3}{8} (\xi^2 - \eta^2) d\xi \, d\eta \, d\phi$$



in (8) and (3), we find

$$J_{\ell r} = \frac{\zeta^3 R^2}{4\pi} \int_0^{2\pi} d\varphi \int_{-1}^{1} d\eta \int_1^{\infty} d\xi \left\{ (\xi^2 - \eta^2)\, e^{-\zeta R(\xi - \eta)} \times \right.$$

$$\left. \times \frac{1}{(\xi + \eta)} \left[1 - e^{-\zeta R(\xi+\eta)} \left(1 + \frac{\zeta}{2} R(\xi + \eta) \right) \right] \right\}$$

$$= \frac{\zeta^3 R^2}{2} \int_{-1}^{1} d\eta \int_1^{\infty} d\xi\, (\xi - \eta) \left[e^{-\zeta R(\xi - \eta)} - e^{-2\zeta R\xi} \left(1 + \frac{\zeta}{2} R(\xi + \eta) \right) \right] \tag{9}$$

or

$$J_{\ell r} = \frac{\zeta^3 R^2}{2} \int_{-1}^{1} d\eta \int_1^{\infty} d\xi\, (\xi - \eta)\, e^{-\zeta R(\xi - \eta)} +$$

$$+ \frac{\zeta^3 R^2}{2} \int_{-1}^{1} d\eta \int_1^{\infty} d\xi\, (\xi - \eta)\, e^{-2\zeta R\xi} + \tag{10}$$

$$+ \frac{\zeta^4 R^3}{4} \int_{-1}^{1} d\eta \int_1^{\infty} d\xi\, (\xi^2 - \eta^2)\, e^{-2\zeta R\xi} .$$

Evaluating these elementary integrals gives the following result

$$J_{\ell r} = \zeta \left[\frac{1}{\zeta R} - e^{-2\zeta R} \left(\frac{1}{\zeta R} + \frac{11}{8} + \frac{3}{4} \zeta R + \frac{1}{6} \zeta^2 R^2 \right) \right] \tag{11}$$

Problem: Evaluate $\langle \chi_\ell(1)\, \chi_\ell(1) \,|\, \frac{1}{r_{12}} \,|\, \chi_r(2)\, \chi_\ell(2) \rangle$

2-D.2 The Exchange Integral $K_{\ell r}$

Now we evaluate the exchange integral

$$K_{\ell r} = \langle \chi_\ell(1)\, \chi_r(2) | \frac{1}{r_{12}} | \chi_r(1)\, \chi_\ell(2) \rangle = [\chi_\ell \chi_r | \chi_\ell \chi_r]. \qquad (12)$$

Again we can define a quantity

$$I(2) = \int d\tau_1 [\chi_\ell(1)\, \chi_r(1) \frac{1}{r_{12}}] \qquad (13)$$

involving integration over the first electron. Unfortunately the Laplace expansion of $\frac{1}{r_{12}}$ will now lead to an infinite sum because $\chi_\ell(1)\, \chi_r(1)$ is not spherically symmetric.

Instead we expand $\frac{1}{r_{12}}$ in terms of elliptical coordinates using the Neuman expansion,

$$\frac{1}{r_{12}} = \frac{2}{R} \sum_{k=0}^{\infty} \sum_{m=-k}^{k} (-1)^m (2k+1) \left[\frac{(k-|m|)!}{(k+|m|)!} \right]^2 \times$$

$$\times P_k^{|m|}[\xi_<]\, Q_k^{|m|}[\xi_>]\, P_k^{|m|}(\eta_1)\, P_k^{|m|}(\eta_2)\, e^{im(\varphi_1 - \varphi_2)} \qquad (14)$$

where $P_k^{|m|}$ are the associated Legendre functions and

$Q_k^{|m|}$ are the associated Legendre functions of the second kind.

Our function $\chi_\ell \chi_r$ is independent of φ so the only nonzero term in the m summation is $m = 0$.

To simplify the k summation we use the property

$$\int_{-1}^{1} P_k(\eta)\, P_{k'}(\eta)\, d\eta = 0 \quad \text{if } k \neq k'$$

together with the facts that

$$P_0(\eta) = \text{constant}$$

and

$$P_2(\eta) = \tfrac{3}{2}(\eta^2 - \tfrac{1}{3}) .$$

Thus since the volume element for integration is $\frac{R^3}{8}(\xi_1^2 - \eta_1^2)\,d\xi_1\,d\eta_1, d\phi_1$, we find that by integration with respect to η, the only nonzero terms are for $k = 0$ and $k = 2$.

We will now skip pages of tedious algebra to the result (see, for example, J. C. Slater, Quantum Theory of Molecules and Solids, Vol. I, pp 266-273 for the details).

It is first convenient to define

$$S = e^{-\zeta R}(1 + \zeta R + \tfrac{1}{3}\zeta^2 R^2)$$

$$\sigma = e^{+\zeta R}(1 - \zeta R + \tfrac{1}{3}\zeta^2 R^2)$$

$$C = \int_0^1 \frac{1 - e^t}{t}\,dt - \int_1^\infty \frac{e^{-t}}{t}\,dt = 0.57722 \quad \text{(Euler's Constant)}$$

$$Ei(-x) = -\int_x^\infty \frac{e^{-t}}{t}\,dt \quad \text{(integral logarithm)} .$$

With these definitions the result is

$$K_{\ell r} = \frac{1}{10}\zeta\left\{-e^{-2\zeta R}\left(-\frac{25}{8} + \frac{23}{4}\zeta R + 3\zeta^2 R^2 + \tfrac{1}{3}\zeta^3 R^3\right) + \right.$$

$$\left. + \frac{6}{\zeta R}\left[S^2\left(C + \ell n(\zeta R)\right) + \sigma^2\,Ei(-4\zeta R) - 2S\sigma\,Ei(-2\zeta R)\right]\right\}$$

or for small R

$$K_{\ell r} = \tfrac{1}{2}\zeta\left[\frac{5}{4} - \tfrac{1}{2}\zeta^2 R^2 + \left(\frac{3}{50} + \frac{8}{75}\,\ell n\, 4\right)\zeta^4 R^4\right] + \text{(higher order terms).}$$

Note also for small R that if we include terms through R^2,

$$J_{\ell r} = \tfrac{1}{2}\zeta\left(\frac{5}{4} - \frac{1}{6}\,\zeta^2 R^2 + \ . \ . \ . \ \right)$$

$$K_{\ell r} = \tfrac{1}{2}\zeta\left(\frac{5}{4} - \tfrac{1}{2}\zeta^2 R^2 + \ . \ . \ . \ \right)$$

$$\underline{\therefore\ K_{\ell r} < J_{\ell r}\ .}$$

APPENDIX 2-E. DETAILED ANALYSIS OF THE EXCHANGE TERMS

In this section we will provide more detailed analysis of the classical and exchange terms for H_2^+ discussed in § 2.2 and § 2.3.

2-E.1 The Potential Energy Terms

Just as with the total energy (see § 2.2.1) the potential energy can be partitioned into classical and exchange terms as follows

$$V_g = \frac{v_{\ell\ell} + v_{rr} + 2v_{\ell r}}{2(1 + S)} + \frac{1}{R}$$

$$= \frac{v_{\ell\ell} + v_{\ell r}}{1 + S} + \frac{1}{R}$$

$$= V^{c\ell} + V_g^x , \qquad (1)$$

where

$$v_{\ell r} = \langle \ell | v | r \rangle .$$

$$V^{c\ell} = v_{\ell\ell} + \frac{1}{R} \qquad (2)$$

$$= \tfrac{1}{2}(v_{\ell\ell} + v_{rr}) + \frac{1}{R}$$

$$= \int dr\, v(\underset{\frown}{r})\rho^{c\ell}(\underset{\frown}{r}) + \frac{1}{R}$$

$$V_g^x = \frac{v_{\ell r} - S\, v_{\ell\ell}}{1 + S}$$

$$= \frac{\tau_v}{1 + S} \qquad (3)$$

$$\tau_v \equiv v_{\ell r} - S\, v_{\ell\ell} \qquad (4)$$

($\rho^{c\ell}$ is given in 2.3-3). Similarly

$$V_u = V^{c\ell} + V_u^x$$

where

$$V_u^x = \frac{-\tau_v}{1 - S} \quad . \tag{5}$$

First we examine the form of $V^{c\ell}$. Substituting (2.1-4) leads to

$$\begin{aligned} V^{c\ell} &= \langle \chi_\ell | -\frac{1}{r_a} - \frac{1}{r_b} | \chi_\ell \rangle + \frac{1}{R} \\ &= \langle \chi_\ell | -\frac{1}{r_a} | \chi_\ell \rangle + \langle \chi_\ell | \frac{1}{R} - \frac{1}{r_b} | \chi_\ell \rangle \end{aligned} \tag{6}$$

The first term is just the potential energy of an isolated hydrogen atom. The second term is the net Coulomb interaction between a proton (on the right) and a hydrogen atom (on the left). As shown in App. A [eqn. (25)]

$$\Delta V^{c\ell} \equiv \langle \chi_\ell | \frac{1}{R} - \frac{1}{r_b} | \chi_\ell \rangle = (1 + \frac{1}{R}) e^{-2R}$$

and hence

$$V^{c\ell} = -1 + (1 + \frac{1}{R}) e^{-2R} \tag{7}$$

Consequently in the simple classical description (superposition of atomic densities), there is no bonding of H_2^+. [This classical description is equivalent to bringing up a proton to a hydrogen atom without allowing any changes in the wavefunction of the hydrogen atom.] The other terms in the potential energy arise from interference effects. That is, they occur because we superimpose amplitudes rather than densities.

The total electron density for the g state is

$$\rho_g = \frac{\chi_\ell \chi_\ell + \chi_r \chi_r + 2 \chi_\ell \chi_r}{2 (1 + S)} \quad ,$$

which can be partitioned into classical and exchange parts as

$$\rho_g = \rho^{c\ell} + \rho_g^x \quad , \tag{8}$$

where $\rho^{c\ell}$ is given in (2.3-3) and

$$\rho_g^x = \frac{[\chi_\ell \chi_r - S\rho^{c\ell}]}{(1 + S)} \quad . \tag{9}$$

Since

$$\int d\tau \rho = 1$$

and

$$\int d\tau \rho^{c\ell} = 1$$

the integral of ρ^x must be zero

$$\int d\tau \rho^x = 0 \ . \tag{10}$$

That is, ρ^x merely shifts density around with no net contribution to the total electron charge. As a result we can determine the sign of

$$V_g^x = \int d\tau \, v(\underset{\frown}{r}) \, \rho_g^x(\underset{\frown}{r}) \tag{11}$$

from Fig. 2-8. Here we see that $\rho_g^x > 0$ near the bond midpoint while $\rho_g^x < 0$ near the nuclei; that is, ρ_g^x leads to a shift of charge from the nuclear region to the bond region. Since $v(\underset{\frown}{r})$ is much more negative near the nuclei than near the bond midpoint, this shift of charge into the bond region leads to a positive value for $V_g(R)$ as shown in Fig. 36.

EXERCISE:

(a) Evaluate ρ_g^x and $\rho^{c\ell}$ at the bond midpoint for $R = 2.5\ a_0$.

[Answer: $\rho_g^x(\frac{R}{2}) = \frac{0.033}{\pi}$, $\rho^{c\ell}(\frac{R}{2}) = \frac{0.286}{\pi}$] .

(b) Evaluate ρ_g^x and $\rho^{c\ell}$ at the left nucleus.

[Answer: $\rho_g^x(0) = \frac{-0.10}{\pi}$ and $\rho^{c\ell}(0) = \frac{0.50}{\pi}$] .

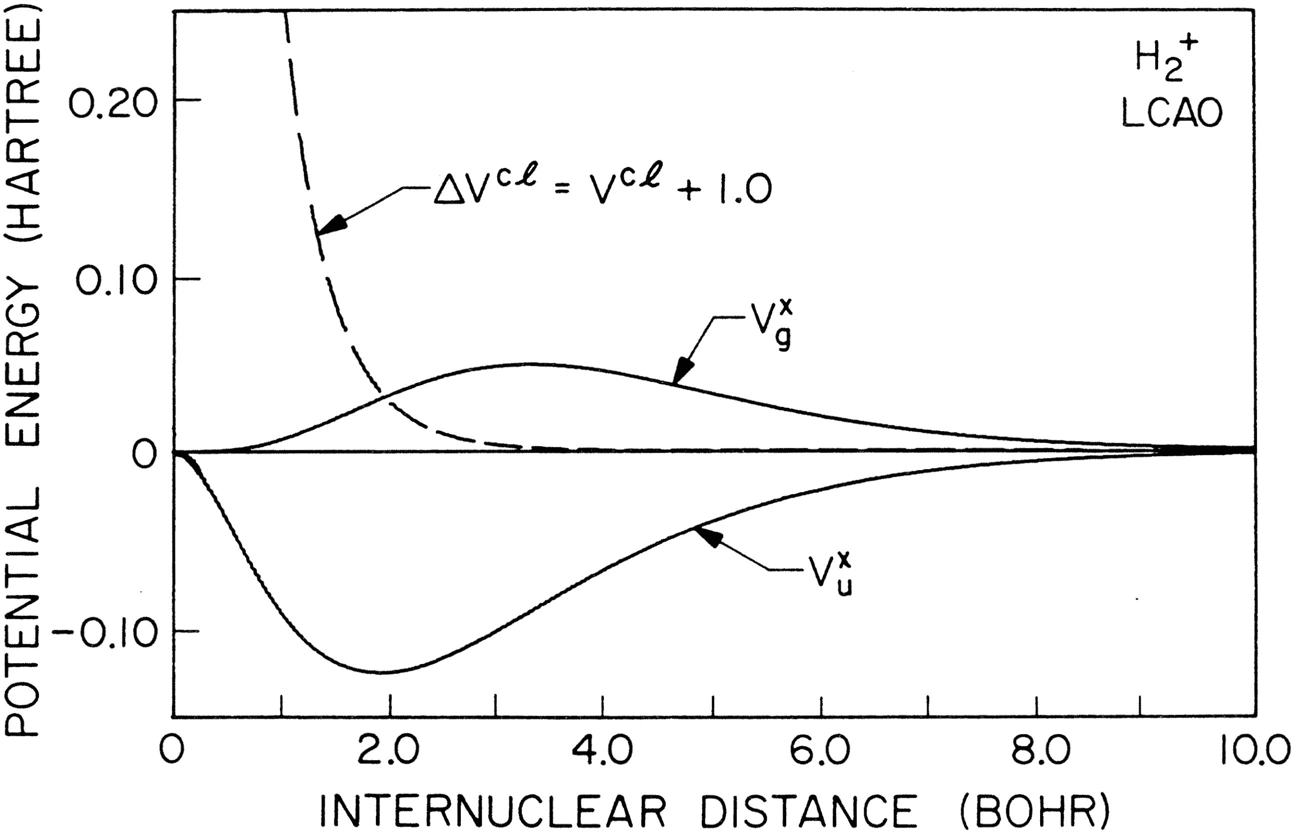


Figure 2-36. The classical and exchange potential energies for the LCAO wavefunction of H_2^+.

2-E.2 The Kinetic Energy Terms

The kinetic energy of the ϕ_g state can be written as

$$T_g = \frac{t_{\ell\ell} + t_{rr} + 2t_{\ell r}}{2(1 + S)}$$

$$= \frac{t_{\ell\ell} + t_{\ell r}}{1 + S} , \tag{12}$$

where

$$t_{\ell\ell} = \langle \chi_\ell | \hat{t} | \chi_\ell \rangle$$

$$= t_{rr} ,$$

$$t_{\ell r} = \langle \chi_\ell | \hat{t} | \chi_r \rangle .$$

We will write

$$T_g = T^{c\ell} + T_g^x , \tag{13}$$

where

$$T^{c\ell} = \tfrac{1}{2} (t_{\ell\ell} + t_{rr}) = t_{\ell\ell} \tag{14}$$

$$T_g^x = \frac{t_{\ell r} - S\, T^{c\ell}}{1 + S}$$

$$= \frac{\tau_t}{1 + S} \tag{15}$$

$$\tau_t \equiv t_{\ell r} - S\, T^{c\ell} \tag{16}$$

Similarly $T_u = T^{c\ell} + T_u^x$, where

$$T_u^x = -\frac{t_{\ell r} - S\,T^{c\ell}}{1 - S} = -\frac{\tau_t}{1 - S} \tag{17}$$

Since $T^{c\ell}$ is just the atomic value of the kinetic energy (independent of R), the changes in T responsible for bonding must all be contained in T^x. Thus the plots of T_g and T_u in Fig. 12 are actually plots of T_g^x and T_u^x.

The large negative value of T_g responsible for the bond in H_2^+ results from the large negative value of τ_t. We will now examine why τ_t is large and negative. From Appendix 1-A we know that

$$\begin{aligned} t_{\ell r} &= -\tfrac{1}{2}\langle \chi_\ell | \nabla^2 | \chi_r \rangle = \tfrac{1}{2}\langle \nabla\chi_\ell \cdot \nabla\chi_r \rangle \\ &= \tfrac{1}{2}\int d\tau (\nabla\chi_\ell^*)\cdot \nabla\chi_r \; ; \end{aligned} \tag{18}$$

$$t_{\ell\ell} = \tfrac{1}{2} < |\nabla\chi_\ell|^2 > \;,$$

and

$$t_{rr} = \tfrac{1}{2} < |\nabla\chi_r|^2 > \;.$$

Thus

$$\tau_t = t_{\ell r} - \tfrac{1}{2} S (t_{\ell\ell} + t_{rr}) \tag{19}$$

$$= \tfrac{1}{2}\int d^3\underset{\wedge}{r}\, \{\nabla\chi_\ell \cdot \nabla\chi_r - \tfrac{S}{2}[(\nabla\chi_\ell)^2 + (\nabla\chi_r)^2]\} \tag{20}$$

In order to understand the significance of the terms in (20), we will consider first the case where τ_t is <u>modified</u> by replacing

$\nabla\chi_\ell \cdot \nabla\chi_r$ in (20) by $|\nabla\chi_\ell|\,|\nabla\chi_r|$. This leads to an integrand of the form

$$|\nabla\chi_r|\,|\nabla\chi_\ell| - \frac{S}{2}\left[(\nabla\chi_\ell)^2 + (\nabla\chi_r)^2\right] \quad . \tag{21}$$

Since $\chi_\ell = e^{-r_a}$ we obtain

$$\nabla\chi_\ell = -\chi_\ell \hat{e}_r$$

(where $\hat{e}_r$ is a unit vector in the r direction) and hence (21) becomes

$$[\chi_r \chi_\ell - \frac{S}{2}(\chi_\ell^2 + \chi_r^2)]$$

However the term in brackets is just proportional to ρ^x in (9) and hence from (10) the resulting integral is zero. Thus it is the difference between the dot product term

$$\nabla\chi_\ell \cdot \nabla\chi_r$$

in (20) and the absolute value term

$$|\nabla\chi_\ell|\,|\nabla\chi_r|$$

in (21) that is responsible for the large negative value of τ_t and hence of the chemical bond. To emphasize this we define a function called the contragradience

$$C(\underset{\sim}{r}) = |\nabla\chi_\ell|\,|\nabla\chi_r| - \nabla\chi_\ell \cdot \nabla\chi_r \tag{2.3-7}$$

such that

$$\tau_t = -\tfrac{1}{2}\int d^3\underset{\sim}{r}\; C(\underset{\sim}{r}). \tag{2.3-6}$$

Large contragradiences lead to a large negative τ_t and hence strong bonds. As discussed in § 2.3.3 and illustrated in Fig. 14, the largest values of C(r) occur for points in between the nuclei.

2-E.3 Specific Results for H_2^+

From App. A the explicit form of τ_t for H_2^+ is

$$\tau_t = -\tfrac{1}{3}R^2 e^{-R}$$

Thus as expected, $\tau_t \rightarrow 0$ as $R \rightarrow 0$ and as $R \rightarrow \infty$. The minimum in τ_t occurs for $R = 2$. Thus we would expect the maximum bonding effect to occur near $R = 2a_0$. Indeed this is the optimum R of the exact wavefunction of H_2^+. Approximating the bond strength as

$$T_g^x = -\frac{\tau_t}{1+S}$$

we obtain for $R = 2$ (where $S = 0.6$)

$$\begin{aligned} T_g^x &= \frac{4e^{-2}}{(3)(1.6)} = -0.12h \\ &= 3.1\,\mathrm{eV} \end{aligned}$$

In fact the bond energy is only $0.1h = 2.5$ eV, and the T_g^x term does dominate the bonding. For quantitative considerations we should, of course, use the total E^x.

From Appendix A the explicit form of τ_v for H_2^+ is

$$\tau_v = e^{-R}\left[\frac{1}{R} - \frac{2}{3}R + \frac{1}{3}R^2\right] , \tag{22}$$

neglecting terms of order e^{-2R}. Combining with τ_t leads to

$$\tau = e^{-R}\left[\frac{1}{R} - \frac{2}{3}R\right] \tag{23}$$

(neglecting terms of order e^{-2R}), whereas

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

Thus

$$\frac{\tau}{S} = -\frac{2}{R}\left(1 - \frac{3}{R} + \frac{9}{2R^2}\right) + 0\left(\frac{1}{R^4}\right)$$

and hence $\tau \approx -\frac{2}{R} S$. (24)

Various energies for H_2^+ are tabulated in Table I.

Table 2-1. Energy quantities for the LCAO wavefunctions of the g state of H_2^+. All quantities are in atomic units.

R	S	$\Delta V^{c\ell}$	V^x	ΔV^{total}	$T^x = \Delta T^{total}$	ΔE^{total}
∞		0.0[a]	0.0	0.0[a]	0.0[a]	0.0[a]
10.0	0.00201	0.00000	0.00121	0.00121	-0.00151	-0.00030
8.0	0.01018	0.00000	0.00536	0.00536	-0.00708	-0.00173
6.0	0.04710	0.00001	0.01933	0.01934	-0.02841	-0.00907
5.0	0.09658	0.00005	0.03195	0.03200	-0.05120	-0.01920
4.0	0.18926	0.00042	0.04485	0.04527	-0.08214	-0.03687
3.5	0.25919	0.00117	0.04858	0.04975	-0.09792	-0.04817
3.0	0.34851	0.00331	0.04837	0.05168	-0.11076	-0.05908
2.5	0.45831	0.00943	0.04301	0.05244	-0.11727	-0.06483
2.0	0.58645	0.02747	0.03250	0.05997	-0.11374	-0.05377
1.5	0.72517	0.08298	0.01901	0.10199	-0.09700	+0.00499
1.0	0.85839	0.27067	0.00695	0.27762	-0.06599	0.21163
0.5	0.96034	1.10364	0.00080	1.10443	-0.02578	1.07865

[a] The values at R = ∞ are $V^{c\ell} = -1.0$, $V^{total} = -1.0$, $T^{total} = 0.5$, $E^{total} = 0.5$.

Ch 120a

Chapter 3. More Exact Wavefunctions for One- and Two-Electron Systems

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* There is no Section 3.4 in this Chapter.

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Appendices:

Summary

The energy ϵ_0 of any approximate wavefunction ϕ_0 is an upper bound on the exact energy of the ground state E_0,

$$\epsilon_0 \geqslant E_0, \tag{3.1-3}$$

leading to the variational condition: If an approximate wavefunction (and hence the energy) is a function of some parameter λ, then the optimum wavefunction satisfies the (necessary) condition

$$\frac{\partial \epsilon}{\partial \lambda} = 0. \tag{3.1-4}$$

Expanding the unknown wavefunction ϕ in terms of a basis

$$\phi = \sum_{\mu=1}^{P} C_\mu \chi_\mu \tag{3.1-6}$$

and applying the variational condition leads to a set of matrix equations,

$$\underset{\sim}{H}\,\underset{\sim}{C} = E\,\underset{\sim}{S}\,\underset{\sim}{C} \tag{3.1-25}$$

for obtaining the optimum coefficients (i.e., wavefunction).

More exact wavefunctions of H_2^+ are considered in § 3.2, but in § 3.3 we find that the description of bonding in terms of exchange energies is retained.

In § 3.5 we present an overview of three useful methods for wavefunctions: (a) The Hartree Fock (HF) method is a generalization of the MO wavefunction in which the wavefunction (ground state of a two-electron system) is taken as

$$\Phi^{HF}(1,2) = \phi(1)\,\phi(2) \tag{3.5-10}$$

and the orbitals ϕ optimized by solving the differential equation

$$H^{HF}\phi = (h + J_{\phi})\,\phi = \epsilon\,\phi \tag{3.5-20}$$

or the matrix equation

$$\underline{H}^{HF}\underline{C} = \epsilon\,\underline{S}\,\underline{C}\ . \tag{3.5-18b}$$

These equations are nonlinear and must be solved iteratively.

(b) The generalized valence bond (GVB) method is a generalization of the VB method with the wavefunction taken of the form

$$\Phi^{GVB}(1,2) = \phi_a(1)\,\phi_b(2) + \phi_b(1)\,\phi_a(2) \tag{3.5-22}$$

and the orbitals ϕ_a and ϕ_b optimized. This leads to two matrix equations

$$\begin{aligned}\underline{H}^{a}\underline{C}_a &= \epsilon_a\underline{S}\,\underline{C}_a\\ \underline{H}^{b}\underline{C}_b &= \epsilon_b\underline{S}\,\underline{C}_b\end{aligned} \tag{3.5-31}$$

analogous to the HF equations (3.5-18) and to two differential equations analogous to (3.5-20).

(c) The configuration interaction (CI) method with the wavefunction taken of the form

$$\Phi^{CI}(1,2) = \sum_{\mu,\nu} C_{\mu\nu}\,\chi_\mu(1)\,\chi_\nu(2)$$

For the ground state this wavefunction can always be written in terms of natural orbitals $\{\overline{\chi}_\mu\}$ as

$$\Phi^{CI}(1,2) = \sum_{\mu} \overline{C}_\mu\,\overline{\chi}_\mu(1)\,\overline{\chi}_\mu(2)\ . \tag{3.5-53}$$

In § 3.5.5 we find that the ground state of any two electron system is nodeless and symmetric

$$\Phi(1,2) = \Phi(2,1).$$

In § 3.6 and § 3.7 we find that the HF wavefunction accounts for all but about 1.1 eV of the energy for He and H_2 and that a CI wavefunction with five NO's accounts for all but about 0.15 eV. The four correlating NO's for this wavefunction all involve one nodal plane.

All these methods involve expansions in terms of basis sets. For He it is possible to obtain highly accurate HF and GVB wavefunctions with only two (s-like) basis functions [the double valence (DV) basis] and for H_2 similar quality wavefunctions can be obtained with six basis functions (two s and one p on each center), [the DVP or double valence plus polarization basis].

Chapter 3. More Exact Wavefunctions for One- and Two-Electron Systems

In Chapter 2 we discussed approximate wavefunctions for H_2^+

$$\chi_\ell \pm \chi_r$$

and for H_2

$$\chi_\ell \chi_r \pm \chi_r \chi_\ell \, .$$

In this chapter we will consider some aspects of more exact wavefunctions for these molecules and for the two-electron atom, He. Our emphasis will be on qualitative ideas, explicit methods for solving for the wavefunctions will not be developed until Ch120c.

In §3.1 we examine the variational principle and in § 3.5 we use this principle to examine some of the useful methods for calculating wavefunctions: Hartree-Fock (HF), generalized valence bond (GVB), and configuration interaction (CI).

Accurate wavefunctions for H_2^+, He, and H_2 are discussed in sections § 3.2, § 3.6 and § 3.7, respectively. In § 3.3 we reexamine the nature of the bond in H_2^+ and in § 3.7.2 we reexamine the bond in H_2.

§3.1 The Variational Principle

The wavefunction for the ground state of the hydrogen atom has the form e^{-r} and the wavefunction for the ground state of the harmonic oscillator is

$$e^{-\alpha r^2} .$$

However, there are very few interesting systems for which the Schrödinger equation can be solved exactly. Even so there are general procedures allowing one to obtain highly accurate (indeed arbitrarily accurate) wavefunctions. The powerful tool needed is the variational principle which will be discussed extensively in Ch120c. Here we will outline some of the key results of this principle in order to clarify the qualitative discussions of Ch120a. These key results are:

a. Upper bound theorem.

If ψ_0 and E_0 are the exact ground state wavefunction and energy of a system

$$\mathcal{H}\psi_0 = E_0\psi_0 \tag{1}$$

and if ϕ_0 is an approximate wavefunction with energy

$$\epsilon_0 = \frac{\langle\phi_0|\mathcal{H}|\phi_0\rangle}{\langle\phi_0|\phi_0\rangle} , \tag{2}$$

then

$$\epsilon_0 \geqslant E_0 . \tag{3}$$

That is, the energy evaluated using any approximate wavefunction is an upper bound in the exact energy of the ground state.

b. Variational condition

Given an approximate wavefunction $\phi_\lambda(r)$ depending upon some parameter λ,

$$\text{e.g., } \phi_\lambda = e^{-\lambda r},$$

then the optimum value of λ for describing the system must satisfy the necessary condition

$$\frac{\partial \epsilon(\lambda)}{\partial \lambda} = 0, \tag{4}$$

where

$$\epsilon(\lambda) = \frac{\langle \phi_\lambda | \mathcal{H} | \phi_\lambda \rangle}{\langle \phi_\lambda | \phi_\lambda \rangle} .$$

Equation (4) is referred to as the variational condition.

c. Basis set expansions

Given a set of functions

$$\{\chi_\mu(r) \, , \ \mu = 1, 2, \cdots P\} \, , \tag{5}$$

the optimum wavefunction of the form

$$\phi = \sum_{\mu=1}^{P} C_\mu \chi_\mu \tag{6}$$

satisfies the condition

$$\sum_\nu H_{\mu\nu} C_\nu = E \sum_\nu S_{\mu\nu} C_\nu \, , \tag{7a}$$

or in matrix notation

$$\underset{\frown}{H} \, \underset{\frown}{C} = E \, \underset{\frown}{S} \, \underset{\frown}{C} \, , \tag{7b}$$

where

$$H_{\mu\nu} \equiv \langle \chi_\mu | \mathcal{H} | \chi_\nu \rangle$$
$$S_{\mu\nu} \equiv \langle \chi_\mu | \chi_\nu \rangle \; . \qquad (8)$$

The set of functions (5) used for expansion of the unknown function ϕ is called a <u>basis set</u>. The unknowns are the coefficients

$$\{C_\mu ; \; \mu = 1, \cdots P\} \qquad (9)$$

which are obtained by solving the matrix equations (7).

§3.1.1 Discussion Of Upper Bound Theorem

The upper bound theorem (3) is easy to derive. Consider that the exact eigenstates $\{\psi_i\}$ of the Hamiltonian were known

$$\mathcal{H}\,\psi_i = E_i \psi_i \qquad (10)$$

with $i = 0$ as the ground state.

Since the set of functions $\{\psi_i\}$ is complete, we can expand any approximate wavefunction ϕ_0 as

$$\phi_0 = \sum_i C_i \psi_i \quad . \qquad (11)$$

Of course, in a real problem we will not know the functions $\{\psi_i\}$, and hence we will not be able to calculate the $\{C_i\}$. However, the analysis in this section will serve to establish a relation between the approximate and exact solutions. From (10) and (11)

$$\hat{\mathcal{H}}\phi_0 = \sum_i C_i \mathcal{H}\psi_i = \sum_i C_i E_i \psi_i \qquad (12)$$

and the energy of the approximate wavefunction ϕ_0 is

$$\epsilon_0 \equiv \langle \phi_0 | \hat{\mathcal{H}} | \phi_0 \rangle = \sum_i \sum_j C_j^* C_i E_i \langle \psi_j | \psi_i \rangle = \sum_i |C_i|^2 E_i \, . \qquad (13)$$

Assuming ϕ_0 is normalized,

$$1 = \langle \phi_0 | \phi_0 \rangle = \sum_{ij} C_j^* C_i \langle \psi_j | \psi_i \rangle = \sum_i |C_i|^2 . \qquad (14)$$

Using (14) in (13) we obtain

$$\epsilon_0 - E_0 = \sum_i |C_i|^2 \, (E_i - E_0) \, . \qquad (15)$$

Since $E_i \geqslant E_0$ and $|C_i|^2 \geqslant 0$, the right-hand side of (15) is necessarily positive, and hence

$$\epsilon_0 - E_0 \geqslant 0$$

or

$$\boxed{\epsilon_0 \geqslant E_0} \, . \qquad (16)$$

That is, the energy calculated for *any* wavefunction is *never* lower than the exact energy for the ground state wavefunction.* Thus we say that ϵ_0 is an *upper bound* on E_0.

---

*In deriving (16) we assumed that ϕ_0 could be expanded in terms of the eigenfunctions of $\hat{\mathcal{H}}$. This requires that ϕ_0 satisfy the boundary conditions for $\hat{\mathcal{H}}$. For example, if the boundary conditions for the system described by (10) were such that all wavefunctions are anti-symmetric, then we could not allow ϕ_0 to contain a symmetric part.

§3.1.2 Discussion of the Variational Principle

Since any approximate wavefunction must yeild an energy above the energy of the exact (ground state) wavefunction, we have a useful criterion for improving approximate wavefunctions. Namely, if you can find some change in the wavefunction that leads to a lower energy, then do it! And reject any changes that increase the energy. Ultimately if we consider all possible changes in the wavefunction, this procedure must yield the exact wavefunction. Normally we lose patience before considering all changes in the wavefunction, and instead we consider functions of certain restricted classes. Here our basic criterion for approximating the wavefunction will be to select that function of our specific restricted class leading to the lowest energy. If λ is some variable parameter for the restricted set of functions being considered, then the optimum wavefunction must satisfy

$$\boxed{\frac{\partial E}{\partial \lambda} = 0}, \qquad (17)$$

since otherwise a lower energy could be obtained by changing λ a bit, as illustrated in Fig. 1.

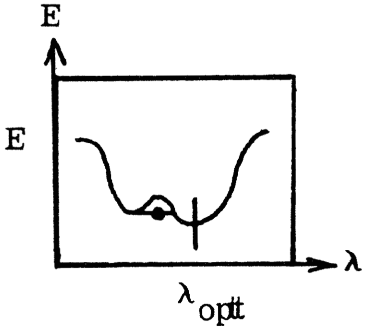

Figure 3-1,

This criterion for optimizing a wavefunction is called the variational principle and forms the basis of all methods we will consider for determining wavefunctions. It should be noted here that (17) is not sufficient to guarantee a minimum with respect to variations in λ (this requires $\frac{\partial^2 E}{\partial \lambda^2} > 0$) and even if a minimum is found it need not in general be the minimum leading to the lowest energy. Fortunately for the types of problems we deal with, these potential difficulties can usually be avoided.

§3.1.2a Parameter Optimization

Consider as an approximation to the ground state of the hydrogen atom the function

$$\phi_0(\alpha) = e^{-\alpha r^2} \qquad (18)$$

where α is a parameter. To determine the value of α minimizing the energy, we first calculate the energy as a function of α,

$$E(\alpha) = \langle \phi_0 | -\tfrac{1}{2}\nabla^2 - \tfrac{1}{r} \ |\phi_0\rangle / \langle \phi_0 | \phi_0 \rangle$$

$$= \frac{3\alpha}{2} - \left(\frac{8\alpha}{\pi}\right)^{\frac{1}{2}} \quad . \qquad (19)$$

The optimum value of α is given by

$$\frac{dE(\alpha)}{d\alpha} = 0 = \tfrac{3}{2} - \tfrac{1}{2}\left(\frac{8}{\pi\alpha}\right)^{\frac{1}{2}}$$

or

$$\alpha_{\text{opt}} = \frac{8}{9\pi} = 0.283\ldots$$

Substituting this into (19) we obtain

$$E(\alpha_{\text{opt}}) = -\frac{4}{3\pi} = -0.4244\ldots$$

(recalling that the exact energy is $E = -0.5$). Thus, even though (18) is considerably different from the exact eigenfunction for the ground state of the hydrogen atom, by optimizing α we are able to account for 84.9% of the energy.

Exercise. (a) Derive the energy expression (19).

(b) Consider

$$ze^{-\alpha r^2}$$

as an approximation to the 2p orbital of hydrogen atom. Find the optimum α.

(c) How would you proceed to obtain a corresponding approximation to the 2s orbital of hydrogen atom?

§3.1.3 Basis Set Expansions

We will now use the variational principle to determine the best representation of an approximate wavefunction as an expansion (6) in terms of the functions of some finite basis set (5). The energy is

$$E = \frac{\langle \phi | \mathcal{H} | \phi \rangle}{\langle \phi | \phi \rangle} = \frac{N}{D} , \tag{20}$$

where

$$N \equiv \sum_{\mu,\nu} C^*_\mu H_{\mu\nu} C_\nu \tag{21}$$

$$D \equiv \sum_{\mu,\nu} C^*_\mu S_{\mu\nu} C_\nu \tag{22}$$

and $H_{\mu\nu}$, $S_{\mu\nu}$ are given in (8). (We do not assume here that the basis functions are orthonormal; they must of course be linearly independent.)

The energy (20) depends on the P parameters $\{C_\mu\}$, and thus from the variational principle we require that

$$\frac{\partial E}{\partial C_\mu} = 0, \quad \text{for } \mu = 1, 2, \ldots, P .$$

From (20) this leads to

$$\frac{\partial E}{\partial C_\mu} = \frac{1}{D} \frac{\partial N}{\partial C_\mu} - \frac{N}{D^2} \frac{\partial D}{\partial C_\mu}$$

$$= \frac{1}{D} \left[\frac{\partial N}{\partial C_\mu} - E \frac{\partial D}{\partial C_\mu} \right] = 0$$

and hence

$$\frac{\partial N}{\partial C_\mu} - E \frac{\partial D}{\partial C_\mu} = 0 . \tag{23}$$

Assuming that the basis functions $\{\chi_\mu\}$ and coefficients $\{C_\mu\}$ are all real,[*] we obtain[#]

$$2\left[\sum_\nu (H_{\mu\nu} - ES_{\mu\nu})\, C_\nu\right] = 0 \tag{24}$$

and hence

$$\sum_\nu H_{\mu\nu} C_\nu = E \sum_\nu S_{\mu\nu} C_\nu \quad . \tag{7}$$

In matrix notation (7) becomes

$$\underset{\wedge}{H}\,\underset{\wedge}{C} = E\,\underset{\wedge}{S}\,\underset{\wedge}{C}\,. \tag{25}$$

If the basis functions are <u>orthonormal</u>

$$S_{\mu\nu} = \delta_{\mu\nu}\,, \tag{26}$$

the variational condition (25) becomes

$$\underset{\wedge}{H}\,\underset{\wedge}{C} = E\,\underset{\wedge}{C}\,. \tag{27}$$

Thus the variational principle leads to a finite matrix equation directly analogous to the Schrödinger equation. Indeed if a complete set of basis functions is used, the solution of (17) or (27) is the exact solution of the Schrödinger equation! Although the wavefunction and basis functions were written as one electron functions, this procedure applies identically for many-electron wavefunctions.

---

[*] The more general case leads to the same equations.

[#] Note that if the basis functions are real then $H_{\mu\nu} = H_{\nu\mu}$ and $S_{\mu\nu} = S_{\nu\mu}$.

§ 3.2 Accurate Wavefunctions for H_2^+

The LCAO wavefunction of H_2^+ discussed in § 2.2 is an approximate wavefunction and does not provide a quantitatively accurate description of H_2^+ near R_e. In this section we will discuss more accurate wavefunctions of H_2^+. First we consider a useful intermediate level description, the MBS wavefunction.

§3.2.1 Scaled LCAO Wavefunctions

We will describe the wavefunction of H_2^+ in terms of linear combinations of two orbitals, χ_ℓ and χ_r, centered on each proton, but rather than atomic orbitals we will use scaled atomic-like orbitals

$$\begin{aligned} \chi_\ell &= \sqrt{(\zeta^3/\pi)}\, e^{-\zeta r_a} \\ \chi_r &= \sqrt{(\zeta^3/\pi)}\, e^{-\zeta r_b} \end{aligned} \qquad (1)$$

The scaling parameter ζ is referred to as an orbital exponent. Use of $\zeta = 1$ leads back to the LCAO description of §2.2, $\zeta > 1$ leads to more contracted orbitals, while $\zeta < 1$ leads to more diffuse orbitals.

Using the basis set (1) the wavefunctions of H_2^+ have the form

$$\begin{aligned} \phi_g &= (\chi_\ell + \chi_r)/\sqrt{2(1+S)} \\ \phi_u &= (-\chi_\ell + \chi_r)/\sqrt{2(1-S)} \end{aligned} \qquad (2)$$

just as in § 2.2. However the energies of these wavefunctions depend upon both ζ and R (see App. 2A for the specific dependence of the integrals on ζ). At each R we will now use the ζ leading to the lowest energy. Since the forms of E_g and E_u are different, the optimum ζ will be different for the g and u states, as shown in Fig. 1.

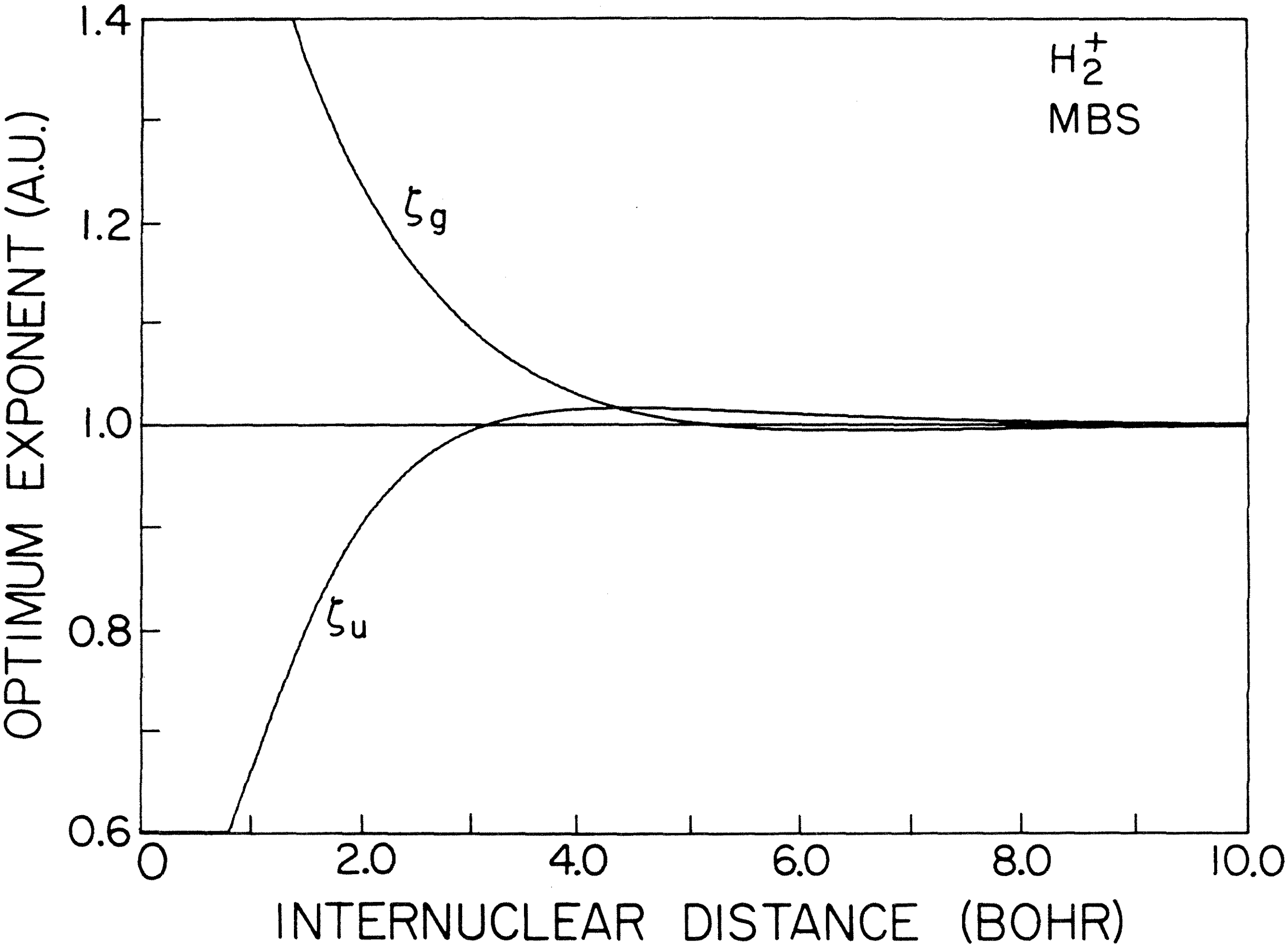

Figure 3-1. The optimum orbital exponents for the MBS descriptions of the g and u states of H_2^+.

As shown in Fig. 2 and Table 1, the improvement in the energy for the g state is quite remarkable, leading to energies close to the exact answer. For the u state both the LCAO and MBS energies are quite close to the exact answer.

In discussing such wavefunctions we will use the following terminology

(a) LCAO denotes the use of a linear combination of atomic orbitals using the orbital exponents of the atoms.

(b) MBS (minimal basis set) indicates the smallest set of atomic-like functions that would describe the case of $R = \infty$. For finite R the orbital exponents will generally be optimized. The results of MBS calculations will be discussed further after a discussion of the exact wavefunctions of H_2^+.

Table 3-1

Optimum Bond Length (R_e) and Bond Strength (D_e) for the g state of H_2^+. All quantities in atomic units.

	Non-Relativistic Neglect Nuclear Kinetic Energy			Relativistic[c]	
				Neglect Nuclear Kinetic Energy	Include Nuclear Kinetic Energy[d]
	LCAO[a]	MBS[a]	EXACT[b]	EXACT ψ	EXACT ψ
R_e	2.493	2.00	2.00379[c]	2.00376[c]	2.00562[c]
D_e	0.06500	0.08651	$0.10263\underline{5}$[c]	0.10264[c]	$0.10178\underline{5}$[c]

a. Unpublished calculations, Wadt, Olafson and Goddard.

b. D. R. Bates, K. Ledsham, and A. L. Stewart, Phil. Trans. Roy. Soc. A246 215 (1953).

c. S. K. Luke, G. Hunter, R. P. McFachran, and M. Cohen, JCP 50 1644 (1969).

d. G. Hunter and H. O. Pritchard, JCP 46 2153 (1967).

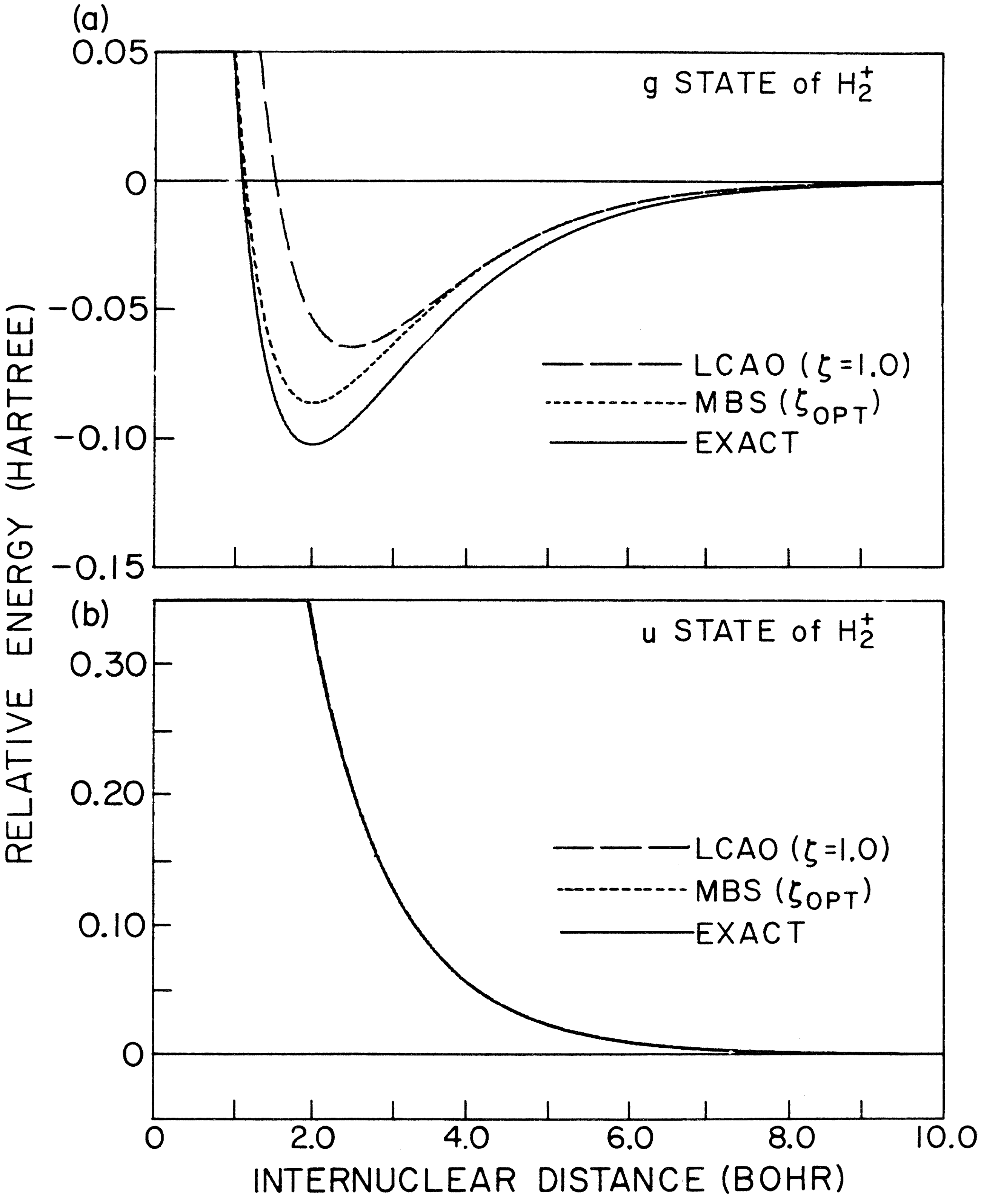

Figure 3-2 The LCAO ($\zeta = 1.0$), MBS (optimum ζ), and exact energies for the g and u states of H_2^+. Note that Fig. (b) does contain three different lines. The vertical scale of (b) is twice that of (a).

§3.2.2 The Exact Wavefunction for H_2^+

Previously we considered approximate solutions of the Schrödinger equation

$$\mathcal{H}\,\psi_R(r) = E(R)\,\psi_R(r), \tag{3}$$

where the Hamiltonian is

$$\mathcal{H} = -\tfrac{1}{2}\nabla^2 - \frac{1}{r_a} - \frac{1}{r_b} + \frac{1}{R} \tag{4}$$

(see Fig. 2-1 for the coordinate system). Exact solutions to (3) have also been obtained as will now be described.

From § 3.1 we can obtain arbitrarily accurate wavefunctions for H_2^+ by expanding the orbital in terms of a sufficiently general basis $\{\chi_\mu;\ \mu=1,2,\ldots P\}$,

$$\phi(r) = \sum_{\mu=1}^{P} C_\mu \chi_\mu(r) \quad ,$$

where the expansion coefficients are obtained by solving the P by P matrix equation

$$\underline{H}\,\underline{C} = \underline{C}\,E \ ,$$

with

$$H_{\mu\nu} = \langle \chi_\mu | \mathcal{H} | \chi_\nu \rangle$$

(assuming the basis to be orthonormal). As the basis set is made more complete (P → ∞) the wavefunction approaches the exact wavefunction.

Although the above procedure is practical, it is possible for H_2^+ to solve directly for the exact solutions. The procedure is examined in Appendix D.

§3.2.3 Comparison of Wavefunctions and Energies

The various wavefunctions of the g and u states are compared in Fig. 3 for $R = 2a_0$. For the g state we see that the shape of the LCAO wavefunction in the bond region is in good agreement with the exact wavefunction; however, the magnitude of the density in the bond region is ~ 25 to 30% low. The MBS description leads to reasonably good densities near the nuclei but too low a density in the bond region. Thus with MBS the shape of the wavefunction is not well described.

In the u state the LCAO wavefunction is in much better agreement with the exact wavefunction than is the MBS wavefunction. I do not understand the reason for this. In addition, I do not understand why the energies of these wavefunctions are so similar (see Fig. 2b) despite the large differences in the wavefunctions.

In Fig. 4 we compare the LCAO and MBS wavefunctions as a function of R, finding that the LCAO description does reasonably well for $R > 4a_0$. Note the large difference in the behavior of the g and u states for small R. These differences were also manifest in the optimum exponents of Fig. 1.

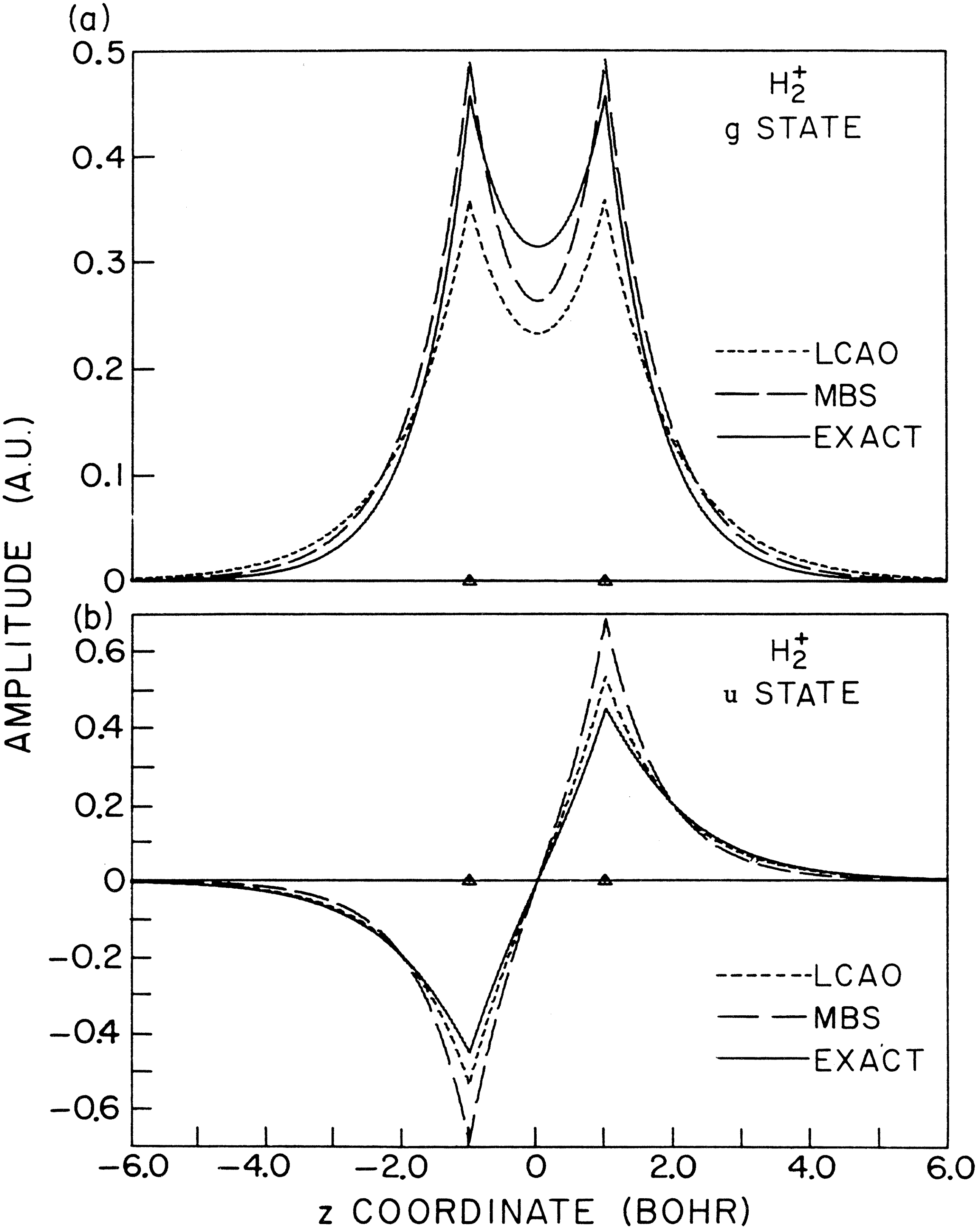

Figure 3-3 The wavefunctions of H_2^+ at $R = 2.0\ a_0$.

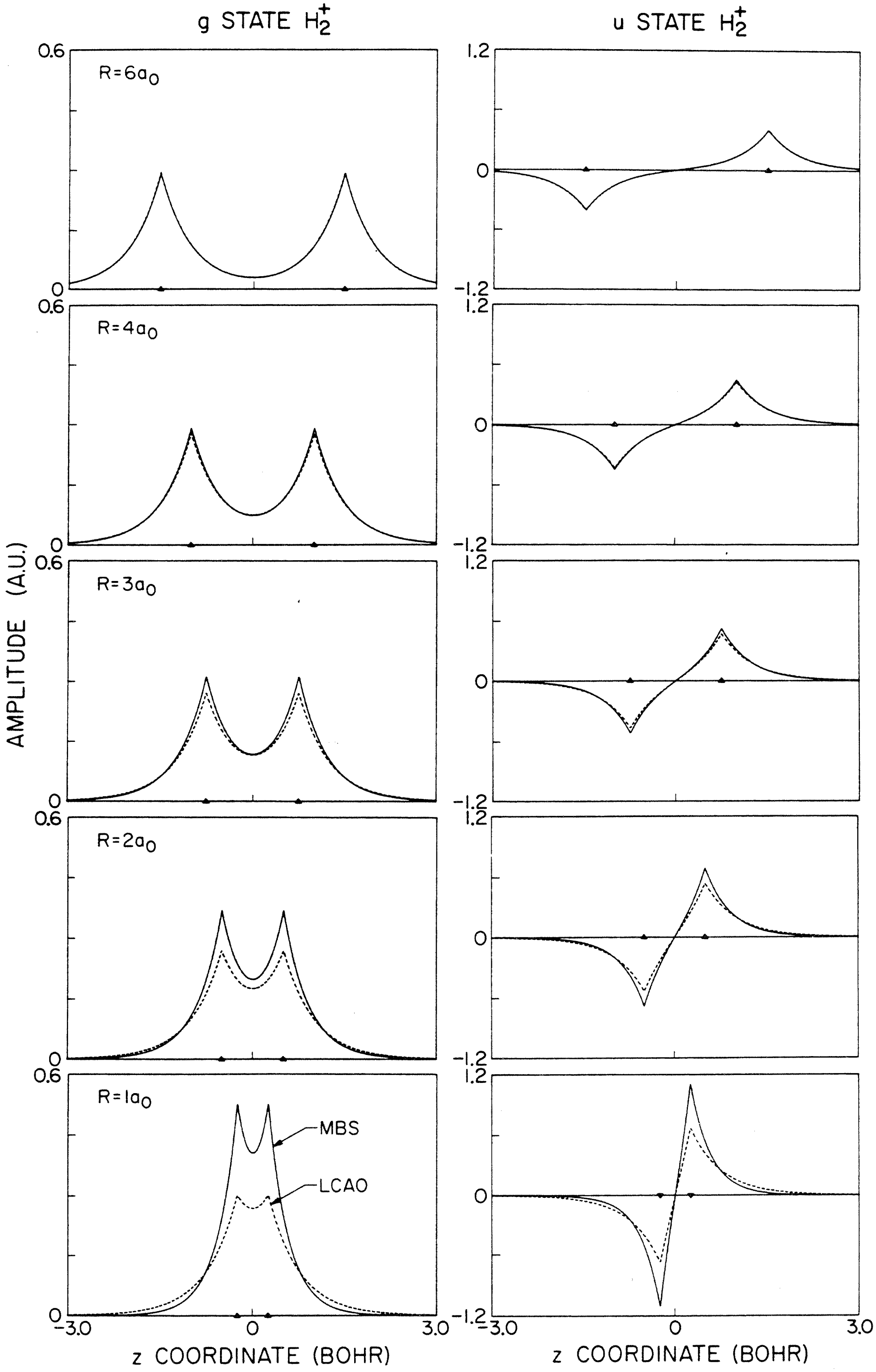

Figure 3-4 The amplitudes of the LCAO (dashed) and MBS (solid) wavefunctions for (a) the g state and (b) the u state of H_2^+.

§3.3 More on the Chemical Bond

In § 2.2 and 2.3 we analyzed the bond of H_2^+ in terms of the LCAO description. Now we will reexamine the bond using more accurate wavefunctions.

With more accurate wavefunctions we still find (§ 3.3.1) that the exchange energy E^x, (more specifically the exchange kinetic energy T^x part of E^x) is responsible for the bonding or antibonding of the g and u states of H_2^+.

On the other hand, partitioning the energy into the total potential energy (V) and the total kinetic energy (T), we find (§ 3.3.2) that neither can be solely responsible for bonding.

§ 3.3.1 The Classical and Exchange Energies

Defining classical and exchange terms just as in § 2.2,

$$E = E^{c\ell} + E^x \qquad (1)$$

$$E^{c\ell} = \langle \chi_\ell | \mathcal{H} | \chi_\ell \rangle \qquad (2)$$

but using the MBS wavefunctions, we obtain the results of Fig. 5. Thus the exchange energy dominates the bonding just as for the LCAO wavefunction. Partitioning the E^x into potential and kinetic parts, V^x and T^x,

$$E^x = V^x + T^x \qquad (3)$$

as in Fig. 5, we see that T^x favors bond formation while V^x opposes it, just as for the LCAO wavefunction.

Thus in terms of the classical and exchange quantities the LCAO and MBS descriptions are quite similar. In both cases it is the large decrease in T^x that is responsible for bond formation. Just as discussed in § 2.3, T^x is large and negative because the atomic orbitals are contragradient in the region between the nuclei. In particular the T^x is similar in character for the LCAO and MBS descriptions. With $\zeta > 1$ the gradients get larger and favor a smaller R so that the differences in T^x for the LCAO and MBS descriptions are easily understood.

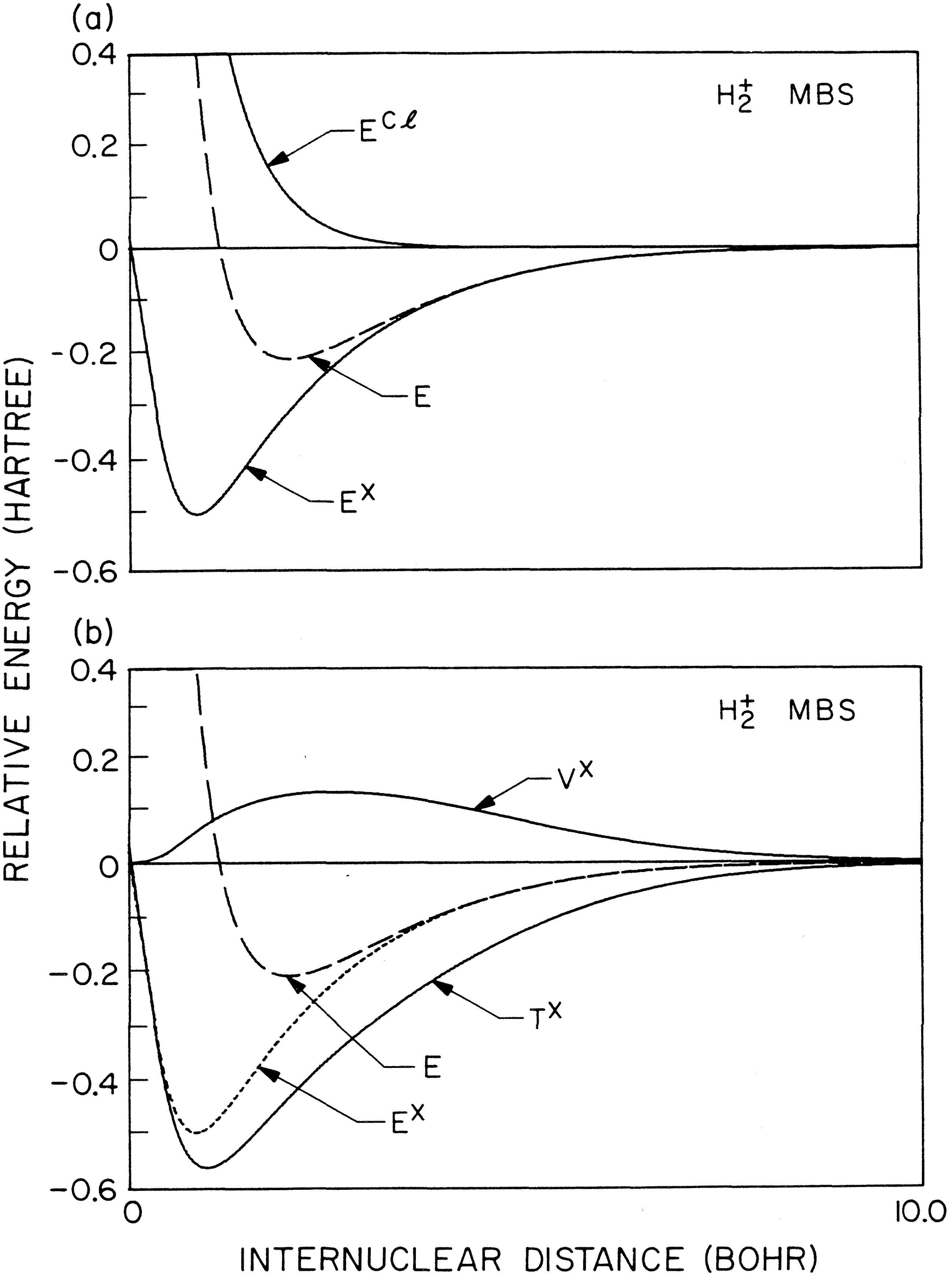

Figure 3-5. (a) The total energy (E) and the components $E^{c\ell}$ and E^X for the MBS wavefunction of the g state of H_2^+. (b) The T^X and V^X components of E^X. All quantities are relative to $R = \infty$.

3.3.1a An Ambiguity

There is a flaw with this procedure of decomposing the energy into classical and exchange parts. Adding a second basis function on each center, say $\chi_{2\ell}$ and χ_{2r}, and optimizing the coefficients (§3.1) leads to

$$\Phi_g = C_1(\chi_{1\ell} + \chi_{1r}) + C_2(\chi_{2\ell} + \chi_{2r})$$

and adding additional functions we ultimately obtain the exact wavefunction in the form

$$\Phi_g = \sum_{k=1}^{\infty} C_k(\chi_{k\ell} + \chi_{kr}). \tag{4}$$

Thus we can define optimum left and right orbitals as

$$\begin{aligned} \chi_\ell &\equiv \sum_k C_k \chi_{k\ell} \\ \chi_r &\equiv \sum_\ell C_k \chi_{kr} \end{aligned} \tag{5}$$

and obtain an exchange energy for the exact wavefunction. The problem is that for the exact wavefunction there is not a unique choice for the left and right functions χ_ℓ and χ_r. As a result, there is some ambiguity in the exchange energy for the exact wavefunction. On the other hand, with optimized basis functions only a few functions (say, two s and one p_z on each center) lead to quite accurate descriptions but with no ambiguity in the decomposition (5).

§3.3.2 Potential and Kinetic Energies

Rather than the partition (1) of the energy into classical and exchange terms, it has been much more common to partition the energy into total potential energy, V, and total kinetic energy, T,

$$E = T + V. \tag{6}$$

I believe that this partition mixes up the things characteristic of bonding with other quantities that are nearly independent of bonding with the result that neither quantity (T or V) consistently contains the bonding stuff. A good illustration of this is to compare the quantities for the LCAO and MBS wavefunctions of H_2^+. As shown in § 3. 3. 1 the classical and exchange energies behave very similarly for these two cases. However as shown in Fig. 6 the behavior of T and V for the MBS and LCAO wavefunctions is markedly different. Thus for LCAO the $T(R)$ is always lower than $T(\infty)$ while $V(R)$ is always higher than $V(\infty)$. This might suggest that it is kinetic energy that is responsible for the bond. However for the MBS wavefunction $T(R)$ is below $T(\infty)$ only for $R > 2.7a_0$. Thus at $R_e = 2a_0$, $T(R) > T(\infty)$ and it would be ludicrous to assert that the total kinetic energy is the quantity dominating bonding! On the other hand, in the MBS wavefunction, $V(R) > V(\infty)$ for $R = 3.5\ a_0$. Thus although $V(R)$ dominates the bond at R_e, it opposes bond formation for $R \geqslant 3.5 a_0$. Furthermore, for LCAO, $V(R)$ opposes bonding for all R.

Such difficulties have convinced me that (6) is not a useful partition of the energy. The key indication of this is that although the total energy changes monotonically from $R = \infty$ to R_e, the V and T for the MBS and exact wavefunctions are not monotonic, each dominating the energy over different regions. Hence neither can be uniquely responsible for bonding.

Occasionally,* energy curves are analyzed by partitioning the V into various parts

$$V = V^{en} + V^{nn} + V^{ee} \tag{7}$$

where ee, en, and nn denote electron-electron repulsion, electron-nuclear attraction, and nuclear-nuclear repulsion terms (ee is not present for H_2^+). As shown in Fig. 7a, each term is monotonic, with V^{en} decreasing with R. One might conclude from this that it is V^{en} that is responsible for bond formation. However as seen from Fig. 7b the

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*Usually in the analysis of rotational and conformational barriers in polyatomic molecules.

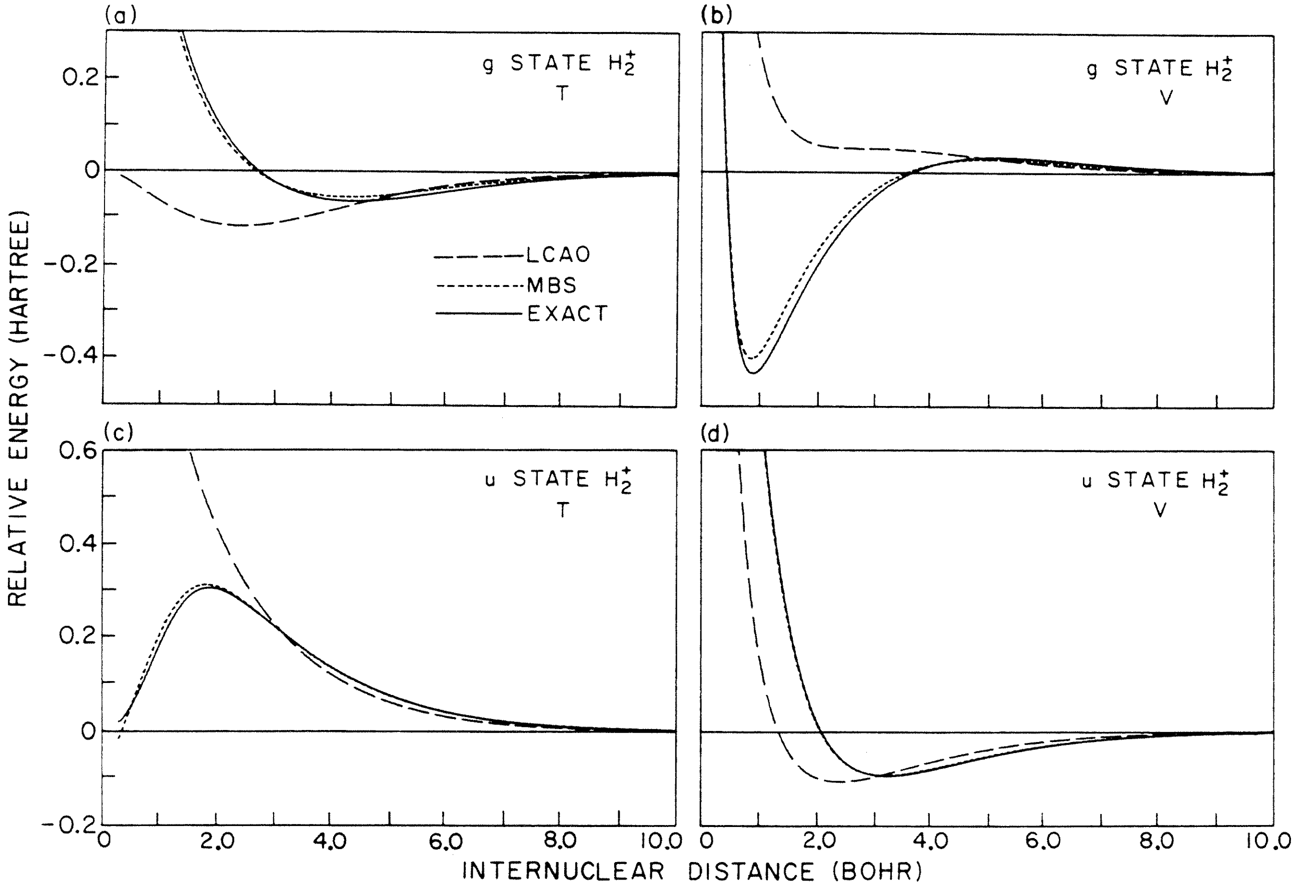

Figure 3-6 The kinetic and total potential energies for (a, b) the g state and (c, d) the u state of H_2^+. All quantities are relative to the value for R = ∞.

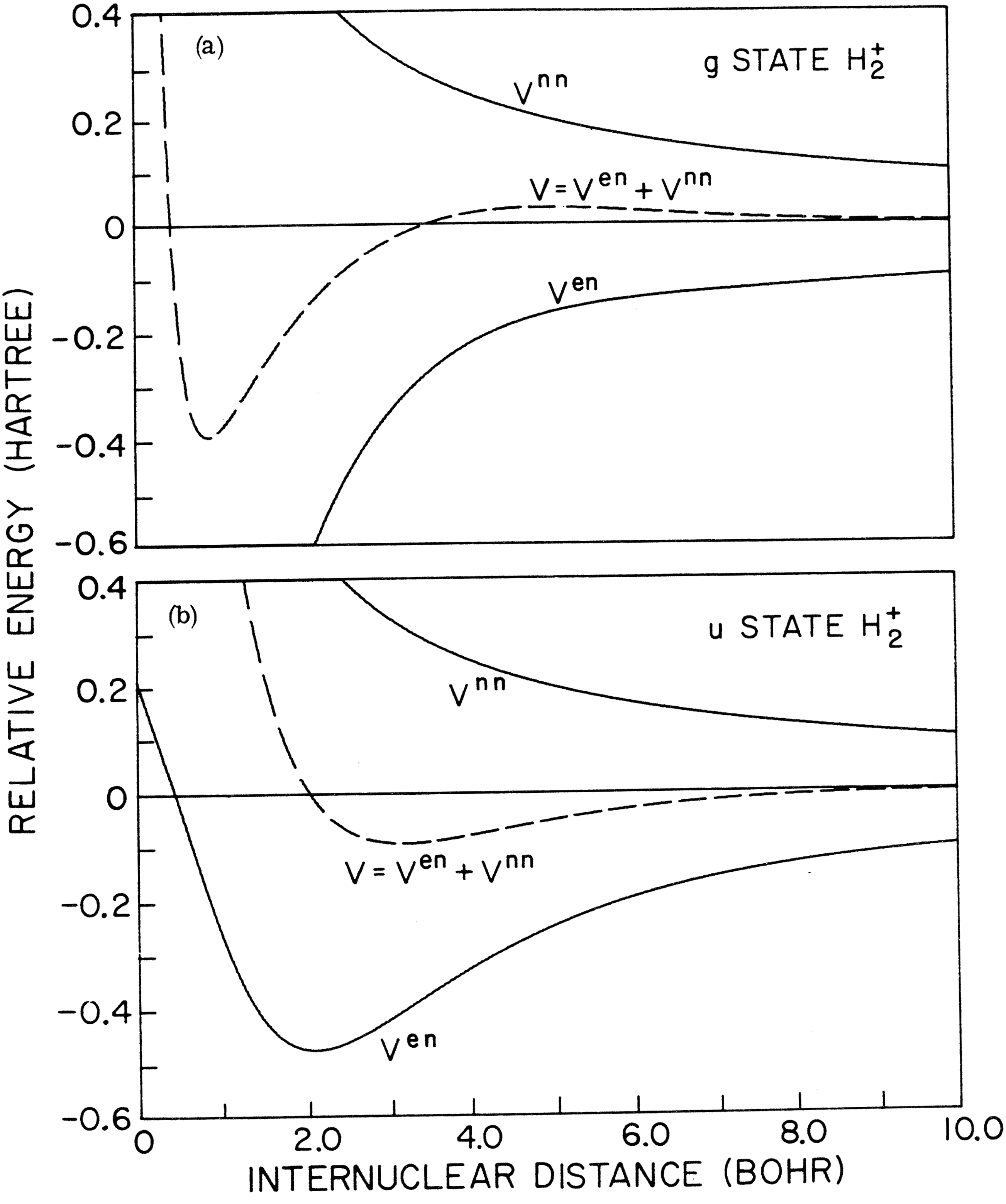

Figure 3-7. The total potential energy (V) and the partition into V^{nn} (nuclear-nuclear energy) and V^{en} (electron-nuclear energy) for (a) the g state and (b) the u state of H_2^+ (exact wavefunctions). All quantities are relative to the value for $R = \infty$.

V^{en} and V^{nn} are also monotonic for the u state and again V^{en} decreases with R, but this state is repulsive! Thus despite similar V^{en} and V^{nn} for g and u, we obtain radically different potential curves. My conclusion is that V^{en} is dominated by quantities other than those responsible for bond formation.

§ 3.5 Overview of Theoretical Methods

In this course the plan is to cover the important qualitative ideas in Ch120a and to examine the theoretical methods in detail in Ch120c. However,

familiarity with the theoretical methods is important for discussing qualitative ideas and hence we will outline these methods.

§3.5.1 Basis Sets

Several methods involve solving for the optimum shape of one-electron orbitals $\phi_i(r)$. The general procedure for carrying out such calculations involves selection of a basis set

$$\{\chi_\mu;\ \mu = 1, \ldots P\}, \tag{1}$$

suitable for describing the optimum orbitals

$$\phi_i(r) = \sum_{\mu=1}^{P} C_{\mu i}\, \chi_\mu(r). \tag{2}$$

Here the basis functions are fixed and hence selection of the optimum coefficients

$$\{C_{1i}, C_{2i}, \cdots, C_{Pi}\} \tag{3}$$

serves to determine the orbital $\phi_i(r)$. This procedure is analogous to a Fourier expansion where harmonic functions (sines and cosines) are used as basis functions in (1).

For an exact description of the optimum orbital it is generally necessary to use an infinite number (a complete set) of basis functions, however for practical reasons we must use a finite set. Indeed from numerous studies of molecular wavefunctions there are principles that can be used to select rather small basis sets that yield quite accurate wavefunctions.

In evaluating the wavefunctions and energies using a basis set as in (1), we must evaluate integrals of the form

$$\langle \chi_\mu | h | \chi_\nu \rangle \tag{4a}$$

$$\langle \chi_\mu(1)\ \chi_\nu(2) | \frac{1}{r_{12}} | \chi_\sigma(1)\ \chi_\eta(2) \rangle , \tag{4b}$$

where the functions may be centered at various regions of space. Thus an important criterion in selecting the basis is that the molecular integrals be practicable to evaluate. In order to obtain the best wavefunctions with the fewest basis functions, we want to choose the basis functions to have shapes characteristic of the eigenstates of the molecular systems.

For a Coulomb potential (i.e. the hydrogen atom), the eigenstates have the form

$$\begin{aligned}
&1s\text{:}\ e^{-Zr}\\
&2s\text{:}\ (r - \alpha)e^{-\frac{1}{2}Zr}\\
&2p_z\text{:}\ r \cos \Theta e^{-\frac{1}{2}Zr}\\
&2p_x\text{:}\ r \sin \Theta \cos \varphi\ e^{-\frac{1}{2}Zr}\\
&2p_y\text{:}\ r \sin \Theta \sin \varphi\ e^{-\frac{1}{2}Zr}\\
&3s\text{:}\ (r^2 - \beta r + \alpha)\, e^{-\frac{1}{3}Zr}\\
&\text{etc.}
\end{aligned} \tag{5}$$

(where normalization is ignored and the constants α and β are unimportant to our considerations here). In order to describe with a finite number of basis functions singular characteristics such as the cusps occurring near the various nuclei, we should include in our basis set functions having similar singular characteristics. Thus for a molecular system we should use atomic functions like (5) centered upon the various nuclei of the molecule.

The radial parts of the functions in (5) all can be built from functions of the form

$$r^n e^{-\zeta r} , \qquad (6)$$

where various values of n and of the orbital exponent, ζ, must be allowed. Functions of the form (6) are preferable to the hydrogen atom orbitals (5) since (6) is more convenient for evaluating the molecular integrals. Combining functions of the form (6) with appropriate angular functions ($Z_{\ell m}$, the real spherical Harmonics) leads to a convenient set of one-particle orbitals

$$r^n e^{-\zeta r} Z_{\ell m}(\theta, \varphi) \qquad (7)$$

for use in atomic and molecular wavefunctions. These functions (7) are referred to as **Slater functions**[#] (or Slater-type orbitals, STO) in honor of an early exponent[*] of such functions. They are denoted as 1s, 2s, 2p, etc. just as for hydrogen atom orbitals. The **orbital exponent**, ζ, in (6) is considered as an adjustable parameter and is generally chosen as the optimum value for the particular molecule and basis set of interest [rather than taken as $\zeta = Z/n$ as suggested by (5a)].

[#] We will use the term function when referring to an arbitrary function as in a basis function and the term orbital when referring to a specific optimized orbital as in a HF or GVB orbital.

[*] J. C. Slater, Phys. Rev., **36**, 57 (1930).

For example, a good basis for describing the wavefunction for H_2 is to use two 1s Slater functions (denoted as 1s and 1s'), a 2s Slater function, and a set of the 2p Slater functions ($2p_z$, $2p_x$, and $2p_y$) on each center. The optimum exponents at R = 1.4 a_0 are[†]

$$\begin{aligned} \zeta(1s) &= 0.965 \\ \zeta(1s') &= 1.43 \\ \zeta(2s) &= 1.16 \\ \zeta(2pz) &= 1.87 \\ \zeta(2px) = \zeta(2py) &= 1.71 \end{aligned} \tag{8}$$

(where the molecular axis is along z).

With this basis the CI wavefunction leads to an energy of -1.16696h (at R = 1.4 a_0), 99.4% of the exact answer[*] -1.17447 h. Note that the optimum orbital exponents are significantly different from the values for the free atom

$$\begin{aligned} \zeta_{1s} &= 1.0 \\ \zeta_{2s} &= 0.5 \\ \zeta_{2p} &= 0.5\ . \end{aligned}$$

[†] A. D. McLean, A. Weiss, and M. Yoshimine, Rev. Mod. Phys., **32**, 211 (1960).

[*] W. Kolos and L. Wolniewicz, JCP **41**, 3663 (1964).

The second type of basis functions commonly used in molecular calculations are Gaussian functions where the $e^{-\zeta r}$ of (7) is replaced by $e^{-\alpha r^2}$ and n is taken as ℓ,

$$r^{\ell} e^{-\alpha r^2} Z_{\ell m}(\theta, \varphi) \tag{9}$$

Although Gaussian functions have the wrong behavior as $r \to 0$ and as $r \to \infty$, they serve just as well as Slater functions in describing the valence orbitals and the bonds of molecules. The major advantage of Gaussian functions is that the molecular integrals (4) required for large molecules are much simpler (and less time consuming) than for Slater functions.

Generally the basis sets are optimized for the atoms. If properly carried out, the atomic basis sets supplemented by a few additional functions (polarization functions) serve to provide very accurate descriptions of the molecular wavefunctions.

§3.5.2 The Hartree-Fock Method

§3.5.2a The Basic Equations

In §2.2 we described the simple MO wavefunction of H_2 in which the two-electron wavefunction is expressed as

$$\Phi(1,2) = \phi(1)\,\phi(2) \tag{10}$$

where ϕ is the MO

$$\phi = (\chi_\ell + \chi_r)/\sqrt{2(1+S)}$$

and χ_ℓ and χ_r are hydrogen orbitals centered on the two nuclei. Now we will consider the case where ϕ is allowed to be completely general.

Thus if $\{\chi_\mu\}$ is some basis set, we write

$$\phi = \sum_\mu C_\mu \chi_\mu \tag{11}$$

with the coefficients $\{C_\mu\}$ chosen so that Φ in (10) leads to the lowest possible energy.

The energy of (10) is

$$\begin{aligned} E &= \langle \Phi | \mathcal{H}^{e\ell} | \Phi \rangle / \langle \Phi | \Phi \rangle \\ &= 2\langle \phi | h | \phi \rangle + J_{\phi\phi} + \frac{1}{R} \quad , \end{aligned} \tag{12}$$

where

$$J_{\phi\phi} = (\phi\phi|\phi\phi) = \int d^3 r_1 \, \phi^*(1)\phi(1) \int d^3 r_2 \, \frac{\phi^*(2)\phi(2)}{r_{12}} \tag{13}$$

and

$$\langle \phi | \phi \rangle = 1. \tag{14}$$

Applying the variational principle to (12)

$$\frac{\partial E}{\partial C_\mu} = 0$$

with the constraint (14), leads to

$$\boxed{\langle \chi_\mu | (h + J_\phi - \epsilon) | \phi \rangle = 0} \tag{15}$$

where ϵ is referred to as the orbital energy,

$$\epsilon = \langle\phi|h|\phi\rangle + J_{\phi\phi}, \tag{16}$$

and

$$J_{\phi}(r_1) = \int d^3r_2 \, \frac{\phi^*(r_2)\,\phi(r_2)}{r_{12}} \tag{17}$$

is the electrostatic potential at point r_1 due to the charge density $|\phi(r_2)|^2$ integrated over all r_2.

Substituting (11) into (15) leads to

$$\sum_{\nu=1}^{P} (H_{\mu\nu} - \epsilon S_{\mu\nu})\, C_{\nu} = 0; \quad \mu = 1, 2, \ldots P. \tag{18a}$$

where

$$\begin{aligned} H_{\mu\nu} &\equiv \langle\chi_{\mu}|(h + J_{\phi})|\chi_{\nu}\rangle \\ S_{\mu\nu} &\equiv \langle\chi_{\mu}|\chi_{\nu}\rangle \quad . \end{aligned} \tag{19}$$

In matrix notation (18a) is written

$$\underline{H}\,\underline{C} = \underline{S}\,\underline{C}\,\epsilon \quad . \tag{18b}$$

Since

$$\langle\chi_{\mu}|J_{\phi}|\chi_{\nu}\rangle = \sum_{\sigma,\eta} C_{\sigma}\, C_{\eta} \langle\chi_{\mu}\,\chi_{\sigma}|\frac{1}{r_{12}}|\chi_{\nu}\,\chi_{\eta}\rangle,$$

$H_{\mu\nu}$ is a function of the unknowns $\{C_{\mu}\}$ and (18) is nonlinear. Since the basis functions $\{\chi_{\mu}\}$ are known, all integrals in (19) can be evaluated just once so that (18) becomes a (nonlinear) algebraic equation.

In order for the variational condition (15) to be satisfied for <u>all</u> χ_{μ} of a complete set, the function

$$(h + J_\phi - \epsilon)\phi$$

must be zero. That is, the differential equation

$$\boxed{(h + J_\phi)\phi = \epsilon\phi} \tag{20}$$

or (for H_2)

$$(-\tfrac{1}{2}\nabla^2 - \frac{1}{r_a} - \frac{1}{r_b} + J_\phi)\phi = \epsilon\phi$$

must be satisfied in order that ϕ be a completely optimum function. The resulting optimum wavefunction (10) is called the *Hartree-Fock (HF) wavefunction*, the optimum orbital of (20) is called the *Hartree-Fock orbital*, and this whole approach is called the *Hartree-Fock method*, all in honor of the Englishman D. R. Hartree and the Russian V. Fock (sometimes Fok) who first developed it.

§3.5.2b Solution of the Hartree-Fock Equations

The differential equation (20) is not linear in ϕ since J_ϕ depends upon ϕ. The usual approach to solving (20) is the iterative method in which we guess the orbital, ϕ_0, evaluate J_{ϕ_0} and solve the linear equation

$$(h + J_{\phi_0})\phi_1 = \epsilon\phi_1$$

for a new orbital ϕ_1. Then ϕ_1 is used to evaluate a new J_{ϕ_1} and

$$(h + J_{\phi_1})\phi_2 = \epsilon\phi_2$$

is solved for a new orbital ϕ_2. This process is continued until it converges, that is, until $\phi_{I+1} \approx \Phi_I$.

For atoms the HF equations (20) can be reduced to one-dimension and solved numerically. However, for molecules the only practical procedure is to use a finite basis set and to solve the resulting matrix equations (18). These are also solved iteratively. One guesses the coefficients $\{C^0_\mu\}$ and evaluates the $H_{\mu\nu}$ of (19). With $H_{\mu\nu}$ fixed, the matrix equations (18) are linear and easy to solve for a new set of coefficients $\{C'_\mu\}$. This process is continued until it converges.

By solving the matrix HF equation (18) for larger and larger basis sets one can in the limit approach the results of solving the numerical equations (20). Indeed by proper choice of the basis functions it is possible to obtain very accurate solutions for very small P, e.g., $P = 2$ for He and $P = 6$ for H_2.

§3.5.2c Historical Note

Before real quantum mechanics (i.e., the work of Schrödinger, Heisenberg, and their contemporaries in 1925, 1926), physicists (and chemists) were attempting to understand the structure of atoms (and molecules) on the basis of a many-electron Bohr atom. The idea was that each electron moved along a different Bohr orbit, experiencing electrostatic interactions due to all the other electrons but satisfying various (postulated) rules in order to obtain agreement with the periodic properties of the elements.

Hartree in 1923 suggested* approximating this problem by assuming that the average interaction with the other electrons leads to a net potential that is a function only of the distance from the nucleus. He then tried to determine the form of V(r) [same V(r) for all orbitals] by fitting to the experimental energies of the orbits of various electrons (e.g., from X-ray data).

After quantum mechanics Hartree realized that he could convert this idea into quantum mechanics and actually solve for the potential and orbital. He thus started directly with (20) (and its generalization for more electrons) and began solving for atomic wavefunctions.† These equations are called the Hartree equations [Hartree, a properly modest English gentleman, continued to call them the Self-Consistent Field (SCF) equations].

Slater in 1930 pointed out# that Hartree's equations could be derived using the variational principle; thus putting Hartree's ad hoc approach on a more fundamental basis. Slater also pointed out that for many-electron atoms there are additional terms (we call them exchange terms) that should be in the wavefunction (from the Pauli principle, see Chapter 4), but Slater showed that these terms were of the same size as the intrinsic (correlation) errors in the Hartree approach and did not pursue them further.

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*Proc. Camb. Phil. Soc. **21**, 625 (1923).

†Proc. Camb. Phil. Soc. **24**, 89 (1927), outlined the mathematical techniques and ibid., p. 111, reported Hartree wavefunctions for He ($\epsilon_{1s} = 0.917^{5}$ h) and approximate calculations for Rb.

#Phys. Rev. **35**, 210 (1930).

V. Fock[*] in 1930 included the Pauli principle and derived the corresponding variational equations obtaining Hartree's equations but with additional exchange terms. These equations are now known as the **Hartree-Fock** equations. (Hartree referred to them as SCF *with exchange*.)

The approach of using a finite basis set for obtaining HF wavefunctions (rather than solving numerically, á la Hartree) is sometimes called HF Roothaan in honor of the early leader in the development and application of this procedure.[†] We will make no such distinctions, although Roothaan's paper is amazingly complete and Roothaan is rightfully credited with the development of the basis set expansion (BSE) approach. An early application of BSE was by C. A. Coulson [Proc. Camb. Phil. Soc. **34**, 204 (1938)] who concluded that BSE was not practical and that SCF orbitals would not prove to be very useful for molecular structures. Basically Coulson showed that the same effort required to obtain an accurate HF wavefunction would, if applied to other forms of the wavefunction (with electron correlation), yield far better energies. The point missed by Coulson is that for larger systems these other methods quickly become much more cumbersome and expensive than HF. Roothaan's work came at just the right time. Application of the BSE approach for larger molecules depends upon electronic computers, the development of which was just starting in 1951.

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[*] Z. Physik **61**, 126 (1930).

[†] C. C. J. Roothaan, Rev. Mod. Phys. **23**, 69 (1951); G. C. Hall, Proc. Roy, Soc. **A205**, 541 (1951).

§3.5.2d Interpretation, Correlation, and the Koopmans' Theorem

The variational condition (20) has the form of a Schrödinger equation for a particle moving in the potential

$$V = -\frac{1}{r_a} - \frac{1}{r_b} + J_\phi$$

(assuming for the moment, H_2).

This is just the classical potential that would be obtained if the second electron were replaced by its classical potential, J_ϕ. Thus the Hartree-Fock orbital is the eigenstate of the motion of an electron in the average potential due to the other electron. Indeed Hartree originally derived his equations from just such classical considerations. In the above derivation however, we applied the variational principle and found that the best possible orbital satisfies such an equation.

Of course, in the real molecule the electron motions will be such as to keep $\frac{1}{r_{12}}$ as small as possible and $\frac{1}{r_a}$ and $\frac{1}{r_b}$ as big as possible, while also minimizing the kinetic energy. Thus at instants for which one of the electrons happens to be close to the left nucleus, we expect that the other electron will tend to be **near** the right nucleus. Such instantaneous correlations in the motion of the electrons are ignored in the Hartree-Fock wavefunction. Both electrons move in the same orbital independently of the instantaneous position of the other electron. Hence the error in the Hartree-Fock wavefunction is called the correlation error.

The energy ϵ in (20) is called the orbital energy. From (16) it has the value

$$\epsilon = \langle \phi | h | \phi \rangle + J_{\phi\phi}$$

$$= E_2 - E_1$$

where

$$E_2 = 2\langle\phi|h|\phi\rangle + J_{\phi\phi}$$

is the energy of the two electron system with both electrons in ϕ while

$$E_1 = \langle\phi|h|\phi\rangle$$

is the energy with only one electron in ϕ.

Thus ϵ is just the negative of the ionization potential. There are two approximations here. One is using the Hartree-Fock energy for the two-electron molecule, leading to too high an energy for the two-electron system. The other error is in describing the ion with the optimum orbital ϕ found for the two-electron molecule, leading to too large an energy for the ion. These errors often tend to cancel yielding ionization potentials within $\sim$10% of the exact value. This approximation[‡] of using the orbital energy to approximate the ionization potential is often called the Koopmans theorem.[*] Although not strictly the theorem that Koopmans proved [T. Koopmans, Physica, 1, 104 (1933)];[†] we will also refer to this approximation as Koopmans Theorem.[‡]

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[*] Note that there is an s at the end of this name and that the Dutch oo sounds about like our long o.

[†] Shortly after this work Koopmans switched to economics. He is on the Economics faculty at Yale and in 1975 won a Nobel prize for his work in optimization theory in economics.

[‡] The first application of this approximation was by D. R. Hartree, Proc. Camb. Phil. Soc. 24, 111 (1927).

§3.5.3 The Generalized Valence Bond Method

In §2.3 we described the simple VB wavefunction of H_2 in which the two-electron wavefunction is expressed as:

$$\Phi(1,2) = (\chi_\ell \chi_r + \chi_r \chi_\ell) , \tag{21}$$

where χ_ℓ and χ_r are atomic orbitals.

We will now consider wavefunctions of the VB form (21)

$$\Phi(1,2) = \phi_a \phi_b + \phi_b \phi_a \tag{22}$$

but where the orbitals ϕ_a and ϕ_b are allowed to be completely general. To obtain the best such orbitals we will apply the variational principle, requiring the orbitals to lead to the lowest possible energy. The optimum orbitals are called the generalized valence bond orbitals and the resulting wavefunction is called the generalized valence bond (GVB) wavefunction.

§3.5.3a The Basic Equations

The energy of the GVB wavefunction (22) is

$$E = \frac{N}{D} + \frac{1}{R} \tag{23}$$

where

$$N = [\langle a|h|a\rangle + \langle b|h|b\rangle + J_{ab}] + [2\langle a|h|b\rangle S_{ab} + K_{ab}] \tag{24}$$

$$D = 1 + S_{ab}^2$$

$$S_{ab} = \langle a|b\rangle .$$

Here and in most of the following we will use orbital subscripts (e.g., a and b) to denote orbitals (e.g., ϕ_a and ϕ_b, respectively). Just as in §3.5.2 we will consider that ϕ_a and ϕ_b are expanded in a basis $\{\chi_\mu\}$

$$\phi_a = \sum_\mu \chi_\mu C_{\mu a}$$

$$\phi_b = \sum_\mu \chi_\mu C_{\mu b} \ , \tag{26}$$

and require that

$$\frac{\partial E}{\partial C_{\mu a}} = 0 \tag{27a}$$

$$\frac{\partial E}{\partial C_{\mu b}} = 0 \ . \tag{27b}$$

condition (27a) leads to

$$\langle \chi_\mu | (H^a - \epsilon_a) | \phi_a \rangle = 0 \ , \tag{28}$$

where

$$\epsilon_a \equiv E - \langle b | h | b \rangle \tag{29}$$

and H^a is an operator taking care of all other terms.* To solve (28) we expand ϕ_a with (26) leading to

$$\sum_\nu \langle \chi_\mu | (H^a - \epsilon_a) | \chi_\nu \rangle C_{\nu a} = 0 \ , \tag{30}$$

---

* The form of H^a is

$$H^a = (h + J_b + K_b) + P_b h + h P_b - E P_b$$

where $P_b \equiv |b\rangle\langle b|$ is a projection operator. However, the explicit form is of no importance here.

which in matrix notation is

$$\underline{H}^a \underline{C}_a = \epsilon_a \underline{S}\,\underline{C}_a \quad , \tag{31a}$$

where the elements of the $\underline{H}^a$ and $\underline{S}$ matrices are

$$\begin{aligned} H^a_{\mu\nu} &= \langle \chi_\mu | H^a | \chi_\nu \rangle \\ &= \langle \chi_\mu | (h + J_b + K_b) | \chi_\nu \rangle + \langle \chi_\mu | b \rangle \langle b | h | \chi_\nu \rangle + \\ &\quad \langle \chi_\mu | h | b \rangle \langle b | \chi_\nu \rangle - E \langle \chi_\mu | b \rangle \langle b | \chi_\nu \rangle \end{aligned} \tag{32}$$

and

$$S_{\mu\nu} = \langle \chi_\mu | \chi_\nu \rangle \ .$$

For the HF wavefunction the corresponding matrix is

$$H^{HF}_{\mu\nu} = \langle \chi_\mu | (h + J_b) | \chi_\nu \rangle \tag{33}$$

The presence of the second (exchange) term in the wavefunction (22) leads to the other terms in (32). Of these additional terms only the K_b term would be present if the orbitals ϕ_a and ϕ_b were orthogonal.

Equation (31a) is the condition for orbital ϕ_a to be optimum, there is a similar equation

$$\underline{H}^b \underline{C}_b = \epsilon_b \underline{S}\,\underline{C}_b \tag{31b}$$

to solve for the optimum orbital ϕ_b. Thus in the GVB method we must solve self-consistently for <u>two</u> orbitals whereas in the HF method we have just <u>one</u> orbital and hence one equation to solve. Otherwise both involve similar computational procedures.

As shown in Fig. 8, the GVB orbital of H_2 corresponds closely to the VB orbital.

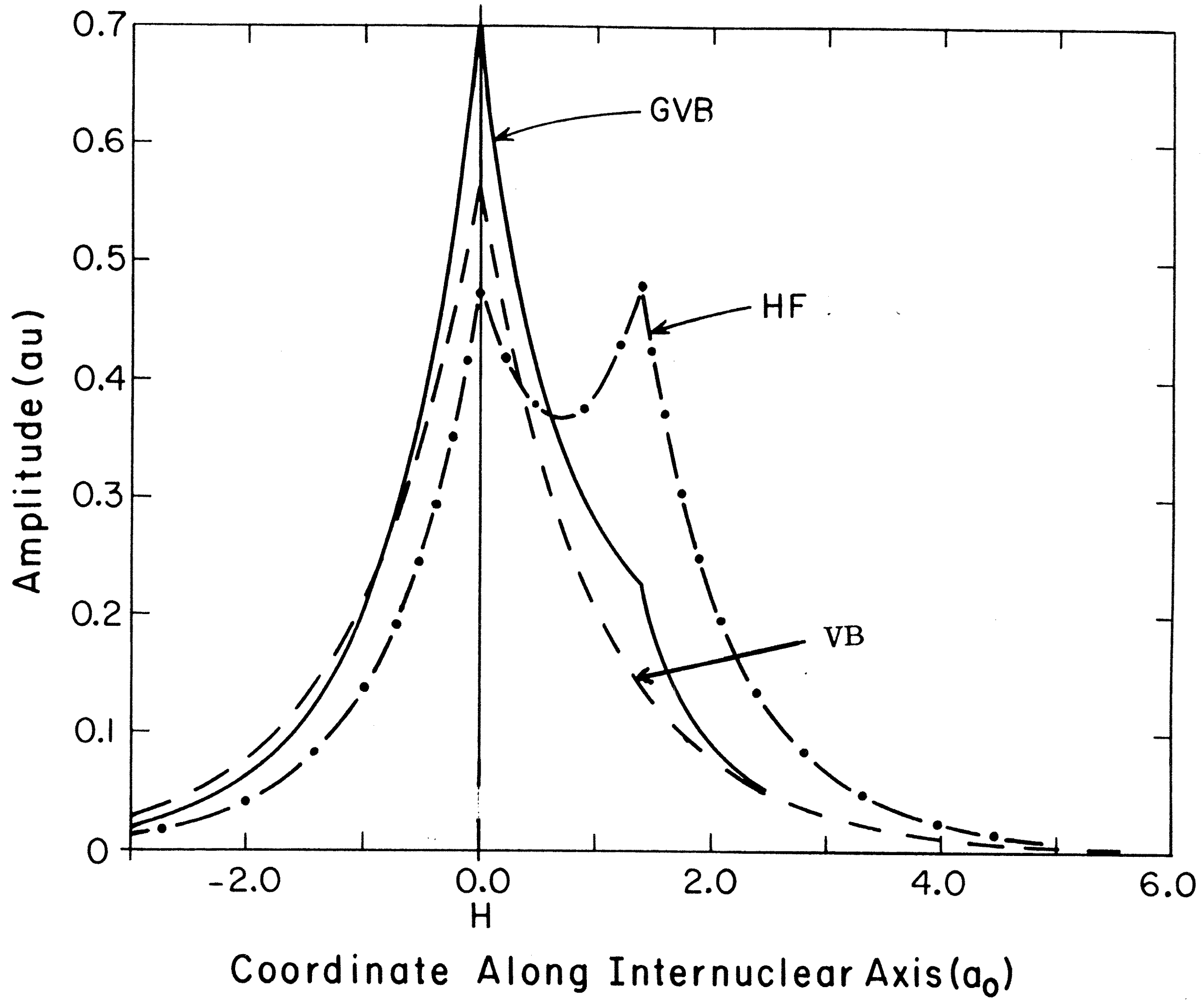


Figure 3-8. Comparison of the GVB, VB, and HF orbitals of H_2 at $R = 1.4\ a_0$. Only one of the GVB and VB orbitals is shown.

§3.5.3b Interpretation

If (28) is satisfied for all basis functions χ_μ of a complete set, then ϕ_a satisfies the differential equation,

$$H^a \phi_a = \epsilon_a \phi_a \ . \tag{34}$$

The H^a in (34) can be written as

$$H^a = h + V_b \tag{35}$$

where V_b contains all the terms depending upon orbital ϕ_b. We can consider V_b as the average potential* seen by the electron in ϕ_a due to the electron in ϕ_b. The average potential is not just the Coulomb potential J_b due to the electron on ϕ_b (as would be expected classically), but also contains other terms arising from the quantum mechanical form of the wavefunction. However, these additional terms are not chosen arbitrarily and indeed were determined through the variational principle as the terms required in order that ϕ_a be the optimum orbital to place in the two-electron wavefunction. Thus we can consider the potential V_b as the quantum mechanical generalization of the classical Coulomb term for the interaction between electrons in overlapping orbitals ϕ_a and ϕ_b.

The operator, H^a, in (35) is equivalent to the Hamiltonian for an electron moving in the potential due to the nuclei (contained in h) plus a potential V_b due to the electron in orbital ϕ_b. Since orbital ϕ_a is an eigenfunction of H^a, we can <u>interpret</u> ϕ_a as the eigenstate of an electron moving in the <u>average</u> potential (V_b) due to the other electron of the system. Similarly, of course, we can interpret ϕ_b as the eigenstate of an electron moving in the average potential (V_a) due to the other electron. Thus with this interpretation we can describe the two-electron

---

*Note well that V_b is not a <u>local</u> potential (that is, a function of $\underset{\sim}{r}$). Rather V_b contains integral operators and upon operating on ϕ_a, puts ϕ_a inside an integral. Even so we can consider V_b as the effective potential due to ϕ_b as seen by ϕ_a.

system in terms of two one-electron systems each of which contains the average potential due to the other electron. Such a description of a multi-electron system in terms of electrons moving independently of each other will be termed an independent particle interpretation (IPI). We will find, especially for larger molecules, that such IPI's will be very useful in understanding the wavefunctions.

It is important to note here that the IPI comes about from the one-particle Schroedinger equation, such as (34), arising from application of the variational principle to a special type of wavefunction (22). The real electrons of a molecule are quite indistinguishable, and we do not imply that one of the electrons moves in one orbital (say ϕ_a) while the other electron moves in the other orbital (ϕ_b). What we say is that the orbitals satisfy a one-electron Schroedinger equation for which the field term is the average potential of an electron in the other orbital. This is not the equation describing the motion of one of the real electrons. However, considering the eigenstates of two fictitious, distinguishable electrons, we do obtain the optimum orbitals for the many-electron wavefunction (22). It is really the orbitals which are distinguishable here, not the electrons.

§3.5.3c GVB Natural Orbitals

In order to obtain another view of the GVB wavefunction we will define the GVB natural orbitals* ϕ_g and ϕ_u as the sum and difference of the GVB orbitals ϕ_ℓ and ϕ_r

$$\begin{aligned} \phi_g &= (\phi_\ell + \phi_r)/D_g \\ \phi_u &= (\phi_r - \phi_\ell)/D_u \ , \end{aligned} \tag{36}$$

where

$$\begin{aligned} D_g &= \sqrt{2(1 + S)} \\ D_u &= \sqrt{2(1 - S)} \end{aligned} \qquad (37)$$

and S is the overlap of the GVB orbitals

$$S = \langle \phi_\ell | \phi_r \rangle .$$

Rearranging (36) leads to

$$\begin{aligned} 2\phi_r &= D_g \phi_g + D_u \phi_u \\ 2\phi_\ell &= D_g \phi_g - D_u \phi_u \end{aligned}$$

and hence the total wavefunction becomes

$$\Phi = \phi_\ell \phi_r + \phi_r \phi_\ell = [D_g^2 \phi_g \phi_g - D_u^2 \phi_u \phi_u]/2 ,$$

Thus we may view the GVB wavefunction in terms of ϕ_ℓ and ϕ_r where there is always one electron in ϕ_ℓ and one in ϕ_r <u>or</u> one may view this wavefunction in terms of GVB natural orbitals ϕ_g and ϕ_u where part of the time both electrons are in ϕ_g and part of the time both are in ϕ_u. Here ϕ_g resembles the bonding orbital and ϕ_u the antibonding orbital. The equivalence of these two descriptions may be clear in Figure 9, where Figure 9d and Figure 9g are equivalent. The first natural orbital ϕ_g has a good kinetic energy but a bad two-electron energy. Mixing in a small amount of ϕ_u causes an increase in the kinetic energy, but this is more than compensated by the decrease in the electron-repulsion energy, leading to the optimum wavefunction Fig. 9d or g.

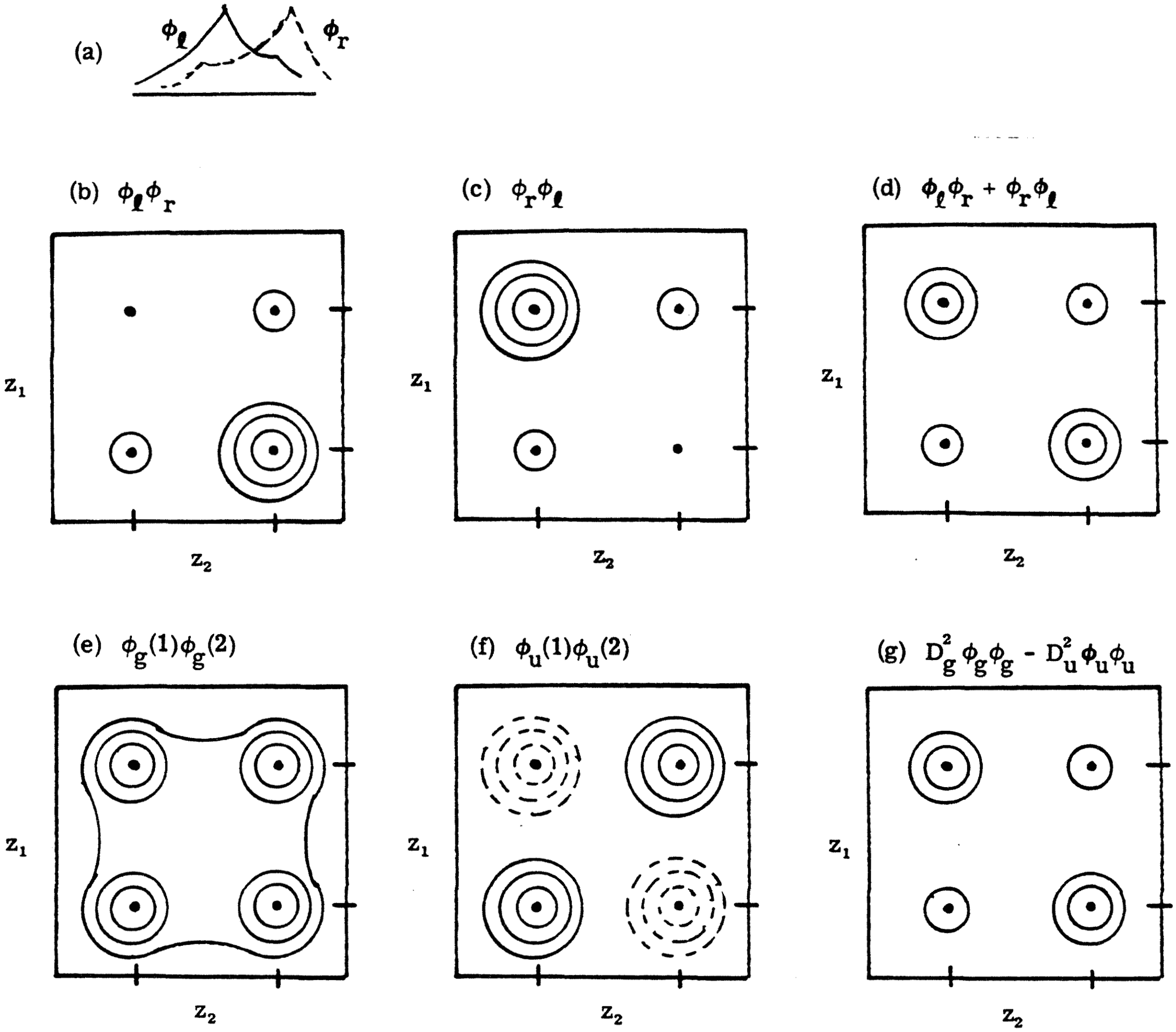

(a) ϕ_ℓ ϕ_r
(b) $\phi_\ell \phi_r$
(c) $\phi_r \phi_\ell$
(d) $\phi_\ell \phi_r + \phi_r \phi_\ell$
(e) $\phi_g(1)\phi_g(2)$
(f) $\phi_u(1)\phi_u(2)$
(g) $D_g^2 \phi_g \phi_g - D_u^2 \phi_u \phi_u$
z_1
z_2

Figure 3-9.

Requiring that the total wavefunction be normalized leads to

$$\begin{aligned}\Phi &= (\phi_\ell \phi_r + \phi_r \phi_\ell)/\sqrt{2(1 + S^2)} \\ &= C_g \phi_g \phi_g - C_u \phi_u \phi_u \end{aligned} \tag{38}$$

where from (37),

$$\frac{C_u}{C_g} = \frac{D_u^2}{D_g^2} = \frac{(1 - S)}{(1 + S)} \tag{39}$$

That is, if the overlap between the two orbitals is nearly zero (H_2 for $R \rightarrow \infty$), then the two configurations come in with nearly equal coefficients. On the other hand, for H_2 at $R = 1.4\ a_0$ $S = 0.8$ and hence

$$\frac{C_u}{C_g} = \frac{1}{9} = 0.11$$

---

*In this section we use g and u for the orbitals as appropriate for H_2. However, the discussion does not depend upon inversion symmetry and all results apply also to a GVB pair for an unsymmetric system.

§3.5.4 Electron Correlation

In a real atom the electrons are expected to move somewhat in concert so that they avoid getting too close to each other while remaining close to the nucleus. That is, their motions are somewhat correlated. On the other hand, in the HF wavefunction, $\phi(1)\,\phi(2)$, each electron is placed in the same orbital and hence the probability of either electron being at a particular position is independent of where the other electron is. That is, the electrons in the HF orbital are uncorrelated in their motions. For this reason the difference between the HF energy and the exact energy is called the correlation error. For the ground states of two-electron atoms (H^-, He, Li^+, etc.) the correlation error is about 1.1 eV. In addition, for H_2 (at R_e) the correlation error is 1.1 eV. Although this correlation energy is small compared to the total energy of these systems (e.g., 1.5% for He), it is comparable to many quantites of interest.

In the GVB wavefunction for H_2

$$\phi_\ell(1)\,\phi_r(2) + \phi_r(1)\,\phi_\ell(2)\ , \tag{40}$$

one electron is in ϕ_ℓ while the other electron is in ϕ_r regardless of which electron is in which. Hence, there is static correlation in the sense that the orbitals for each electron are in a slightly different region of space, and hence on the average the electrons stay farther apart. However, the presence of electron 1 at a particular location of the ϕ_ℓ orbital does not affect the probability of electron 2 being at any particular position in orbital ϕ_r, and hence we may consider that the GVB wavefunction does not provide for instantaneous correlations among the motions of the electrons. Since the

GVB wavefunction is the most general wavefunction involving just two spatial orbitals, we may consider that all correlation error beyond GVB involves instantaneous correlation of the electrons. When important to distinguish these effects we will refer to the latter as dynamic electron correlations and the difference between HF and GVB as static electron correlation.

Now consider the description of correlation in the natural orbital (NO) representation of the GVB wavefunction

$$\Phi^{NO}_{(1,2)} = C_g \phi_g(1) \phi_g(2) - C_u \phi_u(1) \phi_u(2) \ . \tag{41}$$

Assume that electron 1 is at some position R on the right side of the molecule and consider the likelihood of electron 2 being at equivalent positions R or L on the right and left sides of the molecule. In the HF wavefunction

$$\Phi^{HF}(R,R) = \phi(R)\phi(R)$$

$$\Phi^{HF}(R,L) = \phi(R)\phi(L),$$

and since

$$\phi(R) = \phi(L),$$

we have equal probabilities

$$|\Phi^{HF}(R,R)|^2 = |\Phi^{HF}(R,L)|^2 \tag{42}$$

of the electrons being on the same or opposite sides.

In the GVB wavefunction (40) we find

$$\Phi^{GVB}(R,R) = \phi_\ell(R)\phi_r(R) + \phi_r(R)\phi_\ell(R)$$

$$\Phi^{GVB}(R,L) = \phi_\ell(R)\phi_r(L) + \phi_r(R)\phi_\ell(L) \ ,$$

and hence

$$\Phi^{GVB}(R,R) < \Phi^{GVB}(R,L) \ , \tag{43}$$

that is, we obtain the static correlation referred to above. Using the NO form of the wavefunction we obtain

$$\begin{aligned}\Phi^{NO}(R,R) &= C_g \phi_g(R)\, \phi_g(R) - C_u \phi_u(R)\, \phi_u(R)\\ \Phi^{NO}(R,L) &= C_g \phi_g(R)\, \phi_g(L) - C_u \phi_u(R)\, \phi_u(L)\\ &= C_g \phi_g(R)\, \phi_g(R) + C_u \phi_u(R)\, \phi_u(R)\end{aligned}$$

(using the symmetries of ϕ_g and ϕ_u) and hence

$$\Phi^{NO}(R,R) < \Phi^{NO}(R,L). \tag{44}$$

Just as in (43). Comparing (41) with the HF wavefunction

$$\Phi^{HF}(1,2) = \phi_g(1)\, \phi_g(2) \tag{45}$$

we see that in order to obtain effective electron correlation, the second NO must have a shape similar to that of the first (dominant) NO but with an extra nodal plane bisecting the first NO. This allows maximal difference between $\Phi^{NO}(R,R)$ and $\Phi^{NO}(R,L)$ and hence maximal electron correlation. We will later find such arguments in terms of nodal planes to be useful in describing other electron correlation effects.

The above discussion should be made clear in Fig. 9.

§3.5.4a Ionization Potentials

In general we expect the correlation error to increase with the number of electrons (since there are more and more complicated interrelationships ignored). Thus the ionization potentials calculated from HF and GVB should be too small. On the other hand we can get an approximate IP from Koopmans' theorem. The Koopmans IP is the energy difference between the self-consistent energy of the N-electron system, E_N, and an energy of the N-1 electron system, E_{N-1}, obtained using orbitals from the N-electron wavefunction. Thus the description of the ionic (N-1 electron) state is non-optimum leading to too high a value for E_{N-1} and hence too large a prediction of IP. However, the IP calculated using selfconsistent wavefunctions of the N and N-1 electron systems should be too small. Hence there is a cancelling of errors such that the Koopmans theorem value of IP is usually rather good (within ~10%). These effects are indicated in Fig. 10.

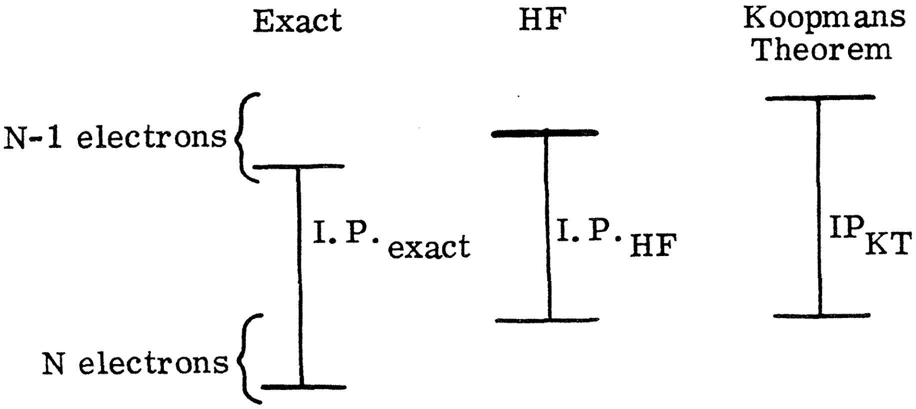


Figure 3-10.

§3.5.5 Configuration Interaction Wavefunctions

Starting with a one-electron basis

$$\{\chi_\mu \,;\, \mu = 1, 2 \ldots P\}$$

we can construct a two-electron basis

$$\{\chi_\mu(1)\, \chi_\nu(2);\ \mu, \nu = 1, 2, \cdots P\}$$

by combining all products of one-electron functions. In terms of this basis the most general wavefunction is

$$\Phi(1,2) = \sum_{\mu,\nu=1}^{P} C_{\mu\nu}\, \chi_\mu(1)\, \chi_\nu(2) \,. \tag{46}$$

The terms in (46) are called configurations and the resulting wavefunction is called an configuration interaction (CI) wavefunction.

Applying the variational principle §3.1, the optimum coefficients for (46) are solutions of equations

$$\sum_{\mu\nu} (H_{\sigma\eta,\mu\nu} - E)\, C_{\mu\nu} = 0 \tag{47}$$

analogous to (3.1-7) except that each simple index μ or ν is replaced by a combined index $\sigma\eta$ or $\mu\nu$. For a complete basis ($P = \infty$) the resulting CI wavefunction is the exact wavefunction of the system.

§3.5.5a Permutational Symmetry

Because the electrons are identical the Hamiltonian must be invariant (unchanged) upon permutation (interchange) of the electrons

$$\mathcal{H}(2,1) = \mathcal{H}(1,2) . \tag{48}$$

[Recall that $\mathcal{H}(1,2) = h(1) + h(2) + \frac{1}{r_{12}}$.]

As a result of this permutational symmetry the exact eigenstates of $\mathcal{H}$ can always be taken as either symmetric

$$\Psi^s(2,1) = \Psi^s(1,2) \tag{49}$$

or antisymmetric

$$\Psi^a(2,1) = -\Psi^a(1,2) \tag{50}$$

under permutation.

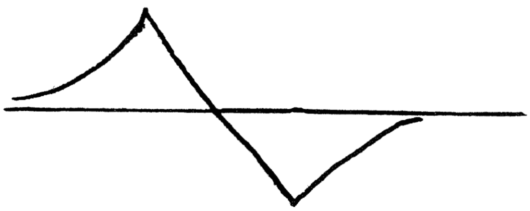
The proof (see App. A) is quite analogous to that in §2.1 where we found that for a system with inversion symmetry, all eigenfunctions are either g or u.

Later when we discuss the Pauli principle and spin we will find that symmetric spatial wavefunctions Ψ^s are allowed only for singlet ($S = 0$) spin states and antisymmetric spatial wavefunctions Ψ^a are allowed only for triplet ($S = 1$) spin states.

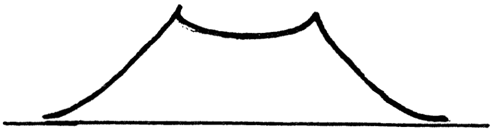
§3.5.5b The Nodal Theorem

Next we will show that the lowest state of $\mathcal{H}(1,2)$ [assuming $\mathcal{H}$ is symmetric (48)] is always a symmetric wavefunction, $\Psi^s(1,2)$, (49).

As shown in §1.2 the ground state of a system is nodeless, that is, the wavefunction of the ground state has the same sign everywhere. For a one-electron system this means that



cannot be the ground state* whereas



can.

The nodal theorem applies also for many electron systems, such as

$$\mathcal{H}(1,2) = -\tfrac{1}{2}\nabla_1^2 - \tfrac{1}{2}\nabla_2^2 + v(r_1) + v(r_2) + \frac{1}{r_{12}} \tag{51}$$

(the proof is exactly as in §1.2). We will now use the nodal theorem to show that the ground state of any two-electron system must be a symmetric wavefunction.

Letting $\underset{\sim}{r}_1 = \underset{\sim}{r}_2$ in an antisymmetric wavefunction

$$\psi^a(\underset{\sim}{r}_2, \underset{\sim}{r}_1) = -\psi^a(\underset{\sim}{r}_1, \underset{\sim}{r}_2)$$

leads to

$$\psi^a(\underset{\sim}{r}_1, \underset{\sim}{r}_1) = -\psi^a(\underset{\sim}{r}_1, \underset{\sim}{r}_1)$$

and hence

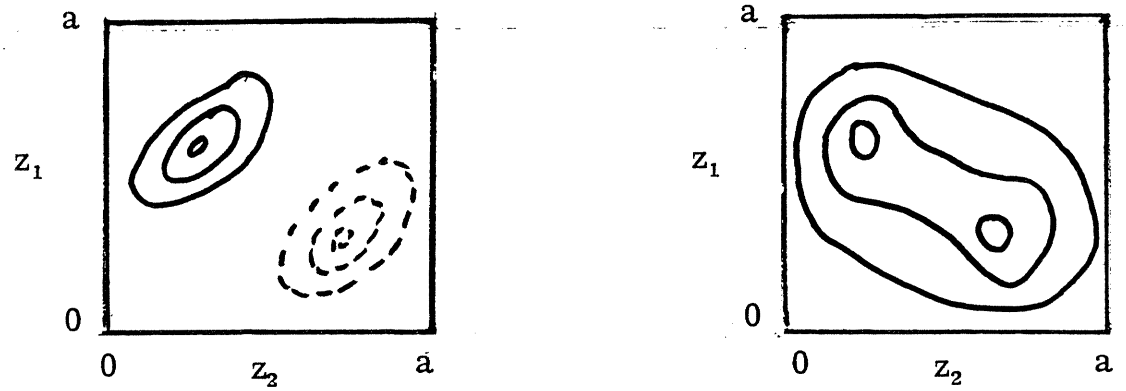
$$\psi^a(\underset{\sim}{r}_1, \underset{\sim}{r}_2) = 0, \quad \text{if } \underset{\sim}{r}_1 = \underset{\sim}{r}_2 . \tag{52}$$

---

* except for R = ∞, where this state is degenerate with the nodeless state.

[For example, typical one-dimensional cases are illustrated in Fig. 11.] Thus every antisymmetric function has a nodal plane whereas symmetric functions need not have nodal planes. Since the nodal theorem implies that the ground state is nodeless, then the ground state must be permutationably symmetric, (49). Later we will find that a symmetric spatial wavefunction must correspond to a singlet spin state and hence the ground state of a two-electron system <u>must</u> be a singlet state.

In the case of a sufficiently singular potential it is possible for the lowest wavefunction having a node to be as low as the lowest nodeless wavefunction. However, in three dimensions our Hamiltonian (51) is not this singular and hence the inequalities apply.



a) Antisymmetric Wavefunction (triplet state)

b) Symmetric Wavefunction (singlet state)

Figure 3-11. Illustration of nodal patterns of two-electron systems (in one dimension).

§3.5.5c Natural Orbitals

In App. B we show that the CI wavefunction (46) for the ground state of any two-electron system can be written as

$$\Psi^0(1,2) = \sum_{\mu=1} \bar{C}_\mu \, \bar{\chi}_\mu(1) \, \bar{\chi}_\mu(2) \tag{53}$$

(that is, double occupied orbitals only) where the orbitals $\{\bar{\chi}_\mu\}$, called natural orbitals, are orthonormal

$$\langle \bar{\chi}_\mu | \bar{\chi}_\nu \rangle = \delta_{\mu\nu} \ . \tag{54}$$

Since (53) has only P terms rather than P^2 as in (46), it is obviously easier to interpret.

The density of electrons in a two-electron system is defined as

$$\rho(1) = \int d^3r_2 \ \Psi(1,2)^* \ \Psi(1,2).$$

Thus using (53) leads to

$$\begin{aligned}\rho(1) &= \sum_{\mu,\nu} \bar{C}_\mu^* \bar{C}_\nu \ \bar{\chi}_\mu(1)^* \bar{\chi}_\nu(1) \ \langle \chi_\mu(2) | \chi_\nu(2) \rangle \\ &= \sum_\mu p_\mu |\chi_\mu(1)|^2\end{aligned}$$

where $p_\mu = |C_\mu|^2$.

Since there is a total of two electrons in the system

$$\int d^3r_1 \, \rho(1) = 2,$$

the coefficients must sum to two,

$$\sum_\mu p_\mu = 2.$$

Consequently, in terms of natural orbitals, the total density of the CI wavefunction is just the sum of the densities of the natural orbitals weighted by a population p_μ that sums to two.

§3.6 Wavefunctions for He

In this section we will illustrate the HF, GVB and CI methods by describing the wavefunctions for He atom.

§3.6.1 HF Wavefunctions for He Atom

First we consider various approximations to the HF wavefunction

$$\Phi^{HF}(1,2) = \phi(1)\,\phi(2),$$

where the HF orbital ϕ is expanded in a basis set.

§3.6.1a MBS

The simplest description of He atom is to place two electrons in the 1s orbital of He^+

$$\chi = e^{-\zeta r} \tag{1}$$

where $\zeta = 2.0$. The total energy in hartrees is just

$$E = 2\epsilon_1 + J = -2.75,$$

where

$$\epsilon_1 = -2.0$$

is the energy of He^+ and

$$J = \tfrac{5}{8}\zeta = 1.25,$$

is the Coulomb interaction of the two electrons (see App. C).

This description can be improved by optimizing ζ (leading to the MBS description). As shown in App. C the energy has the form

$$E = \zeta^2 T_1 + \zeta V_1 \ , \tag{2}$$

where

$$T_1 = (2)\left(\tfrac{1}{2}\right) = 1$$
$$V_1 = -2Z + \frac{5}{8}$$

(i.e., T_1 and V_1 are the kinetic and potential energies for the case of $\zeta = 1$). Requiring that $\partial E/\partial\zeta = 0$, to obtain the optimum ζ, leads to

$$\zeta_{OPT} = -\frac{V_1}{2T_1} = Z - \frac{5}{16} \ . \tag{3}$$
$$= 1.6875$$

for He. Since the optimum ζ for the <u>one-electron</u> atom is

$$\zeta = Z \ ,$$

we can interpret the ζ_{OPT} as an effective charge that has decreased from Z due to the presence of the second electron. It is as if the second electron partially shields the nucleus; hence the quantity

$$\sigma = \frac{5}{16}$$

is sometimes referred to as the shielding correction.

Substituting (3) into (2) leads to

$$E_{OPT} = -\frac{V_1^2}{4T_1} = +\frac{V_1}{2}\zeta_{OPT} = -\zeta_{OPT}^2 \tag{4}$$
$$= -2.84766 \text{ h} \ .$$

This energy is the same as if there had been two non-interacting electrons each experiencing the Coulomb field due to a nucleus of charge $\zeta_{OPT} = Z - \frac{5}{16}$.

The exact energy for He atom is

$$-2.9037$$

Thus the above simple wavefunction accounts for 98.5% of the exact energy! Since the correct energy of He^+ is

$$-2.0 \, ,$$

the use of the calculated E of (4) leads to a predicted IP of 0.84766 or 94% of the exact value. Use of the Koopmans theorem leads to

$$-IP = \langle\phi|h|\phi\rangle + J_{\phi\phi} = \tfrac{1}{2}\zeta_{OPT}^2 - Z\zeta_{OPT} + \tfrac{5}{8}\zeta_{OPT}$$

$$= -\tfrac{1}{2}\zeta_{OPT}^2 + \frac{5}{16}\zeta_{OPT} = -0.89648 \, ,$$

99.2% of the experimental value (a better value is obtained because we describe the ion badly).

§3.6.1b Bigger Basis Sets

The results of using various-sized basis sets for HF calculations on He are listed in Table 2. In the cases P = 1, 2, and 3 extensive optimization of the parameters was carried out, leading to quite short expansions. Thus with P = 2 we are within 0.000007 h = 0.0002 eV = 0.005 kcal/mol of the HF limit ($P = \infty$). With P = 3 the energy is correct to 6 decimal places (comparing to the HF limit). Bear in mind here that the exact (nonrelativistic) energy for He is -2.903 so that even the exact HF wavefunction is off by 0.042 h = 1.1 eV = 25 kcal/mol.

The HF orbitals in these various approximations are plotted in Figure 15. Note that even though P = 3 and P = 12 lead to the same energy (to 6 decimal places) there are still noticeable changes in the orbitals.

The conclusion here is that two suitably chosen basis functions are adequate for describing He. Such a basis is referred to as double zeta (DZ) or double valence (DV).

Table 3-2. Parameters for HF wavefunctions of the ground state of He. E is the total energy, ϵ is the orbital energy. The orbital exponents are shown in parentheses while the expansion coefficients are not. All quantities are in Hartree atomic units.

P	1	2^a	3^a	12^b
E	-2.847656	-2.861673	-2.861680	-2.861680
ϵ	-0.89648	-0.91792	-0.91795	-0.91796
ns(ζ) C_i	1s(1.68750) 1.0	1s(1.453) 0.84289	1s(1.450) 1.36211	1s(3.0) 0.45742
		1s(2.906) 0.18159	2s(1.723) -0.28189	1s(1.4) 0.00000
			2s(2.641) -0.10724	2s(3.0) 0.24427
				2s(1.4) 0.12985
				3s(3.0) 0.13657
				3s(1.4) 0.11340
				4s(3.0) 0.09451
				4s(1.4) -0.08686
				5s(3.0) 0.00819
				5s(1.4) 0.02546
				6s(3.0) 0.02767
				6s(1.4) -0.00267

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[a] P. S. Bagus, T. L. Gilbert, H. D. Cohen, and C. C. J. Roothaan, unpublished, 1966.

[b] C. C. J. Roothaan, L. M. Sachs, and A. W. Weiss, Rev. Mod. Phys. **32**, 186 (1960).

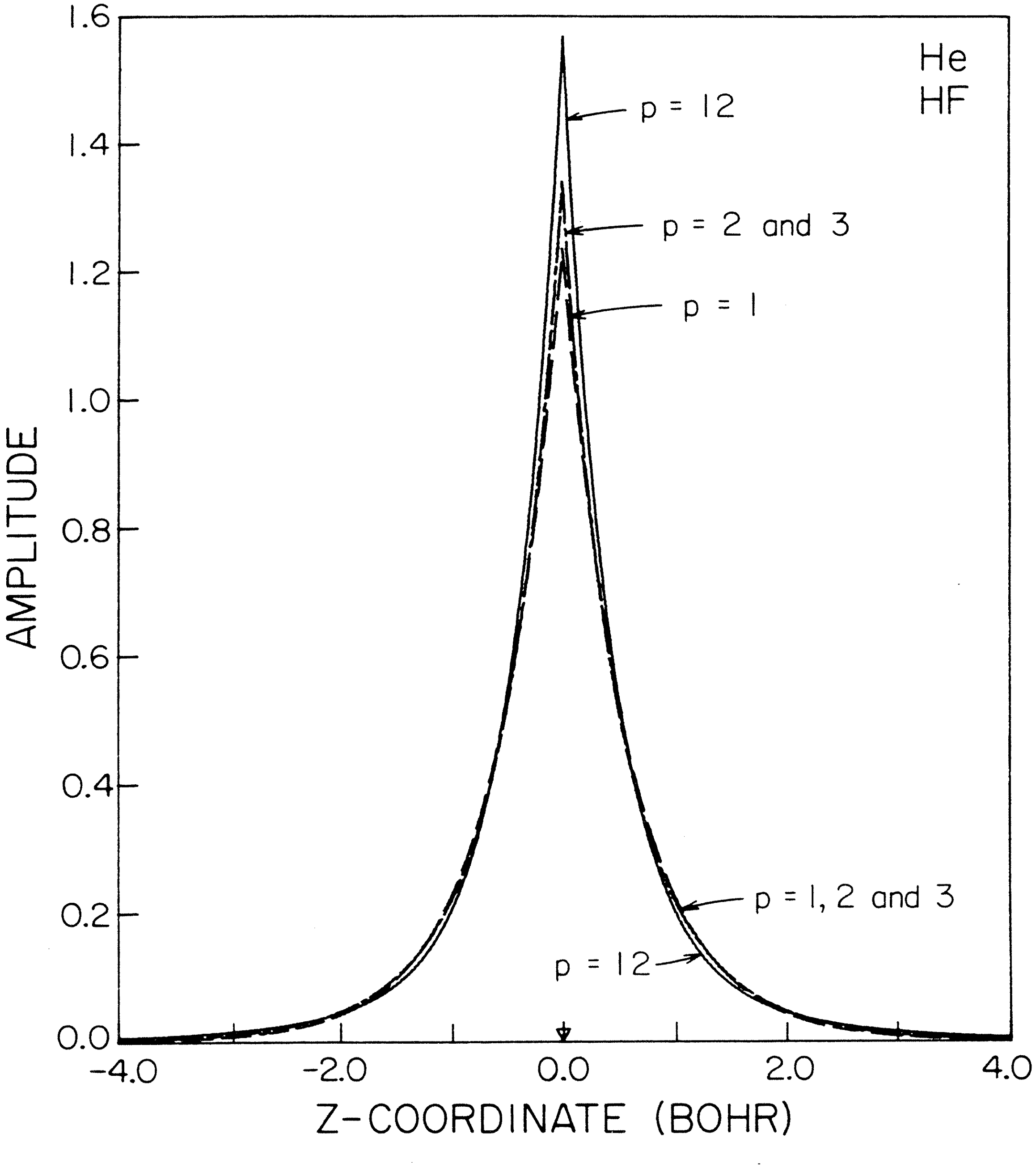

Figure 3-12. Comparison of Hartree-Fock wavefunctions for Helium using various (optimum) basis sets. p indicates the number of functions in the basis set.

§3.6.2 The GVB Wavefunctions for He

For He atom the GVB wavefunction is the optimum wavefunction of the form

$$\Phi^{GVB}(1,2) = \phi_a(1)\phi_b(2) + \phi_b(1)\phi_a(2) \tag{5}$$

The GVB orbitals of He are shown in Fig. 13, where they are compared to the 1s orbital of He^+ and to the HF orbital of He. We see that ϕ_a^{GVB} is very similar to the 1s orbital of He^+, and that ϕ_b^{GVB} is much more diffuse. Thus we envision He as having (i) one electron in the 1s orbital of He^+ (this is orbital ϕ_a) experiencing an effective nuclear charge of $Z \sim 2$ and (ii) the second electron in an orbital (ϕ_b) experiencing an effective charge of $Z \sim 1$ (nuclear charge of 2 but shielded by the ϕ_a electron).*

This type of correlation is referred to as in-out correlation since when one electron is closer to the nucleus, the other tends to be farther away.

This GVB picture is somewhat different from the HF model where both electrons are in the same orbital and one cannot relate the description so simply to that of He^+.

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*Describing both ϕ_a and ϕ_b as simple exponentials and optimizing the exponents leads to effective charges of

$$\zeta_b = 1.189$$

$$\zeta_a = 2.183$$

as expected from the simple picture. [J. N. Silverman, O. Platas, and F. A. Matson, J. Chem. Phys. 32, 1402 (1960).]

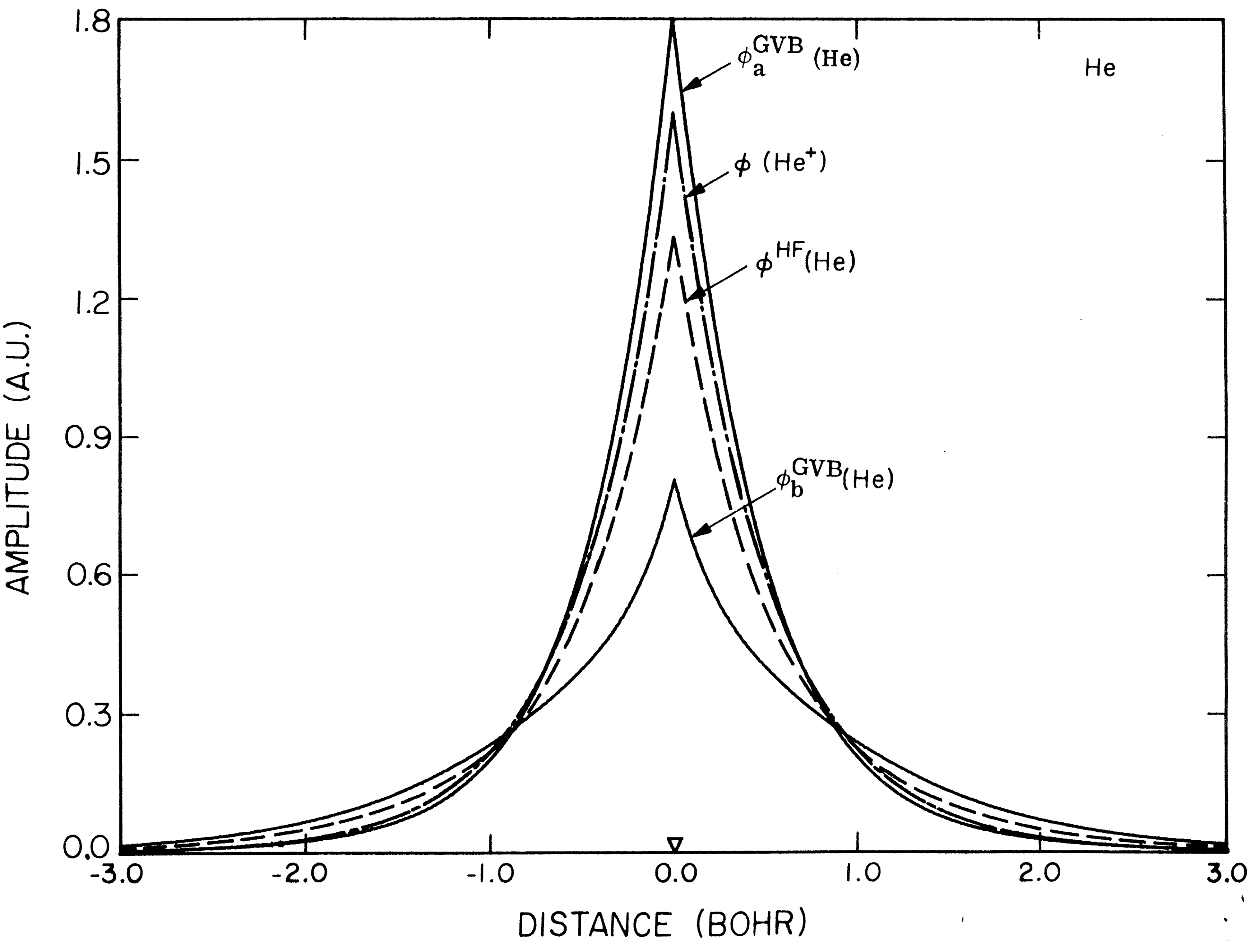

Figure 3-13. HF and GVB Orbitals for He and He$^+$.

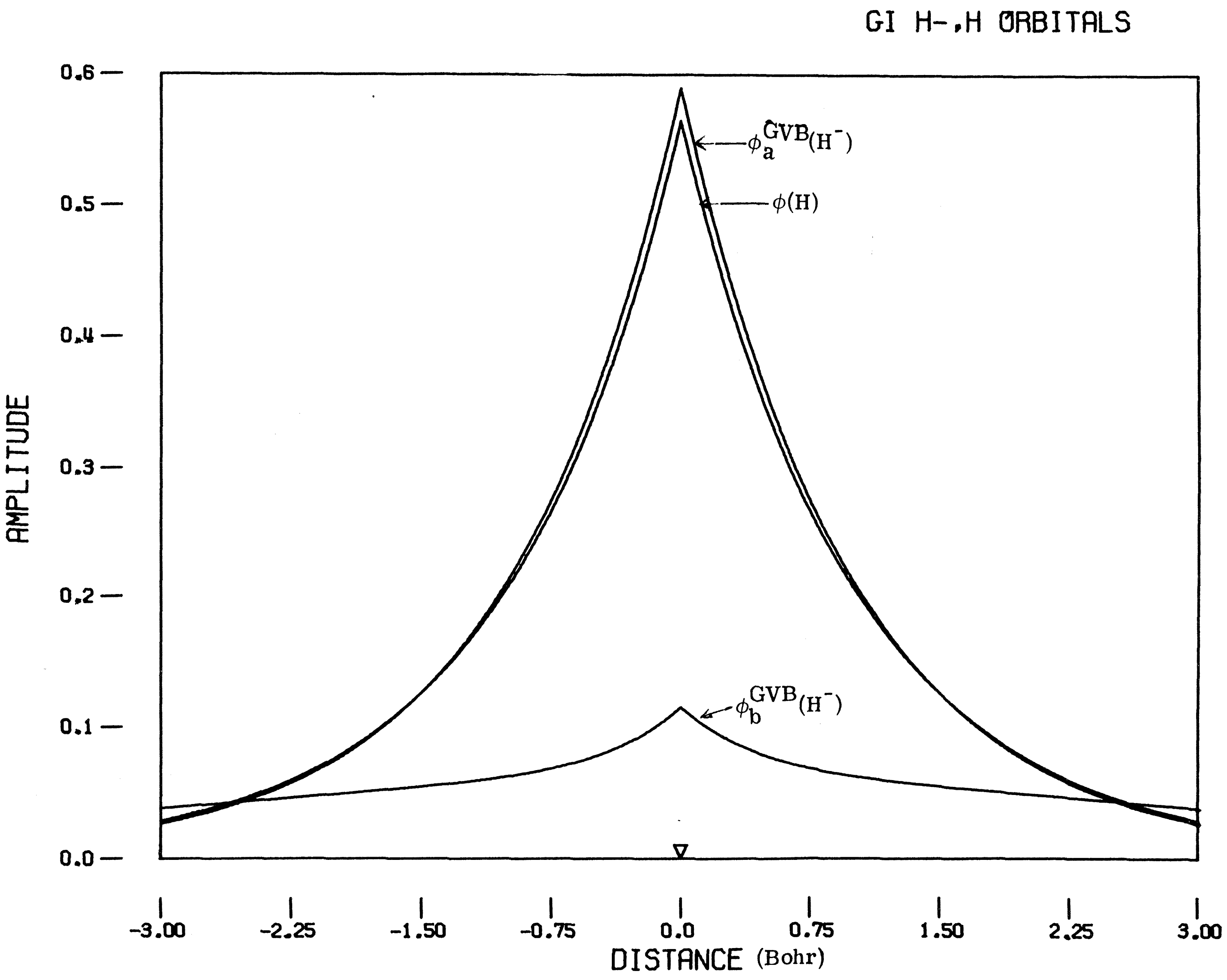

Figure 3-14. GVB Orbitals of H^-.

TABLE 3-3. Comparison of energies for two-electron atoms.

	Exact		Hartree-Fock				GVB					CI
	E^a	I. P.[b]	$E_{HF}{}^c$	$\epsilon_{HF}{}^c$	IP (ΔE)	Corr Energy	E_{GVB}	ϵ_a	ϵ_b	IP (ΔE)	Dynamic Corr Energy	E_{CI}^e
H^-	- 0.527751	0.027751	- 0.4870[d]	- 0.0462[d]	-0.0130	0.0408	- 0.51384[d]	- 0.26800	-0.01471	0.0138	0.0139	- 0.52751
He	- 2.903724	0.903724	- 2.861680	- 0.917956	0.8617	0.0420	- 2.87800[f]	- 1.2152	-0.9039	0.8780	0.0257	- 2.90320
Li^+	- 7.279914	2.779914	- 7.236415	- 2.792365	2.7364	0.0435	- 7.25142[f]	- 3.1965	-2.8149	2.7514	0.0285	- 7.27924
Be^{++}	-13.65557	5.65557	-13.61130	- 5.667116	5.6113	0.0443	-13.62577[f]	- 6.1746	-5.7330	5.6258	0.0298	-13.65481
B^{3+}	-22.03097	9.53097	-21.98623	- 9.541979	9.4862	0.0447	-22.00015[g]	-10.14932	-9.65472	9.5002	0.0308	-22.03016
C^{4+}	-32.40625	14.40625	-32.36119	-14.41689	14.3612	0.0451						-32.40540
N^{5+}	-44.78145	20.28145	-44.73616	-20.29183	20.2362	0.0453						-44.78057
O^{6+}	-59.15660	27.15660	-59.11115	-27.166679	27.1112	0.0455						-59.15570
F^{7+}	-75.53171	35.03171	-75.48613	-35.04176	34.9861	0.0456						
Ne^{8+}	-93.90681	43.90681	-93.86112	-43.91673	43.8611	0.0457						

[a] C. L. Pekeris, Phys. Rev. 112, 1649 (1958).

[b] Calculated using E from Ref. a.

[c] Roothaan, Sachs, and Weiss, Rev. Mod. Phys. 32, 186 (1960).

[d] W. A. Goddard III, Phys. Rev. 172, 7 (1968).

[e] A. W. Weiss, Phys. Rev. 122, 1826 (1961). (35 configurations were used.)

[f] W. A. Goddard III, J. Chem. Phys. 48, 1008 (1968).

[g] R. J. Blint and W. A. Goddard III, unpublished results.

A more extreme case is H^-, the GVB orbitals for which are shown in Fig. 14. Here the first electron (in ϕ_a) is very similar to a hydrogen 1s orbital and the second electron is barely bound, leading to a very diffuse ϕ_b orbital. As shown in Table 3, the HF wavefunction for H^- yields an energy of -0.487, higher than the energy of the hydrogen atom (implying that H^- is not stable with respect to $\underset{\bullet}{H}$ plus an electron). The second electron cannot leave since the HF orbital is doubly occupied; thus either both electrons stay or both leave. The GVB wavefunction yields an energy of -0.513, correctly accounting for the stability of H^- (the exact energy is -0.527).

§3.6.3 CI Wavefunctions for He

The results of several CI calculations on He are shown in Table 4. Analyzing in terms of natural orbitals leads to the results in Table 5. Here we see that the 2s, $2p_x$, $2p_y$, and $2p_z$ natural orbitals provide the dominant electron correlation effects. These are the only natural orbitals containing just one nodal plane. Plots of the 2s and 2p NO's are given in Fig. 15, where we see that the higher NO's are concentrated in the same region as the 1s orbital but with the additional nodal plane (circular for ϕ_{2s} and planar for each ϕ_{2p}).

Table 3-4. Energies for CI wavefunctions of the ground state of He atom.

Number of Basis Functions[a]					Energy
s	p	d	f	g	
5					-2.87896[a]
5	4				-2.90039[a]
5	4	3			-2.90258[a]
5	4	3	2		-2.90307[a]
5	4	3	2	1	-2.90320[a]
Pekeris					-2.90372[b]
HF					-2.86168
GVB					-2.87800

[a] A. W. Weiss, Phys. Rev. **122**, 1826 (1961).

[b] C. L. Pekeris, Phys. Rev. **115**, 1216 (1959).

Table 3-5. Analysis of He CI wavefunction in terms of Natural Orbitals.[a]

Natural Orbital	Energy Lowering Millihartrees	% of Total Correlation Energy[b]
2s	16.30	38.82
2p	19.51	46.46
3s	0.88	2.09
3p	1.63	3.87
3d	1.80	4.28
4s	0.09	0.22
4p	0.26	0.62
4d	0.36	0.86
4f	0.35	0.83
Totals	41.18	98.05

[a] N. Sabelli and J. Hinze, *J. Chem. Phys.*, **50**, 684 (1969).

[b] Total correlation energy = 0.0420 hartree.

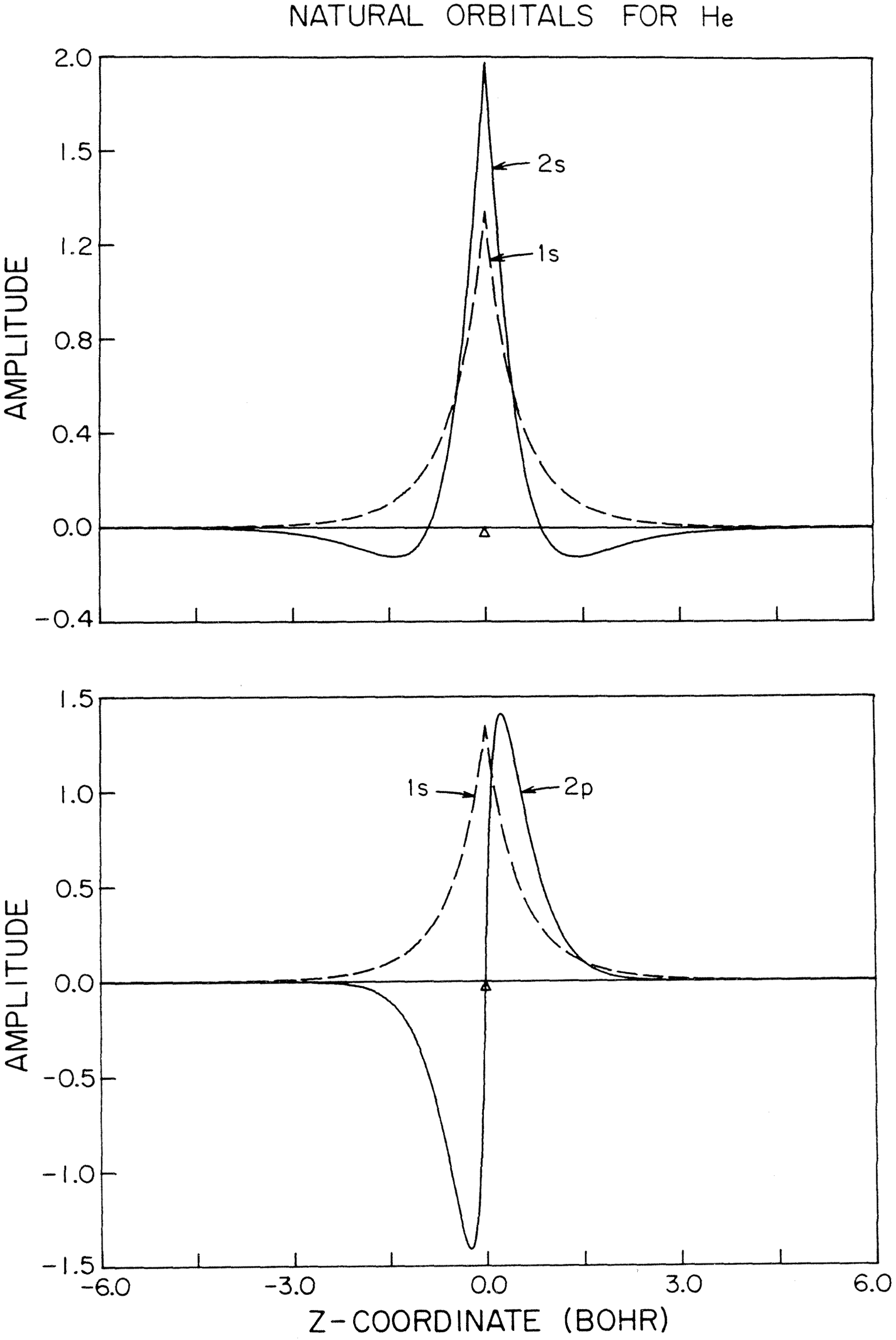

Figure 3-15. The natural orbitals for He (Sabelli and Hinze, loc. cit., Table 4).

Using the five dominant NO's: 1s, 2s, $2p_x$, $2p_y$, $2p_z$, leads to the wavefunction

$$\psi^{CI} = C_{1s}\phi_{1s}\phi_{1s} - C_{2s}\phi_{2s}\phi_{2s} - C_{2p}[\phi_{2p_x}\phi_{2p_x} + \phi_{2p_y}\phi_{2p_y} + \phi_{2p_z}\phi_{2p_z}] \quad (6)$$

where

$$C_{1s} = 0.99599$$

$$C_{2s} = +0.06160$$

$$C_{2p} = +0.06188 \quad .$$

This wavefunction has an energy of -2.8975, just 0.17 eV above the exact (nonrelativistic) energy of -2.9037. This wavefunction is sufficiently accurate that for the purposes of this course we will consider (6) as the exact wavefunction of He.

§3.6.3a Interpretation of the CI Wavefunction

To interpret the wavefunction (6) we will consider one by one the effects of adding any one of the four correlating terms to the dominant (first) term.

The wavefunction

$$C_{1s}\phi_{1s}\phi_{1s} - C_{2s}\phi_{2s}\phi_{2s} \quad (7)$$

can be rewritten in a GVB form

$$\phi_a\phi_b + \phi_b\phi_a \quad (8)$$

where

$$\begin{aligned}\sqrt{2}\phi_a &= \sqrt{C_{1s}}\phi_{1s} + \sqrt{C_{2s}}\phi_{2s}\\ \sqrt{2}\phi_b &= \sqrt{C_{1s}}\phi_{1s} - \sqrt{C_{2s}}\phi_{2s}\end{aligned} \tag{9}$$

are GVB type orbitals. Thus from §3.6.2 we see that the ϕ_{2s} natural orbital in (7) builds in radial correlation, increasing the probability of the second electron being at larger r when the first electron is at smaller r (and vice versa).

Similarly the wavefunction

$$C_{1s}\phi_{1s}\phi_{1s} - C_{2p}\phi_{2p_x}\phi_{2p_x}$$

can also be rewritten as (8) where

$$\begin{aligned}\sqrt{2}\phi_a &= \sqrt{C_{1s}}\phi_{1s} + \sqrt{C_{2p}}\phi_{2p_x}\\ \sqrt{2}\phi_b &= \sqrt{C_{1s}}\phi_{1s} - \sqrt{C_{2p}}\phi_{2p_x}\end{aligned} \tag{10}$$

In (10) we see that when one electron is in the +x direction, the other tends to be in the -x direction. Similar results occur for the ϕ_{2p_y} and ϕ_{2p_z} terms. The three correlations resulting from the terms involving p orbitals are grouped together and referred to as angular correlation.

The three terms of (6) involving p orbitals can be written as

$$[\phi_{2px}\phi_{2px} + \phi_{2py}\phi_{2py} + \phi_{2pz}\phi_{2pz}] =$$

$$= R(1)R(2)[\sin\theta_1 \cos\varphi_1 \sin\theta_2 \cos\varphi_2 + \sin\theta_1 \sin\varphi_1 \sin\theta_2 \sin\varphi_2 + \cos\theta_1 \cos\theta_2]$$

$$= R_{2p}(1)R_{2p}(2) \cos\theta_{12}\ , \tag{11}$$

where R(i) is the radial part of the orbital ϕ_i and θ_{12} is the angle between electron 1 and electron 2. Combining with the first term of (6) we obtain

$$C_{1s} R_{1s}(1) R_{1s}(2) - C_{2p} R_{2p}(1) R_{2p}(2) \cos\theta_{12} . \qquad (12)$$

With this form we see that the magnitude of the wavefunction is increased (with respect to $\phi_{1s}\phi_{1s}$) for $|\theta_{12}| > 90°$ and decreased for $|\theta_{12}| < 90°$. Thus (12) effects an angular correlation of the electrons.

Each of the four dominant correlating orbitals has one nodal plane not contained in* ϕ_{1s} and the correlation effect is across this nodal plane (increased probability of electrons being on opposite sides). Starting with the ϕ_{1s} orbital, there are just four possible orbitals orthogonal to ϕ_{1s} but containing a single nodal plane, namely the above four. All additional correlating terms will involve two or more nodal planes (leading to higher energies) and all are relatively unimportant, leading to a total energy contribution of 6.2 mh = 0.17 eV = 3.9 kcal. For the purposes of most of our considerations of molecules an energy error of 0.1 eV is acceptable, and we will completely ignore these smaller terms. Thus we will consider (6) as the CI wavefunction of He.

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*Of course ϕ_{1s} has no nodal planes; however, we have worded this so as to be appropriate also for correlations of more complicated orbitals than ϕ_{1s}.

§3.7 Wavefunctions for H_2

In this section we will discuss the HF, GVB, and CI wavefunctions for H_2.

§3.7.1 HF Wavefunctions for H_2

In Figure 16 we show how quickly the HF wavefunctions for H_2 converge as a function of basis set size (P). The major effects in the orbital shape are in the bond region.

In Figure 17 we compare the MO wavefunction ($P = 2$, $\zeta = 1$) with the MBS wavefunction ($P = 2$, ζ_{OPT}). Here there are significant changes near the nuclear and bond regions.

Comparing the energies in Table 6 we see that $P = 6$ leads to an energy within 0.00152 h = 0.04 eV = 1 kcal of the HF limit. We consider this as a good level of accuracy. The $P = 6$ basis has two (optimized) s functions on each H and an (optimized) p function on each H. Such a basis is referred to as double valence* (for the two sets of s functions) plus polarization (for the p functions) and will be denoted as DV-P.

With even the best of these HF wavefunctions, the energy is 0.04081 h = 1.1 eV above the exact (nonrelativistic) energy of H_2, about the same as the correlation error of He (and other two-electron ions).

The HF potential curve using the $P = 6$ basis of Table 6 (optimized at each R but restricted so that $\zeta_{1s} = \zeta_{2s}$) is shown in Fig. 18. Just as with the MO wavefunction, the HF wavefunction at large R leads to very serious errors. Thus at $R = 6\ a_0$ with the $P = 6$ wavefunction, the energy is

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*More commonly, double valence is referred to as double zeta.

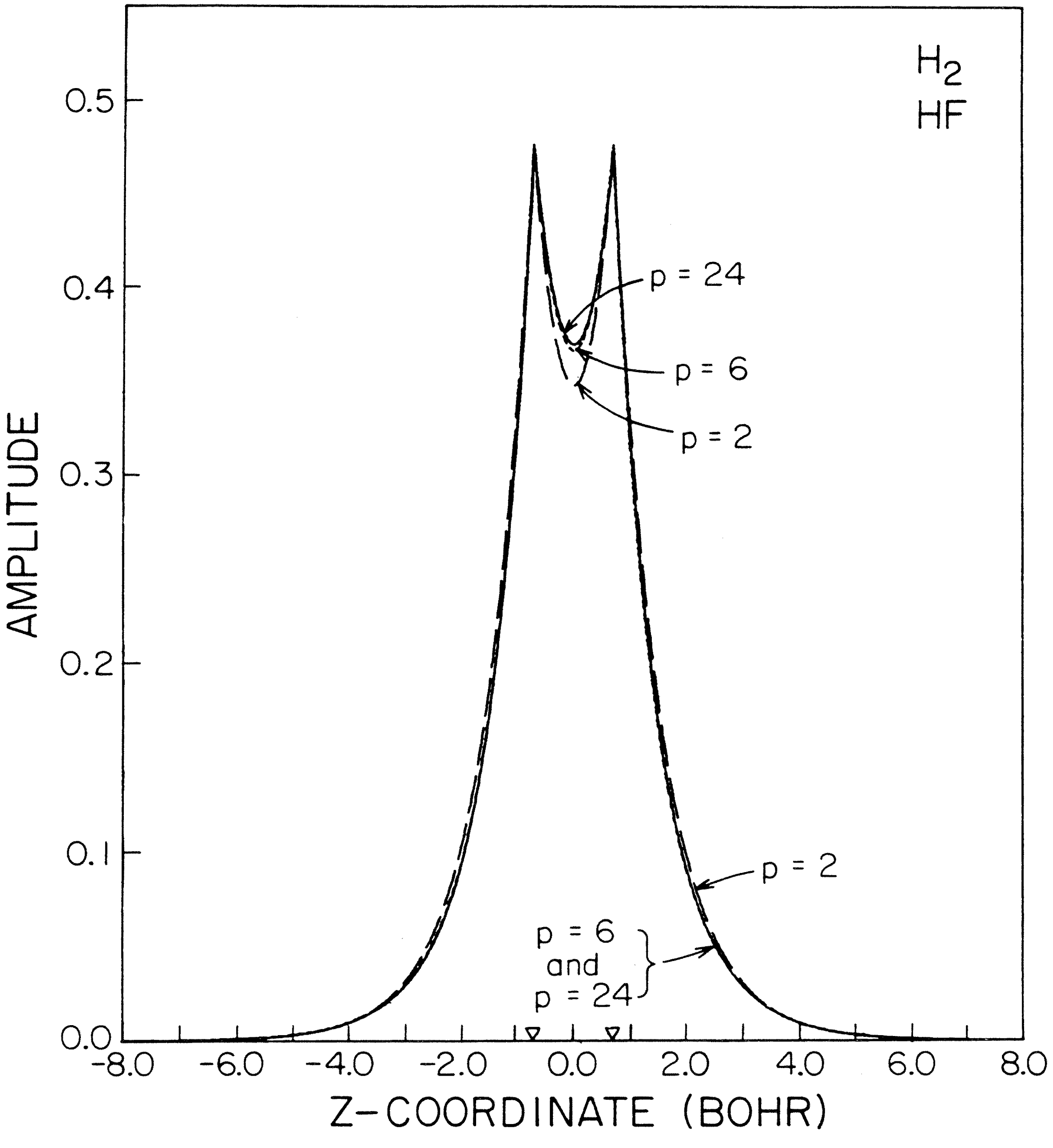

Figure 3-16. Hartree-Fock wavefunctions for H_2 with $R = 1.4\ a_0$. p indicates the number of functions in the basis set.

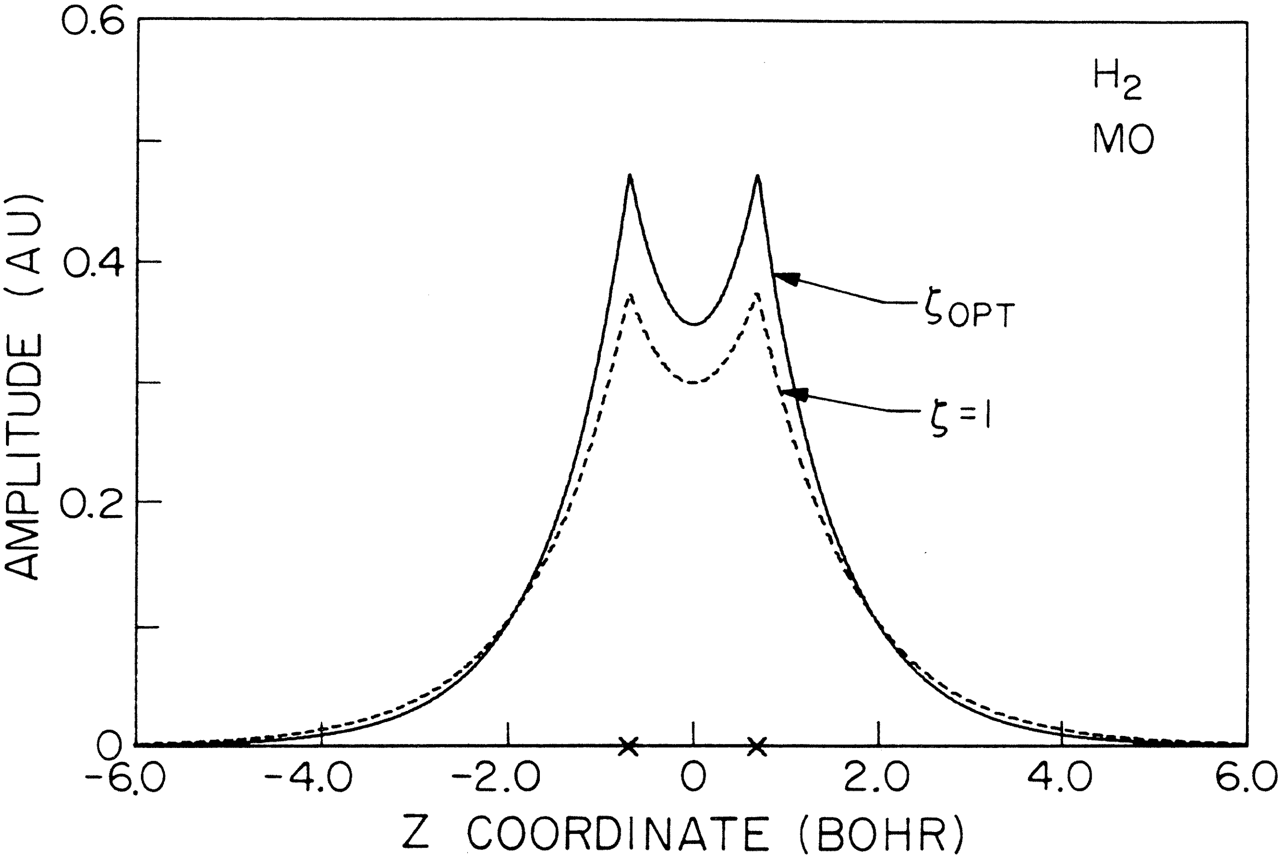

Figure 3-17. MO for H_2 using $\zeta = 1$ and $\zeta_{opt} = 1.1895$ ($R = 1.4a_0$).

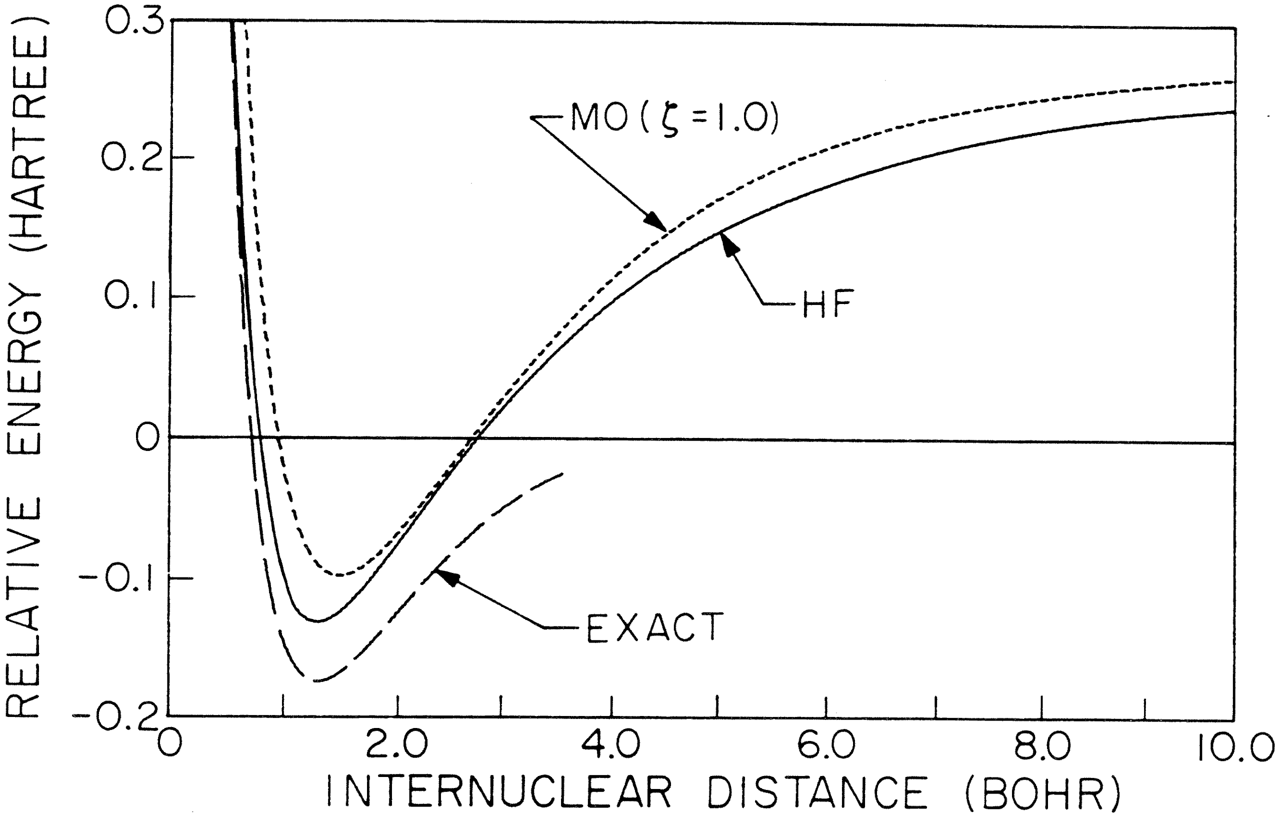

Figure 3-18. Comparison of energies for the MO wavefunction ($\zeta = 1.0$) and the HF wavefunction (six basis functions).

Table 3-6. Energy quantities for HF wavefunctions of H_2 at $R = 1.4 a_0$. Only the coefficients on one atom are shown, the others are equal by symmetry.

P	2		6^a		12^b		18^b		24^b	
E	-1.12819		-1.13211		-1.13353		-1.13359		-1.13363	
ϵ			-0.59443		-0.59463		-0.59466		-0.59465	
	1s(1.1895)	0.54572	1s(1.378)	0.43262	1s(1.19494)	1.03449	1s(1.14615)	0.84994	1s(1.18863)	0.90374
			2s(1.176)	0.12384	1s(3.22156)	-0.06316	1s(3.01720)	-0.01359	1s(2.50021)	-0.04978
			$2p_z$(1.820)	0.02827	2s(1.75027)	-0.22058	2s(0.77682)	0.00894	2s(0.79445)	0.01144
					2s(3.41729)	-0.02034	2s(1.62362)	-0.12071	2s(1.73027)	-0.12832
					$2p_z$(1.81344)	0.04007	3s(3.54949)	0.00753	3s(3.43600)	0.00194
					$2p_z$(3.55649)	-0.00009	$2p_z$(0.98920)	0.08858	$2p_z$(1.05529)	0.03984
							$2p_z$(3.11550)	0.00273	$2p_z$(1.98553)	0.02413
							$3p_z$(3.80593)	0.00790	$2p_z$(4.08182)	-0.00094
							$3d_{z^2}$(1.19687)	0.02029	$3p_z$(3.43359)	0.00129
									$3d_{z^2}$(1.26663)	0.00649
									$3d_{z^2}$(2.68042)	0.00393
									$4f_{z^3}$(2.70808)	0.00103

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[a] S. Fraga and B. J. Ransil, J. Chem. Phys. 35, 1967 (1961).

[b] P. E. Cade, private communication, 1966. Each basis function is normalized to $1/\sqrt{2}$

E = -0.82199 (already far above the dissociation limit, E = -1.0), and the orbital energy is $\epsilon = -0.32170$ (way off from the correct value at large R, $\epsilon = -0.50$). For R = ∞ the HF wavefunction leads to an energy of -0.71542 which is 7.744 eV above the dissociation limit.*

§3.7.2 The GVB Wavefunction for H_2

The GVB wavefunctions and energies for several (optimized) basis sets are given in Table 7. A quite adequate description (0.2 kcal from the limit) is obtained using a single (optimized) s function and a single p_z function on each center. Even the MBS is only 4.1 mh = 0.11 eV above the limit.

The GVB orbitals as a function of R are shown in Fig. 19. At large R the orbitals are atomic-like, but for smaller R the GVB orbital gradually becomes more contracted about each nucleus. These readjustments in the orbitals are such that the contragradience in the bond region is about the same as for the VB wavefunction. From 1 to 6 a_0 the GVB orbitals lead to a much greater overlap than the VB orbital as shown in Fig. 19. For example, at $R = 1.4\ a_0$, $S^{GVB} = 0.804$ as compared to $S^{VB} = 0.753$.

§3.7.2a Energy Analysis

The GVB orbitals for H_2 are compared with the VB orbitals in Fig. 21, where we see that the orbitals readjust in such a way as to maintain the large contragradience in the bond region while concentrating the orbitals more about each nucleus. The GVB energy curves are compared with other energy curves in Fig. 22.

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*W. A. Goddard, J. Chem. Phys., 48, 5337 (1968).

Table 3-7. Energy and wavefunctions for GVB calculations on H_2 at 1.4 a_0. Only the ϕ_ℓ orbital is given, the ϕ_r orbital is the mirror image. The same basis occurs on both centers with the orbitals on the left first (the basis functions on the right have no exponent listed). A p_z basis function with + coefficient is positive toward the second center. All quantities in hartree atomic units.

P	2		4[a]		6[b]	
E	-1.147777		-1.151345		-1.151526	
ϵ	-0.6877		-0.68348		-0.68472	
S	0.79700		0.80093		0.80420	
ns(ζ) C_μ	1s(1.2005)	0.91287	1s(1.1909)	0.88890	1s(1.3129)	0.77499
	1s	0.12303	$2p_z$(2.0928)	-0.00672	2s(1.1566)	0.11116
			1s	0.13631	$2p_z$(1.9549)	-0.00310
			$2p_z$	0.03006	1s	0.12161
					2s	0.04199
					$2p_z$	0.03769

[a] Using 1s(1.262) and 2s(1.191) basis functions on each center leads to E = -1.147804.

[b] Using 1s(1.3092), 2s(1.1273), $2p_z$(1.700), $3d_{z^2}$(2.37) basis functions on each center leads to E = -1.151887.

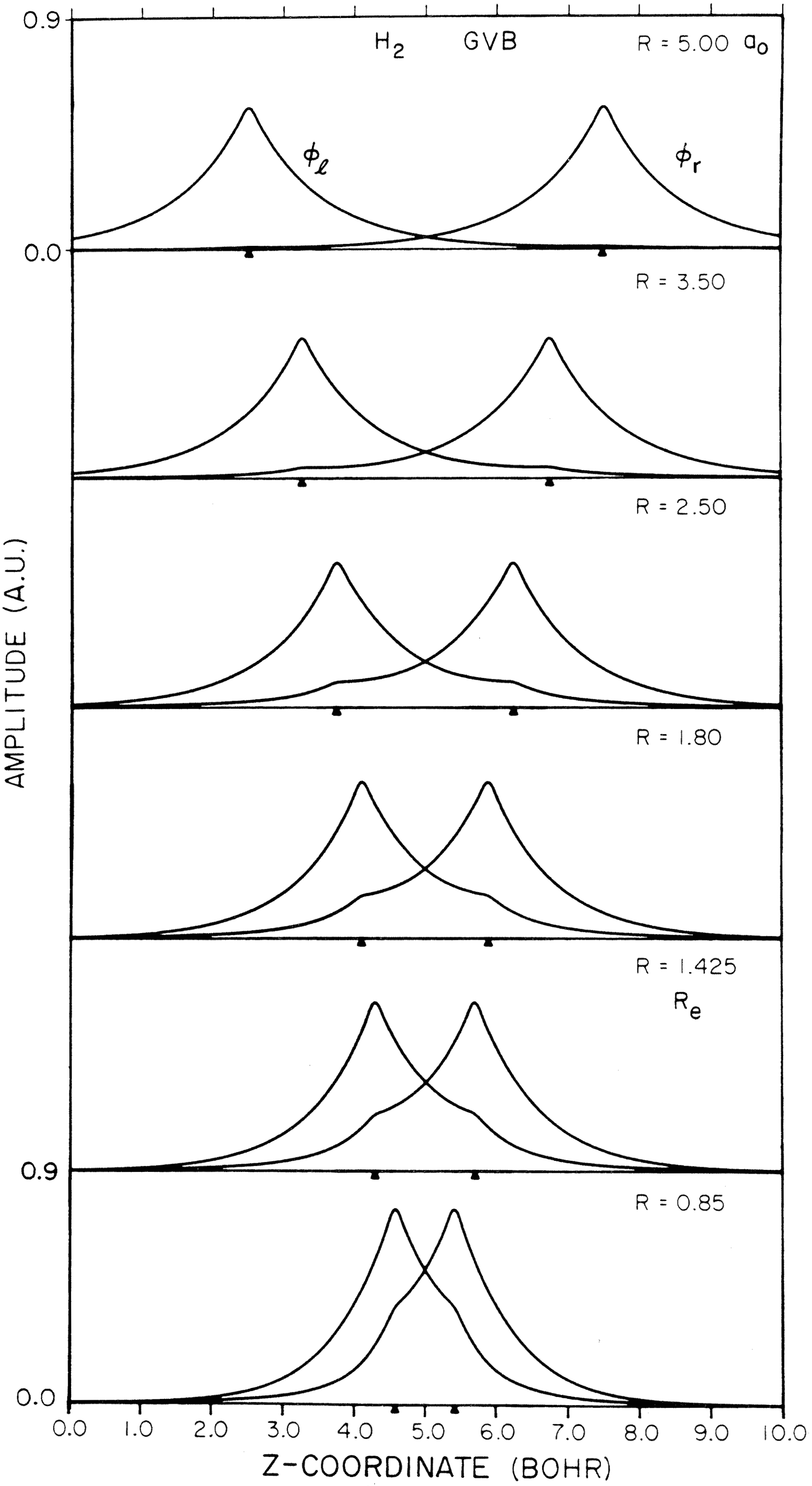

Figure 3-19. The GVB orbitals of H_2 as a function of R (note, the cusps at the nuclei have disappeared due to use of Gaussian basis functions).

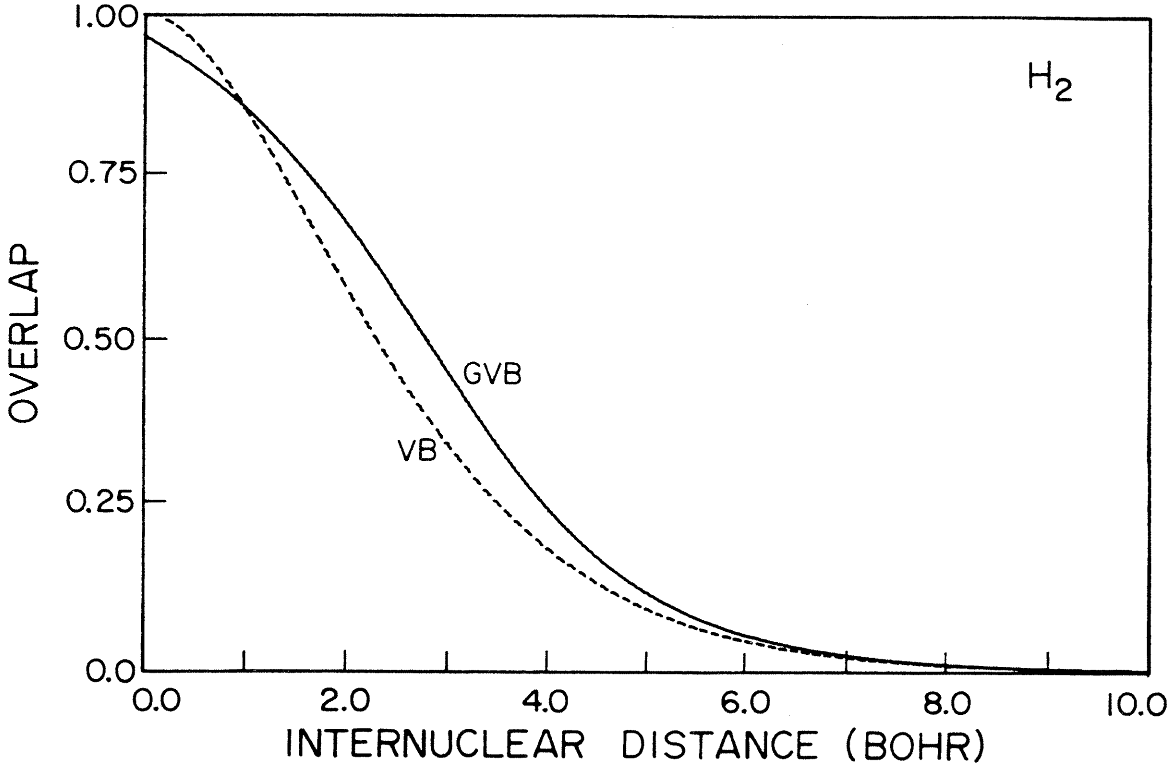

Figure 3-20. Comparison of overlap, $S = \langle\phi_\ell|\phi_r\rangle$ for the VB and GVB wavefunctions.

Some of the energy parameters of the HF, VB, and GVB wavefunctions are compared in Table 8, while the ζ_{opt} as a function of R is given in Fig. 23. For $\zeta = 1.0$ all three wavefunctions yield an R_e far too large (14% to 19%). Optimizing ζ leads to errors of only 1% to 2% in R and improves the calculated bond energies by ~20%. It is characteristic that GVB leads to too large an R while HF leads to too small an R.

Using the form

$$\phi_a \phi_b + \phi_b \phi_a \tag{1}$$

for the GVB wavefunction, we can define classical and exchange terms much as for the VB wavefunction

$$E_{GVB}^{C\ell} \equiv \langle \phi_\ell \phi_r | \mathcal{H} | \phi_\ell \phi_r \rangle$$

$$E_{GVB}^{x} \equiv E_{GVB} - E_{GVB}^{C\ell} ,$$

etc. This leads to the results in Fig. 24, where we see that the exchange term still dominates the bonding. In particular for $R > R_e$ the E^x is very nearly the same for VB and GVB. Thus the main improvement here is in the classical term, $E^{C\ell}$. Similarly, in Fig. 25 we see that it is the exchange part of the kinetic energy that dominates the bonding energy. Again for $R > R_e$ we see only minor changes in T^x between VB and GVB.

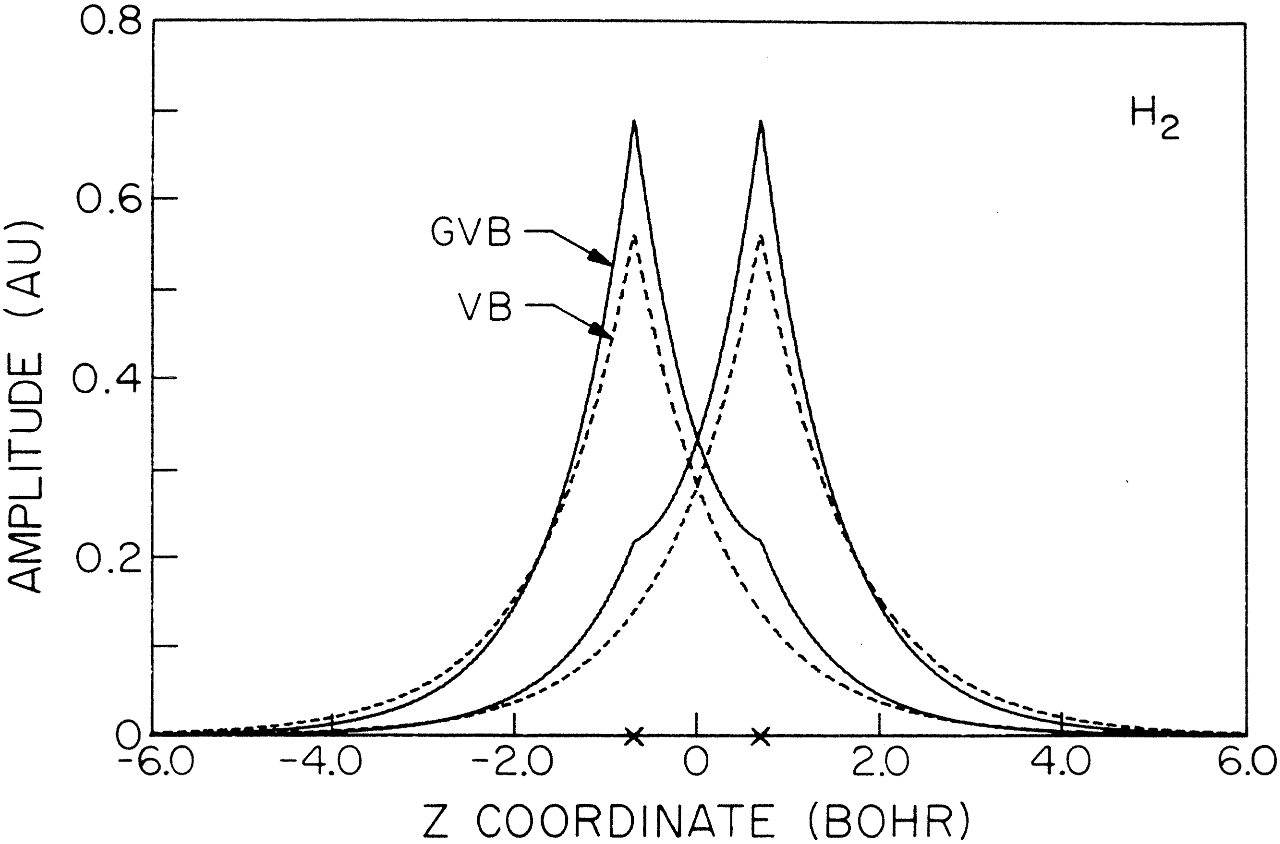

Figure 3-21. Comparison of GVB (two basis functions, $\zeta_{opt} = 1.2005$) and VB ($\zeta = 1$) orbitals for H_2 ($R = 1.4 a_0$).

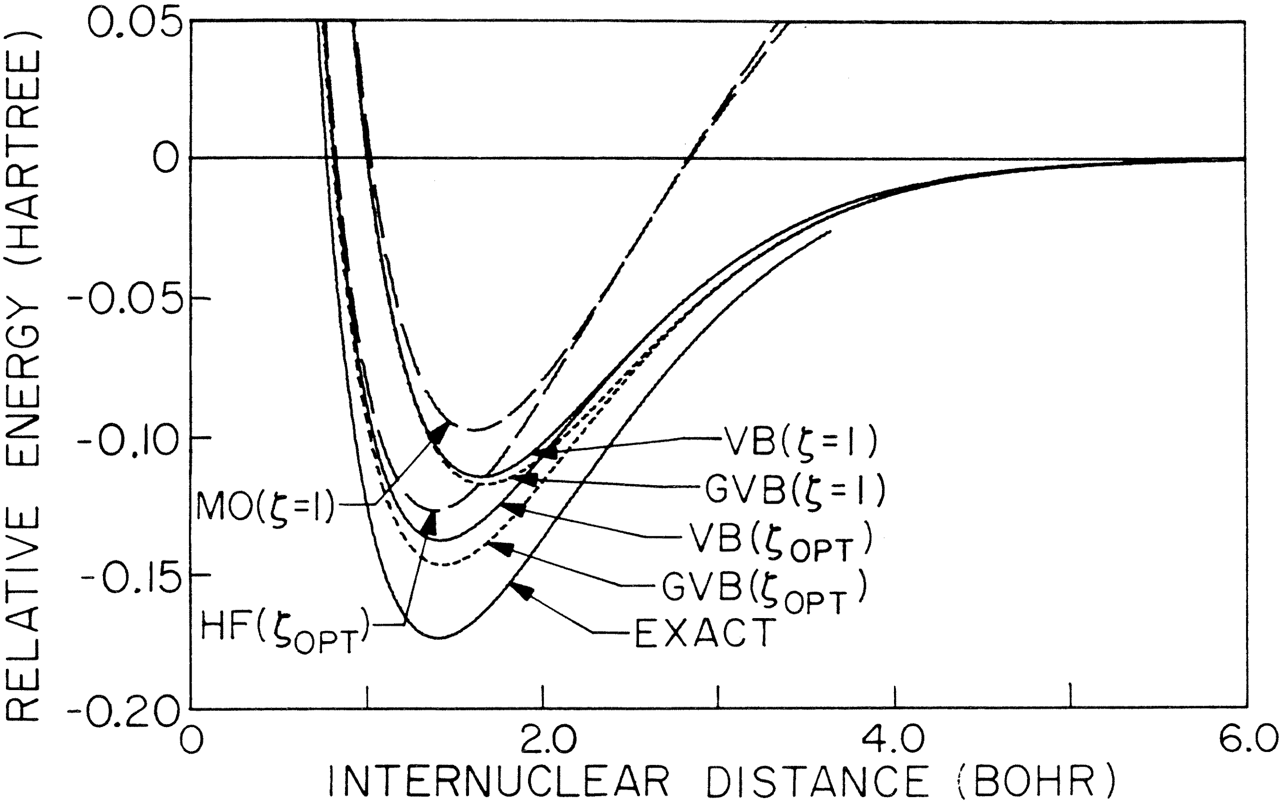

Figure 3-22. Comparison of the energy curves for MO, HF, VB, and GVB wavefunctions of H_2. Only two basis functions were used for HF and GVB. The results for both $\zeta = 1$ and ζ_{opt} are shown. (The ζ_{opt} as a function of R are given in Fig. 2 6.) The energy is relative to the energy of two hydrogen atoms.

Table 3-8. Comparison of results on H_2 for approximate wavefunctions using two basis functions. All quantities are in atomic units; the energies are relative to two hydrogen atoms at $R = \infty$.

		HF	VB	GVB	Exact
$\zeta = 1.0$	R_e	1.603	1.643	1.668	
	E_e	-0.0990808	-0.115971	-0.118651	
ζ_{OPT}	R_e	1.385	1.414	1.431	1.401
	E_e	-0.128231	-0.139083	-0.147938	-0.174470
	ζ_{OPT}	1.1931	1.1661	1.1937	
$R = 1.4a_0$	E	-0.128189	-0.139049	-0.147777	-0.174470
	ζ_{OPT}	1.1895	1.1695	1.2005	

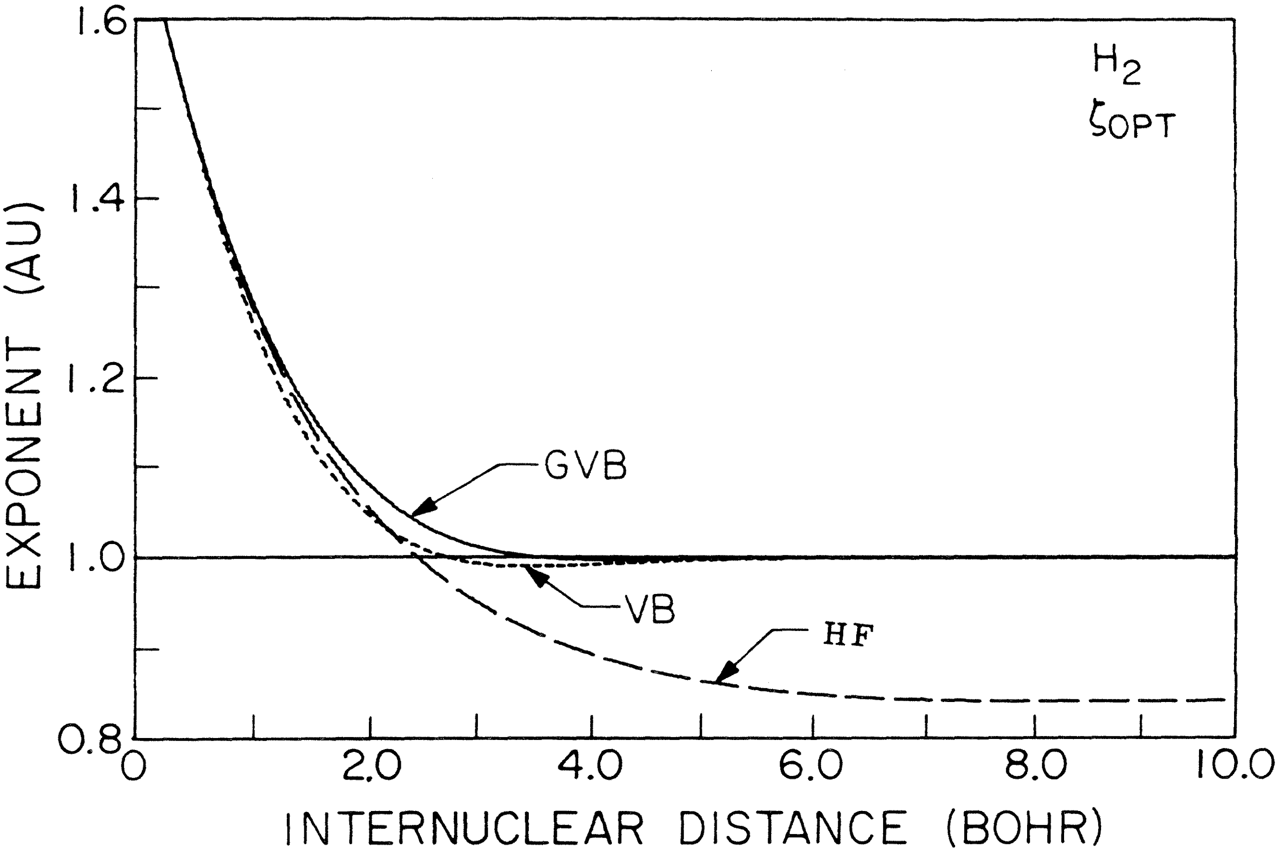

Figure 3-23. ζ_{opt} for the HF, VB, and GVB wavefunctions.

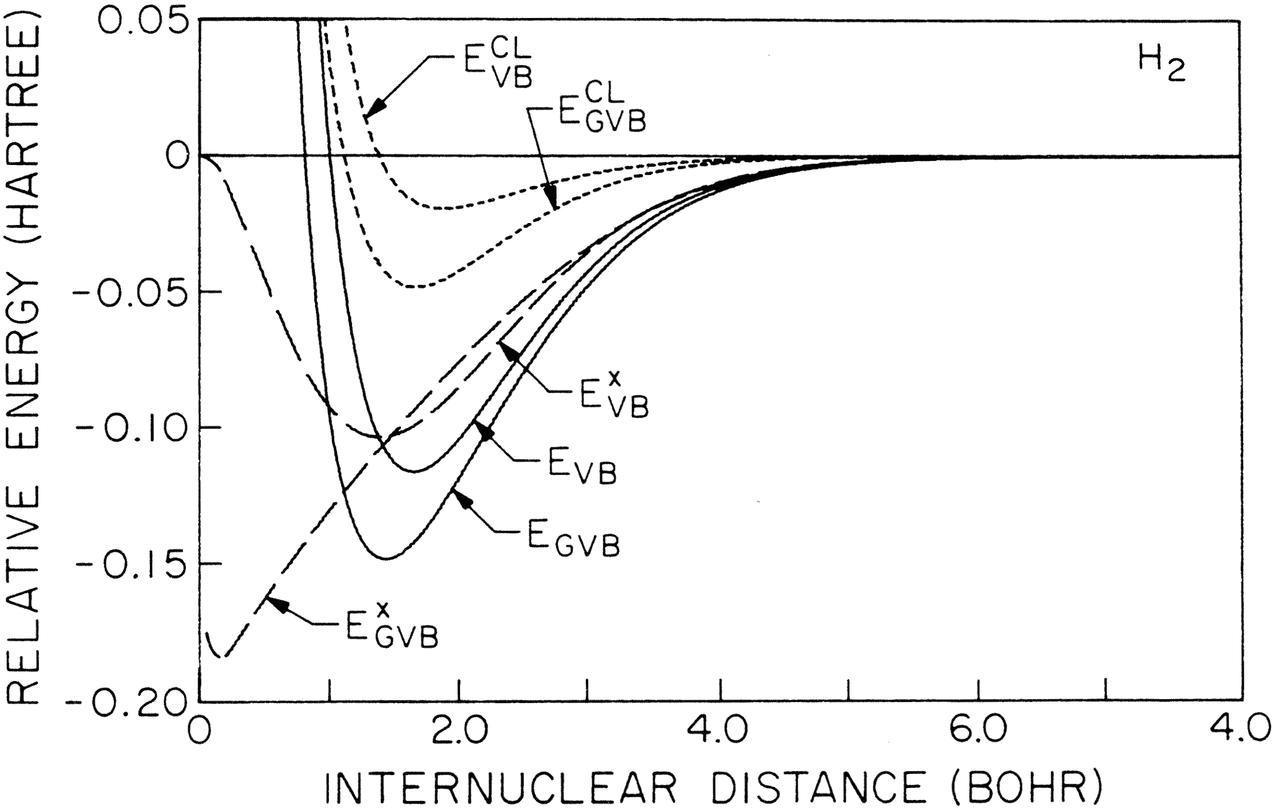

Figure 3-24. Comparison of the classical and exchange energies for the VB and GVB wavefunctions of H_2.

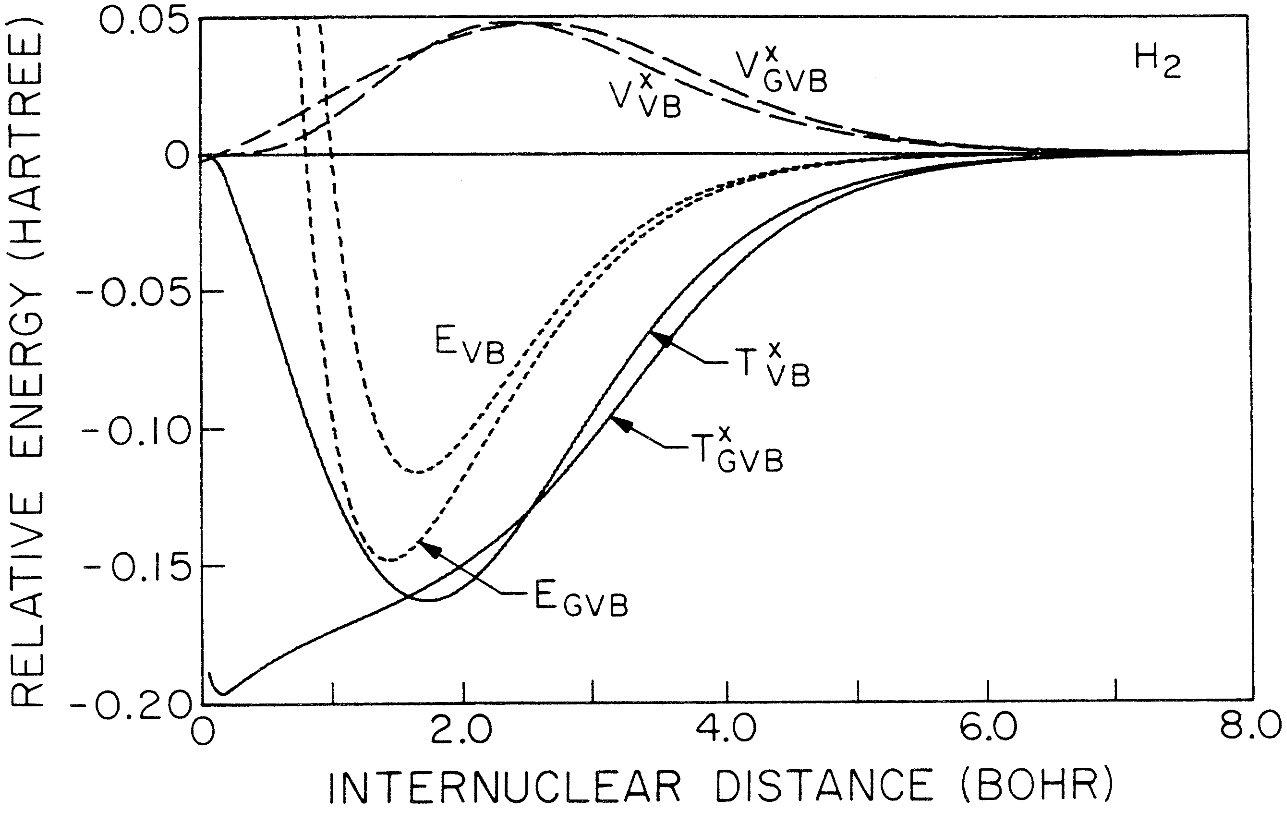

Figure 3-25. The kinetic and potential parts of E^x for the VB and GVB wavefunctions of H_2.

§3.7.3 CI Wavefunctions for H_2

In §3.6.3 we found that in He there are four important correlations each involving a correlating natural orbital having one nodal plane

$$\begin{array}{ll} 2s & \text{radial} \\ \left.\begin{array}{l} 2p_x \\ 2p_y \\ 2p_z \end{array}\right\} & \text{angular} \end{array} \tag{2}$$

For H_2 the HF orbital is nodeless and again we can find four correlating natural orbitals each with one nodal plane. These are illustrated in Fig. 26, where the names $1\sigma_g$, $1\sigma_u$, etc. will be explained below.

As R → 0, the H_2 orbitals in Fig. 26 change smoothly into (we say that they correlate with) the He orbitals in (2):

$$\begin{array}{l} H_2 \quad He \\ \hline 1\sigma_g \rightarrow 1s \\ 2\sigma_g \rightarrow 2s \\ 1\sigma_u \rightarrow 2p_z \\ 1\pi_{ux} \rightarrow 2p_x \\ 1\pi_{uy} \rightarrow 2p_y \quad . \end{array} \tag{3}$$

and hence the correlation effects are closely related:

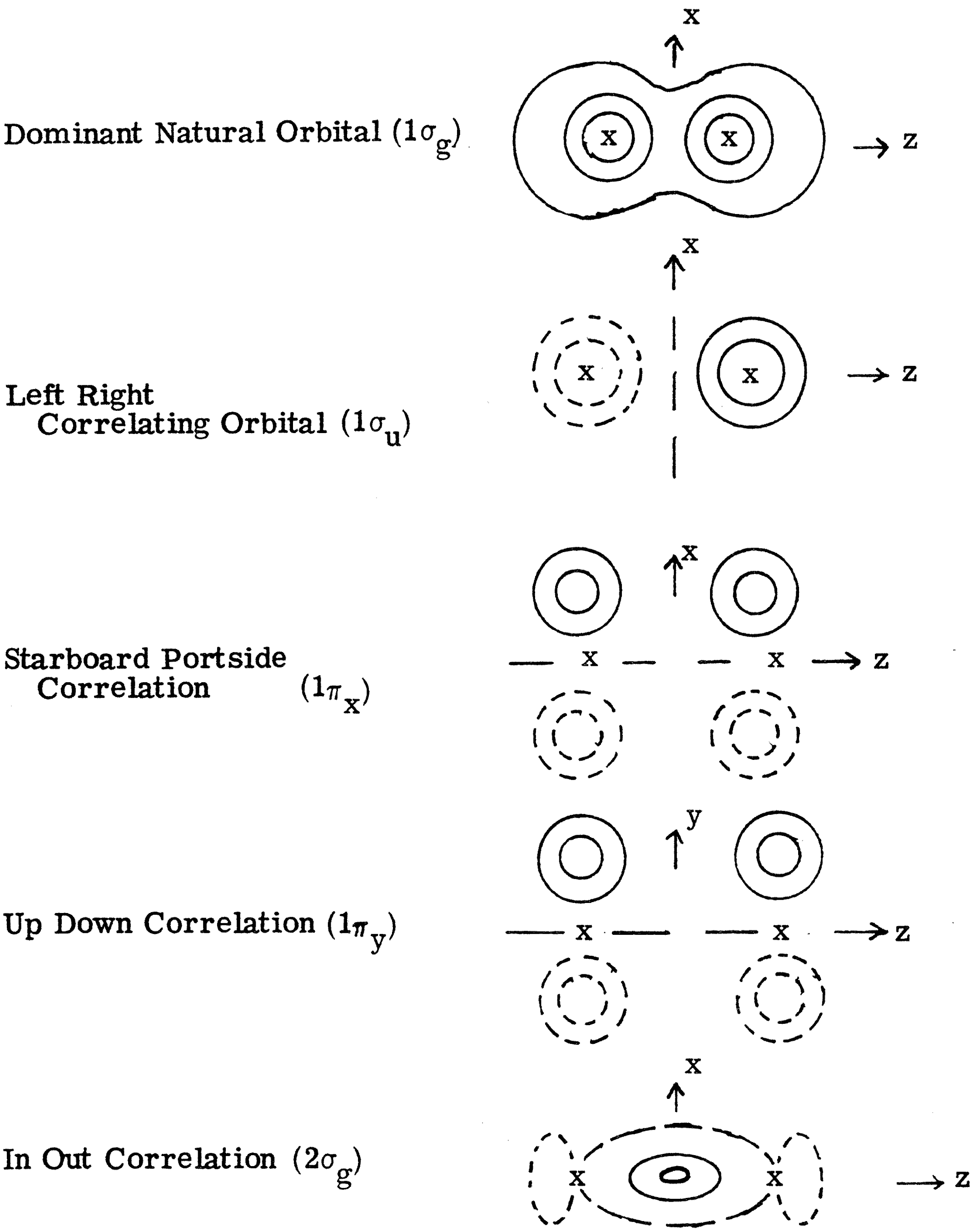

Figure 3-26. Correlating orbitals for H_2. Long dashes indicate nodal planes, solid lines are positive amplitudes and dotted lines negative amplitudes.

$$\begin{array}{rcl} H_2 & & \text{He} \\ \text{left-right } (1\sigma_u) & \longleftarrow & \text{angular-z } (p_z) \\ \text{starboard-portside } (1\pi_{ux}) & \longleftarrow & \text{angular-x } (p_x) \\ \text{up-down } (1\pi_{uy}) & \longleftarrow & \text{angular-y } (p_y) \\ \text{in-out } (2\sigma_g) & \longleftarrow & \text{radial } (2s) \end{array} \qquad (4)$$

The five dominant natural orbitals for H_2 are shown in Fig. 27, which should be compared to Fig. 15 for He. With these five dominant NO's the wavefunction

$$\begin{aligned} \Psi = {} & C_{1\sigma_g}\phi_{1\sigma_g}\phi_{1\sigma_g} - C_{2\sigma_g}\phi_{2\sigma_g}\phi_{2\sigma_g} - C_{1\sigma_u}\phi_{1\sigma_u}\phi_{1\sigma_u} \\ & -C_{1\pi_u}\left[\phi_{1\pi_{ux}}\phi_{1\pi_{ux}} + \phi_{1\pi_{uy}}\phi_{1\pi_{uy}}\right] \end{aligned} \qquad (5)$$

leads to an energy of -1.1699 h. Comparing to the exact energy of -1.1744 h, we see that wavefunction (5) accounts for all but 4.5 mh = 0.12 eV = 2.8 kcal of the exact energy. This is quite adequate for our purposes and we will ignore all other terms.

A more complete analysis [E. R. Davidson and L. L. Jones, J. Chem. Phys., 37, 2966 (1962)] of CI calculations on H_2 (for $R = 1.4\ a_0$) in terms of NO's is given in Table 9.

For the molecule at R_e the dominant correlation is left-right. This becomes even more so for larger R. Thus at $R = \infty$ the exact wavefunction is

$$\Psi(1,2) = C_{1\sigma_g}\ \phi_{1\sigma_g}\ \phi_{1\sigma_g} - C_{1\sigma_u}\ \phi_{1\sigma_u 1\sigma_u}$$

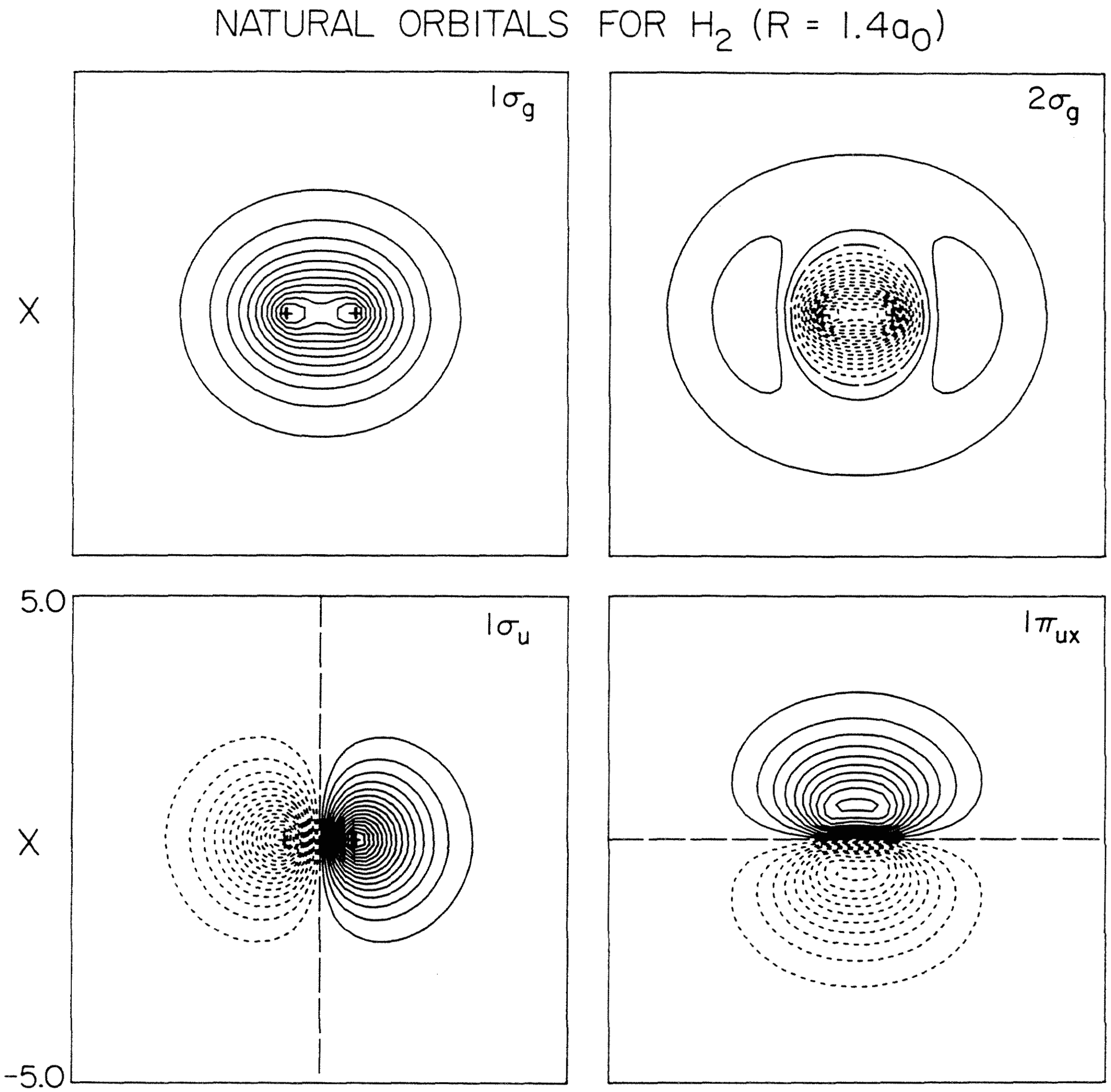

Figure 3-27. The natural orbitals of H_2 for $R = 1.4\ a_0$. [From G. Das and A. C. Wahl, J. Chem. Phys., 44, 87 (1966)].

Table 3-9. Analysis of H_2 CI wavefunction in terms of NO.[a]

Natural Orbital	Energy Lowering Millihartrees	% of Total Correlation Energy[b]
$1\sigma_u$	18.47	45.25
$1\pi_u$	10.34	26.56
$2\sigma_g$	7.03	17.22
$1\pi_g$	0.75	1.84
$3\sigma_g$	0.51	1.25
$2\sigma_u$	0.49	1.20
$1\delta_g$	0.49	1.20
$1\pi_u$	0.56	1.37
$4\sigma_g$	0.29	0.71
Totals	39.43	96.60

[a] E. R. Davidson and L. L. Jones, J. Chem. Phys. 37, 2966 (1962).

[b] Total correlation energy = 0.04082 hartrees.

where

$$C_{1\sigma_g} = C_{1\sigma_u} = \frac{1}{\sqrt{2}}$$

$$\phi_{1\sigma_g} = (\chi_{1s\ell} + \chi_{1sr})/\sqrt{2}$$

$$\phi_{1\sigma_u} = (-\chi_{1s\ell} - \chi_{1sr})/\sqrt{2} \ .$$

That is, only left-right correlation is present at $R = \infty$. For $R < 0.8\ a_0$ in-out correlation becomes more important than left-right correlation.

3.7.3a Notation

For diatomic molecules orbitals are classified in terms of their dependence upon φ [the angle of rotation about the molecular axis (z)]. Thus

$$\sigma \Rightarrow \text{independent of } \varphi$$

$$\pi_x \Rightarrow \cos\varphi$$

$$\pi_y \Rightarrow \sin\varphi$$

where φ is referenced with respect to the xz plane.

§3.8 Open Shell Wavefunctions

In §2.2 we found that the second and third states of H_2 have the form

$$\begin{aligned} {}^1\Phi &= \phi_g\phi_u + \phi_u\phi_g \\ {}^3\Phi &= \phi_g\phi_u - \phi_u\phi_g . \end{aligned} \tag{1}$$

where the orbitals ϕ_g and ϕ_u are orthogonal. Such wavefunctions (with orthogonal orbitals) are referred to as open shell wavefunctions. We will occasionally deal with such wavefunctions and will analyze some aspects of the wavefunctions here.

The energies of the wavefunctions are

$$E = \frac{N}{D} \tag{2}$$

where

$$\begin{aligned} \tfrac{1}{2}D &= \langle \phi_g\phi_u | \phi_g\phi_u \pm \phi_u\phi_g \rangle \\ &= \langle \phi_g | \phi_g \rangle \langle \phi_u | \phi_u \rangle \pm \langle \phi_g | \phi_u \rangle \langle \phi_u | \phi_g \rangle \\ &= 1 \end{aligned} \tag{3}$$

$$\tfrac{1}{2}N = \langle \phi_g\phi_u | \mathcal{H} | \phi_g\phi_u \pm \phi_u\phi_g \rangle \quad . \tag{4}$$

The first term of (4) is

$$\begin{aligned} \langle \phi_g\phi_u | \mathcal{H} | \phi_g\phi_u \rangle &= \langle g|h|g\rangle\langle u|u\rangle + \langle g|g\rangle\langle u|h|u\rangle + \langle gu| \frac{1}{r_{12}} |gu\rangle \\ &= \langle g|h|g\rangle + \langle u|h|u\rangle + J_{gu} , \end{aligned}$$

where

$$\langle \phi_g | \phi_u \rangle = 0 \tag{5}$$

and the second term is

$$\pm \langle \phi_g \phi_u | \mathcal{H} | \phi_u \phi_g \rangle = \pm \{ \langle g|h|u\rangle \langle u|g\rangle + \langle g|u\rangle \langle u|h|g\rangle + \langle gu|\frac{1}{r_{12}}|ug\rangle \}$$

$$= \pm K_{gu} .$$

Thus the energy (2) becomes

$$E = \langle g|h|g\rangle + \langle u|h|u\rangle + J_{gu} \pm K_{gu} \tag{6}$$

$$= \langle g|h|g\rangle + \langle u|h|u\rangle + (gg|uu) \pm (gu|gu) .$$

Thus

$${}^1E - {}^3E = 2K_{gu} . \tag{7}$$

Since $K_{gu} > 0$, the ${}^3\Phi$ state is always below the ${}^1\Phi$ state.

The above analysis shows that the wavefunctions

$$\phi_g \phi_u \pm \phi_u \phi_g$$

lead to an electron repulsion energy

$$E^{c\ell} \pm K_{gu} .$$

Thus the significance of the exchange integral K_{gu} is that it is the <u>change</u> in the energy upon superimposing the exchanged wavefunction $\phi_u^{(1)} \phi_g^{(2)}$ on $\phi_g^{(1)} \phi_u^{(2)}$. See §2.2.

Appendix 3-A. Permutational Symmetry, Two Electrons

Summary: Since the Hamiltonian $\mathcal{H}(1,2)$ for a two-electron system is invariant under permutation of electrons

$$\mathcal{H}(2,1) = \mathcal{H}(1,2) \tag{1}$$

the exact eigenstates of $\mathcal{H}$ are each either symmetric or antisymmetric under permutation.

Proof: Consider that Ψ_0 is an exact eigenfunction of

$$\mathcal{H}(1,2)\Psi_0(1,2) = E_0\Psi_0(1,2) . \tag{2}$$

Renumbering the electrons this becomes

$$\mathcal{H}(2,1)\Psi_0(2,1) = E_0\Psi_0(2,1) . \tag{3}$$

But using (1) in (3) leads to

$$\mathcal{H}(1,2)\Psi_0(2,1) = E_0\Psi_0(2,1) . \tag{4}$$

Thus from (2) and (4) both $\Psi_0(1,2)$ and $\Psi_0(2,1)$ are eigenfunctions of $\mathcal{H}(1,2)$, both with the same energy. There are two possibilities here:

(i) there are two (or more) different (linearly independent) states with energy E_0 or

(ii) there is only one state with energy E_0.

In case (ii) it must be that $\Psi_0(2,1)$ is proportional to $\Psi_0(1,2)$

$$\Psi_0(2,1) = \lambda\Psi_0(1,2) . \tag{5}$$

But interchanging 1 and 2 in (5) leads to

$$\Psi_0(1,2) = \lambda\Psi_0(2,1) \tag{6}$$

and substituting (6) into (5) leads to

$$\Psi_0(2,1) = \lambda^2 \Psi_0(2,1) .$$

Thus

$$\lambda = \pm 1 . \tag{7}$$

That is, for a nondegenerate state the wavefunction must be either symmetric ($\lambda = +1$)

$$\Psi^s(2,1) = \Psi^s(1,2), \tag{8}$$

or antisymmetric ($\lambda = -1$)

$$\Psi^a(2,1) = \Psi^a(1,2) \tag{9}$$

under permutation of the electrons, respectively.

Assuming now case (i) we define new functions

$$\Psi_0^s(1,2) \equiv \Psi_0(1,2) + \Psi(2,1)$$
$$\Psi_0^a(1,2) \equiv \Psi_0(1,2) - \Psi(2,1)$$

Applying $\mathcal{H}$ we obtain

$$\mathcal{H}\,\Psi_0^s = E_0\,\Psi_0^s$$
$$\mathcal{H}\,\Psi_0^a = E_0\,\Psi_0^a$$

and hence the exact eigenfunctions of $\mathcal{H}$ are again either symmetric or antisymmetric. QED

Appendix 3-B. Natural Orbitals

A general CI wavefunction for the ground state of a two-electron system

$$\Psi^S(1,2) = \sum_{\mu,\nu=1}^{P} C_{\mu\nu}\, \chi_\mu(1)\, \chi_\nu(2) \tag{1}$$

can always be rewritten in terms of doubly-occupied orbitals

$$\Psi^S(1,2) = \sum_{\mu=1}^{P} \bar{C}_{\mu\mu}^{Z}\, \bar{\chi}_\mu(1)\, \bar{\chi}_\mu(2) \ , \tag{2}$$

where the natural orbitals $\{\bar{\chi}_\mu\}$ are linear combinations of the original basis functions $\{\chi_\mu\}$.

Proof:

Since ψ^S is symmetric, the coefficient matrix is symmetric.

$$C_{\mu\nu} = C_{\nu\mu}$$

If we choose new basis functions $\{\bar{\chi}_\mu;\ \mu = 1, \ldots P\}$ that are linear combinations of the old basis function $\{\chi_\mu;\ \mu = 1, \ldots P\}$

$$\chi_\mu = \sum_\nu V_{\mu\nu} \bar{\chi}_\nu \quad ,$$

then the wavefunction (1) becomes

$$\begin{aligned}\Psi^S &= \sum_{\mu\nu,\sigma\eta} C_{\mu\nu}\, V_{\mu\sigma} \bar{\chi}_\sigma(1) V_{\nu\eta} \bar{\chi}_\eta(2)\\ &= \sum_{\sigma\eta} \bar{C}_{\sigma\eta}\, \bar{\chi}_\sigma(1)\, \bar{\chi}_\eta(2)\end{aligned}$$

where

$$\bar{C}_{\sigma\eta} \equiv \sum_{\mu,\nu} V_{\mu\sigma} C_{\mu\nu} V_{\nu\eta} \ .$$

The wavefunction Ψ^S is unchanged by this transformation of the basis, but in the new basis the CI expansion coefficients are different.

In matrix notation the new coefficients are given by

$$\underline{\bar{C}} = \underline{\tilde{V}}\,\underline{C}\,\underline{V} \qquad (3)$$

Since $\underline{C}$ is a real symmetric matrix, there is always some transformation $\underline{V}$ for which the transformed matrix $\underline{\bar{C}}$ is diagonal. Thus there is always a particular choice of basis functions such that

$$\Psi^S = \sum_{\mu=1}^{P} \bar{C}_{\mu\mu} \bar{\chi}_\mu(1) \bar{\chi}_\mu(2) \qquad (2)$$

With this basis there are only P terms in the CI expansion rather than P^2 as in (1). Thus (2) is a much simpler wavefunction. To find the V leading to the natural orbitals we must first solve the CI equations to find $\underline{C}$. Hence the natural orbitals do not help us solve for the CI wavefunctions. However, having obtained a CI wavefunction, we will immediately transform to the natural orbitals in order to discuss and interpret the wavefunction.

Appendix 3-C. Evaluation of Energy Quantities For Atoms

Here we consider the evaluation of the various energy quantities for a two-electron system with both electrons in the same 1s orbital,

$$\phi_{1s} = N\, e^{-\zeta r} \tag{1}$$

where the orbital exponent ζ is variable.

3.C.1 One Electron Quantities

First the normalization coefficient, N, is obtained from

$$\begin{aligned} 1 = \langle \phi_{1s} | \phi_{1s} \rangle &= N^2 \int dx\, dy\, dz\, e^{-2\zeta r} \\ &= 4\pi N^2 \int_0^\infty r^2\, dr\, e^{-2\zeta r} \\ &= \frac{4\pi}{(2\zeta)^3} N^2 \int_0^\infty \rho^2\, d\rho\, e^{-\rho} \\ &= \frac{8\pi}{8\zeta^3} N^2 , \end{aligned}$$

so that

$$N = \sqrt{\frac{\zeta^3}{\pi}} \; . \tag{2}$$

The nuclear attraction terms are

$$\begin{aligned} V_{1s}^{en} \equiv \langle 1s | -\frac{Z}{r} | 1s \rangle &= -ZN^2 \int_0^\infty r\, dr\, e^{-2\zeta r} \int_0^\pi \int_0^{2\pi} \sin\theta\, d\theta\, d\varphi \\ &= -\frac{ZN^2 4\pi}{4\zeta^2} \\ &= -\zeta Z \end{aligned} \tag{3}$$

The kinetic energy term is obtained most simply by noting that

$$\underset{\sim}{\nabla} \phi_{1s} = -\zeta \phi_{1s} \hat{e}_r$$

(where $\hat{e}_r$ is a unit vector in the r direction), and hence

$$T_{1s} \equiv \langle 1s|\hat{t}|1s\rangle = \langle 1s|-\tfrac{1}{2}\nabla^2|1s\rangle = \tfrac{1}{2}\langle \nabla\phi_{1s} \cdot \nabla\phi_{1s}\rangle$$
$$= \tfrac{1}{2}\zeta^2 \langle \phi_{1s}|\phi_{1s}\rangle = \tfrac{1}{2}\zeta^2 \qquad (4)$$

To check these quantities consider He^+ where $\zeta = 2$. In this case (3) and (4) lead to

$$E_{1s} = T_{1s} + V_{1s}^{en} = \tfrac{1}{2}\zeta^2 - \zeta Z$$

where Z = 2. Optimizing ζ leads to

$$\zeta = Z$$

and hence

$$E_{1s} = -\tfrac{1}{2}Z^2$$

both of which are correct.

3.C.2 Two Electron Quantities

For He we also need the two-electron interaction term

$$J_{1s,1s} = \langle \phi_{1s}\phi_{1s}|\frac{1}{r_{12}}|\phi_{1s}\phi_{1s}\rangle = \langle \phi_{1s}|J_{1s}|\phi_{1s}\rangle , \qquad (5)$$

where

$$J_{1s}(1) = \int dx_2\, dy_2\, dz_2\, \frac{1}{r_{12}}\, |\phi_{1s}(2)|^2 \qquad (6)$$

is the Coulomb field evaluated at r_1 due to an electron (called 2) in the 1s orbital.

The complication in evaluating such integrals as $J_{1s,1s}$ is that the integrand of (6) depends on r_{12}. The usual solution is to use the Laplace expansion

$$\frac{1}{r_{12}} = \sum_{\ell=0}^{\infty} \frac{r_<^{\ell}}{r_>^{\ell+1}} P_{\ell}(\cos\theta_{12}) \tag{7}$$

where

$$\begin{aligned} r_< &= r_1 \qquad \text{if} \qquad r_1 < r_2 \\ &= r_2 \qquad \text{if} \qquad r_2 < r_1 \end{aligned}$$

and oppositely for $r_>$. With (7), (6) becomes

$$J_{1s}(1) = \sum_{\ell=0}^{\infty} \{ \int_0^{\infty} \frac{r_<^{\ell}}{r_>^{\ell+1}} r_2^2 \, dr_2 \, |\phi_{1s}(2)|^2 \int_0^{\pi} \sin\theta \, d\theta \, P_{\ell}(\cos\theta) \int_0^{2\pi} d\phi \} . \tag{8}$$

The integration over θ is zero unless $\ell = 0$, so that (8) becomes

$$J_{1s}(1) = 4\pi \int_0^{\infty} \frac{r_2^2 \, dr_2}{r_>} |\phi_{1s}(2)|^2 = 4\pi \{ \frac{1}{r_1} \int_0^{r_1} r_2^2 \, dr_2 |\phi_{1s}(2)|^2 + \int_{r_1}^{\infty} r_2 dr_2 |\phi_{1s}(2)|^2 \} \tag{9}$$

Before proceeding to evaluate $J_{1s}(1)$, one should notice that (9) is a well-known result in electrostatics. The quantity

$$Q_1 = 4\pi \int_0^{r_1} r_2^2 \, dr_2 |\phi_{1s}(2)|^2$$

is just the part of the charge distribution inside the point r_1. According to (9) the total contribution of this spherically symmetric charge distribution <u>inside</u> r_1 is the same value

$$\frac{1}{r_1}Q_1$$

as if all that charge (Q_1) were localized at the nucleus. Letting

$$Q_2(r) \doteqdot 4\pi r^2 |\phi_{1s}(r)|^2 ,$$

the quantity

$$Q_2(r)dr$$

is the charge on the spherical shell of radius r and thickness dr. According to (9) the contribution of this charge to the potential is

$$\frac{1}{r}Q_2(r)dr$$

and is the same for <u>all</u> r_1 inside r.

Grunging on, we find

$$Q_1 = 4\pi N^2 \int_0^{r_1} r_2^2 dr_2 \, e^{-2\zeta r_2} = \frac{4\pi N^2}{(2\zeta)^3} \int_0^{\rho_1} \rho^2 \, d\rho \, e^{-\rho}$$

where $\rho_1 = 2\zeta r_1$. Integrating by parts this becomes

$$Q_1 = [1 - e^{-\rho_1}(1 + \rho_1 + \tfrac{1}{2}\rho_1^2)] .$$

Similarly the second term of (9) is

$$I_2 = 4\pi N^2 \int_{r_1}^{\infty} r_2 dr_2 \, e^{-2\zeta r_2} = \zeta[\rho_1 e^{-\rho_1} + e^{-\rho_1}] .$$

Thus

$$J_{1s}(1) = \frac{1}{r_1} Q_1 + I_2 = \frac{1}{r_1}(1 - e^{-2\zeta r_1}) - \zeta e^{-2\zeta r_1} . \qquad (10)$$

For large r_1 this becomes

$$J_{1s} = \frac{1}{r_1} \qquad (11)$$

as expected, and for small r_1 we obtain

$$J_{1s}(1) = \zeta - \tfrac{2}{3}\zeta^3 r_1^2 + O(r_1^3) \tag{12}$$

Thus J_{1s} has the form in Fig. 28.

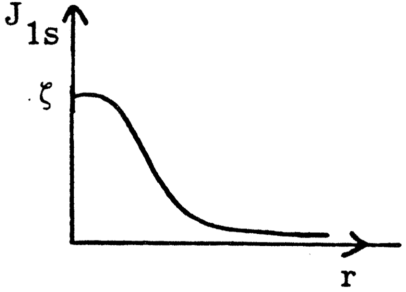

Figure 3-28. The Coulomb potential $J_{1s}(r)$

Using (10) in (5) we obtain

$$\begin{aligned} J_{1s,1s} &= 4\pi N^2 \int_0^\infty r^2\,dr\, e^{-2\zeta r}\left[\frac{1}{r} - \frac{1}{r}e^{-2\zeta r} - \zeta e^{-2\zeta r}\right] \\ &= 4\zeta^3\left\{\frac{1}{(2\zeta)^2} - \frac{1}{(4\zeta)^2} - \frac{2\zeta}{(4\zeta)^3}\right\} \\ &= \tfrac{5}{8}\zeta \end{aligned} \tag{13}$$

Problem 1. Carry through the above analysis for a wavefunction of the form

$$\phi(1)\,\theta(2)$$

where

$$\phi(1) = Ne^{-\zeta r_1}$$

and

$$\theta(2) = N'\,e^{-\eta r_2}$$

with ζ and η different.

3.C.3 Qualitative Analysis of $J_{1s,1s}$

Defining the average size, $\bar{r}$, for the ϕ_{1s} orbital as

$$\langle \phi_{1s} | \frac{1}{r} | \phi_{1s} \rangle = \frac{1}{\bar{r}}$$

we see from (3) that

$$\bar{r} = \frac{1}{\zeta}$$

An approximate value of $J_{1s,1s}$ can be obtained by assuming each electron is at its average radius, $\bar{r} = \frac{1}{\zeta}$, and averaging over the distances between these electrons, assuming each to be on the sphere of radius $\bar{r}$. If the instantaneous location of electron 1 is taken to define the z axis, then the average position of electron 2 will be approximately in the xy plane. This leads to

$$\bar{r}_{12} \approx \sqrt{2}\ \bar{r}$$

and hence to

$$J_{1s,1s} = \frac{1}{\sqrt{2}\ \bar{r}} = \frac{1}{\sqrt{2}} \zeta = 0.707\ \zeta$$

The exact value is

$$J_{1s,1s} = 0.625\ \zeta$$

so that the above estimate is only about 10% high.

APPENDIX 3-D. The Exact Wavefunction of H_2^+

In order to solve for the exact wavefunction of H_2^+ we use elliptic coordinates

$$\xi = (r_a + r_b)/R$$

$$\eta = (r_a - r_b)/R$$

$$\varphi = \text{azimuthal angle}$$

as defined in Appendix 2-A. With elliptic coordinates, the Hamiltonian for H_2^+ becomes separable (expressible as a sum of terms each depending on a different variable), and hence the exact wavefunction of H_2^+ can be factored into terms each depending upon different variables,

$$\Psi(\xi, \eta, \varphi) = \Lambda(\xi) M(\eta) \Phi(\varphi) .$$

For the ground state of H_2^+ at $R = 2a_0$, the resulting (unnormalized) wavefunction is [D.R. Bates, K. Ledsham, and A. L. Stewart, Phil. Trans. Roy. Soc. A246, 215 (1953)]

$$\Lambda(\xi) = (1 + \xi)^{0.34679} (1 + 0.0168\delta + 0.0004\delta^2) e^{-1.48501\xi},$$

$$M(\eta) = [1.1450\, P_0(\eta) + 0.29844\, P_2(\eta) + 0.011461\, P_4(\eta)$$

$$+ 0.000184\, P_6(\eta) + 0.000002\, P_8(\eta)],$$

$$\Phi(\varphi) = 1, \qquad (5)$$

where $\delta = (\xi - 1)/(1 + \xi)$ and $P_\ell(\eta)$ are Legendre polynomials $[P_0 = 1,\ P_2 = \frac{1}{2}(3\eta^2 - 1), \ldots]$

For comparison the MBS wavefunction in elliptic coordinates is

$$\psi^{MBS} = \left(e^{-\zeta r_a} + e^{-\zeta r_b}\right) = \left[e^{\zeta \frac{R}{2} \eta} + e^{-\zeta \frac{R}{2} \eta}\right] e^{-\zeta \frac{R}{2} \xi} . \qquad (6)$$

corresponding to

$$\Lambda(\zeta) = e^{-1.23\xi}$$

$$M(\eta) = \cosh(1.23\eta)$$

at $R = 2a_0$ (the optimum ζ at $R = 2a_0$ is $\zeta = 1.23$). At $R = 2$, the MBS wavefunction leads to $\zeta = 1.23$, somewhat more diffuse than the 1.485 for the exact wavefunction. The optimum energy and bond lengths for the exact wavefunction* are listed in Table 1.

Exercise: expand the $M(\eta)$ expression for the MBS wavefunction in terms of $P_\ell(\eta)$ and compare with the Bates et al. wavefunction.

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*When we say "exact" here we are referring to the exact solutions of (3) and (4). However, (3) and (4) do not lead to an exact description of H_2^+. The two main assumptions here are (1) the neglect of the nuclear kinetic energy terms (referred to as Born-Oppenheimer breakdown) and (2) neglect of relativistic effects. Inclusion of nuclear kinetic energy leads to corrections of order $\frac{1}{2M}$, where M is the proton mass (in Hartree atomic units, e.g., $1/2M = 0.0003\,h = 0.007$ eV). The actual correction to the energy at R_e from the nuclear kinetic energy terms (see Table 1) is $+.00085\,h = 0.023$ eV $= 0.53$ kcal, and from the relativistic effects is $.000005\,h = 0.00013$ eV $= 0.003$ kcal. In order to compare with experiment such terms must be included (actually, for H_2^+ the experimental results are not yet precise enough to require these corrections). However, in this course we will generally ignore such effects and will refer only to results of nonrelativistic, fixed nuclei calculations.