

# Chem120a: The Nature of the Chemical Bond

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# Chapter 1

# The Concepts of Quantum Mechanics

## 1.1 Introduction

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).

This chapter is a review of materials 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 Section 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,  $T = 1/2\langle|\nabla\varphi|^2\rangle$ . 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 Section 0.3. 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].

## 1.2 Basic Principles of Quantum Mechanics

In this section, we highlight the basic concepts of quantum mechanics relevant to 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 given in references [?] and [?].

### 1.2.1 The Need for Quantum Mechanics

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

The total energy is given by  $E = T + V$  where the kinetic energy is

$$T = \frac{1}{2}mv^2 - \frac{1}{2m}p^2 \quad (1.1)$$

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

$$V = \frac{q_p q_e}{r} = -\frac{e^2}{r} \quad (1.2)$$

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

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

$$T = \frac{1}{2}m_p v_p^2 + \frac{1}{2}m_e v_e^2 = \frac{1}{2m_p} (p_p)^2 + \frac{1}{2m_e} (p_e)^2. \quad (1.3)$$

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 equation (1.3) becomes

$$T = \frac{1}{2\mu} (p_e)^2, \quad (1.4)$$

where

$$\frac{1}{\mu} = \frac{1}{m_p} + \frac{1}{m_e} \quad (1.5)$$

or

$$\mu = \frac{m_p m_e}{m_p + m_e} = \frac{m_e}{1 + \frac{m_e}{m_p}}. \quad (1.6)$$

Since  $m_p = 1836m_e$ , then  $\mu = 0.9995m_e$ , and for our purposes we can consider just the kinetic energy of the electron as in equation (1.1).

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. For system containing charges, this is accompanied by emission of light. The lowest kinetic energy occurs for  $p = 0$ , leading to  $T = 0$ , while the lowest potential energy occurs for  $r = 0$ , leading to  $V = -\infty$ . 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 description of atoms, we would not be here pondering the universe.

The solution of this problem is provided in quantum mechanics, as will be discussed. Essentially, the conclusion is that electrons must be described in terms of wavefunctions  $\Psi(\mathbf{r})$ , 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.

### 1.2.2 Interference and Diffraction of Light

Before proceeding, we will review some relevant features concerning the properties of light, interference, and diffraction.

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 ideas are

1. Light is described by a wavefunction  $\psi(x, t)$  that depends upon  $x$  and  $t$ . For example,

$$\psi(x, t) = \cos \left[ \frac{2\pi}{\lambda}x - 2\pi\nu t \right] \quad (1.7)$$

where  $\lambda$  is the wavelength, and  $\nu$  is the frequency.

2. Detection of the light is proportional to the square of the wavefunction, called the intensity, averaged over a long time compared with the frequency

$$I(x) = \langle [\psi(x, t)]^2 \rangle_t \quad (1.8)$$

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

3. Superimposition of two wavefunctions leads to a new wavefunction

$$\psi^{new} = \psi_1^{old} + \psi_2^{old}, \quad (1.9)$$

where the amplitudes add, and

4. The intensity for two superimposed waves is, from 2

$$\begin{aligned} I^{new}(x) &= \langle [\psi_1^{old} + \psi_2^{old}]^2 \rangle_t \\ &= \langle [\psi_1^{old}]^2 \rangle_t + \langle [\psi_2^{old}]^2 \rangle_t + 2\langle \psi_1^{old}\psi_2^{old} \rangle_t \\ &= I_1^{old} + I_2^{old} + I_{int}, \end{aligned} \quad (1.10)$$

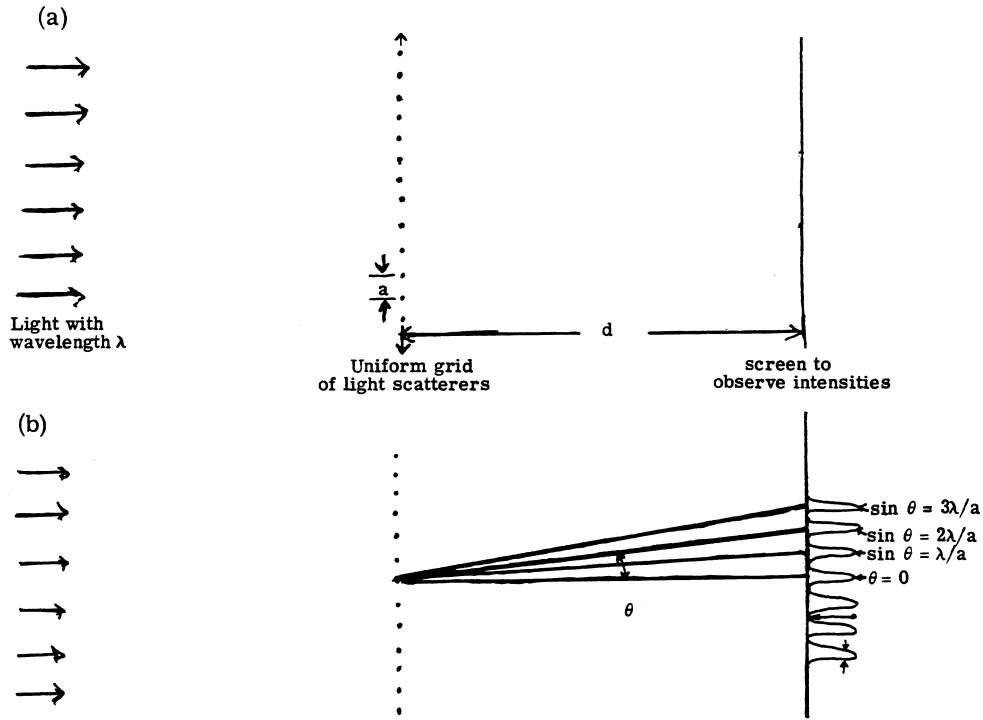


Figure 1.1: Diffraction of light through a grating.

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 terms in 4 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 Figure 1.1. With a set of uniformly spaced scatterers, the observed intensities are sharp spikes at particular angles  $\varphi_n$ , where  $\sin \varphi_n = n(\lambda/a)$ . To have maxima for  $\varphi_n \neq 0$ , we must have  $n\lambda/a$ , the wavelength must be smaller than the spacing of the scattering. From measurements of  $\sin \varphi_{obs}$  one can calculate  $\lambda/a$ . Therefore, knowing the  $\lambda$  of light, we can determine the spacing  $a$ , or vice versa, knowledge of the spacing  $a$  can be used with  $\sin \varphi_{obs}$  to determine  $\lambda$ . A comparison of the observed intensity with that expected if light did not interfere, is given in Figure 1.2.

A particularly exciting application to 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,  $\lambda \approx 1\text{\AA}$ . If so, they should exhibit diffraction, if a grating could be found having equally spaced scatterers with uniform separation of  $\approx 1\text{\AA}$ . 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. Von Laue, an expert on diffraction

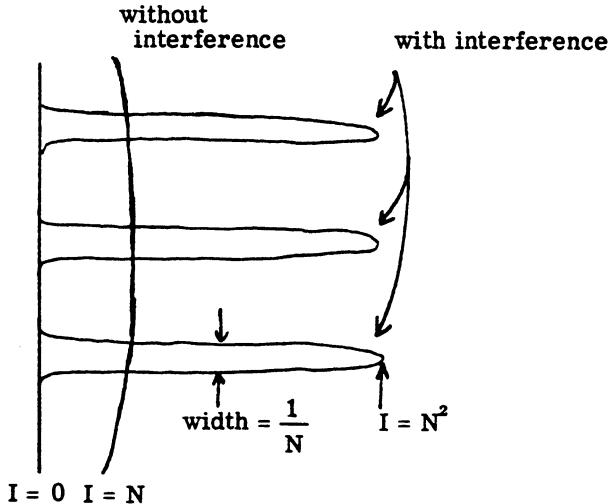


Figure 1.2: Observed intensities if light did not interfere.

theory, suggested the experiment of exposing of 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.

### 1.2.3 Electrons

The critical experiment establishing the wave nature of electrons is that a crystal diffracts a beam of electrons in exactly the same way as it diffracts a beam of X-rays, as illustrated in Figure 1.3. Thus, electrons must be described as waves.

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

$$p = \frac{h}{\lambda}, \quad (1.11)$$

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  $\lambda$  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

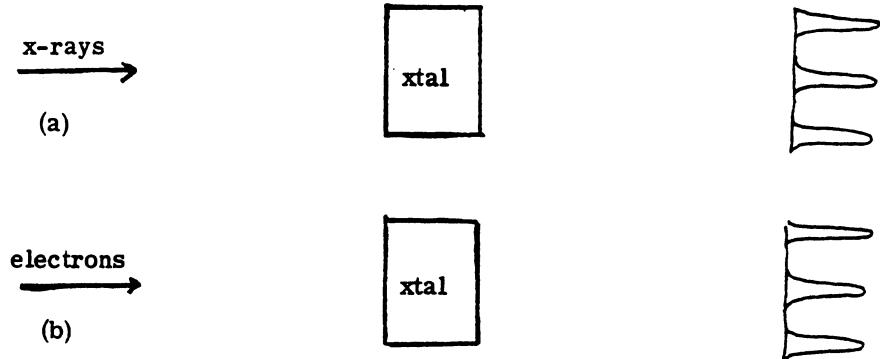


Figure 1.3: Diffraction of electrons.

at some point  $x$  is proportional to the square of the wavefunction,

$$P(x) = \langle [\psi(x, t)]^2 \rangle_t. \quad (1.12)$$

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

#### 1.2.4 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  $\psi_1$  and  $\psi_2$  leads to superposition of the amplitudes

$$\psi = \psi_1 + \psi_2 \quad (1.13)$$

but such that the probability of finding the total system with particular coordinates  $\mathbf{r}$  and  $t$  is given by the, absolute, square of this amplitude.

$$P(\mathbf{r}, t) = |\psi(\mathbf{r}, t)|^2 = \psi^*(\mathbf{r}, t)\psi(\mathbf{r}, t). \quad (1.14)$$

Combining equations (1.13) and (1.14), leads to

$$P(r, t) = \psi_1^*\psi_1 + \psi_2^*\psi_2 + \psi_1^*\psi_2 + \psi_2^*\psi_1, \quad (1.15)$$

and hence, interference effects, as observed.

Putting these ideas together, leads to the basic postulate of quantum mechanics. That is, every physical system is described in terms of a wavefunction  $\psi$  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,

$$\psi = \sum_i \psi_i. \quad (1.16)$$

As part of this basic postulate, we assume that if  $\psi_1$  and  $\psi_2$  are two acceptable wavefunctions of a system, then

$$\psi = c_1\psi_1 + c_2\psi_2, \quad (1.17)$$

where  $c_1$  and  $c_2$  are constants, is also an acceptable wavefunction, 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 equation (1.14). Since the total probability of the system being somewhere is 1, we have the normalization condition of

$$1 = \int P(\mathbf{r}, t) d\tau = \int \psi^* \psi d\tau \equiv \langle \psi | \psi \rangle \quad (1.18)$$

where  $d\tau$  is the incremental volume element and this integration goes over all regions of space. The normalization of the wavefunction 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

$$\psi(\mathbf{r}, t_0 + \delta t) \equiv \varphi_1(\mathbf{r}) \quad (1.19)$$

to

$$\psi(\mathbf{r}, t_0) \equiv \varphi_0(\mathbf{r}). \quad (1.20)$$

Such an association of functions is generally called a transformation and is denoted as

$$\varphi_1(\mathbf{r}) = \hat{A}_{10}\varphi_0(\mathbf{r}). \quad (1.21)$$

where  $\hat{A}_{10}$  is referred to as the operator effecting the particular transformation from state  $\varphi_0$  to state  $\varphi_1$ . Similarly, the time derivative of the wavefunction at time  $t_0$ ,  $\partial\psi/\partial t$ , must be determined by the form of the wavefunction at time  $t_0$ , and hence we can write

$$\left[ \frac{\partial \psi}{\partial t} \right]_{t_0} = \hat{B}\psi(\mathbf{r}, t_0), \quad (1.22)$$

where  $\hat{B}$  is called the time evolution operator. For convenience, we replace  $\hat{B}$  with  $\hat{H} = i\hbar\hat{B}$ , where  $H$  is referred to as the Hamiltonian. Thus, equation (1.22) becomes

$$i\hbar \frac{\partial \psi}{\partial t} = \hat{H}\psi, \quad (1.23)$$

which is known as the time-dependent Schrödinger equation. In equation (1.23),  $i = \sqrt{-1}$ ,  $\hbar$  is Planck's constant,  $1.054589 \cdot 10^{-27}$  erg sec, and  $H$  has the dimensions of energy. 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.

Since equation (1.23) must also apply to any superposition of wavefunctions (1.17),  $H$  must be a linear operator

$$H(\psi_1 + \psi_2) = H\psi_1 + H\psi_2. \quad (1.24)$$

From equation (1.23)

$$i\hbar \frac{\partial}{\partial t} \psi = c_1 \left[ i\hbar \frac{\partial \psi_1}{\partial t} \right] + c_2 \left[ i\hbar \frac{\partial \psi_2}{\partial t} \right] = c_2 H\psi_1 + c_2 H\psi_2, \quad (1.25)$$

where equation (1.23) was applied to  $\psi_1$  and  $\psi_2$ , respectively. Applying equation (1.23) directly to  $\psi$  leads to

$$i\hbar \frac{\partial}{\partial t} \psi = H(c_1 \psi_1 + c_2 \psi_2) \quad (1.26)$$

and hence equation (1.24). 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  $\mathbf{r}$  and time  $t$ .

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

$$\psi(\mathbf{r}, t) = \varphi(\mathbf{r})T(t). \quad (1.27)$$

where

$$\frac{\partial T}{\partial t} = -i\omega T(t) \quad (1.28)$$

and

$$\hat{H}(\mathbf{r})\varphi(\mathbf{r}) = \hbar\omega\varphi(\mathbf{r}). \quad (1.29)$$

Equation (1.28) has the solution

$$T(t) = e^{-i\omega t}, \quad (1.30)$$

so that equation (1.27) becomes

$$\psi(\mathbf{r}, t) = \varphi(\mathbf{r})e^{-i\omega t}, \quad (1.31)$$

where  $\varphi(\mathbf{r})$  is yet to be determined from equation (1.29).

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

$$E = \hbar\omega, \quad (1.32)$$

where

$$\omega = 2\pi\nu = \frac{2\pi c}{\lambda} \quad (1.33)$$

is the angular frequency of the light. This suggests that the  $\hbar\omega$  in equation (1.29) be considered as the energy in equation (1.32). 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

$$k = \frac{2\pi}{\lambda} \quad (1.34)$$

and angular frequency  $\omega$ , where  $\omega$  is given by equation (1.30) and  $k$  is given by  $p = \hbar k$ . Thus, we postulate that the energy and frequency are always related by equation (1.32), leading to

$$\psi(\mathbf{r}, t) = \varphi(\mathbf{r}) e^{-\frac{iE}{\hbar}t} \quad (1.35)$$

$$\hat{H}(\mathbf{r})\varphi(\mathbf{r}) = E\varphi(\mathbf{r}). \quad (1.36)$$

The latter equation, (1.36), is known as the time-independent Schrödinger equation, and is the fundamental equation determining chemical bonding.

### 1.2.5 The Form of the Hamiltonian

In equation (1.36) 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

$$H^{cl} = T^{cl} + V^{cl} \quad (1.37)$$

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

$$\hat{V}(\mathbf{r}) = V(\mathbf{r})^{cl}. \quad (1.38)$$

Thus, for the hydrogen atom,

$$\hat{V}(r) = -\frac{e^2}{r}. \quad (1.39)$$

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

$$T^{cl} = \frac{1}{2m} p^2. \quad (1.40)$$

where  $p = mv$  is the momentum of the particle. We will postulate that the quantum mechanical Hamiltonian operator corresponding to equation (1.38) is

$$\hat{T} = \frac{1}{2m} \hat{p}^2, \quad (1.41)$$

where  $\hat{p}$  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 frequency  $\omega$  has the form

$$\varphi(x, t) = e^{i(kx - \omega t)}, \quad (1.42)$$

and hence the wave vector is given by

$$k = \frac{1}{\varphi} \left[ \frac{1}{i} \frac{d\varphi}{dx} \right]. \quad (1.43)$$

From the diffraction experiments, it was found that  $p = \hbar k$ , leading to

$$p = \frac{1}{\varphi} \left[ \frac{\hbar}{i} \frac{d\varphi}{dx} \right]. \quad (1.44)$$

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

$$\hat{p}_x = \frac{\hbar}{i} \frac{\partial}{\partial x} \quad (1.45)$$

and similarly, for the other directions

$$\hat{p}_y = \frac{\hbar}{i} \frac{\partial}{\partial y} \quad (1.46)$$

and

$$\hat{p}_z = \frac{\hbar}{i} \frac{\partial}{\partial z}. \quad (1.47)$$

Just as the classical momentum is a vector quantity, the three quantities in equations (1.45)–(1.47) are considered as the three components of a vector operator

$$\hat{p} = \frac{\hbar}{i} \nabla \quad (1.48)$$

where  $\nabla$  is the gradient operator.

Now we construct the kinetic energy operator. Since

$$\nabla^2 = \nabla \cdot \nabla = \left[ \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right], \quad (1.49)$$

we obtain

$$\hat{p}^2 = \hat{\mathbf{p}} \cdot \hat{\mathbf{p}} = \left[ \frac{\hbar}{i} \nabla \right] \cdot \left[ \frac{\hbar}{i} \nabla \right] = -\hbar^2 \nabla^2 = -\hbar^2 \left[ \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right], \quad (1.50)$$

and hence,

$$\hat{T} = \frac{1}{2m} \hat{p}^2 = -\frac{\hbar^2}{2m} \nabla^2. \quad (1.51)$$

From equation (1.37), (1.38), and (1.51), we obtain

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \quad (1.52)$$

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

Basically, the Schrödinger equation (1.23) 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 change in  $\psi$ . With suitably ingenious experiments, it is often possible to determine something about how  $\psi$  changes in response to the field and, thereby something about the form of  $\psi$  before changing  $\hat{H}$ . In this way, we can determine various properties of  $\psi$ . 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,  $\hat{O}_p = \Delta \hat{H}$ .

## 1.2.6 More on the Schrödinger Equation

### The Hilbert Space

Given any two functions  $\psi_1$  and  $\psi_2$ , we can generate from equation (1.16) as 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  $\psi_1$  and  $\psi_2$ . Even so, the postulates of quantum mechanics lead to constraints on the functions, and hence, we need not consider every wavefunction. For example, from equation (1.18) we need consider only wavefunctions for which the integral of the square of the wavefunction is unity  $\langle\psi|\psi\rangle = 1$ . Of course, given some wavefunction  $\bar{\psi}$  with

$$\langle\bar{\psi}|\bar{\psi}\rangle = \int d\tau |\bar{\psi}|^2 = a \quad (1.53)$$

with finite, nonzero,  $a$ , we can always define a new function

$$\psi = \frac{\bar{\psi}}{\sqrt{a}} \quad (1.54)$$

that is normalized, i.e.,  $\langle\psi|\psi\rangle = 1$ . Note that  $a$  can never be negative. On the other hand, we need not consider any wavefunctions  $\psi$  for which 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.

### Hermitian Operators

In Section 1.6.1, we consider the implications of requiring that the norm of the wavefunction by unity,  $\langle\psi|\psi\rangle = 1$ , and hence, independent of time for any superposition of wavefunctions,  $\psi = \psi_i + \psi_j$ . The conclusion is that for all possible functions  $\varphi_1$  and  $\varphi_2$ , the Hamiltonian operator  $H$  must satisfy the condition

$$\int d\tau (\hat{H}\psi_i)^* \psi_j = \int d\tau \phi_i^* (\hat{H}\psi_j), \quad (1.55)$$

which we denote as

$$\langle (\hat{H}\psi_i) | \psi_j \rangle = \langle \psi_i | \hat{H} | \psi_j \rangle. \quad (1.56)$$

Such an operator is called Hermitian.

The expectation value

$$\frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle} \quad (1.57)$$

of a Hermitian operator is always real, see Section 1.6.1. Hence, the energy

$$E = \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle} \quad (1.58)$$

in the Schrödinger equation must be real. In Section 1.6.1, we show that the momentum operator

$$\mathbf{P} = \left( \frac{\hbar}{i} \right) \nabla, \quad (1.59)$$

and the kinetic energy operator,

$$\hat{T} = \left( \frac{1}{2m} \right) \hat{p}^2, \quad (1.60)$$

are Hermitian. Similarly, any function of coordinates,  $V(r)$ , is Hermitian, so that the Hamiltonian in equation (1.52) is also Hermitian.

### 1.2.7 Analysis of Kinetic Energy and Potential Energy

In the previous sections, we have established the Schrödinger equation

$$\hat{H}\psi = E\psi, \quad (1.61)$$

where

$$\hat{H} = \hat{T} + \hat{V}, \quad (1.62)$$

$$\hat{T} = -\frac{\hbar^2}{2m} \nabla^2, \quad (1.63)$$

and

$$\hat{V} = V(r). \quad (1.64)$$

Multiplying both sides of equation (1.61) by  $\psi^*$  and integrating, leads to

$$\langle \psi | \hat{H} | \psi \rangle = E \langle \psi | \psi \rangle = E, \quad (1.65)$$

where

$$\langle \psi | \hat{H} | \psi \rangle = \int d\tau \psi^* \hat{H} \psi \quad (1.66)$$

and  $\langle \psi | \psi \rangle = 1$ . Defining the number  $\bar{T}$  and  $\bar{V}$  as

$$\bar{T} = \langle \psi | \hat{T} | \psi \rangle = \int d\tau \psi^*(r) \left[ -\frac{\hbar^2}{2m} \nabla^2 \right] \psi(r) \quad (1.67)$$

and

$$\bar{V} = \langle \psi | \hat{V} | \psi \rangle = \int d\tau \psi^*(r) V(r) \psi(r), \quad (1.68)$$

we see that the total quantum mechanical energy  $E$  can be written as a sum of quantities  $E = \bar{T} + \bar{V}$  interpreted as a kinetic energy ( $\bar{T}$ ) and potential energy ( $\bar{V}$ )

The quantity (1.68) can be rewritten as

$$V = \int d\tau(r) \rho(r) V(r), \quad (1.69)$$

Figure 1.4:

where

$$\rho(r) = \psi^*(r)\psi(r) \quad (1.70)$$

is the probability of finding the system in the volume element  $d\tau$  near configuration  $r$ . 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 equation (1.22),  $\bar{T}$  does not seem to bear much relation to the classical kinetic energy. However, in Section 1.6.2 we show that

$$\langle\psi| -\nabla^2|\psi\rangle = \langle|\nabla\psi|^2\rangle, \quad (1.71)$$

so that equation(1.67) becomes

$$\bar{T} = \frac{\hbar^2}{2m}\langle|\nabla\psi|^2\rangle = \frac{1}{2m}\langle\left|\frac{\hbar}{i}\nabla\psi\right|^2\rangle. \quad (1.72)$$

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

$$\bar{T} = \frac{1}{2m}\langle|\hat{p}\psi|^2\rangle, \quad (1.73)$$

which can be compared with the classical kinetic energy,

$$T^{cl} = \frac{1}{2m}p^2, \quad (1.74)$$

suggesting that  $\langle|\hat{p}\psi|^2\rangle$  corresponds to the square of the classical momentum. Throughout this course, we will find equation (1.72) 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 Figure 1.4, all normalized, we see immediately that  $\psi_c$  has the highest  $\bar{T}$ , which  $\psi_a$  has the lowest. Of course, equation (1.72) assumes that  $\langle\psi|\psi\rangle = 1$ .

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.

### 1.3 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

$$E = \frac{p^2}{2m} - \frac{Ze^2}{r}, \quad (1.75)$$

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  $E = -\infty$ . That is, the classical  $H$  atom collapses to a point.

Quantum mechanically, the Hamiltonian is

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{r}, \quad (1.76)$$

and the energy is obtained by solving the Schrödinger equation,

$$\hat{H}\psi(\mathbf{r}) = E\psi(\mathbf{r}). \quad (1.77)$$

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  $\psi(r)$  for the ground state of  $H$  atoms. The result is that

$$\psi(r, \theta, \varphi) = N_0 e^{-\zeta r}, \quad (1.78)$$

where

$$N_0 = \sqrt{\frac{\zeta^3}{\pi}} \quad (1.79)$$

$$\zeta = \frac{Z}{a_0} \quad (1.80)$$

$$E = -\frac{1}{2}Z^2 \left[ \frac{e^2}{a_0} \right] \quad (1.81)$$

$$a_0 = \frac{\hbar^2}{me^2} \quad (1.82)$$

Later, we define atomic units where  $\hbar = 1$ ,  $m = 1$ , and  $|e| = 1$ . In these units, the unit of length is

$$1 \text{ bohr} = 1 a_0 = \frac{\hbar^2}{me^2} = 0.529177 \text{\AA}, \quad (1.83)$$

and the unit of energy is

$$1 \text{ Hartree} = 1 h_0 = \frac{e^2}{a_0} = \frac{me^4}{\hbar^2} = 27.2116 \text{ eV} = 627.510 \text{ kcal/mol}. \quad (1.84)$$

In these units, the Hamiltonian for  $H$  atom becomes

$$\hat{H} = -\frac{1}{2}\nabla^2 - \frac{Z}{r}, \quad (1.85)$$

the energy becomes

$$E = -\frac{1}{2}Z^2, \quad (1.86)$$

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.

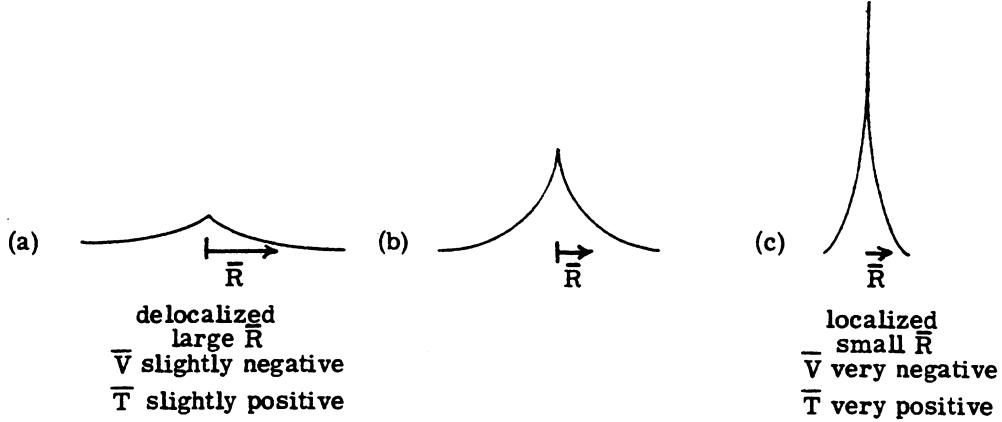


Figure 1.5: Comparison of wavefunctions with different scales.

### 1.3.1 Atoms Exist!

In the last section, we found that the classical description of the atom leads to collapse,

$$T = \frac{1}{2m} p^2 \rightarrow 0 \quad (1.87)$$

as  $p \rightarrow 0$ , and

$$V = -\frac{e^2}{r} \rightarrow -\infty \quad (1.88)$$

as  $r \rightarrow 0$ . 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,

$$\bar{V} = \langle \psi | -\frac{e^2}{r} | \psi \rangle \quad (1.89)$$

$$\bar{T} = \frac{\hbar^2}{2m} \langle [\nabla \psi]^2 \rangle. \quad (1.90)$$

Consider now the sequence of similar wavefunctions in Figure 1.5. To be specific, consider the normalized function

$$\psi = N e^{-\frac{r}{R}}, \quad (1.91)$$

where  $N = 1/\sqrt{\pi R^3}$ . Thus, if  $R$  is very large,  $\psi$  decreases very slowly with  $r$ , leading to the delocalized function  $a$  in Figure 1.5(a), while with very small  $R$ ,  $\psi$  decreases rapidly to zero for small  $r$ , leading to the localized function in Figure 1.5(c).

$$\langle \psi^2 \rangle = \int_0^\pi \sin \theta d\theta \int_{-\pi}^\pi d\varphi \int_0^\infty \psi^2 r^2 dr = 4\pi N^2 \int_0^\infty r^2 dr e^{-2(\frac{r}{R})}$$

$$= 4\pi N^2 \left[ \frac{\bar{R}}{2} \right]^3 \int_0^\infty \rho^2 d\rho e^{-\rho} = \pi N^2 \bar{R}^3 = 1. \quad (1.92)$$

where we used

$$\int_0^\infty \rho^m e^{-\rho} d\rho = m!. \quad (1.93)$$

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

$$\langle \Phi | \frac{1}{r} | \Phi \rangle = \frac{1}{\bar{R}}, \quad (1.94)$$

leading to

$$\bar{V} = -\frac{e^2}{\bar{R}}. \quad (1.95)$$

Consider now, some wavefunction, say  $b$ , in Figure 1.5 as the reference wavefunction, with  $\bar{R} = 1$  in some units, and let  $\bar{V}_1$  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. The technical term is scaled.

From equation (1.95) we see that

$$\bar{V}_{\bar{R}} = \langle \Phi_{\bar{R}} | \frac{1}{r} | \Phi_{\bar{R}} \rangle = \frac{1}{\bar{R}} V_1. \quad (1.96)$$

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

$$\left\langle \left[ \frac{\partial \Phi}{\partial x} \right] \right\rangle^2, \quad (1.97)$$

so that

$$\bar{T}_{\bar{R}} \propto \left[ \frac{1}{\bar{R}} \right]^2. \quad (1.98)$$

Basically, the gradient is proportional to  $1/\bar{R}$ , and hence, the gradient squared is proportional to  $[1/\bar{R}]^2$ . 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 equations (1.96) and (1.98), we see that

$$\frac{\bar{T}_{\bar{R}}}{\bar{V}_{\bar{R}}} = \left[ \frac{1}{\bar{R}} \right] \frac{\bar{T}_1}{\bar{V}_1} \quad (1.99)$$

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

Consider first, the case as  $\bar{R} \rightarrow \infty$ , then from equations (1.96) and (1.98)  $\bar{T} \rightarrow 0$ ,  $\bar{V} \rightarrow 0$ , and  $\bar{E} = \bar{T} + \bar{V} \rightarrow 0$ , as expected. For sufficiently large  $\bar{R}$ , that is,

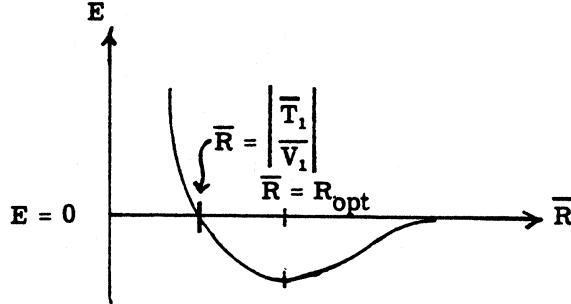


Figure 1.6: H atom is stable in quantum mechanics.

$\bar{R} \gg |\bar{T}_1/\bar{V}_1|$ , we see from equation (1.99) 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 equation (1.99) that  $|\bar{T}| \gg |\bar{V}|$ , and hence, the total energy must be positive. Thus, the energy of the wavefunctions in Figure 1.5 must behave, as in Figure 1.6, 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.

In the above example, we consider just the stretching and compression of the one function considered in Figure 1.5. 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, Figure 1.5(a), 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 diffused wavefunctions, potential energy always wins. We are assuming here, Coulombic attractions. 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.

### 1.3.2 The Ground State Wavefunction

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

$$H\psi(\mathbf{r}) = E\psi(r), \quad (1.100)$$

where

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{r}. \quad (1.101)$$

The Hamiltonian in equation (1.101) is independent of orientation of the atom in space, and hence, the eigenfunctions will have the form

$$f(r)Z(\theta, \varphi), \quad (1.102)$$

where  $f$  is a function of  $r$  only, and  $Z(\theta, \varphi)$  is a function of angular coordinates only. Since kinetic energy favors having smooth wavefunctions, the ground state wavefunction should be as devoid of wiggles as possible. Thus, we will take  $Z(\theta, \varphi)$  as a constant leading to

$$-\frac{\hbar^2}{2m}\nabla^2 f(r) + \frac{Ze^2}{r}f(r) = Ef(r) \quad (1.103)$$

for the Schrödinger equation.

There are straightforward mathematical techniques for solving equation (1.103). For example, see Section 1.6.4. Here we will use a physically oriented approach to examine some features of the solutions. At  $r = \infty$ , the potential in equation (1.101) is zero, thus, the bound states of equation (1.100) have negative energy,  $E < 0$ . Now consider a very large  $r$  so that the Coulomb term is negligible,

$$\frac{Ze^2}{r} \ll |E|. \quad (1.104)$$

In this case, the Schrödinger equation reduces to

$$-\frac{\hbar^2}{2m}\nabla^2 f(r) = Ef(r) \quad (1.105)$$

or

$$\nabla^2 f(r) = +\zeta^2 f(r), \quad (1.106)$$

where

$$\zeta^2 = -\frac{2m}{\hbar^2}E \quad (1.107)$$

note that  $E$  is negative and, hence,  $\zeta$  is real. Consider a point along the positive  $x$  axis. Since  $r$  is very large,

$$\left(\frac{\partial f}{\partial y}\right) \approx 0 \quad (1.108)$$

and

$$\left(\frac{\partial f}{\partial x}\right) \approx 0. \quad (1.109)$$

Thus, equation (1.106) becomes

$$+\frac{\partial^2 f}{\partial x^2} = \zeta^2 f. \quad (1.110)$$

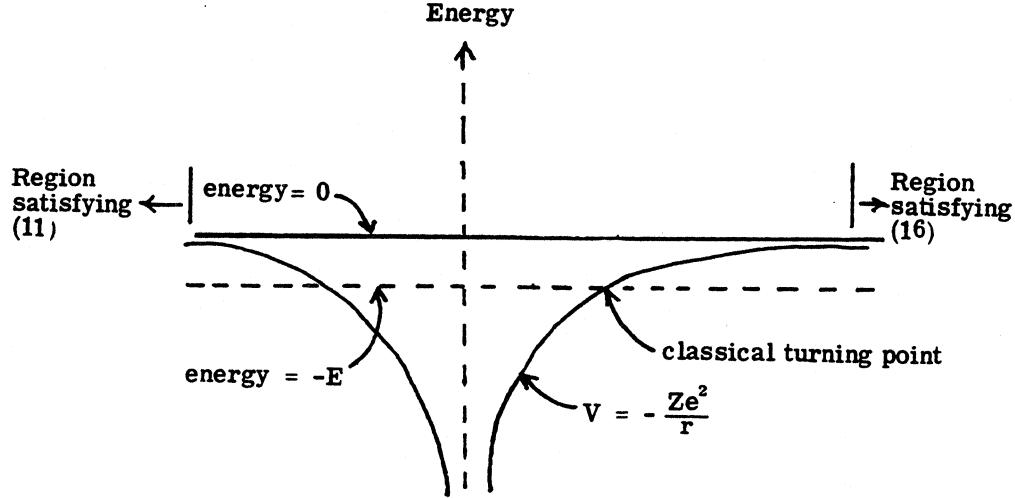


Figure 1.7:  $H$  potential with classical turning points.

Consequently,  $f = e^{-\zeta r}$ , where this 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

$$f(r) = e^{-\zeta r}. \quad (1.111)$$

In Section 1.6.4, we show that the wavefunction (1.111) is an eigenfunction of equation (1.103) for all  $r$  if  $\zeta$  is chosen so that

$$\zeta = \frac{Z}{a_0}, \quad (1.112)$$

where

$$a_0 = \frac{\hbar^2}{me^2}. \quad (1.113)$$

From equations (1.107) and (1.112), we have

$$E = -\frac{\hbar^2}{2m}\zeta^2 = -\frac{\hbar^2}{2m} \frac{Z^2}{a_0^2} = -\frac{1}{2} \frac{Z^2 e^2}{a_0}, \quad (1.114)$$

and hence,

$$E = -\frac{1}{2} Z^2 \left[ \frac{e^2}{a_0} \right]. \quad (1.115)$$

Normalizing the wavefunction (1.111) leads to, see Section 1.6.4

$$\psi(r, \theta, \varphi) = N_0 e^{-\frac{Zr}{a_0}}, \quad (1.116)$$

where

$$N_0 = \sqrt{\frac{Z^3}{\pi a_0^3}}. \quad (1.117)$$

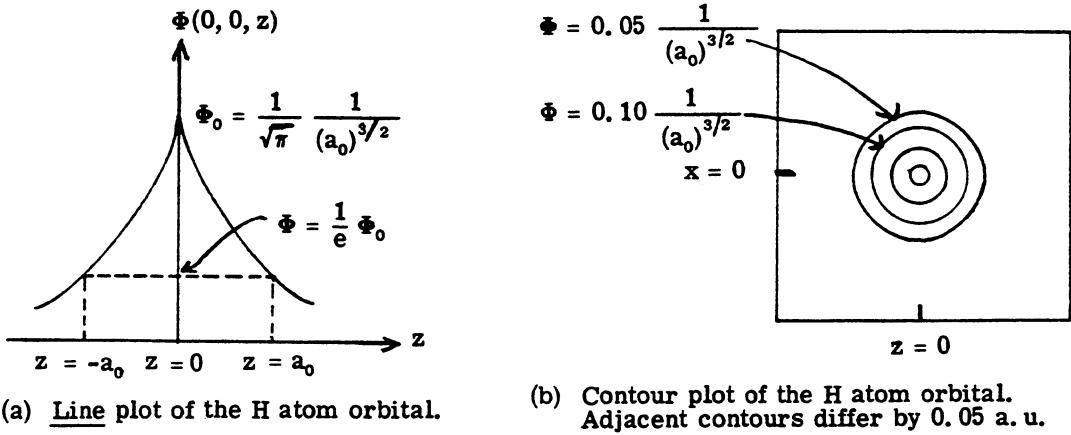


Figure 1.8: Line (a) and contour (b) plots of the  $H$  atom orbital; in (b), the adjacent contours differ by 0.05 a.u.

This wavefunction is plotted in Figure 1.8.

The average radius of the wavefunction (1.113) is

$$\frac{1}{R} = \langle \psi | \frac{1}{r} | \psi \rangle = \frac{Z}{a_0}, \quad (1.118)$$

so that

$$\bar{R} = \frac{a_0}{Z}, \quad (1.119)$$

where  $a_0 = \hbar^2/m e^2$  is referred to as the Bohr radius, or more simply, the Bohr, in honor of Niels Bohr. Substituting into equation (1.112) leads to

$$E = -\frac{1}{2} \frac{Ze^2}{\bar{R}}, \quad (1.120)$$

which can be compared with

$$\bar{V} = \langle \psi | -\frac{Ze^2}{r} | \psi \rangle = -\frac{Ze^2}{\bar{R}}. \quad (1.121)$$

Thus,

$$E = \frac{1}{2} \bar{V} \quad (1.122)$$

and

$$\bar{T} = E - \bar{V} = -\frac{1}{2} \bar{V} = \frac{1}{2} \frac{Ze^2}{\bar{R}}. \quad (1.123)$$

Equation (1.120) provides an easy way to remember the proper energy expression, it is just half the total potential energy.

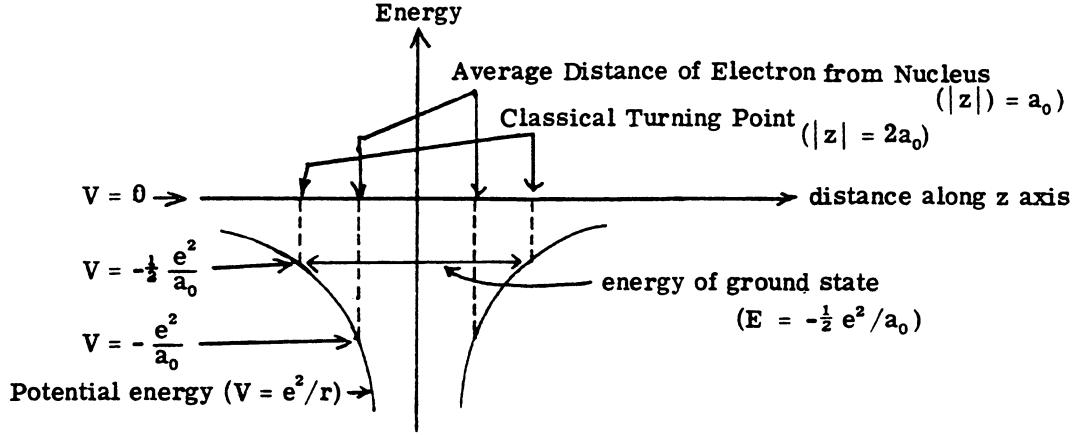


Figure 1.9: The potential energy as a function of distance.

For the hydrogen atom,  $Z = 1$ , the above equations become

$$E = -\frac{1}{2} \frac{e^2}{a_0} \quad (1.124)$$

$$\bar{V} = -\frac{e^2}{a_0} \quad (1.125)$$

$$\bar{T} = +\frac{1}{2} \frac{e^2}{a_0} = +\frac{\hbar^2}{2m} \frac{1}{a_0^2}, \quad (1.126)$$

where

$$\left\langle \frac{1}{r} \right\rangle = \frac{1}{a_0} \quad (1.127)$$

$$\langle [\nabla \varphi]^2 \rangle = \frac{1}{a_0^2}. \quad (1.128)$$

Imagining a classical particle with this same energy  $E$  moving in the potential

$$V(r) = -\left(\frac{e^2}{r}\right), \quad (1.129)$$

we would find the particle bouncing back and forth from  $z = -2a_0$  to  $z = +2a_0$ . The kinetic energy is

$$T = E - V = E + \frac{e^2}{r} = -\frac{e^2}{2a_0} + \frac{e^2}{r}. \quad (1.130)$$

For  $r > 2a_0$ , we would have  $T < 0$ , but this is not possible, classically, since  $T = 1/2mv^2$  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 (1.116) is positive for all finite  $x$ ,  $y$ , and  $z$ . Since it is never zero for finite distances, we say that the wavefunction is nodeless.

### 1.3.3 Atomic Units

As mentioned, the size of the atom is

$$\bar{R} = \frac{a_0}{Z}, \quad (1.131)$$

thus, a natural unit of length for atomic problems is the Bohr radius

$$a_0 = \frac{\hbar^2}{me^2}. \quad (1.132)$$

The quantity

$$\frac{e^2}{a_0} = \frac{me^4}{\hbar^2} \quad (1.133)$$

in the energy expression, equation (1.120) 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,<sup>3</sup> and is denoted as  $h_0$ ,

$$h_0 = \frac{e^2}{a_0} = \frac{me^4}{\hbar^2} \quad (1.134)$$

so that the energy of the hydrogen atom (1.116) becomes

$$E = -\frac{1}{2}Z^2h_0. \quad (1.135)$$

Throughout this course, we will encounter quantities such as  $a_0 = \hbar/me^2$  corresponding to a length,

$$h_0 = \frac{e^2}{a_0} = \frac{me^4}{\hbar^2} \quad (1.136)$$

corresponding to an energy, and dimensionless quantities such as

$$\alpha = \frac{e^2}{\hbar c} = \frac{1}{137.03604} \quad (1.137)$$

the fine structure constant.

We will find it convenient to use a particular set of units, called atomic units, where  $\hbar = 1$ ,  $m_e = 1$ , and  $|e| = 1$ . Atomic units are sometimes called Hartree atomic units to distinguish them from other occasionally used atomic units, see Section 1.6.5.

We use the above unit 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 are include in Section 1.6.6.

With atomic units, the Hamiltonian for the hydrogen atom becomes

$$H = -\frac{1}{2}\nabla^2 - \frac{Z}{r} \quad (1.138)$$

and the ground state wavefunction becomes

$$\psi(r, \theta, \varphi) = N_0 e^{-Zr}, \quad (1.139)$$

where

$$N_0 = \sqrt{\frac{Z^3}{\pi}} \quad (1.140)$$

and the ground state energy becomes

$$E = -\frac{1}{2}Z^2. \quad (1.141)$$

### 1.3.4 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 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 equation (1.139) the ionization potential of the ground state of hydrogen atom is

$$\text{IP}_H = \frac{1}{2} \left( \frac{e^2}{a_0} \right). \quad (1.142)$$

In atomic units, this quantity is

$$\text{IP}_H = 0.5 h_0, \quad (1.143)$$

and experimentally, it is known that

$$\text{IP}_H = 13.605805(37) \text{ eV}. \quad (1.144)$$

This is corrected to correspond to a nucleus of infinite mass. Thus,

$$1h_0 = \frac{e^2}{a_0} = 27.21161 \text{ eV}. \quad (1.145)$$

Similarly, using the known values of  $\hbar$ ,  $m$ , and  $e$

$$\hbar = 1.0545887(56) \times 10^{-27} \text{ gm cm}^2 \text{ sec}^{-1} \quad (1.146)$$

$$m_e = 9.109534(47) \times 10^{-28} \text{ gm} \quad (1.147)$$

$$e = 4.803242(14) \times 10^{-10} \text{ gm}^{\frac{1}{2}} \text{ cm}^{\frac{3}{2}} \text{ sec}^{-1}, \quad (1.148)$$

we find that the atomic unit of length is

$$1a_0 = \frac{\hbar^2}{me^2} = 0.52917704(44) \text{ \AA}. \quad (1.149)$$

Another useful relation is the fine structure constant

$$\alpha = \frac{e^2}{\hbar c} = \frac{1}{137.03604(11)}, \quad (1.150)$$

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

$$c = 137.03604 \text{ a.u.} \quad (1.151)$$

in atomic units. From the cgs value of  $c$ ,

$$c = 2.99792458(l) \times 10^{10} \text{ cm/sec} \quad (1.152)$$

we find the atomic unit of time, denoted as  $\tau_0$ ,

$$\tau_0 = 2.41888 \times 10^{-17} \text{ sec.} \quad (1.153)$$

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

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

$$R = \frac{10}{0.529177} = 18.897 a_0. \quad (1.154)$$

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

$$E = \frac{1}{R} = -0.052918 h_0. \quad (1.155)$$

We can now convert back to electron volts,

$$E = -0.052917 \times 27.2116 = -1.43998 \text{ eV.} \quad (1.156)$$

In general, then

$$E(\text{eV}) = \frac{-14.3998}{R(A)}. \quad (1.157)$$

It would be instructive to calculate other quantities in terms of atomic units. For example, 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?

## 1.4 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.

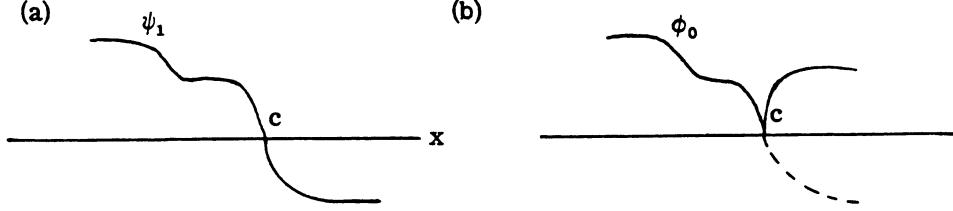


Figure 1.10: Illustration of the nodal theorem.

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

$$H = -\frac{1}{2M} \frac{d^2}{dx^2} + V(x), \quad (1.158)$$

where  $M = m/\hbar^2$  and  $V(x)$  is some function of  $x$  depending only upon the spatial coordinates.  $V(x)$  is independent of momentum and spin, and is not an integral operator. If this potential contains bound states, then we can prove the nodal theorem. First, the ground state wavefunction does not change sign, i.e., has no nodes. Secondly, 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,

$$E_0 < E_n \quad (1.159)$$

$$E_n < E_{n+1} \quad (1.160)$$

where  $n$  is the number of nodal points, internal to the boundaries. In the case of a sufficiently singular potential, some inequalities in equation (1.160) may be equalities.

The nodal theorem is proven, see Section 1.6.3. Here we will provide some intuitive reasoning concerning this theorem.

#### 1.4.1 The Ground State is Nodeless

Consider first  $\psi_1$ , the lowest eigenstate of the Hamiltonian

$$\hat{H}\psi_1 = E_1\psi_1 \quad (1.161)$$

having one sign change as in Figure 1.10(a). From  $\psi_1$  we can form a wavefunction  $\varphi_0 = |\psi_1|$ , not necessarily an eigenfunction of  $\hat{H}$ , that has no sign changes, as in Figure 1.10(b). Since  $\psi_1$  is normalized, then  $\varphi_0$  is also normalized,

$$\langle \varphi_0 | \varphi_0 \rangle = \int dx |\varphi_0(x)|^2 = \int dx |\psi_1(x)|^2 = 1, \quad (1.162)$$

and the energy of  $\varphi_0$  becomes

$$\epsilon_0 = \langle \varphi_0 | H | \varphi_0 \rangle = \langle \varphi_0 | -\frac{1}{2M} \frac{d^2}{dx^2} | \varphi_0 \rangle + \langle \varphi_0 | V | \varphi_0 \rangle. \quad (1.163)$$

The potential energy of  $\varphi_0$  is the same as that of  $\psi_1$ ,

$$\begin{aligned}\langle \varphi_0 | V | \varphi_0 \rangle &= \int dx V(x) |\varphi_0(x)|^2 \\ &= \int dx V(x) |\psi_1(x)|^2 \\ &= \langle \psi_1 | V | \psi_1 \rangle.\end{aligned}\quad (1.164)$$

From Section 1.6.2, the kinetic energy of  $\psi_1$  can be expressed as

$$\begin{aligned}\langle \psi_1 | -\frac{1}{2m} \frac{d^2}{dx^2} | \psi_1 \rangle &= \frac{1}{2M} \langle |\Delta \psi_1|^2 \rangle \\ &= \frac{1}{2M} \int_{-\infty}^{+\infty} dx \left| \frac{d\psi_1}{dx} \right|^2\end{aligned}\quad (1.165)$$

But

$$\frac{1}{2} \int_{-\infty}^{-\infty} dx \left| \frac{d\psi_1}{dx} \right|^2 = \frac{1}{2} \int_{-\infty}^{-\infty} dx \left| \frac{d\varphi_0}{dx} \right|^2\quad (1.166)$$

since the integrands are equal except at one point,  $x_0$ . Thus, the kinetic energies of  $\varphi_0$  and  $\psi_1$  are equal,

$$\langle \psi_1 | -\frac{1}{2M} \frac{d^2}{dx^2} | \psi_1 \rangle = \langle \varphi_0 | -\frac{1}{2M} \frac{d^2}{dx^2} | \varphi_0 \rangle,\quad (1.167)$$

and consequently from equations (1.164) and (1.167) the total energies of  $\psi_1$  and  $\varphi_0$  are equal,

$$\epsilon_0 = \langle \varphi_0 | H | \varphi_0 \rangle = \langle \psi_1 | H | \psi_1 \rangle = E_1.\quad (1.168)$$

That is, given any eigenfunction  $\psi_1$  of  $f\hat{H}$  that changes sign, we can construct a function  $\varphi_0$  which does not change sign and yet has the same energy.

Now consider a new function  $\bar{\varphi}_0$  identical to  $\varphi_0$  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  $\varphi_0$ ,

$$\langle \bar{\varphi}_0 | V | \bar{\varphi}_0 \rangle = \langle \varphi_0 | V | \varphi_0 \rangle.\quad (1.169)$$

However, since

$$\left| \frac{d\bar{\varphi}_0}{dx} \right| \ll \left| \frac{d\varphi_0}{dx} \right|\quad (1.170)$$

in the region near  $c$ ,  $\varphi'_0$  will have a smaller kinetic energy than  $\varphi_0$ ,

$$\frac{1}{2M} \langle \left| \frac{d\bar{\varphi}_0}{dx} \right|^2 \rangle < \frac{1}{2M} \langle \left| \frac{d\varphi_0}{dx} \right|^2 \rangle.\quad (1.171)$$

Consequently, the energy of  $\bar{\varphi}_0$  is lower than that of  $\varphi_0$

$$\bar{\epsilon}_0 < \epsilon_0 = E_1.\quad (1.172)$$

The best, i.e., lowest energy, nodeless, i.e. non-negative, wavefunction has an energy,  $E_0$ , no higher than  $\bar{\epsilon}_0$ , and hence,  $E_0 < E_1$ . 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 Figure 1.12.

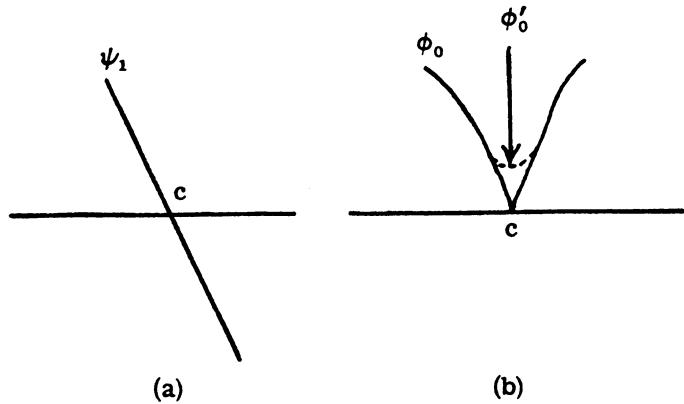


Figure 1.11:

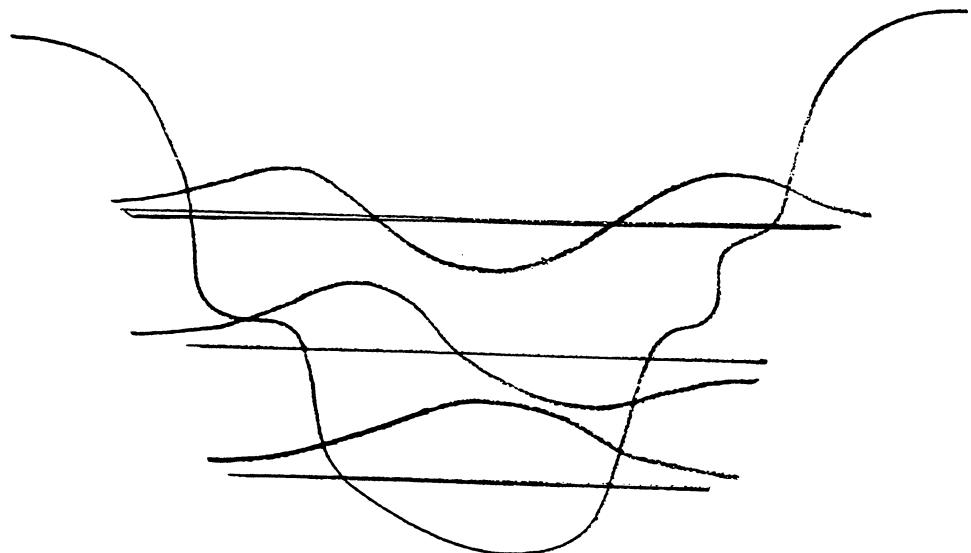


Figure 1.12: The nodal patterns of successive states of a general (one-dimensional) potential.

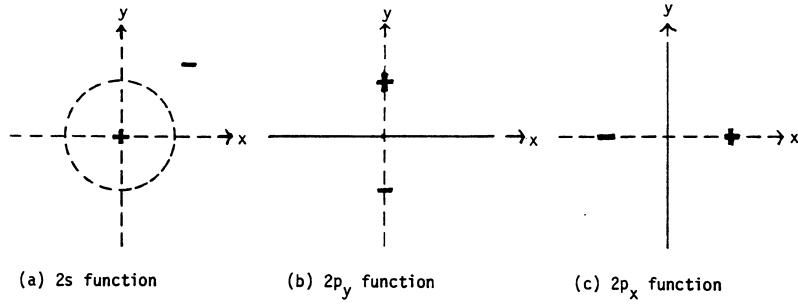


Figure 1.13:

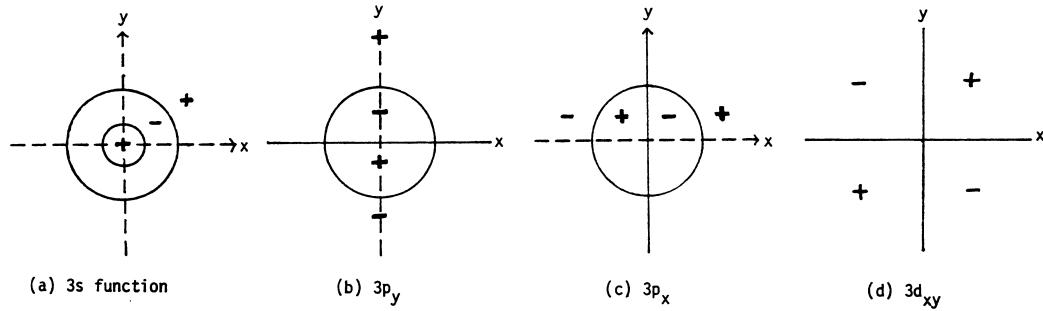


Figure 1.14: Two-Dimensional states with two nodal lines.

### 1.4.2 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. In this section, we will use the same notation  $nl$  as for states of the three-dimensional  $H$  atom. 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 dimension we can construct three orthogonal wavefunctions, all orthogonal to the ground nodeless state, each with one nodal surface, as illustrated in Figure 1.13.

If the potential energy is independent of angle, the wavefunctions in Figure 1.13(b) and 1.13(c) will have the same energy. However, the wavefunction in Figure 1.13(a) 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 Figure 1.14(a) is above, or below, the 2p functions of Figure 1.13(b) and 1.13(c).

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 Figure ???, and change the sign

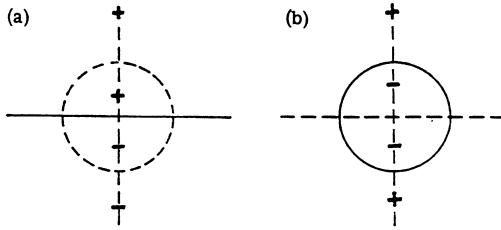


Figure 1.15:

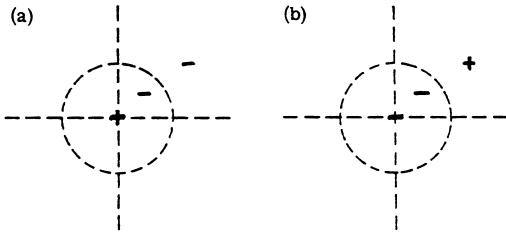


Figure 1.16:

on opposite sides of a single nodal surface to obtain either Figure 1.15(a) or 1.15(b) by the same argument used in equations 1.169–1.172. The new wavefunctions in Figure 1.15(a) and Figure 1.15(b) must have exactly the same energy as Figure 1.14(c).

The wavefunction in Figure 1.15(a) is an upper bound on the  $2p_y$  wavefunction of Figure 1.13(b). The wavefunction in Figure 1.15(b) is an upper bound on the  $2s$  wavefunction of Figure 1.13(a).

Similarly, starting with the  $3s$  wavefunction of Figure 1.14(a), we see that the wavefunctions in Figure 1.16 have the same energy and are upper bounds to the  $2s$  wavefunctions of Figure 1.13(a). 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,

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

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

$$2s < 3p\dots$$

$$3s < 4p\dots$$

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

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

etc.

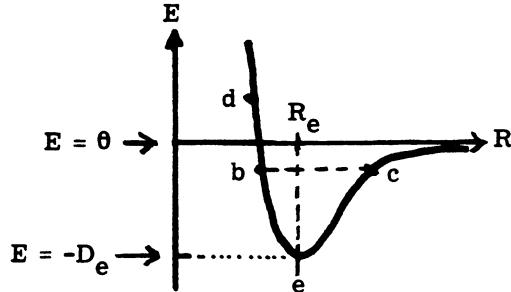


Figure 1.17:

## 1.5 Vibration and Rotation

Throughout this course, we will focus upon the electronic wavefunctions for molecules. Thus, for an  $N$  electronic wavefunction, we determine  $\Psi^{el}(1, 2, \dots, N)$ , with energy

$$E = \frac{\langle \Psi^{el} | H | \Psi^{el} \rangle}{\langle \Psi^{cl} | \Psi^{el} \rangle}, \quad (1.173)$$

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 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 until point  $b$ , and would continue oscillating between these points, assuming no friction. Starting at point  $d$ , the  $R$  would continue increasing until  $R = \infty$ . 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 shown in 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

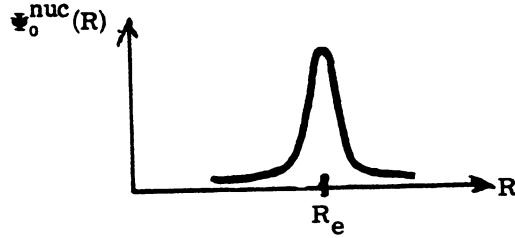


Figure 1.18:

energy. This lowest state, Figure 1.18, is referred to as the ground vibrational state,  $\Phi^{vib}$ , with  $v = 0$ , and one thinks of the molecule as vibrating back and forth with a frequency  $\nu_0$ .

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

$$E(R) = E(R_e) + \frac{1}{2}k(R - R_e)^2, \quad (1.174)$$

where  $k$ , the curvature at the bottom of the well, is called the force constant

$$k = \left[ \frac{\partial^2 E}{\partial R^2} \right]_{R_e}. \quad (1.175)$$

In this approximation, called the harmonic oscillator approximation, the vibrational frequency is given by

$$\nu_0 = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}, \quad (1.176)$$

where  $\mu$  is the reduced mass

$$\mu = \frac{M_1 M_2}{M_1 + M_2} \quad (1.177)$$

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

$$\frac{1}{2}\hbar\nu_0 \quad (1.178)$$

where  $\hbar$  is Planck's constant. Thus, the energy of the ground vibrational state is  $E = -D_0$ , where

$$D_0 = D_e - \frac{1}{2}\hbar\nu_0. \quad (1.179)$$

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

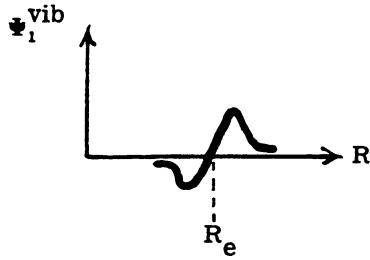


Figure 1.19:

In quantum mechanics, the excited vibrational wavefunctions must be orthogonal to the ground wavefunction, leading to the form in Figure 1.19, for the first excited vibrational state,  $v = 1$ . The excitation energy is

$$E_1 - E_0 = h\nu_0, \quad (1.180)$$

in the harmonic approximation. The separations between vibrational states, as in equation (1.180), can be determined experimentally, thereby providing experimental values for the zero-point energy (1.178), 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 orientation 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

$$E_{rot} = \frac{\hbar^2}{2I} J(J+1), \quad (1.181)$$

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

$$E_{rot}^{cl} = \frac{1}{2I} L^2, \quad (1.182)$$

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  $h\nu_0 = 4401 \text{ cm}^{-1} = 12.58 \text{ kcal/mol}$  for  $H_2$ , and  $h\nu_0 = 2322 \text{ cm}^{-1} = 0.288 \text{ eV} = 6.64 \text{ kcal/mol}$  for  $H_2^+$ , and the rotational energies are  $E_j = BJ(J+1)$ , where  $B = 60.85 \text{ cm}^{-1}$  for  $H_2$ , and  $B = 30.21 \text{ cm}^{-1}$  for  $H_2^+$ . In these systems, the total bond energies are  $D_0 = 36117 \text{ cm}^{-1} = 4.478 \text{ eV} = 103.3 \text{ kcal/mol}$  for  $H_2$ , and  $D_0 = 21382 \text{ cm}^{-1} = 2.651 \text{ eV} = 61.1 \text{ kcal/mol}$  for  $H_2^+$ .

## 1.6 Appendices

### 1.6.1 Hermitian Operators

In Section 1.2, we found that the basic postulate of quantum mechanics implies that the wavefunction  $\psi$  is normalized

$$\langle \psi | \psi \rangle = 1 \quad (1.183)$$

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

$$i\hbar \frac{\partial \psi}{\partial t} = H\psi. \quad (1.184)$$

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

$$\langle \psi_j | H^\dagger | \psi_k \rangle = \langle (H\psi_j) | \psi_k \rangle = \langle \psi_j | H | \psi_k \rangle \quad (1.185)$$

for all allowed functions  $\psi_j$  and  $\psi_k$ . This property results from the requirement that the total integrated probability (1.183) not change with time for any superposition of allowed functions.

#### Notation

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

$$B_{jk} = \langle \psi_j | \hat{B} | \psi_k \rangle = \int d\tau \psi_j^* (\hat{B} \psi_k). \quad (1.186)$$

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

$$(B^\dagger)_{jk} = \langle \psi_j | \hat{B}^\dagger | \psi_k \rangle = \int d\tau (\hat{B} \psi_j)^* \psi_k = \langle (\hat{B} \psi_j) | \psi_k \rangle \quad (1.187)$$

for all  $\psi_j$  and  $\psi_k$ , of the Hilbert space. From equation (1.186) we see that

$$\langle (\hat{B} \psi_j) | \psi_k \rangle = \langle \psi_k | \hat{B} \psi_j \rangle^* = B_{ij}^*, \quad (1.188)$$

and hence, equation (1.187) can be written

$$(B^\dagger)_{jk} = B_{kj}^*. \quad (1.189)$$

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

$$\langle \psi_j | \hat{B}^\dagger | \psi_k \rangle = \langle \psi_i | B | \psi_k \rangle, \quad (1.190)$$

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

$$\hat{B}^\dagger = \hat{B}. \quad (1.191)$$

### Hermitivity of $\hat{H}$

From equation (1.183) the total probability of finding the partial somewhere,  $\langle \psi | \psi \rangle = 1$ , is independent of time. Thus, taking the derivative with respect to time, we have

$$0 = \left\langle \frac{\partial \psi}{\partial t} | \psi \right\rangle + \left\langle \psi | \frac{\partial \psi}{\partial t} \right\rangle = \int d\tau \left[ \frac{\partial \psi^*}{\partial t} \psi + \psi^* \frac{\partial \psi}{\partial t} \right]. \quad (1.192)$$

Substituting the Schrödinger equation (1.184) here, leads to

$$0 = (i\hbar)^{-1} \int d\tau [(-H\psi)^* \psi + \psi^*(\psi)] \quad (1.193)$$

or

$$0 = \{-\langle \psi | H | \psi \rangle^* + \langle \psi | H | \psi \rangle\}, \quad (1.194)$$

which implies that the quantity  $E \equiv \langle \psi | H | \psi \rangle$ , referred to as the energy, is real.

Consider, now, the superposition

$$\psi = C_j \psi_j + C_k \psi_k \quad (1.195)$$

where  $C_j$  and  $C_k$  are numbers, possibly complex, of two states  $\psi_j$  and  $\psi_k$  that are orthogonal

$$\langle \psi_j | \psi_k \rangle = 0 \quad (1.196)$$

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

$$C_k^* C_j \langle \psi_k | \psi_j \rangle + C_j^* C_k \langle \psi_j | \psi_k \rangle = \langle \psi | \psi \rangle - C_j^* C_j \langle \psi_j | \psi_j \rangle - C_k^* C_k \langle \psi_k | \psi_k \rangle \quad (1.197)$$

is also independent of time. Simiarly, considering

$$\psi' = iC_j \psi_j + C_k \psi_k \quad (1.198)$$

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

$$iC_k^* C_j \langle \psi_k | \psi_j \rangle - iC_j^* C_k \langle \psi_j | \psi_k \rangle \quad (1.199)$$

also be independent of time. Combining equations (1.197)and (1.199), leads to the condition that

$$\langle \psi_j | \psi_k \rangle = 0 \quad (1.200)$$

is independent of time. This leads to

$$0 = \left\langle \frac{\partial \psi_j}{\partial t} | \psi_k \right\rangle + \left\langle \psi_j | \frac{\partial \psi_k}{\partial t} \right\rangle = i\hbar \left[ -\langle \psi_j | \hat{H}^\dagger | \psi_k \rangle + \langle \psi_j | \hat{H} | \psi_k \rangle \right], \quad (1.201)$$

and hence

$$\langle \psi_j | \hat{H} \psi_k \rangle = \langle \psi_j | \hat{H}^\dagger | \psi_k \rangle \quad (1.202)$$

which also applies to  $j = k$ . The relation (1.202) must apply to all possible pairs of functions  $\psi_j$  and  $\psi_k$ , 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.

## 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

$$\hat{p} = \frac{\hbar}{i} \frac{d}{dx} \quad (1.203)$$

Hermitian? To find out, we consider

$$\langle \psi_j | \hat{p}^\dagger | \psi_k \rangle = -\frac{\hbar}{i} [\psi_j^*(a)\psi_k(a) - \psi_j^*(0)\psi_k(0)] + \frac{\hbar}{i} \int_0^a dx \psi_j^* \frac{d\psi_k}{dx} \quad (1.204)$$

or

$$\langle \psi_j | \hat{p}^\dagger | \psi_k \rangle = -\frac{\hbar}{i} [\psi_j^*(a)\psi_k(a) - \psi_j^*(0)\psi_k(0)] + \langle \psi_j | \hat{p} | \psi_k \rangle \quad (1.205)$$

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

$$\psi_j^*(a)\psi_k(a) = \psi_j^*(0)\psi_k(0) \quad (1.206)$$

for all allowed functions  $\psi_j$  and  $\psi_k$ . Thus, it is nonsense to say the

$$\hat{p} = \frac{\hbar}{i} \frac{d}{dx} \quad (1.207)$$

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, first that  $\psi(A) = 0$  and  $\psi(0) = 0$  which is the case of a particle in a box. Secondly,  $\psi(a) = \psi(0)$  which corresponds to periodic boundary conditions here the point  $x = a$  is physically equivalent to the point  $x = 0$ . A common example is for angular coordinate  $\varphi$  where  $a = 2\pi$  is identically the same point as  $x = 0$ . And finally, for systems of infinite range  $-\infty < x < +\infty$ , then for  $\varphi$  to be normalized,  $\langle \varphi | \varphi \rangle = 1$ , it must be that  $\varphi \rightarrow 0$  as  $x \rightarrow \pm\infty$ , leading to  $\varphi_j^*(a)\varphi_k(a) \rightarrow 0$  as  $a \rightarrow \pm\infty$ .

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

$$T = \frac{1}{2m} \hat{p}^2 \quad (1.208)$$

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

$$\langle (\hat{p}_x \hat{p}_x \psi_j) | \psi_k \rangle = \langle (\hat{p}_x \psi_j) | \hat{p}_x | \psi_k \rangle = \langle \psi_j | \hat{p}_x \hat{p}_x \psi_k \rangle. \quad (1.209)$$

### 1.6.2 The Kinetic Energy

In this section, we will show that the matrix element

$$t_{ab} = \langle \varphi_a | -\frac{1}{2} \nabla^2 | \varphi_b \rangle \quad (1.210)$$

can be written as

$$t_{ab} = \frac{1}{2} \langle \nabla \varphi_a \cdot \nabla \varphi_b \rangle, \quad (1.211)$$

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

$$t_{aa} = \frac{1}{2} \langle |\nabla \varphi_a|^2 \rangle \quad (1.212)$$

in atomic units, or

$$t_{aa} = \frac{\hbar^2}{2m} \langle |\nabla \varphi_a|^2 \rangle \quad (1.213)$$

in other units.

Consider first the integral

$$\langle \varphi_a | \frac{\partial^2}{\partial x^2} | \varphi_b \rangle - \int \int \int_{-\infty}^{+\infty} dx dy dx \varphi_a^* \frac{\partial^2 \varphi_b}{\partial x^2}. \quad (1.214)$$

Integrating by parts, this becomes

$$Q(x = +\infty) - Q(x = -\infty) - \int \int \int_{-\infty}^{+\infty} dx dy dz \frac{\partial \varphi_a^*}{\partial x} \frac{\partial \varphi_b}{\partial x}, \quad (1.215)$$

where

$$Q = \int \int_{-\infty}^{+\infty} dy dz \varphi_a^* \frac{\partial \varphi_b}{\partial x} \quad (1.216)$$

this is referred to as Green's theorem. However, for  $\varphi_a$  and  $\varphi_b$  to satisfy the basic postulates of quantum mechanics, we must have  $\langle \varphi_a | \varphi_a \rangle = 1$ ,  $\langle \varphi_b | \varphi_b \rangle = 1$ , and hence  $\varphi_a \rightarrow 0$  as  $x \rightarrow \pm\infty$ . Thus,  $Q(x = +\infty) = 0$  and  $Q(x = -\infty) = 0$  we obtain

$$\langle \varphi_a | \frac{\partial^2}{\partial x^2} | \varphi_b \rangle = - \langle \frac{\partial \varphi_a}{\partial x} | \frac{\partial \varphi_b}{\partial x} \rangle. \quad (1.217)$$

Proceeding similarly for the other terms of equation (1.210), we obtain

$$t_{ab} = \frac{1}{2} \int d\tau [\nabla \varphi_a^* \nabla \varphi_b] \equiv \frac{1}{2} \langle \nabla \varphi_a \cdot \nabla \varphi_b \rangle, \quad (1.218)$$

and letting  $\varphi_a = \varphi_b$ , leads to equations (1.212)–(1.213).

### 1.6.3 The Nodal Theorem

In this section, we consider the eigenfunctions  $\varphi_n$  for a general one-dimensional system,  $H\varphi_n = E_n\varphi_n$ , where

$$H = -\frac{1}{2M} \frac{d^2}{dx^2} + V(x) \quad (1.219)$$

is real, so that the eigenfunctions are real, and

$$M = \frac{m}{\hbar^2}. \quad (1.220)$$

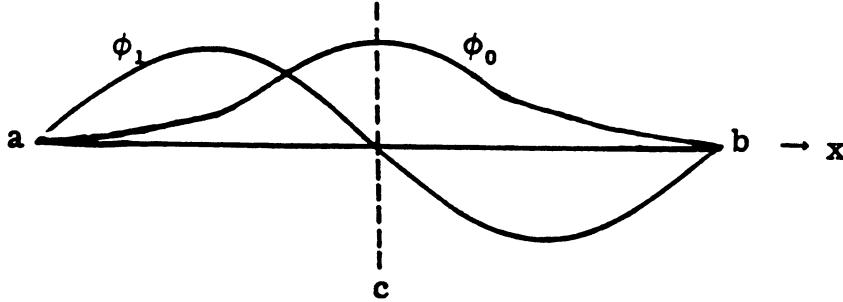


Figure 1.20:  $\varphi_0$  and  $\varphi_1$  Nodal Theorem Proof.

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

$$E_0 < E_n \quad (1.221)$$

and

$$E_n < E_{n+1}. \quad (1.222)$$

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 equations (1.221) and (1.222) become equalities.

### The Inequalities

Consider first the functions  $\varphi_0$  and  $\varphi_1$ , which are the eigenstates of  $\hat{H}$ ,

$$\begin{aligned} \hat{H}\varphi_0 &= (\hat{T} + \hat{V})\varphi_0 = E_0\varphi_0 \\ \hat{H}\varphi_1 &= (\hat{T} + \hat{V})\varphi_1 = E_1\varphi_1, \end{aligned} \quad (1.223)$$

with zero and one node, respectively, as in Figure 1.20. Here  $a$  and  $b$  are the boundaries of the system, they may be at  $\pm\infty$ , and zeroes at the boundaries are not counted.

First we will show that  $E_1 \geq E_0$ . Letting  $c$  be the location of the node in  $\varphi_1$ , we consider the region

$$a < x < c \quad (1.224)$$

so that both  $\varphi_0$  and  $\varphi_1$  are positive. Then from equation (1.223) we have

$$E_0 = V + \frac{1}{\varphi_0} \hat{T}\varphi_0 \quad (1.225)$$

and

$$E_1 = V + \frac{1}{\varphi_1} \hat{T}\varphi_1 \quad (1.226)$$

for all points in region (1.224). Thus, the energy difference is given by

$$E_1 - E_0 = +\frac{1}{\varphi_1} \hat{T}\varphi_1 - \frac{1}{\varphi_0} \hat{T}\varphi_0 = \frac{1}{\varphi_1\varphi_0} [\varphi_0 (\hat{T}\varphi_1) - \varphi_1 (\hat{T}\varphi_0)]. \quad (1.227)$$

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

$$\int_a^b dx [\varphi_0 (\hat{T}\varphi_1) - \varphi_1 (\hat{T}\varphi_0)] = \langle \varphi_0 | \hat{T} | \varphi_1 \rangle - \langle \hat{T} \varphi_0 | \varphi_1 \rangle = 0. \quad (1.228)$$

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 equation (1.227), we multiply by  $\varphi_1\varphi_0$ , then integrate from  $a$  to  $c$ , and then divide appropriately to obtain

$$(E_1 - E_0) = \frac{B}{A}, \quad (1.229)$$

where

$$B = \int_a^c dx \varphi_0 \hat{T} \varphi_1 - \int_a^c dx \varphi_1 \hat{T} \varphi_0 \quad (1.230)$$

and

$$A = \int_a^c dx \varphi_1 \varphi_0. \quad (1.231)$$

Integrating by parts, the first term of equation (1.230) becomes

$$\begin{aligned} \int_a^c dx \varphi_0 \hat{T} \varphi_1 &= \frac{1}{2M} \int_a^c dx \varphi_0 \left[ \frac{\partial^2 \varphi_1}{\partial x^2} \right] \\ &= \left\{ +\frac{1}{2M} \int_a^c dx \left[ \frac{\partial \varphi_0}{\partial x} \right] \left[ \frac{\partial \varphi_1}{\partial x} \right] \right\} - \left\{ \left[ \frac{1}{2M} \varphi_0 \left( \frac{\partial \varphi_1}{\partial x} \right) \right]_a^c \right\} \\ &= \left\{ -\frac{1}{2M} \int_a^c dx \frac{\partial^2 \varphi_0}{\partial x^2} \varphi_1 \right\} + \frac{1}{2M} \left\{ \left[ \left( \frac{\partial \varphi_0}{\partial x} \right) \varphi_1 - \varphi_0 \left( \frac{\partial \varphi_1}{\partial x} \right) \right]_a^c \right\}. \end{aligned} \quad (1.232)$$

Combining equations (1.229) through (1.232), we obtain

$$(E_1 - E_0) = \frac{1}{2M} \left[ \varphi_1 \left( \frac{\partial \varphi_0}{\partial x} \right) - \left( \frac{\partial \varphi_1}{\partial x} \right) \varphi_0 \right]_a^c. \quad (1.233)$$

Since  $\varphi_1(c) = 0$ ,  $\varphi_0(c) > 0$ ,

$$\left( \frac{\partial \varphi_1}{\partial x} \right)_{x=c} < 0 \quad (1.234)$$

and

$$A = \int_a^c dx \varphi_1^* \varphi_0 > 0, \quad (1.235)$$

we obtain

$$E_1 - E_0 = -\frac{1}{2A} \varphi_0(c) \left( \frac{\partial \varphi_1}{\partial x} \right)_{x=c} > 0, \quad (1.236)$$

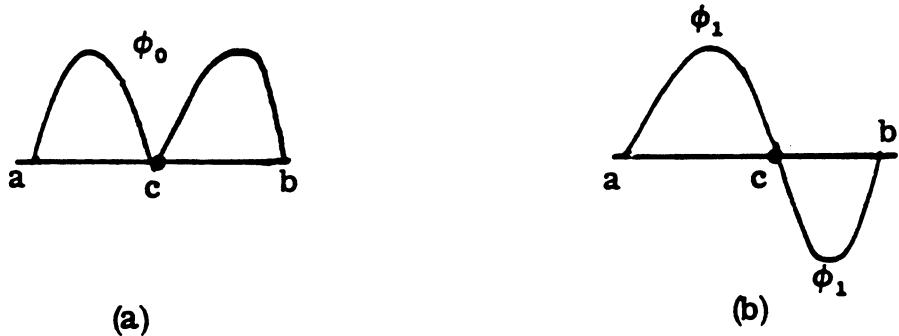


Figure 1.21:

that is,

$$E_1 - E_0 > 0. \quad (1.237)$$

Thus, the nodeless wavefunction has a lower energy than the wavefunction with one node. The same proof shows that  $\varphi_0$  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

$$E_{n+1} > E_n, \quad (1.238)$$

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

### Singular Potentials

To obtain equation (1.237) we assumed in equation (1.236) that

$$\varphi_0(c) \neq 0 \quad (1.239)$$

and that

$$\left( \frac{\partial \varphi_1}{\partial x} \right)_{x=c} \neq 0. \quad (1.240)$$

Usually these conditions (1.239)–(1.240) are satisfied. However, there can be cases where the potential is such that one of the quantities in (1.239)–(1.240) is zero. In this case, we have  $E_1 - E_0 = 0$ , and hence, the general condition (1.237) should be  $E_1 \geq E_0$ , and (1.238) should be  $E_{n+1} \geq E_n$ .

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  $\varphi_0$  and  $\varphi_1$  in Figure 1.20 will have the shapes in Figure 1.21.

From this figure, the first two solutions for a potential, sufficiently singular at point  $c$ , are shown.

From equation (1.236), this leads to  $E_1 = E_0 = 0$ , so that  $E_0$  and  $E_1$  are degenerate. In this case, the functions  $\varphi_0$  and  $\varphi_1$  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  $\varphi_0$  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 1.9(a), 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,  $E_{n+1} = E_n$ .

### A Singular Example

As discussed above, the equal sign in (1.221) would occur when the potential  $V(x)$  is sufficiently singular, that the best non-negative wavefunction  $\varphi_0$  has a node at some point. For example, if

$$V(x) = \frac{1}{|x - x_0|}, \quad (1.241)$$

the potential energy is

$$\langle \varphi(x) | V(x) | \varphi(x) \rangle = \int_{-\infty}^{x_0} dx \frac{|\varphi(x)|^2}{|x - x_0|} + \int_{x_0}^{\infty} dx \frac{|\varphi(x)|^2}{|x - x_0|}. \quad (1.242)$$

Expanding

$$\varphi(x) = \varphi(x_0) + (x - x_0)\varphi'(x_0) + \dots \quad (1.243)$$

we see that the dominant term in the integral

$$\int_{\infty}^{x_0} dx \frac{\varphi(x)^2}{|x - x_0|} \quad (1.244)$$

is

$$\varphi(x_0)^2 \int_{\infty}^{x_0} \frac{dx}{(x - x_0)} = \varphi(x_0)^2 \ln 0 \quad (1.245)$$

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

Thus, for  $\varphi$  to yield an  $E < \infty$ , and hence to describe the ground state, it must be that  $\varphi(x) \rightarrow 0$  as  $x \rightarrow 0$ . In this case,  $E_0 = E_1$ , assuming no other singularities in  $V(x)$ .

### 1.6.4 The Ground State of Hydrogen Atom

In summary, the ground state of the hydrogen-like atom, with nuclear charge  $Z$ , has the wavefunction

$$\psi(r, \nu, \varphi) = N_0 e^{-\frac{Zr}{a_0}}, \quad (1.246)$$

where

$$N_0 = \sqrt{\frac{Z^3}{\pi a_0^3}} \quad (1.247)$$

and

$$a_0 = \frac{\hbar}{me^2} \quad (1.248)$$

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

$$E = -\frac{1}{2}Z^2 \left[ \frac{e^2}{a_0} \right] = -\frac{1}{2} \frac{Ze^2}{\bar{R}}, \quad (1.249)$$

where

$$\bar{R} = \frac{a_0}{A} \quad (1.250)$$

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

### Solution of the Schrödinger Equation

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

$$\left[ -\frac{\hbar^2}{2m} \nabla^2 - \frac{Ze^2}{r} \right] \psi(r, \theta, \varphi) = E\psi(r, \theta, \varphi). \quad (1.251)$$

Since the potential term is independent of angle, the wavefunction has the form

$$\psi(r, \theta, \varphi) = f(r)Z(\theta, \varphi), \quad (1.252)$$

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

$$Z(\theta, \varphi) = \frac{1}{\sqrt{4\pi}}. \quad (1.253)$$

The normalization condition is

$$\int_0^{2\pi} d\varphi \int_0^\pi \sin \theta d\theta [Z(\theta, \varphi)]^2 = 1, \quad (1.254)$$

leading to equation (1.253). Thus, our chore is to solve

$$-\frac{\hbar^2}{2m} \nabla^2 f(r) - \frac{Ze^2}{r} f(r) = Ef(r). \quad (1.255)$$

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

$$z = r \cos \theta, \quad (1.256)$$

$$x = r \sin \theta \cos \varphi, \quad (1.257)$$

$$y = r \sin \theta \sin \varphi, \quad (1.258)$$

and

$$r^2 = x^2 + y^2 + z^2. \quad (1.259)$$

Since

$$\left[ \frac{\partial r}{\partial z} \right]_{x,y} = \frac{\partial}{\partial z} \sqrt{x^2 + y^2 + z^2} = \frac{z}{r} \quad (1.260)$$

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

$$\left[ \frac{\partial}{\partial z} f(r) \right]_{x,y} = \left[ \frac{\partial r}{\partial z} \right]_{x,y} \left[ \frac{\partial f}{\partial r} \right] = \frac{z}{r} f'(r). \quad (1.261)$$

Thus, letting

$$f''(r) = \frac{d^2 f}{dr^2} \quad (1.262)$$

and

$$f'(r) = \frac{df}{dr}, \quad (1.263)$$

we obtain

$$\begin{aligned} \frac{\partial^2}{\partial z^2} f(r) &= \frac{\partial}{\partial z} \left[ \frac{z}{r} f'(r) \right] = \frac{1}{r} f'(r) + z \frac{\partial x}{\partial r} \frac{\partial}{\partial r} \left[ \frac{1}{r} f'(r) \right] \\ &= \frac{1}{r} f'(r) + \frac{z^2}{r} \left[ \frac{1}{r} f''(r) - \frac{1}{r^2} f'(r) \right] \\ &= \left[ \frac{1}{r} - \frac{z^2}{r^3} \right] f'(r) + \frac{z^2}{r^2} f''(r). \end{aligned} \quad (1.264)$$

Combining with  $\partial^2/\partial x^2 f(r)$  and  $\partial^2/\partial y^2 f(r)$  leads, then, to

$$\nabla^2 f(r) = f''(r) + \frac{2}{r} f'(r) \quad (1.265)$$

Substituting equation (1.265) into equation (1.255), leads to

$$-\frac{\hbar^2}{2m} \left[ \frac{d^2 f}{dr^2} + \frac{2}{r} \frac{df}{dr} \right] - \frac{Ze^2}{r} f(r) = Ef(r) \quad (1.266)$$

as the Schrödinger equation. Since the potential in equation (1.251) goes to zero as  $r \rightarrow \infty$ , only the state with  $E < 0$  are bound, and hence we take  $E < 0$ . Consider now a sufficiently larger  $r$  that

$$\left| \frac{Ze^2}{r} \right| \ll |E| \quad (1.267)$$

and

$$\frac{2}{r} \left| \frac{df}{dr} \right| \ll \left| \frac{d^2 f}{dr^2} \right|. \quad (1.268)$$

In this case, equation (1.266) reduces to

$$\frac{d^2 f}{dr^2} = \zeta^2 f(r), \quad (1.269)$$

where

$$\zeta^2 = -\frac{2mE}{\hbar^2} \geq 0. \quad (1.270)$$

The solution of equation (1.269) is

$$f(r) = e^{-\zeta r}. \quad (1.271)$$

Thus, all bound state solutions of equation (1.270) must necessarily go to zero exponentially. Note that in the limit of very large  $r$ , the function  $r^n e^{-\zeta r}$  would also satisfy equation (1.266).

Consider now the substitution of the exponential function (1.271) into the Schrödinger equation (1.266),

$$\frac{d^2 f}{dr^2} + \frac{2}{r} \frac{df}{dr} - \zeta^2 f(r) = -\frac{2mZe^2}{\hbar^2} \frac{1}{r} f(r). \quad (1.272)$$

From equation (1.269) the first term of each side, the long-range terms, cancel at all  $r$  leaving

$$\frac{2}{r} \frac{df}{dr} = -\frac{2\zeta}{r} f(r) = -\frac{2mZe^2}{\hbar^2} \frac{1}{r} f(r). \quad (1.273)$$

Thus, the exponential function (1.271) is an eigenfunction of the Schrödinger equation if

$$\zeta = \frac{mZe^2}{\hbar^2}. \quad (1.274)$$

Since  $\zeta$  has the units of inverse length, e.g., see equation (1.270), it is convenient to consider the length quantity  $a_0 = \hbar/me^2$ , referred to as the Bohr radius or simply the Bohr, as the fundamental atomic length leading to  $\zeta = Z/a_0$ . From equation (1.269) the value of  $\zeta$  is related also to the energy,

$$E = -\frac{\hbar^2}{2m} \zeta^2. \quad (1.275)$$

Thus,

$$E = -\left[ \frac{\hbar^2}{2m} \right] \frac{Z^2}{a_0^2} = -\frac{1}{2} Z^2 \left[ \frac{e^2}{a_0} \right]. \quad (1.276)$$

Summarizing, we find that the wavefunction

$$\psi_0(r, \theta, \varphi) = f(r) = N_0 e^{-\frac{Zr}{a_0}}, \quad (1.277)$$

is an eigenfunction of the Schrödinger equation with an energy of

$$E_0 = -\frac{1}{2} Z^2 \left[ \frac{e^2}{a_0} \right], \quad (1.278)$$

where  $a_0 = \hbar^2/m e^2$ . Since the wavefunction (1.277) 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 (1.277), the average value of  $1/r$  is

$$\frac{1}{\bar{H}} = \langle \psi | \frac{1}{r} | \psi \rangle = \frac{Z}{a_0}. \quad (1.279)$$

Thus, the average potential energy is

$$\bar{V} = \langle \psi | -\frac{Ze^2}{r} | \psi \rangle = -\frac{Ze^2}{r} = -\frac{Z^2 e^2}{a_0} \quad (1.280)$$

and the total energy can be written as

$$E = \frac{1}{2} \bar{V} = -\frac{1}{2} \frac{Ze^2}{R} = -\frac{1}{2} \frac{Z^2 e^2}{a_0} \quad (1.281)$$

In order to normalize the wavefunction (1.277), note that

$$\langle \psi | \psi \rangle = \int_0^\infty r^2 dr \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\varphi [f(r)]^2 = 4\pi \int_z^\infty r^2 dr f(r)^2, \quad (1.282)$$

where the angular integral is

$$\int d\Omega = \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\varphi = 4\pi. \quad (1.283)$$

Since

$$\int_0^\infty r^2 dr f(r)^2 = N_0^2 \int_0^\infty r^2 dr e^{-2\zeta r} = \frac{N_0^2}{(2\zeta)^3} \int_0^\infty \rho^2 d\rho e^{-\rho} = \frac{N_0^2}{(2\zeta)^3} 2!, \quad (1.284)$$

we see that

$$N_0 = \sqrt{\frac{\zeta^3}{\pi}} = \sqrt{\frac{Z^3}{\pi a_0^3}}. \quad (1.285)$$

### Analysis of the Wavefunction

A plot of the orbital along the  $z$  axis is given in Figure 1.22. Note that the slope of 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.

In Figure 1.22, the ground state wavefunction,  $\psi_0$ , for the  $H$  atom, plotted along the  $z$  axis, is illustrated.

The Schrödinger equation (1.253) says that  $Ef(r)$  is equal to

$$-\frac{\hbar^2}{2m} \nabla^2 f(r) - \frac{Ze^2}{r} f(r) \quad (1.286)$$

for every point  $r$ . But, as  $r \rightarrow 0$ , the term

$$-\frac{Ze^2}{r} f(r) \quad (1.287)$$

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

$$-\frac{\hbar^2}{2m} \nabla^2 f(r) \quad (1.288)$$

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

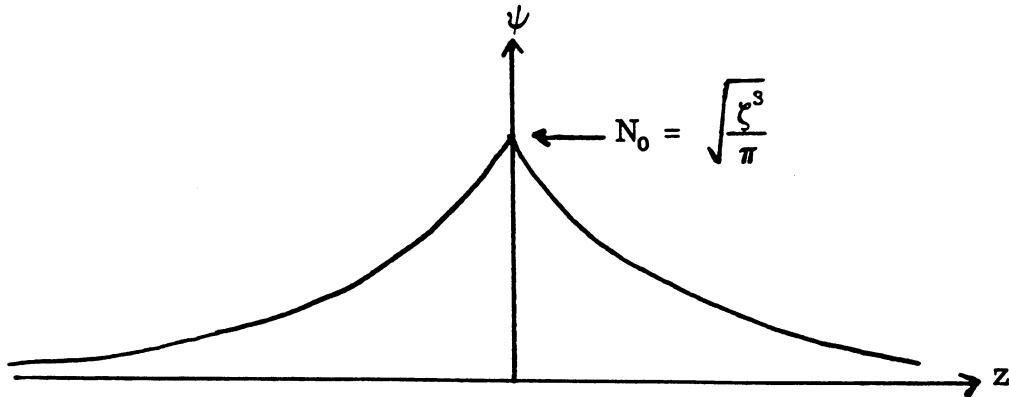


Figure 1.22:

### 1.6.5 Rydberg Atomic Units

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

$$R_\infty = \frac{me^4}{2\hbar^2}. \quad (1.289)$$

This quantity is called the Rydberg and is related to the Hartree by one Rydberg equal to one-half Hartree. With this choice for the unit of energy,  $me^4/2\hbar^2 = 1$ , we cannot use the convenient sets of units in the text. 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,  $(\hbar^2/2m)/k^2$  simply becomes  $k^2$ . Also, some workers reporting band calculations on solids use Rydberg units. The series of books by Slater also used these units. However, the regular atomic units, or Hartree atomic units, as described in the text, are more convenient and more common, and we will always use them.

### 1.6.6 Units and Conversion Factors

#### International System of Units

In an effort to bring some order to the proliferation of units that continues to occur in the sciences, an international group in 1960, adopted what is referred to as the International System of Units, or may be called 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 some 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

$$\frac{\text{mass} \times \text{length}}{\text{time}^2}, \quad (1.290)$$

and it is convenient to define the unit of force, Newton's, as one Newton equal to  $1 \text{ kg m sec}^{-2}$ . Similarly, a constant force  $F$  exerted over a distance  $\ell$  does an amount of work  $W$ , so that the unit of energy, joule, is one joule equal to one newton meter equal to one  $\text{kg m}^2 \text{ sec}^{-2}$ .

Some commonly derived units, in the International System of Units, are:

Unit	Abbreviation	Definition in Fundamental Unit Terms	Physical Quantity
liter	$\ell$	$10^{-3} \text{ m}^3$	volume
newton	N	$\text{mkgsec}^{-2}$	force
joule	J	$N\text{m} = \text{m}^2 \text{ kgsec}^{-2}$	energy
watt	W	$\text{Jsec}^{-1} = \text{m}^2 \text{ kgsec}^{-2}$	power
pascal	Pa	$\text{Nm}^{-2} = \text{m}^{-1} \text{ kgsec}^{-2}$	pressure
coulomb	C	$\text{A sec}$	electric charge
volt	V	$WA^{-1} = \text{m}^2 \text{ kgsec}^{-2} \text{ A}^{-1}$	electric potential
ohm	$\Omega$	$VA^{-1} = \text{m}^2 \text{ kgsec}^{-3} \text{ A}^{-2}$	electrical resistance
hertz	Hz	$\text{sec}^{-1}$	frequency

The acceptable multiples, or fractions, to be used for the basic International Systems of Units are designed by the following prefixes:

Fraction	Prefix	Symbol Quantity
$10^{-18}$	atto	a
$10^{-15}$	femto	f
$10^{-12}$	pico	p
$10^{-9}$	nano	n
$10^{-6}$	micro $\mu$	
$10^{-3}$	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. Some examples include:

Physical Quantity	Abbreviation	Definition in SI Units
Charge on an Electron	e	$1.602189 \times 10^{-19} \text{ C}$
Atmospheric Pressure	atm	101.325 Pa

For the atmospheric pressure, this is at sea level.

Other units are not necessarily superior to the International System of Unit quantities, but their use is so widespread that scientists must be facile with their use. Some examples include:

1. Kilocalorie, the original definition was the energy to heat 1 kg of H<sub>2</sub>O by a temperature of 1°K, at 15°C. Abbreviated as kcal, and its relation to fundamental units is 1 kcal = 4.18 kJ, defined to be exact.
2. Angstrom, abbreviated as Å, and its relation to fundamental units is  $1 \text{ \AA} = 10^{-10} \text{ m} = 10^{-3} \text{ cm}$ .
3. Electron volt, defined as the energy change upon moving a charge of one electron through an electric potential of one volt. Abbreviated as eV, and its relations to fundamental units as  $1 \text{ eV} = 96.483 \text{ kJ mol}^{-1}$ .

### Units for Coulomb's Law

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

$$F_{tot} = \frac{Q_1 Q_2}{R^2} \quad (1.291)$$

where  $F_{tot}$  is the total force. Hence, the energy of interaction is

$$E = \int_{-\infty}^R F \cdot dr = \frac{Q_1 Q_2}{R}. \quad (1.292)$$

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

$$\text{Force(dynes)} = \frac{[Q(\text{esu})]^2}{[R(\text{cm})]^2} \quad (1.293)$$

and

$$\text{Energy(ergs)} = \frac{[Q(\text{esu})]^2}{R(\text{cm})}. \quad (1.294)$$

In the International System of Units, the unit of charge, the Coulomb, is defined in terms of a current, one ampere is equal to one Coulomb/sec. Also the units of current are related to force and distance through a different force law, magnetic induction. The relation between Coulombs and esu, turns out to be

$$1 \text{ Coulomb} = \frac{1 \text{ esu}}{(2.99810^9)}, \quad (1.295)$$

where the 2.998 comes from the speed of light,  $2.998 \cdot 10^8$  m/sec. Since

$$\text{Force(newtons)} = 10^{-5} \text{ Force(dynes)} \quad (1.296)$$

and

$$R(\text{meters}) = 10^{-2} R(\text{cm}), \quad (1.297)$$

the Coulomb law becomes

$$\text{Force(newtons)} = [8.98810^9] \frac{[Q(\text{Coulomb})]^2}{[R(\text{m})]^2} \quad (1.298)$$

and

$$\text{Energy(joules)} = [8.98810^9] \frac{[Q(\text{Coulomb})]^2}{[R(\text{cm})]}. \quad (1.299)$$

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

$$8.988 \times 10^9 = \frac{1}{4\pi\epsilon_0}, \quad (1.300)$$

where

$$\epsilon_0 = 8.85410^{-12} \text{ C}^2\text{N}^{-1}\text{m}^{-2} \quad (1.301)$$

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

$$\text{Energy(N)} = \frac{Q_1(\text{C})Q_2(\text{C})}{4\pi\epsilon_0 R(\text{m})} \quad (1.302)$$

for the Coulomb energy.

In this case, the  $Q_1$  and  $Q_2$  are always some multiple of the fundamental charge on a proton, or electron,

$$1 e = 1.60210^{-19} \text{ C} \quad (1.303)$$

and

$$1 e = 4.80310^{-10} \text{ esu.} \quad (1.304)$$

Thus, we will write

$$Q_1 = q_1 e \quad (1.305)$$

$$Q_2 = q_2 e \quad (1.306)$$

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

$$R = r a_0, \quad (1.307)$$

where  $r$  has no units. In this case, the Coulomb energy becomes

$$E = \frac{q_1 q_2}{r} \left[ \frac{e^2}{a_0} \right] \quad (1.308)$$

where no  $4\pi\epsilon_0$  factor is included. In equation (1.308), the unit of energy is

$$1 h_0 = 1 \text{ hartree} = \frac{e^2}{a_0} \quad (1.309)$$

and

$$1 h_0 = 27.2116 \text{ eV} = 2625.5 \text{ kJ/mol} = 627.51 \text{ kcal/mol.} \quad (1.310)$$

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 equations (1.305)–(1.306) and (1.307), calculate the energy using (1.308) and then to convert from atomic units to SI units using equations (1.309) –(1.310).

For example, calculate the interaction of two protons at a distance of  $R = 5 \text{ \AA}$ . The answer is

$$R = 5 \text{ \AA} = \frac{5}{0.529} a_0 = 9.45 a_0 \quad (1.311)$$

$$E(h_0) = \frac{1}{R(a_0)} = \frac{1}{9.45} = 0.1058 h_0 \quad (1.312)$$

both equal to  $2.88 \text{ eV} = 278 \text{ kJ/mole} = 66.4 \text{ kcal/mol}$ .

Useful conversion factors here, are

$$e^2 = 14.3998 eV \text{ \AA} = 332.059 (\text{kcal/mol}) \text{\AA}. \quad (1.313)$$

## 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.,  $^{12}\text{C}$ , as having a mass of 12.0000. In these units, the mass of the hydrogen atom is 1.00783 amu, the mass of a proton is 1.00728 amu, and the mass of an electron is 1/18.22.89 amu. Thus, in atomic units, hartree, the mass of the proton is

$$1.00728 \times 1822.89 = 1836.16. \quad (1.314)$$

The conversion to SI units is

$$1 \text{ amu} = 1.660566 \times 10^{-27} \text{ kg}. \quad (1.315)$$

## Energy Quantities for Photons

The wavelength,  $\lambda$ , and frequency,  $\nu$ , of light are related by the speed of light,  $c$ ,  $\lambda\nu = c$ . Thus, since  $c = 2.99792458 \times 10^{10} \text{ cm/sec}$ , the frequency for yellow light,  $\lambda = 600 \text{ nm}$ , is

$$\nu = \frac{3 \times 10^{10}}{6 \times 10^{-7}} = 5 \times 10^{16} \text{ Hz} \quad (1.316)$$

where one Hz is equal to one cycle per second, and the wavelength for KZLA,  $\nu = 94 \text{ MHz}$ , is

$$\lambda = \frac{3 \times 10^{10}}{94 \times 10^6} = 319 \text{ cm} = 3.19 \text{ m}. \quad (1.317)$$

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

$$E = h\nu = \frac{hc}{\lambda} = hc\bar{\nu} \quad (1.318)$$

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

$$E(\text{eV}) = \frac{1239.85}{\lambda(\text{nm})} = 8065.480\bar{\nu} (\text{cm}^{-1}) \quad (1.319)$$

and

$$\bar{\nu}(\text{cm}^{-1}) = \frac{10^7}{\lambda(\text{nm})} \quad (1.320)$$

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

## 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

$$1 \text{ eV} = 36.7490 \text{ mh} = 23.0604 \text{ kcal} = 96.4847 \text{ kJpm} = 8065.48 \text{ cm}^{-1}, \quad (1.321)$$

and

$$1 \text{ mh} = 0.27212 \text{ eV} = 0.627511 \text{ kcal} = 2.62550 \text{ kJpm} = 219.475 \text{ cm}^{-1}. \quad (1.322)$$

The average thermal energy of an oscillator, at room temperature, is

$$kT = \frac{1}{40} \text{ eV} = 1 \text{ mh} = 0.6 \text{ kcal} = 200 \text{ cm}^{-1} = 2.4 \text{ kJpm}. \quad (1.323)$$

The strength of the  $\text{H}_2^+$  bond is

$$2.5 \text{ eV} = 92 \text{ mh} = 58 \text{ kcal} = 24l \text{ kJpm}. \quad (1.324)$$

The vibrational energy  $\hbar\omega_e$  of  $\text{H}_2^+$  is

$$3000 \text{ cm}^{-1} = 14 \text{ mh} = 8.6 \text{ kcal} = 0.37 \text{ eV} = 36 \text{ kJpm}. \quad (1.325)$$

## 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

$$\begin{aligned} 1 \left( \frac{\text{eV}}{\text{atom}} \right) & \times 1.60218921 \times 10^{-22} \left( \frac{\text{kJ}}{\text{eV}} \right) \times \frac{1\text{kcal}}{4.184\text{kJ}} \times 6.022045 \times 10^{23} \left( \frac{\text{atoms}}{\text{mol}} \right) \\ & = 23.06036 \text{ kcal/mol}. \end{aligned} \quad (1.326)$$

Therefore,

$$1 \frac{\text{eV}}{\text{atom}} = 23.06036 \text{ kcal/mol}. \quad (1.327)$$

For force constants, we use the following

$$k = M\omega^2 = \frac{\text{mass}}{\text{time}^2} = \frac{\text{Energy}}{\text{length}^2} \quad (1.328)$$

$$\begin{aligned} 1au = \frac{h}{a_0^2} & = \frac{27.21161 \times 1.6021892 \times 10^{-12} \text{ erg}}{(0.52917706 \times 10^{-8} \text{ cm})^2} \\ & = 1.556919 \times 10^6 \frac{\text{dyne}}{\text{cm}} \\ & = 15.56919 \frac{\text{mdyne}}{\text{\AA}}. \end{aligned} \quad (1.329)$$

## Conversion Factors

Included herein, are the fundamental constants as of 1973 [?]. Commonly used constants are as follows. A number in parentheses indicates the standard deviation in the error for the last quoted digit.

1. 1 bohr = 0.5291771(4) Å.
2. 1 hartree = 27.21161(7) eV.
3. 1 hartree = 627.5096(4) kcal/mol = 219474.7 cm<sup>-1</sup>.
4. 1 eV = 23.06036(14) kcal/mol = 96.483 kJ/mol.
5. 1 eV = 8065.48(2) cm<sup>-1</sup>.
6. 1 eV = 1239.852(3)/λ(nm).
7. 1 kcal 4.18400 kJ = 349.755 cm<sup>-1</sup>.
8. 1 amu 1822.887(l)  $m_e$  for atomic masses. This is used to convert atomic masses to hartree atomic units, mass <sup>12</sup>C = 12.000.
9. 1 au = 15.56919 mdyne/Å for force constant.
10. For gas constant, R = 98719(7) cal mol<sup>-1</sup>K<sup>-1</sup>, and R = 82.0568 cc atm mol<sup>-1</sup>K<sup>-1</sup>.
11. Avogadro's constant = 6.022045(31) × 10<sup>23</sup> molecules/mol.
12.  $1/\alpha = \hbar c/e^2 = 137.03604(11)$  for fine structure constant.
13. For dipole moment, 1 au = 2.541765(8) Debye, and 1 au  $2.541765(8) \times (10^{-18} \text{ esu} \times \text{cm})$ .
14. For quadrupole moment, 1 au  $1.345044 \times 10^{-26}$  esu cm<sup>2</sup>, and 1 au = 1.345044 Buckingham.
15. 1 au =  $3.241391 \times 10^{15}$  esu cm<sup>-3</sup> for electric field gradient.
16. For Coulomb energies,  $e^2/R$  (eV) = 14.3998/R(Å), and  $e^2/R$  (kcal) 332.059/R(Å).

## Chapter 2

# The Chemical Bond, $\text{H}_2^+$ and $\text{H}_2$

### 2.1 Introduction

In this chapter we consider the two states of  $\text{H}_2^+$

$$\varphi_g = \chi_\ell + \chi_r \quad (2.1)$$

and

$$\varphi_u = \chi_\ell - \chi_r \quad (2.2)$$

known as the linear combination of atomic orbitals, LCAO, wavefunctions, arising from bringing a proton up to the ground state of hydrogen. We also consider the two states of  $\text{H}_2$

$$\Phi_g = \chi_\ell \chi_r + \chi_r \chi_\ell \quad (2.3)$$

and

$$\Phi_u = \chi_\ell \chi_r - \chi_r \chi_\ell \quad (2.4)$$

the valence bond, 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  $\text{H}_2^+$  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  $\text{H}_2$  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

$$\epsilon_g^x = \frac{\tau}{1 + S} \quad (2.5)$$

and

$$\epsilon_u^x = -\frac{\tau}{1 - S} \quad (2.6)$$

for  $\text{H}_2^+$ , and

$$E_g^x = \frac{2S\tau}{1 - S^2} \quad (2.7)$$

and

$$E_u^x = -\frac{2S\tau}{1 - S^2} \quad (2.8)$$

for  $\text{H}_2$ , where  $S$  is the overlap of the atomic orbitals. The quantity  $\tau$  is the quantitative manifestation of the decreased kinetic energy, and increased potential energy, arising from interference of the  $\chi_\ell$  and  $\chi_r$  orbitals. It has the form

$$\tau \approx -\frac{2}{R}S \quad (2.9)$$

for large  $R$ . Thus, at large  $R$  the bonding of  $\text{H}_2^+$  is proportional to  $S$ , while the bonding of  $\text{H}_2$  is proportional to  $S^2$ . Consequently, for large  $R$  the bond energy of  $\text{H}_2^+$  exceeds that of  $\text{H}_2$ . For small  $R$ , where  $S \approx 1$ , the bond energy of  $\text{H}_2$  is approximately twice that of  $\text{H}_2^+$ . 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  $\epsilon^x$  and  $E^x$ ).

We also examine the molecular orbital (MO) wavefunction for  $\text{H}_2$

$$\Phi_g^{MO}(1, 2) = \varphi_g(1)\varphi_g(2), \quad (2.10)$$

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

## 2.2 The Chemical Bond in $\text{H}_2^+$ and $\text{H}_2$

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 ( $\varphi$ ) and energies ( $\epsilon$ ). Whereas upper-case letters will be used for many-particle wavefunctions ( $\Phi$ ) and energies ( $E$ ).

### 2.2.1 Origin of the Bond in $\text{H}_2^+$

We first consider the smallest possible molecule,  $\text{H}_2^+$ , consisting of one electron, plus two protons, separated by a distance  $R$ . This system is sketched in Figure 2.1, where the two protons are denoted as  $a$  and  $b$ .

### 2.2.2 Linear Combination of Atomic Orbitals Description

Consider first the case with  $R = \infty$ . With the two protons infinitely far apart, the ground state is obtained by placing the electron in the  $1s$  orbital of one or the other of

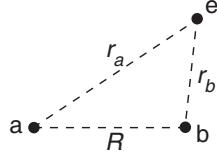


Figure 2.1: Coordinates for  $\text{H}_2^+$ .

the two protons. This leads to the two states,  $HH^+$  and  $H^+H$ , which are described by the wavefunctions,

$$\varphi = \chi_\ell = Ne^{-r_a} \quad (2.11)$$

$$\varphi = \chi_r = Ne^{-r_b} \quad (2.12)$$

respectively, where  $\chi_\ell$  and  $\chi_r$  denote hydrogen 1s orbitals centered on the left and right protons, and  $N$  is the normalization factor.

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 equations (2.11)–(2.12),

$$\varphi = C_\ell \chi_\ell + C_r \chi_r. \quad (2.13)$$

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

$$\varphi_g = \frac{(\chi_\ell + \chi_r)}{D_g} \quad (2.14)$$

where  $D_g$  is a normalization factor. The other combination of the orbitals is the anti-symmetric combination,

$$\varphi_u = \frac{(\chi_\ell - \chi_r)}{D_g} \quad (2.15)$$

where  $D_u$  is the normalization factor.

The energies for the wavefunctions  $\varphi_g$  and  $\varphi_u$  in equations (2.14) and (2.15) are shown as a function of  $R$  in Figure 2.2. Here we see that the  $g$  state is strongly bonding (that is, the energy drops as the nuclei are brought together), whereas 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 character exhibited by the  $\varphi_g$  and  $\varphi_u$  states.

### Electrostatic Energy

First we consider the electron density,

$$\rho_g = \varphi_g^2 = \frac{1}{D_g^2} (\chi_\ell + \chi_r)^2 = \frac{(\chi_\ell^2 + \chi_r^2 + 2\chi_\ell\chi_r)}{D_g^2} \quad (2.16)$$

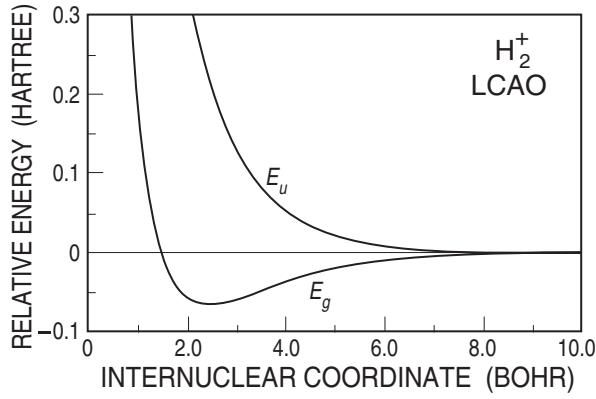


Figure 2.2: The energies of the LCAO wave functions for  $\text{H}_2^+$ .

Integrating  $\varphi_g^2$  over all space must give one electron

$$\langle \varphi_g^2 \rangle = 1, \quad (2.17)$$

and similarly

$$\langle \chi_\ell^2 \rangle = 1 \quad (2.18)$$

$$\langle \chi_r^2 \rangle = 1 \quad (2.19)$$

(recall, these are just the  $1s$  orbitals of  $H$  atom). Thus, equation (2.16) leads to

$$1 = \frac{1 + 1 + 2S}{D_g^2}, \quad (2.20)$$

where  $S = \langle \chi_\ell | \chi_r \rangle$  is called the overlap of the two atomic orbitals. Consequently, the normalization condition of equation (2.14) is

$$D_g = \sqrt{2(1 + S)}. \quad (2.21)$$

If there were no interference terms in equation (2.16), the density would be

$$\rho^{cl} = \frac{1}{2} (\chi_\ell^2 + \chi_r^2) \quad (2.22)$$

where the factor of  $1/2$  leads to the required condition of  $\langle \rho^{cl} \rangle = 1$ . But because of the interference terms the density near the bond midpoint is increased, as shown in Figure 2.3. 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,  $p^+e^-p^+$ . This reasoning is false, as will now be demonstrated. The total potential energy is given by

$$V(r) = -\frac{e^2}{r_a} - \frac{e^2}{r_b} + \frac{e^2}{R}, \quad (2.23)$$

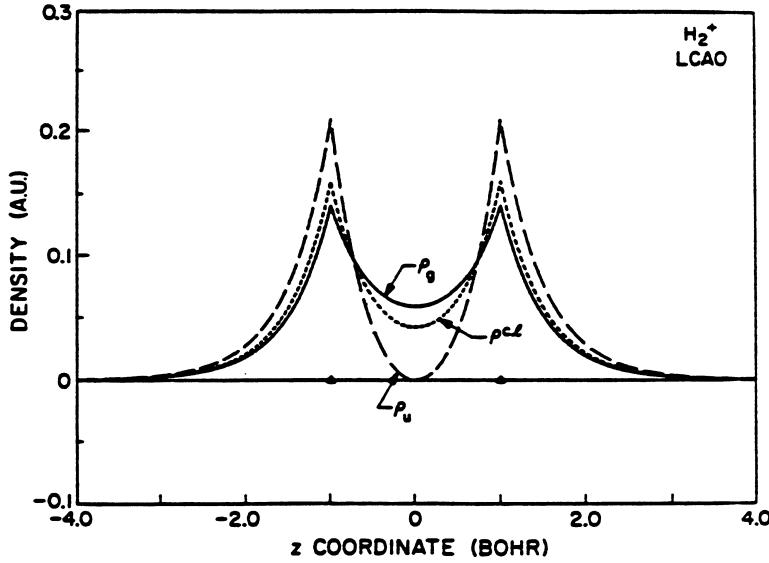


Figure 2.3: The densities  $\rho_g$  and  $\rho_u$  for the LCAO wave functions of  $\text{H}_2^+$  compared with the superposition of atomic densities  $\rho^{cl}$ .

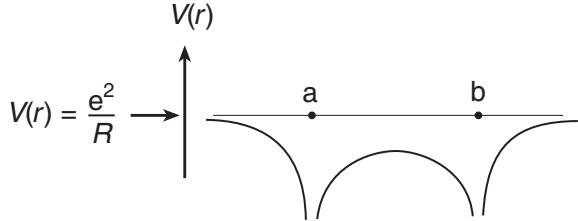


Figure 2.4: The nuclear attraction potential  $V(r)$  for  $\text{H}_2^+$ .

as sketched in Figure 2.4. Here we see that the best place for the electron (lowest energy) is at a nucleus ( $r_a = 0$  or  $r_b = 0$ ) not at the bond midpoint. From Figure 2.3 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 2.5, where

$$V_g = \langle \varphi_g^2 V(\mathbf{r}) \rangle \quad (2.24)$$

is the total potential energy for the  $\varphi_g$  wavefunction.

Our conclusion then is that the 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,

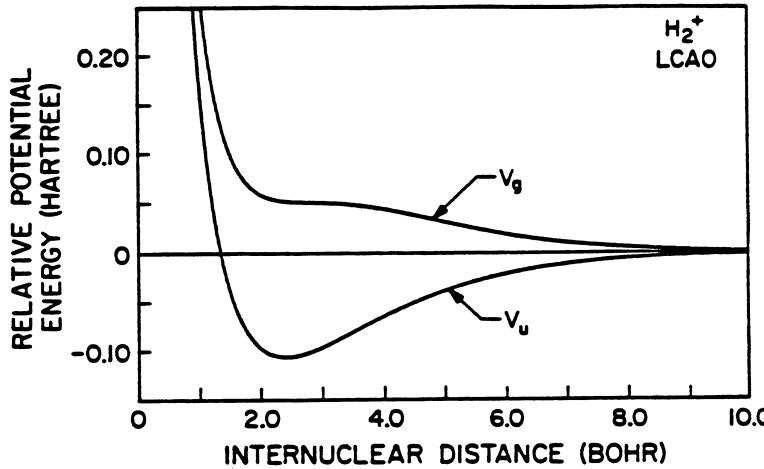


Figure 2.5: The relative potential energies  $V_g$  and  $V_u$  for the LCAO wave functions of  $\text{H}_2^+$ . The absolute values are obtained by noting that  $V_g = V_u = -1.0$  at  $R = \infty$ .

the kinetic energy, as will be discussed next.

### 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

$$T = \left( \frac{\hbar^2}{2m} \right) \langle |\nabla\psi|^2 \rangle. \quad (2.25)$$

Superimposing two atomic orbitals symmetrically, as in  $\varphi_g$ , leads to a large decrease in the slope in the bond region, see Figure 2.6, and hence, a large decrease in the kinetic energy, see  $T_g$  in Figure 2.7,

$$T_g = \left( \frac{\hbar^2}{2m} \right) \langle |\nabla\varphi_g|^2 \rangle \quad (2.26)$$

resulting in a strong bond. On the other hand, the antisymmetric combination in  $\varphi_u$  leads to a large increase in the slope in the bond region (see Figure 2.6) and hence, the kinetic energy opposes bond formation (see  $T_u$  of Figure 2.7).

The resulting total energies are given in Figure 2.2, where we see that  $\varphi_g$  is strongly bonding, while  $\varphi_u$  is strongly antibonding.

### 2.2.3 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

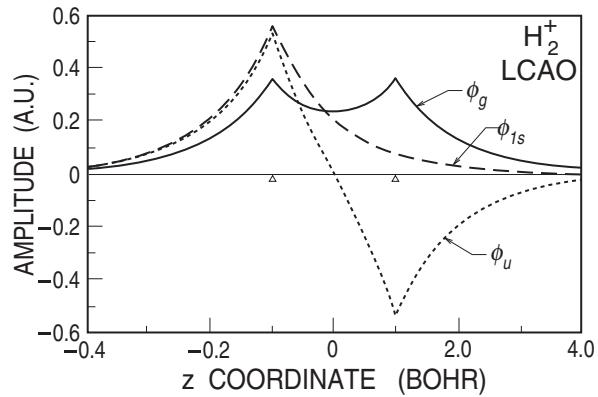


Figure 2.6: Comparison of the  $\varphi_g$  and  $\varphi_u$  LCAO's of  $\text{H}_2^+$  with the hydrogen orbital,  $\varphi_{1s}$ . All wave functions have been normalized.

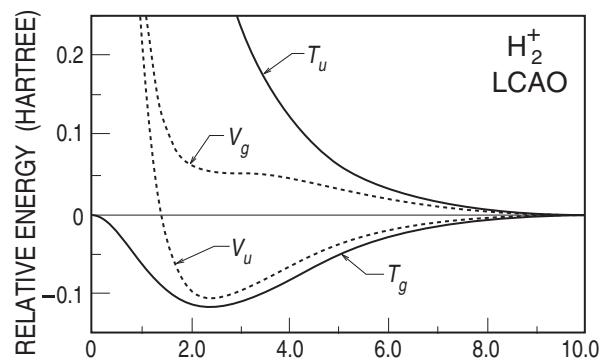


Figure 2.7: The changes in the total kinetic and potential energies for the  $g$  and  $u$  LCAO wave functions of  $\text{H}_2^+$ . The actual values at  $R = \infty$  are  $T_u(\infty) = T_g(\infty) = +\frac{1}{2}$  and  $V_u(\infty) = V_g(\infty) = -1$ .

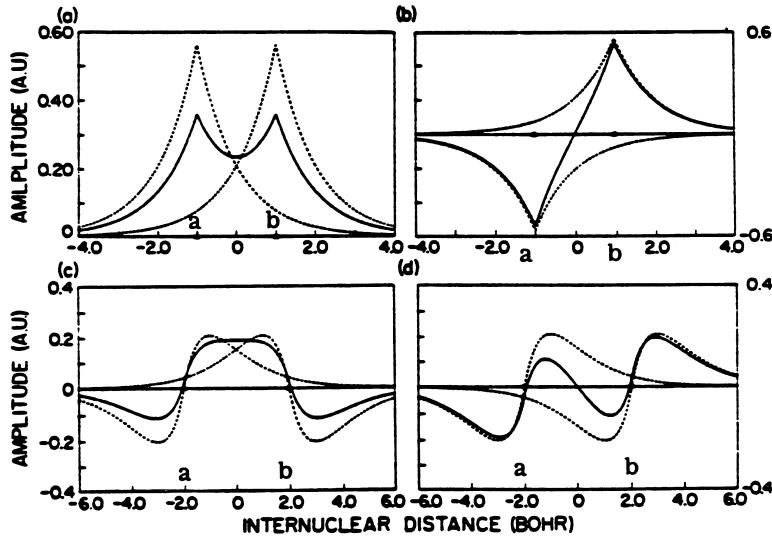


Figure 2.8: (a,b) Symmetric and antisymmetric superposition of  $1s$  atomic orbitals. (c,d) Symmetric and antisymmetric superposition of  $2p_x$  orbitals (oriented along the axis).

so that no new nodal planes are created, as in Figure 2.8(a), then the kinetic energy drops significantly due to 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.

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 2.9. The plus combination,  $\varphi_{zu} = p_{z\ell} + p_{zr}$ , leads to a new nodal plane, higher gradients, and antibonding, as shown in Figure 2.9(d). Meanwhile the minus combination,  $\varphi_{zu} = p_{z\ell} - p_{zr}$ , leads to lower gradients and bonding, as shown in Figure 2.9(c). Similarly, bonding of the  $p_x$  orbitals leads to Figure 2.10. Now the minus combination  $\varphi_{xu} = p_{x\ell} - p_{xr}$  leads to a new nodal plane and antibonding. While the plus combination,  $\varphi_{xg} = p_{x\ell} + p_{xr}$ , leads to bonding.

## 2.2.4 The Optimum Distance for Bonds

There is a natural optimum range for the effects that dominate bonding. First, if  $R$  is very large, near  $\infty$ , 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  $R$ .

Secondly, 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 illustrated in Figure 2.11, where the left

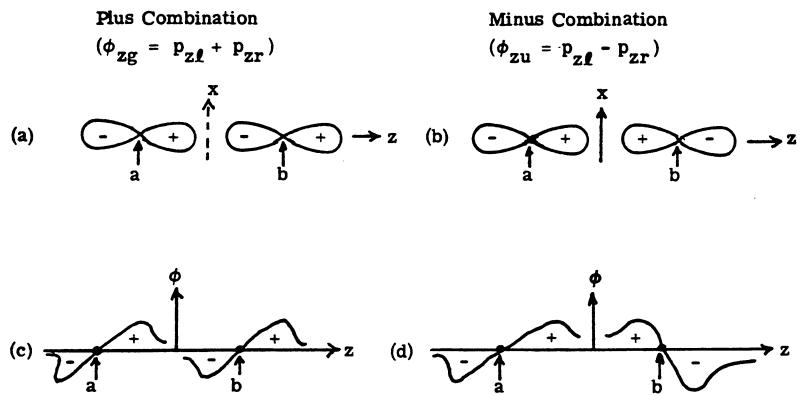


Figure 2.9: Bonding between  $p_x$  orbitals. (a) and (b) are schematic diagrams of the shape of the orbitals in the  $xz$ -plane. (c) and (d) are plots of the orbitals along the  $z$ -axis.

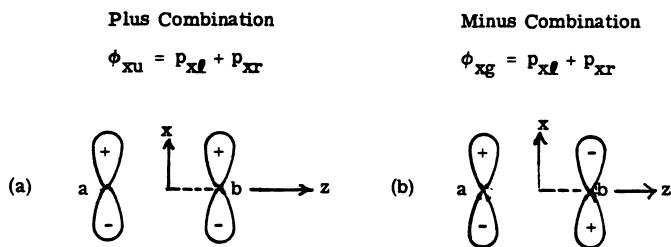


Figure 2.10: Bonding between  $p_x$  orbitals.

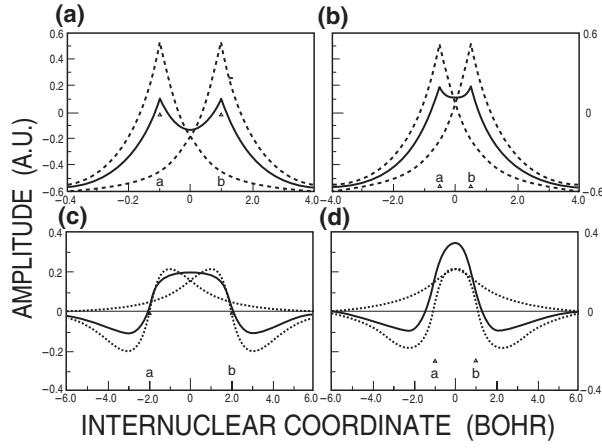


Figure 2.11: Illustrations of the effect of  $R$  on the contragradience of orbitals. In each case the  $R$  for the left case is near optimal, whereas the  $R$  for the right case is too small.

side is for  $R$  near optimum and the right side is for small  $R$ . Figure 2.11 illustrates 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.

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 Figure 2.11(c).

## 2.2.5 Symmetry Considerations

The  $\text{H}_2^+$  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 in both 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  $\text{H}_2^+$ , namely, the inversion symmetry.

### The Hamiltonian

First, we need to consider the form of the Hamiltonian for  $\text{H}_2^+$ . Using the coordinate system of Figure 2.1, the full Hamiltonian for  $\text{H}_2^+$  is

$$\hat{H}(\text{H}_2^+) = -\frac{\hbar^2}{2M_a}\nabla_a^2 - \frac{\hbar^2}{2M_b}\nabla_b^2 - \frac{\hbar^2}{2m}\nabla_1^2 - \frac{Z_a e^2}{r_a} - \frac{Z_b e^2}{r_b} + \frac{Z_a Z_b e^2}{R} \quad (2.27)$$

We will simplify equation (2.27) by assuming the nuclear masses to be infinitely heavy ( $M_a = M_b = \infty$ ) by taking the nuclear charges as unity (as appropriate for  $\text{H}_2^+$ ) and

by using atomic units ( $\hbar = m = e = 1$ ). This reduces equation (2.27) to

$$\hat{H}(\text{H}_2^+) = -\frac{1}{2}\nabla_1^2 - \frac{1}{r_a} - \frac{1}{r_b} + \frac{1}{R}. \quad (2.28)$$

We will group together all the terms depending upon the coordinates of one (and only one) electron as

$$h(1) = -\frac{1}{2}\nabla_1^2 + v(1) \quad (2.29)$$

referred to as the *one-electron Hamiltonian*, where

$$v(1) = -\frac{1}{r_a} - \frac{1}{r_b} \quad (2.30)$$

is the nuclear attraction term, arising from the attractive electron-nuclear interactions. This leads to

$$\hat{H}(\text{H}_2^+) = h(1) + \frac{1}{R}. \quad (2.31)$$

The exact electronic wavefunction of  $\text{H}_2^+$  is obtained by solving

$$\hat{H}\varphi(1) = E\varphi(1), \quad (2.32)$$

where  $H$  is given by equation (2.31). Substituting equation (2.7) into equation (2.32) and rearranging, we obtain

$$h\varphi = \epsilon\varphi, \quad (2.33)$$

where

$$\epsilon = E - \frac{1}{R} \quad (2.34)$$

is referred to as the electronic energy. Although equation (2.33) may appear to involve only the electronic coordinates  $\mathbf{r}$ , the internuclear coordinate  $R$  is involved implicitly, since it determines the spacing of the attractive terms in  $v$ , (2.30). In solving for the wavefunction of  $\text{H}_2^+$ , we choose an  $R$  and solve equation (2.33) to obtain the electronic wavefunction  $\varphi(\mathbf{r})$  and the electronic energy  $\epsilon$ . We then chose a new  $R$  and again solve equation (2.31), obtaining a new  $\varphi(\mathbf{r})$  and an electronic energy  $\epsilon$ , each of which is parametrically dependent upon  $R$ . This procedure is referred to as the Born-Oppenheimer approximation.

### Inversion Symmetry

The operation of inversion through the origin of a coordinate system leads to the changes  $x \rightarrow -x$ ,  $y \rightarrow -y$ , and  $z \rightarrow -z$  in the coordinates, and will be denoted as  $\hat{I}$ . Taking the origin of the coordinate systems as the bond midpoint in Figure 2.1, the inversion of the coordinates of the electron leads to Figure 2.12. The electron is now  $r_a$  from the right nucleus in Figure 2.12(b), and  $r_b$  from the left nucleus as shown in Figure 2.12(a). However, since the nuclear charges are the same, the potential terms in the Hamiltonian are the same.

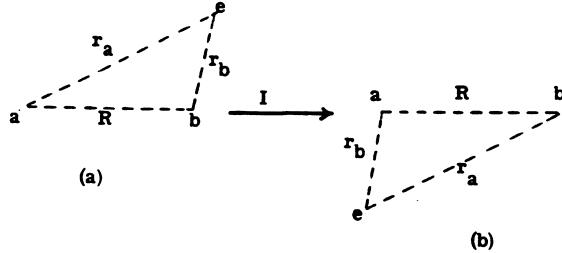


Figure 2.12: The effect of inverting the coordinates of the electron.

Upon inversion, the kinetic energy terms in  $\hat{H}$  are also unchanged

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \rightarrow \frac{\partial^2}{\partial(-x)^2} + \frac{\partial^2}{\partial(-y)^2} + \frac{\partial^2}{\partial(-z)^2} = \nabla^2, \quad (2.35)$$

and hence, the Hamiltonian is invariant upon inversion of the electronic coordinate, through the bond midpoint.

Now consider that we have solved equation (2.32) to obtain eigenstates of  $H_2^+$

$$\hat{H}\varphi = E\varphi, \quad (2.36)$$

and apply  $\hat{I}$  to both sides of equation (2.36). The result is

$$\hat{I}(\hat{H}\Phi) = E(\hat{I}\varphi), \quad (2.37)$$

which we could write as

$$\hat{H}(-\mathbf{r})\varphi(-\mathbf{r}) = E\varphi(-\mathbf{r}), \quad (2.38)$$

indicating the result of inversion. But  $\hat{H}$  is invariant under  $\hat{I}$ ,

$$\hat{H}(-\mathbf{r}) = \hat{H}(\mathbf{r}) \quad (2.39)$$

so that equation (2.38) becomes

$$\hat{H}(\mathbf{r})\varphi(-\mathbf{r}) = E\varphi(-\mathbf{r}) \quad (2.40)$$

or

$$\hat{H}(\mathbf{r})(\hat{I}\varphi) = E(\hat{I}\varphi). \quad (2.41)$$

Equations (2.36) and (2.41) state that  $\varphi$  and  $\hat{I}\varphi$  are each eigenfunctions of exactly the same Hamiltonian with exactly the same energy. There are two possibilities here. The state is nondegenerate, in which case  $\hat{I}\varphi$  and  $\varphi$  must be proportional to each other. Or the state is degenerate, in which case  $\hat{I}\varphi$  and  $\varphi$  may be linearly independent function, i.e., not proportional.

First we consider that the state is nondegenerate. In this case,

$$\hat{I}\varphi = \lambda\varphi, \quad (2.42)$$

where  $\lambda$  is some constant. But applying  $\hat{I}$  twice leads to  $x \rightarrow x$ ,  $y \rightarrow y$ , and  $z \rightarrow z$ . Thus, must return the original function

$$\hat{I}^2\varphi(\mathbf{r}) = \hat{I}\varphi(-\mathbf{r}) = \varphi(\mathbf{r}). \quad (2.43)$$

Whereas applying  $\hat{I}$  to equation (2.42) leads to

$$\hat{I}^2\varphi = \lambda\hat{I}\varphi \quad (2.44)$$

and using equation (2.42) on the right side, leads to

$$\hat{I}^2\varphi = \lambda^2\varphi. \quad (2.45)$$

Combining equations (2.43) and (2.45), leads to

$$\varphi(r) = \lambda^2\varphi(r) \quad (2.46)$$

or

$$\lambda^2 = 1, \quad (2.47)$$

leading to

$$\lambda = \pm 1. \quad (2.48)$$

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  $\varphi_g$  or  $\varphi_u$ .

Consider now the case of a degenerate state with  $\hat{I}\varphi$  not proportional to  $\varphi$ . We can form two new functions,  $\varphi_g = \varphi + \hat{I}\varphi$ , and  $\varphi_u = \varphi - \hat{I}\varphi$ , such that each function is still an eigenfunction of  $H$ , with the same energy,  $H\varphi_g = E\varphi_g$  and  $H\varphi_u = E\varphi_u$  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*.

If a certain state is doubly-degenerate with wavefunctions  $\varphi_a$  and  $\varphi_b$ , then starting with just one function, say  $\varphi_a$ , 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  $\varphi_b$  will be a linear combination of  $\varphi_{ga}$  and  $\varphi_{ua}$ , and nothing need be done with it. However, if  $\varphi_a$  were already *g* or *u*, then  $\varphi_b$  is needed to generate the second function.

The same procedure can be used for higher degeneracies. 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 2.8, 2.9, and 2.10.

### 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. 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.

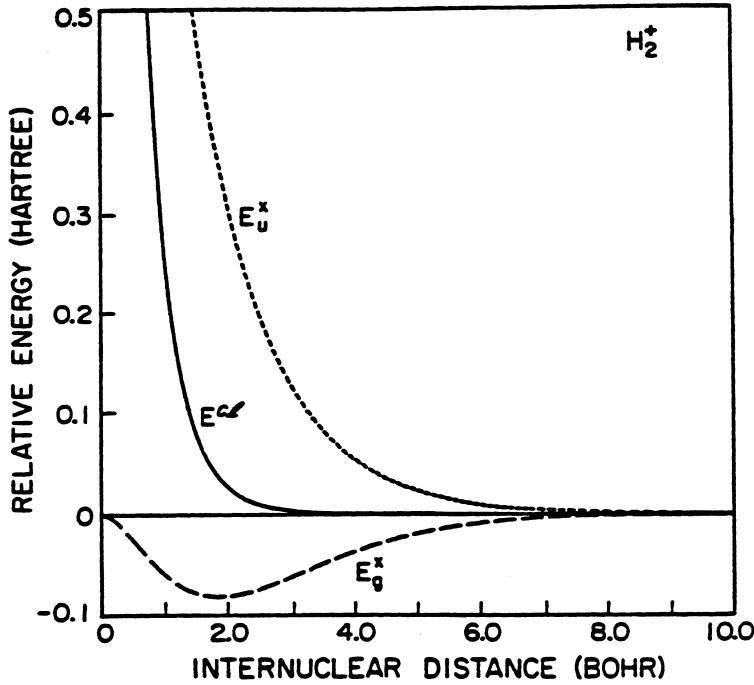


Figure 2.13: The classical energy and the exchange energies for the LCAO wave functions of  $\text{H}_2^+$ .

### 2.2.6 The Exchange Energy

There is a direct relationship between the bonding observed in  $\varphi_g$  and the antibonding observed in  $\varphi_u$ , both being dominated by changes in the kinetic energy as the bond is formed. We will now obtain an explicit form for this relationship.

#### The Classical Energy

Consider first, the wavefunction for  $\text{H}_2^+$  with no superimposition of atomic orbitals,  $\varphi^{cl} = \chi_\ell$ . We refer to this as the classical wavefunction because it does not have interference effects arising from superposition of atomic orbitals. The energy of this wavefunction,  $\epsilon^{cl}$ , is nonbonding, as shown in Figure 2.13. Using equation (2.31), we obtain

$$\epsilon^{cl} = \langle \chi_\ell | H | \chi_\ell \rangle = \langle \chi_\ell | -\frac{1}{2} \nabla^2 - \frac{1}{r_a} - \frac{1}{r_b} | \chi_\ell \rangle = \epsilon_{atom} + \langle \chi_\ell | -\frac{1}{r_b} | \chi_\ell \rangle, \quad (2.49)$$

where

$$\epsilon_{atom} = \langle \chi_\ell | -\frac{1}{2} \nabla^2 - \frac{1}{r_a} | \chi_\ell \rangle = -\frac{1}{2} \left( \frac{e^2}{a_0} \right). \quad (2.50)$$

Thus,

$$\epsilon^{cl} + \frac{1}{R} = \epsilon_{atom} + \delta\bar{v}^{cl}, \quad (2.51)$$

where

$$\delta\bar{v}^{cl} = \left[ \left\langle \chi_\ell^2 \left( -\frac{e^2}{r_b} \right) \right\rangle + \frac{e^2}{r} \right] \quad (2.52)$$

is repulsive.

### The Exchange Energy

Now we consider the wavefunction  $\varphi_g$  with energy

$$\epsilon_g = \frac{\langle l+r|\hat{H}|l+r \rangle}{\langle l+r|l+r \rangle} = \frac{\langle l|\hat{H}|l+r \rangle}{\langle l|l+r \rangle}. \quad (2.53)$$

Since

$$\begin{aligned} \langle l|\hat{H}|l+r \rangle &= \langle l|\hat{H}|l+r \rangle + \langle l|\hat{H}|r \rangle = \epsilon^{cl} + \langle l|\hat{H}|r \rangle \\ \langle l|l+r \rangle &= \langle l|l \rangle + \langle l|r \rangle = 1+S, \end{aligned}$$

we obtain

$$\epsilon_g = \frac{\epsilon^{cl} + \langle l|\hat{H}|r \rangle}{1+S} = \epsilon^{cl} + \frac{\langle l|\hat{H}|r \rangle - \epsilon^{cl}S}{1+S} \quad (2.54)$$

hence

$$\epsilon_g = \epsilon^{cl} + \frac{\tau}{1+S}, \quad (2.55)$$

where

$$\tau = \langle l|\hat{H}|r \rangle - S\epsilon^{cl} = \left[ h_{lr} + S\frac{1}{R} \right] - S \left[ h_{ll} + \frac{1}{R} \right] \quad (2.56)$$

or

$$\tau = h_{lr} - Sh_{ll}. \quad (2.57)$$

Similarly,

$$\epsilon_u = \frac{\langle l-r|\hat{H}|l-r \rangle}{\langle l-r|l-r \rangle} = \frac{\langle l|\hat{H}|l-r \rangle}{\langle l|l-r \rangle} = \frac{\epsilon^{cl} - \langle l|\hat{H}|r \rangle}{1-S} \quad (2.58)$$

or

$$\epsilon_u = \epsilon^{cl} + \frac{\tau}{1-S}, \quad (2.59)$$

where  $\tau$  is again given by equation (2.57). Thus, the interference resulting from superimposing the  $\chi_\ell$  and  $\chi_r$  wavefunctions can be viewed as corrections upon the classical energy,

$$\epsilon_g = \epsilon^{cl} + \epsilon_g^x \quad (2.60)$$

$$\epsilon_u = \epsilon^{cl} + \epsilon_u^x, \quad (2.61)$$

where the correction terms

$$\epsilon_g^x = \frac{\tau}{1+S} \quad (2.62)$$

$$\epsilon_u^x = \frac{-\tau}{1 - S} \quad (2.63)$$

are referred to as interference, exchange, or resonance terms. These energies are shown in Figure 2.12, where we see that  $\epsilon_g^x$  favors bond formation, while  $\epsilon_u^x$  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  $\chi_\ell$  and  $\chi_r$ , that is, due to exchange of the electron between the left and right centers. As shown in Figure 2.12,  $\epsilon^{cl}$  is weakly antibonding, and hence, bonding in the  $g$  state of  $H_2^+$  results from the exchange energy  $\epsilon_g^x$ . On the other hand, the exchange term  $\epsilon_u^x$  for the  $u$  state is strongly repulsive, resulting in a strongly antibonding potential curve.

These quantities  $\epsilon_g^x$  and  $\epsilon_u^x$  constitute a quantitative representation of the effects discussed qualitatively in the first section. 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  $\tau$ . 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  $\tau$ . The net result is a negative  $\tau$ , leading to a negative value for

$$\epsilon_g^x = \frac{\tau}{(1 + S)} \quad (2.64)$$

and a positive value for

$$\epsilon_u^x = \frac{-\tau}{(1 - S)}. \quad (2.65)$$

### Comparison of $g$ and $u$ States

For large  $R$ , where the overlap  $S$  is nearly zero, we see that equations (2.62)–(2.63) lead to

$$\epsilon_g^x = \tau \quad (2.66)$$

and

$$\epsilon_u^x = -\tau, \quad (2.67)$$

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  $R = 2.5 a_0 = 1.32 \text{ \AA}$ , we have  $S = 0.4583$ , and  $\tau = -0.1083(e^2/a_0)$ , leading to

$$\epsilon_g^x = -0.0742 \left( \frac{e^2}{a_0} \right) \quad (2.68)$$

$$\epsilon_u^x = +0.20939 \left( \frac{e^2}{a_0} \right), \quad (2.69)$$

whereas

$$\epsilon^{cl} = 0.00943 \left( \frac{e^2}{a_0} \right). \quad (2.70)$$

## Analytic Results

Explicit evaluation of the various quantities involved in the energy of  $\text{H}_2^+$  is carried out in Section 2.6.1, leading to

$$\begin{aligned} S &= \left[1 + R + \frac{1}{3}R^2\right] e^{-R} \\ \epsilon^{cl} &= -\frac{1}{2} + \left(1 + \frac{1}{R}\right) e^{-2R}, \end{aligned}$$

and

$$\begin{aligned} \tau &= -\left[\frac{2}{3}R - \frac{1}{R}\right] e^{-R} - \left(1 + \frac{1}{r}\right) \left(1 + R + \frac{1}{3}R^2\right) e^{-3R} \\ &\approx -\left[\frac{2}{3}R - \frac{1}{R}\right] e^{-R}, \end{aligned}$$

where terms of order  $e^{-3R}$  are neglected. Thus, for large  $R$

$$\tau \approx -\frac{2}{3}Re^{-R}. \quad (2.71)$$

That is, the quantity  $\tau$  dominating the bond in  $\text{H}_2^+$  is proportional to the overlap between the orbitals. At large  $R$ , this leads to a bond strength of the form

$$\tau \approx -\frac{2}{3}Re^{-R}. \quad (2.72)$$

Thus, the bond energy decreases exponentially with internuclear distance.

This simple relation between bonding does not hold for small  $R$ . We saw, above, that  $\tau$  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  $R = 0$ .

## Contragradience

The above discussions indicate that the interference or exchange part of the kinetic energy dominates the bonding in  $\text{H}_2^+$ . This term is dominated by

$$t^x = \frac{1}{2} \left[ \langle (\nabla \chi_\ell) + (\nabla \chi_r) \rangle - S \langle (\nabla \chi_\ell)^2 \rangle \right], \quad (2.73)$$

which is large and negative in between the atoms. The region of space leading to negative  $\nabla \chi_\ell \cdot \nabla \chi_r$ , and hence, dominating the bond, is indicated for  $\text{H}_2$  in Figure 2.14.

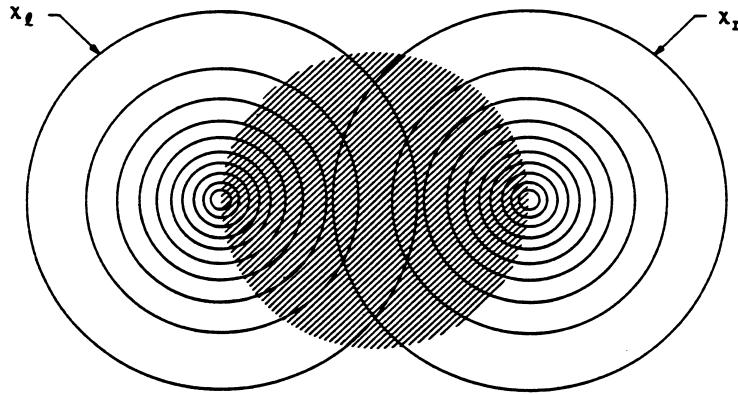


Figure 2.14: Contour plots of two hydrogen atomic orbitals for  $R = 2a_0$  (contour increment 0.05 a.u.). The shaded region leads to negative values of  $\nabla\chi_\ell \cdot \nabla\chi_r$  and hence to a large contragradience. As a result, this region dominates the bonding.

### Historical Development

H. Hellmann [?], after escaping from Hitler Germany into Russia around 1934, and before suddenly vanishing into Stalin Russia around 1937, was the first to suggest that bonding arises essentially from a decrease in kinetic energy. He suggested that the bond in  $H_2^+$  results because the electron is allowed to delocalize over the 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 2.15, where we see that for the  $\varphi_g$  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  $\varphi_g$  state is expected to be stabilized with respect to  $H$  atoms.

On the other hand, since the  $\varphi_u$  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 K. Ruedenberg [?] provided a more quantitative framework showing, for specific cases, that interference terms resulting from the superposition of amplitude 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 Wilson and Goddard [?, ?]. Other, somewhat related viewpoints, have also been proposed by Feinberg and Ruedenberg [?], Feinberg, Ruedenberg and Mebler [?], and Bader and Baudraut [?].

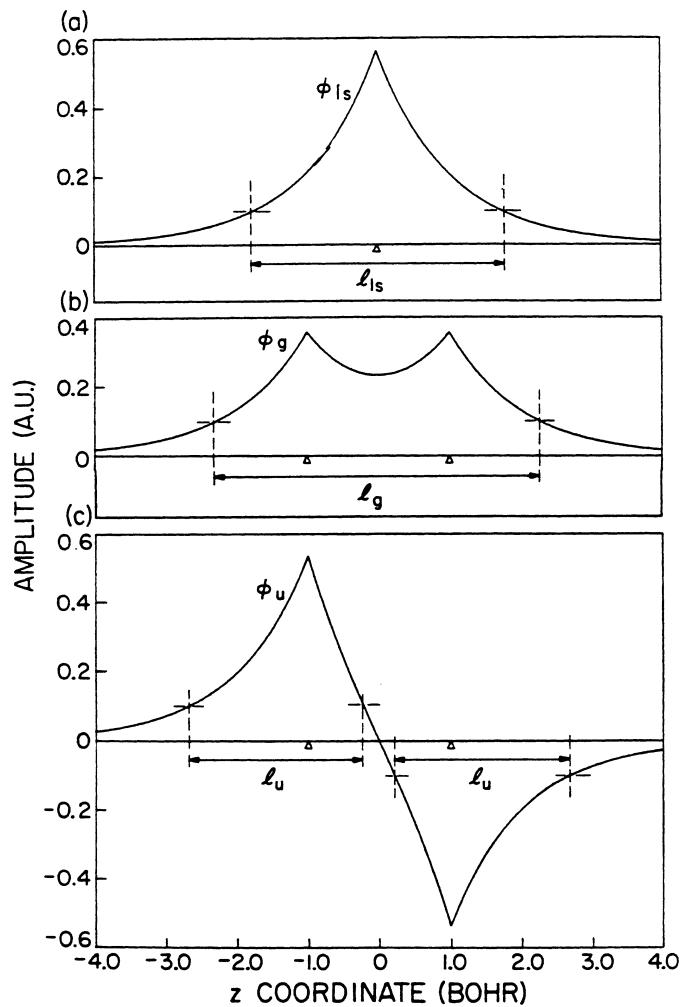


Figure 2.15: Illustration of the differences in the effective size of the box for the electron in the hydrogen atom and in the  $g$  and  $u$  states of  $\text{H}_2^+$ .

## 2.3 The Molecular Orbital Description of H<sub>2</sub>

We will now add a second electron to H<sub>2</sub><sup>+</sup> to obtain the H<sub>2</sub> molecule. The simplest wavefunction for H<sub>2</sub> is to start with an electron in the best molecular orbital of H<sub>2</sub><sup>+</sup>, and to place a second electron in this  $\varphi_g$  orbital. This leads to the molecular orbital (MO) wavefunction for H<sub>2</sub>,

$$\Phi_{gg}^{MO}(\mathbf{r}_1, \mathbf{r}_2) = \varphi_g(\mathbf{r}_1)\varphi_g(\mathbf{r}_2) \quad (2.74)$$

where

$$\varphi_g = \frac{(\chi_\ell + \chi_r)}{D_g}, \quad (2.75)$$

and

$$D_g = \sqrt{2(1 + S)}. \quad (2.76)$$

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 equation (2.74).

First we will examine the meaning of the wavefunction (2.74). 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

$$P(\mathbf{r}_1, \mathbf{r}_2) = |\Phi^{MO}(\mathbf{r}_1, \mathbf{r}_2)|^2 = |\varphi_g(\mathbf{r}_1)|^2|\varphi_g(\mathbf{r}_2)|^2 = P_g(\mathbf{r}_1)P_g(\mathbf{r}_2). \quad (2.77)$$

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. (Consider the analogous case of a red die, electron 1, and a green die, electron 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 1/6 × 1/6 equal to 1/36. The dice are independent so that the probabilities multiply.) Summarizing, a product wavefunction as in equation (2.74) implies that the electrons move independently of each other (no correlations in their motions).

In addition to using the  $\varphi_g$  molecular orbital, as in equations (2.75)–(2.76), we can construct wavefunctions of H<sub>2</sub> using the  $\varphi_u$  molecular orbital,

$$\varphi_u = \frac{(\chi_\ell - \chi_r)}{\sqrt{2(1 - S)}}. \quad (2.78)$$

This leads to wavefunctions of the form

$$\Phi_{ug}(1, 2) = \varphi_u(1)\varphi_g(2), \quad (2.79)$$

$$\Phi_{gu}(1, 2) = \varphi_g(1)\varphi_u(2), \quad (2.80)$$

$$\Phi_{uu}(1, 2) = \varphi_u(1)\varphi_u(2). \quad (2.81)$$

Since the  $\varphi_u$  orbital is antibonding, the above wavefunctions of H<sub>2</sub> lead to much higher energies than equation (2.74), except at large  $R$ , and we expect an energy level diagram as in Figure 2.16.

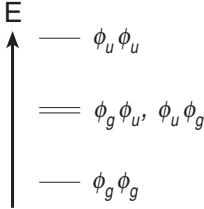


Figure 2.16: Simple energy diagram for MO wave functions of  $\text{H}_2$ .

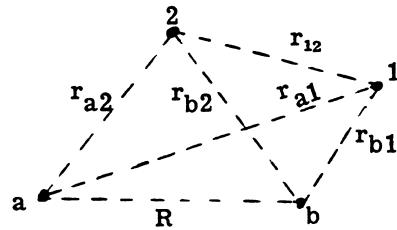


Figure 2.17: Coordinates for  $\text{H}_2$ .

### 2.3.1 Energies

For  $\text{H}_2$ , we use the coordinate system of Figure 2.17. Using the same conventions and assumptions as for  $\text{H}_2^+$  leads to the Hamiltonian

$$\hat{H}(\text{H}_2) = h(1) + h(2) + \frac{1}{r_{12}} + \frac{1}{R}, \quad (2.82)$$

where  $1/r_{12}$  is the Coulomb interaction between the two electrons, and where

$$h(i) = -\frac{1}{2}\nabla_i^2 - \frac{1}{r_{ai}} - \frac{1}{r_{bi}} \quad (2.83)$$

contains all terms depending only upon the coordinates of electron  $i$ .

Consider now the energy of a product wavefunction

$$\Phi_{ab}(1, 2) = \varphi_a(1)\varphi_b(2) \quad (2.84)$$

and note that many two-electron integrals factor into products of one-electron integrals, e.g.,

$$\begin{aligned} \langle \Phi_{ab}(1, 2) | h(2) | \Phi_{ab}(1, 2) \rangle &= \int \int d^2 r_1 d^3 r_2 \varphi_a^*(1) \varphi_b^*(2) h(2) \varphi_a(1) \varphi_b(2) \\ &= \left[ \int d^3 r_1 \varphi_a^*(1) \varphi_a(1) \right] \left[ \int d^3 r_2 \varphi_b^*(2) h(2) \varphi_b(2) \right] \\ &= \langle \varphi_a | \varphi_a \rangle \langle \varphi_b | h | \varphi_b \rangle \end{aligned}$$

$$= \langle \varphi_b | h | \varphi_b \rangle \quad (2.85)$$

since  $\langle \varphi_a | \varphi_a \rangle = 1$ . Note that the  $\langle \rangle$  notation implies integration over however many electrons are in the wavefunctions. In order to simplify the energy expressions, we will define

$$h_{ij} = \langle \varphi_i | h | \varphi_j \rangle. \quad (2.86)$$

The integral that does not factor is the one arising from the  $1/r_{12}$  terms in the Hamiltonian, which we will denote as

$$J_{ij} = \langle \Phi_{ij}(1, 2) | \frac{1}{r_{12}} | \Phi_{ij}(1, 2) \rangle = \int \int d^3 r_1 d^3 r_2 \frac{\varphi_i^*(1) \varphi_i(1) \varphi_j^*(2) \varphi_j(2)}{r_{12}}. \quad (2.87)$$

Note that

$$\rho_i(1) = \varphi_i^*(1) \varphi_i(1) \quad (2.88)$$

is the probability density for finding the electron in orbital  $i$  at a position  $\mathbf{r}_1$ , and

$$\rho_j(2) = \varphi_j^*(2) \varphi_j(2) \quad (2.89)$$

is the probability density for finding the electron in orbital  $j$  at position  $\mathbf{r}_2$ . Thus, we can rewrite equation (2.87) as

$$J_{ij} = \int \int d^3 r_1 d^3 r_2 \frac{\rho_i(1) \rho_j(2)}{r_{12}}. \quad (2.90)$$

But equation (2.90) is just the classical electrostatic interaction energy (the Coulomb energy) between the two charge distributions  $\rho_i$  and  $\rho_j$ . Thus, we refer to  $J_{ij}$  as the *Coulomb integral* between orbitals  $\varphi_i$  and  $\varphi_j$ . This term cannot be factored into a product of one-electron terms because of the

$$r_{12} = \sqrt{(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2} \quad (2.91)$$

term.

Since  $\rho_i$ ,  $\rho_j$ , and  $1/r_{ij}$  are always positive, we see that the Coulomb integral is always positive  $J_{ij} \geq 0$ . Using the above results, we can write

$$E_{gg} = 2h_{gg} + J_{gg} + \frac{1}{R} \quad (2.92)$$

$$E_{gu} = h_{uu} + h_{gg} + J_{gu} + \frac{1}{R} \quad (2.93)$$

$$E_{ug} = E_{gu} \quad (2.94)$$

$$E_{uu} = 2h_{uu} + J_{uu} + \frac{1}{R}. \quad (2.95)$$

The molecular orbital states are ordered as in Figure 2.16. Note there that the Coulomb interactions are not negligible, but nonetheless, overall ordering of states can be predicted solely from considering the one-electron terms.

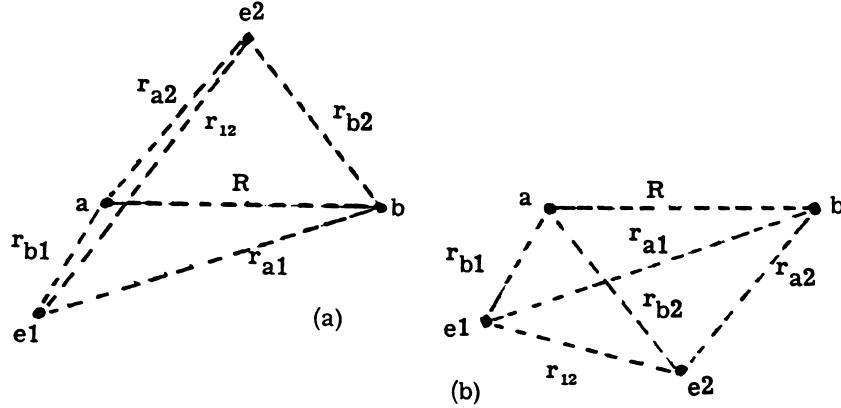


Figure 2.18:

### 2.3.2 Symmetries

Before proceeding further in the discussion of  $H_2$ , we will examine how symmetry can help us in sorting out the states.

#### Inversion

Starting with the configuration of particles in Figure 2.17 and inverting the coordinates of electron 1, leads to Figure 2.18(a), with electron 1 at a distance of  $r_{b1}$  from the nucleus  $a$ , and  $r_{a1}$  from  $b$ . Recall that the center of inversion is the bond midpoint. 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 2.18(b). Thus, we define the inversion operator,  $\hat{I}$ , for  $H_2$  as  $x_1 \rightarrow -x_1$ ,  $y_1 \rightarrow -y_1$ ,  $z_1 \rightarrow -z_1$  and  $x_2 \rightarrow -x_2$ ,  $y_2 \rightarrow -y_2$ , and  $z_2 \rightarrow -z_2$  or  $r_1 \rightarrow -r_1$  and  $r_2 \rightarrow -r_2$ , and the total Hamiltonian is invariant under this inversion,

$$\hat{I}\hat{H}(\mathbf{r}_1, \mathbf{r}_2) = \hat{H}(-\mathbf{r}_1, -\mathbf{r}_2) = \hat{H}(\mathbf{r}_1, \mathbf{r}_2). \quad (2.96)$$

The exact wavefunction for  $H_2$  is obtained by solving

$$\hat{H}(1, 2)\Phi(1, 2) = E\Phi(1, 2) \quad (2.97)$$

do not panic, we will not try this yet. Since  $\hat{H}(1, 2)$  is invariant under the inversion  $\hat{I}$  (2.96), we find that (2.97) implies

$$\hat{H}(I\Phi) = E(I\Phi) \quad (2.98)$$

and hence, just as for  $H_2^+$ , the exact eigenstates of  $H_2$  are either  $g$  or  $u$ ,

$$\hat{I}\Phi_g(1, 2) = +\Phi_g(1, 2) \quad (2.99)$$

$$\hat{I}\Phi_u(1, 2) = -\Phi_u(1, 2). \quad (2.100)$$

Applying the  $\hat{I}$  operator to the MO wavefunctions (2.74), (2.79), (2.80), and (2.81) leads to the conclusion that  $\Phi_{gg}$  and  $\Phi_{uu}$  are  $g$  states, and  $\Phi_{gu}$  and  $\Phi_{ug}$  are  $u$  states. 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 2.16.

### 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,

$$\hat{H}(2, 1) = \hat{H}(1, 2). \quad (2.101)$$

To discuss such symmetries, we define the transposition operator  $\tau_{12}$  as  $\mathbf{r}_1 \rightarrow \mathbf{r}_2$  and  $\mathbf{r}_2 \rightarrow \mathbf{r}_1$ . Thus, starting with the exact wavefunction (2.97), applying  $\tau_{12}$  to both sides, and using equation (2.101), we find that

$$\hat{H}(\tau_{12}\Phi) = E(\tau_{12}\Phi). \quad (2.102)$$

Since  $(\tau_{12})^2$  transposes the electrons twice, taking us back to the original starting point,

$$(\tau_{12})^2 = \tau_{12}\tau_{12} = e \quad (2.103)$$

(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

$$\tau_{12}\Phi^s(1, 2) = \Phi^s(2, 1) = +\Phi^s(1, 2) \quad (2.104)$$

$$\tau_{12}\Phi^a(1, 2) = \Phi^a(2, 1) = +\Phi^a(1, 2) \quad (2.105)$$

under transposition. Examining the wavefunctions (2.74), (2.79), (2.80), and (2.81), we see that

$$\tau_{12}[\varphi_g(1)\varphi_g(2)] = [\varphi_g(1)\varphi_g(2)] \quad (2.106)$$

is symmetric,

$$\tau_{12}[\varphi_g(1)\varphi_u(2)] = [\varphi_u(1)\varphi_g(2)], \quad (2.107)$$

$$\tau_{12}[\varphi_u(1)\varphi_g(2)] = [\varphi_g(1)\varphi_u(2)], \quad (2.108)$$

have no symmetry, and

$$\tau_{12}[\varphi_u(1)\varphi_u(2)] = [\varphi_u(1)\varphi_u(2)], \quad (2.109)$$

is symmetric. Thus, the  $g$  states,  $\Phi_{gg}$  and  $\Phi_{uu}$ , have the proper permutational symmetry, but the  $u$  states,  $\Phi_{gu}$  and  $\Phi_{ug}$ , do not. In the next section, we will fix up this problem with the  $u$  states.

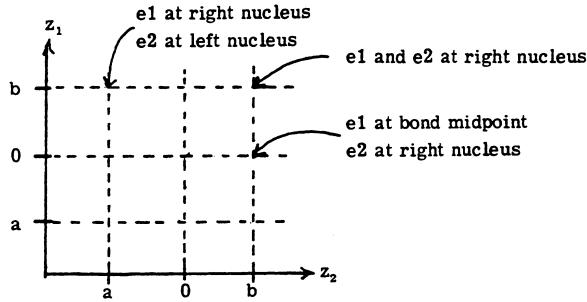


Figure 2.19: Coordinates showing simultaneous positions for  $z_1$  and  $Z_1$

### The $u$ States

Combining the  $u$  wavefunctions as follows

$${}^3\Phi_u = (\varphi_g \varphi_u - \varphi_u \varphi_g) \quad (2.110)$$

$${}^1\Phi_u = (\varphi_g \varphi_u + \varphi_u \varphi_g) \quad (2.111)$$

leads to

$$\tau_{12} {}^3\Phi_u = (\varphi_u \varphi_g - \varphi_g \varphi_u) = -{}^3\Phi_u \quad (2.112)$$

$$\tau_{12} {}^1\Phi_u = (\varphi_u \varphi_g - \varphi_g \varphi_u) = +{}^1\Phi_u \quad (2.113)$$

so that the combinations (2.110) and (2.111) have proper permutational symmetry. The notation will become clear when we discuss spin, in Chapter 4.

Now we must examine the physics behind the combinations (2.110) and (2.111). 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 2.19, where some special points are included.

Multiplying these orbitals leads to the wavefunction  $\Phi_{gu}(z_1, z_2)$  with amplitudes at various points, as given in Figure 2.20(c). Rather than listing numbers as in Figure 2.20(c), we will draw contours of equal amplitude as indicated in Figure 2.20(d), where solid lines indicate positive amplitude, dotted lines indicate negative amplitude, and long dashes indicate zero amplitude. Here, one sees the maximum positive amplitude occurs for  $z_2 = b$  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

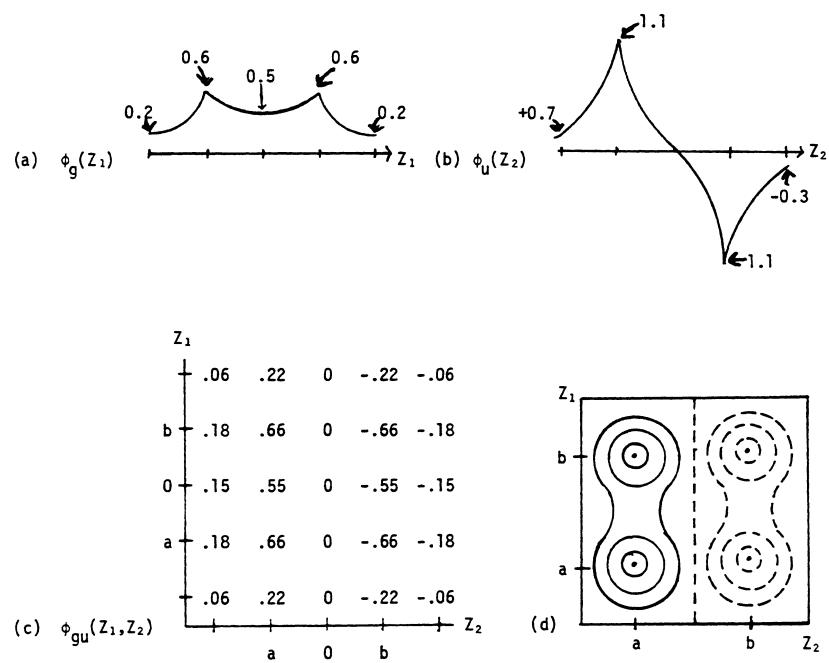


Figure 2.20:

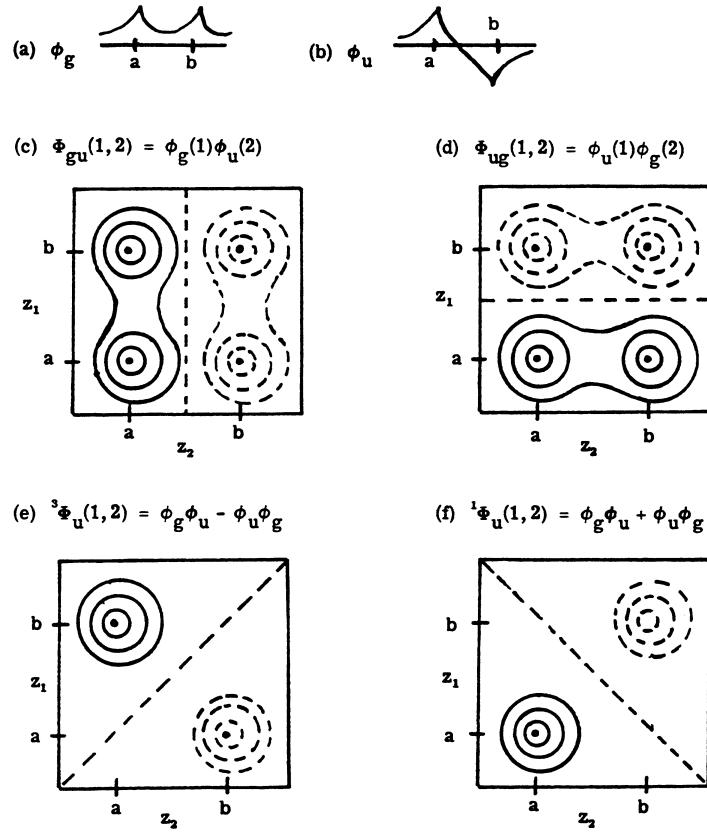


Figure 2.21:

Figure 2.20(d) directly from Figures 2.20(a) and 2.20(b), without going through Figure 2.20(c).

In Figure 2.21, we compare the two-electron wavefunctions of  $\Phi_{gu}$ ,  $\Phi_{ug}$ ,  $^3\Phi_u$ , and  $^1\Phi_u$ . All cases involve a single nodal plane, and if there were no electron-electron interactions, all of these wavefunctions would have the same total energy. Note from equation (2.93) that both  $u$  states have the same total energy, and that any combination of these states leads to the same one-electron energy,  $h_{uu} + h_{gg}$ . The difference lies in the electron-electron interactions. In Figure 2.21(e), we see that the  $^3\Phi_u$  wavefunction is zero along the line with  $z_1 = z_2$ , whereas in Figure 2.21(f) 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  $\Phi_{gu}$  and  $\Phi_{ug}$ , the one with the lowest electron repulsion is just  $^3\Phi_u$ . Thus, the energy diagram for the molecular orbital wavefunctions of  $H_2$ , becomes as in Figure 2.22.

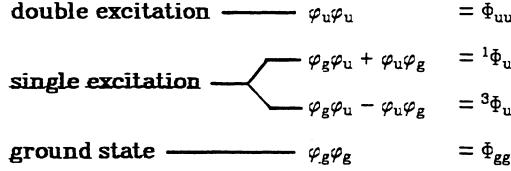


Figure 2.22:

## 2.4 Quantitative Aspects

Now that we see the physics behind why the  $^3\Phi_u$  wavefunction (2.110) is the best  $u$  state, we will examine the quantitative energy expression

$$\begin{aligned} E(^3\Phi_u) &= \frac{\langle ^3\Phi_u | \hat{H} | ^3\Phi_u \rangle}{\langle ^3\Phi_u | ^3\Phi_u \rangle} = \frac{\langle gu - ug | \hat{H} | gu - ug \rangle}{\langle gu - ug | gu - ug \rangle} \\ &= \frac{2\langle gu | \hat{H} | gu - ug \rangle}{2\langle gu | gu - ug \rangle} = \frac{\langle gu | \hat{H} | gu \rangle - \langle gu | \hat{H} | ug \rangle}{\langle gu | gu \rangle - \langle gu | ug \rangle}. \end{aligned} \quad (2.114)$$

Since

$$\langle gu | ug \rangle = \langle g | u \rangle \langle u | g \rangle = 0 \quad (2.115)$$

$$\langle gu | h(1) | ug \rangle = \langle g | h | u \rangle \langle u | g \rangle = 0 \quad (2.116)$$

$$\langle gu | h(2) | ug \rangle = \langle g | u \rangle \langle u | h | g \rangle = 0, \quad (2.117)$$

we are left with

$$E(^3\Phi_u) = E_{gu} - \langle gu | \hat{H} | ug \rangle, \quad (2.118)$$

where

$$\langle gu | \hat{H} | ug \rangle = \langle gu | \frac{1}{r_{12}} | ug \rangle = \int \int d^3 r_1 d^3 r_2 \frac{\varphi_g^*(1) \varphi_u(1) \varphi_u^*(2) \varphi_g(2)}{r_{12}} = K_{gu}, \quad (2.119)$$

where this two-electron term is called the *exchange integral* between orbitals  $\varphi_g$  and  $\varphi_u$ . The net result is

$$E(^3\Phi_u) = E_{gu} - K_{gu} \quad (2.120)$$

and

$$E(^1\Phi_u) = E_{gu} + K_{gu}. \quad (2.121)$$

Since the previous section showed that

$$E(^1\Phi_u) > E(^3\Phi_u), \quad (2.122)$$

we see that the exchange integral must be positive,  $K_{gu} \geq 0$ .

What is the physical significant of  $K_{gu}$ ? It tells us how much the two-electron energy changes when we go from the wavefunctions in Figure 2.21(c), or 2.21(d),

to the wavefunctions in Figure 2.21(e), or 2.21(f). 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 equation (2.93) into (2.118), leading to

$$E({}^3\Phi_u) = \left[ h_{gg} + h_{uu} + \frac{1}{R} \right] + [J_{gu} - K_{gu}] \quad (2.123)$$

$$E({}^1\Phi_u) = \left[ h_{gg} + h_{uu} + \frac{1}{R} \right] + [J_{gu} + K_{gu}] \quad (2.124)$$

Here  $J_{gu} - K_{gu}$  is the total two-electron energy of Figure 2.21(f), while  $J_{gu} + K_{gu}$  is the total two-electron energy of Figure 2.21(e), and  $J_{gu}$  is the two-electron energy of Figures 2.21(c) and 2.21(d). The two-electron energy of  ${}^3\Phi_u$  can also be written as

$$J_{gu} - K_{gu} = \frac{\langle {}^3\Phi_u | \frac{1}{r_{12}} | {}^3\Phi_u \rangle}{\langle {}^3\Phi_u | {}^3\Phi_u \rangle} = \int \int d^3 r_1 d^3 r_2 \frac{{}^3P_u(1, 2)}{r_{12}}, \quad (2.125)$$

where  $1/2$  comes from  $\langle {}^3\Phi_u | {}^3\Phi_u \rangle = 2$ , and where

$${}^3P_u(1, 2) = \frac{1}{2} {}^3\Phi_u^*(1, 2) {}^3\Phi_u(1, 2). \quad (2.126)$$

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 equation (2.125) is always positive, we see that the total two-electron energy of the  ${}^3\Phi_u$  state must be positive

$$J_{gu} - K_{gu} \geq 0, \quad (2.127)$$

and hence

$$J_{gu} \geq K_{gu} \quad (2.128)$$

the exchange integral is always less than the Coulomb integral. Combining (2.128) with  $J_{ij} \geq 0$ , leads then to

$$J_{gu} \geq K_{gu} \geq 0. \quad (2.129)$$

This relation is true for any pairs of orbitals, as shown in Section 2.6.3.

### 2.4.1 Potential Curves

So far we have discussed the MO wavefunction assuming that the bonding orbital  $\varphi_g$  is much better than the antibonding orbital  $\varphi_u$ . This is true for shorter internuclear distance  $R$  but does not remain true as the bond is broken. Thus, in Figure 2.23 we compare the energy of the molecular orbital wavefunction  $\Phi_{gg}$  with the exact energy for the ground state of  $H_2$ . This molecular orbital 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 AO description of the MO (2.75)–(2.76) into the MO wavefunction (2.74), leading to

$$\Phi_{gg}^{MO}(1, 2) = N [\chi_\ell \chi_\ell + \chi_r \chi_r + \chi_\ell \chi_r + \chi_r \chi_\ell] = \Phi_{covalent} + \Phi_{ionic}, \quad (2.130)$$

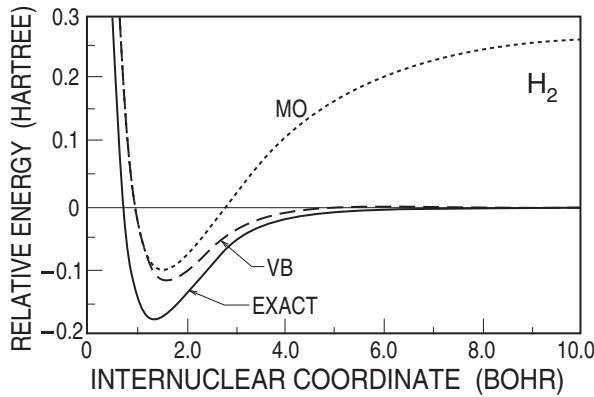


Figure 2.23: The energy of the MO wave function for the ground state of  $\text{H}_2$  with comparison to the VB and exact energies.

where  $N = [2(1 + S)]^{-1}$  and

$$\Phi_{\text{covalent}} = N (\chi_\ell \chi_r + \chi_r \chi_\ell) \quad (2.131)$$

$$\Phi_{\text{ionic}} = N (\chi_\ell \chi_\ell + \chi_r \chi_r). \quad (2.132)$$

At very large  $R$ , the exact wavefunction will have one electron near the left proton and one at the right, as in equation (2.131), which we will refer to as the *covalent* part of the wavefunction. The other terms of (2.130) have both electrons near one proton and none near the other, thus an *ionic* wavefunction. At  $R = \infty$ , these ionic terms lead to the energy of  $\text{H}^-$  and  $\text{H}^+$  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 molecular orbital wavefunction is that both electrons are in the same  $\varphi_g$  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 molecular orbital 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  $R = \infty$ , 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  $R$ .

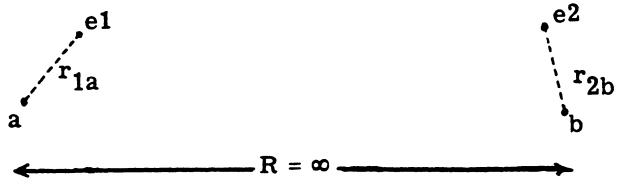


Figure 2.24:

## 2.5 The Valence Bond Description of H<sub>2</sub>

### 2.5.1 The Covalent States

We will now re-examine the ground state of H<sub>2</sub> molecule. However, rather than the approach of the previous section, plotting electrons one by one into the orbital of H<sub>2</sub><sup>+</sup>, 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 2.24. The wavefunction for Figure 2.24 is

$$\Phi_g(\mathbf{r}_1, \mathbf{r}_2) = \chi_\ell(\mathbf{r}_1)\chi_r(\mathbf{r}_2), \quad (2.133)$$

where

$$\chi_\ell(\mathbf{r}_1) = Ne^{-\mathbf{r}_{a1}} \quad (2.134)$$

$$\chi_r(\mathbf{r}_2) = Ne^{-\mathbf{r}_{b2}} \quad (2.135)$$

and  $N$  is the normalization factor.

This wavefunction  $\Phi_a$  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 in (37), namely,

$$\Phi_b(\mathbf{r}_1, \mathbf{r}_2) = \chi_r(\mathbf{r}_1)\chi_\ell(\mathbf{r}_2), \quad (2.136)$$

where the electrons have been interchanged. This wavefunction  $\Phi_b$  is different from  $\Phi_a$  since electron 1 is on the opposite sides of the universe. However, the energies of  $\Phi_b$  and  $\Phi_a$  must be the same, since electrons 1 and 2 have the same properties.

We will find it useful to combine  $\Phi_a$  and  $\Phi_b$  into two new wavefunctions,

$$\Phi_g(1, 2) = \Phi_a(1, 2) + \Phi_b(1, 2) = \chi_\ell(1)\chi_r(2) + \chi_r(1)\chi_\ell(2) \quad (2.137)$$

$$\Phi_u(1, 2) = \Phi_a(1, 2) - \Phi_b(1, 2) = \chi_\ell(1)\chi_r(2) - \chi_r(1)\chi_\ell(2) \quad (2.138)$$

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.

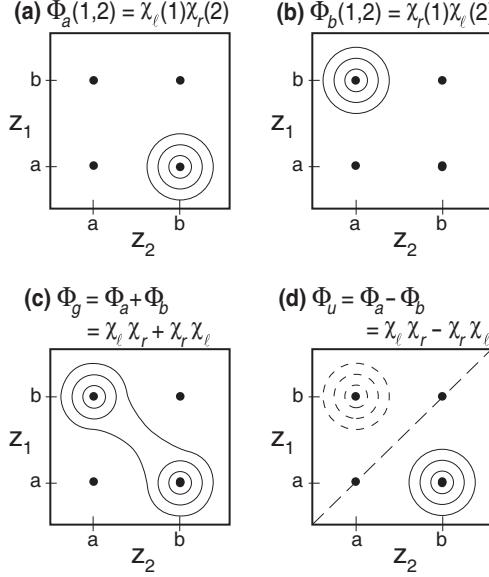


Figure 2.25: (a)  $\Phi_a(1,2) = \chi_\ell(1)\chi_r(2)$ ; (b)  $\Phi_b(1,2) = \chi_r(1)\chi_\ell(2)$ ; (c)  $\Phi_g = \Phi_a + \Phi_b = \chi_\ell\chi_r + \chi_r\chi_\ell$ ; (d)  $\Phi_u = \Phi_a - \Phi_b = \chi_\ell\chi_r - \chi_r\chi_\ell$

In Figure 2.25, we plot the four wavefunctions,  $\Phi_a$ ,  $\Phi_b$ ,  $\Phi_g$ , and  $\Phi_u$ . Here we see that  $\Phi_u$  has a nodal plane, corresponding to  $z_1 = z_2$ , while  $\Phi_g$  does not. Indeed, along the line between the two peaks in Figure 2.25(c), we see that the gradient of the  $\Phi_g$  wavefunction is smaller than that of  $\Phi_a$  or  $\Phi_b$ , while the gradient of the wavefunction is larger. This decrease in the gradient of  $\Phi_g$ , and increase for  $\Phi_u$ , depends upon  $R$  with a bigger effect for smaller  $R$ . Thus, based on kinetic energy, we would expect that  $\Phi_g$  is bonding and  $\Phi_u$  is antibonding, and indeed this is the case, as shown in Figure 2.26.

## 2.5.2 Symmetry

Inversion of the coordinates of the electrons  $r_{a1} \leftrightarrow r_{b1}$  and  $r_{a2} \leftrightarrow r_{b2}$  leads to (see equations (2.134)–(2.135))

$$\chi_\ell(\mathbf{r}_1) \leftrightarrow \chi_r(\mathbf{r}_1). \quad (2.139)$$

Consequently,

$$\hat{I}\Phi_a(\mathbf{r}_1, \mathbf{r}_2) = \chi_r(\mathbf{r}_1)\chi_\ell(\mathbf{r}_2) = \Phi_b(\mathbf{r}_1, \mathbf{r}_2) \quad (2.140)$$

or  $\hat{I}\Phi_b = \Phi_a$ . As a result,

$$\hat{I}\Phi_g = I(\Phi_a + \Phi_b) = (\Phi_b + \Phi_a) = \Phi_g \quad (2.141)$$

$$\hat{I}\Phi_u = I(\Phi_a - \Phi_b) = (\Phi_b - \Phi_a) = -\Phi_u, \quad (2.142)$$

and we see that  $\Phi_g$  and  $\Phi_u$  are indeed gerade and ungerade, respectively.

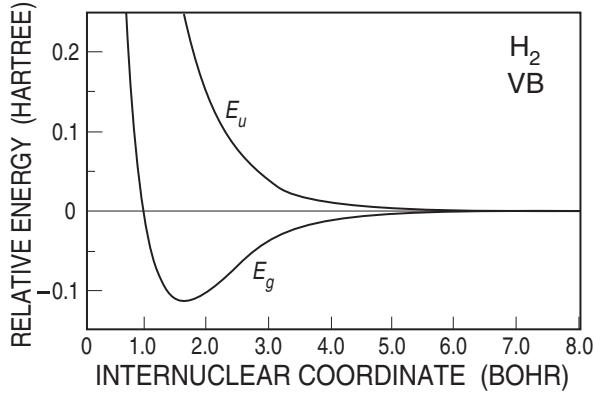


Figure 2.26: The energies  $E_g$  and  $E_u$  for the valence bond wave functions of  $\text{H}_2$ .

### 2.5.3 Comparison of VB and MO Wavefunctions

#### Ground State

The MO wavefunction is (ignoring normalization)

$$\Phi_{gg}^{MO}(1, 2) = \varphi_g(1)\varphi_g(2) = [\chi_\ell\chi_r + \chi_r\chi_\ell] + [\chi_\ell\chi_\ell + \chi_r\chi_r], \quad (2.143)$$

whereas the VB wavefunction is

$$\Phi^{VB}(1, 2) = [\chi_\ell\chi_r + \chi_r\chi_\ell]. \quad (2.144)$$

The energies for these wavefunctions are compared in Figure 2.27, where we see that the valence bond is always better, but that the difference becomes negligible for small  $R$ .

The wavefunctions are compared in Figure 2.28, showing graphically, how the valence bond wavefunction has smaller probability of having  $z_1 = z_2$ , leading to the lower electron repulsion energies. On the other hand, the molecular orbital wavefunction is smoother, leading to smaller kinetic energies. For normal bond distances, the electron repulsion effects dominate so that the valence bond wavefunction is better. However, for very short  $R$ , the kinetic energy becomes dominant so that the molecular orbital and valence bond wavefunctions lead to nearly identical total energies.

#### The $u$ States

Expanding the MOs in terms of AOs, ignoring normalization, leads to

$$\Phi_{gu} = (l+r)(l-r) = ll + rl - lr - rr \quad (2.145)$$

$$\Phi_{ug} = (l-r)(l+r) = ll - rl + lr - rr. \quad (2.146)$$

Thus

$${}^3\Phi_u = \Phi_{gu} - \Phi_{ug} = 2(rl - lr) = \Phi_u^{VB} \quad (2.147)$$

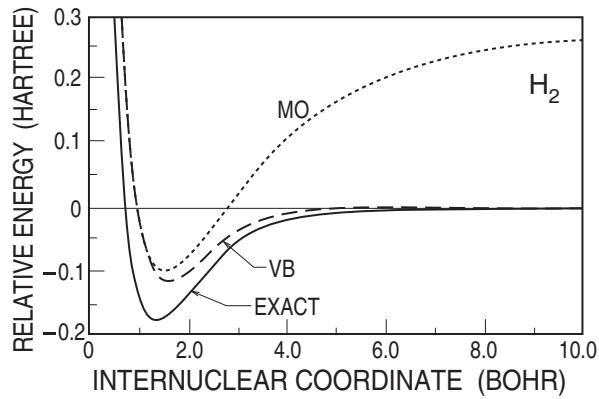


Figure 2.27: The energy of the MO wave function for the ground state of  $H_2$  with comparison to the VB and exact energies.

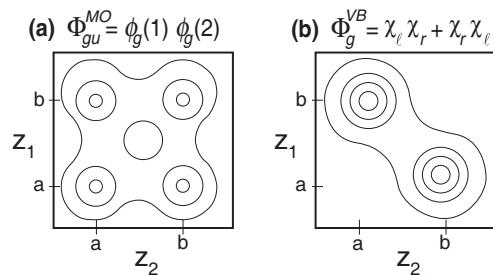


Figure 2.28: (a)  $\Phi_{gu}^{MO} = \varphi_g(1)\varphi_g(2)$  (b)  $\Phi_g^{VB} = \chi_\ell\chi_r + \chi_r\chi_\ell$ .

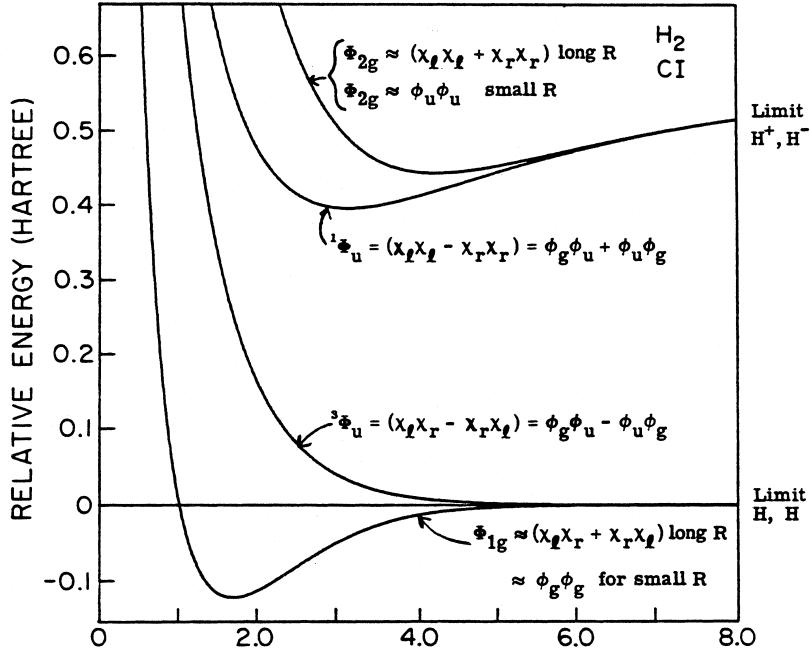


Figure 2.29: Energies for the states of  $H_2$ , using atomic orbitals ( $\zeta = 1.0$ ).

$$^1\Phi_u = gu + ug = 2(l - rr) = \Phi_u^{ION}. \quad (2.148)$$

That is, the first excited state of the MO description  $^3\Phi_u$ , is identical to the first excited state in the valence bond description. Both describe a covalent repulsive state that separates to two free  $H$  atoms, as indicated in Figure 2.29.

### The Second $g$ State

In the MO description

$$\Phi_{uu}^{MO} = (l - r)(l - r) = \frac{[(ll + rr) - (lr + rl)]}{2(1 - S)} \quad (2.149)$$

$$\Phi_{gg}^{MO} = (l + r)(l + r) = \frac{[(ll + rr) + (lr + rl)]}{2(1 + S)} \quad (2.150)$$

(now we include normalization factors). In contrast, the VB description leads to

$$\Phi_g^{VB} = \frac{(lr + rl)}{\sqrt{2(1 + S^2)}} \quad (2.151)$$

$$\Phi_g^{ION} = \frac{(lr + rr)}{\sqrt{2(1 + S^2)}} \quad (2.152)$$

for the covalent and ionic  $g$  states.

The connections between these states are

$$\begin{aligned}\Phi_g^{VB} &= \frac{1}{\sqrt{2(1+S^2)}} [(1+S)\Phi_{gg}^{MO} - (1-S)\Phi_{uu}^{MO}] \\ &= \frac{(1+S)}{\sqrt{2(1+S^2)}} [\Phi_{gg}^{MO} - \lambda\Phi_{uu}^{MO}],\end{aligned}\quad (2.153)$$

where

$$\lambda = \frac{1-S}{1+S}. \quad (2.154)$$

Thus, we can fix up the MO wavefunction so that it behaves like the VB wavefunction, by mixing together the  $\Phi_{gg}^{MO}$  and  $\Phi_{uu}^{MO}$  wavefunctions. This is related to the configuration interaction (CI) wavefunction, as discussed below. For large  $R$ ,  $S = 0$  so that  $\lambda = 1$ , whereas for  $R = 1.6a_0 = 0.8\text{\AA}$ ,  $S = 0.7$ , leading to  $\lambda = 0.18$ . Thus CI is most important at larger  $R$ .

For a more general description of these states, we would consider the wavefunction to have the form

$$\Phi_{1g}^{CI} = C_1\Phi_{gg}^{MO} + C_2\Phi_{uu}^{MO} \quad (2.155)$$

or

$$\Phi_{1g}^{CI} = D_1\Phi_g^{COV} + D_2\Phi_g^{ION} \quad (2.156)$$

and chose the coefficients that lead to the best energy. The equations of (2.155)–(2.156) lead to an equivalent total wavefunction, as can be seen by comparing equations (2.149)–(2.151). This is called the CI wavefunction, and leads to the results shown in Figure 2.29. The excited  $g$  states,  $\Phi_{2g}^{CI}$ , can also be taken to have the form (2.155)–(2.156). However, it must be orthogonal to  $\Phi_{1g}^{CI}$ , leading to

$$\langle \Phi_{2g}^{CI} | \Phi_{1g}^{CI} \rangle = 0. \quad (2.157)$$

The overlap between the covalent and ionic  $g$  states is

$$\langle \Phi_g^{ION} | \Phi_g^{COV} \rangle = \frac{\langle ll + rr | lr + rl \rangle}{2(1+S^2)} = \frac{2S}{1+S^2}. \quad (2.158)$$

Thus, for  $S = 0.7$ ,  $R = 1.6 a_0 = 0.8 \text{\AA}$ , 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 valence bond wavefunction is a close approximation to the  $\Phi_{1g}^{CI}$  wavefunction. However, except for  $S \approx 0$ , the  $\Phi_g^{ION}$  wavefunction is not a good approximation to the excited state,  $\Phi_{2g}^{CI}$ . Instead, we must orthogonalize  $\Phi_g^{ION}$  to  $\Phi_g^{COV}$ , leading to new nodal planes and a much higher energy. This explains why the  $\Phi_{2g}^{CI}$  state is always above the  $\Phi_u^{ION}$  state. Based on the nodal theorem, we would expect that  $\Phi_g^{ION}$ , which has no nodal planes, would have a lower energy than  $\Phi_u^{ION}$ , and it does. However, the only nodeless state is the ground state  $\Phi_{1g}$  which mixes whatever combination of  $\Phi_g^{COV}$  and  $\Phi_g^{ION}$  gives the best energy. The excited  $g$  state,  $\Phi_{2g}^{CI}$ , necessarily has nodal surfaces since it must be orthogonal to the ground state. The result is that the ionic  $g$  state,  $\Phi_{2g}^{CI}$ , is always above the ionic  $u$  state.

### 2.5.4 Quantitative Analysis of Bonding in H<sub>2</sub>

We will analyze the energies of the valence bond wavefunctions for the *g* and *u* states of H<sub>2</sub> in a manner very similar to that used for the LCAO wavefunction of the *g* and *u* states of H<sub>2</sub><sup>+</sup>.

First we consider the energy of the simple product wavefunction

$$\Phi^{cl}(1, 2) = \chi_\ell(1)\chi_r(2) = \chi_\ell\chi_r, \quad (2.159)$$

which is just part of the wavefunction for the *g* and *u* states, equations (2.137) and (2.138). We will refer to this wavefunction as the classical wavefunction, and the energy

$$E^{cl} = \frac{\langle \Phi^{cl} | \hat{H} | \Phi^{cl} \rangle}{\langle \Phi^{cl} | \Phi^{cl} \rangle} = h_{ll} + h_{rr} + J_{lr} + \frac{1}{R} \quad (2.160)$$

as the classical energy.

The total energy of H<sub>2</sub> differs from the classical energy due to the presence of a second term in the wavefunctions (2.137) and (2.138). 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 (2.137), 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

$$E_g = E^{cl} + E_g^x \quad (2.161)$$

$$E_u = E^{cl} + E_u^x \quad (2.162)$$

In Figure 2.30, we show the behavior of these quantities with  $R$ . Just as for H<sub>2</sub><sup>+</sup>, we see that it is the exchange term that dominates the bonding energy.

#### Analysis of $E^{cl}$

At large  $R$ , the one-electron term

$$h_{ll} = \underbrace{\langle \chi_\ell | -\frac{1}{2} \nabla^2 - \frac{1}{r_a} | \chi_1 \rangle}_{\text{atomic energy}} + \underbrace{\langle \chi_\ell | -\frac{1}{r_b} | \chi_\ell \rangle}_{\text{penetration term}}, \quad (2.163)$$

has the form

$$h_{ll} \approx \epsilon_{1s} - \frac{1}{R}. \quad (2.164)$$

(neglecting terms of order  $e^{-2R}$ ), and the Coulomb term has the form

$$J_{lr} \sim \frac{1}{R} \quad (2.165)$$

(neglecting terms of order  $e^{-2R}$ ). Thus, the classical term is just twice the energy of an H atom,  $\epsilon_{1s}$ ,

$$E^{cl} \approx 2\epsilon_{1s} \quad (2.166)$$

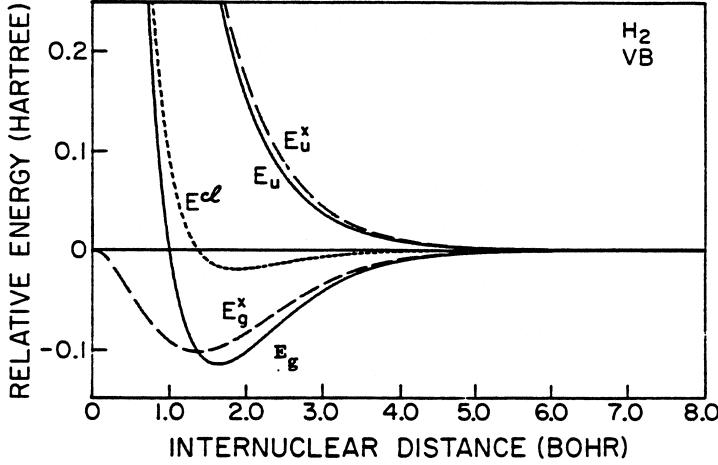


Figure 2.30: The classical ( $E^{cl}$ ), exchange ( $E^x$ ), and total ( $E$ ) energies for the VB wave functions of  $H_2$ . Note that each energy is referenced to the value for  $R = \infty$ , that is,  $E^{cl}(\infty) = E_g(\infty) = E_u(\infty) = -1.0$  and  $E^x(\infty) = E_u^x(\infty) = 0.0$ .

(neglecting terms of order  $e^{-2R}$ ), with no net Coulomb terms. Including the additional penetration terms lead to

$$E^{cl} = 2\epsilon_{1s} + \left[ \frac{1}{R} + \frac{5}{8} + \frac{3}{4}R - \frac{1}{6}R^2 \right] e^{-2R}, \quad (2.167)$$

corresponding to the interpenetration of the two atomic electron clouds. Although negative for  $R > 1.4 a_0$ , this quantity is small, as shown in Figure 2.30. Thus, the bonding of  $H_2$  cannot be explained as due to penetration of the charge clouds of two hydrogen atoms.

### The Exchange Terms

Now we consider the energy of  $\Phi_g^{COV}$ , (2.137),

$$E_g = \frac{\langle \Phi_g | \hat{H} | \Phi_g \rangle}{\langle \Phi_g | \Phi_g \rangle}. \quad (2.168)$$

By symmetry

$$\langle \Phi_g | \Phi_g \rangle = \langle \chi_\ell \chi_r | \Phi_g \rangle + \langle \chi_r \chi_\ell | \Phi_g \rangle = 2 \langle \chi_\ell \chi_r | \Phi_g \rangle \quad (2.169)$$

and

$$\langle \Phi_g | \hat{H} | \Phi_g \rangle = \langle \chi_\ell \chi_r | \hat{H} | \Phi_g \rangle + \langle \chi_r \chi_\ell | \hat{H} | \Phi_g \rangle = 2 \langle \chi_\ell \chi_r | \hat{H} | \Phi_g \rangle. \quad (2.170)$$

Hence,

$$E_g = \frac{\langle \chi_\ell \chi_r | \hat{H} | \Phi_g \rangle}{\langle \chi_\ell \chi_r | \Phi_g \rangle} \quad (2.171)$$

Evaluating the individual terms, we find

$$\langle \chi_\ell \chi_r | \Phi_g \rangle = 1 + \langle \chi_\ell | \chi_r \rangle \langle \chi_r | \chi_\ell \rangle = 1 + S^2 \quad (2.172)$$

and

$$\langle \chi_\ell \chi_r | \hat{H} | \Phi_g \rangle = \langle \chi_\ell \chi_r | \hat{H} | \chi_\ell \chi_r \rangle + \langle \chi_\ell \chi_r | \hat{H} | \chi_r \chi_\ell \rangle = E^{cl} + \mathcal{E}, \quad (2.173)$$

where

$$\mathcal{E} = \langle \chi_\ell \chi_r | \hat{H} | \chi_r \chi_\ell \rangle \quad (2.174)$$

is referred to as the *valence bond exchange term*. Thus,

$$E_g = \frac{E^{cl} + \mathcal{E}}{1 + S^2} = E^{cl} + E_g^x, \quad (2.175)$$

where the exchange energy is

$$E_g^x = \frac{(\mathcal{E} - S^2 E^{cl})}{(1 + S^2)}. \quad (2.176)$$

The same analysis for the  $\Phi_u^{VB}$  wavefunction (2.138) leads to

$$E_u = \frac{E^{cl} - \mathcal{E}}{1 - S^2} = E^{cl} + E_u^x, \quad (2.177)$$

where

$$E_u^x = -\frac{(\mathcal{E} - S^2 E^{cl})}{(1 - S^2)}. \quad (2.178)$$

The close relationship between  $E_g^x$  and  $E_u^x$  is emphasized by defining

$$\bar{\tau} = (\mathcal{E} - S^2 E^{cl}) \quad (2.179)$$

so that

$$E_g^x = \frac{\bar{\tau}}{(1 + S^2)} \quad (2.180)$$

$$E_u^x = \frac{-\bar{\tau}}{(1 - S^2)}. \quad (2.181)$$

We use  $\bar{\tau}$  here in order to distinguish this quantity for  $\text{H}_2$  from the  $\tau$  of  $\text{H}_2^+$ . From equations (2.180) and (2.181), the energy separation between the  $g$  and  $u$  states is

$$E_g - E_u = \frac{2\bar{\tau}}{1 - S^4}. \quad (2.182)$$

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  $\varphi_g$  and  $\varphi_u$  state have energies

$$\epsilon_g = \epsilon^{cl} + \left[ \frac{1}{1+S} \right] \tau \quad (2.183)$$

$$\epsilon_u = \epsilon^{cl} - \left[ \frac{1}{1-S} \right] \tau \quad (2.184)$$

$$\epsilon_g - \epsilon_u = \frac{2\tau}{(1-S^2)}, \quad (2.185)$$

with

$$\epsilon^{cl} = h_{ll} + \frac{1}{R} \quad (2.186)$$

$$\tau = h_{lr} - Sh_{ll}. \quad (2.187)$$

### Analysis of $\mathcal{E}$

The components of  $\mathcal{E}$  (2.174) are

$$\langle \chi_\ell \chi_r | h(1) | \chi_r \chi_\ell \rangle = \langle \chi_\ell | h | \chi_r \rangle \langle \chi_r | \chi_\ell \rangle = h_{lr} S \quad (2.188)$$

$$\langle \chi_\ell \chi_r | h(2) | \chi_r \chi_\ell \rangle = \langle \chi_\ell | \chi_r \rangle \langle \chi_r | h | \chi_\ell \rangle = Sh_{rl} \quad (2.189)$$

$$\langle \chi_\ell \chi_r | \frac{1}{r_{12}} | \chi_r \chi_\ell \rangle = \int d\tau \chi_\ell^*(1) \chi_r(1) \int d\tau_2 \frac{1}{r_{12}} \chi_r^*(2) \chi_\ell(2) = K_{lr} \quad (2.190)$$

$$\langle \chi_\ell \chi_r | \frac{1}{R} | \chi_r \chi_\ell \rangle = \frac{S^2}{R}, \quad (2.191)$$

where  $S$  is the overlap and  $K_{lr}$  is referred to as an exchange integral. Note the distinction between  $\mathcal{E}$ , the VB exchange term, and  $K_{lr}$ , the exchange integral. Thus,

$$\mathcal{E} = 2Sh_{lr} + K_{lr} + \frac{S^2}{R}. \quad (2.192)$$

### Analysis of $\bar{\tau}$

Using  $E^{cl}$  from equation (2.160) in (2.179), we find that  $\bar{\tau} = \bar{\tau}_1 + \bar{\tau}_2$ , where

$$\bar{\tau}_1 = [2Sh_{lr} - S^2(h_{ll} + h_{rr})] = 2S[h_{lr} - Sh_{ll}] = 2S\tau \quad (2.193)$$

$$\bar{\tau}_2 = [K_{lr} - S^2 J_{lr}] \quad (2.194)$$

are the one- and two-electron parts, respectively (the  $1/R$  terms cancel). These quantities are plotted in Figure 2.31, where we see that  $\bar{\tau}_2$  has a smaller magnitude than  $\bar{\tau}_1$ . Thus,  $\bar{\tau} \approx \bar{\tau}_1$ . Comparing equations (??) and (??), we see that

$$\bar{\tau} = 2S\tau. \quad (2.195)$$

That is, the one-electron part of  $\bar{\tau}$  for  $H_2$  is related directly to the  $\tau$  of  $H_2^+$ , leading to

$$\bar{\tau} \approx \bar{\tau}_1 - 2S\tau, \quad (2.196)$$

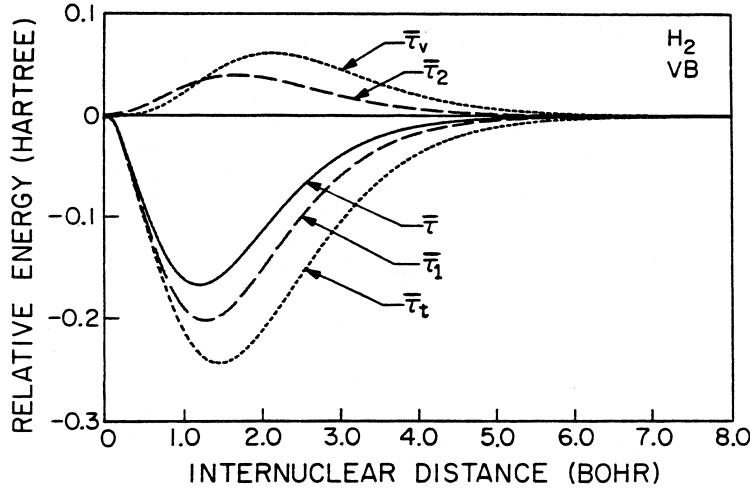


Figure 2.31: The total exchange term ( $\bar{\tau}$ ) and the one-electron ( $\bar{\tau}_1$ ) and two-electron ( $\bar{\tau}_2$ ) parts. The potential ( $\bar{\tau}_v$ ) and kinetic ( $\bar{\tau}_t$ ) parts of  $\bar{\tau}_1$  are also shown separately. All results are for  $H_2$ .

where  $\tau$  is the quantity for  $H_2^+$ . Thus, for  $H_2$  the bonding energy is determined by

$$E_g^x \approx \frac{2S\tau}{1+S^2} = \bar{E}_g^x \quad (2.197)$$

$$E_u^x \approx -\frac{2S\tau}{1-S^2} = \bar{E}_u^x \quad (2.198)$$

whereas for  $H_2^+$  it is determined by

$$\epsilon_g^x = \frac{\tau}{1+S} \quad (2.199)$$

$$\epsilon_u^x = -\frac{\tau}{1-S}. \quad (2.200)$$

These quantities are compared in Figure 2.32.

#### Analysis of $\bar{\tau} + 1 = 2S\tau$

Since the quantities  $\bar{\tau}_1$  and  $\tau$  dominating the bonding in  $H_2$  and  $H_2^+$  are related,

$$\bar{\tau}_1 = 2S\tau, \quad (2.201)$$

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 Figures 2.33(a) and 2.33(b). In both cases, the kinetic energy is decreased from that in the classical wavefunctions, Figures 2.33(c)

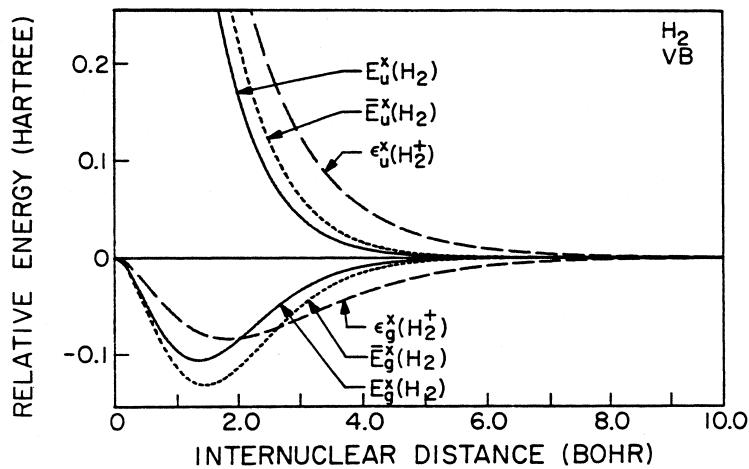


Figure 2.32: The exchange energies ( $E_g^x$  and  $E_u^x$ ) for  $H_2^+$  and  $H_2$ . In addition, the one-electron approximation  $\bar{E}^x$  to the  $E^x$  for  $H_2$  is shown for each state.

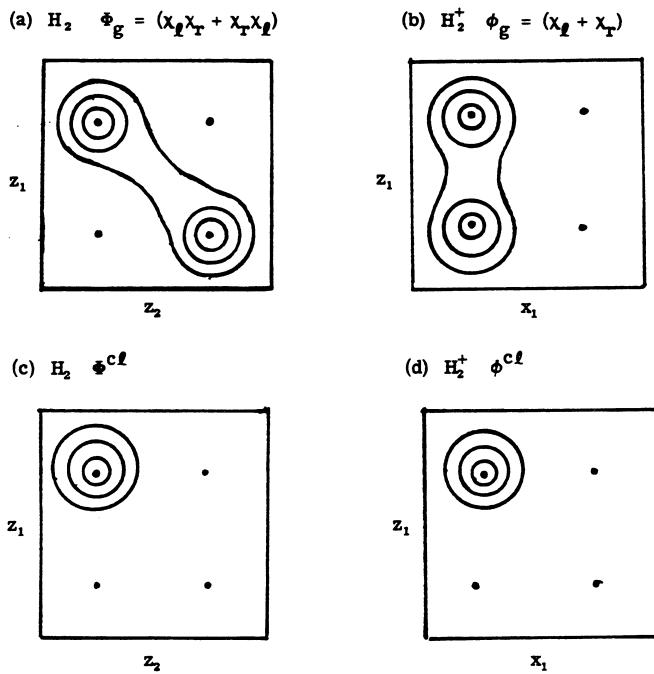


Figure 2.33: (a)  $H_2$ ,  $\Phi_g = (\chi_\ell \chi_r + \chi_r \chi_\ell)$ ; (b)  $H_2^+$ ,  $\varphi_g = \phi_g = (\chi_\ell + \chi_r)$ ; (c)  $H_2$ ,  $\Phi^{cl}$ ; (d)  $H_2^+$ ,  $\varphi^{cl}$

and 2.33(d). The decrease in the kinetic energy for electron 1 is obtained by examining the gradients in the vertical direction (ordinate) of Figure 2.33. Here we see that  $\text{H}_2^+$  leads to larger decrease than  $\text{H}_2$ . Thus, the combination is  $S\tau$  for  $\text{H}_2$ , but  $\tau$  for  $\text{H}_2^+$ . However, for  $\text{H}_2$  there is a second electron (number 2) that has a similar decrease. Thus, for  $\text{H}_2$  the net is  $2S\tau$  as compared to  $\tau$  for  $\text{H}_2^+$ .

### Comparison of Bonding in $\text{H}_2$ and $\text{H}_2^+$

Although the bonding energies of  $\text{H}_2$  and  $\text{H}_2^+$  are both determined by  $\tau$ , we see from (2.197) to (2.200) that the value of the overlap  $S$  also plays an important role. From an earlier section, the form of  $\tau$  at large  $R$  is

$$\tau \approx -\left(\frac{2}{R}\right)S, \quad (2.202)$$

hence,

$$\bar{\tau}_1 = 2S\tau \approx -\left(\frac{4}{R}\right)S^2. \quad (2.203)$$

Thus, the bonding in  $\text{H}_2^+$  is proportional to  $S$ , but the bonding in  $\text{H}_2$  is proportional to the square of  $S$ .

At  $R = 1.6 a_0$ , the value of  $S$  is  $S = 0.7$ , and hence, for  $\text{H}_2$ ,  $E_g^x = 0.94\tau$  and  $E_u^x = -2.75\tau$ . For  $\text{H}_2^+$ ,  $\epsilon_g^x = 0.67\tau$  and  $\epsilon_u^x = -3.33\tau$ . Thus, the  $g$  state of  $\text{H}_2$  should have a bond energy about 50% larger than the  $g$  state of  $\text{H}_2^+$ , while the  $u$  state of  $\text{H}_2$  should be 17% less repulsive than the  $u$  state of  $\text{H}_2^+$ . In addition, we see that the  $u$  state of  $\text{H}_2$  should be about three times as repulsive as the  $g$  state is attractive.

At  $R = 3 a_0$ , the overlap is  $S = 0.1$ , and hence, we obtain for  $\text{H}_2$ ,  $E_g^x = 0.20\tau$  and  $E_u^x = -0.20\tau$ . For  $\text{H}_2^+$ ,  $\epsilon_g^x = 0.91\tau$  and  $\epsilon_u^x = -1.11\tau$ . Thus, at this large  $R$ , the  $g$  and  $u$  states of  $\text{H}_2^+$  are five times as attractive, or repulsive, as the  $g$  and  $u$  states of  $\text{H}_2$ . That is, at large  $R$ , the one-electron bond is much stronger than the two-electron bond. This difference is relative bond strengths of  $\text{H}_2$  and  $\text{H}_2^+$  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 for  $\text{H}_2$ ,  $E_g^x = \tau$  and for  $\text{H}_2^+$ ,  $\epsilon_g^x = 1/2\tau$ , leading to an  $\text{H}_2$  bond twice that of  $\text{H}_2^+$ , the commonly expected result. Actually,  $S = 1$  implies  $R = 0$ , which in turn implies  $\tau = 0$ .

## 2.6 Appendices

### 2.6.1 Energy Quantities of $\text{H}_2^+$

We will consider an atomic orbital of the form

$$\chi = \sqrt{\frac{\zeta^3}{\pi}} e^{-\zeta r} \quad (2.204)$$

centered at each of the two nuclei of  $\text{H}_2^+$ . The coordinates are indicated in Figure 2.34.

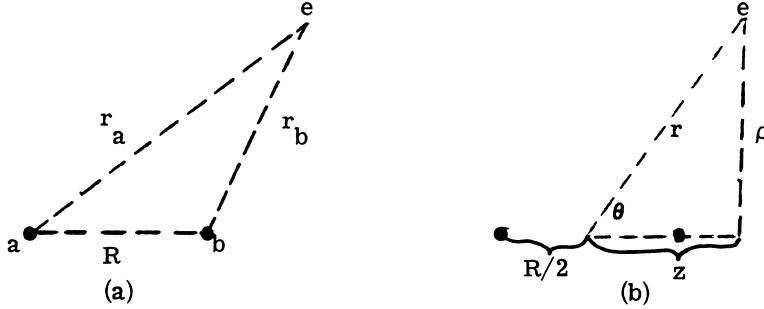


Figure 2.34:

With  $\zeta = 1$ , the orbitals (2.204) correspond to hydrogen  $1s$  orbitals on each center. First, we evaluate the atomic integrals for general  $\zeta$ , then the new energy quantities occurring in  $H_2^+$ . First we consider the atomic energy quantities.

### Atomic Energy Quantities

The norm of  $\chi$  is

$$\begin{aligned} \langle \chi | \chi \rangle &= \left( \frac{\zeta^3}{\pi} \right) \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\varphi \int_0^\infty r^2 dr e^{-2\zeta r} \\ &= 4\zeta^3 \int_0^\infty r^2 dr e^{-2\zeta r} = \frac{1}{2} \int_0^\infty p^2 e^{-p} dp = 1, \end{aligned} \quad (2.205)$$

where we set  $p = 2\zeta r$  and used

$$\int_0^\infty p^m e^{-p} dp = m!. \quad (2.206)$$

Similarly, the atomic potential energy is

$$\langle \chi | -\frac{1}{r} | \chi \rangle = -4\zeta^3 \int_0^\infty r^2 dr e^{-2\zeta r} = -\zeta \quad (2.207)$$

and the kinetic energy is

$$\langle \chi | -\frac{1}{2} \nabla^2 | \chi \rangle = \frac{1}{2} \langle |\nabla \chi|^2 \rangle = \frac{1}{2} \zeta^2 \langle \chi | \chi \rangle = \frac{1}{2} \zeta^2. \quad (2.208)$$

## Elliptic Coordinates

In evaluating the energy quantities for diatomic molecules, it is convenient to use elliptic coordinates

$$\xi = \frac{(r_a + r_b)}{R} \quad (2.209)$$

$$\eta = \frac{(r_a - r_b)}{R} \quad (2.210)$$

and  $\varphi$  equal to azimuthal angle about the  $z$  axis, measured from the  $xz$  plane, in place of the cylindrical polar coordinate  $\rho$ ,  $\varphi$ , and  $z$  or spherical coordinates  $r$ ,  $\theta$ , and  $\varphi$ , see Figure 2.34(b). The geometric condition defining an ellipse is that the sum of the distances to the two foci is a constant. Hence, each curve of constant  $\xi$  corresponds to an ellipse. Similarly, from the defining condition of a hyperbola, each surface of constant  $\eta$  corresponds to a hyperbola. The range of the elliptic coordinates is

$$0 \leq \xi < \infty \quad (2.211)$$

$$-1 \leq \eta \leq +1 \quad (2.212)$$

$$0 \leq \varphi < 2\pi \quad (2.213)$$

The volume increments in the various coordinate systems are

$$\begin{aligned} d\tau &= dx dy dz \\ d\tau &= \rho d\rho d\varphi dz \\ d\tau &= r^2 \sin \theta dr d\theta d\varphi \\ d\tau &= \frac{1}{8} R^3 (\xi^2 - \eta^2) d\xi d\eta d\varphi \end{aligned} \quad (2.214)$$

The latter relationship can be derived from

$$\begin{aligned} x &= \frac{1}{2} R \sqrt{(\xi^2 - 1)(1 - \eta^2)} \cos \varphi \\ y &= \frac{1}{2} R \sqrt{(\xi^2 - 1)(1 - \eta^2)} \sin \varphi \\ z &= \frac{1}{2} R \xi \eta \end{aligned}$$

since the Jacobian  $\frac{1}{8} R^3 (\xi^2 - \eta^2)$  is just the determinant of the derivative matrix.

From Figure 2.34(b), we see that

$$\begin{aligned} r_b^2 &= \rho^2 + \left( z - \frac{R}{2} \right)^2 \\ r_a^2 &= \rho^2 + \left( z + \frac{R}{2} \right)^2 \\ r^2 &= \rho^2 + z^2, \end{aligned} \quad (2.215)$$

and hence,

$$\frac{1}{2} (r_a^2 + r_b^2) = r^2 + \left( \frac{R}{2} \right)^2 \quad (2.216)$$

and

$$r_a^2 - r_b^2 = 2zR. \quad (2.217)$$

From (2.209)–(2.210) we find

$$\begin{aligned} \frac{1}{2} (\xi^2 + \eta^2) &= \frac{(r_a^2 + r_b^2)}{R^2} \\ \xi\eta &= \frac{(r_a^2 - r_b^2)}{R^2} \\ \xi^2 - \eta^2 &= \frac{4r_a r_b}{R^2} \end{aligned} \quad (2.218)$$

and hence,

$$r^2 = \frac{1}{4} R^2 [\xi^2 + \eta^2 - 1]. \quad (2.219)$$

These relations will be useful in the next section.

In evaluating integrals over  $\xi$ , the following integral will be useful

$$\int_{x_0}^{\infty} x^m e^{-\alpha x} dx = \frac{m! e^{-\alpha x_0}}{a^{m+1}} \sum_{k=0}^m \frac{(ax_0)^k}{k!} = A_m(\alpha x_0) \quad (2.220)$$

For  $x_0 = 1$  and  $m = 0, 1$ , and  $2$ , this becomes

$$A_0(\alpha) = \frac{1}{\alpha} e^{-\alpha} \quad (2.221)$$

$$A_1(\alpha) = \frac{1}{\alpha^2} e^{-\alpha} [1 + \alpha] \quad (2.222)$$

$$A_2(\alpha) = \frac{2}{\alpha^3} e^{-\alpha} \left[ 1 + \alpha + \frac{1}{2} \alpha^2 \right] \quad (2.223)$$

### Diatom Energy Quantities

First we evaluate the overlap integral,

$$S = \langle \chi_\ell | \chi_r \rangle. \quad (2.224)$$

Using (2.204), (2.214), (2.221) andqn (2.223), this becomes

$$\begin{aligned} S = \int d\tau \chi_\ell \chi_r &= \left( \frac{\zeta^3}{\pi} \right) \left( \frac{R^3}{8} \right) (2\pi) \int_1^{\infty} d\xi \int_{-1}^{+1} d\eta (\xi^2 - \eta^2) e^{-2\zeta R\xi} \\ &= e^{-\zeta r} \left[ 1 + (\zeta R) + \frac{1}{3} (\zeta R)^2 \right] \end{aligned} \quad (2.225)$$

There are two terms involved in evaluating the potential energy of  $H_2^+$ , the exchange terms

$$V_{lr} = \langle \chi_\ell | \hat{v} | \chi_r \rangle, \quad (2.226)$$

where

$$\hat{v} = -\frac{1}{r_a} - \frac{1}{r_b} \quad (2.227)$$

and

$$V_{ll} = \langle \chi_\ell | \hat{v} | \chi_\ell \rangle. \quad (2.228)$$

In this section, we evaluate  $V_{lr}$ .

First we convert  $\hat{v}$  to elliptic coordinates

$$\hat{v} = -\frac{(r_a + r_b)}{r_a r_b} = -\frac{4\xi}{R(\xi^2 - \eta^2)} \quad (2.229)$$

using (2.209)–(2.218). Combining (2.229) with (2.214) leads to

$$\hat{v} d\tau = -\frac{1}{2} R^2 \xi d\xi d\eta d\varphi, \quad (2.230)$$

and integrating over  $\varphi$ , we obtain

$$V_{lr} = \left(-\frac{R^2}{2}\right) \left(\frac{\zeta^3}{\pi}\right) (2\pi) \int_1^\infty \xi d\xi e^{-\zeta R\xi} \int_{-1}^{+1} d\eta = -2\zeta e^{-\zeta R} (1 + \zeta R). \quad (2.231)$$

The other potential energy term  $V_{ll}$  has two parts

$$V_{ll} = \langle \chi_\ell | -\frac{1}{r_a} | \chi_\ell \rangle + \langle \chi_\ell | -\frac{1}{r_b} | \chi_\ell \rangle, \quad (2.232)$$

the first of which is

$$V_{ll}^{(1)} = \langle \chi_\ell | -\frac{1}{r_a} | \chi_\ell \rangle \quad (2.233)$$

is a one center integral, involving only the left nucleus, and the other of which is

$$V_{ll}^{(2)} = \langle \chi_\ell | -\frac{1}{r_b} | \chi_\ell \rangle \quad (2.234)$$

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 on the right nucleus and is referred to as the *penetration integral*.

As shown below,

$$V_{ll}^{(2)} = A + B, \quad (2.235)$$

where

$$A = -\frac{Q}{R} \quad (2.236)$$

$$B = -4\pi \left(\frac{\zeta^3}{\pi}\right) \int_R^\infty r_a dr_a e^{-2\zeta r_a} \quad (2.237)$$

and

$$Q = 4\pi \left( \frac{\zeta^3}{\pi} \right) \int_0^R r_a^2 dr_a e^{-2\eta r_a}. \quad (2.238)$$

Using

$$\int_0^R r_a^2 dr e^{-\alpha r} = \frac{2}{\alpha^3} \left[ 1 - \left( 1 + \alpha R + \frac{1}{2}\alpha^2 R^2 \right) e^{-\alpha R} \right], \quad (2.239)$$

we obtain

$$Q = \left[ 1 - (1 + 2\zeta R + 2\zeta^2 R^2) e^{-2\zeta R} \right]. \quad (2.240)$$

Using (2.220), we obtain

$$B = -\zeta e^{-2\zeta R} (1 + 2\zeta R), \quad (2.241)$$

and hence,

$$V_{ll}^{(2)} = -\frac{1}{R} (1 - e^{-2\zeta R}) + \zeta e^{-2\zeta R}. \quad (2.242)$$

The two-center kinetic energy integral is

$$t_{lr} = \langle \chi_\ell | -\frac{1}{2} \nabla^2 | \chi_r \rangle, \quad (2.243)$$

which, from the Appendix in Chapter 1, becomes

$$t_{lr} = \frac{1}{2} \langle \nabla \chi_\ell \cdot \nabla \chi_r \rangle = \frac{1}{2} \int d\tau (\nabla \chi_\ell \cdot \nabla \chi_r). \quad (2.244)$$

Since

$$r_b = \sqrt{x^2 + y^2 + \left( z - \frac{R}{2} \right)^2} \quad (2.245)$$

$$r_a = \sqrt{x^2 + y^2 + \left( z + \frac{R}{2} \right)^2}, \quad (2.246)$$

we obtain

$$\hat{\nabla} e^{-\zeta r_a} = -\frac{\zeta}{r_a} e^{-\zeta r_a} \left[ x\hat{e}_x + y\hat{e}_y + \left( z + \frac{1}{2}R \right) \hat{e}_z \right] \quad (2.247)$$

$$\hat{\nabla} e^{-\zeta r_b} = -\frac{\zeta}{r_b} e^{-\zeta r_b} \left[ x\hat{e}_x + y\hat{e}_y + \left( z - \frac{1}{2}R \right) \hat{e}_z \right] \quad (2.248)$$

where  $\hat{e}_x$  denotes a unit vector in the  $x$  direction. Hence,

$$(\nabla e^{-\zeta r_a}) \cdot (\nabla e^{-\zeta r_b}) = \left( \frac{\zeta^2}{r_a r_b} \right) e^{-\zeta R \xi} \left[ x^2 + y^2 + \left( z^2 - \frac{1}{4}R^2 \right) \right] \quad (2.249)$$

Using (2.214), (2.219), and (2.218), we obtain

$$d\tau (\nabla \chi_\ell \cdot \nabla \chi_r) = \left( \frac{R^3}{8} \right) \left( \frac{4\zeta^2}{R^2} \right) \left( \frac{\zeta^3}{\pi} \right) \left( \frac{R^2}{4} \right) e^{-\zeta R \xi} (\xi^2 + \eta^2 - 2) d\xi d\eta d\varphi. \quad (2.250)$$

Integrating over  $\varphi$ , and substituting into (2.244), leads to

$$\begin{aligned} t_{lr} &= \frac{1}{8} R^3 \zeta^5 \int_1^\infty d\xi e^{-\zeta R \xi} \int_{-1}^{+1} d\eta (\xi^2 + \eta^2 - 2) \\ &= \frac{1}{4} R^2 \zeta^5 \int_1^\infty \left( \zeta^2 - \frac{5}{3} \right) e^{-\zeta R \xi} d\xi \\ &= \frac{1}{2} \zeta^2 e^{-\zeta R} \left[ 1 + \zeta R - \frac{1}{3} (\zeta R)^2 \right]. \end{aligned} \quad (2.251)$$

### Summary

Collecting together the quantities of the previous sections, we have

$$\chi = \sqrt{\frac{\zeta^3}{\pi}} e^{-\zeta r} \quad (2.252)$$

$$t_{ll} = \langle \chi_\ell | t | \chi_\ell \rangle = \frac{1}{2} \zeta^2 \quad (2.253)$$

$$V_{ll}^{(1)} = \langle \chi_\ell | -\frac{1}{r_a} | \chi_\ell \rangle = -\zeta \quad (2.254)$$

$$S = \langle \chi_\ell | \chi_r \rangle = e^{-\zeta R} \left[ 1 + \zeta R + \frac{1}{3} (\zeta R)^2 \right] \quad (2.255)$$

$$t_{lr} = \langle \chi_\ell | t | \chi_r \rangle = \frac{1}{2} \zeta^2 e^{-\zeta R} \left[ 1 + \zeta R - \frac{1}{3} (\zeta R)^2 \right] \quad (2.256)$$

$$V_{lr} = \langle \chi_\ell | \left( -\frac{1}{r_a} - \frac{1}{r_b} \right) | \chi_r \rangle = -2\zeta e^{-\zeta R} (1 + \zeta R) \quad (2.257)$$

$$V_{ll}^{(2)} = -\frac{1}{R} [1 - (1 + \zeta R) e^{-1\zeta R}] \quad (2.258)$$

### Qualitative Examination of Diatomic Quantities

The amplitude of  $\chi_r$  evaluated at the left nucleus is

$$\chi_r(R) = \sqrt{\frac{\zeta^3}{\pi}} e^{-\zeta R} \quad (2.259)$$

while the amplitude of  $\chi_\ell$  at the left nucleus is

$$\chi_\ell(0) = \sqrt{\frac{\zeta^3}{\pi}} \quad (2.260)$$

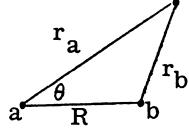


Figure 2.35:

Thus,

$$\chi_r(R) = e^{-\zeta R} \chi_\ell(0) \quad (2.261)$$

If  $\chi_\ell$  were highly concentrated about the left nucleus, the overlap would be given by

$$S = e^{-\zeta R} \quad (2.262)$$

Comparing with the correct formula (2.225), we see that the approximate form (2.262) has the correct exponential behavior on  $R$  but the numerical coefficient in (2.262) is correct only for  $R = 0$ . Using  $R = 2.0 a_0$  and  $\zeta = 1.0$  in (2.225), leads to a coefficient of 3.33, and using  $R = 6.0 a_0$  leads to a coefficient of 19.0, many times the value obtained with (2.262).

## 2.6.2 The Legendre Expansion

Consider a system such as in Figure 2.34. 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 Figure 2.35.

The relation between these coordinates is

$$r_b^2 = r_a^2 + R^2 - 2r_a R \cos \theta \quad (2.263)$$

A case of particular importance, is to convert  $1/r_b$  over to the new coordinates. This leads to

$$\frac{1}{r_b} = \frac{1}{r_a \sqrt{1 + \rho^2 - 2\rho \cos \theta}} \quad (2.264)$$

where  $\rho = R/r_a$ . If  $\rho < 1$ , the radical in (2.264) can be expanded as

$$\frac{1}{\sqrt{1 + \rho^2 - 2\rho \cos \theta}} = \sum_{l=0}^{\infty} \rho^l P_l(\cos \theta), \quad (2.265)$$

where the  $P_\ell(\cos \theta)$  are the Legendre polynomials

$$P_0(\cos \theta) = 1, \quad (2.266)$$

$$P_1(\cos \theta) = \sin \theta, \quad (2.267)$$

$$P_2(\cos \theta) = \frac{1}{2} (3 \cos^2 \theta - 1) \quad (2.268)$$

etc. Thus (2.264) becomes

$$\frac{1}{r_b} = \sum_{t=0}^{\infty} \frac{(r_<)^t}{(r_>)^{l+1}} P_\ell(\cos \theta), \quad (2.269)$$

where  $r_<$  and  $r_>$  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

$$V = \int d\tau \rho_a(r_a) \frac{1}{r_b} = 2\pi \sum_{t=0}^{\infty} \int_0^{\infty} r_a^2 dr_a \rho_a(r_a) \left[ \frac{(r_<)^t}{(r_>)^{l+1}} \right] \int_0^{\pi} \sin \theta d\theta P_\ell(\cos \theta), \quad (2.270)$$

where we integrated over the  $\varphi$  coordinate. The Legendre polynomials have the property that

$$\int_0^{\pi} \sin \theta d\theta P_\ell(\cos \theta) = 2\delta_{l0}, \quad (2.271)$$

so that (2.270) becomes

$$V = 4\pi \sum_{t=0}^{\infty} \int_0^{\infty} r_a^2 dr_a \rho_a(r_a) \frac{1}{r_>} = 4\pi \left\{ \frac{1}{R} \int_0^R r_a^2 dr_a \rho_a(r_a) + \int_R^{\infty} r_a dr_a \rho_a(r_a) \right\}. \quad (2.272)$$

The quantity

$$Q = 4\pi \int_0^R r_a^2 dr_a \rho_a(r_a) \quad (2.273)$$

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

$$\delta Q = 4\pi r_a^2 \rho_a(r_a) \delta r_a \quad (2.274)$$

is the amount of charge on a sphere of radius  $r_a$  and thickness  $\delta r_a$ . The potential within such a uniformly charged sphere, is constant and equal to  $1/r_a \delta Q$  as implied by the second term of (2.272).

### 2.6.3 Coulomb and Exchange Integrals

In the text, we indicated that

$$J_{ij} \geq K_{ij} \geq 0. \quad (2.275)$$

These relationships are now derived.

$$J_{ij} \geq 0$$

The Coulomb integral is

$$J_{ij} = \int d\tau_1 \varphi_i^*(1) \varphi_i(1) \int d\tau_2 \frac{1}{r_{12}} \varphi_j^*(2) \varphi_j(2) = \int d\tau_1 d\tau_2 \frac{\varphi_i^*(1) \varphi_i(1) \varphi_j^*(2) \varphi_j(2)}{r_{12}}. \quad (2.276)$$

Since the integrand is positive for all values of  $\mathbf{r}_1$  and  $\mathbf{r}_2$ , the integral must be positive. This integral is also denoted as

$$J_{ij} = [\varphi_i^* \varphi_i | \varphi_j^* \varphi_j], \quad (2.277)$$

where the orbitals on the left are for electron 1, and those on the right are for electron 2. This is often called *chemist's notation* for the two-electron integrals.

$$K_{ij} \geq 0$$

The exchange integral is

$$K_{ij} = \int d\tau_1 \varphi_i^*(1) \varphi_i(1) \int d\tau_2 \frac{1}{r_{12}} \varphi_j^*(2) \varphi_i(2) = [\varphi_i^* \varphi_j | \varphi_j^* \varphi_i]. \quad (2.278)$$

To prove that  $K_{ij} \geq 0$ , we set

$$\varphi_i = \xi + i\eta_i \quad (2.279)$$

$$\varphi_j = \xi_j + i\eta_j \quad (2.280)$$

where  $\xi_i$ ,  $\eta_i$ ,  $\xi_j$ , and  $\eta_j$  are real. This substitution leads to

$$\begin{aligned} K_{ij} &= [\{\xi_i(1) - i\eta_i(1)\} \{\xi_j(1) + i\eta_j(1)\} | \{\xi_i(2) + i\eta_i(2)\} \{\xi_j(2) - i\eta_j(2)\}] \\ &= \{\xi_i \xi_j + \eta_i \eta_j + i(\xi_i \eta_j - \eta_i \xi_j)\} |\xi_i \xi_j + \eta_i \eta_j - i(\xi_i \eta_j - \eta_i \xi_j)|. \end{aligned}$$

We now define the charge distributions  $\rho_1$  and  $\rho_2$  as

$$\rho_1 = \xi_i \xi_j + \eta_i \eta_j \quad (2.281)$$

$$\rho_2 = \xi_i \xi_j - \eta_i \eta_j. \quad (2.282)$$

This leads to

$$K_{ij} = [\rho_1 + i\rho_2 | \rho_1 - i\rho_2] = \underbrace{[\rho_1 | \rho_1]}_{\geq 0} + i \underbrace{\{[\rho_2 | \rho_1] - [\rho_1 | \rho_2]\}}_{=0} + \underbrace{[\rho_2 | \rho_2]}_{\geq 0}, \quad (2.283)$$

and hence,  $K_{ij} \geq 0$ .

$$J_{ij} \geq K_{ij}$$

To show that  $J_{jj} \geq K_{ij}$ , we consider the wavefunction

$$\Psi(1, 2) = \varphi_i \varphi_j - \varphi_j \varphi_i \quad (2.284)$$

The electron-electron interaction energy for this state is

$$\langle \Psi | \frac{1}{r_{12}} | \Psi \rangle = \int \int d\tau_1 d\tau_2 \frac{1}{r_{12}} |\psi(1, 2)|^2 \geq 0, \quad (2.285)$$

since the integrand is positive everywhere. Substituting the wavefunction from above leads to

$$\langle \Psi | \frac{1}{r_{12}} | \Psi \rangle = 2(J_{ij} - K_{ij}) \quad (2.286)$$

and hence,  $J_{ij} \geq K_{ij}$ . Expression (16) provides the physical significance of  $K_{ij}$ . It is the change in electron repulsion energy upon superimposing both products of orthogonal orbitals  $\varphi_i \varphi_j$ . That is, wavefunctions

$$\frac{1}{\sqrt{2}} [\varphi_i \varphi_j \pm \varphi_j \varphi_i] \quad (2.287)$$

lead to Coulomb repulsion energies of  $J_{ij} \pm K_{ij}$ .

## 2.6.4 Two-Electron Integrals of H<sub>2</sub>

### The Coulomb Integral

The Coulomb integral,  $J_{lr}$  has the form

$$J_{lr} = \langle \chi_\ell(1) \chi_\ell(1) | \frac{1}{r_{12}} | \chi_r(2) \chi_r(2) \rangle = \int d\tau_2 \left[ \int d\tau_1 \chi_\ell^*(1) \chi_\ell(1) \frac{1}{r_{12}} \right] \chi_r^*(2) \chi_r(2) \quad (2.288)$$

where  $\chi_\ell$  and  $\chi_r$  are 1s atomic orbitals centered on the left and right protons. Letting

$$J_\ell(2) = \int d\tau_1 \chi_\ell^*(1) \chi_\ell(1) \frac{1}{r_{12}}, \quad (2.289)$$

we have

$$J_{lr} = \int d\tau_1 J_\ell(2) \chi_r^*(2) \chi_r(2). \quad (2.290)$$

In the remainder of this section, we will assume  $\chi_\ell$  and  $\chi_r$  are real.

First we evaluate  $J_\ell$  by expanding  $1/r_{12}$  as

$$\frac{1}{r_{12}} = \sum_{k=0}^{\infty} \sum_{m=-k}^k \frac{(k-|m|)! r_{<}^k}{(k+|m|)! r_{>}^{k+1}} P_k^{|m|}(\cos \theta_1) P_k^{|m|}(\cos \theta_2) e^{im(\varphi_1 - \varphi_2)} \quad (2.291)$$

the Laplace expansion, where  $r_{12}$  is the distance between the points with spherical coordinates  $r_1, \theta_1$ , and  $\varphi_1$ , and  $r_2, \theta_2$ , and  $\varphi_2$ .

Note that both  $r_1$  and  $r_2$  are with respect to the left-hand center. Since  $\chi_\ell$  is spherically symmetric, about center  $l$ , the integrals over  $\theta_1$  and  $\theta_2$  will be nonzero only when  $k = m = 0$

$$J_\ell = 4\pi \int_0^\infty r_{a1}^2 dr_{a1} \chi_\ell^2(r_{a1}) \frac{1}{r_>}. \quad (2.292)$$

Breaking the interval of integration to remove the  $r_>$  yields,

$$J_\ell(2) = \frac{1}{r_{a2}} 4\pi \left[ \int_0^{r_{a2}} \chi_\ell^2(r_{a1}) r_{a1}^2 dr_{a1} + \int_{r_{a2}}^\infty \chi_\ell^2(r_{a1}) r_{a1} r_{a2} dr_{a1} \right] \quad (2.293)$$

Letting

$$\chi_\ell(1) = \sqrt{\frac{\zeta^3}{\pi}} e^{-\zeta r_{a1}}, \quad (2.294)$$

we find

$$J_\ell(r_{a2}) = \frac{1}{r_{a2}} [1 - e^{-2\zeta r_{a2}} (1 + \zeta r_{a2})] \quad (2.295)$$

Now we must change to elliptic coordinates in order to evaluate the integral over the coordinates of electron 2.

Using elliptical coordinates  $\xi$  and  $\eta$ ,

$$\xi = \frac{(r_a + r_b)}{R} \quad (2.296)$$

$$\eta = \frac{(r_a - r_b)}{R} \quad (2.297)$$

$$d\tau = \frac{R^3}{8} (\xi^2 - \eta^2) d\xi d\eta d\varphi \quad (2.298)$$

in (2.295) and (2.290), we find

$$\begin{aligned} J_{lr} &= \frac{\xi^3 R^2}{4\pi} \int_0^{2\pi} d\varphi \int_{-1}^1 d\eta \int_1^\infty d\xi \left\{ (\xi^2 - \eta^2) e^{-\zeta R(\xi - \eta)} \right. \\ &\quad \times \frac{1}{(\xi + \eta)} \left[ 1 - e^{-\zeta R(\xi + \eta)} \left( 1 + \frac{\zeta}{2} R(\xi + \eta) \right) \right] \Big\} \\ &= \frac{\zeta^3 R^2}{2} \int_{-1}^1 d\eta \int_1^\infty d\xi (\xi - \eta) \left[ e^{-\zeta R(\xi - \eta)} - e^{-2\zeta R\xi} \left( 1 + \frac{\zeta}{2} R(\zeta + \eta) \right) \right] \end{aligned}$$

or

$$J_{lr} = \frac{\zeta^3 R^2}{2} \int_{-1}^1 d\eta \int_1^\infty d\xi (\xi - \eta) e^{-\zeta R(\xi - \eta)}$$

$$+ \frac{\zeta^3 R^2}{2} \int_{-1}^1 d\eta \int_1^\infty d\xi (\xi - \eta) e^{-2\zeta R \xi} + \frac{\zeta^4 R^3}{2} \int_{-1}^1 d\eta \int_1^\infty d\xi (\xi^2 - \eta^2) e^{-2\zeta R \xi}$$

Evaluating these elementary integrals, gives the following result

$$J_{lr} = \zeta \left[ \frac{1}{\zeta R} - e^{-2\zeta R} \left( \frac{1}{\zeta R} + \frac{11}{8} + \frac{3}{4}\zeta R + \frac{1}{6}\zeta^2 R^2 \right) \right] \quad (2.299)$$

### The Exchange Integral

Now we evaluate the exchange integral

$$K_{lr} = \langle \chi_\ell(1)\chi_r(2) | \frac{1}{r_{12}} | \chi_r(1)\chi_\ell(2) \rangle = [\chi_\ell\chi_r | \chi_\ell\chi_r]. \quad (2.300)$$

Again, we can define a quantity

$$I(2) = \int d\tau_1 \left[ \chi_\ell(1)\chi_r(1) \frac{1}{r_{12}} \right] \quad (2.301)$$

involving integration over the first electron. Unfortunately, the Laplace expansion of  $1/r_{12}$  will now lead to an infinite sum because  $\chi_\ell(1)\chi_r(1)$  is not spherically symmetric.

Instead, we expand  $1/r_{12}$  in terms of elliptical coordinates using the Neuman expansion,

$$\begin{aligned} \frac{1}{r_{12}} &= \frac{2}{R} \sum_{k=0}^{\infty} \sum_{m=-k}^k (-1)^m (2k+1) \left[ \frac{(k-|m|)!}{(k+|m|)!} \right]^2 \\ &\times P_k^{|m|}[\xi_<] Q_k^{|m|}[\xi_>] P_k^{|m|}(\eta_1) P_k^{|m|}(\eta_2) e^{im(\varphi_1-\varphi_2)} \end{aligned}$$

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  $\varphi$  so the only nonzero term in the  $m$  summation is  $m = 0$ . To simplify the  $k$  summation, we use the property

$$\int_{-1}^1 P_k(\eta) P_{k'}(\eta) d\eta = 0 \quad (2.302)$$

if  $k \neq k'$ , together with the facts that  $P_0(\eta)$  is constant, and

$$P_2(\eta) = \frac{3}{2} \left( \eta^2 - \frac{1}{3} \right). \quad (2.303)$$

Thus, since the volume element for integration is

$$\frac{R^3}{8} (\zeta_1^2 - \eta_1^2) d\zeta_1 d\eta_1 d\varphi_1, \quad (2.304)$$

we find that by integration with respect to  $\eta$ , the only nonzero terms are for  $k = 0$  and  $k = 2$ .

We will now skip pages of tedious algebra to the result (see reference ??). It is convenient to define

$$S = e^{-\zeta R} \left( 1 + \zeta R + \frac{1}{3} \zeta^2 R^2 \right) \quad (2.305)$$

$$\sigma = e^{+\zeta R} \left( 1 - \zeta R + \frac{1}{3} \zeta^2 R^2 \right) \quad (2.306)$$

$$C = \int_0^1 \frac{1 - e^t}{t} dt - \int_1^\infty dt = 0.57722 \quad (2.307)$$

(Euler's constant), and

$$Ei(-x) = - \int_x^\infty \frac{e^{-t}}{t} dt \quad (2.308)$$

(the integral logarithm).

With these definitions, the result is

$$\begin{aligned} K_{lr} &= \frac{1}{10} \zeta \left\{ -e^{-2\zeta R} \left( -\frac{25}{6} + \frac{23}{4} \zeta R + 3\zeta^2 R^2 + \frac{1}{3} \zeta^3 R^3 \right) \right. \\ &\quad \left. + \frac{6}{\zeta R} [S^2 (C + \ln(\zeta R)) + \sigma^2 Ei(-4\zeta R) - 2S\sigma Si(-2\zeta R)] \right\} \end{aligned}$$

or, for small  $R$

$$K_{lr} = \frac{1}{2} \zeta \left[ \frac{5}{4} - \frac{1}{2} \zeta^2 R^2 + \left( \frac{3}{50} + \frac{8}{75} \ln 4 \right) \zeta^4 R^4 \right] \quad (2.309)$$

(plus higher-order terms). Note, also for small  $R$ , that if we include terms through  $R^2$ ,

$$J_{lr} = \frac{1}{2} \zeta \left( \frac{5}{4} - \frac{1}{6} \zeta^2 R^2 + \dots \right) \quad (2.310)$$

$$K_{lr} = \frac{1}{2} \zeta \left( \frac{5}{4} - \frac{1}{2} \zeta^2 R^2 + \dots \right) \quad (2.311)$$

and therefore

$$K_{lr} < J_{lr}. \quad (2.312)$$

## 2.6.5 Analysis of the Exchange Terms

In this section, we will provide more detailed analysis of the classical and exchange terms for  $H_2^+$  as discussed above.

## The Potential Energy Terms

Just as with the total energy, the potential energy can be partitioned into classical and exchange terms as follows

$$V_g = \frac{v_{ll} + v_{rr} + 2v_{lr}}{2(1+S)} + \frac{1}{R} = \frac{v_{ll} + v_{lr}}{(1+S)} + \frac{1}{R} = V^{cl} + V_g^x, \quad (2.313)$$

where

$$v_{lr} = \langle l|v|r\rangle \quad (2.314)$$

$$V^{cl} = v_{ll} + \frac{1}{R} = \frac{1}{2}(v_{ll} + v_{rr}) + \frac{1}{R} = \int d\mathbf{r} v(\mathbf{r}) \rho^{cl}(\mathbf{r}) + \frac{1}{R} \quad (2.315)$$

$$V_g^x = \frac{v_{lr} - S v_{ll}}{1+S} = \frac{\tau_v}{1+S} \quad (2.316)$$

and

$$\tau_v = v_{lr} - S v_{ll} \quad (2.317)$$

Similarly,

$$V_u = V^{cl} + V_u^x \quad (2.318)$$

where

$$V_u^x = \frac{-\tau_v}{1-S}. \quad (2.319)$$

First, we examine the form of  $V^{cl}$ . Substituting leads to

$$V^{cl} = \langle \chi_\ell | -\frac{1}{r_a} - \frac{1}{r_b} | \chi_\ell \rangle + \frac{1}{r} = \langle \chi_\ell | -\frac{1}{r_a} | \chi_\ell \rangle + \langle \chi_\ell | \frac{1}{R} - \frac{1}{r_b} | \chi_\ell \rangle \quad (2.320)$$

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 above

$$\Delta V^{cl} = \langle \chi_\ell | \frac{1}{R} - \frac{1}{r_b} | \chi_\ell \rangle = \left( 1 + \frac{1}{R} \right) e^{-2R} \quad (2.321)$$

and, hence

$$V^{cl} = -1 + \left( 1 + \frac{1}{R} \right) e^{-2R} \quad (2.322)$$

Consequently, in the simple classical description (superposition of atomic densities) there is no bonding of  $\text{H}_2^+$ . 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

$$\rho_g = \frac{\chi_\ell \chi_\ell + \chi_r \chi_r + 2\chi_\ell \chi_r}{2(1+S)}, \quad (2.323)$$

which can be partitioned into classical and exchange parts, as

$$\rho_g = \rho^{cl} + \rho_g^x, \quad (2.324)$$

where  $\rho^{cl}$  is given in the text, and

$$\rho_g^x = \frac{[\chi_\ell \chi_r - S \rho^{cl}]}{(1 + S)}. \quad (2.325)$$

Since

$$\int d\tau \rho = 1, \quad (2.326)$$

and

$$\int d\tau \rho^{cl} = 1, \quad (2.327)$$

the integral of  $\rho^x$  must be zero

$$\int d\tau \rho^x = 0. \quad (2.328)$$

That is,  $\rho^x$  merely shifts density around with no net contribution to the total electron charge. As a result, we can determine the sign of

$$V_g^x = \int d\tau v(\mathbf{r}) \rho_g^x(\mathbf{r}) \quad (2.329)$$

from Figure 2.36. Here we see that  $\rho_g^x > 0$  near the bond midpoint, while  $\rho_g^x < 0$  near the nuclei. That is,  $\rho_g^x$  leads to a shift of charge from the nuclear region to the bond region. Since  $v(\mathbf{r})$  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 Figure 2.36.

### The Kinetic Energy Terms

The kinetic energy of the  $\varphi_g$  state, can be written as

$$T_g = \frac{t_{ll} + t_{rr} + 2t_{lr}}{2(1 + S)} = \frac{t_{ll} + t_{lr}}{1 + S}, \quad (2.330)$$

where

$$t_{ll} = \langle \chi_\ell | \hat{t} | \chi_\ell \rangle = t_{rr}, \quad (2.331)$$

$$t_{lr} = \langle \chi_\ell | \hat{t} | \chi_r \rangle. \quad (2.332)$$

We will write

$$T_g = T^{cl} + T_g^x, \quad (2.333)$$

where

$$T^{cl} = \frac{1}{2} (t_{ll} + t_{rr}) = t_{ll} \quad (2.334)$$

$$T_g^x = \frac{t_{lr} - ST^{cl}}{1 + S} = \frac{\tau_t}{1 + S} \quad (2.335)$$

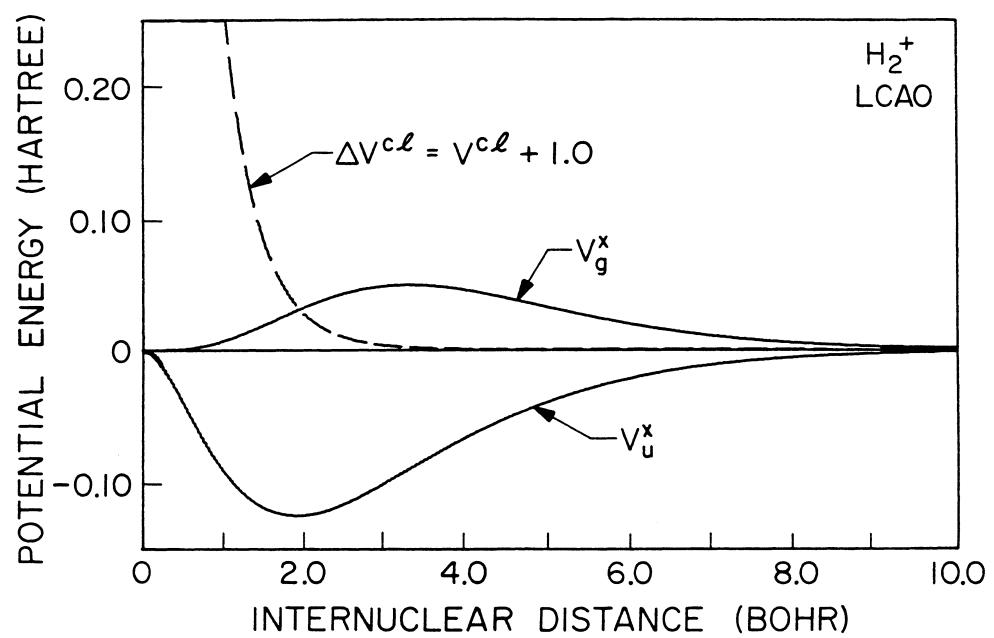


Figure 2.36:

$$\tau_t = t_{lr} - ST^{cl} \quad (2.336)$$

Similarly,

$$T_u = T^{cl} + T_u^x, \quad (2.337)$$

where

$$T_u^x = -\frac{t_{lr} - ST^{cl}}{1 - S} = -\frac{\tau_t}{1 - S} \quad (2.338)$$

Since  $T^{cl}$  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 Figure 2.7 are actually plots of  $T_g^x$  and  $T_u^x$ .

The large negative value of  $T_g$  responsible for the bond in  $\text{H}_2^+$  results from the large negative value of  $\tau_t$ . We will now examine why  $\tau_t$  is large and negative. We know that

$$t_{lr} = -\frac{1}{2}\langle \chi_\ell | \nabla^2 | \chi_r \rangle = \frac{1}{2}\langle \nabla \chi_\ell \cdot \nabla \chi_r \rangle = \frac{1}{2} \int d\tau (\nabla \chi_\ell^*) \cdot \nabla \chi_r \quad (2.339)$$

$$t_{ll} = \frac{1}{2}\langle |\nabla \chi_\ell|^2 \rangle, \quad (2.340)$$

$$t_{rr} = \frac{1}{2}\langle |\nabla \chi_\ell|^2 \rangle. \quad (2.341)$$

Thus,

$$\tau_t = t_{lr} - \frac{1}{2}S(t_{ll} + t_{rr}) = \frac{1}{2} \int d^3\mathbf{r} \left\{ \nabla \chi_\ell \cdot \nabla \chi_r - \frac{S}{2} \left[ (\nabla \chi_\ell)^2 + (\nabla \chi_r)^2 \right] \right\} \quad (2.342)$$

In order to understand the significance of the terms above, we will consider first the case where  $\tau_t$  is modified by replacing  $\nabla \chi_\ell \cdot \nabla \chi_r$  in the equation, by  $|\nabla \chi_\ell||\nabla \chi_r|$ . This leads to an integrand of the form

$$|\nabla \chi_r||\nabla \chi_\ell| - \frac{S}{2} \left[ (\nabla \chi_\ell)^2 + (\nabla \chi_r)^2 \right]. \quad (2.343)$$

Since

$$\chi_\ell = e^{-r_a} \quad (2.344)$$

we obtain

$$\nabla \chi_\ell = -\chi_\ell \hat{e}_r, \quad (2.345)$$

where  $\hat{e}_r$  is a unit vector in the  $r$  direction, and hence, (22) becomes

$$\left[ \chi_r \chi_\ell - \frac{S}{2} (\chi_\ell^2 + \chi_r^2) \right] \quad (2.346)$$

However, the term in brackets is just proportional to  $\rho^x$  in (2.325) and hence, from (2.328) the resulting integral is zero. Thus, it is the difference between the dot product term  $\nabla \chi_\ell \cdot \nabla \chi_r$  in (2.342) and the absolute value term  $|\nabla \chi_\ell||\nabla \chi_r|$  in (2.343) that is responsible for the large negative value of  $\tau_t$ ; hence, of the chemical bond. To emphasize this, we define a function called the contragradient

$$C(\mathbf{r}) = |\nabla \chi_\ell||\nabla \chi_r| - \nabla \chi_\ell \cdot \nabla \chi_r \quad (2.347)$$

such that

$$\tau_t - \frac{1}{2} \int d^3\mathbf{r} C(\mathbf{r}). \quad (2.348)$$

Large contragradiences lead to a large negative  $\tau_t$ , and hence, strong bonds. As discussed in the text and illustrated in Figure 2.14, the larger values of  $C(\mathbf{r})$  occur for points in between the nuclei.

### Specific Results for $\text{H}_2^+$

The explicit form of  $\tau_t$  for  $\text{H}_2^+$  is

$$\tau_t = -\frac{1}{3} R^2 e^{-R} \quad (2.349)$$

Thus, as expected  $\tau_t \rightarrow 0$  as  $R \rightarrow 0$  and as  $R \rightarrow \infty$ . The minimum in  $\tau_t$  occurs for  $R = 2$ . Thus, we would expect the maximum bonding effect to occur near  $R = 2 a_0$ . Indeed this is the optimum  $R$  of the exact wavefunction of  $\text{H}_2^+$ . Approximating the bond strength as

$$T_g^x = -\frac{\tau_t}{1 + S} \quad (2.350)$$

we obtain for  $R = 2$ , where  $S = 0.6$ ,

$$T_g^x = \frac{4e^{-2}}{(3)(1.6)} = -0.12 h = 3.1 \text{ eV} \quad (2.351)$$

In fact, the bond energy is only  $0.1 h = 2.5 \text{ eV}$ , and the  $T_g^x$  term does dominate the bond. For quantitative considerations we should, of course, use the total  $E^x$ .

The explicit form of  $\tau_v$  for  $\text{H}_2^+$  is

$$\tau_v = e^{-R} \left[ \frac{1}{R} - \frac{2}{3}R + \frac{1}{3}R^2 \right], \quad (2.352)$$

neglecting terms of order  $e^{-2R}$ . Combining with  $\tau_t$  leads to

$$\tau = e^{-R} \left[ \frac{1}{R} - \frac{2}{3}R \right] \quad (2.353)$$

neglecting terms of order  $e^{-2R}$ , whereas

$$S = e^{-R} \left[ 1 + R + \frac{1}{3}R^2 \right] \quad (2.354)$$

Thus,

$$\frac{\tau}{S} = -\frac{2}{R} \left( 1 - \frac{3}{R} + \frac{9}{2R^2} \right) + 0 \left( \frac{1}{R^4} \right) \quad (2.355)$$

and, hence

$$\tau \approx -\frac{2}{R} S. \quad (2.356)$$

Various energies for  $\text{H}_2^+$  are tabulated in Table 2.1.

Table 2.1: Energy quantities for the linear combinations of atomic orbital wavefunctions of the  $g$  state of  $\text{H}_2^+$ . All quantities are in atomic units.

$R$	$S$	$\Delta V^{cl}$	$V^x$	$\Delta V^{tot}$	$T^x = \Delta T^{tot}$	$\Delta E^{tot}$
$\infty$		O.O <sup>a</sup>	0.0	0.0 <sup>a</sup>	O.O <sup>a</sup>	O.O <sup>a</sup>
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	0.34581	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

<sup>a</sup> The values at  $R = \infty$  are  $V^{cl} = -1.00$ ,  $V^{total} = -1.0$ ,  $T^{total} = 0.5$ , and  $E^{total} = 0.5$ .

## Chapter 3

# More Exact Wavefunctions

### 3.1 Introduction

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 of these molecules and for the two-electron atom, He. Our emphasis here will be on qualitative ideas.

We first examine the variational principle and later we use this principle to examine some of the useful methods for calculating wavefunctions such as HF, GVB, and CI.

Accurate wavefunctions for  $H_2^+$ , He, and  $H_2$  are discussed in Sections 3.3, 3.7, and 3.8, respectively. In Section 3.4 we re-examine the nature of the bond in  $H_2^+$  and in Section 3.8 we re-examine the bond in  $H_2$ .

The energy  $\epsilon_0$  of any approximate wavefunction  $\varphi_0$  is an upper bound on the exact energy of the ground state  $E_0$ ,

$$\epsilon_0 \geq E_0, \quad (3.1)$$

leading to the variational condition. If an approximate wavefunction, and hence the energy, is a function of some parameter  $\lambda$ , then the optimum wavefunction satisfies the necessary condition

$$\frac{\partial \epsilon}{\partial \lambda} = 0. \quad (3.2)$$

Expanding the unknown wavefunction  $\varphi$  in terms of a basis

$$\varphi = \sum_{\mu=1}^p C_\mu \chi_\mu \quad (3.3)$$

and applying the variational condition, leads to a set of matrix equations,

$$\mathbf{H}\mathbf{C} = E\mathbf{S}\mathbf{C} \quad (3.4)$$

for obtaining the optimum coefficients, i.e., wavefunction.

More exact wavefunctions of  $H_2^+$  are also considered, but later we find that the description of bonding, in terms of exchange energies is retained. In Section 3.6 we

present an overview of three useful methods for wavefunctions. They are, first, the *Hartree-Fock* (HF) method, a generalization of the MO wavefunction in which the wavefunction (ground state of a two-electron system) is taken as

$$\Phi^{HF}(1, 2) = \varphi(1)\varphi(2) \quad (3.5)$$

and the orbitals  $\varphi$  optimized by solving the differential equation

$$H^{HF}\varphi = (h + J_\varphi)\varphi = \epsilon\varphi \quad (3.6)$$

or the matrix equation

$$\mathbf{H}^{HF}\mathbf{C} = \epsilon\mathbf{SC}. \quad (3.7)$$

These equations are nonlinear and must be solved iteratively.

Secondly, the *generalized valence bond* (GVB) method, a generalization of the VB method with the wavefunction taken of the form

$$\Phi^{GVB}(1, 2) = \varphi_a(1)\varphi_b(2) + \varphi_b(1)\varphi_a(2) \quad (3.8)$$

and the orbitals  $\varphi_a$  and  $\varphi_b$  optimized. This leads to two matrix equations

$$\mathbf{H}^a\mathbf{C}_a = \epsilon_a\mathbf{SC}_a \quad (3.9)$$

$$\mathbf{H}^b\mathbf{C}_b = \epsilon_b\mathbf{SC}_b \quad (3.10)$$

analogous to the HF equations (3.7) and to two differential equations analogous to (3.6).

Third, the *configuration interaction* (CI) method with the wavefunction taken of the form

$$\Phi^{CI}(1, 2) = \sum_{\mu, \nu} C_{\mu\nu} \chi_\mu(1) \chi_\nu(2) \quad (3.11)$$

For the ground state this wavefunction can always be written in terms of natural orbitals  $\{\bar{\chi}_\mu\}$  as

$$\Phi^{CI}(1, 2) = \sum_{\mu} \bar{C}_{\mu\nu} \bar{\chi}_\mu(1) \bar{\chi}_\nu(2). \quad (3.12)$$

Later in Section 3.6 we find that the ground state of any two electron systems is nodeless and symmetric

$$\Phi(1, 2) = \Phi(2, 1). \quad (3.13)$$

In Sections 3.7 and 3.8 we find that the HF wavefunction accounts for all but about 1.1 eV of the energy for He and H<sub>2</sub>, and that a CI wavefunction with five natural orbitals accounts for all but about 0.15 eV. The four correlating natural orbitals for this wavefunction all involve one nodal plane.

All of 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<sub>2</sub> similar quality wavefunctions can be obtained with six basis functions, two *s* and one *p* on each center, the *double valence plus polarization* (DVP) basis.

## 3.2 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*. Here, we will outline some of the key results of this principle.

### 3.2.1 Upper Bound Theorem

If  $\psi_0$  and  $E_0$  are the exact ground state wavefunction, and energy of a system

$$H\psi_0 = E_0\psi_0 \quad (3.14)$$

and if  $\varphi_0$  is an approximate wavefunction with energy

$$\epsilon_0 = \frac{\langle \varphi_0 | H | \varphi_0 \rangle}{\langle \varphi_0 | \varphi_0 \rangle}, \quad (3.15)$$

then

$$\epsilon_0 \geq E_0. \quad (3.16)$$

That is, the energy evaluated using any approximate wavefunction is an upper bound in the exact energy of the ground state.

### 3.2.2 Variational Condition

Given an approximate wavefunction  $\varphi_\lambda(r)$  depending upon some parameter  $\lambda$ , e.g.,

$$\varphi_\lambda = e^{-\lambda r}, \quad (3.17)$$

then the optimum value of  $\lambda$ , for describing the system, must satisfy the necessary condition

$$\frac{\partial \epsilon(\lambda)}{\partial \lambda} = 0, \quad (3.18)$$

where

$$\epsilon(\lambda) = \frac{\langle \varphi_\lambda | H | \varphi_\lambda \rangle}{\langle \varphi_\lambda | \varphi_\lambda \rangle}. \quad (3.19)$$

Equation (3.18) is referred to as the *variational condition*.

### 3.2.3 Basis Set Expansions

Given a set of functions

$$\{\chi_\mu(r), \mu = 1, 2, \dots, P\}, \quad (3.20)$$

the optimum wavefunction of the form

$$\varphi = \sum_{\mu=1}^P C_\mu \chi_\mu \quad (3.21)$$

satisfies the condition

$$\sum_{\nu} H_{\mu\nu} C_{\nu} = E \sum_{\nu} S_{\mu\nu} C_{\nu}, \quad (3.22)$$

or in matrix notation

$$\mathbf{H}\mathbf{C} = E\mathbf{S}\mathbf{C}, \quad (3.23)$$

where

$$H_{\mu\nu} \equiv \langle \chi_{\mu} | H | \chi_{\nu} \rangle \quad (3.24)$$

and

$$S_{\mu\nu} \equiv \langle \chi_{\mu} | \chi_{\nu} \rangle. \quad (3.25)$$

The set of functions (3.20) used for expansion of the unknown function  $\varphi$ , is called a basis set. The unknowns are the coefficients

$$\{C_{\mu}; \mu = 1, \dots, P\} \quad (3.26)$$

which are obtained by solving the matrix equations 3.22–3.23.

### 3.2.4 Discussion of Upper Bound Theorem

The upper bound theorem (3.16) is easy to derive. Consider that the exact eigenstates  $\{\psi_i\}$  of the Hamiltonian were known

$$H\psi_i = E_i\psi_i \quad (3.27)$$

with  $i = 0$  as the ground state.

Since the set of functions  $\{\psi_i\}$  is complete, we can expand any approximate wavefunction  $\varphi_0$  as

$$\varphi_0 = \sum_i C_i \psi_i. \quad (3.28)$$

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 equations (3.27) and (3.28)

$$H\varphi_0 = \sum_i C_i H\psi_i = \sum_i C_i E_i \psi_i \quad (3.29)$$

and the energy of the approximate wavefunction  $\varphi_0$  is

$$\epsilon_0 \equiv \langle \varphi_0 | H | \varphi_0 \rangle = \sum_i \sum_j C_j^* C_i E_i \langle \psi_j | \psi_i \rangle = \sum_i |C_i|^2 E_i. \quad (3.30)$$

Assuming  $\varphi_0$  is normalized,

$$1 = \langle \varphi_0 | \varphi_0 \rangle = \sum_{ij} C_j^* C_i \langle \psi_j | \psi_i \rangle = \sum_i |C_i|^2. \quad (3.31)$$

Using (3.31) in (3.30), we obtain

$$\epsilon_0 - E_0 = \sum_i |C_i|^2 (E_i - E_0). \quad (3.32)$$

Since  $E_i \geq E_0$  and  $|C_i|^2 \geq 0$ , the right-hand side of (3.32) is necessarily positive, and hence

$$\epsilon_0 - E_0 \geq 0 \quad (3.33)$$

or

$$\epsilon_0 \geq E_0. \quad (3.34)$$

That is, the energy calculated for any wavefunction is never lower than the exact energy for the ground state wavefunction. Thus, we say that  $\epsilon_0$  is an upper bound on  $E_0$ .

In deriving (3.34), we assumed that  $\varphi_0$  could be expanded in terms of the eigenfunctions of  $H$ . For example, if the boundary conditions for the system described by (3.27) were such that all wavefunctions are antisymmetric, then we could not allow  $\varphi_0$  to contain a symmetric part.

### 3.2.5 Discussion of the Variational Principle

Since any approximate wavefunction must yield 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. Then reject any change 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 the function of our specific restricted class leading to the lowest energy. If  $\lambda$  is some variable parameter for the restricted set of functions being considered, then the optimum wavefunction must satisfy

$$\frac{\partial E}{\partial \lambda} = 0 \quad (3.35)$$

since otherwise a lower energy could be obtained by changing  $\lambda$  a bit, as illustrated in 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 (3.35) is not sufficient to guarantee a minimum, with respect to variations in  $\lambda$  (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.

### 3.2.6 Parameter Optimization

Consider, as an approximation to the ground state of the hydrogen atom, the function

$$\varphi_0(\alpha) = e^{-\alpha r^2} \quad (3.36)$$

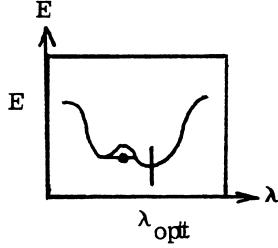


Figure 3.1:

where  $\alpha$  is a parameter. To determine the value of  $\alpha$  minimizing the energy, we first calculate the energy as a function of  $\alpha$ ,

$$E(\alpha) = \frac{\langle \varphi_0 | -\frac{1}{2} \nabla^2 - \frac{1}{r} | \varphi_0 \rangle}{\langle \varphi_0 | \varphi_0 \rangle} = \frac{3}{2}\alpha - \left( \frac{8}{\pi\alpha} \right)^{\frac{1}{2}} \quad (3.37)$$

The optimum value of  $\alpha$  is given by

$$\frac{dE(\alpha)}{d\alpha} = 0 = \frac{3}{2} - \frac{1}{2} \left( \frac{8}{\pi\alpha} \right)^{\frac{1}{2}} \quad (3.38)$$

or

$$\alpha_{opt} = \frac{8}{9\pi} = 0.283\dots \quad (3.39)$$

Substituting this into (3.37), we obtain

$$E(\alpha_{opt}) = -\frac{4}{3\pi} = -0.4244\dots \quad (3.40)$$

recalling that the exact energy is  $E = -0.5$ . Thus, even though (3.36) is considerably different from the exact eigenfunction for the ground state of the hydrogen atom, by optimizing  $\alpha$  we are able to account for 84.9% of the energy.

### 3.2.7 Basis Set Expansions

We will now use the variational principle to determine the best representation of an approximate wavefunction as an expansion (3.21), in terms of the functions of some finite basis set (3.20). The energy is

$$E = \frac{\langle \varphi | H | \varphi \rangle}{\langle \varphi | \psi \rangle} = \frac{N}{D}, \quad (3.41)$$

where

$$N = \sum_{\mu,\nu} C_\mu^* H_{\mu\nu} C_\nu, \quad (3.42)$$

$$D = \sum_{\mu,\nu} C_\mu^* S_{\mu\nu} C_\nu, \quad (3.43)$$

and,  $H_{\mu\nu}$  and  $S_{\mu\nu}$  are given in (3.24)–(3.25). We do not assume here that the basis functions are orthonormal; they must, of course, be linearly independent.

The energy (3.41) depends on the  $P$  parameters  $\{C_\mu\}$ , and thus, from the variational principle we require that

$$\frac{\partial E}{\partial C_\mu} = 0; \mu = 1, 2, \dots, P. \quad (3.44)$$

From (3.41), this leads to

$$\frac{\partial E}{\partial C_\mu} = \frac{1}{D} \frac{\partial N}{\partial C_\mu} - \frac{N}{D^2} \frac{\partial D}{\partial C_\mu} = \frac{1}{D} \left[ \frac{\partial N}{\partial C_\mu} - E \frac{\partial D}{\partial C_\mu} \right] = 0 \quad (3.45)$$

and hence,

$$\frac{\partial N}{\partial C_\mu} - E \frac{\partial D}{\partial C_\mu} = 0. \quad (3.46)$$

Assuming that the basis function  $\{\chi_\mu\}$  and coefficients  $\{C_\mu\}$  are all real, we obtain

$$2 \left[ \sum_\nu (H_{\mu\nu} - ES_{\mu\nu}) C_\nu \right] = 0 \quad (3.47)$$

and hence,

$$\sum_\nu H_{\mu\nu} C_\nu E \sum_\nu S_{\mu\nu} C_\nu. \quad (3.48)$$

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  $S_{\mu\nu} = S_{\nu\mu}$ .

In matrix notation, (3.48) becomes

$$\mathbf{HC} = E\mathbf{SC}. \quad (3.49)$$

If the basis functions are orthonormal

$$S_{\mu\nu} = \delta_{\mu\nu}, \quad (3.50)$$

the variational condition (3.49) becomes

$$\mathbf{HC} = E\mathbf{C}. \quad (3.51)$$

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 (3.35) or (3.51) 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.

Table 3.1: Optimum bond length,  $R_e$ , and bond strength,  $D_e$ , for the  $g$  state of  $\text{H}_2^+$ . All quantities in atomic units.

	Non-Relativistic			Relativistic	
	Neglect $T_{nuc}$		Exact <sup>b</sup>	Neglect $T_{nuc}$	Include $T_{nuc}$
LCAO <sup>a</sup>	MBS <sup>a</sup>	Exact <sup>b</sup>	Exact	Exact	Exact
$R_e$	2.493	2.00	2.00379 <sup>c</sup>	2.00376 <sup>c</sup>	2.00562 <sup>c</sup>
$D_e$	0.065	0.08651	0.102635 <sup>c</sup>	0.10264 <sup>c</sup>	0.101785 <sup>c</sup>

<sup>a</sup>See reference 1. <sup>b</sup>See reference 2. <sup>c</sup>See reference 3. <sup>d</sup>See reference 4.

### 3.3 Accurate Wavefunctions for $\text{H}_2^+$

The LCAO wavefunction of  $\text{H}_2^+$  discussed in Chapter 2, is an approximate wavefunction and does not provide a quantitatively accurate description of  $\text{H}_2^+$  near  $R_e$ . In this section, we will discuss more accurate wavefunctions of  $\text{H}_2^+$ . First we consider a useful intermediate level description, the MBS wavefunction.

#### 3.3.1 Scaled LCAO Wavefunctions

We will describe the wavefunction of  $\text{H}_2^+$  in terms of linear combinations of two orbitals,  $\chi_\ell$  and  $\chi_r$ , centered on each proton, but rather than atomic orbitals, we will use scaled atomic-like orbitals

$$\chi_\ell = \sqrt{\left(\frac{\zeta^3}{\pi}\right)} e^{-\zeta r_a} \quad (3.52)$$

and

$$\chi_r = \sqrt{\left(\frac{\zeta^3}{\pi}\right)} e^{-\zeta r_b} \quad (3.53)$$

The scaling parameter  $\zeta$  is referred to as an *orbital exponent*. Use of  $\zeta = 1$  leads to the LCAO description of Chapter 2,  $\zeta > 1$  leads to more contracted orbitals, while  $\zeta < 1$  leads to more diffuse orbitals.

Using the basis set (3.52)–(3.53), the wavefunctions of  $\text{H}_2^+$  have the form

$$\varphi_g = \frac{(\chi_\ell + \chi_r)}{\sqrt{2(1+S)}} \quad (3.54)$$

$$\varphi_u = \frac{(-\chi_\ell + \chi_r)}{\sqrt{2(1-S)}} \quad (3.55)$$

just as in Chapter 2. However, the energies of these wavefunctions depend upon both  $\zeta$  and  $R$  (see Section 2.6.1 in Chapter 2 for the specific dependence of the integrals on  $\zeta$ ). At each  $R$  we will use the  $\zeta$  leading to the lowest energy. Since the forms of  $E_g$  and  $E_u$  are different, the optimum  $\zeta$  will be different for the  $g$  and  $u$  states, as shown in Figure 3.2.

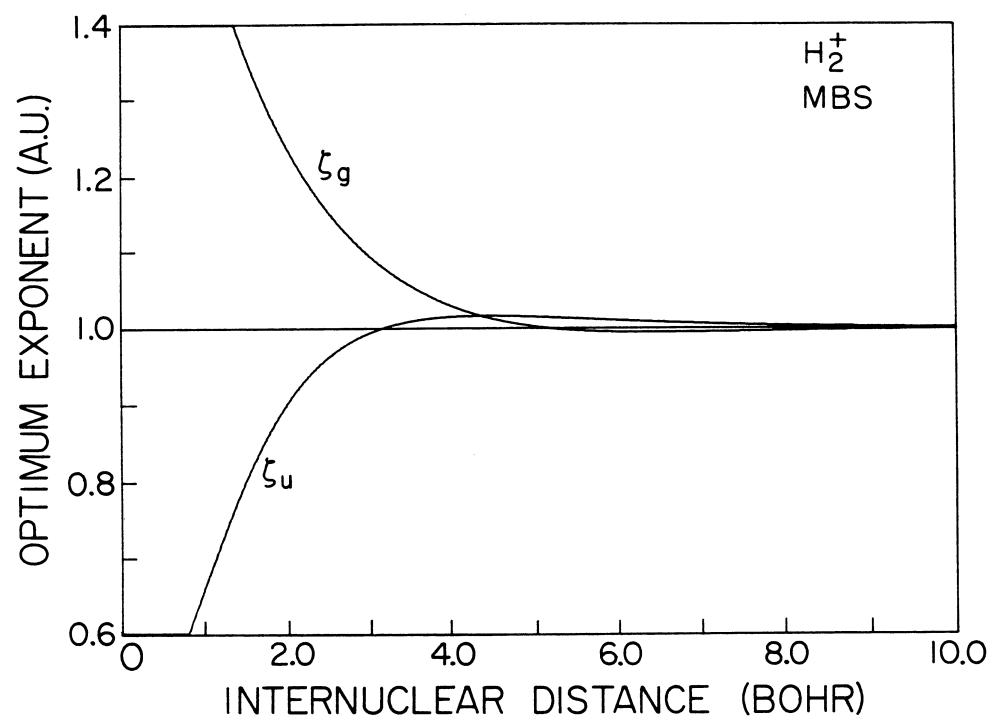


Figure 3.2: The optimal orbital exponents for the MBS descriptions of the *g* and *u* states of  $\text{H}_2^+$ .

As shown in Figure 3.2 and seen in Table 3.1, 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 the MBS energies are quite close to the exact answer.

In discussing such wavefunctions, we will use the following terminology. First, linear combination of atomic orbitals, LCAO, denotes the use of a linear combination of atomic orbitals using the orbital exponents of the atoms. Second, minimal basis set, MBS, 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 result of MBS calculations will be discussed further, after a discussion of the exact wavefunctions of  $\text{H}_2^+$

### 3.3.2 The Exact Wavefunction for $\text{H}_2^+$

Previously, we considered approximate solutions of the Schrödinger equation

$$H\psi_R(r) = E(R)\psi_R(r), \quad (3.56)$$

where the Hamiltonian is

$$H = -\frac{1}{2}\nabla^2 - \frac{1}{r_a} - \frac{1}{r_b} + \frac{1}{R}. \quad (3.57)$$

Exact solutions to (3.56) have also been obtained, as will now be described.

We can obtain arbitrarily accurate wavefunctions of  $\text{H}_2^+$  by expanding the orbital in terms of a sufficiently general basis

$$\{\chi_\mu : \mu = 1, 2, \dots, P\}, \quad (3.58)$$

$$\varphi(r) = \sum_{\mu=1}^P C_\mu \chi_\mu(r), \quad (3.59)$$

where the expansion coefficients are obtained by solving the  $P$  by  $P$  matrix equation

$$\mathbf{HC} = \mathbf{CE}, \quad (3.60)$$

with

$$H_{\mu\nu} = \langle \chi_\mu | H | \chi_\nu \rangle \quad (3.61)$$

assuming the basis to be orthonormal. As the basis set is made more complete ( $P \rightarrow \infty$ ) the wavefunction approaches the exact wavefunction.

Although the above procedure is practical, it is possible for  $\text{H}_2^+$  to solve directly for the exact solutions. The procedure is examined in more detail in Section 3.9.4.

### 3.3.3 Comparison of Wavefunctions and Energies

The various wavefunctions of the  $g$  and  $u$  states are compared in Figure 3.4 for  $R = 2a_0$ . For the  $g$  state, we see that the shape of the linear combination of atomic orbitals wavefunction in the bond region, is in good agreement with the exact wavefunction. However, the magnitude of the density in the bond region is  $\approx 25$  to  $30\%$  low.

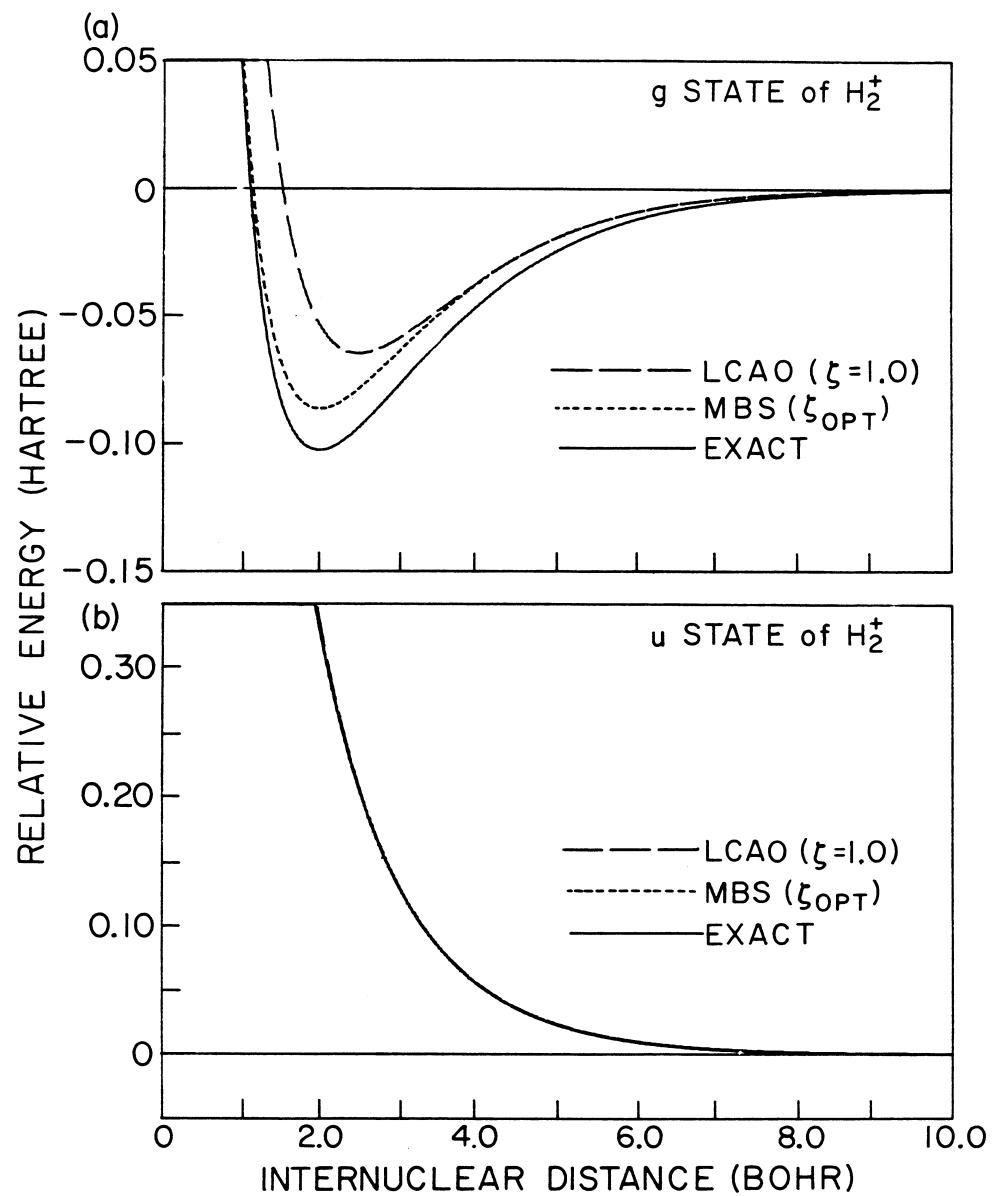


Figure 3.3: The LCAO ( $\zeta = 1.0$ ) MBS (optimum  $\zeta$ ) and the exact energies for the  $g$  and  $u$  states of  $H_2^+$ . Note that (b) does contain three different lines. The vertical scale of (b) is twice that of (a).

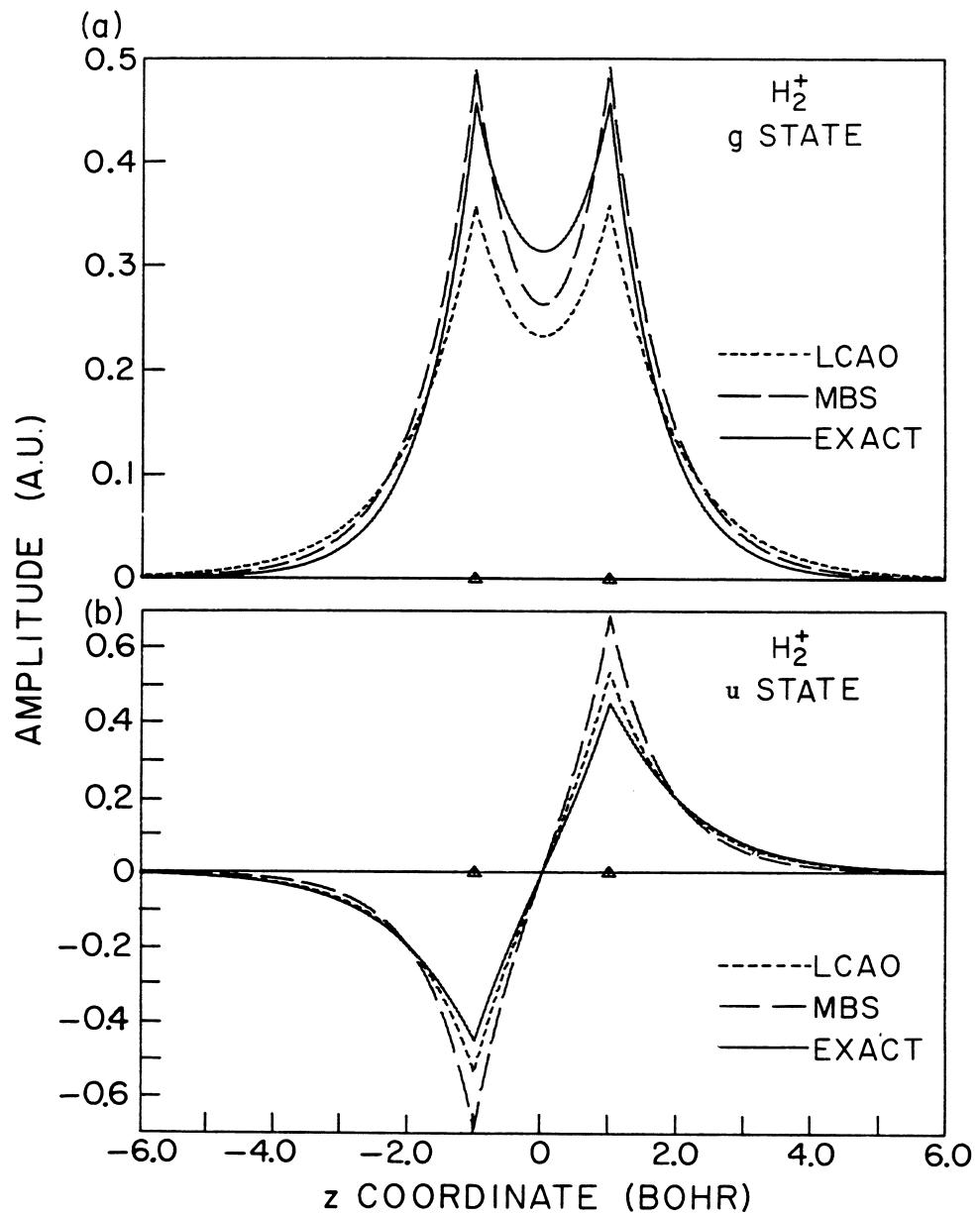


Figure 3.4: The wavefunctions of  $\text{H}_2^+$  at  $R = 2.0a_0$ .

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.

In Figure 3.5, we compare the LCAO and MBS wavefunctions as a function of  $R$ , finding that the LCAO description does reasonably well for  $R > 4 a_0$ . 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 Figure 3.2.

## 3.4 More on the Chemical Bond

In Chapter 2 we analyzed the bond of  $\text{H}_2^+$  in terms of the linear combination of atomic orbitals description. Now we will re-examine the bond using more accurate wavefunctions. With more accurate wavefunctions, we still find 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  $\text{H}_2^+$ . On the other hand, partitioning the energy into the total potential energy ( $V$ ) and the total kinetic, energy ( $T$ ) we find that neither can be solely responsible for bonding.

### 3.4.1 The Classical and Exchange Energies

Defining the classical and exchange terms, just as in Chapter 2,

$$E = E^{cl} + E^x \quad (3.62)$$

and

$$E^{cl} = \langle \chi_\ell | H | \chi_\ell \rangle \quad (3.63)$$

but using the MBS wavefunctions, we obtain the results of Figure 3.6.

Thus the exchange energy dominates the bonding just as for the linear combination of atomic orbitals wavefunction. Partitioning the  $E^x$  into potential and kinetic parts,  $V^x$  and  $T^x$ ,

$$E^x = V^x + T^x \quad (3.64)$$

as in Figure 3.6, 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 linear combination of atomic orbitals 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 Chapter 2,  $T^x$  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.

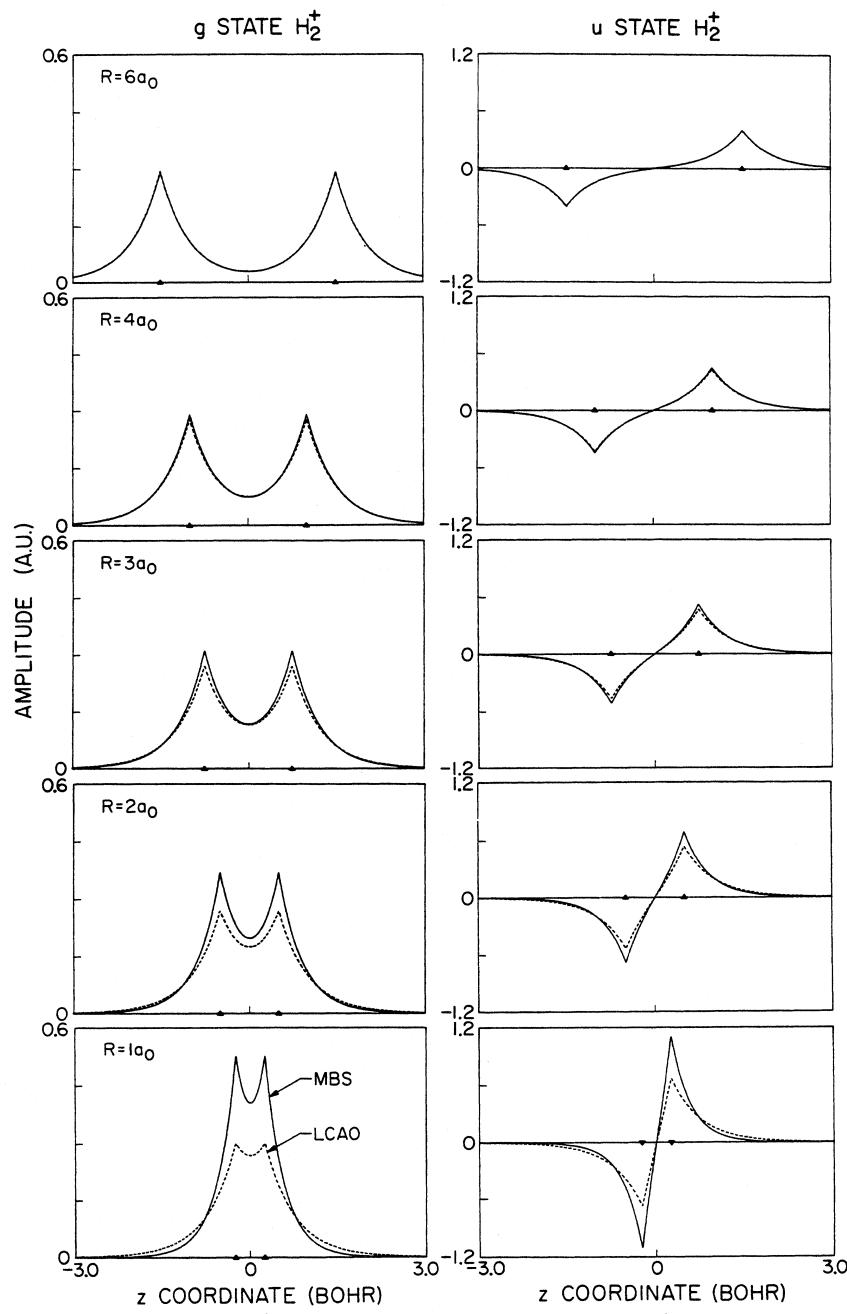


Figure 3.5: Amplitudes of the LCAO (dashed) and MBS (solid) wave functions for (a) the *g* state and (b) the *u* state of  $H_2^+$

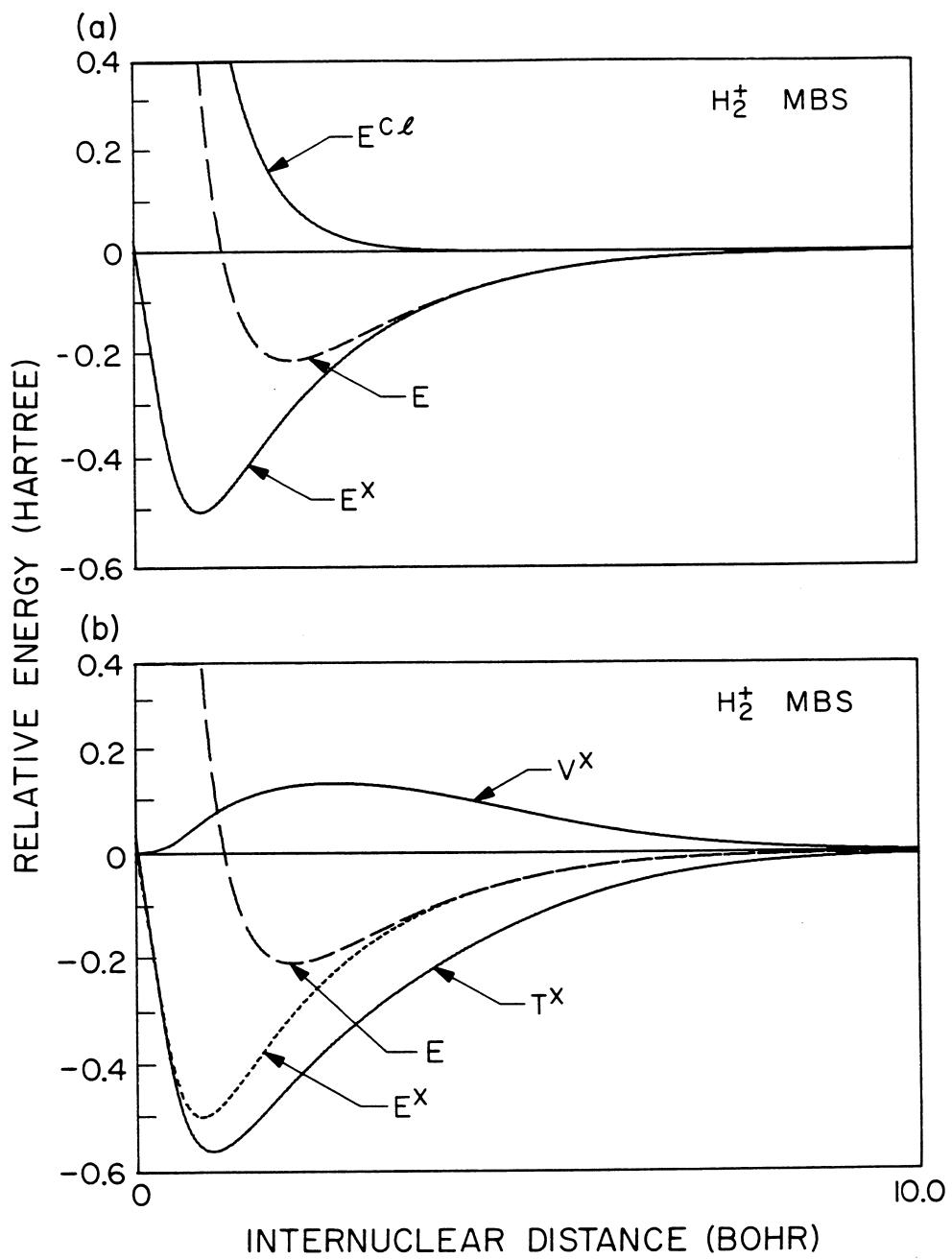


Figure 3.6: (a) The total energy,  $E$ , and the components  $E^{cl}$  and  $E^x$  for the MBS wavefunction of the  $g$  state of  $H_2^+$ . (b) The  $T^x$  and  $V^x$  components of  $E^x$  is shown. All quantities are relative to  $R = \infty$ .

### 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  $\chi_{2r}$ , and optimizing the coefficients, leads to

$$\Phi_g = C_1 (\chi_{1\ell} + \chi_{1r}) + C_2 (\chi_{2\ell} + \chi_{2r}) \quad (3.65)$$

and adding additional functions, we ultimately obtain the exact wavefunction in the form

$$\Phi_g = \sum_{k=1}^{\infty} C_k (\chi_{k\ell} + \chi_{kr}) . \quad (3.66)$$

Thus, we can define optimum left and right orbitals as

$$\chi_{\ell} = \sum_k C_k \chi_{k\ell} \quad (3.67)$$

$$\chi_r = \sum_k C_k \chi_{kr} \quad (3.68)$$

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  $\chi_{\ell}$  and  $\chi_r$ . 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 (3.67)–(3.68).

### 3.4.2 Potential and Kinetic Energies

Rather than the partition (3.62) 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,  $T$ ,

$$E = T + V \quad (3.69)$$

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 earlier, the classical and exchange energies behave very similarly for these two cases. However, as shown in Figure 3.7, the behavior of  $T$  and  $V$  for the LCAO and MBS 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  $R > 2.7 a_0$ . Thus, at  $R_e = 2 a_0$ ,  $T(R) > T(\infty)$  and it would be ludicrous to assume 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

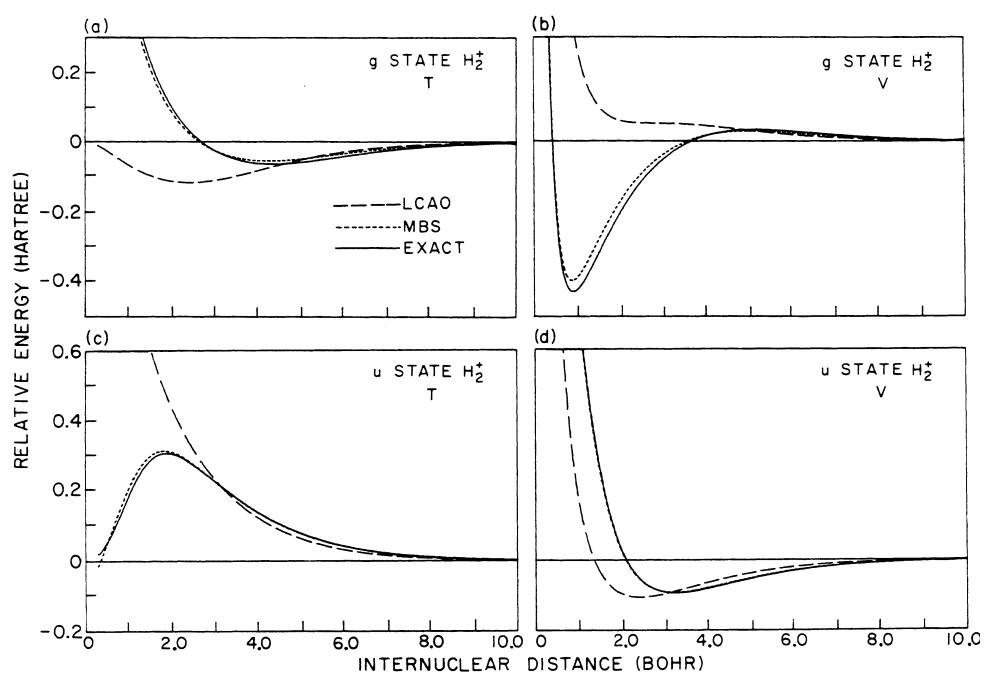


Figure 3.7: The kinetic and total potential energies for (a,b) the  $g$  state, and (c,d) the  $u$  state of  $H_2^+$ . All quantities are relative to the value for  $R = \infty$ .

bond at  $R_e$ , it opposes bond formation for  $R < 3.5 a_0$ . Furthermore, for the LCAO,  $V(R)$  opposes bonding for all  $R$ .

Such difficulties show that (3.69) 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, usually in the analysis of rotational and conformational barriers in polyatomic molecules, energy curves are analyzed by partitioning the  $V$  into various parts

$$V = V^{en} + V^{nn} + V^{ee} \quad (3.70)$$

where  $ee$  denotes electron-electron repulsion,  $en$  denotes electron-nuclear attraction, and  $nn$  denotes nuclear-nuclear repulsion terms,  $ee$  is not present for  $H_2^+$ . As shown in Figure 3.8, 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 Figure 3.8(b), the  $V^{en}$  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. Thus,  $V^{en}$  is dominated by quantities other than those responsible for bond formation.

## 3.5 Overview of Theoretical Methods

This course focuses primarily on *qualitative* ideas of chemical bonding rather than particular theoretical methods. 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  $\varphi_i(r)$ . The general procedure for carrying out such calculations, involve selection of a basis set

$$\{\chi_\mu; \mu = 1, \dots, P\}, \quad (3.71)$$

suitable for describing the optimum orbitals

$$\varphi_i(r) = \sum_{\mu=1}^P C_{\mu i} \chi_\mu(r). \quad (3.72)$$

Here, the basis functions are fixed and hence, selection of the optimum coefficients

$$\{C_{1i}, C_{2i}, \dots, C_{Pi}\} \quad (3.73)$$

serves to determine the orbital  $\varphi_i(r)$ . This procedure is analogous to a Fourier expansion where harmonic functions (sines and cosines) are used as basis functions in (3.71).

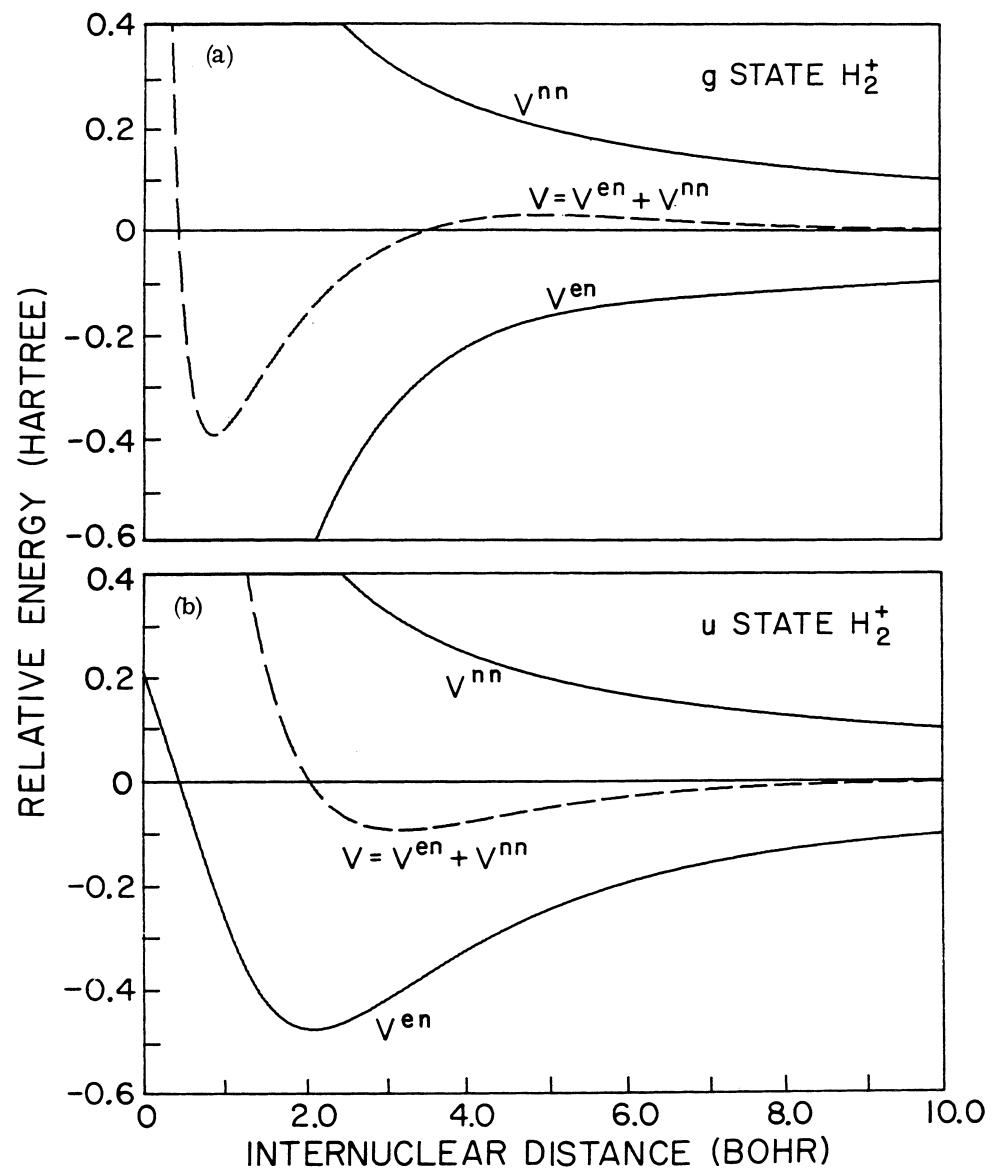


Figure 3.8: The total potential energy,  $V$ , and the partition into  $V^{nn}$  and  $V^{en}$  for (a) the  $g$  state and (b) the  $u$  state of  $\text{H}_2^+$ , exact wavefunctions is shown. All quantities are relative to the value for  $R = \infty$ .

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 (3.71), we must evaluate integrals of the form

$$\langle \chi_\mu | h | \chi_\nu \rangle \quad (3.74)$$

$$\langle \chi_\mu(1) \chi_\nu(2) | \frac{1}{r_{12}} | \chi_\sigma(1) \chi_\eta(2) \rangle, \quad (3.75)$$

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

$$1s : e^{-Zr} \quad (3.76)$$

$$2s : (r - \alpha) e^{-\frac{1}{2} Zr} \quad (3.77)$$

$$2p_z : r \cos \theta e^{-\frac{1}{2} Zr} \quad (3.78)$$

$$2p_x : r \sin \theta \cos \varphi e^{-\frac{1}{2} Zr} \quad (3.79)$$

$$2p_y : r \sin \theta \sin \varphi e^{-\frac{1}{2} Zr} \quad (3.80)$$

$$3s : (r^2 - \beta r + \alpha) e^{-\frac{1}{2} Zr} \quad (3.81)$$

etc.

where normalization is ignored and the constants  $\alpha$  and  $\beta$  are unimportant to our considerations here. In order to describe, with 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 (3.79) centered upon the various nuclei of the molecule.

The radial parts of the functions in (3.79) all can be built from functions of the form

$$r^n e^{-\zeta r}, \quad (3.82)$$

where various values of  $n$  and of the orbital exponents,  $\zeta$ , must be allowed. Functions of the form (3.82) are preferable to the hydrogen atom orbitals (3.79), since (3.82) is more convenient for evaluating the molecular integrals. Combining functions of the form (3.82) with appropriate angular functions,  $Z_{lm}$  the real spherical harmonics, leads to a convenient set of one-particle orbitals

$$r^n e^{-\zeta r} Z_{lm}(\theta, \varphi) \quad (3.83)$$

for use in atomic and molecular wavefunctions. These functions (3.83) are referred to as *Slater functions*, or *Slater-type orbitals* (STO) in honor of an early exponent [?] of such functions. 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 orbitals as in a HF or GVB orbital. They are denoted as  $1s$ ,  $2s$ ,  $2p$ , etc., just as for hydrogen atom orbitals. The orbital exponent,  $\zeta$ , in (3.82) 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 (3.79)).

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 [?]

$$\zeta(1s) = 0.965 \quad (3.84)$$

$$\zeta(1s') = 1.43 \quad (3.85)$$

$$\zeta(2s) = 1.16 \quad (3.86)$$

$$\zeta(2pz) = 1.87 \quad (3.87)$$

$$\zeta(2px) = \zeta(2py) = 1.71 \quad (3.88)$$

where the molecular axis is along  $z$ . With this basis, the CI wavefunction leads to an energy of  $-1.16696$  h, at  $R = 1.4a_0$ , 99.4% of the exact answer<sup>7</sup>  $-1.17447$  h. Note that the optimum orbital exponents are significantly different from the values for the free atom

$$\zeta_{1s} = 1.0 \quad (3.89)$$

$$\zeta_{2s} = 0.5 \quad (3.90)$$

$$\zeta_{2p} = 0.5. \quad (3.91)$$

The second type of basis functions, commonly used in molecular calculations, are *Gaussian functions* where the  $e^{-\zeta r}$  of (3.83) is replaced by  $e^{-\alpha r^2}$  and  $n$  is taken as  $l$ ,

$$r^l e^{-\alpha r^2} Z_{lm}(\theta, \varphi) \quad (3.92)$$

Although Gaussian functions have the wrong behavior as  $r \rightarrow 0$ , and as  $r \rightarrow \infty$ , 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 (3.74)–(3.75) required for large molecules are much simpler, and less time consuming, than for Slater functions.

Generally, basis sets are optimized for 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 HF Method

#### The Basic Equations

In Chapter 2 we described the simple MO wavefunction of  $H_2$  in which the two-electron wavefunction is expressed as

$$\Phi(1, 2) = \varphi(1)\chi(2) \quad (3.93)$$

where  $\varphi$  is the MO

$$\varphi = \frac{(\chi_\ell + \chi_r)}{\sqrt{2(1+S)}} \quad (3.94)$$

and  $\chi_\ell$  and  $\chi_r$  are hydrogen orbitals centered on the two nuclei. Now we will consider the case where  $\varphi$  is allowed to be completely general. Thus, if  $\{\chi_\mu\}$  is some basis set, we write

$$\varphi = \sum_\mu C_\mu \chi_\mu \quad (3.95)$$

with the coefficients  $\{C_\mu\}$  chosen so that  $\Phi$  in (3.93) leads to the lowest possible energy.

The energy of (3.93) is

$$E = \frac{\langle \Phi | H^{el} | \Phi \rangle}{\langle \Phi | \Phi \rangle} = 2\langle \varphi | h | \varphi \rangle + J_{\varphi\varphi} + \frac{1}{R}, \quad (3.96)$$

where

$$J_{\varphi\varphi} = (\varphi\varphi | \varphi\varphi) = \int d^3r_1 \varphi^*(1)\varphi(1) \int d^3r_2 \frac{\varphi^*(2)\varphi(2)}{r_{12}} \quad (3.97)$$

and

$$\langle \varphi | \varphi \rangle = 1. \quad (3.98)$$

Applying the variational principle to (3.96)

$$\frac{\partial E}{\partial C_\mu} = 0 \quad (3.99)$$

with the constraint (3.98), leads to

$$\langle \chi_\mu | (h + J_\varphi - \epsilon) | \varphi \rangle = 0 \quad (3.100)$$

where  $\epsilon$  is referred to as the orbital energy,

$$\epsilon = \langle \varphi | h | \varphi \rangle + J_{\varphi\varphi}, \quad (3.101)$$

and

$$J_\varphi(r_1) = \int d^3r_2 \frac{\varphi^*(r_2)\varphi(r_2)}{r_{12}} \quad (3.102)$$

is the electrostatic potential at point  $r_1$  due to the charge density  $|\varphi(r_2)|^2$  integrated over all  $r_2$ .

Substituting (3.95) into (3.100) leads to

$$\sum_{\nu=1}^P (H_{\mu\nu} - \epsilon S_{\mu\nu}) C_\nu = 0; \mu = 1, 2, \dots, P. \quad (3.103)$$

where

$$H_{\mu\nu} = \langle \chi_\mu | (h + J_\varphi) | \chi_\nu \rangle \quad (3.104)$$

$$S_{\mu\nu} = \langle \chi_\mu | \chi_\nu \rangle. \quad (3.105)$$

In matrix notation, (3.103) is written as

$$\mathbf{HC} = \mathbf{SC}\epsilon. \quad (3.106)$$

Since

$$\langle \chi_\mu | J_\varphi | \chi_\nu \rangle = \sum_{\sigma, \eta} C_\sigma C_\eta \langle \chi_\mu \chi_\sigma | \frac{1}{r_{12}} | \chi_\nu \chi_\eta \rangle, \quad (3.107)$$

$H_{\mu\nu}$  is a function of the unknowns  $\{C_\mu\}$  and (3.103) is nonlinear. Since the basis functions  $\{\chi_\mu\}$  are known, all integrals in (3.104)–(3.105) can be evaluated just once so that (3.106) becomes a nonlinear algebraic equation.

In order for the variational condition of (3.100) to be satisfied for all  $\chi_\mu$  of a complete set, the function  $(h + J_\varphi - \epsilon)\varphi$  must be zero. That is, the differential equation

$$(h + J_\varphi)\varphi = \epsilon\varphi \quad (3.108)$$

or (for  $H_2$ )

$$\left( -\frac{1}{2} \nabla^2 - \frac{1}{r_a} - \frac{1}{r_b} + J_\varphi \right) \varphi = \epsilon\varphi \quad (3.109)$$

must be satisfied in order that  $\varphi$  be a completely optimum function. The resulting optimum wavefunction of (3.93) is called the HF wavefunction, the optimum orbital of (3.108) is called the HF orbitals, and this whole approach is called the HF method, all in honor of the Englishman D. R. Hartree, and the Russian V. Fock (sometimes Fok) who first developed it.

### Solution of the HF Equations

The differential equation (3.108) is not linear in  $\varphi$  since  $J_\varphi$  depends upon  $\varphi$ . The usual approach to solving (3.108) is the iterative method in which we guess the orbital,  $\varphi_0$ , evaluate  $J_{\varphi_0}$ , and solve the linear equation

$$(h + J_{\varphi_0})\varphi_1 = \epsilon\varphi_1 \quad (3.110)$$

for a one orbital  $\varphi_1$ . Then  $\varphi_1$  is used to evaluate a new  $J_{\varphi_1}$  and

$$(h + J_{\varphi_1})\varphi_2 = \epsilon\varphi_2 \quad (3.111)$$

is solved for a new orbitals. This process is continued until it converges, that is, until

$$\varphi_{I+1} \approx \Phi_I. \quad (3.112)$$

For atoms, the HF equation (3.108) 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 (3.103) and (3.106). These are also solved iteratively. One guesses the coefficients  $\{C_\mu^0\}$  and evaluates the  $H_{\mu\nu}$  of (3.104)–(3.105). With  $H_{\mu\nu}$  fixed, the matrix equations (3.103) and (3.106) 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 equations (3.104)–(3.105) and (3.106) for larger and larger basis sets, one can in the limit approach the results of solving the numerical equation (3.108). 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<sub>2</sub>.

### Historical Note

Before real quantum mechanics, i.e., the work of Schrödinger, Heisenberg, and their contemporaries in 1925 and 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 suggested [?] approximating this problem by assuming that the average interaction with the other electrons leads to a new 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 (3.108), 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.

In 1930, Slater 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. However, 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.

Also in 1930, V. Fock [?] 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 HF equations. Hartree referred to them as self-consistent field with exchange.

The approach of using a finite basis set for obtaining HF wavefunctions, rather than solving numerically, via 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 he is rightfully credited with the development of the basis set expansion (BSE) approach. An early

application of BSE was by Coulson [?] who concluded that the basis set expansion was not practical and that self-consistent field 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 basis set expansion approach for larger molecules depends upon electronic computers, the development of which was just starting in 1951.

### Interpretation, Correlation and Koopmans' Theorem

The variational condition of (3.108) has the form of a Schrödinger equation for a particle moving in the potential

$$V = -\frac{1}{r_a} - \frac{1}{r_b} + J_\varphi \quad (3.113)$$

assuming for the moment,  $\text{H}_2$ . This is just the classical potential that would be obtained if the second electron were replaced by its classical potential,  $J_\varphi$ . Thus, the HF 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  $1/r_{12}$  as small as possible, and  $1/r_a$  and  $1/r_b$  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 HF wavefunction. Both electrons move in the same orbital independently of the instantaneous position of the other electron. Hence, the error in the HF wavefunction is called the *correlation error*.

The energy  $\epsilon$  in (3.108) is called the *orbital energy*. From (3.101) it has the value

$$\epsilon = \langle \varphi | h | \varphi \rangle + J_{\varphi\varphi} = E_2 - E_1 \quad (3.114)$$

where

$$E_2 = 2\langle \varphi | h | \varphi \rangle + J_{\varphi\varphi} \quad (3.115)$$

is the energy of the two electron system with both electrons in  $\varphi$ , while

$$E_1 = \langle \varphi | h | \varphi \rangle \quad (3.116)$$

is the energy with only one electron in  $\varphi$ . Thus,  $\epsilon$  is just the negative of the *ionization potential*. There are two approximations here. One is using the HF 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  $\varphi$  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 about 10% of the exact value. This approximation, the first [?] of using the orbital energy to approximate the ionization potential is often called *Koopmans theorem*. Note that there is an ess at the end of this name, and the Dutch oo sounds about like our long o. Although not strictly the theorem that Koopmans proved,<sup>14</sup> we will also refer to this approximation as Koopmans theorem. Shortly after this work, Koopmans switched to economics. Koopmans is on the Economic faculty at Yale, and in 1975 won a Nobel Prize for his work in optimization theory of economics.

### 3.5.3 The GVB Method

In Chapter 2 we described the simple VB wavefunctions of H<sub>2</sub>, in which the two-electron wavefunction is expressed as

$$\Phi(1, 2) = (\chi_\ell \chi_r + \chi_r \chi_\ell), \quad (3.117)$$

where  $\chi_\ell$  and  $\chi_r$  are atomic orbitals.

We will not consider wavefunctions of the VB form

$$\Phi(1, 2) = \varphi_a \varphi_b + \varphi_b \varphi_a \quad (3.118)$$

but where the orbitals  $\varphi_a$  and  $\varphi_b$  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 GVB orbitals and the resulting wavefunction is called the *GVB wavefunction*.

#### The Basic Equations

The energy of the GVB wavefunction (3.118) is

$$E = \frac{N}{D} + \frac{1}{R} \quad (3.119)$$

where

$$N = [\langle a|h|a \rangle + \langle b|h|b \rangle + J_{ab}] + [2\langle a|h|b \rangle S_{ab} + K_{ab}] \quad (3.120)$$

$$D = 1 + S_{ab}^2 \quad (3.121)$$

$$S_{ab} = \langle a|b \rangle. \quad (3.122)$$

Here, and in most of the following, we will use orbital subscripts, e.g.,  $a$  and  $b$ , to denote orbitals (e.g.,  $\varphi_a$  and  $\varphi_b$ , respectively). Just as in the previous section, we will consider that  $\varphi_a$  and  $\varphi_b$  are expanded in a basis  $\{\chi_\mu\}$

$$\varphi_a = \sum_\mu \chi_\mu C_{\mu a} \quad (3.123)$$

and

$$\varphi_b = \sum_\mu \chi_\mu C_{\mu b} \quad (3.124)$$

and require that

$$\frac{\partial E}{\partial C_{\mu a}} = 0 \quad (3.125)$$

$$\frac{\partial E}{\partial C_{\mu b}} = 0. \quad (3.126)$$

This condition leads to

$$\langle \chi_\mu | (H^a - \epsilon_a) | \varphi_a \rangle = 0, \quad (3.127)$$

where

$$\epsilon_a = E - \langle b | h | b \rangle \quad (3.128)$$

and  $H^a$  is an operator taking care of all other terms. The form of  $H^a$  is

$$H^a = (h + J_b + K_b) + P_b h + h P_b - EP_b \quad (3.129)$$

where  $P_b = |b\rangle\langle b|$  is a projection operator. However, the explicit form is of no importance here. To solve (3.127), we expand  $\varphi_a$  with (3.123)–(3.124) leading to

$$\sum_\nu \langle \chi_\mu | (H^a - \epsilon_a) | \chi_\nu \rangle C_{\nu a} = 0, \quad (3.130)$$

which, in matrix notation, is

$$\mathbf{H}^a \mathbf{C}_a = \epsilon_a \mathbf{S} \mathbf{C}_a, \quad (3.131)$$

where the elements of the  $\mathbf{H}^a$  and  $\mathbf{S}$  matrices are

$$\begin{aligned} H_{\mu\nu}^a &= \langle \chi_\mu | H^a | \chi_\nu \rangle \\ &= \langle \chi_\mu | (h + J_b + K_b) | \chi_\nu \rangle + \langle \chi_\mu | b \rangle \langle b | h | \chi_\nu \rangle + \langle \chi_\mu | h | b \rangle \langle b | \chi_\nu \rangle - E \langle \chi_\mu | b | \chi_\nu \rangle \end{aligned} \quad (3.132)$$

and

$$S_{\mu\nu} = \langle \chi_\mu | \chi_\nu \rangle. \quad (3.134)$$

For the HF wavefunction, the corresponding matrix is

$$H_{\mu\nu}^{HF} = \langle \chi_\mu | (h + J_b) | \chi_\nu \rangle \quad (3.135)$$

The presence of the second (exchange) term in the wavefunction (3.118) leads to the other terms in (3.133). Of these additional terms, only the  $K_b$  term would be present if the orbitals  $\varphi_a$  and  $\varphi_b$  were orthogonal.

Equation (3.131) is the condition for orbital  $\varphi_a$  to be optimum, there is a similar equation

$$\mathbf{H}^b \mathbf{C}_b = \epsilon_b \mathbf{S} \mathbf{C}_b \quad (3.136)$$

to solve for the optimum orbital  $\varphi_b$ . Thus, in the GVB method, we must solve self-consistently for *two* orbitals, whereas in the HF method we have just one orbital, and hence, one equation to solve. Otherwise both involve similar computational procedures.

As shown in Figure 3.9, the GVB orbital of  $\text{H}_2$  corresponds closely to the VB orbital.

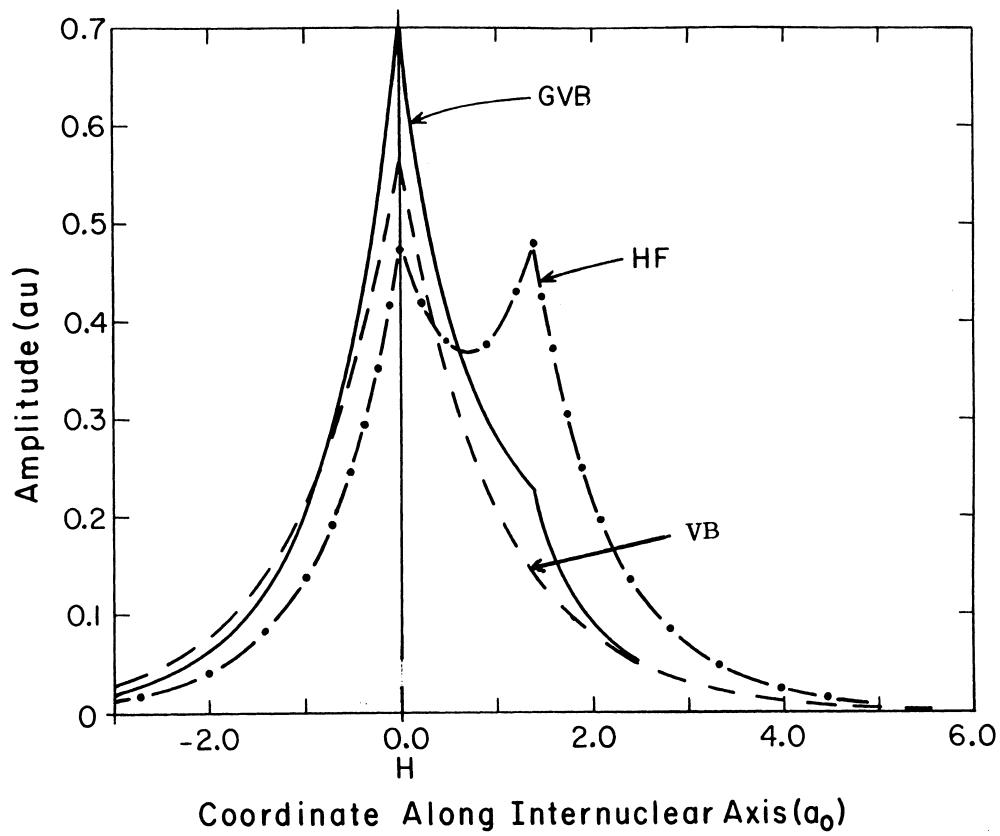


Figure 3.9: Comparison of the GVB, VB and HF orbitals of  $H_2$  at  $R = 1.4a_0$ . Only one of the GVB and VB orbitals is shown.

## Interpretation

If (3.127) is satisfied for all basis functions  $\chi_\mu$  of a complete set, then  $\varphi_a$  satisfies the differential equation

$$H^a \varphi_a = \epsilon_a \varphi_a. \quad (3.137)$$

The  $H^a$  in (3.137), can be written as

$$H^a = h + V_b \quad (3.138)$$

where  $V_b$  contains all the terms depending upon orbital  $\varphi_b$ . We can consider  $V_b$  as the average potential seen by the electron in  $\varphi_a$  due to the electron in  $\varphi_b$ . Note that  $V_b$  is not a local potential, that is, a function of  $\mathbf{r}$ . Rather,  $V_b$  contains integral operators and upon operating on  $\varphi_a$  and  $\varphi_b$  inside the integral. Even so, we can consider  $V_b$  as the effective potential due to  $\varphi_b$  as seen by  $\varphi_a$ . The average potential is not just the Coulomb potential  $J_b$  due to the electron on  $\varphi_b$ , 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  $\varphi_a$  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  $\varphi_a$  and  $\varphi_b$ .

The operator  $H^a$ , in (3.138) 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  $\varphi_b$ . Since orbital  $\varphi_a$  is an eigenfunction of  $H^a$ , we can interpret  $\varphi_b$  as the eigenstate of an electron moving in the average potential,  $V_b$ , due to the other electron of the system. Similarly, of course, we can interpret  $\varphi_b$  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 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 independent particle interpretations will be very useful in understanding the wavefunctions.

It is important to note here that the independent particle interpretation comes about from the one-particle Schrödinger equation, such as (3.137), arising from application of the variational principle to a special type of wavefunction (3.118). The real electrons of a molecule are quite indistinguishable, and we do not imply that one of the electrons moves in one orbital, say  $\varphi_a$ , while the other electron moves in the other orbital,  $\varphi_b$ . What we say is that the orbitals satisfy a one-electron Schrödinger equation for which the field term is the average potential of an electron in the other orbital. This is not the equation describing the moving of one of the real electrons. However, consider the eigenstates of two fictitious, distinguishable electrons, we do obtain the optimum orbitals for the many-electron wavefunction (3.118). It is really the orbitals which are distinguishable here, not the electrons.

## GVB Natural Orbitals

In order to obtain another view of the GVB wavefunction, we will define the GVB orbitals  $\varphi_g$  and  $\varphi_u$  as the sum and difference of the GVB orbitals  $\varphi_\ell$  and  $\varphi_r$

$$\varphi_g = \frac{(\varphi_\ell + \varphi_r)}{D_g} \quad (3.139)$$

$$\varphi_u = \frac{(\varphi_r - \varphi_\ell)}{D_u} \quad (3.140)$$

where

$$D_g = \sqrt{2(1+S)} \quad (3.141)$$

and

$$D_u = \sqrt{2(1-S)} \quad (3.142)$$

and  $S$  is the overlap of the GVB orbitals

$$S = \langle \varphi_\ell | \varphi_r \rangle. \quad (3.143)$$

Rearranging (3.139)–(3.140) leads to

$$2\varphi_r = D_g\varphi_g + D_u\varphi_u \quad (3.144)$$

and

$$2\varphi_\ell = D_g\varphi_g - D_u\varphi_u \quad (3.145)$$

and hence, the total wavefunction becomes

$$\Phi = \varphi_\ell\varphi_r + \varphi_r\varphi_\ell = \frac{[D_g^2\varphi_g\varphi_g - D_u^2\varphi_u\varphi_u]}{2}, \quad (3.146)$$

Thus, we may view the GVB wavefunction in terms of  $\varphi_\ell$  and  $\varphi_r$ , where there is always one electron in  $\varphi_\ell$  and one in  $\varphi_r$ . Or, one may view this wavefunction in terms of GVB *natural orbitals*  $\varphi_g$  and  $\varphi_u$ , where part of the time both electrons are in  $\varphi_g$  and part of the time both are in  $\varphi_u$ . Here,  $\varphi_g$  resembles the bonding orbital and  $\varphi_u$  the antibonding orbital. The equivalence of these two descriptions may be clear in Figure 3.10, where (d) and (g) are equivalent.

The first natural orbital  $\varphi_g$  has a good kinetic energy, but a bad two-electron energy. Mixing in a small amount of  $\varphi_u$  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 wave function in Figure 3.10 (d) or (g).

Requiring that the total wavefunction be normalized, leads to

$$\Phi = \frac{(\varphi_\ell\varphi_r + \varphi_r\varphi_\ell)}{\sqrt{2(1+S^2)}} = C_g\varphi_g\varphi_g - C_u\varphi_u\varphi_u \quad (3.147)$$

where from (3.141)–(3.142),

$$\frac{C_u}{C_g} = \frac{D_u^2}{D_g^2} = \frac{(1-S)}{(1+S)} \quad (3.148)$$

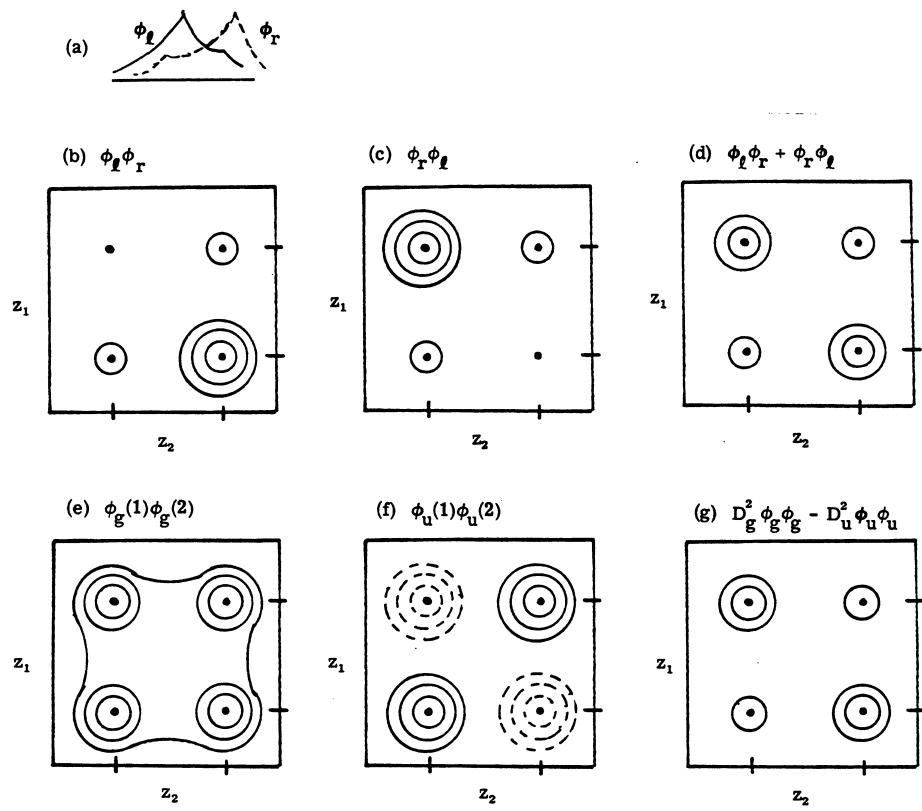


Figure 3.10:

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  $R = 1 a_0$ , and  $S = 0.8$ , and hence

$$\frac{C_u}{C_g} = \frac{1}{9} = 0.11. \quad (3.149)$$

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 the 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,  $\varphi(1)\varphi(2)$ , 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 state 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 system, e.g., 1.5% of He, it is comparable to many quantities of interest.

In the GVB wavefunction of  $H_2$

$$\varphi_\ell(1)\varphi_r(2) + \varphi_r(1)\varphi_\ell(2), \quad (3.150)$$

one electron is in  $\varphi_\ell$ , while the other electron is in  $\varphi_r$ , 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  $\varphi_\ell$  orbital, does not affect the probability of electron 2 being at any particular position in orbital  $\varphi_r$ , 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

$$\Phi_{(1,2)}^{NO} = C_g\varphi_g(1)\varphi_g(2) - C_u\varphi_u(1)\varphi_u(2). \quad (3.151)$$

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

$$\Phi^{HF}(R, R) = \varphi(R)\varphi(R) \quad (3.152)$$

$$\Phi^{HF}(R, L) = \varphi(R)\varphi(L), \quad (3.153)$$

and since  $\varphi(R) = \varphi(L)$ , we have equal probabilities

$$|\Phi^{HF}(R, R)|^2 = |\Phi^{HF}(R, L)|^2 \quad (3.154)$$

of the electrons being on the same, or opposite, sides. In the GVB wavefunction (3.150), we find

$$\Phi^{GVB}(R, R) = \varphi_\ell(R)\varphi_r(R) + \varphi_r(R)\varphi_\ell(R) \quad (3.155)$$

and

$$\Phi^{GVB}(R, L) = \varphi_\ell(R)\varphi_r(L) + \varphi_r(R)\varphi_\ell(L), \quad (3.156)$$

and hence,

$$\Phi^{GVB}(R, R) < \Phi^{GVB}(R, L), \quad (3.157)$$

that is, we obtain the static correlation referred to above. Using the NO form of the wavefunction, we obtain

$$\Phi^{NO}(R, R) = C_g\varphi_g(R)\varphi_g(R) - C_u\varphi_u(R)\varphi_u(R) \quad (3.158)$$

$$\Phi^{NO}(R, L) = C_g\varphi_g(R)\varphi_g(L) - C_u\varphi_u(R)\varphi_u(L) \quad (3.159)$$

$$= C_g\varphi_g(R)\varphi_g(R) + C_u\varphi_u(R)\varphi_u(R) \quad (3.160)$$

using the symmetries of  $\varphi_g$  and  $\varphi_u$ , and hence,

$$\Phi^{NO}(R, R) < \Phi^{NO}(R, L) \quad (3.161)$$

just as in (3.157). Comparing (3.151) with the HF wavefunction

$$\Phi^{HF}(1, 2) = \varphi_g(1)\varphi_g(2) \quad (3.162)$$

we see that in order to obtain effective electron correlation, the second natural orbital must have a shape similar to that of the first, dominant, natural orbital, but with an extra nodal plane bisecting the first natural orbital. 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. This discussion should all be clear from Figure 3.10.

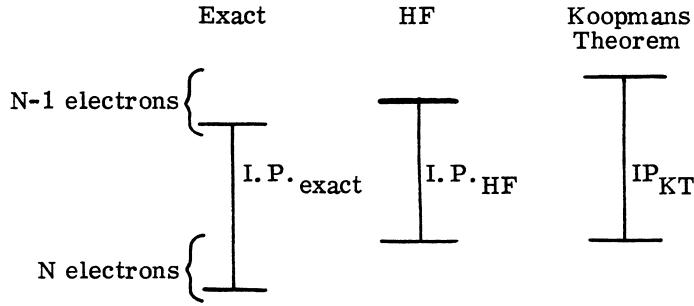


Figure 3.11:

### **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 the HF and GVB should be too small. On the other hand, we can get an approximate independent particle from Koopmans' theorem. The Koopmans independent particle 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 nonoptimum leading to too high a value for  $E_{N-1}$  and, hence too large a prediction of independent particle. However, the independent particle calculated using self-consistent 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 independent particle is usually rather good, within about 10%. These effects are indicated in Figure 3.11.

#### **3.5.5 CI Wavefunctions**

Starting with a one-electron basis

$$\{\chi_\mu : \mu = 1, 2, \dots, P\} \quad (3.163)$$

we can construct a two-electron basis

$$\{\chi_\mu(1)\chi_\nu(2); \mu, \nu = 1, 2, \dots, P\} \quad (3.164)$$

by combining all products of one-electron functions. In terms of this basis, the most general wavefunction is

$$\Phi(1, 2) = \sum_{\mu, \nu=1}^P C_{\mu\nu} \chi_\mu(1) \chi_\nu(2). \quad (3.165)$$

The terms in (3.165) are called *configurations*, and the resulting wavefunction is called a *CI wavefunction*.

Applying the variational principle from earlier, the optimum coefficients for (3.165) are solutions of the equation

$$\sum_{\mu\nu} (H_{\mu\nu,\sigma\eta} - E) C_{\mu\nu} = 0. \quad (3.166)$$

For a complete basis ( $P \rightarrow \infty$ ) the resulting CI wavefunction is the exact wavefunction of the system.

### Permutational Symmetry

Because the electrons are identical, the Hamiltonian must be invariant (unchanged) upon permutation (interchange) of the electrons

$$H(2, 1) = H(1, 2). \quad (3.167)$$

As a result of this permutational symmetry, the exact eigenstates of  $H$  can always be taken as either symmetric

$$\Psi^s(2, 1) = \Psi^s(1, 2) \quad (3.168)$$

or antisymmetric

$$\Psi^a(2, 1) = -\Psi^a(1, 2) \quad (3.169)$$

under permutation. The proof is quite analogous to that in Chapter 2 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  $\Psi^s$  are allowed only for singlet ( $S = 0$ ) spin states and antisymmetric spatial wavefunctions  $\Psi^a$  are allowed only for triplet ( $S = 1$ ) spin states.

### The Nodal Theorem

Next we will show that the lowest state of  $H(1, 2)$  (assuming  $H$  is symmetric (3.167)) is always a symmetric wavefunction,  $\Psi^s(1, 2)$ , (3.168).

As shown in Chapter 1, 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 the top wave function in Figure 3.12 cannot be the ground state, except for  $R = \infty$ , where this state is degenerate with the nodeless state. Whereas the bottom state in Figure 3.12 can. The nodal theorem applies also for many electron systems, such as

$$H(1, 2) = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 + v(r_1) + v(r_2) + \frac{1}{r_{12}} \quad (3.170)$$

(the proof is exactly as in Chapter 1). We will now use the nodal theorem to show that the ground state of any two-electron system must be a symmetric wavefunction.

Letting  $\mathbf{r}_1 = \mathbf{r}_2$  in an antisymmetric wavefunction

$$\psi^a(\mathbf{r}_2, \mathbf{r}_1) = -\psi^a(\mathbf{r}_1, \mathbf{r}_2) \quad (3.171)$$

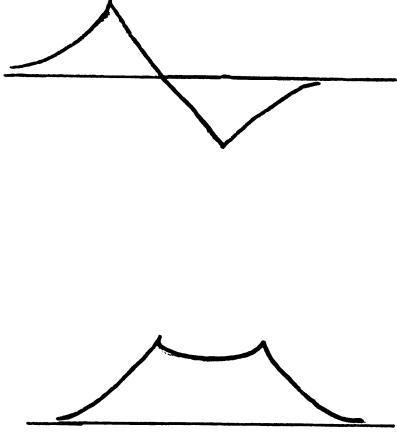


Figure 3.12: LCAO combinations with (top) and without (bottom) a node.

leads to

$$\psi^a(\mathbf{r}_1, \mathbf{r}_1) = -\psi^a(\mathbf{r}_1, \mathbf{r}_1) \quad (3.172)$$

and hence,

$$\psi^a(\mathbf{r}_1, \mathbf{r}_2) = 0 \quad (3.173)$$

if  $\mathbf{r}_1 = \mathbf{r}_2$ . (For example, typical one-dimensional cases are illustrated in Figure 3.13.)

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 permutationally symmetric (3.168). 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 must 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 (3.170) is not this singular and, hence, the inequalities apply.

### Natural Orbitals

In Section 3.9.2 we show that the CI wavefunction (3.165) for the ground state of any two-electron system, can be written as

$$\Psi^0(1, 2) = \sum_{\mu=1} \bar{C}_{\mu} \bar{\chi}_{\mu}(1) \bar{\chi}_{\mu}(2) \quad (3.174)$$

(that is, double occupied orbitals only) where the orbitals  $\{\bar{\chi}_{\mu}\}$ , called *natural orbitals*, are orthonormal

$$\langle \bar{\chi}_{\mu} | \bar{\chi}_{\nu} \rangle = \delta_{\mu\nu}. \quad (3.175)$$

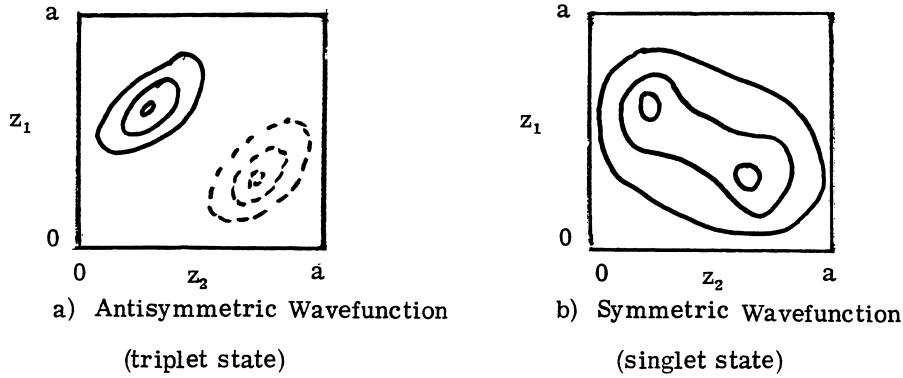


Figure 3.13: Illustration of nodal patterns of two-electron systems, in one dimension.

Since (3.174) has only  $P$  terms rather than  $P^2$ , as in (3.165), it is obviously easier to interpret.

The density of electrons in a two-electron system is defined as

$$\rho(1) = \int d^3r_2 \Psi(1, 2)^* \Psi(1, 2). \quad (3.176)$$

Thus, using (3.174) leads to

$$\rho(1) = \sum_{\mu, \nu} \bar{C}_\mu^* \bar{C}_\nu \bar{\chi}_\mu(1)^* \bar{\chi}_\nu(1) \langle \chi_\mu(2) | \chi_\nu(2) \rangle = \sum_\mu p_\mu |\chi_\mu(1)|^2 \quad (3.177)$$

where

$$p_\mu = |C_\mu|^2. \quad (3.178)$$

Since there is a total of two electrons in the system

$$\int d^3r_1 \rho(1) = 2, \quad (3.179)$$

the coefficients must sum to two,

$$\sum_\mu p_\mu = 2. \quad (3.180)$$

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  $p_\mu$  that sums to two.

## 3.6 Wavefunctions of 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 the He Atom

First, we consider various approximations of the HF wavefunction

$$\Phi^{HF}(1, 2) = \varphi(1)\varphi(2), \quad (3.181)$$

where the HF orbital  $\varphi$  is expanded in a basis set.

#### MBS

The simplest description of He atom is to place two electrons in the  $1s$  orbital of  $\text{He}^+$

$$\chi = e^{-\zeta r} \quad (3.182)$$

where  $\zeta = 2.0$ . The total energy in hartrees is just

$$E = 2\epsilon_1 + J = -2.75, \quad (3.183)$$

where  $\epsilon_1 = -2.0$  is the energy of  $\text{He}^+$ , and

$$J = \frac{5}{8}\zeta = 1.25, \quad (3.184)$$

is the Coulomb interaction of the two electrons, see Section 3.9.3.

This description can be improved by optimizing  $\zeta$ , leading to the MBS description. As shown in Section 3.9.3, the energy has the form

$$E = \zeta^2 T_1 + \zeta V_1, \quad (3.185)$$

where

$$T_1 = (2) \left( \frac{1}{2} \right) = 1 \quad (3.186)$$

and

$$V_1 = -2Z + \frac{5}{8} \quad (3.187)$$

(i.e.,  $T_1$  and  $V_1$  are the kinetic and potential energies for the case of  $\zeta = 1$ ). Requiring that

$$\frac{\partial E}{\partial \zeta} = 0, \quad (3.188)$$

to obtain the optimum  $\zeta$ , leads to

$$\zeta_{OPT} = -\frac{V_1}{2T_1} = Z - \frac{5}{16} = 1.6875 \quad (3.189)$$

for He. Since the optimum  $\zeta$  for the one-electron atom is  $\zeta = Z$ , we can interpret the  $\zeta_{OPT}$  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

$$\sigma = \frac{5}{16} \quad (3.190)$$

Table 3.2: Parameters of HF wavefunctions of the ground state of He.  $E$  is the total energy,  $E$  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 <sup>a</sup>	3 <sup>a</sup>	12 <sup>b</sup>
$E$	-2.847656	-2.861673	-2.861680	-2.861680
$\epsilon$	-0.89648	-0.91792	-0.91795	-0.91796
$ns(\zeta)C_i$	$1s(1.68750)1.0$	$1s(1.453)0.84289$ $1s(2.906)0.18159$	$1s(1.450)1.36211$ $2s(1.723)-0.28189$ $2s(2.641)-0.10724$	$1s(3.0)0.45742$ $1s(1.4)0.00000$ $2s(3.0)0.24427$ $2s(1.4)0.12985$ $3s(3.0)0.13657$ $3s(1.4)0.11340$ $4s(3.0)0.09451$ $4s(1.4)-0.08606$ $5s(3.0)0.00819$ $5s(1.4)0.02546$ $6s(3.0)0.02767$ $6s(1.4)-0.00267$

<sup>a</sup>See reference 19. <sup>b</sup>See reference 20.

is sometimes referred to as the *shielding correction*.

Substituting (3.189) into (??)–(??) leads to

$$E_{OPT} - \frac{V_1^2}{4T_1} = +\frac{V_1}{2}\zeta_{OPT} = -\zeta_{OPT}^2 = -2.84766h. \quad (3.191)$$

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

$$\zeta_{OPT} = Z - \frac{5}{16}. \quad (3.192)$$

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  $\text{He}^+$  is -2.0, the use of the calculated  $E$  of (3.191), leads to a predicted independent particle of 0.84766 or 94% of the exact value. Use of the Koopmans theorem leads to

$$-IP = \langle \varphi | h | \varphi \rangle + J_{\varphi\varphi} = \frac{1}{2}\zeta_{OPT}^2 = Z\zeta_{OPT} + \frac{5}{8}\zeta_{OPT} = -\frac{1}{2}\zeta_{OPT}^2 + \frac{5}{16}\zeta_{OPT} = -0.89648, \quad (3.193)$$

99.2% of the experimental value (a better value is obtained because we describe the ion badly).

### Bigger Basis Sets

The results of using various-sized basis sets for HF calculations on He, are listed in Table ???. In the cases  $P = 1, 2$ , and  $3$ , extensive optimization of the parameters

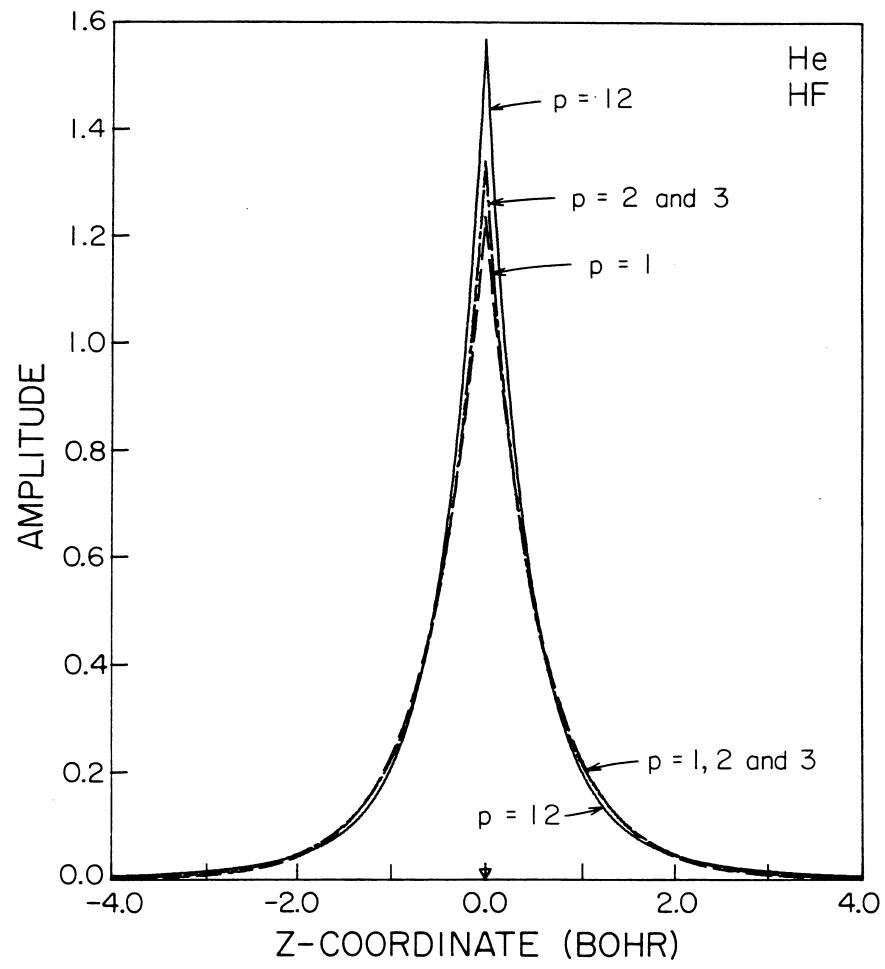


Figure 3.14: Comparison of HF wavefunctions for He using various (optimum) basis sets.  $p$  indicates the number of functions in the basis set.

was carried out, leading to quite short expansions. Thus, with  $P = 2$  we are within  $0.000007 \text{ h} = 0.0002 \text{ eV} = 0.005 \text{ kcal/mol}$  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  $0.042 \text{ h} = 1.1 \text{ eV} = 25 \text{ kcal/mol}$ . The HF orbitals in these various approximations, are plotted in Figure 3.14. Note that even though  $P = 3$  and  $P = 12$  lead to the same energy, to 6 decimal places, there are still noticeable change in the orbitals. The conclusion 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).

### 3.6.2 The GVB Wavefunctions for the He Atom

For He atom, the GVB wavefunction is the optimum wavefunction of the form

$$\Phi^{GVB}(1, 2) = \varphi_a(1)\varphi_b(2) + \varphi_b(1)\varphi_a(2) \quad (3.194)$$

The GVB orbitals of He are shown in Figure 3.15, where they are compared to the  $1s$  orbital of  $\text{He}^+$  and to the HF orbital of He.

We see that  $\varphi_a^{GVB}$  is very similar to the  $1s$  orbital of  $\text{He}^+$ , and that  $\varphi_b^{GVB}$  is much more diffuse. Thus, we envision He as having, first, one electron in the  $1s$  orbital of  $\text{He}^+$  (this is orbital  $\varphi_a$ ) experiencing an effective nuclear charge of  $Z \approx 2$ , and secondly, the second electron in an orbital ( $\varphi_b$ ) experiencing an effective charge of  $Z \approx 1$ , nuclear charge of 2 but shielded by the  $\varphi_a$  electron. Describing both  $\varphi_a$  and  $\varphi_b$  as simple exponentials and optimizing the exponents, leads to effective charges of  $\zeta_b = 1.189$  and  $\zeta_a = 2.183$ , as expected from the simple picture [?].

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  $\text{He}^+$ .

A more extreme case is  $\text{H}^-$ , the GVB orbitals for which are shown in Figure 3.16. Here, the first electron (in  $\varphi_a$ ) is very similar to a hydrogen  $1s$  orbital, and the second electron is barely bound, leading to a very diffuse  $\varphi_b$  orbital. As shown in Tables 3.3-3.6, the HF wavefunction of  $\text{H}^-$  yields an energy of  $-0.487$ , higher than the energy of the hydrogen atom, implying that  $\text{H}^-$  is not stable with respect to 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  $\text{H}^-$ , the exact energy is  $-0.527$ .

### 3.6.3 CI Wavefunctions for the He Atom

The results of several CI calculations on He are shown in Table 3.7. Analyzing in terms of natural orbitals leads to the results in Table 3.8. 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  $2p$  natural orbitals are given in Figure 3.17, where we see that the higher natural orbitals are concentrated in the same region as the  $1s$  orbital but with the additional nodal plane, circular for  $\psi_{2s}$  and planar for each  $\varphi_{2p}$ .

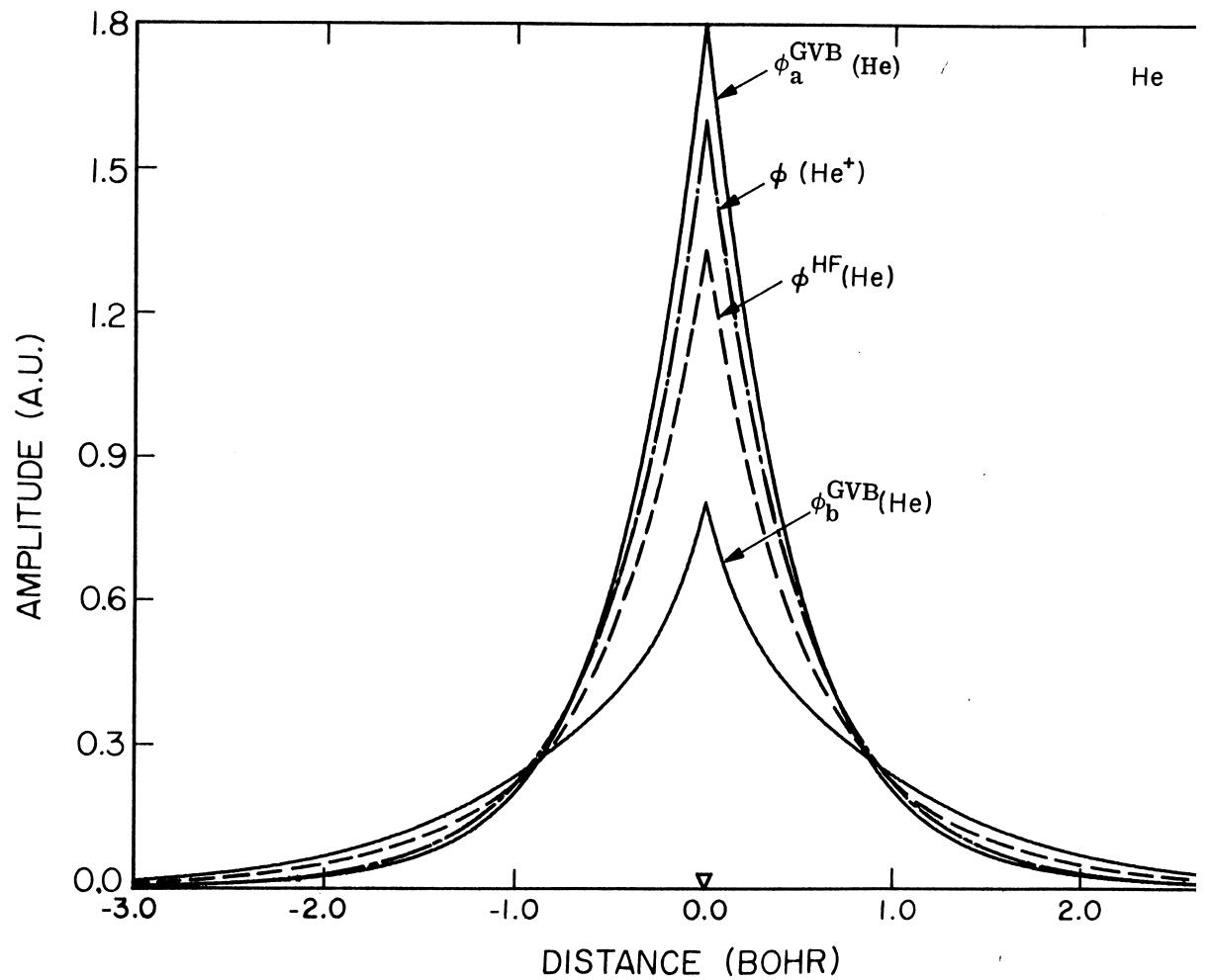


Figure 3.15: The HF and GVB orbitals for He and He<sup>+</sup>.

GI H-,H ORBITAL

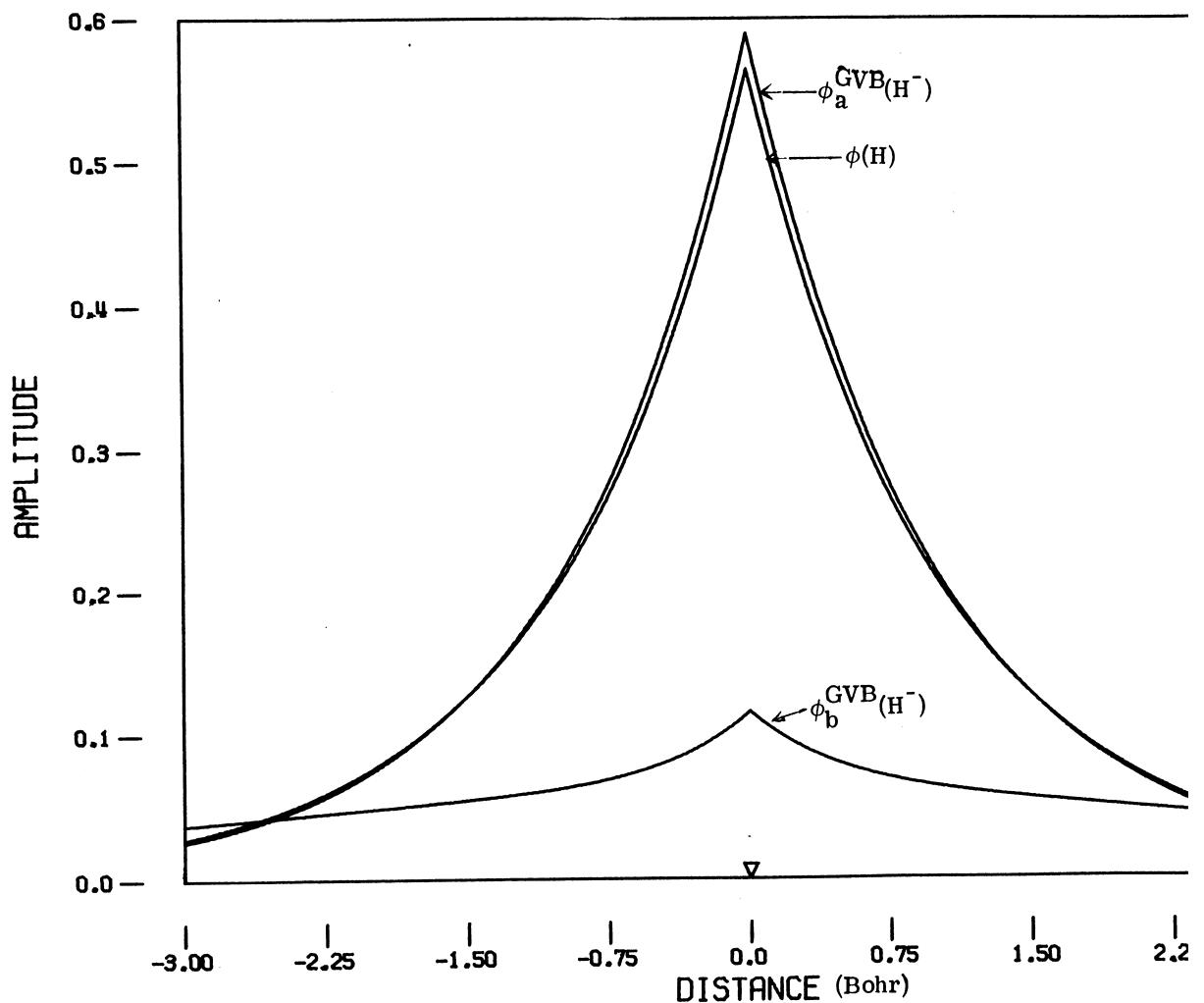


Figure 3.16: The GVB orbitals of  $\text{H}^-$ .

Table 3.3: Comparison of energies for two-electron atoms: Exact.

	$E^a$	I.P. <sup>b</sup>
H <sup>-</sup>	-0.527751	0.027751
He	-2.903724	0.903724
Li <sup>+</sup>	-7.279914	2.779914
Be <sup>++</sup>	-13.65557	5.65557
B <sup>3+</sup>	-22.03097	9.53097
C <sup>4+</sup>	-32.40625	14.40625
N <sup>5+</sup>	-44.78145	20.28145
O <sup>6+</sup>	-59.15660	27.15660
F <sup>7+</sup>	-75.53171	35.03171
Ne <sup>8+</sup>	-93.90681	43.90681

Table 3.4: Comparison of energies for two-electron atoms. HF

	$E_{HF}^c$	$\epsilon_{HF}^C$	IP ( $\Delta E$ )	$E_{corr}$
H <sup>-</sup>	-0.4870 <sup>d</sup>	-0.0642 <sup>d</sup>	-0.0130	0.0408
He	-2.861680	-0.917956	0.8617	0.0420
Li <sup>+</sup>	-7.2364150	-2.792365	2.7364	0.0435
Be <sup>++</sup>	-13.61130	-5.667116	5.6113	0.0443
B <sup>3+</sup>	-21.98623	-9.541979	9.4862	0.0447
C <sup>4+</sup>	-32.36119	-14.41689	14.3612	0.0451
N <sup>5+</sup>	-44.73616	-20.29183	20.2362	0.0453
O <sup>6+</sup>	-59.11115	-27.166679	27.1112	0.0455
F <sup>7+</sup>	-75.48613	-35.04176	34.9861	0.0456
Ne <sup>8+</sup>	-93.86112	-43.91673	43.8611	0.0457

Table 3.5: Comparison of energies for two-electron atoms: GVB.

	$E_{GVB}$	$\epsilon_a$	$\epsilon_b$	IP ( $\Delta E$ )	$E_{corr}$
H <sup>-</sup>	-0.51384 <sup>d</sup>	-0.26800	-0.01471	0.0138	0.0139
He	-2.87800 <sup>f</sup>	-1.2152	-0.9039	0.8780	0.0257
Li <sup>+</sup>	-7.25142 <sup>f</sup>	-3.1965	-2.8149	2.7514	0.0285
Be <sup>++</sup>	-13.62577 <sup>f</sup>	-6.1746	-5.7330	5.6258	0.0298
B <sup>3+</sup>	-22.000159	-10.14932	-9.65472	9.5002	0.0308
C <sup>4+</sup>					
N <sup>5+</sup>					
O <sup>6+</sup>					
F <sup>7+</sup>					
Ne <sup>8+</sup>					

Table 3.6: Comparison of energies for two-electron atoms: CI.

	$E_{CI}^e$
H <sup>-</sup>	-0.52751
He	-2.90320
Li <sup>+</sup>	-7.27924
Be <sup>++</sup>	-13.65481
B <sup>3+</sup>	-2.03016
C <sup>4+</sup>	-32.40540
N <sup>5+</sup>	-44.78057
O <sup>6+</sup>	-59.15570
F <sup>7+</sup>	-
Ne <sup>8+</sup>	-

<sup>a</sup>See reference 21. <sup>b</sup>Calculated using  $E$  from reference 21. <sup>c</sup>See reference 20. <sup>d</sup>See reference 22. <sup>e</sup>See reference 23. 35 configurations were used. <sup>f</sup>See reference 24. <sup>g</sup>See reference 25.

Table 3.7: Energies for CI wavefunctions of the ground state of He atom.

Number of Basis Functions <sup>a</sup>					Energy
s	p	d	f	g	
5					-2.87896 <sup>a</sup>
5	4				-2.90039 <sup>a</sup>
5	4	3			-2.90258 <sup>a</sup>
5	4	3	2		-2.90307 <sup>a</sup>
5	4	3	2	1	-2.90320 <sup>a</sup>
Pekeris					-2.90372 <sup>b</sup>
HF					-2.86168
GVB					-2.87800

<sup>a</sup>See reference 23. <sup>b</sup>See reference 26.

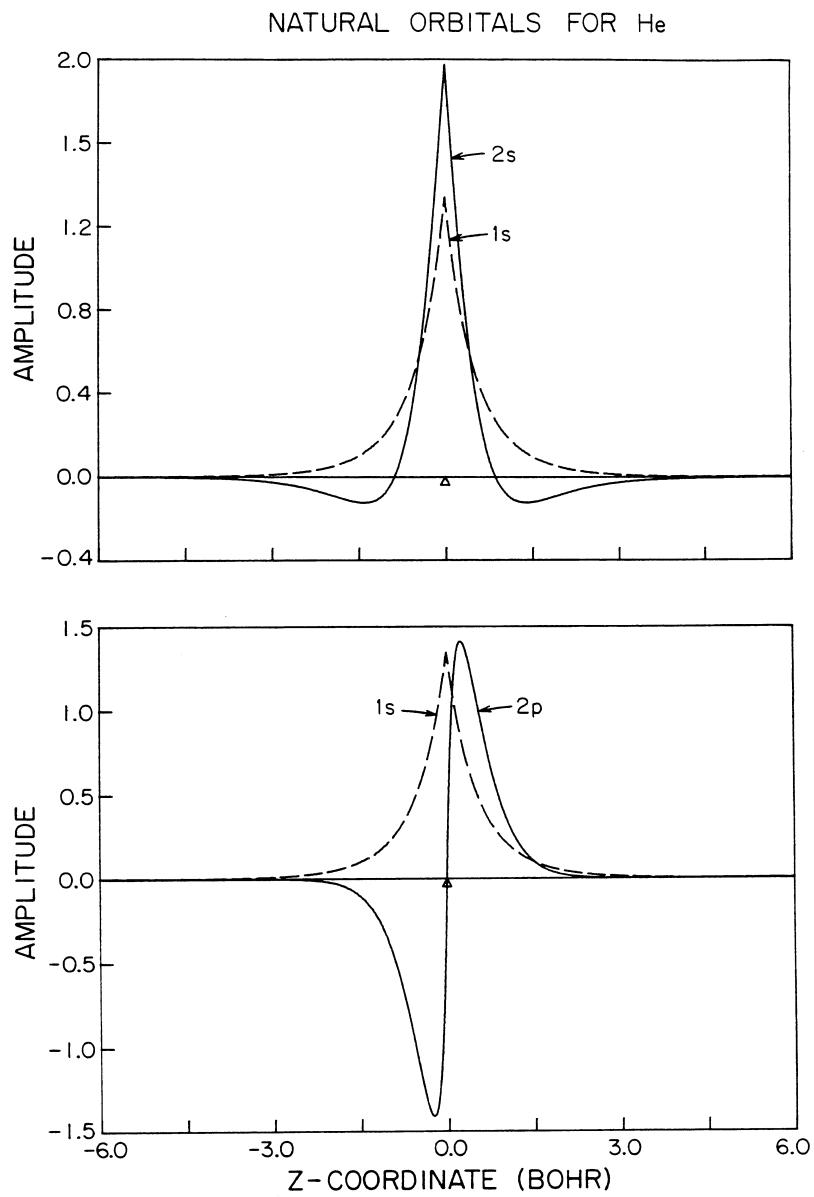


Figure 3.17: The natural orbitals for He.

Table 3.8: Analysis of He CI wavefunction in terms of natural orbitals.<sup>a</sup>

Natural Orbital	Energy Lowering (mh)	% $E_{corr}$
2s	16.30	38.83
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

<sup>a</sup>See reference 27. <sup>b</sup>Total correlation energy is equal to 0.0420 hartree.

Using the five dominant natural orbitals, 1s, 2s, 2p<sub>x</sub>, 2p<sub>y</sub>, and 2p<sub>z</sub>, leads to the wavefunction

$$\psi^{CI} = C_{1s}\varphi_{1s}\varphi_{1s} - C_{2s}\varphi_{2s}\varphi_{2s} - C_{2p} [\varphi_{2p_x}\varphi_{2p_x} + \varphi_{2p_y}\varphi_{2p_y} + \varphi_{2p_z}\varphi_{2p_z}] \quad (3.195)$$

where  $C_{1s} = 0.99599$ ,  $C_{2s} = 0.06160$ , and  $C_{2p} = 0.06188$ . 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 (3.195) as the exact wavefunction of He.

### CI Wavefunction Interpretation

To interpret the wavefunction (3.195), we will consider one by one the effects of adding any one of the four correlating terms to the dominant, first, term. The wavefunction

$$C_{1s}\varphi_{1s}\varphi_{1s} - C_{2s}\varphi_{2s}\varphi_{2s} \quad (3.196)$$

can be rewritten in the GVB form

$$\varphi_a\varphi_b + \varphi_b\varphi_a \quad (3.197)$$

where

$$\sqrt{2}\varphi_a = \sqrt{C_{1s}}\varphi_{1s} + \sqrt{C_{2s}}\varphi_{2s} \quad (3.198)$$

$$\sqrt{2}\varphi_b = \sqrt{C_{1s}}\varphi_{1s} - \sqrt{C_{2s}}\varphi_{2s} \quad (3.199)$$

are the GVB orbitals. Thus, from earlier in this section, we see that the  $\varphi_{2s}$  natural orbital in (3.196) 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

$$C_{1s}\varphi_{1s}\varphi_{1s} - C_{2p}\varphi_{2p_x}\varphi_{2p_x} \quad (3.200)$$

can also be rewritten as (3.197), where

$$\sqrt{2}\varphi_a = \sqrt{C_{1s}}\varphi_{1s} + \sqrt{C_{2p}}\varphi_{2p_x} \quad (3.201)$$

$$\sqrt{2}\varphi_b = \sqrt{C_{1s}}\varphi_{1s} - \sqrt{C_{2p}}\varphi_{2p_x} \quad (3.202)$$

In (3.201)–(3.202) we see that when one electron is in the  $+x$  direction, the other tends to be in the  $-x$  direction. Similar results occurs for the  $\varphi_{2p_y}$  and  $\varphi_{2p_z}$  terms. The three correlations resulting from the terms involving  $p$  orbitals, are grouped together and referred to as *angular correlation*.

The three terms of (3.195) involving  $p$  orbitals, can be written as

$$[\varphi_{2px}\varphi_{2px} + \varphi_{2py}\varphi_{2py} + \varphi_{2pz}\varphi_{2pz}] = R(1)R(2)[\sin\theta_1 \cos\varphi_1 \sin\theta_2 \cos\varphi_2 + \sin\theta_1 \sin\varphi_1 \sin\theta_2 \sin\varphi_2 + \cos\theta_1 \cos\theta_2] \quad (3.203)$$

$$= R_{2p}(1)R_{2p}(2) \cos\theta_{12}, \quad (3.204)$$

where  $R(i)$  is the radial part of the orbital  $\varphi_i$ , and  $\theta_{12}$  is the angle between electron 1 and electron 2. Combining with the first term of (3.195), we obtain

$$C_{1s}R_{1s}(1)R_{1s}(2) - C_{2p}R_{2p}(1)R_{2p} \cos\theta_{12}. \quad (3.205)$$

With this form, we see that the magnitude of the wavefunction is increased (with respect to  $\varphi_{1s}\varphi_{1s}$ ) for  $|\theta_{12}| > 90^\circ$  and decreased for  $|\theta_{12}| < 90^\circ$ . Thus, (3.205) effects an angular correlation of the electrons.

Each of the four dominant correlating orbitals has one nodal plane not contained in  $\varphi_{1s}$ , and the correlation effect is across the nodal plane, increased probability of electrons being on opposite sides. Of course,  $\varphi_{1s}$  has no nodal planes, however, we have worded this so as to be appropriate also for correlations of more complicated orbitals than  $\varphi_{1s}$ . Starting with the  $\varphi_{1s}$  orbital, there are just four possible orbitals orthogonal to  $\varphi_{1s}$  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 (3.195) as the CI wavefunction of He.

## 3.7 Wavefunctions of H<sub>2</sub>

In this section we will discuss the HF, GVB, and CI wavefunctions for H<sub>2</sub>.

### 3.7.1 HF Wavefunctions for H<sub>2</sub>

In Figure 3.18, we show how quickly the HF wavefunctions for H<sub>2</sub> converge as a function of basis set size,  $P$ . The major effects in the orbital shape are in the bond region.

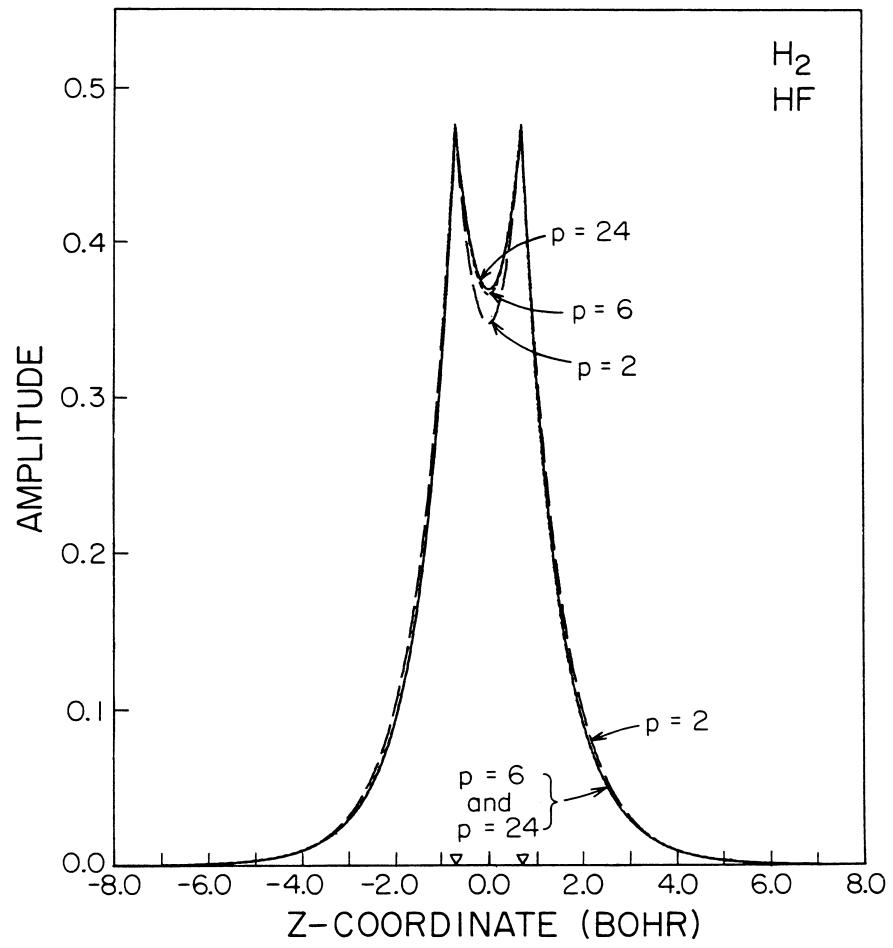


Figure 3.18: HF wavefunctions for  $\text{H}_2$  with  $R = 1.4a_0$ .  $p$  indicates the number of functions in the basis set.

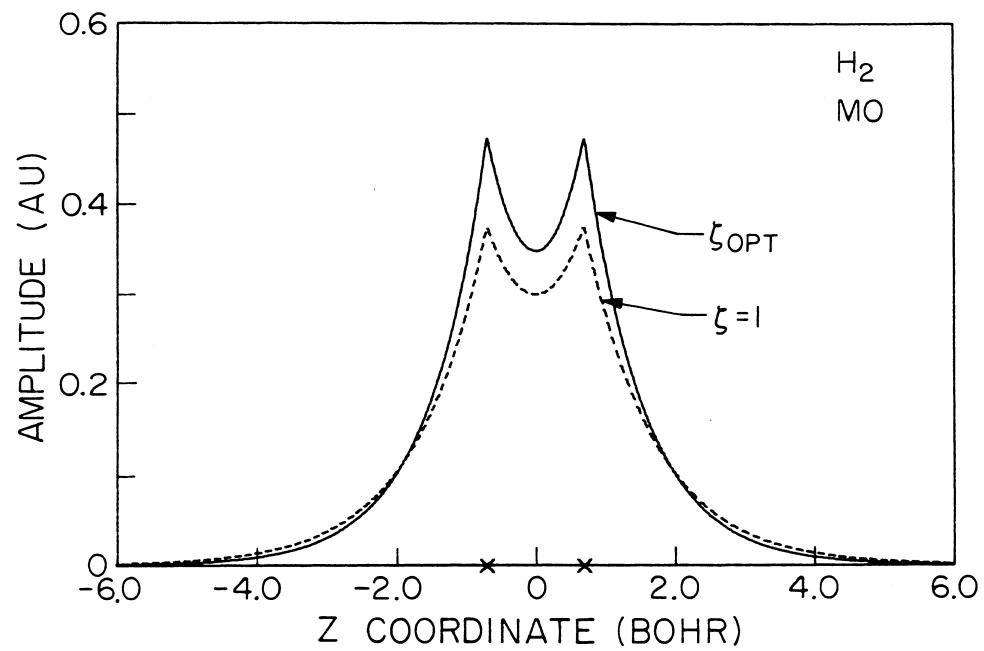


Figure 3.19: MO for H<sub>2</sub> using  $\zeta = 1$ , and  $\zeta_{OPT} = 1.1895$  ( $R = 1.4a_0$ ).

Table 3.9: Energy quantities for HF wavefunctions of  $H_2$  at  $R = 1.4a_0$ . Only the coefficients on one atom are shown, the others are equal by symmetry.

$P$	2	6 <sup>a</sup>	12 <sup>b</sup>	18 <sup>b</sup>	24 <sup>b</sup>
$E$	-1.12819	-1.13211	-1.13353	-1.13359	-1.13360
$\epsilon$		-0.59443	-0.59463	-0.59466	-0.59467
	1s(1.1895) 0.54572	1s(1.378) 0.43262	1s(1.19494) 1.03449	1s(1.14615) 0.84994	1s(1.18863) 0.84994
		2s(1.176) 0.12384	1s(3.22156) -0.6316	1s(3.01720) -0.01359	1s(2.50021) -0.01359
		2p <sub>x</sub> (1.820) 0.02827	2s(1.75027) -0.22058	2s(0.77682) 0.00894	2s(0.79445) 0.00894
			2s(3.41729) -0.02034	2s(1.62362) -0.12071	2s(1.73027) -0.12071
			2p <sub>z</sub> (1.81344) 0.04007	3s(3.54949) 0.00753	3s(3.43600) 0.00753
			2p <sub>z</sub> (3.55649) -0.00009	2p <sub>z</sub> (0.98920) 0.08858	2p <sub>z</sub> (1.05529) 0.08858
				2p <sub>z</sub> (3.11550) 0.00273	2p <sub>z</sub> (1.98553) 0.00273
				3p <sub>z</sub> (3.80593) 0.00790	2p <sub>z</sub> (4.08182) 0.00790
				3d <sub>z^2</sub> (1.19687) 0.02029	3p <sub>z</sub> (3.43359) 0.02029
					3d <sub>z^2</sub> (1.26663) 0.02029
					3d <sub>z^2</sub> (2.68042) 0.02029
					4f <sub>z^3</sub> (2.70808)

<sup>a</sup>See reference 28. <sup>b</sup>See reference 29. Each basis function is normalized to  $2/\sqrt{2}$ .

In Figure 3.19, we compare the MO wavefunction ( $P = 2, \zeta = 1$ ) with the MBS wavefunction ( $P = 2, \zeta_{OPT}$ ). Here there are significant changes near the nuclear and bond regions.

Comparing the energies in Table 3.9, we see that  $P = 6$  leads to an energy within  $0.00152 \text{ h} = 0.04 \text{ eV} = 1 \text{ kcal}$  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 *DVP*. More commonly, double valence is referred to as double zeta.

With even the best of these HF wavefunctions, the energy is  $0.04081 \text{ h} = 1.1 \text{ eV}$  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 3.9, optimized at each  $R$  but restricted so that  $\zeta_{1s} = \zeta_{2s}$ , is shown in Figure 3.20.

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  $E = -0.82199$  (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  $R = \infty$ , the HF wavefunction leads to an energy of  $-0.71542$  which is  $7.744 \text{ eV}$  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 3.10. A quite adequate description (0.2 kcal for the limit) is obtained using a

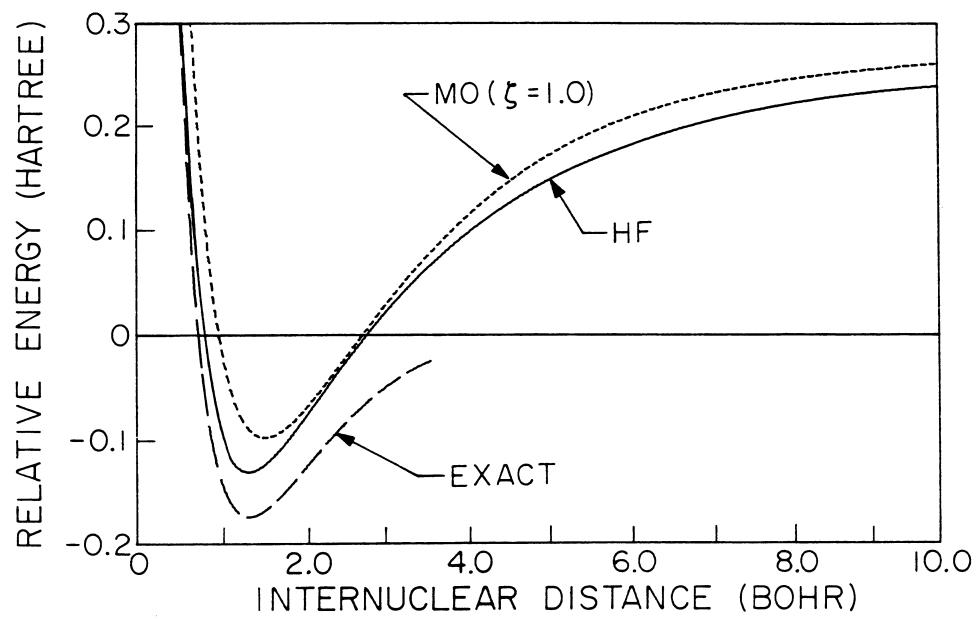


Figure 3.20: Comparison of energies for the MO wave function ( $\zeta = 1.0$ ) and the HF wavefunction (six basis functions).

Table 3.10: Energy and wavefunctions for GVB calculations on  $\text{H}_2$  at  $1.4a_0$ . Only the  $\varphi_\ell$  orbitals are given, the  $\varphi_r$  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 plus coefficient is positive toward the second center. All quantities in hartree atomic units.

P	2	4 <sup>a</sup>	6 <sup>b</sup>
E	-1.147777	-1.151345	-1.151526
$\epsilon$	-0.6877	-0.68348	-0.68472
S	0.79700	0.80093	0.80420
ns( $\zeta$ ) $C_\mu$	1s(1.2005) 0.91287 1s 0.12303	1s(1.1909) 0.8890 $2p_z$ (2.0928) -0.00672 1s 0.13631 $2P_z$ 0.03006	1s(1.3129) 0.77499 2s(1.1566) 0.11116 $2p_z$ (1.9549) -0.00310 1s 0.12161 2s 0.04199 $2p_z$ 0.03769

<sup>a</sup>Using 1s(1.262) and 2s(1.191) basis functions on each center, leads to  $E = -1.147804$ .

<sup>b</sup>Using 1s(1.3092), 2s(1.1273),  $2p_z$ (1.700), and  $3d_z^2$ (2.37) basis functions on each center, leads to  $E = -1.151887$ .

single optimized  $s$  function and a single  $p_z$  function on each center. Even the MBS is only  $4.1 \text{ mH} = 0.11 \text{ eV}$  above the limit.

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 orbital leads to a much greater overlap than the VB orbital, as shown in Figure 3.22. For example, at  $R = 1.4 a_0$ ,  $S^{GVB} = 0.804$  as compared to  $S^{VB} = 0.753$ .

### Energy Analysis

The GVB orbitals of  $\text{H}_2$  are compared with the VB orbitals in Figure 3.23, 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 Figure 3.24.

Some of the energy parameters of the HF, VB, and GVB wavefunctions are compared in Table 3.11, while the  $\zeta_{OPT}$  as a function of  $R$ , is given in Figure 3.25.

For  $\zeta = 1.0$ , all three wavefunctions yield an  $R_e$  for too large, 14% to 19%. Optimizing  $\zeta$  leads to errors of only 1% to 2% in  $R$ , and improves the calculated bond energies by about 20%. It is characteristic that GVB leads to too large an  $R$ , while HF leads to too small an  $R$ .

Using the form

$$\varphi_a \varphi_b + \varphi_b \varphi_a \quad (3.206)$$

for the GVB wavefunction, we can define classical and exchange terms much as for the

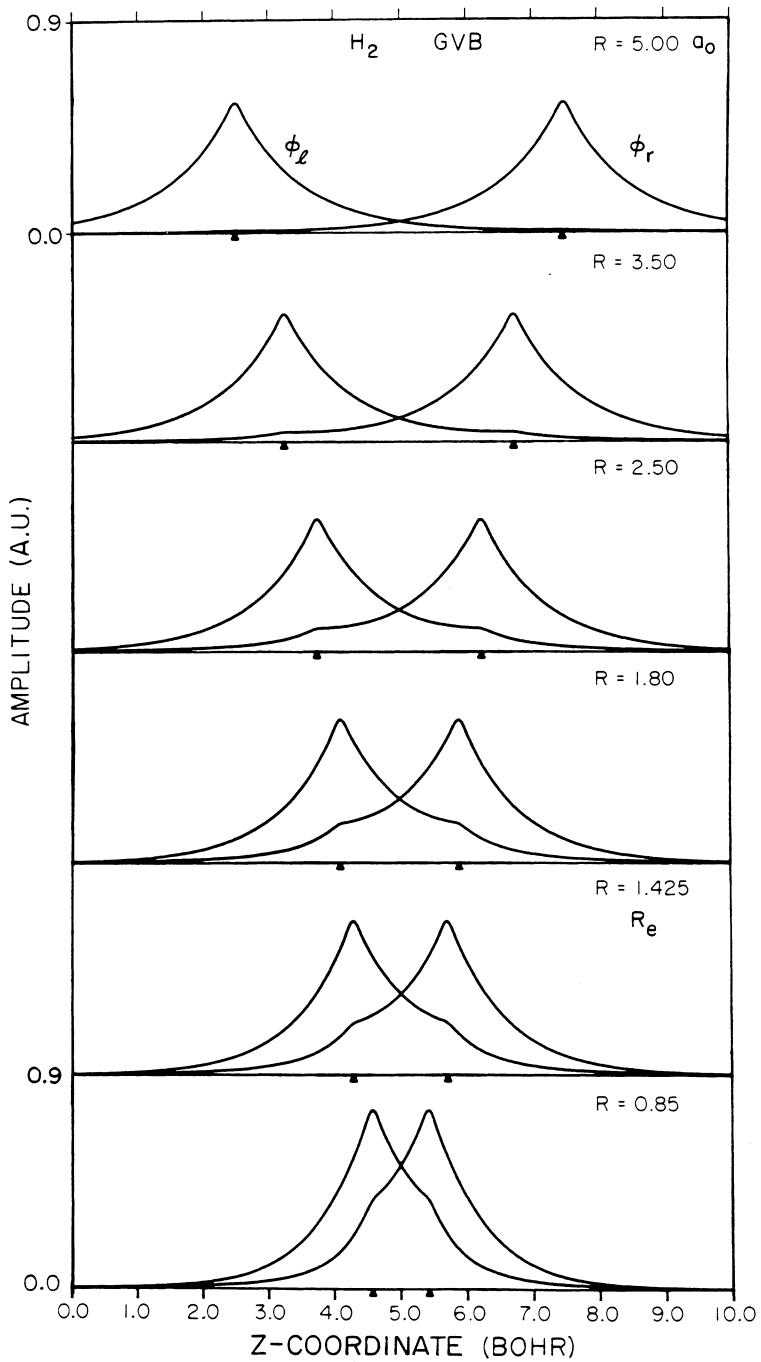


Figure 3.21: The GVB orbitals as a function of  $R$ . Note the cusps at the nuclei have disappeared due to use of Gaussian basis functions.

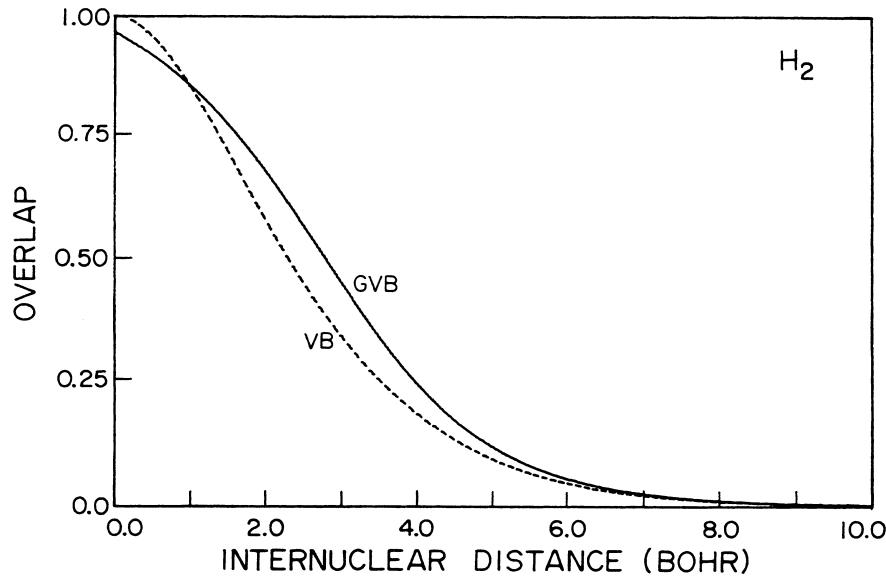


Figure 3.22: Comparison of overlap,  $S = \langle \varphi_\ell | \varphi_r \rangle$  for the VB and GVB wave functions.

Table 3.11: Comparison of results on  $\text{H}_2$  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	
$\zeta_{OPT}$	$R_e$	1.385	1.414	1.431	1.401
	$E_e$	-0.128231	-0.139083	-0.147938	-0.174470
$\zeta_{OPT}$		1.1931	1.1661	1.1937	-
$R = 1.4a_0$	$E$	-0.128189	-0.139049	-0.147777	-0.174470
	$\zeta_{OPT}$	1.1895	1.1695	1.2005	

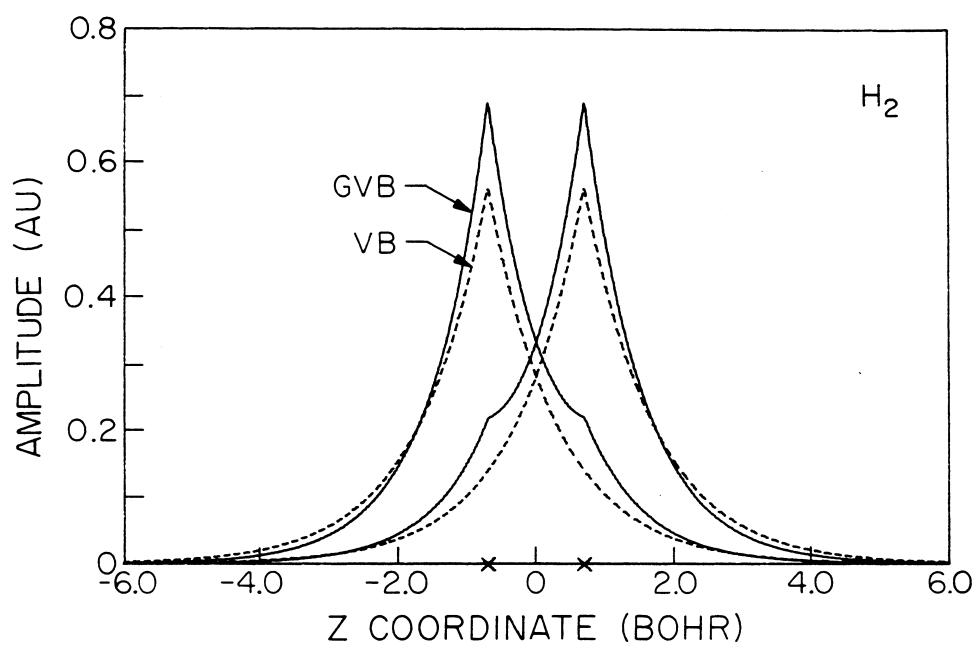


Figure 3.23: Comparison of GVB (two basis functions,  $\zeta_{OPT} = 1.2005$ ) and VB ( $\zeta = 1$ ) orbitals for H<sub>2</sub>,  $R = 1.4a_0$ .

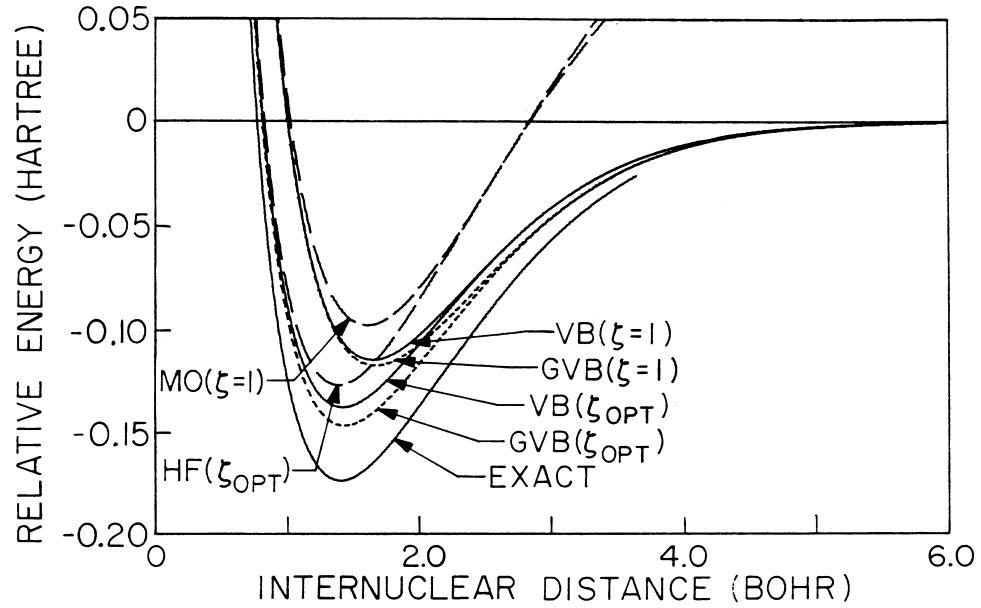


Figure 3.24: Comparison of the energy curves for MO, HF, VB, and GVB wave functions of  $H_2$ . Only two basis functions were used for HF and GVB. The results for both  $\zeta = 1$  and  $\zeta_{OPT}$  are shown. The  $\zeta_{OPT}$  as a function of  $R$  are given in Figure 3.25 later. The energy is relative to the energy of two hydrogen atoms.

Figure 3.25:  $\zeta_{OPT}$  for HF, VB and GVB wave functions.

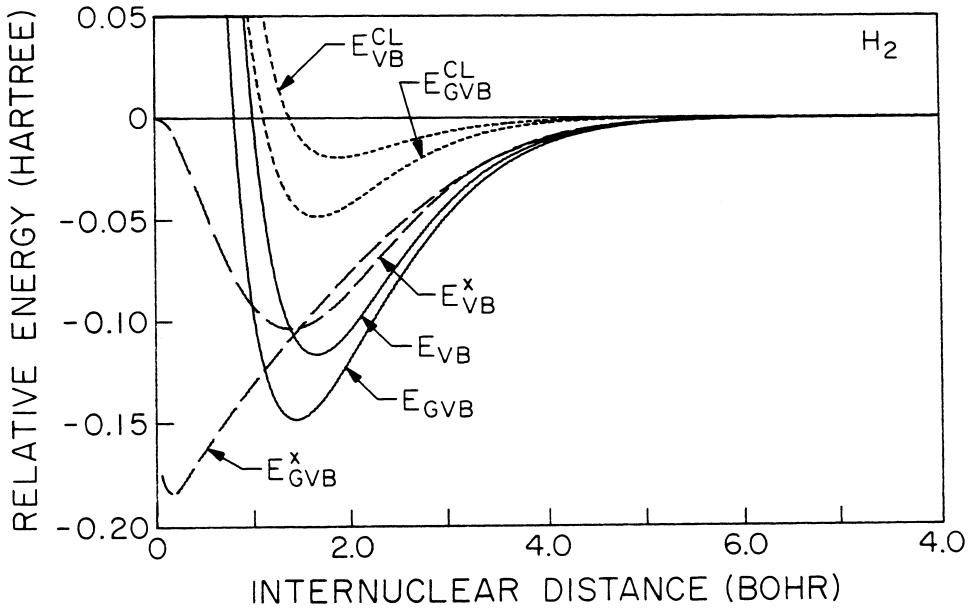


Figure 3.26: Comparison of the classical and exchange energies for the VB and GVB wave functions of  $\text{H}_2$ .

VB wavefunction

$$E_{GVB}^{Cl} = \langle \varphi_\ell \varphi_r | H | \varphi_\ell \varphi_r \rangle, \quad (3.207)$$

and

$$E_{GVB}^x = E_{GVB} - E_{GVB}^{Cl}, \quad (3.208)$$

etc. This leads to the results in Figure 3.26, 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,  $E^{Cl}$ . Similarly, in Figure 3.27 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.

### 3.7.3 CI Wavefunctions for $\text{H}_2$

Earlier, we found that in He there are four important correlations each involving a correlating natural orbital having one nodal plane

$$2s \quad \text{radial} \quad (3.209)$$

$$2p_x \quad \text{angular} \quad (3.210)$$

$$2p_y \quad \text{angular} \quad (3.211)$$

$$2p_z \quad \text{angular} \quad (3.212)$$

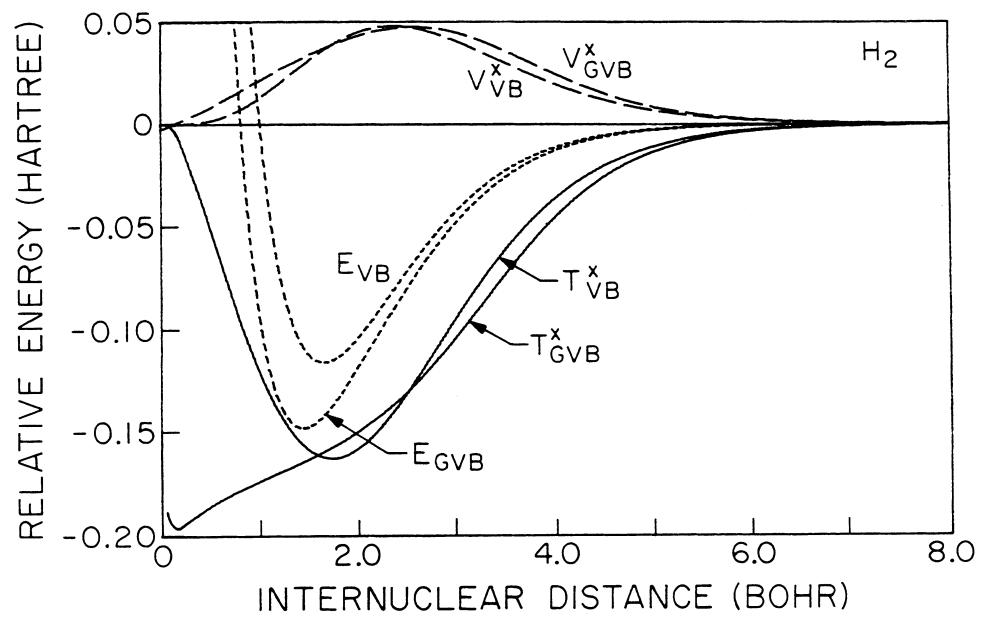


Figure 3.27: The kinetic and potential parts of  $E^x$  for the VB and GVB wave functions of  $H_2$

(3.213)

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 Figure 3.28, where the names  $1\sigma_g$ ,  $1\sigma_u$ , etc., will be explained next.

As  $R \rightarrow 0$ , the  $H_2$  orbitals change smoothly into (we say that they *correlate with*) the He orbitals in (3.213), ( $H_2$  on the left and He on the right)

$$1\sigma_g \rightarrow 1s \quad (3.214)$$

$$2\sigma_g \rightarrow 2s \quad (3.215)$$

$$1\sigma_u \rightarrow 2p_z \quad (3.216)$$

$$1\pi_{ux} \rightarrow 2p_x \quad (3.217)$$

$$1\pi_{uy} \rightarrow 2p_y \quad (3.218)$$

(3.219)

and hence, the correlation effects are closely related, ( $H_2$  on the left and He on the right)

$$\text{left - right, } (1\sigma_u) \leftrightarrow \text{angular - } z(p_z) \quad (3.220)$$

$$\text{starboard - portside, } (1\pi_{ux}) \leftrightarrow \text{angular - } x(p_x) \quad (3.221)$$

$$\text{up - down, } (1\pi_{uy}) \leftrightarrow \text{angular - } y(p_y) \quad (3.222)$$

$$\text{in - out, } (2\sigma_g) \leftrightarrow \text{radial}(2s) \quad (3.223)$$

(3.224)

The five dominant natural orbitals of  $H_2$  are shown in Figure 3.29, which should be compared to Figure 3.17 for He.

With these five dominant natural orbitals, the wavefunction

$$\begin{aligned} \Psi = & C_{1\sigma_g} \varphi_{1\sigma_g} \varphi_{1\sigma_g} - C_{2\sigma_g} \varphi_{2\sigma_g} \varphi_{2\sigma_g} \\ & - C_{1\sigma_u} \varphi_{1\sigma_u} \varphi_{1\sigma_u} - C_{1\pi_u} [\varphi_{1\pi_{ux}} \varphi_{1\pi_{ux}} + \varphi_{1\pi_{uy}} \varphi_{1\pi_{uy}}] \end{aligned} \quad (3.225)$$

leads to an energy of  $-1.1699$  h. Comparing to the exact energy of  $-1.1744$  h, we see that wavefunction (3.226) accounts for all but  $4.5 \text{ mh} = 0.12 \text{ eV}$   $2.8 \text{ kcal}$  of the exact energy. This is quite adequate for our purposes and we will ignore all other terms. A more complete analysis [?] of CI calculations on  $H_2$ , for  $R = 1.4 a_0$ , in terms of natural orbitals is given in Table 3.12.

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

$$\Psi(1, 2) = C_{1\sigma_g} \varphi_{1\sigma_g} \varphi_{1\sigma_g} - C_{1\sigma_u} \varphi_{1\sigma_u} \varphi_{1\sigma_u} \quad (3.226)$$

where

$$C_{1\sigma_g} = C_{1\sigma_u} = \frac{1}{\sqrt{2}}, \quad (3.227)$$

$$\varphi_{1\sigma_g} = \frac{(\chi_{1sl} + \chi_{1sr})}{\sqrt{2}}, \quad (3.228)$$

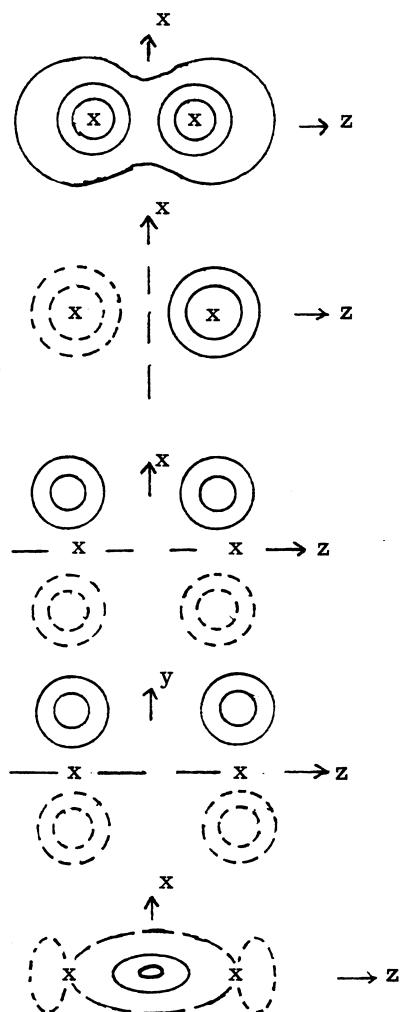


Figure 3.28: Correlating orbitals of  $H_2$ . Long dashes indicate nodal planes, solid lines are positive amplitudes and dotted lines negative amplitudes.

NATURAL ORBITALS FOR  $\text{H}_2$  ( $R = 1.4a_0$ )

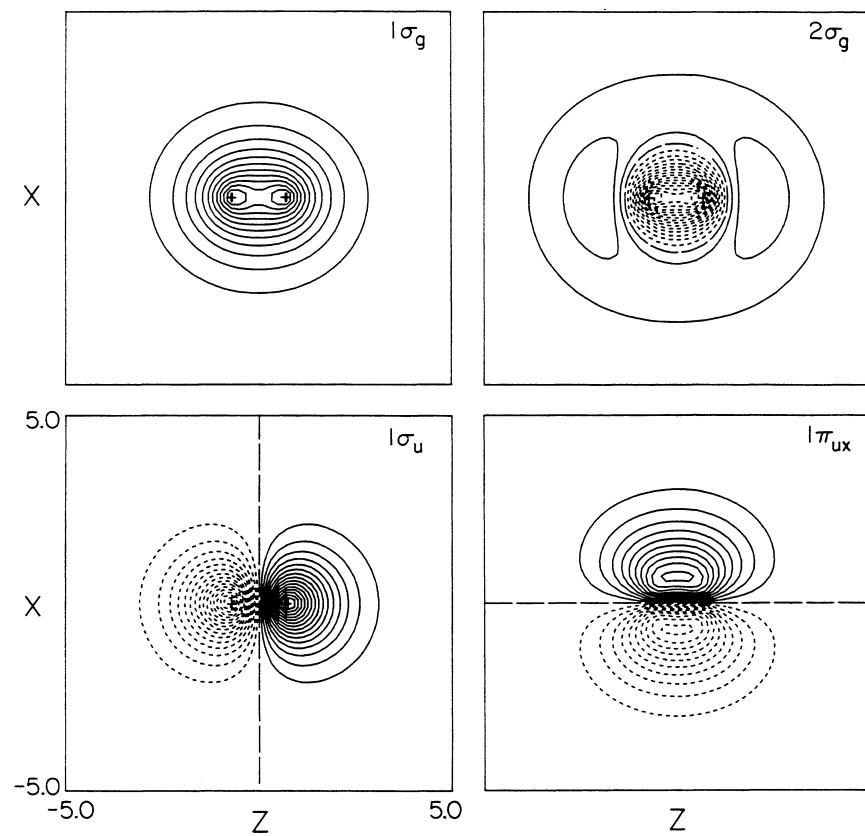


Figure 3.29: The natural orbitals of  $\text{H}_2$  for  $R = 1.4a_0$ .<sup>17</sup>

Table 3.12: Analysis of H<sub>2</sub> CI wavefunction in terms of natural orbitals.<sup>a</sup>

Natural Orbital	Energy Lowering (mh)	% E <sub>corr</sub>
1σ <sub>u</sub>	18.47	45.25
1π <sub>u</sub>	10.34	26.56
2σ <sub>g</sub>	?7.03	17.22
1π <sub>g</sub>	?0.75	1.84
3σ <sub>g</sub>	?0.51	1.25
2σ <sub>u</sub>	?0.49	1.20
1δ <sub>g</sub>	?0.49	1.20
1π <sub>u</sub>	?0.56	1.37
4σ <sub>g</sub>	?0.29	0.71
Totals	39.43	96.60

<sup>a</sup>See reference 18. <sup>b</sup>Total correlation energy is equal to 0.04082 hartrees.

and

$$\varphi_{1\sigma_u} = \frac{(-\chi_{1sl} - \chi_{1sr})}{\sqrt{2}}, \quad (3.229)$$

That is, only left-right correlation is present at R = ∞. For R < 0.8 a<sub>0</sub>, in-out correlation becomes more important than left-right correlation.

### Notation

For diatomic molecules, orbitals are classified in terms of their dependence upon φ, the angle of rotation about the molecular axis, z. Thus,

$$\sigma \implies \text{independent of } \varphi \quad (3.230)$$

$$\pi_x \implies \cos \varphi \quad (3.231)$$

$$\pi_y \implies \sin \varphi \quad (3.232)$$

$$(3.233)$$

where φ is referenced with respect to the xz plane.

## 3.8 Open Shell Wavefunction

In Chapter 2, we found that the second and third states of H<sub>2</sub> have the form

$$^1\Phi = \varphi_g \varphi_u + \varphi_u \varphi_g \quad (3.234)$$

and

$$^3\Phi = \varphi_g \varphi_u - \varphi_u \varphi_g \quad (3.235)$$

where the orbitals φ<sub>g</sub> and φ<sub>u</sub> 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

$$E = \frac{N}{D} \quad (3.236)$$

where

$$\frac{1}{2}D = \langle \varphi_g \varphi_u | \varphi_g \varphi_u \pm \varphi_u \varphi_g \rangle = \langle \varphi_g | \varphi_g \rangle \langle \varphi_u | \varphi_u \rangle \pm \langle \varphi_g | \varphi_u \rangle \langle \varphi_u | \varphi_g \rangle = 1 \quad (3.237)$$

$$\frac{1}{2}N = \langle \varphi_g \varphi_u | H | \varphi_g \varphi_u \pm \varphi_u \varphi_g \rangle. \quad (3.238)$$

The first term of (3.238), is

$$\langle \varphi_g \varphi_u | H | \varphi_g \varphi_u \rangle = \langle g | h | g \rangle \langle u | u \rangle + \langle g | g \rangle \langle u | h | u \rangle + \langle gu | \frac{1}{R_{12}} | gu \rangle \quad (3.239)$$

$$= \langle g | hg \rangle \langle u | h | u \rangle + J_{gu}, \quad (3.240)$$

$$(3.241)$$

where  $\langle \varphi_g | \varphi_u \rangle = 0$  and the second term is

$$\pm \langle \varphi_g \varphi_u | H | \varphi_u \varphi_g \rangle = \pm \left\{ \langle g | h | u \rangle \langle u | g \rangle + \langle g | u \rangle \langle u | h | g \rangle + \langle gu | \frac{1}{r_{12}} | ug \rangle \right\} \quad (3.242)$$

$$= \pm K_{gu}. \quad (3.243)$$

$$(3.244)$$

Thus,

$$^1E - ^3E = 2K_{gu}. \quad (3.245)$$

Since  $K_{gu} > 0$ , the the  ${}^3\Phi$  state is always below the  ${}^1\Phi$  state.

The above analysis shows that the wavefunctions

$$\varphi_g \varphi_u \pm \varphi_u \varphi_g \quad (3.246)$$

lead to an electron repulsion energy

$$E^{cl} \pm K_{gu}. \quad (3.247)$$

Thus, the significance of the exchange integral  $K_{gu}$  is that it is the change in the energy upon superimposing the exchanged wavefunction  $\varphi_u^{(1)} \varphi_g^{(2)}$  or  $\varphi_g^{(1)} \varphi_u^{(2)}$ . See Chapter 2.

## 3.9 Appendices

### 3.9.1 Permutational Symmetry

Since the Hamiltonian  $H(1, 2)$  for a two-electron system is invariant under permutation of electrons

$$H(2, 1) = H(1, 2) \quad (3.248)$$

the exact eigenstates of  $H$  are each either symmetric or antisymmetric under permutation.

For the proof, consider that  $\Psi_0$  is an exact eigenfunction of

$$H(1, 2)\Psi_0(1, 2) = E_0\Psi_0(1, 2). \quad (3.249)$$

Renumbering the electrons, this becomes

$$H(2, 1)\Psi_0(2, 1) = E_0\Psi_0(2, 1). \quad (3.250)$$

But, using (3.249) in (3.250) leads to

$$H(1, 2)\Psi_0(2, 1) = E + 0\Psi(2, 1). \quad (3.251)$$

Thus, for (3.249) and (3.251), both  $\Psi_0(1, 2)$  and  $\Psi_0(2, 1)$  are eigenfunctions of  $H(1, 2)$ , both with the same energy. There are two possibilities here. First there are two, or more, different (linearly independent) state with energy  $E_0$ , or there is only one state with energy  $E_0$ .

Where there is only one state with energy  $E_0$ , it must be that  $\Psi_0(2, 1)$  is proportional to  $\Psi_0(1, 2)$

$$\Psi_0(2, 1) = \lambda\Psi_0(1, 2). \quad (3.252)$$

But interchanging 1 and 2 in (3.252), leads to

$$\Psi_0(1, 2) = \lambda\Psi_0(2, 1) \quad (3.253)$$

and substituting (3.253) into (3.252), leads to

$$\Psi_0(2, 1) = \lambda^2\Psi_0(2, 1). \quad (3.254)$$

Thus,  $\lambda = \pm 1$ . That is, for a nondegenerate state, the wavefunction must be either symmetric,  $\lambda = +1$ ,

$$\Psi^s(2, 1) = \Psi^s(1, 2), \quad (3.255)$$

or antisymmetric,  $\lambda = -1$ ,

$$\Psi^a(2, 1) = \Psi^a(1, 2), \quad (3.256)$$

under permutation of the electrons, respectively.

Assuming now, that there are two or more different, linearly independent, states with energy  $E_0$ , we define new functions

$$\Psi_0^s(1, 2) = \Psi_0(1, 2) + \Psi(2, 1) \quad (3.257)$$

and

$$\Psi_0^a(1, 2) = \Psi_0(1, 2) - \Psi(2, 1). \quad (3.258)$$

Applying  $H$ , we obtain

$$H\Psi_0^s = E_0\Psi_0^s \quad (3.259)$$

and

$$H\Psi_0^a = E_0\Psi_0^a \quad (3.260)$$

and hence, the exact eigenfunctions of  $H$  are, again, either symmetric or antisymmetric.

### 3.9.2 Natural Orbitals

A general CI wavefunction, for the ground state of a two-electron system

$$\Psi^s(1, 2) = \sum_{\mu, \nu=1}^P C_{\mu\nu} \chi_\mu(1) \chi_\nu(2) \quad (3.261)$$

can always be rewritten in terms of doubly-occupied orbitals

$$\Psi^s(1, 2) = \sum_{\mu=1}^P \bar{C}_{\mu\mu}^Z \bar{\chi}_\mu(1) \bar{\chi}_\mu(2) \quad (3.262)$$

where the natural orbitals  $\{\bar{\chi}_\mu\}$  are linear combinations of the original basis functions  $\{\chi_\mu\}$ .

The proof is that since  $\psi^s$  is symmetric, the coefficient matrix is symmetric

$$C_{\mu\nu} = C_{\nu\mu} \quad (3.263)$$

If we choose new basis functions

$$\{\bar{\chi}_\mu; \mu = 1, \dots, P\} \quad (3.264)$$

that are linear combinations of the old function

$$\{\chi_\mu; \mu = 1, \dots, P\} \quad (3.265)$$

$$\chi_\mu = \sum_\nu V_{\mu\nu} \bar{\chi}_\nu, \quad (3.266)$$

then the wavefunction (3.261) becomes

$$\Psi^s = \sum_{\mu\nu, \sigma\eta} C_{\mu\nu} V_{\mu\sigma} \bar{\chi}_\sigma(1) V_{\nu\eta} \bar{\chi}_\eta(2) = \sum_{\sigma\eta} \bar{C}_{\sigma\eta} \bar{\chi}_\sigma(1) \bar{\chi}_\eta(2) \quad (3.267)$$

where

$$\bar{C}_{\sigma\eta} = \sum_{\mu, \nu} V_{\mu\sigma} C_{\mu\nu} V_{\nu\eta}. \quad (3.268)$$

The wavefunction  $\Psi^s$  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

$$\bar{\mathbf{C}} = \tilde{\mathbf{V}} \mathbf{C} \mathbf{V} \quad (3.269)$$

Since  $\mathbf{C}$  is a real symmetric matrix, there is always some transformation  $\mathbf{V}$  for which the transformed matrix  $\bar{\mathbf{C}}$  is diagonal. Thus, there is always a particular choice of basis functions such that

$$\Psi^s = \sum_{\mu=1}^P \bar{C}_{\mu\mu} \bar{\chi}_\mu(1) \bar{\chi}_\mu(2) \quad (3.270)$$

With this basis, there are only  $P$  terms in the CI expansion rather than  $P^2$  as in (3.261). Thus, (3.270) is a much simpler wavefunction. To find the  $V$  leading to the natural orbitals, we must first solve the CI equations to find  $\mathbf{C}$ . Hence, the natural orbitals do not help us solve for the CI wavefunction. However, having obtained a CI wavefunction, we will immediately transform to the natural orbitals in order to discuss and interpret the wavefunction.

### 3.9.3 Evaluating 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,

$$\varphi_{1s} = Ne^{-\zeta r} \quad (3.271)$$

where the orbital exponent  $\zeta$  is variable.

#### One Electron Quantities

First the normalization coefficient,  $N$ , is obtained from

$$1 = \langle \varphi_{1s} | \varphi_{1s} \rangle = N^2 \int dx dy dz e^{-2\zeta r} = 4\pi N^2 \int_0^\infty r^2 dr e^{-2\zeta r} = \frac{4\pi}{(2\zeta)^3} N^2 \int_0^\infty \rho^2 d\rho e^{-\rho} = \frac{8\pi}{8\zeta^3} N^2, \quad (3.272)$$

so that

$$N = \sqrt{\frac{\zeta^3}{\pi}}. \quad (3.273)$$

The nuclear attraction terms are

$$\begin{aligned} V_{1s}^{en} = \langle 1s | -\frac{Z}{r} | 1s \rangle &= -ZN^2 \int_0^\infty r dr e^{-2\zeta r} \int_0^\pi \int_0^{2\pi} \sin \theta d\theta d\varphi \\ &= -\frac{ZN^2 4\pi}{4\zeta^2} = -\zeta Z \end{aligned} \quad (3.274)$$

The kinetic energy term is obtained, most simply, by noting that

$$\nabla \varphi_{1s} = -\zeta \varphi_{1s} \hat{e}_r \quad (3.275)$$

where  $\hat{e}_r$  is a unit vector in the  $r$  direction, and hence

$$T_{1s} = \langle 1s | t | 1s \rangle = \langle 1s | -\frac{1}{2} \nabla^2 | 1s \rangle = \frac{1}{2} \langle \nabla \varphi_{1s} \cdot \nabla \varphi_{1s} \rangle = \frac{1}{2} \zeta^2 \langle \varphi_{1s} | \varphi_{1s} \rangle = \frac{1}{2} \zeta^2 \quad (3.276)$$

To check these quantities consider  $\text{He}^+$  where  $\zeta = 2$ . In this case, (3.274) and (3.276) lead to

$$E_{1s} = T_{1s} + V_{1s}^{en} = \frac{1}{2} \zeta^2 - \zeta Z \quad (3.277)$$

where  $Z = 2$ . Optimizing  $\zeta$ , leads to  $\zeta = Z$ , and hence,

$$E_{1s} = -\frac{1}{2} Z^2 \quad (3.278)$$

both of which are correct.

## Two Electron Quantities

For He, we also need the two-electron interaction term

$$J_{1s,1s} = \langle \varphi_{1s}\varphi_{1s} | \frac{1}{r_{12}} | \varphi_{1s}\varphi_{1s} \rangle = \langle \varphi_{1s} | J_{1s} \varphi_{1s} \rangle, \quad (3.279)$$

where

$$J_{1s}(1) = \int dx_2 dy_2 dz_2 \frac{1}{r_{12}} |\varphi_{1s}(2)|^2 \quad (3.280)$$

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 (3.280) depends on  $R_{12}$ . The usual solution is to use the Laplace expansion

$$\frac{1}{r_{12}} = \sum_{l=0}^{\infty} \frac{r_{<}^l}{r_{>}^{l+1}} P_l(\cos \theta_{12}) \quad (3.281)$$

where  $r_{<} = r_1$  if  $r_1 < r_2$  or  $r_{<} = r_2$  if  $r_2 < r_1$ , and oppositely for  $r_{>}$ . With (3.281), (3.280) becomes

$$J_{1s} = \sum_{l=0}^{\infty} \left\{ \int_0^{\infty} \frac{r_{<}^l}{r_{>}^{l+1}} r_2^2 dr_2 |\varphi_{1s}(2)|^2 \int_0^{\pi} \sin \theta d\theta P_l(\cos \theta) \int_0^{2\pi} d\varphi \right\}. \quad (3.282)$$

The integration over  $\theta$  is zero unless  $l = 0$ , so that (3.282) becomes

$$J_{1s}(1) = 4\pi \int_0^{\infty} \frac{r_2^2 dr_2}{r_{>}} |\varphi_{1s}(2)|^2 = 4\pi \left\{ \frac{1}{r_1} \int_0^{r_1} r_2^2 dr_2 |\varphi_{1s}(2)|^2 + \int_0^{\infty} r_2 dr_2 |\varphi_{1s}(2)|^2 \right\} \quad (3.283)$$

Before proceeding to evaluate  $J_{1s}(1)$ , one should notice that (3.283) is a well-known result in electrostatic. The quantity

$$Q_1 = 4\pi \int_0^{r_1} r_2^2 dr_2 |\varphi_{1s}(2)|^2 \quad (3.284)$$

is just the part of the charge distribution inside the point  $r_1$ . According to (3.283), the total contribution of this spherically symmetric charge distribution inside  $r_1$ , is the same value

$$\frac{1}{r_1} Q_1 \quad (3.285)$$

as if all the charge,  $Q_1$ , were localized at the nucleus. Letting

$$Q_2(r) = 4\pi r^2 |\varphi_{1s}(r)|^2, \quad (3.286)$$

the quantity  $Q_2(r)dr$  is the charge on the spherical shell of radius  $r$ , and thickness  $dr$ . According to (3.283), the contribution of this charge to the potential is

$$\frac{1}{r} Q_2(r) dr \quad (3.287)$$

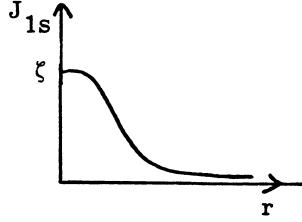


Figure 3.30: The Coulomb potential  $J_{1s}(r)$ .

and is the same for all  $r_1$  inside  $r$ .

Grunging on, we find

$$Q_1 = 4\pi N^2 \int_0^{r_1} r_2^2 dr_2 e^{-2\zeta r_2} = \frac{4\pi N^2}{(2\zeta)^3} \int_0^{\rho_1} \rho^2 d\rho e^{-\rho} \quad (3.288)$$

where  $\rho_1 = 2\zeta r_1$ . Integrating by parts, this becomes

$$Q_1 = \left[ 1 - e^{-\rho_1} \left( 1 + \rho_1 + \frac{1}{2}\rho_1^2 \right) \right]. \quad (3.289)$$

Similarly, the second term of (3.283) is

$$I_2 = 4\pi N^2 \int_{r_1}^{\infty} r_2 dr_2 e^{-2\zeta r_2} = \zeta [ \rho_1 e^{-\rho_1} + e^{-\rho_1} ]. \quad (3.290)$$

Thus

$$J_{1s}(1) = \frac{1}{r_1} Q_1 + I_2 = \frac{1}{r_1} (1 - e^{-2\zeta r_1}) - \zeta e^{-2\zeta r_1}. \quad (3.291)$$

For large  $r_1$ , this becomes

$$J_{1s} = \frac{1}{r_1} \quad (3.292)$$

as expected, and for small  $r_1$  we obtain

$$J_{1s}(1) = \zeta - \frac{2}{3}\zeta^3 r_1^2 + O(r_1^3) \quad (3.293)$$

Thus,  $J_{1s}$  has the form in Figure 3.30.

Using (3.291) in (3.279), we obtain

$$\begin{aligned} J_{1s,1s} &= 4\pi N^2 \int_0^{\infty} r^2 dr e^{-2\zeta r} \left[ \frac{1}{r} - \frac{1}{r} e^{-2\zeta r} - \zeta e^{-2\zeta r} \right] \\ &= 4\zeta^3 \left\{ \frac{1}{(2\zeta)^2} - \frac{1}{(4\zeta)^2} - \frac{2\zeta}{(4\zeta)^3} \right\} = \frac{5}{8}\zeta \end{aligned} \quad (3.294)$$

### Qualitative Analysis of $J_{1s,1s}$

Defining the average size,  $\bar{r}$ , for the  $\varphi_{1s}$  orbital as

$$\langle \varphi_{1s} | \frac{1}{r} | \varphi_{1s} \rangle = \frac{1}{\bar{r}} \quad (3.295)$$

we see from (3.283) that

$$\bar{r} = \frac{1}{\zeta}. \quad (3.296)$$

An approximate value of  $J_{1s,1s}$  can be obtained by assuming each electron is at its average radius,  $\bar{r} = 1/\zeta$ , 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

$$\bar{r}_{12} \approx \sqrt{2}\bar{r} \quad (3.297)$$

and, hence, to

$$J_{1s,1s} = \frac{1}{\sqrt{2}\bar{r}} = \frac{1}{\sqrt{2}}\zeta = 0.707\zeta \quad (3.298)$$

The exact value is  $J_{1s,1s} = 0.625\zeta$  so that the above estimate is only about 10 percent high.

### 3.9.4 The Exact Wavefunction of $\text{H}_2^+$

In order to solve for the exact wavefunction of  $\text{H}_2^+$ , we use elliptic coordinates

$$\xi = \frac{(r_a + r_b)}{R}, \quad (3.299)$$

$$\eta = \frac{(r_a - r_b)}{R}, \quad (3.300)$$

and  $\varphi$  equal to azimuthal angle as defined in Chapter 2. With elliptic coordinates, the Hamiltonian for  $\text{H}_2^+$  becomes separable, expressible as a sum of terms each depending on a different variable. Hence, the exact wavefunction of  $\text{H}_2^+$  can be factored into terms, each depending upon different variables,

$$\Psi(\xi, \eta, \varphi) = \Lambda(\xi)M(\eta)\Phi(\varphi). \quad (3.301)$$

For the ground state of  $\text{H}^+$  at  $R = 2a_0$ , the resulting, unnormalized wavefunction is<sup>2</sup>

$$\Lambda(\xi) = (1 + \xi)^{0.34679}(1 + 0.0168\delta + 0.0004\delta^2)e^{-1.48501\xi}, \quad (3.302)$$

$$M(\eta) = [1.1450P_0(\eta) + 0.29844P_2(\eta) + 0.011461P_4(\eta) + 0.000184P_6(\eta) + 0.000002P_8(\eta)], \quad (3.303)$$

$$\Phi(\varphi) = 1, \quad (3.304)$$

where

$$\delta = \frac{(\xi - 1)}{(1 + \xi)} \quad (3.305)$$

and  $P_\ell(\eta)$  are Legendre polynomials [ $P_0 = 1, P_2 = \frac{1}{2}(3\eta^2), \dots$ ]. For comparison, the MBS wavefunction in elliptic coordinates is

$$\psi^{MBS} = (e^{-\zeta r_a} + e^{-\zeta r_b}) = \left[ e^{\zeta \frac{R}{2}\eta} + e^{-\zeta \frac{R}{2}\eta} \right] e^{-\zeta \frac{R}{2}\xi} \quad (3.306)$$

corresponding to

$$\Lambda(\zeta) = e^{-1.23\zeta} \quad (3.307)$$

and

$$M(\eta) = \cos h(1.23\eta) \quad (3.308)$$

at  $R = 2 a_0$  (the optimum  $\zeta$  at  $R = 2 a_0$  is  $\zeta = 1.23$ ). At  $R = 2$ , the MBS wavefunction leads to  $\zeta = 1.23$ , somewhat more diffused than the 1.485 for the exact wavefunction. The optimum energy and bond lengths for the exact wavefunction are listed in Table 3.1.

When we say *exact* here, we are referring to the exact solutions of (3.274) and (3.276). However, (3.274) and (3.276) do not lead to an exact description of  $H_2^+$ . The two main assumptions here are, first, the neglect of the nuclear kinetic energy terms, referred to as Born-Oppenheimer breakdown, and, secondly, neglect or relativistic effects. Inclusion of nuclear kinetic energy leads to corrections of order  $1/2M$ , where  $M$  is the proton mass, in Hartree atomic units, e.g.,  $1/2M = 0.0003 \text{ h} = 0.007 \text{ eV}$ . The actual correction to the energy at  $R_e$  from the nuclear kinetic energy terms, see Table 3.1, is  $+0.00085 \text{ h} = 0.023 \text{ eV} = 0.53 \text{ kcal}$ , and from the relativistic effects is  $.000005 \text{ h} = 0.00013 \text{ eV} = 0.003 \text{ kcal}$ . 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.

## Chapter 4

# Electron Spin and the Pauli Principle

### 4.1 Introduction

In previous chapters, we considered one-electron and two-electron systems. In these cases, the ground state is obtained by starting with the Hamiltonian  $H(1)$  or  $H(2)$ , and solving for the wavefunction yielding the lowest possible energy. This is a very reasonable procedure; however, it does not work for more than two electrons. For many-electron systems, the wavefunction leading to the lowest energy, is not allowed. The fundamental reasons for this are obscure; however, there is a simple principle that correctly tells us which wavefunctions are allowed. This principle is called the *Pauli principle* and is one of the two major subjects of this chapter.

In previous chapters we have considered the electron as an entity localized at a point, and having only a mass and a charge. However, there is internal structure to the electron resulting in a net angular momentum (spin) for the electron. Thus, the total wavefunction for an electron can be written as

$$\psi(\mathbf{r}, \sigma) = \varphi(\mathbf{r})\chi(\sigma), \quad (4.1)$$

where  $\psi$  is a spin orbital,  $\varphi$  is a spatial orbital, and  $\chi$  is a spin function ( $\alpha$  or  $\beta$  corresponding to the two components for spin 1/2). Without magnetic fields, the Hamiltonian is approximately independent of electron spin. Hence, spin does not enter directly into determining the bond strengths, ordering of state, etc. However, in collusion with the Pauli principle, the spin plays a crucial role in chemistry, eliminating many eigenstate of  $H$  having energies far below the actual ground state of the molecule. For atoms having  $Z > 54$ , Xe, effects involving spin are quite important in bonding, and for atoms having  $Z > 36$ , Kr, the effects are moderately important, we shall ignore such complications.

The simplest wavefunction satisfying the Pauli principle is the Slater determinant

wavefunction

$$\mathcal{A}\Psi = \mathcal{A}\psi_a\psi_b\psi_c = \begin{vmatrix} \psi_a(1) & \psi_b(1) & \cdots \\ \psi_a(2) & \psi_b(2) & \cdots \\ \vdots & & \ddots \end{vmatrix}, \quad (4.2)$$

where  $\mathcal{A}$  is the antisymmetrizer, or determinant operator. In the case that two of the spin orbitals of a Slater determinant are equal, we obtain  $\mathcal{A}\Psi = 0$ , and the spin orbitals of a Slater determinant can be taken as orthonormal

$$\langle \psi_i | \psi_j \rangle = \delta_{ij} \quad (4.3)$$

with no affect on the energy or properties of the wavefunction. We will find that the Slater determinant is invariant under recombinations of these spin orbitals.

The energy of the Slater determinant wavefunction is

$$E = \sum_i^N \langle i | h | i \rangle + \sum_{i>j}^N (J_{ij} - K_{ij}), \quad (4.4)$$

where  $h$  is the one-electron operator, and  $\mathcal{G}_{ij}$  and  $\mathcal{K}_{jj}$  are Coulomb and exchange integrals over spin orbitals.

Factoring the spin orbitals into spatial and spin functions leads to the following important wavefunctions and energies. Here,  $J_{ij}$  and  $K_{ij}$  are integrals over spatial functions only.

For closed-shell Hartree-Fock

$$\mathcal{A}(\varphi_1\alpha)(\varphi_1\beta) \cdots (\varphi_m\alpha)(\varphi_m\beta), \quad (4.5)$$

where  $m = N/2$

$$E = 2 \sum_{i=1}^m \langle i | h | i \rangle + \sum_{ij}^m (eJ_{ij} - K_{ij}). \quad (4.6)$$

For high-spin multiplet

$$\mathcal{A}(\varphi_1\alpha) \cdots (\varphi_n\alpha) \quad (4.7)$$

$$E = \sum_i^n \langle i | h | i \rangle + \sum_{i>j}^n (J_{ij} - K_{ij}). \quad (4.8)$$

Finally, for intermediate spin

$$\mathcal{A}(\varphi_1\alpha)(\varphi_1\beta) \cdots (\varphi_m\alpha\varphi_m\beta)(\varphi_{m+1}\alpha) \cdots (\varphi_n\alpha), \quad (4.9)$$

with the energy given in Section 4.5.3.

## 4.2 Electron Spin, One Electron

### 4.2.1 Spin Orbitals

So far, in this course, we have considered the electron to be a point particle having mass  $m$  and charge  $-e$ . Thus, we described the electron wavefunction as

$$\varphi(\mathbf{r}) = \varphi(x, y, z), \quad (4.10)$$

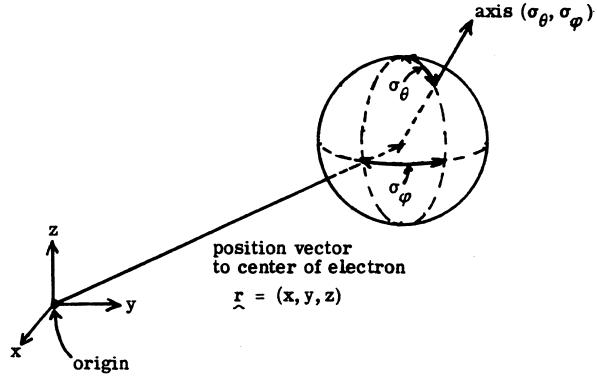


Figure 4.1:

presuming that only the position of the electron need be given. Imagine now that the electron has some finite size, say a small sphere. Then we would need to specify, not only the position  $x$ ,  $y$ , and  $z$  of the electron, but also the orientation of the sphere, say  $\sigma_v$ ,  $\sigma_\varphi$ , as indicated in Figure 4.1. Thus, we would have to specify five coordinates in order to completely describe the total wavefunction,

$$\psi(x, y, z, \sigma_v, \sigma_\varphi). \quad (4.11)$$

If the orientation is independent of the absolute position, the wavefunction will factor into two parts,

$$\varphi(x, y, z, \sigma_v, \sigma_\varphi) = \varphi(x, y, z)\chi(\sigma_v, \sigma_\varphi) = \varphi(\mathbf{r})\chi(\sigma), \quad (4.12)$$

where, as usual,  $\varphi$  is the probability amplitude of finding the electron at some point  $x$ ,  $y$ ,  $z$ . Here,  $\mathbf{r}$  is symbolic for the collection of coordinates  $x$ ,  $y$ ,  $z$ , and  $\sigma$  is symbolic for the collection of coordinates  $\sigma_v$ ,  $\sigma_\varphi$ . The other function,  $\chi$  gives the probability amplitude of finding some particular orientation  $\sigma_v$ ,  $\sigma_\varphi$  on the electron. These orientation coordinates  $\sigma_v$ ,  $\sigma_\varphi$  would be called *internal coordinates*.

Imagine now that the electron is spinning about its axis with some angular momentum  $s$ . Since the electron is charged, the spin would lead to a magnetic moment  $\mu = \gamma s$ . This magnetic moment could be detected by its interaction with an external magnetic field, say in the  $z$  direction,

$$\Delta E = -\mu_z B_z = -\gamma B_z s_z. \quad (4.13)$$

Classically,  $s_z$  could have any value from  $s_z = +|s|$  to  $s_z = -|s|$ , where  $|s|$  is the total angular momentum. Experimentally, the electron leads to only two values of  $s_z$ ,

$$s_z = +\frac{1}{2}\hbar \quad (4.14)$$

$$s_z = -\frac{1}{2}\hbar \quad (4.15)$$

This description of the electron as a finite size charged sphere should not be taken literally. It is only to indicate how one might think of the internal coordinates. However, it is the case that the electron does have an internal angular momentum (called *spin*) which leads to a magnetic moment that can interact with external magnetic fields. There are only two possible states for the internal coordinates of the electron, up-spin (4.14), denoted as  $\alpha(\sigma)$  and down-spin (4.15), denoted as  $\beta(\sigma)$ . These two states,  $\alpha$  and  $\beta$  are orthogonal, and normalized so that we write

$$\langle \alpha | \beta \rangle = 0 \quad (4.16)$$

$$\langle \alpha | \alpha \rangle = 1 \quad (4.17)$$

$$\langle \beta | \beta \rangle = 1 \quad (4.18)$$

where the integration is over the internal (spin) coordinates.

Consider now, the product of spatial functions, hereafter called orbitals, e.g.,  $\varphi_i$  and  $\varphi_j$ , and spin functions, e.g.,  $\alpha$  and  $\beta$ , to form spin orbitals such as

$$\begin{aligned} \psi_{i\alpha}(\mathbf{r}, \sigma) &= \varphi_i(\mathbf{r})\alpha(\sigma) \\ \psi_{i\beta} &= \varphi_i\beta \\ \psi_{j\alpha} &= \varphi_j\alpha \\ \psi_{j\beta} &= \varphi_j\beta \end{aligned} \quad (4.19)$$

Then,

$$\langle \psi_{i\alpha} | \psi_{j\alpha} \rangle = \langle \varphi_i | \varphi_j \rangle \langle \alpha | \alpha \rangle = \langle \varphi_i | \varphi_j \rangle \quad (4.20)$$

and

$$\langle \psi_{i\alpha} | \psi_{j\beta} \rangle = \langle \varphi_i | \varphi_j \rangle \langle \alpha | \beta \rangle = 0. \quad (4.21)$$

Thus, states with different spin are always orthogonal, independent of the relation between  $\varphi_i$  and  $\varphi_j$ . States with the same spin are orthonormal if the  $\varphi_i$  are orthonormal.

Now consider the  $\{\varphi_i\}$  to be eigenstates of the Hamiltonian

$$H\varphi_i = E_i\varphi_i, \quad (4.22)$$

where  $H$  is independent of spin. There are actually terms in the Hamiltonian that are dependent upon spin (e.g., spin-orbital coupling). These terms can usually be neglected in discussing the chemistry of nontransition metals and are ignored here.

Then

$$H\psi_{i\alpha} = (H\varphi_i)\alpha = E_i\varphi_{i\alpha} = E_i\psi_{i\alpha} \quad (4.23)$$

and

$$H\psi_{i\beta} = E_i\psi_{i\beta}, \quad (4.24)$$

so that there are two spin orbital eigenstates corresponding to each orbital eigenstate. Thus, with spin there are twice as many states as without spin. For example, the state of the  $H$  atoms become  $\psi_{1s\alpha}$ , and  $\psi_{1s\beta}$  with energy

$$E = -\frac{1}{2} \left( \frac{e^2}{a_0} \right) \quad (4.25)$$

$\psi_{2s\alpha}, \psi_{2s\beta}, \psi_{2py\beta}, \psi_{2pz\alpha}, \psi_{2pz\beta}$ , with energy

$$E = -\frac{1}{8} \left( \frac{e^2}{a_0} \right) \quad (4.26)$$

and  $\psi_{3s\alpha}, \psi_{3s\beta}$ , etc., with energy

$$E = -\frac{1}{18} \left( \frac{e^2}{a_0} \right), \quad (4.27)$$

etc.

In quantum mechanics, a state with total angular momentum quantum number  $L$  leads to a total of  $2L + 1$  states having component along the  $z$  axis of

$$M_L = +L, +L - 1, +L - 2, \dots, -L + 1, -L. \quad (4.28)$$

A more proper review of angular momentum is given in Section 4.6.2. Thus, with  $L = 1$  we obtain three states,  $M_L = +1, 0, -1$ . With  $L = 1/2$  we obtain two states,  $M_L = +1/2$ , and  $-1/2$ . The spin of an electron has two possible states,  $M_S = +1/2$  and  $-1/2$ , and we say that the electron has a spin of *one-half*.

### 4.2.2 Two Electrons

If  $\Phi(1, 2)$  is an eigenfunction of the two-electron Hamiltonian  $H(1, 2)$ ,

$$H(1, 2)\Phi(1, 2) = E\Phi(1, 2), \quad (4.29)$$

the inclusion of electron spin leads to a total of four states,

$$\Psi_{\alpha\alpha}(1, 2) = \Psi(1, 2)\alpha(1)\alpha(2) \quad (4.30)$$

$$\Psi_{\alpha\beta}(1, 2) = \Psi(1, 2)\alpha(1)\beta(2) \quad (4.31)$$

$$\Psi_{\beta\alpha}(1, 2) = \Psi(1, 2)\beta(1)\alpha(2) \quad (4.32)$$

$$\Psi_{\beta\beta}(1, 2) = \Psi(1, 2)\beta(1)\beta(2) \quad (4.33)$$

all of which are eigenfunctions of  $H$

$$H\Psi_{ij} = E\Psi_{ij} \quad (4.34)$$

with the same energy. In Chapter 2 we found that since the Hamiltonian is unchanged upon transposing the electrons,

$$H(1, 2) = H(2, 1), \quad (4.35)$$

then its eigenstates (4.29) must each be either symmetric or antisymmetric upon transposition,  $\tau$ ,

$$\tau\Phi = \pm\Phi \quad (4.36)$$

Thus, for H<sub>2</sub>, we found that the lowest two states have the form

$$\Phi_g(1, 2) = \chi_l \chi_r + \chi_r \chi_l \quad (4.37)$$

and

$$\Phi_u(1, 2) = \chi_l \chi_r - \chi_r \chi_l, \quad (4.38)$$

which satisfy

$$\tau \Phi_g = +\Phi_g \quad (4.39)$$

and

$$\tau \Phi_u = -\Phi_u \quad (4.40)$$

Similarly, for He we found that the ground state was

$$\Phi(1, 2) = \varphi_{1s}(1) \varphi_{1s}(2), \quad (4.41)$$

which satisfies

$$\tau \Phi = +\Phi. \quad (4.42)$$

Including spin, the Hamiltonian remains rigorously symmetric under interchange of the electrons, since the electrons are identical. We now must interchange both spatial and spin coordinates simultaneously, denoting this as  $\bar{\tau}$ . Thus, the spatial spin eigenstates  $\Psi_{ij}$  in (4.34) must also satisfy

$$\bar{\tau} \Psi_{ij} = \pm \Psi_{ij} \quad (4.43)$$

Since

$$\Psi_{ij} = \Phi \chi_{ij}, \quad (4.44)$$

where  $\chi_{ij}$  is a two-electron spin function, and since  $\Phi$  satisfied (4.36), then (4.43) becomes

$$\bar{\tau} \Psi_{ij} = (\bar{\tau} \Phi) (\bar{\tau} \chi_{ij}) = (\pm) \Phi (\bar{\tau} \chi_{ij}) = (\pm) \Psi_{ij} = (\pm) \Phi \chi_{ij}. \quad (4.45)$$

The  $(\pm)$  in various terms indicates only that either + or - may appear here, the  $(\pm)$  of different terms need not be correlated.

Thus, we must have

$$\bar{\tau} \chi_{ij} = \pm \chi_{ij} \quad (4.46)$$

that is, the spin functions must be either symmetric or antisymmetric under transposition of the electrons. But

$$\bar{\tau} \alpha \alpha = +\alpha \alpha, \quad (4.47)$$

$$\bar{\tau} \alpha \beta = \beta \alpha, \quad (4.48)$$

$$\bar{\tau} \beta \alpha = \alpha \beta \quad (4.49)$$

$$\bar{\tau} \beta \beta = \beta \beta \quad (4.50)$$

so that the  $\alpha \beta$  and  $\beta \alpha$  terms do not satisfy (4.46). Recombining spin terms, we get

$${}^3 \chi_{\alpha \alpha} = \alpha \alpha, \quad (4.51)$$

Table 4.1: Permutational symmetries for wavefunctions of H<sub>2</sub> and He.

		Permutation Symmetry			Observed?
		Spatial	Spin	Total	
H <sub>2</sub>	(χ <sub>I</sub> χ <sub>r</sub> + χ <sub>r</sub> χ <sub>I</sub> )(αα)	+	+	+	no
	(χ <sub>I</sub> χ <sub>r</sub> + χ <sub>r</sub> χ <sub>I</sub> )(αβ + βα)	+	+	+	no
	(χ <sub>I</sub> χ <sub>r</sub> + χ <sub>r</sub> χ <sub>I</sub> )(ββ)	+	+	+	no
	(χ <sub>I</sub> χ <sub>r</sub> + χ <sub>r</sub> χ <sub>I</sub> )(αβ - βα)	+	-	-	yes
	(χ <sub>I</sub> χ <sub>r</sub> - χ <sub>r</sub> χ <sub>I</sub> )(αα)	-	+	-	yes
	(χ <sub>I</sub> χ <sub>r</sub> - χ <sub>r</sub> χ <sub>I</sub> )(αβ + βα)	-	+	-	yes
	(χ <sub>I</sub> χ <sub>r</sub> - χ <sub>r</sub> χ <sub>I</sub> )(ββ)	-	+	-	yes
	(χ <sub>I</sub> χ <sub>r</sub> - χ <sub>r</sub> χ <sub>I</sub> )(αβ - βα)	-	-	+	no
He	(φ <sub>1s</sub> φ <sub>1s</sub> )(αα)	+	+	+	no
	(φ <sub>1s</sub> φ <sub>1s</sub> )(αβ + βα)	+	+	+	no
	(φ <sub>1s</sub> φ <sub>1s</sub> )(ββ)	+	+	+	no
	(φ <sub>+1s</sub> φ <sub>1s</sub> )(αβ - βα)	+	-	-	yes

$${}^3\chi_{\alpha\beta} = (\alpha\beta + \beta\alpha), \quad (4.52)$$

$${}^3\chi_{\beta\beta} = \beta\beta \quad (4.53)$$

$${}^1\chi_{\alpha\beta} = (\alpha\beta - \beta\alpha), \quad (4.54)$$

where the three  ${}^3\chi_{ij}$  terms are symmetric and the  ${}^1\chi$  terms is antisymmetric, the notation will become clear momentarily.

Combining the above results on spin and permutational symmetry, we obtain the states of H<sub>2</sub> and He in Table 4.1. As expected, there are four possible spatial-spin states for each spatial state, leading to a quadrupling of the states of the system, just as the number of states for a one-electron system doubled. In each case, all four states are equally good, all being eigenstates of the Hamiltonian with the same energy. However, some of these states are never observed. For two-electron systems, the only states that have ever been observed are those that are permutationally antisymmetric,

$$\bar{\tau}\Psi = -\Psi. \quad (4.55)$$

This fact, that only antisymmetric states are observed, is incorporated into quantum mechanics by adding a new postulate called the *Pauli principle*, as will be discussed in the next section.

### 4.3 The Pauli Principle

In the previous section, we saw that for two electrons the identity of the electrons leads to the expectation that each eigenstates of  $H$  has the symmetry

$$\bar{\tau}\Psi = \pm\Psi, \quad (4.56)$$

where  $\bar{\tau}$  interchanges all coordinates, spatial and spin, of the two particles. However, we noted that all experiments on electrons suggest that

$$\bar{\tau}\Psi = -\Psi \quad (4.57)$$

is the only allowed permutational symmetry for electrons. Section 4.6.4 has some of the historical development leading to these ideas. We incorporate these observations into quantum mechanics with the following postulate. The Pauli principle states that the wavefunction for any system of electrons must change sign upon interchange (transposition) of all coordinates (space and spin) of any two electrons. This is a basic postulate of quantum mechanics, and is justified by correct predictions for numerous systems.

To see what the Pauli Principle means, consider a simple two-electron wavefunction,

$$\Psi_A(1, 2) = \psi_a(1)\psi_b(2), \quad (4.58)$$

where 1 symbolizes all spatial and spin coordinates of electron 1 and 2, the same for electron 2.

After interchanging the electrons, we get a new wavefunction,

$$\Psi_B(1, 2) = \Psi_A(2, 1) = \psi_b(1)\psi_a(2). \quad (4.59)$$

The Pauli principle states that

$$\Psi_B(1, 2) = -\Psi_A(1, 2) \quad (4.60)$$

and hence, that

$$\psi_b(1)\psi_a(2) = \psi_a(1)\psi_b(2). \quad (4.61)$$

This is obviously not true, and, thus, the simple wavefunction (4.58) is not acceptable for describing electrons.

However, it is easy to fix up a suitable wavefunction by subtracting (4.59) from (4.58),

$$\Psi_C(1, 2) = \Psi_A(1, 2) - \Psi_A(2, 1) = \psi_a(1)\psi_b(2) - \psi_b(1)\psi_a(2). \quad (4.62)$$

Thus, starting with (10) and interchanging electrons, leads to

$$\begin{aligned} \Psi_C(2, 1) &= \psi_a(2)\psi_b(1) - \psi_b(2)\psi_a(1) \\ &= \psi_b(1)\psi_a(2) - \psi_a(1)\psi_b(2) \\ &= -\psi_a(1)\psi_b(2) + \psi_b(1)\psi_a(2) \\ &= -\Psi_C(1, 2), \end{aligned} \quad (4.63)$$

so that the wavefunction (4.62) does indeed satisfy the Pauli principle.

For convenience in describing wavefunctions such as (4.62), we will define the antisymmetrizer  $\mathcal{A}$

$$\mathcal{A}\psi_a(1)\psi_b(2) = \psi_a(1)\psi_b(2) - \psi_b(1)\psi_a(2), \quad (4.64)$$

which takes a spin orbital product and converts it into a wavefunction satisfying the Pauli principle. Now let us consider some simple cases.

### 4.3.1 Identical Spin Orbitals

Assume that  $\psi_b = \psi_a$ . In this case, the wavefunction (4.62) and (4.64) becomes

$$\psi_a(1)\psi_a(2) - \psi_a(1)\psi_a(2) = 0. \quad (4.65)$$

Therefore, the Pauli principle says that we cannot have two electrons in the same spin orbital.

### 4.3.2 Orthogonality of Spin Orbitals

Consider a case where  $\psi_a$  and  $\psi_b$  are orthogonal,

$$\langle \psi_a | \psi_b \rangle = 0 \quad (4.66)$$

and define a new function

$$\psi_c = \psi_b + \lambda\psi_a, \quad (4.67)$$

where  $\lambda \neq 0$ , so that  $\psi_c$  is not orthogonal to  $\psi_a$ ,

$$\langle \psi_a | \psi_c \rangle = \langle \psi_a | \psi_b \rangle + \lambda \langle \psi_a | \psi_a \rangle = 0 + \lambda = \lambda \neq 0. \quad (4.68)$$

Forming a new wavefunction, using  $\psi_a$  and  $\psi_c$  V), we obtain

$$\begin{aligned} \psi_a(1)\psi_c(2) - \psi_c(1)\psi_a(2) &= \psi_a\psi_b + \lambda\psi_a\psi_a - \psi_b\psi_a - \lambda\psi_a\psi_a \\ &= \psi_a\psi_b - \psi_a\psi_a. \end{aligned} \quad (4.69)$$

Because of the Pauli principle, the wavefunction with partially overlapping spin orbitals  $\psi_a$  and  $\psi_b$  is identical to the waverfunction in which these spin orbitals are orthogonal. Consequently, we say that the Pauli principle leads to orthogonality of spin orbitals. Since the spin orbitals are normalized, we can require that the spin orbitals of antisymmetric wavefunctions (4.62) and (4.64), be orthonormal,

$$\langle \psi_i | \psi_j \rangle = \delta_{ij}. \quad (4.70)$$

### 4.3.3 Nonuniqueness

Starting with the wavefunctions (4.62) and (4.64), consider the new wavefunction

$$\Psi_2 = \mathcal{A}\bar{\psi}_a\bar{\psi}_b = \bar{\psi}_a\bar{\psi}_b - \bar{\psi}_b\bar{\psi}_a, \quad (4.71)$$

where

$$\bar{\psi}_a = \cos \theta \psi_a + \sin \theta \psi_b \quad (4.72)$$

and

$$\bar{\psi}_b = -\sin \theta \psi_a + \cos \theta \psi_b. \quad (4.73)$$

If  $\psi_a$  and  $\psi_b$  are orthonormal, (4.70), then the new orbitals  $\bar{\psi}_a$  and  $\bar{\psi}_b$  are also orthonormal,

$$\langle \bar{\Psi}_i | \bar{\Psi}_j \rangle = \delta_{ij}. \quad (4.74)$$

Substituting (4.72)–(4.73) into (4.71) leads to

$$\Psi_2 = -\sin \theta \cos \theta \mathcal{A} \psi_a \psi_a + \sin \theta \cos \theta \mathcal{A} \psi_b \psi_b \quad (4.75)$$

$$+ \cos^2 \theta \mathcal{A} \psi_a \psi_b - \sin^2 \theta \mathcal{A} \psi_b \psi_a \quad (4.76)$$

$$= \mathcal{A} \psi_a \psi_b = \Psi_1 \quad (4.77)$$

or

$$\mathcal{A} \bar{\psi}_a \bar{\psi}_b = \mathcal{A} \psi_a \psi_b. \quad (4.78)$$

Thus, given an antisymmetrized wavefunction written in terms of spin orbitals  $\psi_a$  and  $\psi_b$ , this wavefunction is unchanged upon recombining the spin orbitals; the wavefunction retains orthonormality. The Pauli principle states that only the two-dimensional space spanned by  $\psi_a$  and  $\psi_b$  is significant, but not the particular axis or basis functions used to describe this space.

#### 4.3.4 Summary for Two Electrons

Starting with two spin orbitals  $\psi_a$  and  $\psi_b$ , one could construct four possible wavefunctions,

$$\psi_a(1)\psi_a(2) \quad (4.79)$$

$$\psi_a(1)\psi_b(2) \quad (4.80)$$

$$\psi_b(1)\psi_a(2) \quad (4.81)$$

$$\psi_b(1)\psi_b(2). \quad (4.82)$$

Of these four possibilities, only the following combination of the second and third functions

$$\psi_a(1)\psi_b(2) = \psi_a(1)\psi_b(2) - \psi_b(1)\psi_a(2) \quad (4.83)$$

are allowed by the Pauli principle.

For convenience in writing such wavefunctions, we define the antisymmetrizer  $\mathcal{A}$ , so that  $\mathcal{A}\psi_a\psi_b$  is always understood to denote  $\psi_a\psi_b - \psi_b\psi_a$ . If the two spin orbitals are identical, the wavefunction (4.83) is zero and, indeed, the spin orbitals can be taken as orthogonal without affecting the wavefunction. Moreover, the spin orbitals  $\psi_a$  and  $\psi_b$  can be recombined, retaining orthonormality, without changing the wavefunction. For the antisymmetrized wavefunction (4.83), any overlap between the spinorbitals gets zapped, deleted, by the antisymmetrizer; hence, the spin orbitals can be taken as orthogonal, with no restriction.

#### 4.3.5 Determinants

There is a simple way to use determinants in writing wavefunctions satisfying the Pauli principle. The determinant is defined as

$$\begin{vmatrix} a & b \\ c & d \end{vmatrix} = ad - bc \quad (4.84)$$

and

$$\begin{vmatrix} a & b & c \\ d & e & f \\ g & h & i \end{vmatrix} = aei + bfg + chd - ceg - bdi - ahf \quad (4.85)$$

etc. For matrices of orders 2 and 3, the determinant is most rapidly calculated by assigning a +1 coefficient for products arising from multiplying along the downward diagonals, including parallel shifted diagonals, and assigning a -1 coefficient for products arising from multiplying along upward diagonals. The general definition is

$$\det [a_{11}a_{12}\cdots a_{nn}] = \sum_{ij\cdots\omega} \epsilon_{ij\cdots\omega} a_{1i}a_{2j}\cdots a_{n\omega}, \quad (4.86)$$

where  $\epsilon_{ij\cdots\omega} = 0$ , unless all indices are different, say  $\epsilon_{ij\cdots\omega} = +1$  when  $ij\cdots\omega$  is an even permutation of  $12\cdots n$ , and  $\epsilon_{ij\cdots\omega} = -1$  when  $ij\cdots\omega$  is an odd permutation of  $12\cdots n$ . An odd permutation is one that is constructed from an odd number of transpositions, and an even permutation is one that is constructed from an even number of transpositions. Thus, the determinant automatically changes sign upon interchange of any two rows or columns.

Important properties of a determinant are:

1. The determinant changes sign upon interchange of any two rows or any two columns, e.g.,

$$\begin{vmatrix} b & c \\ d & e \end{vmatrix} = bd - ad = - \begin{vmatrix} a & b \\ c & d \end{vmatrix}. \quad (4.87)$$

2. The determinant is zero, if any two columns, or any two rows, are identical, e.g.,

$$\begin{vmatrix} a & a \\ c & c \end{vmatrix} = ac - ac = 0. \quad (4.88)$$

3. Adding some amount of any one column to any other column, leaves the determinant unchanged,

$$\begin{vmatrix} a & b + \lambda a \\ c & d + \lambda c \end{vmatrix} = a(d + \lambda c) - (b + \lambda a)c = ad + \lambda ac - bd - \lambda ac = \begin{vmatrix} a & b \\ d & d \end{vmatrix} \quad (4.89)$$

(the same is true for rows). Thus, each row can be made as orthogonal to each other row without changing the determinant.

The wavefunction (4.83) can be written as a determinant, as follows

$$\begin{vmatrix} \psi_a(1) & \psi_b(1) \\ \psi_a(2) & \psi_b(2) \end{vmatrix} = \psi_a(1)\psi_b(2) - \psi_b(1)\psi_a(2) = \mathcal{A}\psi_a(1)\psi_b(2) \quad (4.90)$$

where the antisymmetrizer  $\mathcal{A}$  can be referred to as the *determinant operator*.

Similarly, starting with the  $3! = 6$  product wavefunctions,

$$\psi_a(1)\psi_b(2)\psi_c(3) \quad (4.91)$$

the only combination satisfying the Pauli principle is

$$\Psi(1, 2, 3) = \mathcal{A}\psi_a(1)\psi_b(2)\psi_c(3) \quad (4.92)$$

$$\begin{aligned} &= [\psi_a\psi_b\psi_c + \psi_b\psi_c\psi_a + \psi_c\psi_a\psi_b - \psi_b\psi_a\psi_c - \psi_c\psi_b\psi_a - \psi_a\psi_c\psi_b] \\ &= \begin{vmatrix} \psi_a(1) & \psi_b(1) & \psi_c(1) \\ \psi_a(2) & \psi_b(2) & \psi_c(2) \\ \psi_a(3) & \psi_b(3) & \psi_c(3) \end{vmatrix} \end{aligned} \quad (4.94)$$

For example, interchanging electrons 1 and 3, leads to

$$\Psi(3, 2, 1) = [\psi_c\psi_b\psi_a + \psi_a\psi_c\psi_b + \psi_b\psi_a\psi_c - \psi_c\psi_a\psi_b - \psi_a\psi_b\psi_c - \psi_b\psi_c\psi_a] \quad (4.95)$$

$$\begin{aligned} &= -\psi_a\psi_b\psi_c - \psi_b\psi_c\psi_a - \psi_c\psi_a\psi_b + \psi_b\psi_a\psi_c + \psi_c\psi_b\psi_a + \psi_a\psi_c\psi_b \\ &= -\Psi(1, 2, 3). \end{aligned} \quad (4.96)$$

Note also, from the properties of determinants, that interchange of any two columns of (4.94) (i.e. interchanging two spin orbitals) merely changes the sign of the wavefunction so that

$$\mathcal{A}\psi_b\psi_a\psi_c = -\mathcal{A}\psi_a\psi_b\psi_c. \quad (4.98)$$

Using the properties of the determinant, one can show that:

1.  $\mathcal{A}\psi_a\psi_b\psi_c \dots$  changes sign upon interchange of any pair of electrons, thus the Pauli principle is always satisfied.
2.  $\mathcal{A}\psi_a\psi_b\psi_c \dots = 0$  if any two spin orbitals are equal (e.g.  $\mathcal{A}\psi_a\psi_a\psi_c = 0$ ).
3. All orbitals in  $\mathcal{A}\psi_a\psi_b\psi_c$  can be taken as orthogonal with no restrictions. Thus, we take  $\langle \psi_i | \psi_j \rangle = \delta_{ij}$ .
4. Interchange of any two spin orbitals of  $\mathcal{A}\psi_a\psi_b\psi_c \dots$  merely changes the sign of the wavefunction. Thus, any permutation of the spin orbitals leads back to the original wavefunction, or else changes the sign. Since the sign of the total wavefunction has no significance, the order of the spin orbitals in  $\mathcal{A}\psi_a\psi_b\psi_c \dots$  is of no significance.
5. We may take any recombination of the  $\psi_i$ , preferring orthonormality to obtain  $\mathcal{A}\bar{\psi}_a\bar{\psi}_b\bar{\psi}_c \dots = \mathcal{A}\psi_a\psi_b\psi_c \dots$ .

For an  $N$ -electron system, there are  $N!$  possible product terms, such as

$$\psi_a(1)\psi_b(2) \cdots \psi_z(N). \quad (4.99)$$

Of these, there is one combination that satisfies the Pauli principle. This combination can be written as an  $N$  by  $N$  determinant

$$\det \psi_a(1)\psi_b(2) \cdots \psi_z(N), \quad (4.100)$$

where the spin orbitals are orthonormal

$$\langle \psi_i | \psi_j \rangle = \delta_{ij}. \quad (4.101)$$

Such determinants of functions are referred to in the mathematical literature as Stäckel determinants. They were first used to describe electronic wavefunctions by Heisenberg and were popularized by J. L. Slater [?]. They are often referred to as *Slater determinants*.

For  $N$  noninteracting but identical particles, there would be  $N!$  possible states, all with the same energy. Of these, only one is allowed by quantum mechanics. In developing statistical mechanics, the famous engineer J. W. Gibbs, realized that use of  $N!$  factor led to ridiculous entropies and arbitrarily just divided the total number of states by  $N!$ . He got the right answer but missed a golden opportunity to invent quantum mechanics before the physicists stumbled into it.

### 4.3.6 More on Spins for Two Electrons

Defining the total  $M_s$  quantum number for a spin function, as the sum of the  $M_s$  numbers for each electron, leads to

$$\left. \begin{array}{ll} \alpha\alpha & M_s = +1 \\ \alpha\beta + \beta\alpha & M_s = 0 \\ \beta\beta & M_s = -1 \end{array} \right\} s = 1 \quad (4.102)$$

$$\alpha\beta - \beta\alpha \quad M_s = 0 \} s = 0. \quad (4.103)$$

The three states of the triplet have  $M_S = +1, 0, -1$ , and we refer to this as the *spin-one states* ( $S = 1$ ). Whereas the singlet state has only  $M_S = 0$ , we refer to this as the *spin-zero states* ( $S = 0$ ). Spin states are discussed more carefully in a following section.

### 4.3.7 Noninteracting Particles

Consider, for the moment, a simple system in which the electrons do not interact, say one electron in California and the other on the moon. The Hamiltonian of the system is

$$H(1, 2) = h(1) + h(2), \quad (4.104)$$

and if  $\psi_a$  and  $\psi_b$  are eigenstates of  $h$ ,

$$h\psi_a = \epsilon_a \psi_a \quad (4.105)$$

and

$$h\psi_b = \epsilon_b \psi_b, \quad (4.106)$$

then either produce wavefunction is an eigenfunction of  $H$

$$H\psi_a\psi_b = (\epsilon_a + \epsilon_b)\psi_a\psi_b \quad (4.107)$$

and

$$H\psi_b\psi_a = (\epsilon_a + \epsilon_b)\psi_b\psi_a. \quad (4.108)$$

However, the Pauli principle says that only the wavefunction (4.83)

$$\psi = \varphi_a \varphi_b - \varphi_b \varphi_a \quad (4.109)$$

is allowed. Thus, even electrons 200,000 miles apart have a phase relation connecting them. Quantum mechanics is stranger than fiction!

## 4.4 Spin for Two or More Electrons

### 4.4.1 Two Electrons

Because of the Pauli principle, only one spin state is consistent with the symmetric spatial wavefunction,

$$(\varphi_a \varphi_b + \varphi_b \varphi_a) (\alpha\beta - \beta\alpha) \quad (4.110)$$

and, consequently, this is called a *singlet state*. On the other hand, three spin states are allowed for an antisymmetric spatial wavefunction,

$$(\varphi_a \varphi_b - \varphi_b \varphi_a) (\alpha\alpha) \quad (4.111)$$

$$(\varphi_a \varphi_b - \varphi_b \varphi_a) (\alpha\beta + \beta\alpha) \quad (4.112)$$

$$(\varphi_a \varphi_b - \varphi_b \varphi_a) (\beta\beta) \quad (4.113)$$

and these are collectively referred to as a *triplet state*.

Since the energy expression does not depend upon spin, the energies of the allowed wavefunctions (4.110) and (4.111)–(4.113) are the same as for the forbidden states,

$$(\varphi_a \varphi_b + \varphi_b \varphi_a) (\alpha\alpha) \quad (4.114)$$

$$(\varphi_a \varphi_b + \varphi_b \varphi_a) (\alpha\beta + \beta\alpha) \quad (4.115)$$

$$(\varphi_a \varphi_b + \varphi_b \varphi_a) (\beta\beta) \quad (4.116)$$

$$(\varphi_a \varphi_b - \varphi_b \varphi_a) (\alpha\beta - \beta\alpha), \quad (4.117)$$

respectively. However, because of the Pauli principle, only (4.110)–(4.113) are allowed, leading to a correlation between spatial symmetry (and hence, energy) and spin. Thus, if  $\varphi_a$  and  $\varphi_b$  are the  $\chi_l$  and  $\chi_r$  orbitals of  $H_2$ , state 1 is better, leading to the singlet spin state. In this case, we say that bonding electrons prefer to have their spins aligned antiparallel. On the other hand, if  $\varphi_a$  and  $\varphi_b$  are the  $\varphi_g$  and  $\varphi_u$  orbitals of the excited state of  $H_2$ , then state 2 is better and we say that electrons in orthogonal orbitals prefer to have their spin aligned parallel. Of course the spin has nothing to do with the energy, but such descriptions do serve to keep track of the spatial symmetries that do determine energy.

Since the three spin functions in (4.111)–(4.113) all lead to the same energy, it is sufficient to consider just one. We will always use the maximum value of  $M_S$ , namely,  $\alpha\alpha$  for  $S = 1$  and,  $\alpha\beta - \beta\alpha$  for  $S = 0$ . Thus, (4.110) becomes

$$(\varphi_a \varphi_b - \varphi_b \varphi_a) \alpha\alpha = [\varphi_a(1)\varphi_b(2) - \varphi_b(1)\varphi_a(2)] \alpha(1)\alpha(2)$$

$$\begin{aligned}
&= (\varphi_a \alpha) (\varphi_b \alpha) - (\varphi_b \alpha) (\varphi_a \alpha) \\
&= \mathcal{A} [(\varphi_a \alpha) (\varphi_b \alpha)]
\end{aligned} \tag{4.118}$$

On the other hand, the wavefunction (4.117) requires two determinants,

$$\begin{aligned}
(\varphi_a \varphi_b + \varphi_b \varphi_a) (\alpha \beta - \beta \alpha) &= \mathcal{A} (\varphi_a \varphi_b + \varphi_b \varphi_a) \alpha \beta \\
&= \mathcal{A} (\varphi_a \alpha) (\varphi_b \beta) + \mathcal{A} (\varphi_b \alpha) (\varphi_a \beta) \\
&= \mathcal{A} (\varphi_a \varphi_b) (\alpha \beta - \beta \alpha).
\end{aligned} \tag{4.119}$$

#### 4.4.2 Three Electrons

For three electrons, there are eight spin functions,  $\alpha\alpha\alpha$ ,  $\alpha\alpha\beta$ ,  $\alpha\beta\alpha$ ,  $\beta\alpha\alpha$ ,  $\alpha\beta\beta$ ,  $\beta\alpha\beta$ ,  $\beta\beta\alpha$ , and  $\beta\beta\beta$ . You should check to see that all eight functions are orthogonal. Combining these into proper spin functions, leads to

$$\left. \begin{array}{ll} \alpha\alpha\alpha & M_S = \frac{3}{2} \\ \alpha\alpha\beta + \alpha\beta\alpha & M_S = \frac{1}{2} \\ \alpha\beta\beta + \beta\alpha\beta + \beta\beta\alpha & M_S = -\frac{1}{2} \\ \beta\beta\beta & M_S = -\frac{3}{2} \end{array} \right\} s + \frac{3}{2} \text{ quartet} \tag{4.120}$$

$$\left. \begin{array}{ll} (\alpha\beta - \beta\alpha)\alpha & M_s = \frac{1}{2} \\ (\alpha\beta - \beta\alpha)\beta & M_s = -\frac{1}{2} \end{array} \right\} s = \frac{1}{2} \text{ doublet} \tag{4.121}$$

$$\left. \begin{array}{ll} 2(\alpha\alpha)\beta - (\alpha\beta + \beta\alpha)\alpha & M_S = \frac{1}{2} \\ (\alpha\beta + \beta\alpha)\beta - 2(\beta\beta)\alpha & M_S = -\frac{1}{2} \end{array} \right\} s = \frac{1}{2} \text{ doublet} \tag{4.122}$$

The particular combinations involved here, for  $M_s = 1/2$  and  $M_S = -1/2$  are of no concern here. In discussing the  $S = 3/2$  or quartet, it is sufficient to consider the  $M_S = 3/2$  function of  $\alpha(1)\alpha(2)\alpha(3)$ .

#### 4.4.3 Spin States for N Electrons

Given two choices,  $\alpha$  and  $\beta$ , for the spin of each electron, there are  $2N$  possible spin functions for an  $N$ -electron system. These functions are most conveniently discussed using the theory of angular momentum. In this course, we make little explicit use of angular momentum theory. However, the terminology incorporates aspects of this theory; hence, some discussion is appropriate.

Section 4.6.2 contains a review of the formalism. The results (relevant here) are the following. A set of  $2S + 1$  states,

$$\chi_{S,S}, \chi_{S,S-1}, \dots, \chi_{S,-S} \tag{4.123}$$

is said to be an angular momentum  $S$  state if

$$\hat{S}^2 \chi_{S,M} = S(S+1) \chi_{S,M} \tag{4.124}$$

and

$$\hat{S}_z \chi_{S,M} = M \chi_{S,M} \tag{4.125}$$

where  $\hat{S}^2$  and  $\hat{S}_z$  are referred to as the total angular momentum operator and the angular momentum projection operator. The numbers  $S$  and  $M$  must be integers or half-integers, leading to the following possible cases. For singlet

$$S = 0, M = 0 \quad (4.126)$$

for doublet

$$S = \frac{1}{2}, M = \pm \frac{1}{2} \quad (4.127)$$

for triplet

$$S = 1, M = 0, \pm 1 \quad (4.128)$$

for quartet

$$S = \frac{3}{2}, M = \pm \frac{1}{2}, \pm \frac{3}{2} \quad (4.129)$$

etc. Since the Hamiltonian does not depend on spin, no magnetic field, the  $2S+1$  states in (4.123) all have the same energy. The states of  $\chi_{S,M}$  with the same  $S$  but different  $M$ , are related by the raising and lowering operators,  $\hat{S}^+$  and  $\hat{S}^-$ ,

$$\hat{S}^+ \chi_{S,M} = \sqrt{S(S+1) - M_S(M_S+1)} \chi_{S,M+1} \quad (4.130)$$

$$\hat{S}^- \chi_{S,M+1} = \sqrt{S(S+1) - M_S(M_S+1)} \chi_{S,M}. \quad (4.131)$$

Thus, in particular,

$$\hat{S}^+ \chi_{S,S} = 0 \quad (4.132)$$

$$\hat{S}^- \chi_{S,-S} = 0. \quad (4.133)$$

A convenient test for whether a function is a spin eigenfunction, is as follows, using (4.132)–(4.133). If

$$\hat{S}_z \psi_M = M \psi_M \quad (4.134)$$

and

$$\hat{S}^+ \psi_M = 0, \quad (4.135)$$

then  $\psi_M$  is an angular momentum state with  $M = S$ .

## One Electron

Applying these properties to the one-electron case,  $S = 1/2$ , and  $M = \pm 1/2$ , leads to

$$\hat{s}_z \alpha = \frac{1}{2} \alpha \quad (4.136)$$

$$\hat{s}_z \beta = -\frac{1}{2} \beta \quad (4.137)$$

$$\hat{s}^2 \alpha = s(s+1)\alpha = \frac{3}{4} \alpha \quad (4.138)$$

$$\hat{s}^2 \beta = s(s+1)\beta = \frac{3}{4} \beta \quad (4.139)$$

where  $s = 1/2$ . From (4.130)–(4.131)

$$\hat{s}^+ \alpha = 0 \quad (4.140)$$

$$\hat{s}^- \alpha = \beta \quad (4.141)$$

$$\hat{s}^+ \beta = \alpha \quad (4.142)$$

$$\hat{s}^- \beta = 0. \quad (4.143)$$

The one electron spin functions are orthonormal, that is

$$\begin{aligned} \langle \alpha | \beta \rangle &= 0 \\ \langle \alpha | \alpha \rangle &= 1 \\ \langle \beta | \beta \rangle &= 1. \end{aligned} \quad (4.144)$$

## Two Electrons

With two electrons, we define the spin operators as

$$\begin{aligned} \hat{S}_z &= \hat{s}_z(1) + \hat{s}_z(2) \\ \hat{S}^+ &= \hat{s}^+(1) + \hat{s}^+(2) \\ \hat{S}^- &= \hat{s}^-(1) + \hat{s}^-(2) \end{aligned} \quad (4.145)$$

and

$$\hat{S}_2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2. \quad (4.146)$$

Applying the theory leads two-electron spin eigenfunctions of the form

$$S = 1 : \begin{cases} \chi_{11} = \alpha\alpha \\ \chi_{10} = \frac{1}{\sqrt{2}}(\alpha\beta + \beta\alpha) \\ \chi_{1\bar{1}} = \beta\beta \end{cases} \quad (4.147)$$

$$S = 0 : \chi_{00} = \frac{1}{\sqrt{2}}(\alpha\beta - \beta\alpha) \quad (4.148)$$

Using the orthogonality of the one-electron spin functions (4.144) we see that the four two-electron functions (4.147) and (4.148) are orthonormal. Since  $\hat{S}^+ \chi_{11} = 0$  and  $\hat{S}^+ \chi_{00} = 0$ , we see from (4.132)–(4.133) that these are spin eigenfunctions with  $S = 1$  and  $S = 0$ , respectively. Since

$$\hat{S}^- \chi_{11} = \sqrt{2} \chi_{10} \quad (4.149)$$

and

$$\hat{S}^- \chi_{10} = \sqrt{2} \chi_{1\bar{1}}, \quad (4.150)$$

we find that  $\chi_{10}$  and  $\chi_{1\bar{1}}$  are also  $S = 1$  functions.

As derived in Section 4.3, from the Pauli principle, a triplet spin function (symmetric) such as  $\alpha\alpha$  of (4.147) must go with an antisymmetric spatial function such as

$$\varphi_a\varphi_b - \varphi_b\varphi_a, \quad (4.151)$$

while a single spin function (antisymmetric) such as  $(\alpha\beta - \beta\alpha)$  of (4.148) must go with a symmetric spatial function such as

$$\varphi_a\varphi_b + \varphi_b\varphi_a \quad (4.152)$$

These permutational symmetries of wavefunctions are sometimes illustrated by diagrams as in (4.151) and (4.152), where orbitals in the same row are symmetrical (permutationally), while orbitals in the same column are antisymmetrical.

In Chapter 3 we used the nodal theorem to show that the ground state of any two-electron system must have a symmetric spatial function. Thus, because of the Pauli principle the ground state of any two-electron system must be a singlet spin state.

### Many Electrons

Section 4.6.3 shows how to construct spin eigenfunctions for systems with more electrons. An understanding of such functions is important for discussing the states of transition metal systems but will be deferred for now. We will instead consider the spin properties of some Slater determinant wavefunctions.

Consider first

$$\Psi_{11} = \mathcal{A}(\varphi_a\alpha)(\varphi_b\alpha). \quad (4.153)$$

Since

$$\hat{S}_x\Psi_{11} = \left(\frac{1}{2} + \frac{1}{2}\right)\Psi_{11} = \Psi_{11} \quad (4.154)$$

and

$$\hat{S}^+\Psi_{11} = 0, \quad (4.155)$$

we see that  $\Psi_{11}$  has  $S = 1$  and  $M = 1$ . This, of course, is obvious since expanding  $\Psi_{11}$  leads to

$$\Psi_{11} = (\varphi_a\alpha)(\varphi_b\alpha) - (\varphi_b\alpha)(\varphi_a\alpha) = (\varphi_a\varphi_b - \varphi_b\varphi_a)\alpha\alpha. \quad (4.156)$$

Applying  $\hat{S}$  to  $\Psi_{11}$  leads to

$$\begin{aligned} \Psi_{10} &= \frac{1}{\sqrt{2}} [\mathcal{A}(\varphi_a\beta)(\varphi_b\alpha) + \mathcal{A}(\varphi_a\alpha)(\varphi_b\beta)] \\ &= \frac{1}{\sqrt{2}} [(\varphi_a\beta)(\varphi_b\alpha) - (\varphi_b\alpha)(\varphi_a\beta) + (\varphi_a\alpha)(\psi_b\beta) - (\varphi_b\beta)(\varphi_a\alpha)] \\ &= \frac{1}{\sqrt{2}} [(\varphi_a\varphi_b - \varphi_b\varphi_a)(\alpha\beta + \beta\alpha)] \end{aligned} \quad (4.157)$$

with  $S = 1$  and  $M = 0$ . Note, particularly, that the  $M = 0$  triplet function requires two Slater determinants.

Now consider

$$\Psi_0 = \mathcal{A}(\varphi_a\alpha)(\varphi_b\beta). \quad (4.158)$$

Applying  $\hat{S}_z$  leads to  $M = 0$ . However, this is not a singlet state since

$$\hat{S}^+\Psi_0 = \mathcal{A}(\varphi_a\alpha)(\varphi_b\alpha) = (\varphi_a\varphi_b - \varphi_b\varphi_a)\alpha\alpha. \quad (4.159)$$

On the other hand, comparison with  $\Psi_{10}$  shows that  $\Psi_0$  is not a triplet state either. Noting that the singlet function is

$$\begin{aligned}\Psi_{00} &= \mathcal{A}(\varphi_a\varphi_b + \varphi_b\varphi_a)(\alpha\beta - \beta\alpha) \\ &= \mathcal{A}(\varphi_a\alpha)(\varphi_b\beta) - \mathcal{A}(\varphi_a\beta)(\varphi_b\alpha)\end{aligned} \quad (4.160)$$

we see that

$$\Psi_0 = \Psi_{00} + \Psi_{10}. \quad (4.161)$$

There is one exception to the above conclusion. From (4.159) we see that if  $\varphi_a = \varphi_b$ , then  $\hat{S}^+\Psi_0 = 0$ , and hence,  $\Psi_0$  is a proper spin eigenstate. Thus, the wavefunction with a doubly-occupied orbitals,

$$\mathcal{A}(\varphi_a\alpha)(\varphi_a\beta) \quad (4.162)$$

is a singlet state. Alternative, applying  $\hat{S}^+$  to (4.162) leads to

$$\hat{S}^+\mathcal{A}(\varphi_a\alpha)(\varphi_a\beta) = \mathcal{A}(\varphi_a\alpha)(\varphi_a\alpha) = 0, \quad (4.163)$$

that is, (4.162) is a singlet ( $S = 0$ ) state. Since the Hamiltonian does not contain spin, the exact wavefunctions are spin eigenstates, and we will deal only with approximate wavefunctions that are also spin eigenstates. Thus, for two electrons, we deal only with the closed-shell singlet wavefunction of (4.170) and the open-shell triplet wavefunction of (4.162), and the open-shell triplet wavefunction

$$\mathcal{A}(\varphi_a\alpha)(\varphi_b\alpha) \quad (4.164)$$

as shown earlier,  $\psi_a$  and  $\psi_b$  can be taken as orthogonal in (4.153) and (4.156).

For a many-electron system, the generalization of (4.162) is the closed-shell wavefunction,

$$\Psi^{cs} = \mathcal{A}(\varphi_a\alpha)(\varphi_a\beta)(\varphi_b\alpha)(\varphi_b\beta) \cdots (\varphi_m\alpha)(\varphi_m\beta), \quad (4.165)$$

where the number of electrons  $N$  must be even,  $m = N/2$ . Equation (4.165) is a single eigenstate since  $M_s = 0$  and since applying  $\hat{S}^+$  leads to  $\hat{S}^+\Psi^{cs} = 0$ , because of the antisymmetrizer. The generalization of the open-shell wavefunction (4.153) and (4.156) is

$$\Psi^{HS} = \mathcal{A}(\varphi_a\alpha)(\varphi_b\alpha) \cdots (\varphi_N\alpha), \quad (4.166)$$

where all orbitals have the same spin leading to  $S = N/2$ .

In addition, we can have an intermediate case of the form

$$\Psi^{IS} = \mathcal{A}(\varphi_a\alpha)(\varphi_a\beta) \cdots (\varphi_m\alpha)(\varphi_m\beta)(\varphi_{m+1}\alpha) \cdots (\varphi_n\alpha) \quad (4.167)$$

with  $m$  doubly-occupied (or closed-shell) orbitals

$$\varphi_a \cdots \varphi_m \quad (4.168)$$

and  $n - m$  singly-occupied (or open-shell) orbitals

$$\varphi_{m+1}, \dots, \varphi_n \quad (4.169)$$

all coupled to high spin  $S = 1/2(n - m)$ .

## 4.5 The Energy of a Determinant Wavefunction

### 4.5.1 Permutational Symmetry

The energy of the wavefunction  $\mathcal{A}\Psi$  is

$$E = \frac{\langle \mathcal{A}\varphi | H | \mathcal{A}\psi \rangle}{\langle \mathcal{A}\Psi | \mathcal{A}\Psi \rangle}, \quad (4.170)$$

where for  $N$  electrons each  $\mathcal{A}\Psi$  involves  $N!$  terms. Thus, the numerator and denominator in (4.170) each involved  $(N!)^2$  terms. However, (4.170) can always be rewritten as

$$E = \frac{\langle \Psi | H | \mathcal{A}\Psi \rangle}{\langle \Psi | \mathcal{A}\Psi \rangle}, \quad (4.171)$$

reducing the numerator and denominator to only  $N!$  terms each.

For example, with two electrons,

$$\Psi_1 = \mathcal{A}\psi = \Psi - \tau\Psi \quad (4.172)$$

and, thus

$$\langle \mathcal{A}\Psi | H | \mathcal{A}\Psi \rangle = \langle \Psi | H | \Psi_1 \rangle - \langle \tau\Psi | H | \Psi_1 \rangle, \quad (4.173)$$

where

$$\langle \tau\Psi | H | \Psi_1 \rangle = \int d^3r_1 d^3r_2 [\tau\Psi(1, 2)H\Psi_1(1, 2)] \quad (4.174)$$

Renumbering the dummy indices in (4.174), and noting that

$$\begin{aligned} \tau\Psi(2, 1) &= \Psi(1, 2) \\ H(2, 1) &= H(1, 2) \\ \Psi_1(2, 1) &= -\Psi_1(1, 2) \end{aligned} \quad (4.175)$$

we see that

$$\langle \tau\Psi | H | \Psi_1 \rangle = -\langle \Psi | H | \Psi_1 \rangle. \quad (4.176)$$

Thus, (4.173) becomes

$$\langle \mathcal{A}\Psi | H | \mathcal{A}\Psi \rangle = 2\langle \Psi | H | \Psi_1 \rangle \quad (4.177)$$

and similarly

$$\langle \mathcal{A}\Psi | \mathcal{A}\Psi \rangle = 2\langle \Psi | \mathcal{A}\Psi \rangle \quad (4.178)$$

leading to (4.171).

For an  $N$ -electron wavefunction, expansion of the numerator for the energy, leads to  $N!$  terms of the form

$$\zeta_\pi \langle \pi \Psi | H | \Psi_1 \rangle, \quad (4.179)$$

where each  $\pi$  is expressed as a product of transpositions. Each term comes in with  $\zeta_\pi = -1$  if  $\pi$  involves an odd number of transpositions, and  $\zeta_\pi = +1$  if  $\pi$  involves an even number of transpositions. Because  $H$  is invariant under all permutations, and since  $\Psi_1$  changes sign under every transposition, we obtain

$$\zeta_\pi \langle \pi \Psi | H | \Psi_1 \rangle = \zeta_\pi \zeta_\pi \langle \Psi | H | \Psi_1 \rangle \quad (4.180)$$

and, hence

$$\langle \mathcal{A} \Psi | H | \mathcal{A} \Psi \rangle = N! \langle \Psi | H | \mathcal{A} \Psi \rangle \quad (4.181)$$

and

$$\langle \mathcal{A} \Psi | \mathcal{A} \Psi \rangle = N! \langle \Psi | \mathcal{A} \Psi \rangle, \quad (4.182)$$

leading to (4.171).

### 4.5.2 The Energy in Terms of Spin Orbitals

#### Two Electrons

For two electrons, the Slater determinant wavefunction is

$$\mathcal{A} \psi_a \psi_b = \psi_a(1) \psi_b(2) - \psi_b(1) \psi_a(2) \quad (4.183)$$

and the energy is

$$E = \frac{\langle ab | H | \mathcal{A} ab \rangle}{\langle ab | \mathcal{A} ab \rangle}, \quad (4.184)$$

where we use the subscripts  $a$  and  $b$  to denote the spin orbitals  $\psi_a$  and  $\Psi_b$ . Since the spin orbitals are orthonormal,

$$\langle \psi_i | \psi_j \rangle = \delta_{ij} \quad (4.185)$$

the denominator of (4.184) becomes

$$\langle ab | \mathcal{A} ab \rangle = \langle ab | ab \rangle - \langle ab | ba \rangle = \langle a | a \rangle \langle b | b \rangle - \langle a | b \rangle \langle b | a \rangle = 1 \quad (4.186)$$

and (4.184) becomes

$$E = \langle ab | H | ab \rangle - \langle ab | H | ba \rangle. \quad (4.187)$$

Since

$$H(1, 2) = h(1) + h(2) + \frac{1}{r_{12}}, \quad (4.188)$$

the two terms of (4.187) are

$$\begin{aligned} \langle ab | H | ab \rangle &= \langle a | h | a \rangle \langle b | b \rangle + \langle a | a \rangle \langle b | h | b \rangle + \langle ab | \frac{1}{r_{12}} | ab \rangle \\ &= \langle a | h | a \rangle + \langle b | h | b \rangle + J_{ab} \end{aligned} \quad (4.189)$$

and

$$\langle ab|H|ba\rangle = \langle a|h|b\rangle \underbrace{\langle b|a\rangle}_0 + \underbrace{\langle a|b\rangle}_0 + \langle ab|\frac{1}{r_{12}}|ba\rangle = K_{ab} \quad (4.190)$$

where

$$J_{ab} = \langle a(1)b(2)|\frac{1}{r_{12}}|a(1)b(2)\rangle \quad (4.191)$$

and

$$K_{ab} = \langle a(1)b(2)|\frac{1}{r_{12}}|b(1)a(2)\rangle \quad (4.192)$$

are Coulomb and exchange integrals between spin orbitals  $\psi_a$  and  $\psi_b$ . Note we will use script  $J$  and  $K$  to denote integrals involving spin orbitals, and Roman  $J$  and  $K$  to denote integrals involving spatial orbitals. Thus, the energy of the Slater determinant wavefunction is

$$E = \langle \psi_a | h | \psi_a \rangle + \langle \psi_b | h | \psi_b \rangle + J_{ab} - K_{ab}. \quad (4.193)$$

### Three Electrons

For three electrons, the normalization term is

$$\langle abc | \mathcal{A}abc \rangle = \langle abc | abc + bca + cab - bac - cba - acb \rangle = 1 \quad (4.194)$$

because of orthogonality, and hence, the energy is

$$E = \langle abc | H | \mathcal{A}abc \rangle = \langle abc | \mathcal{H} | abc + bca + cab - bac - cba - acb \rangle. \quad (4.195)$$

Considering the one-electron part of  $H$ ,

$$H_1 = h(1) + h(2) - h(3), \quad (4.196)$$

only the first term of (4.195) is nonzero, because of orthogonality, leading to

$$E_1 = \langle abc | H_1 | abc \rangle = \sum_{i=a}^c \langle i | h | i \rangle. \quad (4.197)$$

Considering the two-electron term,  $1/r_{12}$ , (4.195) becomes

$$\begin{aligned} & \langle ab|\frac{1}{r_{12}}|ab\rangle\langle c|c\rangle + \langle ab|\frac{1}{r_{12}}|bc\rangle\langle c|a\rangle + \langle ab|\frac{1}{r_{12}}|ca\rangle\langle c|b\rangle \\ & - \langle ab|\frac{1}{r_{12}}|ba\rangle\langle c|c\rangle - \langle ab|\frac{1}{r_{12}}|cb\rangle\langle c|a\rangle - \langle ab|\frac{1}{r_{12}}|ac\rangle\langle c|b\rangle. \end{aligned} \quad (4.198)$$

But, because of orthogonality, only the first and fourth terms are nonzero, leading to  $J_{ab} - K_{ab}$ . Similarly,  $1/r_{13}$  leads to  $J_{ac} - K_{ac}$  and  $1/r_{23}$  leads to  $J_{bc} - K_{bc}$ . Thus,

$$\begin{aligned} E_2 &= \langle abc | H_2 | \mathcal{A}abc \rangle \\ &= (J_{ab} - K_{ab}) + (J_{ac} - K_{ac}) + (J_{bc} - K_{bc}), \\ &= \sum_{i>j=a}^c (J_{ij} - K_{ij}), \end{aligned}$$

(4.199)

and the total energy is

$$E = \sum_{i=1}^3 \langle i|h|i \rangle + \sum_{i>j=1}^3 (J_{ij} - K_{ij}) \quad (4.200)$$

### Many Electrons

Generalizing from the three-electron case, the  $N$ -electron wavefunction  $\Psi$  leads to the energy

$$E = \sum_{i=1}^N \langle i|h|i \rangle + \sum_{i>j=1}^N (J_{ij} - K_{ij}) . \quad (4.201)$$

Thus, the energy of a Slater determinant wavefunction consists of the one-electron energy of each of the  $N$  spin orbitals, plus the two-electron Coulomb interaction  $J_{ij}$  between each pair of electrons (this leads to  $N(N - 1)/2$  terms) plus the two-electron exchange interaction  $K_{ij}$  between each pair of electrons (leading also to  $N(N - 1)/2$  terms).

### 4.5.3 Factor into Spatial and Spin Parts

#### Two Electrons

If the spin orbitals in the determinant have different spin,

$$\mathcal{A}(\varphi_a\alpha)(\varphi_b\beta), \quad (4.202)$$

then orthonormality of the spin orbitals (4.185) and of the spin functions  $\langle \alpha|\alpha \rangle = \langle \beta|\beta \rangle = 1$ , and  $\langle \alpha|\beta \rangle = 0$ , leads to

$$1 = \langle \psi_a|\psi_a \rangle = \langle \varphi_a|\varphi_a \rangle \langle \alpha|\alpha \rangle = \langle \varphi_a|\varphi_a \rangle \quad (4.203)$$

and

$$1 = \langle \psi_b|\psi_b \rangle = \langle \varphi_b|\varphi_b \rangle \langle \beta|\beta \rangle = \langle \varphi_b|\varphi_b \rangle \quad (4.204)$$

as before, but

$$\langle \psi_a|\psi_b \rangle = \langle \varphi_a|\varphi_b \rangle \langle \alpha|\beta \rangle = 0 \quad (4.205)$$

independent of  $\varphi_a$  and  $\varphi_b$ . Thus, the requirement that the spin orbitals be orthogonal is satisfied whether  $\psi_a$  and  $\psi_b$  overlap or not. Substituting the spin orbitals into (4.191) and (4.192), leads to

$$\begin{aligned} J_{ab} &= \langle (\varphi_a\alpha)(\varphi_b\beta) | \frac{1}{r_{12}} | (\varphi_a\alpha)(\varphi_b\beta) \rangle \\ &= \langle \varphi_a\varphi_b | \frac{1}{r_{12}} | \psi_a\varphi_b \rangle \langle \alpha|\alpha \rangle \langle \beta|\beta \rangle = J_{ab}, \end{aligned} \quad (4.206)$$

and

$$K_{ab} = \langle (\varphi_a\alpha)(\varphi_b\beta) | \frac{1}{r_{12}} | (\varphi_b\beta)(\psi_a\alpha) \rangle$$

$$= \langle \varphi_a \varphi_b \left| \frac{1}{r_{12}} \right| \varphi_b \varphi_a \rangle \langle \alpha | \beta \rangle \langle \beta | \alpha \rangle = 0. \quad (4.207)$$

Thus, because the spins are different, the exchange term is zero and the energy becomes

$$E = \langle \varphi_a | h | \varphi_a \rangle + \langle \varphi_b | h | \varphi_b \rangle + J_{ab}. \quad (4.208)$$

### Many Electrons

For the many-electron case, the Slater determinant is

$$\mathcal{A} (\varphi_{1a}\alpha) (\varphi_{2a}\alpha) \cdots (\varphi_{na}\alpha) (\varphi_{1b}\beta) (\varphi_{2b}\beta) \cdots (\varphi_{mb}\beta), \quad (4.209)$$

where  $n$  is the number of spin up orbitals, and  $m$  is the number of spin-down orbitals. From the orthonormality of spin orbitals (4.185), we obtain

$$\delta_{ij} = \langle \varphi_{ia}\alpha | \varphi_{ja}\alpha \rangle = \langle \psi_{ia} | \varphi_{ja} \rangle \langle \alpha | \alpha \rangle = \langle \varphi_{ia} | \varphi_{ja} \rangle \quad (4.210)$$

$$\delta_{ij} = \langle \varphi_{ib}\beta | \varphi_{jb}\beta \rangle = \langle \psi_{ib} | \varphi_{jb} \rangle \langle \beta | \beta \rangle = \langle \varphi_{ib} | \varphi_{jb} \rangle \quad (4.211)$$

$$0 = \langle \varphi_{ia}\alpha | \varphi_{ib}\beta \rangle = \langle \varphi_{ia} | \varphi_{jb} \rangle \langle \alpha | \beta \rangle. \quad (4.212)$$

Thus, the orbitals  $\{\varphi_{ia}\}$  are orthonormal, and the orbitals  $\{\varphi_{ib}\}$  are orthonormal, but there is no special relation between the  $a$  and  $b$  orbitals.

The terms in the energy (4.201) become

$$\langle \varphi_{ia}\alpha | h | \varphi_{ia}\alpha \rangle = \langle \varphi_{ia} | h | \varphi_{ia} \rangle \quad (4.213)$$

$$J_{ia,ja} = J_{ia,ja} \langle \alpha | \alpha \rangle \langle \alpha | \alpha \rangle = J_{ia,ja} \quad (4.214)$$

$$K_{ia,ja} = K_{ia,ja} \langle \alpha | \alpha \rangle \langle \alpha | \alpha \rangle = K_{ia,ja} \quad (4.215)$$

where Roman letter  $J_{ij}$  and  $K_{ij}$  indicate integrals involving spatial orbitals only. The  $b$  orbitals, also lead to results as in (4.213)–(4.215). However,

$$J_{ia,jb} = J_{ia,jb} \langle \alpha | \alpha \rangle \langle \beta | \beta \rangle = J_{ia,jb} \quad (4.216)$$

and

$$K_{ia,jb} = K_{ia,jb} \langle \alpha | \beta \rangle \langle \beta | \alpha \rangle = 0. \quad (4.217)$$

Thus, there are exchange terms only between electrons of the same spin. As a result, the energy of the wavefunction (4.201) is

$$E = \sum_{ia}^n \langle ia | h | ia \rangle + \sum_{ib}^m \langle ib | h | ib \rangle + \sum_{ia>ja}^n (J_{ia,ja} - K_{ia,ja}) \quad (4.218)$$

$$+ \sum_{ib>jb}^m (J_{ib,jb} - K_{ib,jb}) + \sum_{ia,jb}^{n,m} J_{ia,jb}. \quad (4.219)$$

### Closed-Shell Wavefunctions

A very important special case of the wavefunction (4.209), is the closed-shell wavefunction where  $n = m$  and

$$\varphi_{ia} = \varphi_{ib}, i = 1, 2, \dots, n. \quad (4.220)$$

Thus, each spatial orbital is doubly-occupied, one with each spin, leading to

$$\mathcal{A}(\varphi_1\alpha)(\varphi_1\beta)(\varphi_2\alpha)(\varphi_2\beta)\cdots. \quad (4.221)$$

Note, we have permuted the spin orbitals of the wavefunction (4.201). At most, this can change the sign of the wavefunction but cannot change the energy.

From (4.219) we see that the energy of (4.221) is

$$E = 2 \sum_i^n \langle i | h | i \rangle + 2 \sum_{i>j}^n (J_{ij} - K_{ii}) + \sum_{i,j}^n J_{ij}. \quad (4.222)$$

Since  $J_{ii} = K_{ii}$ , we obtain

$$\sum_{i,j} (J_{ij} - K_{ij}) = \sum_i (J_{ii} - K_{ii}) + 2 \sum_{i>j} (J_{ij} - K_{ij}) = 2 \sum_{i>j} (J_{ij} - K_{ij}). \quad (4.223)$$

and hence, (49) can be written as

$$E = 2 \sum_i^n \langle i | h | i \rangle + \sum_{i,j}^n (2J_{ij} - K_{ii}). \quad (4.224)$$

Note that the sum in (4.224) is over orbitals, not electrons. That is, for  $N$  electrons, the sums in (4.224) go over the  $n = N/2$  orbitals.

In order to remember the energy expression (4.224), note that each orbital has two electrons leading to two one-electron terms,  $\langle i | h | i \rangle$  and four two-electron Coulomb terms,  $J_{ij}(j \neq i)$ . Since exchange terms exist only between orbitals with the same spin, there should be two exchange terms,  $K_{ij}$  if  $i \neq j$ , one when both orbitals are spin  $\alpha$  and one when both are  $\beta$ . The sum in (4.224) is over all  $i$  and  $j$ , leading to a total of

$$4J_{ij} - 2K_{ij}, \quad (4.225)$$

if  $i \neq j$ . The  $i = j$  term in (4.224) is

$$2J_{ii} - K_{ii} = J_{ii}. \quad (4.226)$$

### High Spin Multiplet

In the case that all spin orbitals have the same spin,  $n = N$  and  $m = 0$ , the wavefunction (4.201) becomes

$$\mathcal{A}(\varphi_1\alpha)(\varphi_2\alpha)\cdots(\varphi_n\alpha), \quad (4.227)$$

and the energy (4.219) becomes

$$E = \sum_i^n \langle i | h | i \rangle + \sum_{i>j}^n (J_{ij} - K_{ij}) \quad (4.228)$$

and

$$E = \sum_i \langle i | h | i \rangle + \frac{1}{2} \sum_{i>j} (J_{ij} - K_{ij}). \quad (4.229)$$

### Intermediate Spin

Now consider the case with  $m$  doubly-occupied orbitals,  $\varphi_1, \varphi_2, \dots, \varphi_m$ , and  $p$  singly-occupied orbitals,  $\varphi_{m+1}, \dots, \varphi_{m+p}$ , all coupled to high-spin  $S = 1/2p$ . The wavefunction is

$$\mathcal{A}(\varphi_1\alpha)(\varphi_1\beta)\cdots(\varphi_m\alpha)(\varphi_m\beta)(\varphi_{m+1}\alpha)\cdots(\varphi_{m+p}\alpha), \quad (4.230)$$

and the energy is

$$E = E_c + E_o + E_{co}, \quad (4.231)$$

where

$$E_c = 2 \sum_i^m \langle i | h | i \rangle + \sum_{i,j}^m (2J_{ij} - K_{ij}) \quad (4.232)$$

$$E_o = 2 \sum_{i=m+1}^{m+p} \langle i | h | i \rangle + \frac{1}{2} \sum_{i>j=m+1}^{m+p} (J_{ij} - K_{ij}) \quad (4.233)$$

$$E_{co} = \sum_{i=1}^m \sum_{j=m+1}^{m+p} (2J_{ij} - K_{ij}). \quad (4.234)$$

## 4.6 Appendices

### 4.6.1 An Examination of the Pauli Exclusion

In this section, we will examine the experimental basis for the Pauli exclusion principle. We will do this by obtaining approximate wavefunctions for the  $(1s)^n$  states of atoms, and showing that for  $n > 2$  the resulting ionization potentials would exhibit behavior inconsistent with the experimental results. On the other hand, limiting the occupation to two for any orbital, leads to the  $(1s)^2(2s)$  configuration as the ground state for Li, and exact agreement with experiment. The details of the approximations used here are not important for Chemistry 120.

## The Ground States of Atoms

We will start by solving, approximately, for the energy of the ground states of two-electron and three-electron atoms. By comparing with the energies of the corresponding positive ions, we will find the lowest state Li would have an ionization potential over six times the experimental value. The Pauli principle tells us that this state is not allowed. The next highest state of Li is found to have an ionization potential (IP) exactly equal to the experimental value. Thus, providing one direct verification of the Pauli exclusion principle.

### Two Electrons

In Chapter 1, we found that the ground state of H atom is

$$\frac{1}{\sqrt{\pi}} e^{-r}. \quad (4.235)$$

In Chapter 3, we obtained an approximate wavefunction for He by putting two electrons in such an orbital, allowing scale factor  $\zeta$  for the orbitals

$$\sqrt{\frac{\zeta^3}{\pi}} e^{-\zeta r} \quad (4.236)$$

to be optimized. With two electrons in this orbital, we found the energy to be

$$E = 2 \left[ \langle \varphi | t | \varphi \rangle + \langle \varphi | -\frac{Z}{r} | \varphi \rangle \right] + J \quad (4.237)$$

where

$$J = \int d\tau_1 |\varphi(1)|^2 \int d\tau_2 |\varphi(2)|^2 \frac{1}{r_{12}} = \frac{5}{8} \zeta \quad (4.238)$$

is the Coulomb interaction between the electrons and

$$\langle \varphi | t | \varphi \rangle = \frac{1}{2} \zeta^2 \quad (4.239)$$

and

$$\langle \varphi | -\frac{Z}{r} | \varphi \rangle = -\zeta Z. \quad (4.240)$$

Thus, the total energy is

$$E = \zeta^2 T_1 + \zeta V_1, \quad (4.241)$$

where  $T_1 = 1/2$  and  $V_1 = -Z + 5/8$ , leading to

$$\zeta_{OPT} = Z - \frac{5}{16} \quad (4.242)$$

and

$$E_{OPT} = -2 \left( \frac{\zeta_{OPT}^2}{2} \right) = -\zeta_{OPT}^2 = -2.848 h \quad (4.243)$$

and predicting an ionization potential of about 94% of the experimental value, 0.9037.

### Three Electrons

With three electrons all the same  $1s$  orbital (4.236), we obtain an energy expression of the form (4.241) with

$$T_1 = 3 \left( \frac{1}{2} \right) = \frac{3}{2} \quad (4.244)$$

and

$$V_1 = 3(-Z) + 3 \left( \frac{5}{8} \right) = -3Z + \frac{15}{8}. \quad (4.245)$$

In this case, the optimum  $\zeta$  is

$$\zeta_{OPT} = -\frac{V_1}{2T_1} = Z - \frac{5}{8}. \quad (4.246)$$

This is, the shielding is twice as great as for a two-electron system.

The optimum energy is

$$E = -\frac{V_1^2}{4T_1} = -\frac{3}{2} \zeta_{OPT}^2 = -8.4609h \quad (4.247)$$

for Li. From (4.243), the energy of  $\text{Li}^+$  is expected to be  $E(\text{Li}^+) = -7.2227 h$ , and hence, the ionization potential of Li is expected to be  $\text{IP(Li)} = 1.2382 h = 33.693 \text{ eV}$ . In fact, however, the experimental ionization potential of Li is  $0.19808 h = 5.390 \text{ eV}$ . Thus, our predicted value is 600% higher. Something is definitely wrong.

### General $N$

For  $N$  electrons in a  $1s$  orbital, the energy components are

$$T_1 = \frac{N}{2} \quad (4.248)$$

and

$$V_1 = N(Z) + \frac{N(N-1)}{2} \frac{5}{8} = -N\zeta_{OPT} \quad (4.249)$$

where

$$\zeta_{OPT} = Z - (N-1) \frac{5}{16}. \quad (4.250)$$

This leads to

$$E_{OPT} = \frac{M}{2} \zeta_{OPT}^2 \quad (4.251)$$

and hence,

$$\text{IP} = \frac{1}{2} \zeta_{OPT}^2 + a \quad (4.252)$$

where

$$a = \frac{(2N-3)(N-1)}{21} \left( \frac{5}{16} \right)^2 \quad (4.253)$$

is a correction term involving the change in shielding between the  $N$  and  $N-1$  electron systems. Assuming  $a = 0$  is equivalent to use of Koopmans' theorem, probably a better approximation. Thus, the ionization potential is expected to be essentially quadratic in  $Z$

$$\text{IP} \approx \frac{Z^2}{2}. \quad (4.254)$$

This, however, is quite far from the experimental results, as Table 4.1.

## The 2s and 2p Orbitals

The first excited state of H atoms are the 2s and 2p states with an energy

$$E = -\frac{1}{2} \frac{Z^2}{n^2} = -\frac{1}{8} = -0.125h \quad (4.255)$$

and a scale parameter of

$$\zeta = \frac{Z}{n} = 0.5. \quad (4.256)$$

If the electrons did not interact with each other, the states of He, first column, would be  $E$ , second column

$$\varphi_{1s}\varphi_{1s} = -4.0 \quad (4.257)$$

$$\varphi_{1s}\varphi_{2s} = -2.5 \quad (4.258)$$

$$\varphi_{1s}\varphi_{1p} = -2.5 \quad (4.259)$$

$$\varphi_{1s}\varphi_{3s} = -2.222 \quad (4.260)$$

We saw, earlier, that the form  $\varphi_{1s}\varphi_{1s}$  leads to a good description of the ground states. Thus, we expect that the wavefunctions  $\varphi_{1s}\varphi_{2s}$  and  $\varphi_{1s}\varphi_{2p}$  would yield reasonably good descriptions of the excited states of He.

The energy of the wavefunction  $\varphi_{1s}\varphi_{2s}$  is

$$E = \langle 1s|h|1s \rangle + \langle 2s|h|2s \rangle + J_{1s,2s} \quad (4.261)$$

and, hence, the ionization potential is given by

$$IP_{2s} = \langle 2s|h|2s \rangle + J_{1s,2s}. \quad (4.262)$$

Assuming that the  $\varphi_{2s}$  orbital is completely outside the  $\varphi_{1s}$  orbital, the  $1s-2s$  Coulomb repulsion becomes

$$J_{1s,2s} = \langle 2s | \frac{1}{r} | 2s \rangle \quad (4.263)$$

and, hence

$$IP_{2s} = \langle 2s | t - \frac{1}{r} | 2s \rangle \quad (4.264)$$

so that

$$IP_{2s} = -0.125 \quad (4.265)$$

just as for the H atom.

The experimental values for He are

$$IP_{2s} = 0.161 h \quad (4.266)$$

and

$$IP_{2p} = 0.129 h. \quad (4.267)$$

As we will see later, there are two states, singlet and triplet, corresponding to the  $1s2s$  and  $1s2p$  states. We have averaged the experimental energies to obtain the numbers used above.

Writing

$$IP = \frac{1}{2} \left( \frac{Z_{eff}}{n} \right)^2 \quad (4.268)$$

we see that

$$Z_{eff}(2s) = n\sqrt{.322} = 1.135 \quad (4.269)$$

and

$$Z_{eff}(2p) = n\sqrt{.258} = 1.012 \quad (4.270)$$

Thus, it is as if the  $\varphi_{1s}$  electron shielded only .865 of the charge of the nucleus from the  $2s$  orbital, but shielded 0.988 of the charge from the  $2p$  orbital. This is reasonable, since the  $2p$  orbital is zero at  $r = 0$ , and tends to be small for small  $r$ , while the  $2s$  orbital is large for small  $r$ .

Now we consider Li atom. Neglecting electron-electron repulsion leads to the following states of Li, first column, equal to  $E$ , second column

$$\begin{aligned} \varphi_{1s}\varphi_{1s}\varphi_{1s} &= -13.5 \\ \varphi_{1s}\varphi_{1s}\varphi_{2s} &= -10.125 \\ \varphi_{1s}\varphi_{1s}\varphi_{2p} &= -10.125 \\ \varphi_{1s}\varphi_{1s}\varphi_{3s} &= -9.5 \end{aligned} \quad (4.271)$$

Including the electron interactions but ignoring penetration of the  $2s$  and  $2p$  orbitals into the core, we would expect

$$IP_{n=2} = -0.125. \quad (4.272)$$

Including the shielding effects found for the  $n = 2$  states of He, we find

$$IP_{2s} = \frac{1}{8}(3 - 0.865 - 0.865)^2 = .202 \quad (4.273)$$

and

$$IP_{2p} = \frac{1}{8}(3 - 0.988 - 0.988) = .131. \quad (4.274)$$

The interesting fact here is that experimentally the first two ionization potentials of Li are 0.19808  $h = 5.390$  eV and 0.13018  $h = 3.542$  eV, in agreement with the ionization potentials calculated for the

$$\varphi_{1s}\varphi_{1s}\varphi_{2s} \quad (4.275)$$

and

$$\varphi_{1s}\varphi_{1s}\varphi_{2p} \quad (4.276)$$

states. It is as if the  $\varphi_{1s}\varphi_{1s}\varphi_{1s}$  state of Li, which would have had an ionization potential of 1.2382  $h$ , is for some reason excluded, leaving the first two states of Li as the states in (4.275) and (4.276). Of course, this is just what the Pauli exclusion principle states.

### 4.6.2 Brief Review of Angular Momentum

Herein, we will summarize some relationships about angular momentum. The student is already expected to be familiar with them. The notation used is appropriate for spin, but all relationships are general. Note, we take  $\hbar = 1$ .

A set of operators  $\hat{S}_x$ ,  $\hat{S}_y$ , and  $\hat{S}_z$  are said to be angular momentum operators, if they satisfy the commutation relations

$$\begin{aligned} [\hat{S}_x, \hat{S}_y] &= i\hat{S}_z \\ [\hat{S}_y, \hat{S}_z] &= i\hat{S}_x \\ [\hat{S}_z, \hat{S}_x] &= i\hat{S}_y \end{aligned} \quad (4.277)$$

where

$$[\hat{S}_x, \hat{S}_y] = \hat{S}_x\hat{S}_y - \hat{S}_y\hat{S}_x. \quad (4.278)$$

Constructing the total angular momentum operator

$$\hat{S}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2, \quad (4.279)$$

the angular momentum eigenstates  $\psi_{SM}$  satisfy

$$\hat{S}^2\psi_{SM} = S(S+1)\psi_{SM} \quad (4.280)$$

$$\hat{S}_z\psi_{SM} = M\psi_{SM}, \quad (4.281)$$

where  $S$  is integer or half-integer, and where  $M$  ranges in integer increments from  $-S$  through  $+S$ . Defining the raising and lowering operators

$$\hat{S}^+ = \hat{S}_x + i\hat{S}_y \quad (4.282)$$

and

$$\hat{S}^- = \hat{S}_x - i\hat{S}_y \quad (4.283)$$

we find that

$$\hat{S}^-\psi_{SM} = \sqrt{S(S+1) - M_S(M_S - 1)}\psi_{S,M-1} \quad (4.284)$$

and

$$\hat{S}^+\psi_{S,M-1} = \sqrt{S(S+1) - M_S(M_S - 1)}\psi_{S,M} \quad (4.285)$$

Note  $S^-\psi_{S,-S} = 0$  and  $\hat{S}^+\psi_{S,S=0}$ . We should point out that use of (4.284)–(4.285) specifies a phase convention between states  $\psi_{SM}$  of differing  $M$ . In general, the fact that  $\hat{S}^+$  is the Hermitian conjugate of  $\hat{S}^-$  would lead in (4.284)–(4.285) that are complex conjugates of each other. With appropriate choices of the phases of the  $\psi_{SM}$ , these coefficients can be made real, as we have done. Thus, given a state  $\psi_{SM}$  of some particular  $M$ , we can obtain the additional  $2S$  states of the same  $S$  by applying  $\hat{S}^+$  and  $\hat{S}^-$  an appropriate number of times.

It is useful to rewrite  $\hat{S}^-$  in terms of  $\hat{S}^\pm$  and  $\hat{S}_z$ . Using (4.277), we obtain

$$\hat{S}^- \hat{S}^+ = \hat{S}_x^2 + \hat{S}_y^2 + i [\hat{S}_x, \hat{S}_y] = \hat{S}_x^2 + \hat{S}_y^2 - \hat{S}_z \quad (4.286)$$

and

$$\hat{S}^+ \hat{S}^- = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z, \quad (4.287)$$

and hence,

$$\hat{S}^2 = \hat{S}_z^2 + \hat{S}_z + \hat{S}^- \hat{S}^+ \quad (4.288)$$

and

$$\hat{S}^2 = \hat{S}_z^2 - \hat{S}_z - \hat{S}^+ \hat{S}^- \quad (4.289)$$

For example, for any function  $\psi_M$  satisfying

$$\hat{S}_z \psi_M = M \psi_M \quad (4.290)$$

and

$$\hat{S}^+ \psi_M = 0, \quad (4.291)$$

we see that

$$\hat{S}^2 \psi_M = (M^2 + M) \psi_M, \quad (4.292)$$

and, hence,  $\psi_M$  is an eigenfunction of  $\hat{S}^2$  corresponding to  $S = M$ . This is useful in constructing angular momentum eigenfunctions. We construct  $\psi_M$  such at  $\hat{S}^+ \psi_M = 0$ , and hence, automatically get an eigenfunction of  $\hat{S}^2$ .

In the case of a many particle system, the fact that the sets  $\{\hat{s}_x(1), \hat{s}_y(1), \hat{s}_z(1)\}$ ,  $\{\hat{s}_x(2), \hat{s}_y(2), \hat{s}_z(2)\}$ , etc., are individually angular momentum operators, satisfying (6), and hence, (7) through (12), the sum

$$\begin{aligned} \hat{S}_x &= \hat{s}_x(1) + \hat{s}_x(2) + \dots \\ \hat{S}_y &= \hat{s}_y(1) + \hat{s}_y(2) + \dots \\ \hat{S}_z &= \hat{s}_z(1) + \hat{s}_z(2) + \dots \end{aligned} \quad (4.293)$$

also satisfy (4.277), and hence, are angular momentum operators. The total angular momentum eigenstates satisfy (4.280) and (4.281). However, these many particle eigenstates are not in general eigenstates of the one-particle operators  $\hat{s}^2$  and  $\hat{s}_z$ .

### 4.6.3 Spin Eigenfunctions

Combining two spin 1/2 particles, leads to three functions with  $S = 1$

$$\begin{aligned} \chi_{11} &= \alpha\alpha \\ \chi_{10} &= \frac{1}{\sqrt{2}} (\alpha\beta + \beta\alpha) \\ \chi_{1\bar{1}} &= \beta\beta \end{aligned} \quad (4.294)$$

$$[1 \boxed{2}] \quad (4.295)$$

and one function with  $S = 0$

$$\chi_{00} = \frac{1}{\sqrt{2}} (\alpha\beta - \beta\alpha) \quad (4.296)$$

1
2

(4.297)

Notice that the three triplet spin eigenfunctions are symmetric under interchange of the spin coordinates of the electrons, while the singlet spin eigenfunction is antisymmetric. This close relationship between permutational symmetry and spin symmetry, is quite general. A function of symmetric permutational symmetry is symbolized by the diagram

1	2
---	---

(4.298)

called a Young tableau, while a function of antisymmetric permutational symmetry is symbolized by

1
2

(4.299)

as indicated in (4.294) and (4.296).

The point of this appendix is to show how to build the spin eigenfunctions for a system with  $N$  electrons. First, we consider the spin eigenfunctions for three electrons.

### Three Electrons

Altogether, there are  $2^3$ , or eight, spin functions for three electrons

$$\begin{aligned} M &= \frac{3}{2} : \alpha\alpha\alpha \\ M &= \frac{1}{2} : \alpha\alpha\beta, \alpha\beta\alpha, \beta\alpha\alpha \\ M &= -\frac{1}{2} : \beta\beta\alpha, \beta\alpha\beta, \alpha\beta\beta \\ M &= -\frac{3}{2} : \beta\beta\beta \end{aligned} \quad (4.300)$$

The high spin case is obvious

$$\chi = \alpha\alpha\alpha \quad (4.301)$$

corresponds to  $S = 3/2$  since  $\hat{S}^+ \chi = 0$ . Applying  $\hat{S}^-$  we then get

$$\begin{aligned} S = \frac{3}{2} : \quad \chi_{\frac{3}{2}\frac{3}{2}} &= \alpha\alpha\alpha \\ \chi_{\frac{3}{2}\frac{1}{2}} &= \frac{1}{\sqrt{3}} (\alpha\alpha\beta + \alpha\beta\alpha + \beta\alpha\alpha) \\ \chi_{\frac{3}{2}, -\frac{1}{2}} &= \frac{1}{\sqrt{3}} (\alpha\beta\beta + \beta\alpha\beta + \beta\beta\alpha) \\ \chi_{\frac{3}{2}, -\frac{3}{2}} &= \beta\beta\beta \end{aligned} \quad (4.302)$$

1	2	3
---	---	---

(4.303)

as the quartet spin eigenfunctions. This leaves two functions with  $M = +1/2$  and two with  $M = -1/2$

$$S = \frac{1}{2} : \quad \chi_{\frac{1}{2}, \frac{1}{2}}^{(1)} = \frac{1}{\sqrt{2}} (\alpha\beta - \beta\alpha) \alpha \quad (16a)$$

$$\chi_{\frac{1}{2}, -\frac{1}{2}}^{(1)} = \frac{1}{\sqrt{2}} (\alpha\beta - \beta\alpha) \beta \quad (4.304)$$

1	3
2	

(4.305)

and

$$S = \frac{1}{2} : \quad \begin{aligned} \chi_{\frac{1}{2}, \frac{1}{2}}^{(2)} &= \sqrt{\frac{2}{3}} \left[ \alpha\alpha\beta - \frac{1}{2} (\alpha\beta + \beta\alpha) \alpha \right] \\ \chi_{\frac{1}{2}, -\frac{1}{2}}^{(2)} &= \sqrt{\frac{2}{3}} \left[ \frac{1}{2} (\alpha\beta + \beta\alpha) \beta - \beta\beta\alpha \right] \end{aligned} \quad (4.306)$$

1	2
3	

(4.307)

Applying  $\hat{S}^+$  we see that

$$\hat{S}^+ \chi_{\frac{1}{2}, \frac{1}{2}}^{(1)} = 0 \quad (4.308)$$

and

$$\hat{S}^+ \chi_{\frac{1}{2}, \frac{1}{2}}^{(2)} = 0, \quad (4.309)$$

and hence, these functions do correspond to  $S = 1/2$  states. The functions  $\chi^{(1)}$  and  $\chi^{(2)}$  are orthogonal, e.g.,

$$\langle \chi^{(1)} | \chi^{(2)} \rangle = \frac{1}{2\sqrt{3}} \underbrace{\langle \alpha\beta\alpha - \beta\alpha\alpha | 2\alpha\alpha\beta - \alpha\beta\alpha - \beta\alpha\alpha \rangle}_{-1+1} = 0. \quad (4.310)$$

That is, there are two sets of doublet states.

The quartet functions (4.302) are all symmetric under all permutations of the spin coordinates, of the electron, which symmetry we denote as

1	2	3
---	---	---

(4.311)

The permutational symmetry of the functions (??) and (??) are more complicated. Function (??) was obtained by starting with the antisymmetric  $S = 0$  function

1
2

(4.312)

and combining with an appropriate third spin function to raise  $S$  to 1/2. This symmetry is then denoted as

$$\begin{array}{|c|c|} \hline 1 & 3 \\ \hline 2 & \\ \hline \end{array} \quad (4.313)$$

On the other hand, (??) was obtained by starting with  $S = 1$  function

$$\begin{array}{|c|c|} \hline 1 & 2 \\ \hline \\ \hline \end{array} \quad (4.314)$$

and combining with appropriate third spin functions to obtain a lower spin. This is denoted as

$$\begin{array}{|c|c|} \hline 1 & 2 \\ \hline 3 & \\ \hline \end{array} \quad (4.315)$$

Note that it is not possible to construct a spin function which is antisymmetric under all electron interchanges

$$\begin{array}{|c|} \hline 1 \\ \hline 2 \\ \hline 3 \\ \hline \end{array} \quad (4.316)$$

To do so would require at least three different spin functions

$$\alpha\beta\gamma + \beta\gamma\alpha + \gamma\alpha\beta - \alpha\gamma\beta - \gamma\beta\alpha - \beta\alpha\gamma \quad (4.317)$$

whereas we have but two. For three electrons the total theorem leads to the result that the ground state should have a totally symmetry spatial function. But because of the Pauli principle, this would require a totally antisymmetric spin which is not possible for spin 1/2 particles. For Li, the totally symmetric wavefunction would corresponds to  $(1a)^3$ . Because of this exclusion, due to the Pauli principle, the nodal theorem cannot be used for such universal states in multi-electron systems.

### Many Electrons

Starting with two spin 1/2 electrons, we get one set of states with  $S = 1$  and one with  $S = 0$ . Starting with  $S = 1$  and combining with a third electron, yields one set of  $S = 3/2$  states and one set of  $S = 1/2$  states. Another set of three-electron  $S = 1/2$  states is obtained by cominging the two-electron  $S = 0$  state with a third electron. Thus, there are two sets of  $S = 1/2$  states for  $N = 3$ . The results of continuing this process for more electrons is indicated in Figure 4.2, in what is referred to as the branching diagram. For example, with six electrons, there are five different singlet states.

This suggests an inductive procedure for building up the spin eigenfunctions  $\chi_{SM}^N$  for an arbitrary  $N$ . We take a spin eigenfunction  $\chi_{SS}^N$  and combine it with either  $\alpha(N+1)$  or  $\beta(N+1)$  to obtain

$$\chi_{SS}^N (1 \cdots N) \alpha (N+1) \quad (4.318)$$

and

$$\chi_{SS}^N (1 \cdots N) \beta (N+1). \quad (4.319)$$

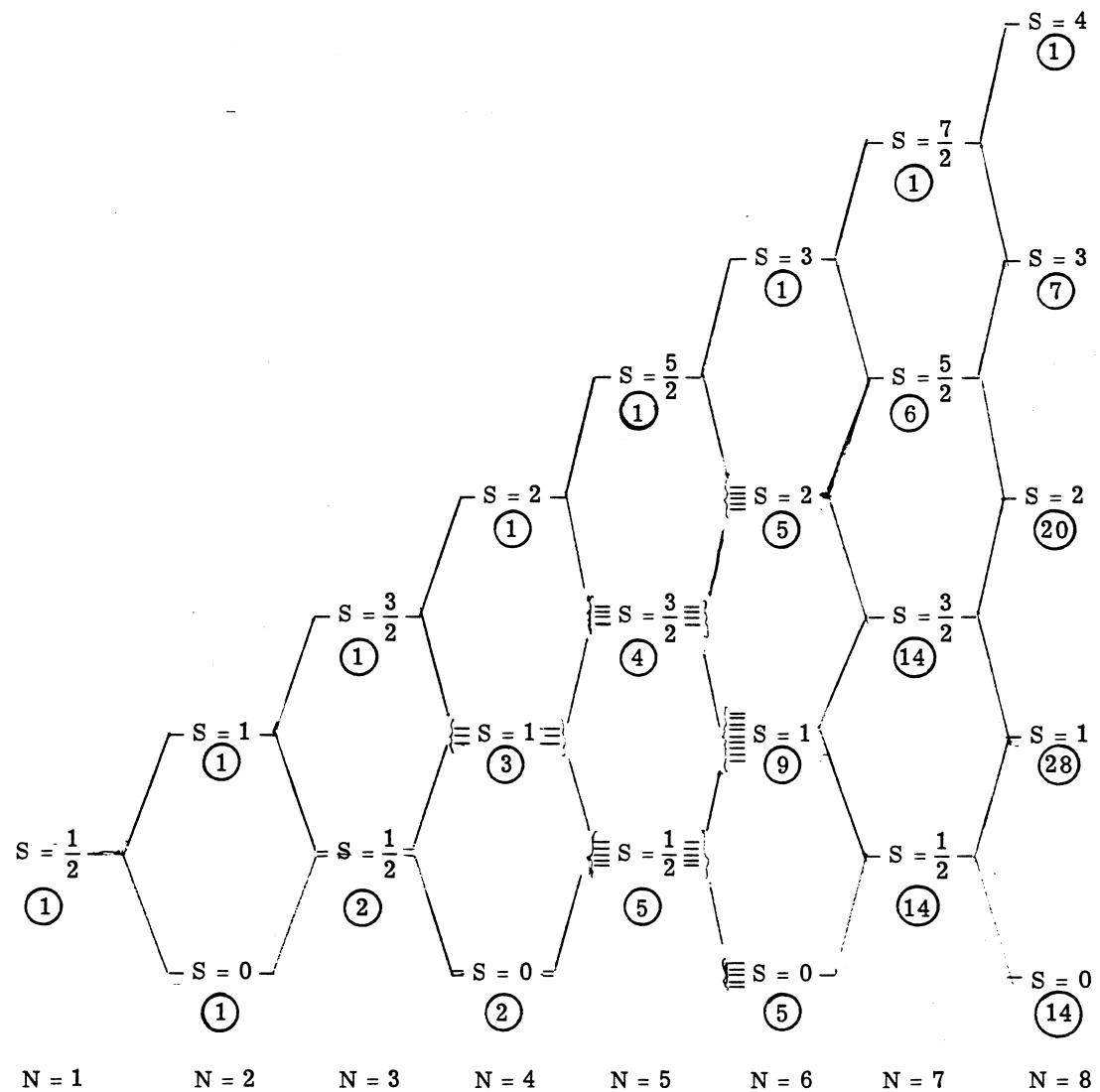


Figure 4.2: Branching diagram for combining electron spins. The number of electrons is indicated by  $N$  and the number of independent sets of spin states of each spin  $S$  is indicated by the encircled number lying below the spin value.

Partitioning the raising operator  $\hat{S}_{N+1}^+$  for  $N + 1$  electrons into the  $\hat{S}_N^+$  for the first  $N$  electrons, plus  $\hat{s}^+(N + 1)$ , we see that

$$\hat{S}_{N+1}^+ [\chi_{SS}^N \alpha(N + 1)] = [\hat{S}_N^+ \chi_{SS}^N] \alpha + \chi_{SS}^N [\hat{s}^+(N + 1) \alpha] = 0 \quad (4.320)$$

and

$$\hat{S}_z [\chi_{SS}^N \alpha(N + 1)] = S + \frac{1}{2}. \quad (4.321)$$

Thus,

$$\chi_{S+\frac{1}{2}, S+\frac{1}{2}}^{N+1} = \chi_S^N \alpha(N + 1) \quad (4.322)$$

is a spin eigenfunction with spin  $S + 1/2$ .

The function

$$\chi_{SS}^N \beta(N + 1) \quad (4.323)$$

has

$$M = S - \frac{1}{2}, \quad (4.324)$$

but it is not an eigenfunction of  $\hat{S}^2$ . However, by combining this function with the function

$$\chi_{S,S-1}^N \alpha(N + 1) = \frac{1}{2S} (\hat{S}_N^- \chi_{S,S}^N) \alpha(N + 1) \quad (4.325)$$

we can get an eigenfunction of  $\hat{S}^2$ . Thus,

$$\hat{S}^+ [\chi_{SS}^N \beta(N + 1) - \chi_{S,S-1}^N \alpha(N + 1)] = \chi_{SS}^N \alpha(N + 1) - \chi_{S,S}^N \alpha(N + 1) = 0 \quad (4.326)$$

and

$$\chi_{S-\frac{1}{2}, S-\frac{1}{2}}^{N+1} = \chi_{S,S}^N \beta(N + 1) - \frac{1}{2S} (\hat{S}_N^- \chi_{S,S}^N) \alpha(N + 1) \quad (4.327)$$

is an eigenfunction of  $\hat{S}^2$  corresponding to  $S - 1/2$ .

Using (4.322) and (4.327) successively, following any pathway in Figure 4.2, we can generate spin eigenfunctions of arbitrary  $N$  and  $S$ , assuming we have sufficient patience. A following section contains a tabulation of all spin eigenfunctions up through  $N = 6$ , generated by a computer program. Note, the tableaux have the rows and columns interchanged as compared to those in this section.

For example, application of (4.322) to the  $S = 0$  state of (4.294) leads to the  $S = 1/2$  state of (??), while application of (4.327) to the  $S = 1$  states of (4.296) to the  $S = 1/2$  state of (??).

As another example, application of (4.327) to the  $S = 1/2$  states of (??) and (??) lead to the  $S = 0$  states of  $N = 4$ ,

$$\chi_{00}^{(1)} = \frac{1}{2} (\alpha\beta - \beta\alpha) (\alpha\beta - \beta\alpha) = \quad (4.328)$$

1	3
2	4

(4.329)

and

$$\chi_{00}^{(2)} = \frac{1}{\sqrt{3}} \left[ \alpha\alpha\beta\beta + \beta\beta\alpha\alpha - \frac{1}{2} (\alpha\beta + \beta\alpha)(\alpha\beta + \beta\alpha) \right] = \quad (4.330)$$

1	2
3	4

(4.331)

There are a number of separate spin eigenfunctions  $\chi_{S,S}^N$  for most cases, and the above inductive procedure for obtaining these eigenstates leads to a particular sequence. Always starting with the lowest  $S$  for a given  $N$ , we number the state for  $N+1$  and any given  $S'$  in the order in which they are constructed, for a given  $S'$ . This has already been done in (??) and (??), and in (4.328) and (4.330). In general, we will refer to this first, second, etc., spin eigenfunctions of a given spin  $S$  as  $Y1$ ,  $Y2$ , etc., in honor of the English clergyman and mathematician Young<sup>1</sup> and the Japanese physicist Yamanouchi,<sup>2</sup> who laid the mathematical foundations for this particular set of spin eigenfunctions.<sup>3</sup>

### Tabulation of Spin Eigenfunctions

Here we list all spin eigenfunctions for up through six electrons.<sup>4</sup> In each case, only the  $M_S = S$  component is given. A spin term of 110101 implies  $\alpha\alpha\beta\alpha\beta\alpha$ . The tableau, e.g.,

1	2
3	
4	

(4.332)

associated with each spin eigenfunction, is in the form appropriate for the spatial wavefunction corresponding to the particular spin function, through the Pauli principle. Thus, compared to the diagrams of the earlier sections, row and columns are interchanged.

The Caltech programs use slightly different sign conventions. For three electrons, it is  $-Y1$  for doublet. For four electrons, it is  $-Y1$  for singlet and  $-Y2$  for triplet. For five electrons, it is  $-Y1$  and  $-Y4$  for doublet. And, for six electrons, it is  $-Y1$  and  $-Y4$  for singlet, and  $-Y1, -Y4, -Y6$ , and  $-Y8$  for triplet. These spin eigenfunctions were generated by the MQM program SEFGEN, MQM number 26, written by G. Levin and F. W. Bobrowicz. The following listing has been taken from that program.

#### 4.6.4 Historical Development

In this section, we will provide some of the historical development. From these developments, two very important postulates of quantum mechanics, neither of which has an analog in the classical description of electrons, will be shown. The first, is the idea that an electron has an internal quantum number called the spin. The second, in a simplified form referred to as the Pauli exclusion principle, is that only one electron can have the same set of quantum number, including spin. The basic character and properties of molecules are most profoundly affected by the combination of the Pauli principle with electron spin.

Table 4.2: Spin-Eigenfunction Listing

	Normalization	Coefficient	Spin Term
1E Doublet	$1/\sqrt{1}$	1	1
2E Singlet	$1/\sqrt{2}$	1	10
		-1	01
2E Triplet	$1/\sqrt{1}$	1	11
3E Doublet Y1	$1/\sqrt{2}$	1	010
		-1	011
3E Doublet Y2	$1/\sqrt{6}$	2	110
		-1	011
		-1	101
3E Quartet	$1/\sqrt{1}$	1	111
4E Singlet Y1	$1/\sqrt{4}$	1	1010
		-1	1001
		-1	0110
		1	0101
4E Singlet Y2	$1/\sqrt{12}$	2	1100
		-1	0101
		-1	1001
		-1	1010
		2	0011
		-1	0110
4E Triplet Y1	$1/\sqrt{2}$	1	1011
		-1	0111
4E Triplet Y2	$1/\sqrt{6}$	2	1101
		-1	1011
		-1	0111
4E Triplet Y3	$1/\sqrt{12}$	3	1110
		-1	0111
		-1	1011
		-1	1101
4E Quintet	$1/\sqrt{1}$	1	1111

	Normalization	Coefficient	Spin Term
5E Doublet Y2	$1/\sqrt{12}$	2	11001
		-1	01011
		-1	10011
		-1	10101
		2	00111
		-1	01101
5E Doublet Y3	$1/\sqrt{12}$	2	10110
		-1	10011
		-1	10101
		-2	01110
		1	01011
		1	01101
5E Doublet Y4	$1/\sqrt{36}$	4	11010
		-1	01011
		-1	10011
		-2	11001
		-2	10110
		2	00111
		1	10101
		-2	01110
		1	01101
		6	11100
5E Doublet Y5	$1/\sqrt{72}$	-2	01101
		-2	10101
		-2	11001
		-2	01110
		2	00111
		2	01011
		-2	10110
		2	10011
		-2	11010

	Normalization	Coefficient	Spin Term
6E Singlet Y1	$1/\sqrt{8}$	1	101010
5E Quartet Y1	$1/\sqrt{2}$	1	101111
		-1	011111
5E Quartet Y2	$1/\sqrt{6}$	2	110111
		-1	101111
		-1	011111
5E Quartet Y3	$1/\sqrt{12}$	3	111011
		-1	011111
		-1	101111
		-1	110111
5E Quartet Y4	$1/\sqrt{20}$	4	111101
		-1	011111
		-1	101111
		-1	110111
		-1	111011
5E Sextet	$1/\sqrt{1}$	1	111111
		-1	101001
		-1	100110
		1	100101
		-1	011010
		1	011001
		1	010110
		-1	010101
6E Singlet Y2	$1/\sqrt{24}$	2	110010
		-2	110001
		-1	010110
		1	010101
		-1	100110
		1	100101
		-1	101010
		1	101001
		2	001110
		-2	001101
		-1	011010
		1	011001

	Normalization	Coefficient	Spin Term
6E Singlet Y3	$1/\sqrt{24}$	2	101100
		-1	100101
		-1	101001
		-1	100110
		2	100011
		-1	101010
		-2	011100
		1	010101
		1	011001
		1	010110
		-2	010011
		1	011010
6E Singlet Y1	$1/\sqrt{8}$	1	101010
6E Singlet Y4	$1/\sqrt{72}$	4	110100
		-1	010101
		-1	100101
		-2	110001
		-1	010110
		2	010011
		-1	100110
		2	100011
		-2	110010
		-2	101100
		2	001101
		1	101001
		2	001110
		-4	001011
		1	101010
		-2	011100
		1	011001
		1	011010
		2	001011
		2	010011
		-2	101010
		2	100011
		-2	110010
		-2	011100
		1	011001
		1	011010

	Normalization	Coefficient	Spin Term
6E Singlet Y5	$1/\sqrt{144}$	6	111000
		-2	011001
		-2	101001
		-2	110001
		-2	011010
		2	001011
		2	010011
		-2	101010
		2	100011
		-2	110010
		-2	011100
		2	001101
		2	010101
		2	001110
		-6	000111
		2	010110
		-2	101100
		2	100101
		2	100110
		-2	110100
6E Singlet Y1	$1/\sqrt{8}$	1	101010
6E Triplet YI	$1/\sqrt{4}$	1	101011
		-1	100111
		-1	011011
		1	010111
6E Triplet Y2	$1/\sqrt{12}$	2	110011
		-1	010111
		-1	100111
		-1	101011
		2	001111
		-1	011011

	Normalization	Coefficient	Spin Term
6E Triplet Y3	$1/\sqrt{12}$	2	101101
		-1	100111
		-1	101011
		-2	011101
		1	010111
		1	011011
6E Triplet Y4	$1/\sqrt{36}$	4	110101
		-1	010111
		-1	100111
		-2	110011
		-2	101101
		2	001111
		1	101011
		-2	011101
		1	011011
6E Triplet Y5	$1/\sqrt{72}$	6	111001
		-2	011011
		-2	101011
		-2	110011
		-2	011101
		2	001111
		2	010111
		-2	101101
		2	100111
		-2	110101
6E Triplet Y6	$1/\sqrt{24}$	3	101110
		-1	100111
		-1	101011
		-1	101101
		-3	011110
		1	010111
		1	011011
		1	011101

	Normalization	Coefficient	Spin Term
6E Triplet Y7	$1/\sqrt{72}$	6	110110
		-1	010111
		-1	100111
		-2	110011
		-2	110101
		-3	101110
		2	001111
		1	101011
		1	101101
		-3	011110
		1	011011
		1	011101
6E Singlet Y8	$1/\sqrt{144}$	9	111010
		-2	011011
		-2	101011
		-2	110011
		-3	111001
		-3	011110
		2	001111
		2	010111
		1	011101
		-3	101110
		2	100111
		1	101101
		-3	110110
		1	110101
6E Triplet Y9	$1/\sqrt{240}$	12	111100
		-3	011101
		-3	101101
		-3	110101
		-3	111001
		-3	011110
		2	001111
		2	010111
		2	011011
		-3	101110
		2	100111
		2	101011
		-3	110110
		2	110011
		-3	111010

	Normalization	Coefficient	Spin Term
6E Quintet Y1	$1/\sqrt{2}$	1	101111
		-1	011111
6E Quintet Y2	$1/\sqrt{6}$	2	110111
		-1	101111
		-1	011111
6E Quintet Y3	$1/\sqrt{12}$	3	111011
		-1	011111
		-1	101111
		-1	101111
		-1	110111
6E Quintet Y4	$1/\sqrt{20}$	4	111101
		-1	011111
		-1	101111
		-1	110111
		-1	111011
6E Quintet Y5	$1/\sqrt{30}$	5	111110
		-1	011111
		-1	101111
		-1	110111
		-1	111011
		-1	111101
6E Septet	$1/\sqrt{1}$	1	111111

### Effect of Magnetic Fields

So far, in this course, we have considered the electron to be point particle having mass  $m$  and charge  $-e$ . Thus, we described the electron wavefunction as  $\varphi(\mathbf{r}) = \varphi(x, y, z)$  presuming that only the position of the electron need be given. This is, of course, an approximation. We can expect that there must be some sort of internal structure for the electron. However, since the size of an electron is about  $10^{-16}$  cm, while the size of the hydrogen atom is about  $10^{-8}$  cm, we would expect that the internal structure of the electron would be of no importance to us. In fact, this is quite far from the truth. The internal structure of the electron plays a very important, although indirect, role in chemistry.

### Effect of Magnetic Fields

The effect of magnetic fields on atomic spectral lines is meant only to provide background on the hypothesis of electron spin. The student is not responsible for this material.

Classically, an electron moving in a magnetic field  $\mathbf{B}$  experiences a force

$$\mathbf{F}_B = -e(\mathbf{v} \times \mathbf{B}) \quad (4.333)$$

called the Lorentz force. For a uniform  $B$ , this force, being perpendicular to  $\mathbf{v}$  and  $\mathbf{B}$ , leads to a circular orbit of radius  $R$ , where the radius is determined by

$$\frac{mv^2}{R} = evB \quad (4.334)$$

or

$$v = \left( \frac{e}{m} B \right) R. \quad (4.335)$$

For distances far from this current loop, the magnetic field due to this electron motion, is given by

$$\mathbf{B} = \frac{\mu}{r^3}, \quad (4.336)$$

where

$$\mu = iA = \left( \frac{e\omega}{2\pi c} \right) (\pi R^2) = -\left( \frac{e}{2c} \right) \omega R^2 \quad (4.337)$$

here  $i$  is the current in the loop,  $A$  is the area of the loop, and the  $e/c$  is needed to correctly convert units from electrostatic unit of charge, and  $\omega$  is the angular velocity

$$\omega = \frac{v}{R}. \quad (4.338)$$

Since the angular momentum is

$$l = mvR = m\omega R^2, \quad (4.339)$$

we see that

$$\mu = -\left( \frac{e}{2mc} \right) l = -\mu_B l, \quad (4.340)$$

where  $\mu_B = e/2mc$  is called the Bohr magneton.

For a state with angular momentum  $l$ , the component of angular momentum along some axis is

$$l_z = \hbar m_l, \quad (4.341)$$

where  $m_l = l, l-1, \dots, -l$ . The magnetic moment along this axis is

$$\mu_z = -(\hbar\mu_B) m_l, \quad (4.342)$$

leading to  $2l+1$  different magnetic moments. Now consider an external magnetic field along the z axis,  $B$ . The interaction energy is

$$\Delta E_{m_l} = \mu \cdot B = -\left(\frac{e\hbar B}{2mc}\right) m_l. \quad (4.343)$$

Thus, the  $2l+1$  states with the same total  $l$ , which are degenerate in the absence of a magnetic field, are split by the magnetic field into  $2l+1$  states having different energy. Hence, in a magnetic field, the absorption or emission lines corresponding to a transition between the  $1s$  and  $2p$  states of hydrogen, should be split into three lines, a multiplet, corresponding to the three values of  $m_l$  for the  $2p$  states.

In fact, experimentally one observed two sets of lines, one corresponding to  $m_l = 2, 2/3, -2/3, -2$ , and the other to  $m_l = 1/3, -1/3$ . Landé, in 1921 and 1923, showed that the multiplets observed with magnetic fields could all be expressed as

$$E(m_j) = E_j - \left(\frac{e\hbar B}{2mc}\right) g m_j, \quad (4.344)$$

where  $g$  has the form

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \quad (4.345)$$

where  $L$ ,  $S$ , and  $J$  are integers, or half integers, and  $m_j$  ranges in integer increments from  $+J$  to  $-J$ , inclusive. For one-electron atoms, such as H and Na, the value of  $S$  is always one half.

Uhlenbeck and Goudsmit, in 1925, showed that the Landé formula could be derived by assuming that electrons have an intrinsic angular momentum  $s$  and an associated magnetic moment  $\mu_s$  where

$$\mu_s = -\left(\frac{e}{mc}\right) s \quad (4.346)$$

that is, the proportionality constant is twice the value obtained in (??), i.e.,  $g = 2$  in (4.345), and where the allowed values of  $s$  parallel to the magnetic field are  $s_z = \hbar m_s$  with  $m_s = \pm 1/2$ . For a one-electron atom, the resulting values of  $J$  are then  $J = L + 1/2$  and  $J = L - 1/2$ , so that  $L = 1$  leads to  $J = 3/2$ , with four values of  $M_J$ , and  $J = 1/2$ , with two values of  $M_J$ . This led to an excellent rationalization of the observed multiplet structures of atom, and provided convincing evidence of the existence of electron spin.

## The Dirac Equation

Dirac, in about 1930, reformulated the Schrödinger equation

$$\left[ -\frac{1}{2m} \nabla^2 + V(R) \right] \psi = i\hbar \frac{\partial \psi}{\partial t} \quad (4.347)$$

to make it relativistically correct. He found that this relativistic formulation lead to the possibility of an angular momentum associated with the internal coordinates with the smallest nonzero value being 1/2. This leads to two possible projections,  $m_s = \pm 1/2$ . He found, directly from relativist quantum mechanics, that the magnetic moment  $\mu$  associated with the spin angular momentum  $s$  is given by (4.346), just as assumed by Uhlenbeck and Goudsmit. The fact that relativistic quantum mechanics leads directly to  $g = 2$  for an electron, was considered quite a success and provided a firm foundation for the concept of electron spin. It is known now, that  $g = 2.00231931$ . However, the deviation from  $g = 2$  is understood as arising from quantum effects involving the radiation field.

## The Pauli Exclusion Principle

Pauli introduced new quantum numbers  $m_s = \pm 1/2$  in the exclusion principle he formulated in explaining the periodic table. Thus the existence of electron spin angular momenta, having quantum number  $m_s = \pm 1/2$ , provides a physical basis for Pauli's hypothesis.

On the basis of the Sommerfeld-Bohr model of the atom, there were two quantum numbers  $n$  and  $k$ , written as  $n_k$ , describing the major and minor axes of the elliptical orbitals. The energy depended only on  $n$ , and  $k$  ranged from  $l$  to  $n$ , in integer increments. Small  $k$  orbits penetrated the core, more than large  $k$ , so that for many-electron atoms  $n_1$  is lowest and  $n_n$  is higher in energy. Indeed, we can think of  $k$  as analogous to  $l + 1$ , although  $k$  did not have the significance of an angular momentum. Initially, Bohr thought that many-electron atoms had all the electrons in the  $l_1$  type orbits, but he soon realized, from experimental observations, that the stable configurations for most atoms must have some electrons in higher energy orbits. There were, of course, an infinite number of possible orbits for even the  $l_1$  level, so it was assumed that particular arrangements of orbits were particularly stable so that additional electrons would be forced to go into higher orbits. Since the inert gases must have such stable configurations, Bohr by 1922 had concluded that the inert gas configurations are as shown in Table 4.3.

The major difficulty here was that no one knew what led to the closing of the electronic shells. Why 2 for  $1_1$ , but 4 for  $2_1$ , and two different limits for  $3_1$ ? In 1924, Pauli was trying to understand the doublet nature of the Na spectrum. Noticing that the Landé scheme led to half-integral quantum number for Na, Pauli suggested that it was due to a new quantum theoretical property of the electron, that he called, classically nondescribable two-valuedness. At the time, the doublet spectrum was thought to be due to a nonvanishing angular momentum of the atomic core. We would now call this spin, with  $m_s = \pm 1/2$  as the two values.

In 1925, Pauli suggested his exclusion principle. It is that now two electrons can have the same set of quantum numbers, including  $m_s$ . This, then, provided the mechanism for closing the shells, and hence, for understanding the periodic table. To do this correctly also required the quantum mechanics of Schrödinger, in 1926, which leads to three spatial quantum number  $nlm_l$  supplemented by  $m_s$ . Assuming a proper sequence of  $nl$  shells, these ideas led to the Aufbau principle providing the explanation of the periodic table, and also, a systematic understanding of the spectrum of the various atoms.

### The Aufbau Principle

The first ionization potentials of the first twenty elements, are listed in Table 4.4. The striking feature is sequences of continuously increasing ionization potentials separated by breaks after He, Ne and Ar, at which the ionization potentials decrease drastically.

In Section 4.6.2 we include a simple calculation indicating that describing He as having two electrons in an optimum 1s-like orbital, leads to an ionization potential of 23.1 eV, in good agreement with experiment, while describing Li as having three electrons in an optimum 1s-like orbitals, leads to an ionization potential of 377 eV, in gross disagreement with experiment. On the other hand, if we arbitrarily restrict each spatial orbital to contain, at most, two electrons, then Li must have the third electron in a loosely bound 2s orbital, in agreement with the small ionization potential of Li. Assuming the atomic orbitals to have energies in the order 1s, 2s, 2p, 3s, 3p, 4s, 3d, and 4p, with big jumps to energy after 1s, after 2p, after 3p, etc., leads to the configurations indicated in Table 4.5, and provides and explanation of the pattern of ionization potentials in Table 4.4. This simple approach, of describing the states of atoms, is called the Aufbau principle. Although not exact, the principle has been extremely useful in understanding the periodic table and in explaining atomic spectroscopy. These successes can be taken as strong empirical evidence, in favor of the hypotheses of the Pauli principle and of electron spin.

Table 4.3:

	He	Ne	Ar	Kr	Xe	Rd
1 <sub>1</sub>	2	2	2	2	2	2
2 <sub>1</sub>		4	4	4	4	4
2 <sub>2</sub>		4	4	4	4	4
3 <sub>1</sub>			4	6	6	6
3 <sub>2</sub>			4	6	6	6
3 <sub>3</sub>				6	6	6
4 <sub>1</sub>				4	6	8
4 <sub>2</sub>				4	6	8
4 <sub>3</sub>					-	8
4 <sub>4</sub>					-	8
5 <sub>1</sub>					4	6
5 <sub>2</sub>						6
5 <sub>3</sub>						6
5 <sub>4</sub>						-
5 <sub>5</sub>						-
6 <sub>1</sub>						4
6 <sub>2</sub>						4

Table 4.4: First IP for atoms.

	IP (eV)
H	13.595
He	24.580
Li	5.390
Be	9.320
B	8.296
C	11.264
N	14.54
O	13.614
F	17.42
Ne	21.559
Na	5.138
Mg	7.644
Al	5.984
Si	8.149
P	11.0
S	10.357
Cl	13.01
Ar	15.755
K	4.339
Ca	6.111

Table 4.5: Aufbau principle for atoms.

	H	He	Li	Be	B	F	Ne	Na
4p								
3d								
4s								
3p								
3s					x	xxxxx	xxxxxx	x
2p				x	xx	xx	xx	xxxxxx
2s			x	xx	xx	xx	xx	xx
1s	x	xx	xx	xx	xx	xx	xx	xx

# Chapter 5

## Atoms

### 5.1 Introduction

In this chapter, we will examine the wavefunctions for the ground states of atoms. A key idea is the Aufbau principle, which forms the basis for understanding chemical regularities of atoms.

Throughout this chapter, we will use atomic units of  $\hbar = 1$ ,  $|e| = 1$ , and  $m_e = 1$ . Consequently, the unit of energy is  $h_0 = 1$  hartree = 27.2116 eV = 627.51 kcal/mole, and the unit of length is  $a_0 = 1$  bohr = 0.52918 Å. First, we will examine the excited states of the H atom.

### 5.2 Excited States H Atoms

Rather than derive the eigenstates of the hydrogen atom, by standard techniques of partial differential equations, we prefer to examine the qualitative reasons behind the forms of the solutions. Although the Schrödinger equation

$$H\phi = E\phi \quad (5.1)$$

can be solved for the H atom, it cannot for most other systems of interest, and hence, qualitative reasoning will be almost essential in most systems.

In atomic units

$$H = -\frac{1}{2}\nabla^2 - \frac{Z}{r}. \quad (5.2)$$

Because  $H$  is independent of orientation, the exact eigenstates can be factored into a radial part  $R(r)$ , and an angular part  $Z(\theta, \varphi)$

$$\phi(r, \theta, \varphi) = R(r)Z(\theta, \varphi) \quad (5.3)$$

where  $z = r \cos \theta$ ,  $x = r \sin \theta \cos \varphi$ , and  $y = r \sin \theta \sin \varphi$ .

### 5.2.1 Angular Functions

From  $H\phi = E\phi$ , we obtain

$$E = \langle \phi | H | \phi \rangle = T + V, \quad (5.4)$$

where, using atomic units, from (5.2)

$$V = \langle \phi | -\frac{Z}{r} | \phi \rangle \quad (5.5)$$

and

$$T = -\frac{1}{2} \langle |\nabla^2| \phi \rangle = \frac{1}{2} \langle |\nabla \phi|^2 \rangle. \quad (5.6)$$

Using spherical coordinates,  $r, \theta, \varphi$ , we will first fix the radial coordinate  $r$  and examine functions of angular coordinates  $\theta, \varphi$  only.

At fixed  $r$ , the potential energy  $V$  is independent of angular coordinate and hence, it is the kinetic energy that is affected by the angular part of the wavefunction. Since the kinetic energy is proportional to the average square of the gradient of the wavefunction, the best, least energy, angular function is the smoothest, i.e., a constant

$$\phi_0(\theta, \varphi) = 1. \quad (5.7)$$

It is convenient to define an integer  $l$  indicating the number of angular nodal planes. Later,  $l$  will be referred to as the total orbital angular momentum quantum number. The function (5.7) has the same sign for all  $\theta$  and  $\varphi$ , and hence, is  $l = 0$ .

All other angular functions must be orthogonal to (5.7), and hence, all must have an equal number of positive and negative regions,  $l \geq 1$ . As the number of angular nodal planes,  $l$  increases, the average square of the gradient increases, and hence, the angular kinetic energy increases. Thus, the angular functions will be ordered as  $l = 0, l = 1, l = 2$ , and  $l = 3$ , etc.

There are three orthogonal functions, all having one nodal plane. For example,

$$\begin{aligned} \phi_z(\theta, \varphi) &= \frac{z}{r} = \cos \theta \\ \phi_x(\theta, \varphi) &= \frac{x}{r} = \sin \theta \cos \varphi \\ \phi_y(\theta, \varphi) &= \frac{y}{r} = \sin \theta \sin \varphi \end{aligned} \quad (5.8)$$

Any other function, with one nodal plane, and orthogonal to  $l = 0$ , can be written as a linear combination of the functions in (5.8). It is easy to see that these functions are orthogonal. For example,

$$\phi_z \phi_x = \left( \frac{zx}{r^2} \right) \quad (5.9)$$

leads to two nodal planes and phases as shown following and hence, the angular integral,

$$\langle \phi_z | \phi_x \rangle = \int d\Omega \phi_z \phi_x, \quad (5.10)$$

must yield zero. Since there are three  $l = 1$  functions, we will introduce an additional number  $m$  to distinguish them.  $m$  is chosen so that  $|m|$  is equal to the number of nodal lines as  $\varphi$  goes from 0 to  $2\pi$ , for a fixed  $\theta$ . Thus,  $\phi_z$  has  $m = 0$ , while  $\phi_x$  and  $\phi_y$  have  $|m| = 1$ . We take  $m = +|m|$  if the function is symmetric with respect to  $\varphi$ , and  $m = -|m|$  is the function of antisymmetric with respect to  $\varphi$ . Thus,  $m = 1$  for  $\phi_x$ , and  $m = -1$  for  $\phi_y$ . Consequently, the allowed values for  $m$  for  $l = 1$  are  $l = 1 : m = -1, 0, +1$ .

Similarly, to construct angular functions orthogonal to  $\phi_0, \phi_x, \phi_y$ , and  $\phi_z$  requires two, or more, angular nodal planes. There are six such functions with two nodal planes, namely,

$$\begin{aligned}\phi_{xy} &= \frac{xy}{r^2} = \sin^2 \theta \sin \varphi \cos \varphi = \frac{1}{2} \sin^2 \theta \sin^2 \varphi \\ \phi_{yx} &= \frac{yz}{r^2} = \sin \theta \cos \theta \sin \varphi \\ \phi_{zx} &= \frac{zx}{r^2} = \sin \theta \cos \theta \cos \varphi \\ \phi_{x^2-y^2} &= \frac{x^2-y^2}{r^2} = \cos^2 \theta (\cos^2 \varphi - \sin^2 \varphi) = \cos^2 \theta \cos^2 \varphi \\ \phi_{y^2-z^2} &= \frac{y^2-z^2}{r^2} \\ \phi_{z^2-x^2} &= \frac{z^2-x^2}{r^2}. \end{aligned} \tag{5.11}$$

Taking the sum, and the difference of the last two functions, leads to

$$\begin{aligned}\phi_{z^2-x^2} + \phi_{y^2-z^2} &= \frac{y^2-x^2}{r^2} = -\phi_{x^2-y^2} \\ \phi_{z^2-x^2} - \phi_{y^2-z^2} &= \frac{2z^2-x^2-y^2}{r^2} = \frac{3z^3-r^2}{r^2} = 3 \cos^2 \theta - 1. \end{aligned} \tag{5.12}$$

The second function will be denoted as

$$\phi_{z^2} = 3 \cos^2 \theta - 1. \tag{5.13}$$

The first function is just the negative of the  $\phi_{x^2-y^2}$  function, and hence, there are only five orthogonal  $l = 2$  functions. Introducing the  $m$  quantum number, we see that  $\phi_{x^2-y^2}$  is  $m = 2$ ,  $\phi_{xy}$  is  $m = -2$ ,  $\phi_{zx}$  is  $m = 1$ ,  $\phi_{yz}$  is  $m = -1$ , and  $\phi_{z^2}$  is  $m = 0$ . Of the two functions having the same  $|m|$ , the  $\cos m\varphi$  function will always be taken as  $+|m|$ , and the  $\sin m\varphi$  function will be taken as  $-|m|$ . Thus, the allowed value of  $m$  for  $l = 2$  are  $l = 2 : m = +2, +1, 0, -1, -2$ . Continuing, we find seven functions with  $l = 3$ , nine with  $l = 4$ , etc.

The set of angular functions generated above, are referred to as the real spherical harmonics  $Z_{lm}(\theta, \varphi)$ , and are tabulated in Tables 5.1–5.2. These functions have been normalized so that

$$\int_0^\pi \sin \theta d\theta \int_{-\pi}^{+\pi} d\varphi |Z_{lm}(\theta, \varphi)|^2 = 1. \tag{5.14}$$

Table 5.1: The complex spherical harmonics  $Y_{lm}$ .

$Y_{00}$	=	$\sqrt{\frac{1}{4\pi}}$
$rY_{1\bar{1}}$	=	$\sqrt{\frac{3}{8\pi}}(x - iy)$
$rY_{10}$	=	$\sqrt{\frac{3}{4\pi}}z$
$rY_{11}$	=	$\sqrt{\frac{3}{8\pi}}(x + iy)$
$r^2Y_{2\bar{2}}$	=	$\sqrt{\frac{5}{4}}\sqrt{\frac{3}{8}}(x - iy)^2$
$r^2Y_{2\bar{1}}$	=	$\sqrt{\frac{5}{4\pi}}\sqrt{\frac{3}{2}}z(x - iy)$
$r^2Y_{20}$	=	$\sqrt{\frac{5}{4\pi}}\sqrt{\frac{1}{4}}(3z^2 - r^2)$
$r^2Y_{21}$	=	$\sqrt{\frac{5}{4\pi}}\sqrt{\frac{3}{2}}z(x + iy)$
$r^2Y_{22}$	=	$\sqrt{\frac{5}{4\pi}}\sqrt{\frac{3}{8}}(x + iy)^2$
$r^3Y_{3\bar{3}}$	=	$\sqrt{\frac{7}{4\pi}}\sqrt{\frac{5}{16}}(x - iy)^3$
$r^3Y_{3\bar{2}}$	=	$\sqrt{\frac{7}{4\pi}}\sqrt{\frac{15}{8}}z(x - iy)^2$
$r^3Y_{3\bar{1}}$	=	$\sqrt{\frac{7}{4\pi}}\sqrt{\frac{3}{16}}(x - iy)(5z^2 - r^2)$
$r^3Y_{30}$	=	$\sqrt{\frac{7}{4\pi}}\sqrt{\frac{1}{4}}z(5z^2 - 3r^2)$
$r^3Y_{31}$	=	$\sqrt{\frac{7}{4\pi}}\sqrt{\frac{3}{16}}(x + iy)(5z^2 - r^2)$
$r^3Y_{32}$	=	$\sqrt{\frac{7}{4\pi}}\sqrt{\frac{15}{8}}(x + iy)^2$
$r^3Y_{33}$	=	$\sqrt{\frac{7}{4\pi}}\sqrt{\frac{5}{16}}(x + iy)^3$

Table 5.2: The real spherical harmonics  $Z_{lm}$ .

$Z_{00}$	=	$\bar{Y}_{00}$
$rZ_{11}$	=	$\sqrt{\frac{3}{4\pi}}x$
$rZ_{1\bar{1}}$	=	$\sqrt{\frac{3}{4\pi}}y$
$rZ_{10}$	=	$\sqrt{\frac{3}{4\pi}}z$
$r^2Z_{22}$	=	$\sqrt{\frac{5}{4\pi}}\sqrt{\frac{3}{4}}(x^2 - y^2)$
$r^2Z_{2\bar{1}}$	=	$\sqrt{\frac{5}{4\pi}}\sqrt{3}xy$
$r^2Z_{21}$	=	$\sqrt{\frac{5}{4\pi}}\sqrt{3}xz$
$r^2Z_{2\bar{2}}$	=	$\sqrt{\frac{5}{4\pi}}\sqrt{3}yz$
$r^2Z_{20}$	=	$\sqrt{\frac{5}{4\pi}}\sqrt{\frac{1}{4}}(3z^2 - r^2)$
$r^3Z_{33}$	=	$\sqrt{\frac{7}{4\pi}}\sqrt{\frac{5}{8}}x(x^2 - 3y^2)$
$r^3Z_{3\bar{2}}$	=	$\sqrt{\frac{7}{4\pi}}\sqrt{\frac{5}{8}}y(3x^2 - y^2)$
$r^3Z_{32}$	=	$\sqrt{\frac{7}{4\pi}}\sqrt{\frac{15}{4}}z(x^2 - y^2)$
$r^3Z_{32}$	=	$\sqrt{\frac{7}{4\pi}}\sqrt{15}zxy$
$r^3Z_{31}$	=	$\sqrt{\frac{7}{4\pi}}\sqrt{\frac{3}{8}}x(5z^2 - r^2)$
$r^3Z_{31\bar{1}}$	=	$\sqrt{\frac{7}{4\pi}}\sqrt{\frac{3}{8}}y(5z^2 - r^2)$
$Z_{30}$	=	$\sqrt{\frac{7}{4\pi}}\sqrt{\frac{1}{4}}z(5z^2 - 3r^2)$

Note that a bar over a number indicates a negative number, e.g.,  $\bar{3} = -3$ .  $Z_{lm}$  with  $m > 0$  are also denoted as  $Z_{lm}^c$  and  $Z_{lm}$  where  $m < 0$  are denoted as  $Z_{lm}^s$ , cosine and sine forms, respectively.

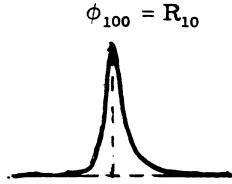


Figure 5.1:

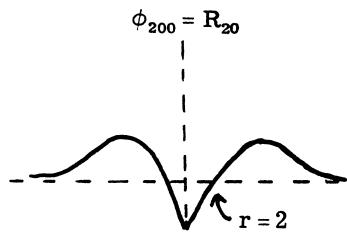


Figure 5.2:

### 5.2.2 Radial Functions

Now we will consider a wavefunction with a specific angular form,  $Z_{lm}(\theta, \varphi)$ , and examine the optimum radial forms  $R(r)$  of the wavefunction. In this section, we will ignore normalization in  $Z_{lm}(\theta, \varphi)$ , in  $R(r)$ , and in the total wavefunction

$$\phi(r, \theta, \varphi) = R(r)Z_{lm}(\theta, \varphi). \quad (5.15)$$

In addition, we will take the nuclear charge as unity, hydrogen atom.

First, we consider the  $l = 0$  angular function,  $Z_{lm}(\theta, \varphi) = 1$ . The potential energy favors concentrating the wavefunction at  $r = 0$ , while the kinetic energy favors spreading the wavefunction over a finite region. The compromise is

$$R_{10}(r) = e^{-r} \quad (5.16)$$

Plotting the total wavefunction

$$\varphi_{100}(r, \theta, \varphi) = R_{10}(r)Z_{lm}(\theta, \varphi) \quad (5.17)$$

along the z axis, leads to Figure 5.1.

The first excited  $l = 0$  states, denoted as  $R_{20}(r)$ , must be orthogonal to  $R_{10}(r)$  and hence, it has the form in Figure 5.2. Forcing a radial node as in Figure 5.3, necessarily leads to higher gradients, for normalized wavefunctions, and hence, a higher kinetic energy. Hence, the optimum  $R_{20}(r)$  orbital is much more extended than  $R_{10}(r)$  in

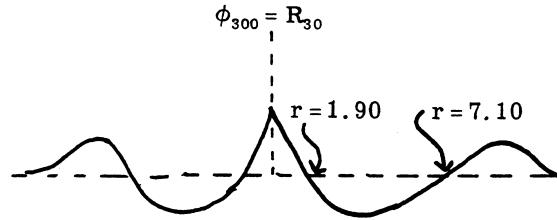


Figure 5.3:

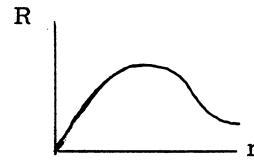


Figure 5.4:

order to decrease the gradients due to the radial node. Of course, expanding the wavefunction increases  $\bar{r}$ , and hence, makes the potential energy less negative. The final orbital is

$$R_{20}(r) = \left( \frac{1}{2}r - 1 \right) e^{-\frac{1}{2}r}. \quad (5.18)$$

Higher states have additional nodal planes.

In order to refer quickly to these various solutions, we will introduce a number  $n$ , defined to be one greater than the total number of nodal planes, radial plus angular. Thus, the ground state wavefunction (5.16) is  $n = 1$ . The function  $R_{20}(r)$  is zero for  $r = 2$  independent of  $\theta$  and  $\varphi$ . Thus, the wavefunction

$$\phi_{200}(r, \theta, \varphi) = R_{20}(r) Z_{l m}(\theta, \varphi) \quad (5.19)$$

has one spherical nodal surface, at  $r = 2a_0$ , and consequently,  $n = 2$ . The next  $l = 0$  state is

$$\phi_{300} = R_{30} Z_{00} \quad (5.20)$$

where

$$R_{30}(r) = \left( \frac{2}{27}r^2 - \frac{2}{3}r + 1 \right) e^{-\frac{1}{2}r} \quad (5.21)$$

with radial nodes at  $r = 1.902$  and  $r = 7.098$ , note that the inner node lies close to that of  $R_{20}$ .

Consider now, the functions with  $l = 1$  and  $m = 0$ ,

$$\phi(r, \theta, \varphi) = R(r) Z_{10}(\theta, \varphi) = R(r) \cos \theta. \quad (5.22)$$

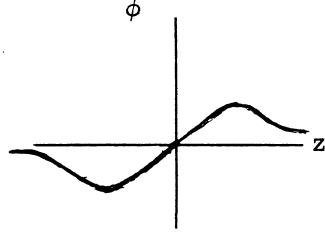


Figure 5.5:

In this case, we must have  $R(r) \rightarrow 0$  and  $r \rightarrow 0$ , since otherwise  $\phi$  would be multi-valued at  $r = 0$ . Thus, the smoothest allowed radial function, i.e., the lowest energy, is of the form in Figure 5.4. Combining this radial form with  $\cos \theta$ , and plotting along the Z axis, leads to the form in Figure 5.5, a function with one planar nodal surface, the xy plane. Thus, this state has  $n = 2$ . The precise form of the radial function is

$$R_{21} = r e^{-\frac{1}{2}r} \quad (5.23)$$

and the total wavefunction is

$$\phi_{210} = r \cos \theta e^{-\frac{1}{2}r} = z e^{-\frac{1}{2}r}. \quad (5.24)$$

Just as for the  $R_{20}(r)$  function, the presence of the nodal plane in  $R_{21}$  leads to an increase in the spatial extent of the wavefunction. Since the three  $l = 1$  functions are equivalent in shape, differing only in the orientation of the nodal plane, the radial function is independent of  $m$ .

The radial function for the next higher  $l = 1$  states,  $n = 3$ , must have an additional radial nodal plane in order to be orthogonal to  $R_{21}$ , as in Figure 5.6. The precise form is

$$R_{31}(r) = r \left( \frac{1}{6}r - 1 \right) e^{-\frac{1}{3}r}. \quad (5.25)$$

Combining  $R_{31}(r)$  with the angular function  $Z_{10}(\theta, \varphi)$  leads to

$$\phi_{310}(r, \theta, \varphi) = z \left( 1 - \frac{1}{6}r \right) e^{-\frac{1}{3}r}. \quad (5.26)$$

Thus,  $\phi_{310}$  has two nodal surfaces, one is spherical at  $r = 6a_0$ , and the other is planar, the xy plane, as illustrated in Figure 5.7.

For higher angular momenta,  $l$ , we find that  $R_{nl}(r) \rightarrow r^l$  as  $r \rightarrow 0$ , in order that  $\phi(r, \theta, \varphi)$  be single valued at  $r = 0$ . The lowest  $n$ , no radial nodal surfaces, is  $n = l+1$ , leading to the general form

$$R_{nl}(r) = r^l e^{-\frac{1}{n}r} \quad (n = l+1) \quad (5.27)$$

see the next section for derivation.

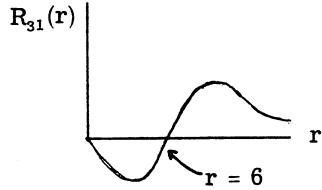


Figure 5.6:

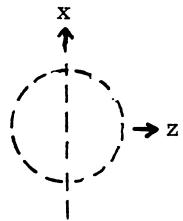


Figure 5.7:

The final energy of these states is given by

$$E = -\frac{1}{2} \frac{Z^2}{n^2}. \quad (5.28)$$

Thus, increasing the number of nodal surfaces ( $n$ ) leads to an increase of the energy (less negative). The unexpected result here is that the energy is determined only by the total number of nodal surfaces, independent of whether they are radial or angular. This result is special to the Coulomb potential  $V(r) = -\frac{Z}{r}$ . For a more general potential  $V(r)$ , the energy depends on  $n$  and  $l$ .

### 5.2.3 Quantitative Aspects of Hydrogen Atom

Using atomic units, the Hamiltonian for the hydrogen atom becomes

$$H = -\frac{1}{2} \nabla^2 - \frac{Z}{r}. \quad (5.29)$$

To solve for the eigenfunctions of (5.29), it is convenient to transform to spherical polar coordinates where the Laplacian becomes

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} - \frac{\hat{l}^2}{r^2} \quad (5.30)$$

and

$$\hat{l}^2 = \hat{l}_x^2 + \hat{l}_y^2 + \hat{l}_z^2 \quad (5.31)$$

is the angular momentum operator. The eigenfunctions of  $H$  can then be written as

$$H\Psi_{nlm} = E_{nlm}\Psi_{nlm}, \quad (5.32)$$

where

$$\Psi_{nlm} = R_{nl}(r)Y_{lm}(\theta, \varphi) \quad (5.33)$$

and  $Y_{lm}(\theta, \varphi)$  are the complex spherical harmonic functions (angular momentum eigenfunctions) shown in Tables 5.1–5.2. The states given here all have energies  $E < 0$ . For  $E \geq 0$  the eigenfunctions of (5.6) are not square-integrable, and we will discuss them no further. The spherical harmonic functions satisfy

$$\hat{l}^2 Y_{lm}(\theta, \varphi) = l(l+1)Y_{lm}(\theta, \varphi) \quad (5.34)$$

$$\hat{l}_z Y_{lm}(\theta, \varphi) = mY_{lm}(\theta, \varphi) \quad (5.35)$$

and are simple combinations of the real spherical harmonics,  $Z_{lm}$ . The  $Z_{lm}$  are eigenfunctions of  $\hat{l}^2$  but not of  $\hat{l}_z$ . That is,  $\hat{l}_z Z_{lm} \neq mZ_{lm}$ , so that the  $m$  in  $Z_{lm}$  is not strictly the angular momentum projection. The real form is more convenient for molecular systems. Although  $l$  and  $m$  refer to the number of angular nodal planes,  $l$  is generally referred to as the *angular momentum*, and  $m$  is referred to as the *angular momentum projection* (along the z axis).

Using (5.29), (5.30), and (5.33) in (??), leads to the differential equation for the radial function,  $R(r)$ ,

$$\left[ -\frac{1}{2} \left( \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} - \frac{l(l+1)}{r^2} \right) - \frac{Z}{r} \right] R_{nl}(r) = E_n R_{nl}(r), \quad (5.36)$$

where the energy is given by

$$E_n = -\frac{Z^2}{2n^2} \quad (5.37)$$

Thus, the energy is independent of the angular momentum,  $l$ . However, only  $l \leq n-1$  are allowed for any given  $n$ .

In solving (5.36), it is customary to substitute

$$P_{nl}(r) = rR_{nl}(r) \quad (5.38)$$

so that (5.36) becomes

$$\left[ -\frac{1}{2} \frac{d^2}{dr^2} + V_l(r) \right] P_{nl}(r) = E_n P_{nl}(r) \quad (5.39)$$

where

$$V_l(r) = \frac{l(l+1)}{2r^2} - \frac{Z}{r}. \quad (5.40)$$

This is just the Schrödinger equation for a particle moving in a one-dimensional potential  $V_l(r)$ . The potential depends upon the value of the angular momentum, leading to a different sequence (denoted by  $n$ ) of solutions for each angular momentum.

Table 5.3:

$n$	$l$	notation
1	0	$1s$
2	0	$2s$
2	1	$2p$
3	0	$3s$
3	1	$3p$
3	2	$3d$

where s, p, d, f, g, etc., denote  $l = 1, 2, 3, 4$ , etc.

The lowest solution for each angular momentum is easy. It has the form

$$R(r) = r^l e^{-\zeta r} \quad (5.41)$$

or

$$P(r) = r^{l+1} e^{-\zeta r} \quad (5.42)$$

Substituting into (5.39), we obtain

$$\left\{ \frac{(l+1)l}{2r^2} + \zeta \frac{(l+1)}{r} - \frac{1}{2}\zeta^2 + \frac{l(l+1)}{2r^2} - \frac{Z}{r} - E \right\} P_{nl}(r) = 0 \quad (5.43)$$

and hence,

$$E = -\frac{1}{2}\zeta^2 \quad (5.44)$$

where

$$\zeta = \frac{Z}{n} \quad (5.45)$$

and  $n = l + 1$ . Substituting (5.45) into (5.44) leads, then, to the total energy

$$E_n = -\frac{Z^2}{2n^2}. \quad (5.46)$$

Higher energy solutions are obtained corresponding to each larger value of  $n$ . The other solutions of (5.36) are listed in Tables 5.4–5.5, using the real form of the angular functions, and plotted in Figures 5.8 and 5.9, for the  $n = 1, 2, 3$ , and  $n = 4$  states, respectively.

For each  $n$  there are solutions corresponding to  $l = 0, 1, \dots, n - 1$ . The eigenfunction of the H atom are shown in Table 5.3.

Throughout this course, orbitals will be represented by *contour plots*, such as in Figures 5.8 and 5.9, and hence, you should be sure to learn how to interpret them. In Figure 5.8, all but one plot is in the plane passing through the origin and lying in the  $xz$  plane, the exception is in the  $xy$  plane. Each contour line corresponds to a particular amplitude for this plane. The lines with long dashes, indicate zero amplitude while solid and dotted lines indicate positive and negative amplitude, respectively. When

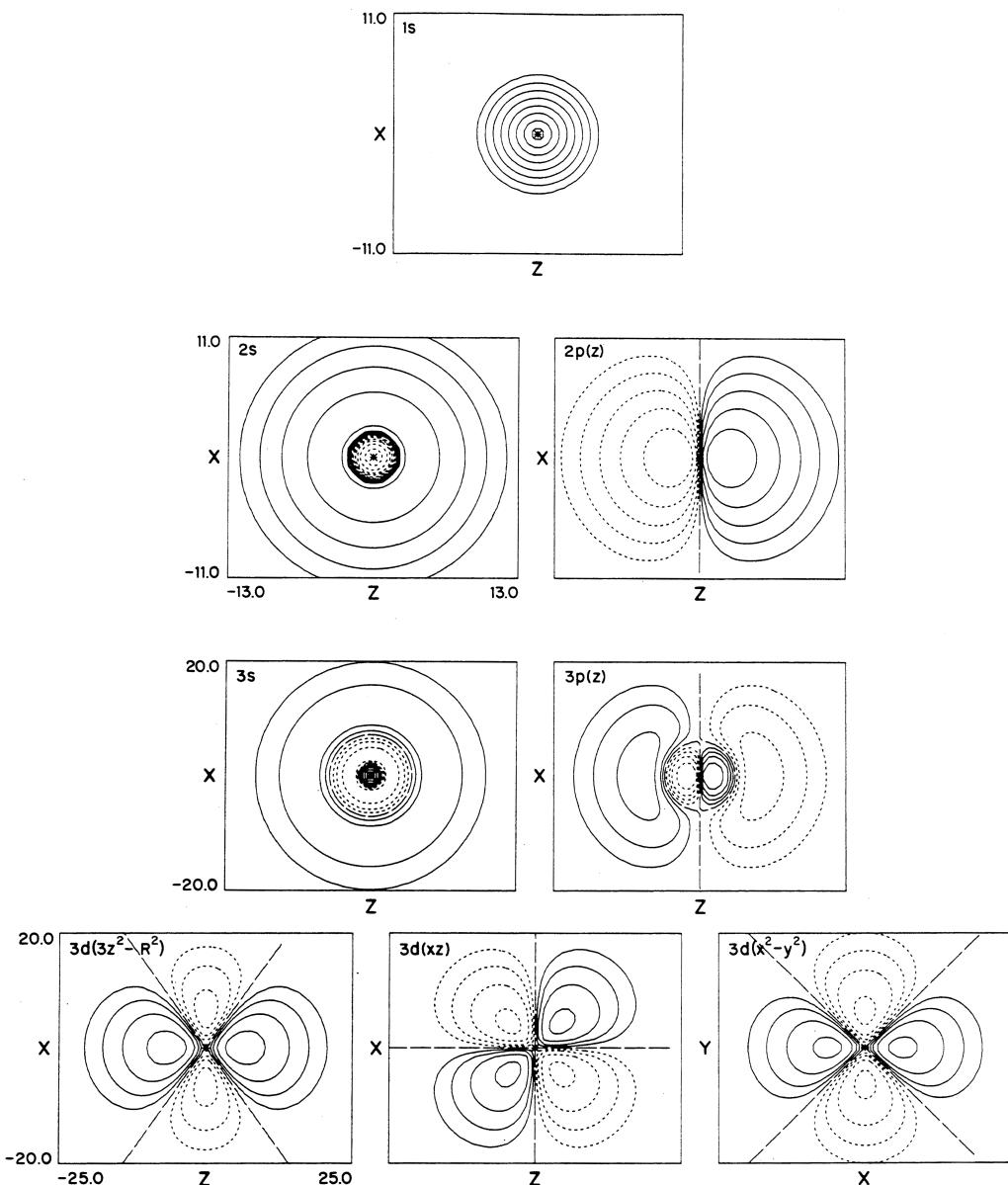


Figure 5.8: Contour plots of selected  $n = 1, 2$ , and  $3$  atomic orbitals,  $Z = 1$ , i.e., for the hydrogen atom. Long dashed lines indicate nodal planes; solid lines indicate positive contours, and short dashed lines indicate negative contours. The most diffuse contour is .0025 atomic unit. Each successive contour is a factor of 2 larger. The contours plotted are 0.0025, 0.0050, 0.0100, 0.0200, 0.0400, etc. All quantities are in atomic units.

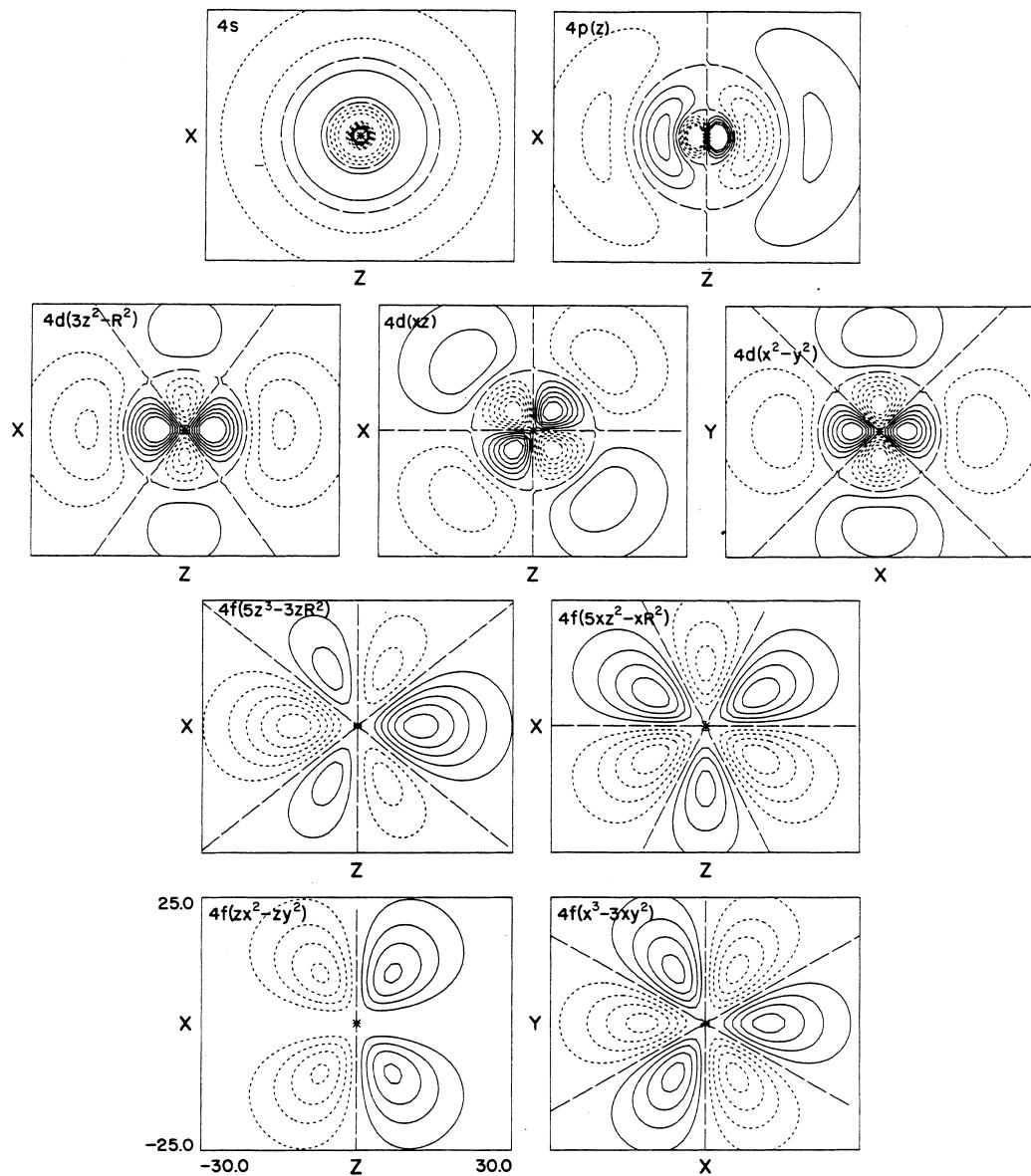


Figure 5.9: Contour plots for selected  $n = 4$  orbitals,  $Z = 1$ . Contour conventions, as in Figure 1. However, the contour values are .0025, .0050, .0075, .0100, and .0125.

Table 5.4: The radial functions, in atomic units, for the hydrogen-like atoms. The sign convention used here is that  $R_{nl}(r) > 0$  for large  $r$ , a more common convention is  $R_{nl}(r) > 0$ , as  $r \rightarrow 0$ . This is convenient for considerations of interactions of orbitals of different atoms of a molecule.

$(nl)$	Spectroscopic	$R_{nl}(r)$
(10)	1s	$2Z^{\frac{3}{2}}e^{-Zr}$
(20)	2s	$\frac{1}{\sqrt{2}}Z^{\frac{3}{2}}(-1 + \frac{Z}{2}r)e^{-\frac{Z}{2}r}$
(21)	2p	$\frac{1}{2\sqrt{6}}Z^{\frac{5}{2}}re^{-\frac{Z}{2}r}$
(30)	3s	$\frac{2}{3\sqrt{3}}Z^{\frac{3}{2}}(1 - \frac{2}{3}Zr + \frac{2}{27}Z^2r^2)e^{-\frac{Z}{3}r}$
(31)	3p	$\frac{8}{27\sqrt{6}}Z^{\frac{5}{2}}r(-1 + \frac{Zr}{6})e^{-\frac{Z}{3}r}$
(32)	3d	$\frac{4}{81\sqrt{30}}Z^{\frac{7}{2}}r^2e^{-\frac{Z}{3}r}$
(40)	4s	$\frac{1}{4}Z^{\frac{3}{2}}(-1 + \frac{3}{4}Zr - \frac{1}{8}Z^2r^2 + \frac{1}{192}Z^3r^3)e^{-\frac{Z}{4}r}$
(41)	4p	$\frac{10}{32\sqrt{15}}Z^{\frac{5}{2}}(1 - \frac{1}{4}Zr + \frac{1}{80}Z^2r^2)re^{-\frac{Z}{4}r}$
(42)	4d	$\frac{1}{64\sqrt{5}}Z^{\frac{7}{2}}(-1 + \frac{1}{12}Zr)r^2e^{-\frac{Z}{4}r}$
(43)	4f	$\frac{1}{768\sqrt{35}}Z^{\frac{9}{2}}r^3e^{-\frac{Z}{4}r}$

Table 5.5: Wavefunctions for the hydrogen-like atoms, through  $n = 3$ , in real form. In atomic units.

State	Wavefunction
1s	$\left(\frac{Z^3}{\pi}\right)^{\frac{1}{2}}e^{-Zr}$
2s	$\left(\frac{Z^3}{8\pi}\right)^{\frac{1}{2}}(1 - \frac{1}{2}r)e^{-\frac{1}{2}Zr}$
2p <sub>x,y,z</sub>	$\left(\frac{Z^5}{32\pi}\right)^{\frac{1}{2}}\begin{Bmatrix} x \\ y \\ z \end{Bmatrix}e^{-\frac{1}{2}Zr}$
3s	$\left(\frac{Z^3}{27\pi}\right)^{\frac{1}{2}}(1 - \frac{2}{3}Zr + \frac{2}{27}Z^2r^2)e^{-\frac{1}{3}Zr}$
3p <sub>x,y,z</sub>	$\left(\frac{8Z^5}{729\pi}\right)^{\frac{1}{2}}(1 - \frac{1}{6}Zr)\begin{Bmatrix} x \\ y \\ z \end{Bmatrix}e^{-\frac{1}{3}Zr}$
3d <sub>z<sup>2</sup>,xz,yz,x<sup>2</sup>-y<sup>2</sup>,xy</sub>	$\frac{1}{81}\left(\frac{Z^7}{\pi}\right)^{\frac{1}{2}}\begin{Bmatrix} 6^{-\frac{1}{2}}(3z^2 - r^2) \\ y^{\frac{1}{2}}xz \\ 2^{\frac{1}{2}}(x^2 - y^2) \\ 2^{-\frac{1}{2}}xy \end{Bmatrix}e^{1\frac{1}{3}Zr}$

comparing a bunch of orbitals, as in Figures 5.8 and 5.9, we will generally use the same scale and will always use the same amplitudes for all plots.

Two standard conventions are used for spacing the amplitudes being plotted. Our normal convention involves use of a constant increment in contour amplitudes. Thus, in Figure 5.9, contours corresponding to  $\pm 0.0125$ ,  $\pm 0.0075$ ,  $\pm 0.0050$ ,  $\pm 0.0025$ ,  $0.00$  are plotted. This is appropriate when all orbitals being shown have similar sizes, in Figure 5.9 all orbitals correspond to  $n = 4$ , and hence, are of nearly the same size. The other convention, referred to as a log plot, involves a constant factor in space the contours. Thus, in Figure 5.8, the contours corresponding to  $0.0$ ,  $0.0025$ ,  $0.0050$ ,  $0.0100$ ,  $0.0200$ ,  $0.0400$ , etc., are plotted. This is appropriate for showing orbitals of widely disparate sizes, as in Figure 5.8 where  $n = 1$ ,  $n = 2$ , and  $n = 3$  orbitals are shown.

For the  $1s$  and  $2p$  orbitals, each contour amplitude occurs once and interpretation is straightforward. For the  $2s$ , and certain other orbitals, interpretation is a little more difficult since there are maxima with  $r \neq 0$ , as illustrated in Figure 5.10. In this case, the presence and position of the maximum is not obvious without careful examination of the positions of the nodal lines, e.g., examine the  $4s$  orbital in Figure 5.

### 5.2.4 Sizes of the Orbitals

The bound eigenstates of a particle moving in a Coulomb potential

$$V(r) = -\frac{Z}{r}, \quad (5.47)$$

lead to total kinetic and potential energies,  $T$  and  $V$ , that are related by  $2T = -V$ . Since the total energy is  $E = T + V$ , we have  $E = -T$  and  $E = 1/2V$ . This result is called the *virial theorem*. Since

$$E = -\frac{Z^2}{2n^2}, \quad (5.48)$$

we find that

$$T = \frac{Z^2}{n^2} \quad (5.49)$$

and

$$V = -\frac{Z^2}{n^2}. \quad (5.50)$$

Since the potential energy of a particle in state  $\phi$  is given by

$$V = \langle \phi | -\frac{Z}{r} | \phi \rangle, \quad (5.51)$$

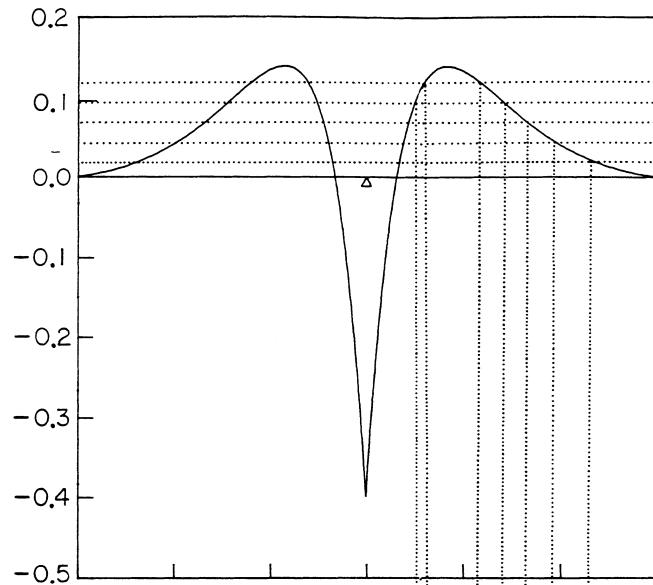
we will define the average distance of the electron from the nucleus,  $\bar{r}$ , as

$$V = -\frac{Z}{\bar{r}}. \quad (5.52)$$

Thus,  $\bar{r}$  is the radius for a classical particle to have the same potential energy. This definition leads to

$$\frac{1}{\bar{r}} = \langle \phi | \frac{1}{r} | \phi \rangle, \quad (5.53)$$

(a) LINE PLOT



(b) CONTOUR PLOT

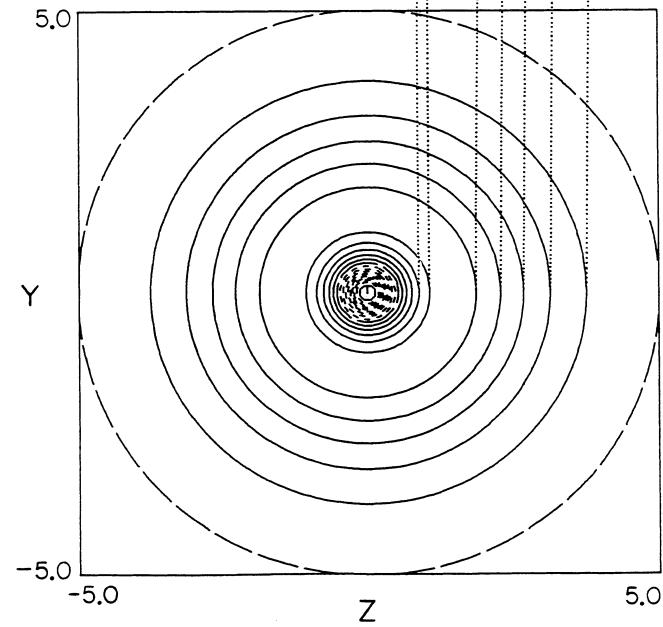


Figure 5.10: Comparison of line and contour plots for a 2s-like orbital (the orbital plotted is not a 2s orbital, but has been modified to go to zero at  $r = 5a_0$ ). Note that with the contour plot, the maximum is indicated by a wide space between positive contours.

and hence, from (5.49) we obtain

$$\bar{r} = \frac{n^2}{Z}. \quad (5.54)$$

Thus, for the hydrogen atom, the average radial distance  $\bar{r}$  for the  $n = 1, 2, 3, 4$ , states are  $\bar{r} = 1a_0 = 0.53\text{\AA}$ ,  $4a_0 = 2.1\text{\AA}$ ,  $9a_0 = 4.7\text{\AA}$ , and  $16a_0 = 8.5\text{\AA}$ , respectively. Since the bond length of the  $\text{H}_2$  molecules is  $1.4a_0 = 0.75\text{\AA}$ , and a typical CH bond length is  $2.1a_0 = 1.0\text{\AA}$ , we see that even the  $n = 2$  excited H orbitals are much larger than a bond, and the  $n = 3$  excited orbitals are very large indeed. Considering a fixed  $n$ , say  $n = 1$ , and varying nuclear charge  $Z$ , we see that the large atoms have much smaller orbitals, with the average radius of the 1s orbital of  $\text{C}^{5+}$  being one-sixth that of hydrogen.

With the definition of size used above, the states of various  $l$ , but the same  $n$ , have the same size. Other definitions of size, say

$$\bar{r} = \langle \phi | r | \phi \rangle \quad (5.55)$$

or

$$\bar{r} = \sqrt{\langle \phi | r^2 | \phi \rangle}, \quad (5.56)$$

lead to slightly different  $\bar{r}$  for different  $l$  with the same  $n$ . However, all such definitions lead to overall sizes comparable to (5.40).

In Figure 5.11(a), we present line plots of the 1s, 2s and 3s orbitals of hydrogen, but with the sign changes for 2s. These orbitals are not normalized, rather the amplitude at the nucleus was taken to be the same value for each orbital. Note that in the region near the nucleus,  $r < la_0$ , the  $\psi_{2s}$  and  $\phi_{3s}$  orbitals are very similar to  $\phi_{1s}$ . For  $r < 4a_0$ , the outer maximum in  $\psi_{2s}$ , the  $\psi_{3s}$  orbital is very similar to  $\psi_{2s}$ . These observations are general and result from the orthogonality conditions on the higher energy orbitals.

From Figure 5.6 it would appear that the  $\psi_{2s}$  and  $\psi_{3s}$  orbitals are concentrated mainly in the same region as  $\phi_{1s}$ . However, in spherical coordinates, the volume element for the radial integration is  $d\tau = r^2 dr$ , and hence, the probability density for the electron to be a distance  $r$  from the nucleus is

$$r^2 \phi^2(r) = [r\phi(r)]^2. \quad (5.57)$$

The quantity  $r\phi(r)$  is plotted in Figure 5.11(b), where we see that the probability density is a maximum at  $r = 1a_0$  for the 1s orbital,  $r = 5a_0$  for the 2s orbital, and  $r = 13a_0$  for the 3s orbital.

Given an energy

$$E_n = -\frac{1}{2n^2}, \quad (5.58)$$

the classical motion of an electron about a nucleus of charge 1, would be confined within the radius

$$r_{cl} = \frac{1}{n^2} = 2\bar{r}. \quad (5.59)$$

From Figure 5.11(b), we see that the maximum probability amplitude always occurs within this classically allowed region. However, there are quite significant amplitudes in the classically forbidden region.

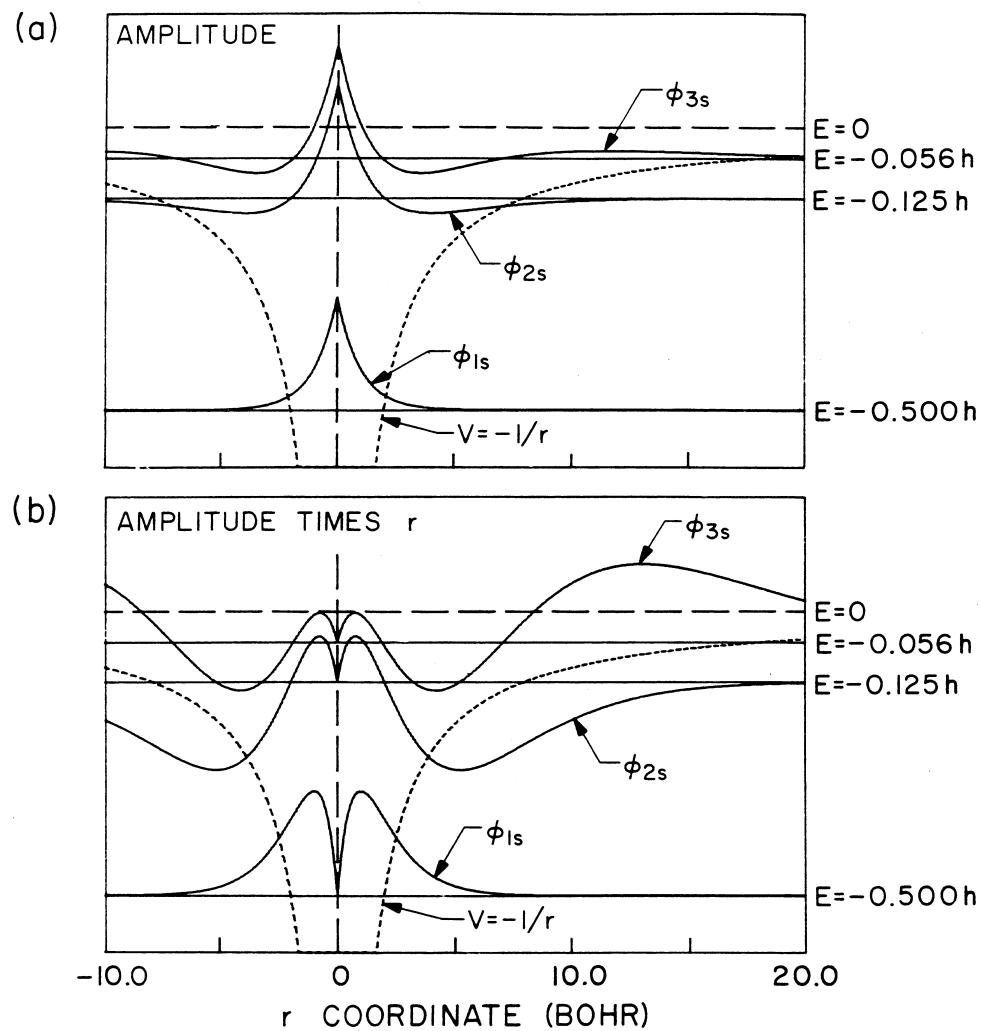


Figure 5.11: (a) The amplitudes of the 1s, 2s, and 3s orbitals of hydrogen (sign changed for 2s). Also included is a plot of the potential energy,  $V = -1/r$  (dotted line). The line with the long dashes is the zero of energy for the potential. For each state, a solid horizontal line is drawn at the energy for the orbital. The orbital is then plotted with this line as the origin. The orbitals are not normalized. (b) The  $r\phi$  for the 1s, 2s, and 3s levels. Since  $(r\phi)^2$  is the probability density for an electron at distance  $r$  from the nucleus, the figure provides the relative amplitude of being at various  $r$ .

Table 5.6:

Table 5.7:

From (5.40) we see that if  $l \neq 0$ , the potential becomes positively infinite for  $r = 0$ . As a result, the wavefunctions for  $l \neq 0$  must go to zero for  $r = 0$ . The potentials (5.40) for  $l = 0, 1$ , and  $2$  are shown in Figure 5.12 along with the amplitudes of the  $1s$ ,  $2p$ , and  $3s$  orbitals.

### 5.3 The Aufbau Principle of Atoms

In this section, we develop the Aufbau principle for atoms. This is based upon the sequence of states for the H atom, except that inclusion of average electron-electron repulsion effects of many-electron atoms, leads to an ordering of orbitals in this sequence

Row 0	$1s$	H to He
Row 1	$2s, 3p$	Li to Ne
Row 2	$3s, 3p$	Na to Ar
Row 3	$4s, 3d, 4p$	K to Kr
Row 4	$5s, 4d, 5p$	Rb to Xe
Row 5	$6s, 4f, 5d, 6p$	Cs to Rn
Row 6	$7s, 5f, 6d, 7p$	Fr to -

where  $1s$  is lowest and large gaps occur between rows. These rows will be denoted as indicated with Li-Ne as the *first row* (this is convenient when discussing periodic trends). The schematic energy diagram, the *Aufbau diagram*, is given in Figure 5.13. The ground state of a  $Z$  electron atom is thus constructed by filling these orbitals, 2 electrons per spatial orbital, starting with the lowest and working up.

If the highest occupied orbitals are in the  $r$ th row, then all orbitals of the earlier rows are too small to play a special role in bonding and are referred to as *core orbitals*. The various occupied orbitals of the  $r$ th row are referred to as *valence orbitals*. States in different rows, but with the same occupation of valence orbitals, have similar chemical properties leading to the *periodic table*, as indicated in Table 5.6 and 5.7.

The  $d$  and  $f$  orbitals complicate the above description. Thus, for the third row, the  $3d$  orbitals are approximately 30 % the size of the  $4s$  and  $4p$  orbitals. As a result, they play a somewhat smaller role in the chemistry. For atoms in which the  $d$  and  $f$  orbitals are empty, or full, we can generally ignore the  $d$  and  $f$  orbitals in considering the chemistry. Thus, Se is analogous to S despite the  $(3d)^{10}$  configuration in Se. Cases with partially occupied  $d$  or  $f$  shells are chemically analogous only to other cases with similar partial occupations.

The valence orbitals for H through Xe are shown in Figure 10. The ionization potentials and electron affinities for various atoms are shown in Tables 5.6 and 5.7.

Figures 5.14–5.20 illustrate the valence orbitals of H through Xe. In this figure, we plot  $r\phi_{nl}$  for the valence orbitals as obtained from accurate Hartree-Fock calculations.

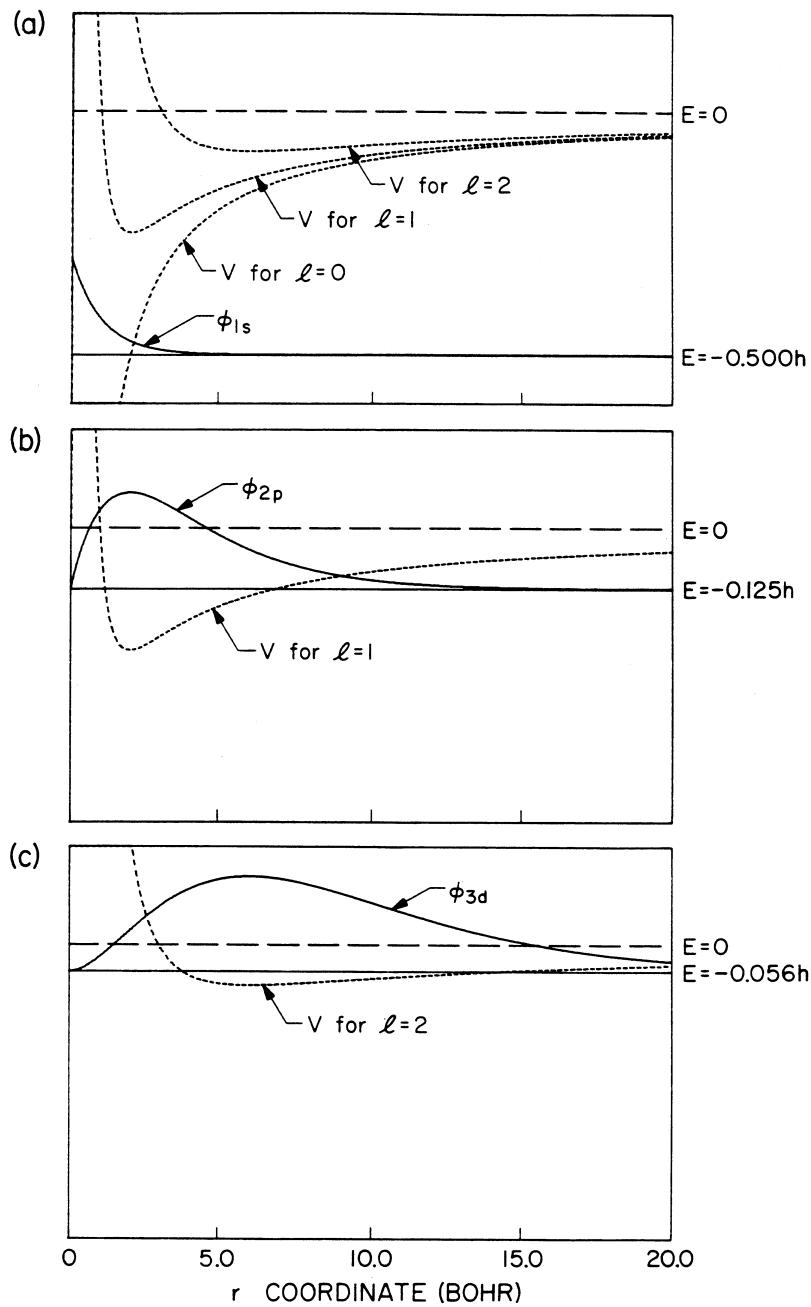


Figure 5.12: Comparison of  $1s$ ,  $2p$ , and  $3s$  orbitals and the potentials,  $V_l$ , including centrifugal terms.

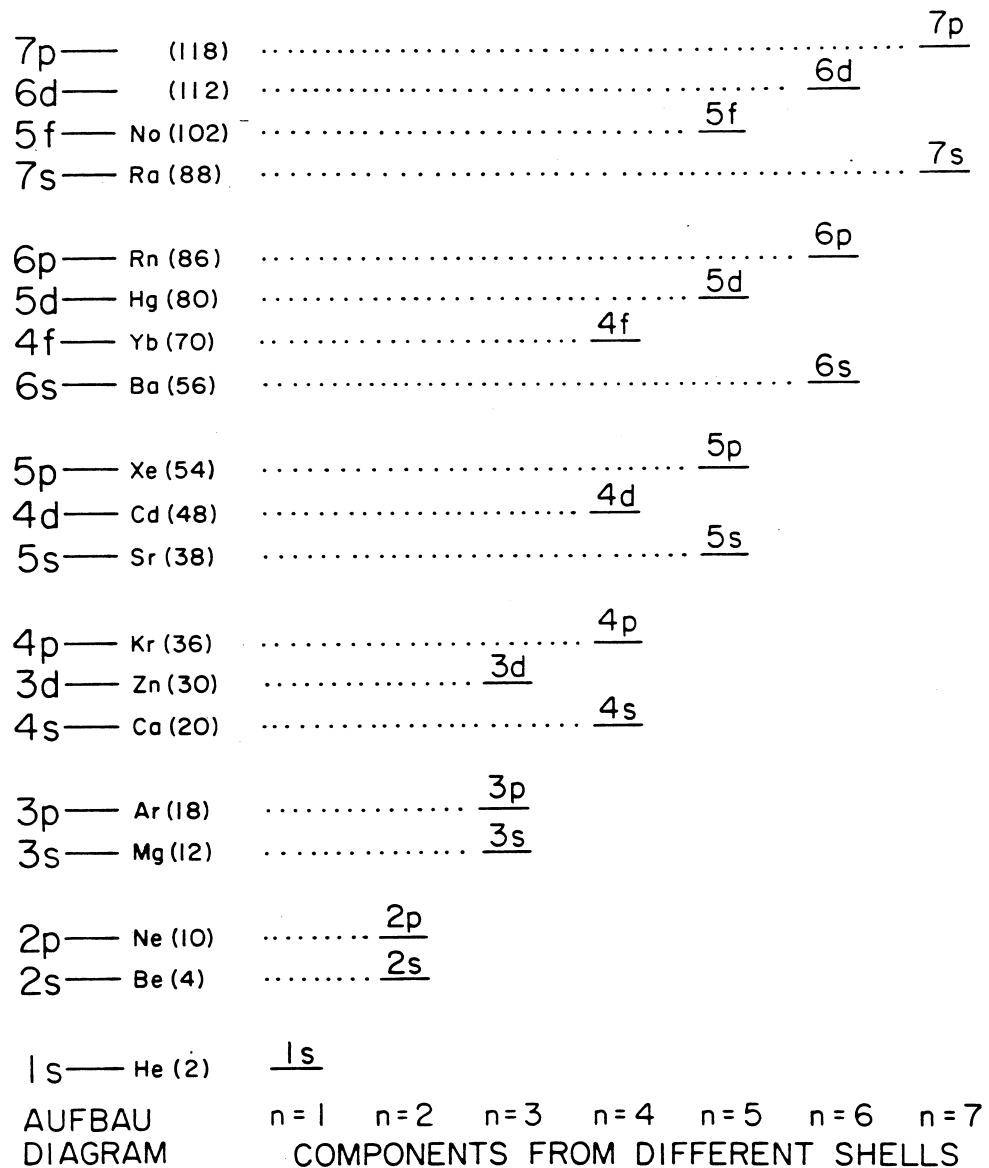


Figure 5.13: The Aufbau diagram. Also indicated is the element ( $Z$  in parentheses) for which a given level (and all deeper levels) is filled. The components for different shells are also listed separately.

The bond radius of each atom is indicated by an x on the abscissa, metallic radius for metal, covalent single-bond radius for nonmetals. All plots are to the same distance scale. However, for the Li and Be columns, an extra piece was added, the vertical dotted line shows where the cutoff would have been. The same vertical scale is used for all atoms of the same column. However, different columns may have different scales, all plots in the same figure have the same vertical scale. For the transition elements, Sc-Zn columns, the  $4s$  orbital has been multiplied by three, indicated by \*3 in the figure.

### 5.3.1 The Ground State Configurations of Atoms

In Section 5.2 we found that the exact eigenfunctions of the H atom are as follows. For  $1s$

$$E = -\frac{1}{2\hbar} = -13.6\text{eV} \quad (5.60)$$

For  $2s$ ,  $2p$

$$E = -\frac{1}{8}\hbar = -3.40\text{eV} \quad (5.61)$$

For  $3s$ ,  $3p$ , and  $3d$

$$E = -\frac{1}{18}\hbar = -1.51\text{eV} \quad (5.62)$$

and for  $4s$ ,  $4p$ ,  $4d$ , and  $4f$

$$E = -\frac{1}{32}\hbar = -0.85\text{eV} \quad (5.63)$$

with all energies relative to a free electron, plus a proton. Except for scaling of all energies by  $Z^2$ , the same results are obtained for a nucleus of arbitrary  $Z$ , still one electron, of course.

Now we want to consider a many-electron atom. In the simple approximation we might completely ignore electron repulsion effects, placing the electrons in the lowest orbitals, consistent with the Pauli principle. In this case, the  $Z$  electron atom would be built up by placing two electrons in the  $1s$  orbital, the next eight electrons in  $2s$  and  $2p$  orbitals, the next 18 into the  $3s$ ,  $3p$ , and  $3d$  orbitals, etc. In this model, there would be a sharp break after filling each  $n$  shell, since the next electron would go in a much higher orbital. Thus,  $Z = 2, 10, 28$ , and  $60$  would be particularly stable and unreactive. These  $Z$  correspond to He, Ne, Ni, and Nd, whereas in fact it is He, Ne, Ar, Kr, and Xe that are particularly stable and unreactive. Consequently, we must include electron-electron interaction effects.

Rather than include these electron repulsion effects exactly, we will include them in an average way. Each orbital will be allowed to adjust to this average electric field due to the electrons in the other orbitals.

#### Effects of Shielding

Consider, first, the case of a nucleus of charge  $Z$  with two electrons in a  $1s$  orbital. Neglecting electron-electron repulsion, this optimum  $1s$  orbital is  $e^{-Zr}$ . Including

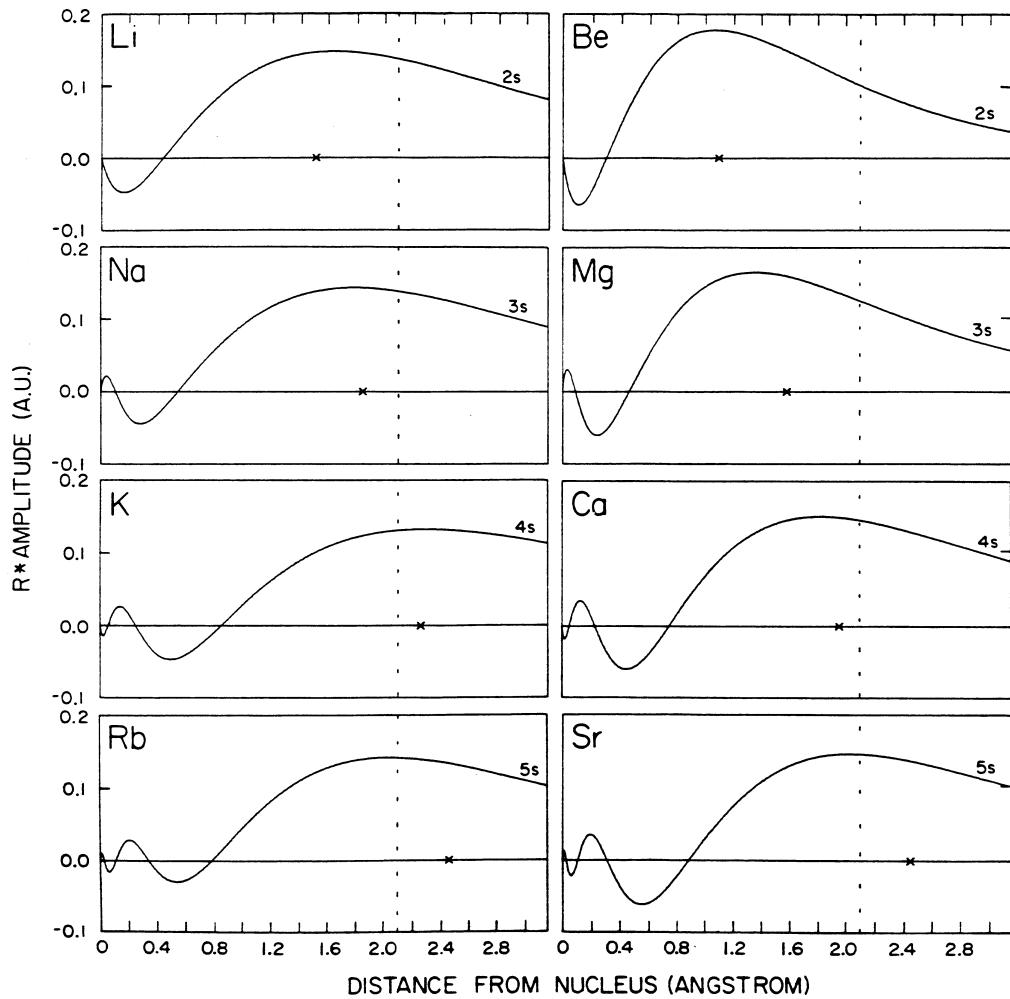


Figure 5.14: The valence orbitals of alkali and alkali earth metals. We plot  $r\phi_{nl}$  for the valence orbitals as obtained from accurate Hartree-Fock calculations. The bond radius of each atom is indicated by an x on the abscissa, metallic radius for metal, covalent single-bond radius for nonmetals.

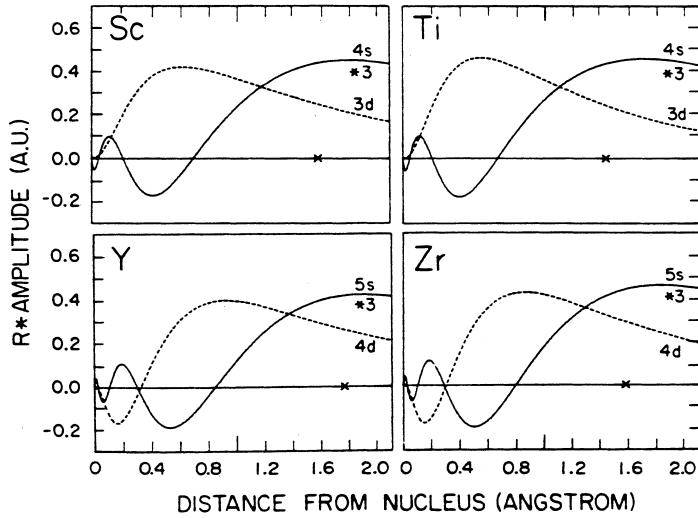


Figure 5.15: The valence orbitals of early transition metals. We plot  $r\phi_{nl}$  for the valence orbitals as obtained from accurate Hartree-Fock calculations. The bond radius of each atom is indicated by an x on the abscissa, metallic radius for metal, covalent single-bond radius for nonmetals.

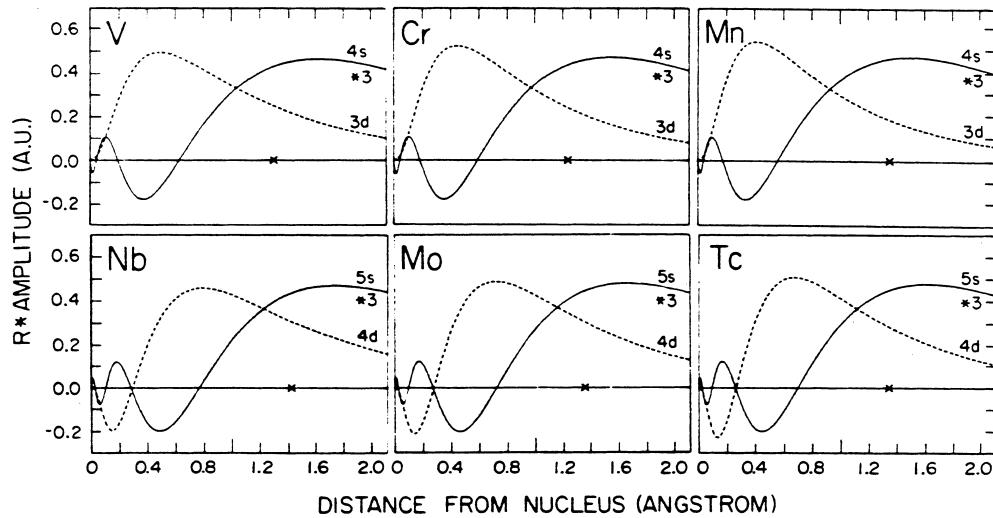


Figure 5.16: The valence orbitals of middle transition metals. We plot  $r\phi_{nl}$  for the valence orbitals as obtained from accurate Hartree-Fock calculations. The bond radius of each atom is indicated by an x on the abscissa, metallic radius for metal, covalent single-bond radius for nonmetals.

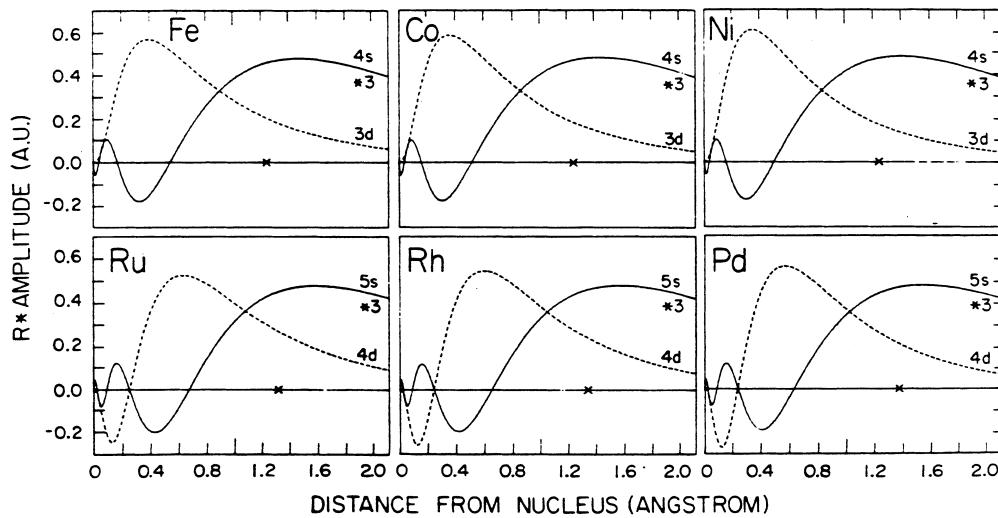


Figure 5.17: The valence orbitals of late transition metals. We plot  $r\phi_{nl}$  for the valence orbitals as obtained from accurate Hartree-Fock calculations. The bond radius of each atom is indicated by an x on the abscissa, metallic radius for metal, covalent single-bond radius for nonmetals.

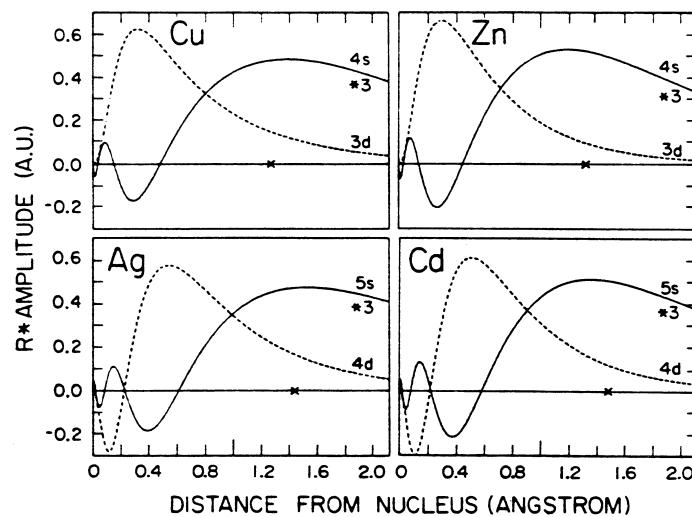


Figure 5.18: The valence orbitals of Cu, Zn, Ag, and Cd. We plot  $r\phi_{nl}$  for the valence orbitals as obtained from accurate Hartree-Fock calculations. The bond radius of each atom is indicated by an x on the abscissa, metallic radius for metal, covalent single-bond radius for nonmetals.

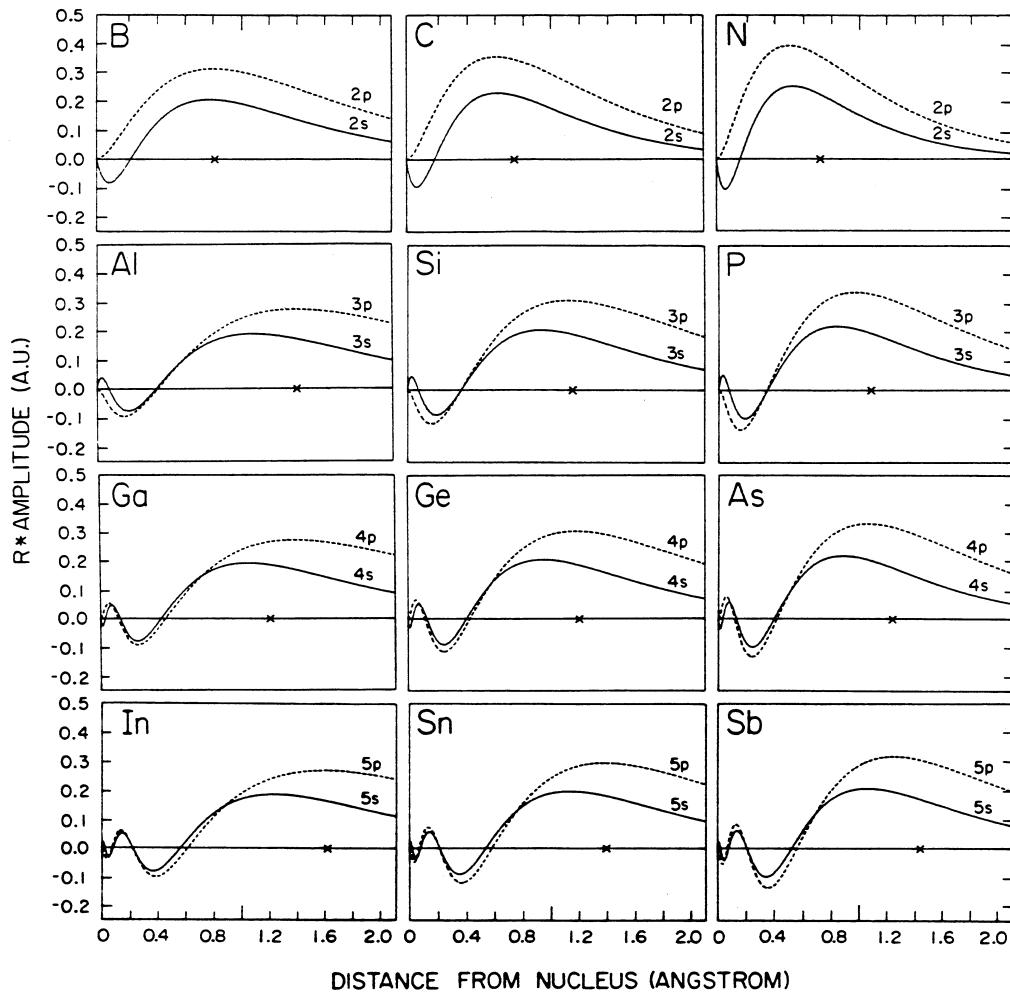


Figure 5.19: The valence orbitals of main group columns III, IV, and V. We plot  $r\phi_{nl}$  for the valence orbitals as obtained from accurate Hartree-Fock calculations. The bond radius of each atom is indicated by an x on the abscissa, metallic radius for metal, covalent single-bond radius for nonmetals.

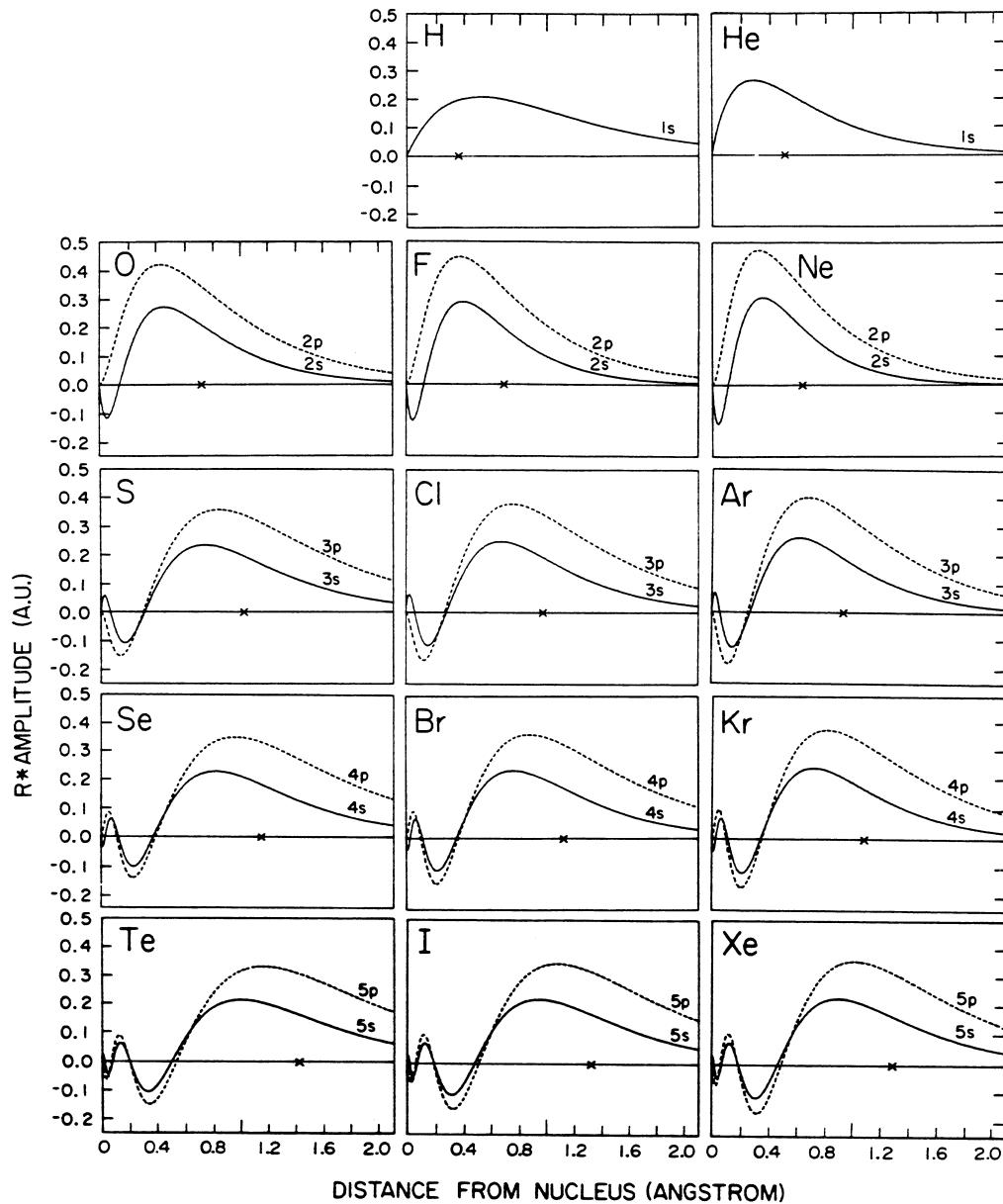


Figure 5.20: The valence orbitals of main group columns VI, VII, and VIII. We plot  $r\phi_{nl}$  for the valence orbitals as obtained from accurate Hartree-Fock calculations. The bond radius of each atom is indicated by an x on the abscissa, metallic radius for metal, covalent single-bond radius for nonmetals.

electron repulsion, the optimum orbital is  $e^{-Z^*r}$  where  $Z^* = Z - 5/16$ . Thus, the average effect of one  $1s$  electron upon the other, is equivalent to cancelling (or *shielding*)  $5/16$  of a positive charge of the nucleus.

Now consider the Li atom. Two electrons go into the  $1s$  orbital, one with each spin, and the remaining electron goes into an  $n = 2$  orbital,  $2s$  or  $2p$  orbital. If the density for the  $n = 2$  orbital were entirely outside the density of the  $1s$  orbital, then the optimum  $Z^*$  for the  $1s$  orbital would be unchanged by the  $n = 2$  orbital, while the  $1s$  electrons would completely shield two protons from the  $n = 2$  orbital. Thus, we would obtain

$$Z_{1s}^* = 3 - \frac{5}{16} = 2.69 \quad (5.64)$$

$$Z_{2s}^* = Z_{2p}^* = 3 - 2 = 1. \quad (5.65)$$

In fact, this is a good approximation for the  $2p$  orbital since this orbital goes to zero at the nucleus. However, the  $2s$  orbital is nonzero at the nucleus and has a significant density within the  $1s$  region. As a result, the  $1s$  electrons only partially shield the nucleus. The result is, for Li

$$Z_{1s}^* = 3 - \frac{5}{16} = 2.69 \quad (5.66)$$

$$Z_{2s}^* = 3 - 1.72 = 1.28 \quad (5.67)$$

$$Z_{2p}^* = 3 - 2 = 1.00. \quad (5.68)$$

Since the nucleus is less completely shielded from the  $2s$  orbital than from  $2p$ , the  $2s$  orbital is more strongly bound than  $2p$ , and hence, the ground state of Li is  $(1s)^2(2s)^1$ , while  $(1s)^2(2p)^1$  is the first excited states, 2 eV excitation energy.

Similar differential shielding effects lead to a splitting of the various  $nl$  states of H atom, having the same  $n$  with the result that for many-electron atoms, the energies satisfy

$$2s < 2p, \quad (5.69)$$

$$3s < 3p < 3d, \quad (5.70)$$

$$4s < 4p < 4d < 4f, \quad (5.71)$$

etc. In all cases, higher  $l$  leads to less penetration of the core, resulting in greater shielding by the core orbitals, leading thereby to higher energy. These  $l$ -splitting effects depend somewhat upon the precise occupation of the various orbitals, but the ground states of most atoms can be qualitatively explained by the simple *Aufbau diagram* in Figure 5.13. Magnitudes of the separations in the Aufbau diagram are not to scale.

As illustrated, the  $l$ -splitting is sometimes larger than the  $n$  splitting, resulting in the general sequences

1s,  
 2s, 2p,  
 3s, 3p  
 4s, 3d, 4p  
 5s, 4d, 5p,

$$\begin{array}{c} 6s, 4f, 5d, 6p \\ 7s, 5f, 6d, 7p \end{array} \quad (5.72)$$

where we have used separate rows to indicate a big break after filling the  $np$  orbital of each row.

### The Aufbau Principle

Using the ordering of levels in (5.72), or Figure 5.13, leads to the Aufbau principle. For an atom of atomic number  $Z$ , we fill in the lowest orbitals in Figure 5.13, allowing 2 electrons per orbital, until all electrons are used up. Counting spatial degeneracies, this allows two electrons for  $s$  shell, six electrons for  $p$  shell, ten electrons for  $d$  shells, and fourteen electrons for  $f$  shells. For example, this leads to

$$\begin{aligned} Z &= 2, \text{He} : (1s)^2 \\ Z &= 6, \text{C} : (\text{He})(2s)^2(2p)^2 \\ Z &= 10, \text{Ne} : (\text{He})(2s)^2(2p)^6 \\ Z &= 18, \text{Ar} : (\text{Ne})(3s)^2(3p)^6 \\ Z &= 26, \text{Fe} : (\text{Ar})(4s)^2(3d)^6 \\ Z &= 36, \text{Kr} : (\text{Ar})(4s)^2(3d)^10(4p)^6 \\ Z &= 54, \text{Xe} : (\text{Kr})(5s)^2(4d)^10(5p)^6 \\ Z &= 86, \text{Rn} : (\text{Xe})(6s)^2(4f)^14(5d)^10(6p)^6, \end{aligned} \quad (5.73)$$

where the configuration of the core electrons is indicated by the corresponding atomic symbol, for example (Ar) indicates the configuration of, ground state, Ar. Large gaps occur after the  $1s$ ,  $2p$ ,  $3p$ ,  $4p$ ,  $5p$ , and  $6p$ , shells are filled, resulting in particularly unreactive and stable atoms, the noble gases of He, Ne, Ar, Kr, Xe, and Rn.

Actually, things are more complicated than this. The ordering of the levels depends somewhat upon the  $Z$ , and the state of ionization of the atoms and exceptions of the simple Aufbau principle, do occur even for ground state atoms. In Table 5.8 we compiled the configurations for the ground state of each atom. Exceptions from the simple Aufbau principle are Cr, Cu, Nb, Mo, Ru, Rh, Pd, Ag, La, Gd, Pt, Au, Ac, Th, Pa, U, Np, Cm.

### 5.3.2 The Periodic Table

The ionization potentials, IP, of the elements, are listed in Table 5.6. Here we see a general build-up of ionization potentials with  $Z$ , but with sudden drops after He, Ne, Ar, Kr, Xe, and Rn. These elements, the noble gases, involve completely filled shells and are particularly inert and unreactive. The elements immediately after a noble gas, Li, Na, K, Rb, Cs, and Fr, referred to as the alkali metals, are all easily ionized, are unit reactive and tend to become positively charge in bonding to other elements. The elements immediately preceding the inert gases, H, F, Cl, Br, I, and At, all have large ionization potentials and, except for H, tend to become negatively charge upon bonding to other elements. Excepting H, these elements are referred to as halogens. Laying out the elements in successive rows, with the final elements of each row being an inert gas atom, leads to the periodic tables of Tables 4 and 5, which automatically group into

Table 5.8: The ground configurations for atoms H-Ar. Also included is the term for the ground state and the ionization potential.

	Z	Configuration	Symmetry	Lowest Orb <sup>a</sup>	IP (eV) <sup>a</sup>
H	1	(1s)	$^2S_{g\frac{1}{2}}$	1s	13.595
He	2	(1s) <sup>2</sup>	$^1S_{g0}$	1s	24.481
Li	3	(1s) <sup>2</sup> (2s)	$^2S_{g\frac{1}{2}}$	2s	5.390
Be	4	(1s) <sup>2</sup> (2s) <sup>2</sup>	$^1S_{g0}$	2s	9.320
B	5	(1s) <sup>2</sup> (2s)(2p)	$^2P_{u\frac{1}{2}}$	2p	8.296
C	6	(1s) <sup>2</sup> (2s)(2p) <sup>2</sup>	$^3P_{g0}$	2p	11.256
N	7	(1s) <sup>2</sup> (2s)(2p) <sup>3</sup>	$^4S_{u\frac{3}{2}}$	2p	14.53
O	8	(1s) <sup>2</sup> (2s)(2p) <sup>4</sup>	$^3P_{g2}$	2p	13.614
F	9	(1s) <sup>2</sup> (2s)(2p) <sup>5</sup>	$^2P_{u\frac{3}{2}}$	2p	17.418
Ne	10	(1s) <sup>2</sup> (2s)(2p) <sup>6</sup>	$^1S_g$	2p	21.559
Na	11	(Ne)(3s)	$^2S_{g\frac{1}{2}}$	3s	5.138
Mg	12	(Ne)(3s) <sup>2</sup>	$^1S_{g0}$	3s	7.644
Al	13	(Ne)(3s) <sup>2</sup> (3p)	$^2P_{u\frac{1}{2}}$	3p	5.984
Si	14	(Ne)(3s) <sup>2</sup> (3p) <sup>2</sup>	$^3P_{g0}$	3p	8.149
P	15	(Ne)(3s) <sup>2</sup> (3p) <sup>3</sup>	$^4S_{u\frac{3}{2}}$	3p	10.484
S	16	(Ne)(3s) <sup>2</sup> (3p) <sup>4</sup>	$^3P_{g2}$	3p	10.357
Cl	17	(Ne)(3s) <sup>2</sup> (3p) <sup>5</sup>	$^2P_{u\frac{3}{2}}$	3p	13.01
Ar	18	(Ne)(3s) <sup>2</sup> (3p) <sup>6</sup>	$^1S_{g0}$	3p	15.755

Table 5.9: The ground configurations for atoms K-Kr. Also included is the term for the ground state and the ionization potential.

	Z	Configuration	Symmetry	Lowest Orb <sup>a</sup>	IP (eV) <sup>a</sup>
K	19	(Ar)(4s)	$^2S_{g\frac{1}{2}}$	4s	4.339
Cs	20	(Ar)(4s) <sup>2</sup>	$^1S_{g0}$	4s	6.111
Sc	21	(Ar)(4s) <sup>2</sup> (3d)	$^2D_{g\frac{3}{2}}$	4s	6.54
Ti	22	(Ar)(4s) <sup>2</sup> (3d) <sup>2</sup>	$^3F_{g2}$	4s	6.82
V	23	(Ar)(4s) <sup>2</sup> (3d) <sup>3</sup>	$^4F_{g\frac{3}{2}}$	b	6.74
Cr	24	(Ar)(4s) <sup>2</sup> (3d) <sup>4</sup>	$^7S_{g3}$	4s	6.764
Mn	25	(Ar)(4s) <sup>2</sup> (3d) <sup>5</sup>	$^6S_{g\frac{5}{2}}$	4s	7.432
Fe	26	(Ar)(4s) <sup>2</sup> (3d) <sup>6</sup>	$^5D_{g4}$	4s	7.87
Co	27	(Ar)(4s) <sup>2</sup> (3d) <sup>7</sup>	$^4F_{g\frac{9}{2}}$	c	7.86
Ni	28	(Ar)(4s) <sup>2</sup> (3d) <sup>8</sup>	$^3F_{g4}$	d	7.633
Cu	29	(Ar)(4s)(3d) <sup>10</sup>	$^2S_{g\frac{1}{2}}$	4s	7.724
Zn	30	(Ar)(4s) <sup>2</sup> (3d) <sup>10</sup>	$^1S_{g0}$	4s	9.391
Ga	31	(Ar)(4s) <sup>2</sup> (3d) <sup>10</sup> (4p)	$^2P_{u\frac{1}{2}}$	4p	6.00
Ge	32	(Ar)(4s) <sup>2</sup> (3d) <sup>10</sup> (4p) <sup>2</sup>	$^3P_{g0}$	4p	7.88
As	33	(Ar)(4s) <sup>2</sup> (3d) <sup>10</sup> (4p) <sup>3</sup>	$^4S_{u\frac{3}{2}}$	4p	9.81
Se	34	(Ar)(4s) <sup>2</sup> (3d) <sup>10</sup> (4p) <sup>4</sup>	$^3P_{g0}$	4p	9.75
Br	35	(Ar)(4s) <sup>2</sup> (3d) <sup>10</sup> (4p) <sup>5</sup>	$^2P_{u\frac{3}{2}}$	4p	11.84
Kr	36	(Ar)(4s) <sup>2</sup> (3d) <sup>10</sup> (4p) <sup>6</sup>	$^1S_{g0}$	4p	13.996

Table 5.10: The ground configurations for atoms Rb-Xe. Also included is the term for the ground state and the ionization potential.

	Z	Configuration	Symmetry	Lowest Orb <sup>a</sup>	IP (eV) <sup>a</sup>
Rb	37	(Kr)(5s)	$^2S_{g\frac{1}{2}}$	5s	4.176
Sr	38	(Kr)(5s) <sup>2</sup>	$^1S_{g0}$	5s	5.692
Y	39	(Kr)(5s) <sup>2</sup> (4d)	$^2D_{g\frac{3}{2}}$	4d	6.38
Zr	40	(Kr)(5s) <sup>2</sup> (4d) <sup>2</sup>	$^3F_{g2}$	5s	6.84
Nb	41	(Kr)(5s) <sup>1</sup> (4d) <sup>4</sup>	$^6D_{g\frac{1}{2}}$	5s	6.88
Mo	42	(Kr)(5s) <sup>1</sup> (4d) <sup>5</sup>	$^7S_{g3}$	5s	7.10
Tc	43	(Kr)(5s) <sup>2</sup> (4d) <sup>5</sup>	$^6S_{g\frac{5}{2}}$	5s	7.28
Ru	44	(Kr)(5s) <sup>1</sup> (4d) <sup>7</sup>	$^5F_{g5}$	5s	7.364
Rh	45	(Kr)(5s) <sup>1</sup> (4d) <sup>8</sup>	$^4F_{g\frac{9}{2}}$	5s	7.46
Pd	46	(Kr)(5s) <sup>0</sup> (4d) <sup>10</sup>	$^1S_{g9}$	4d	8.33
Ag	47	(Kr)(5s) <sup>1</sup> (4d) <sup>10</sup>	$^2S_{g\frac{1}{2}}$	5s	7.574
Cd	48	(Kr)(5s) <sup>2</sup> (4d) <sup>10</sup>	$^1S_{g0}$	5s	8.991
In	49	(Kr)(5s) <sup>2</sup> (4d) <sup>10</sup> (5p)	$^2P_{u\frac{1}{2}}$	5p	5.785
Sn	50	(Kr)(5s) <sup>2</sup> (4d) <sup>10</sup> (5p) <sup>2</sup>	$^3P_{g0}$	5p	7.342
Sb	51	(Kr)(5s) <sup>2</sup> (4d) <sup>10</sup> (5p) <sup>3</sup>	$^4S_{u\frac{3}{2}}$	5p	8.639
Te	52	(Kr)(5s) <sup>2</sup> (4d) <sup>10</sup> (5p) <sup>4</sup>	$^3P_{g2}$	5p	9.01
I	53	(Kr)(5s) <sup>2</sup> (4d) <sup>10</sup> (5p) <sup>5</sup>	$^2P_{u\frac{3}{2}}$	5p	10.454
Xe	54	(Kr)(5s) <sup>2</sup> (4d) <sup>10</sup> (5p) <sup>6</sup>	$^1S_{g0}$	5p	12.127

Table 5.11: The ground configurations for atoms Cs-Rn. Also included is the term for the ground state and the ionization potential.

	Z	Configuration	Symmetry	Lowest Orb <sup>a</sup>	IP (eV) <sup>a</sup>
Cs	55	(Xe)(6s)	$^2S_{g\frac{1}{2}}$	6s	3.893
Ba	56	(Xe)(6s) <sup>2</sup>	$^1S_{g0}$	6p	5.21
La	57	(Xe)(6s) <sup>2</sup> (5d)	$^2D_{g\frac{3}{2}}$	e	5.61
Ce	58	(Xe)(6s) <sup>2</sup> (4f) <sup>2</sup>	6p	5.6	
Pr	59	(Xe)(6s) <sup>2</sup> (4f) <sup>3</sup>	6p	5.46	
Nd	60	(Xe)(6s) <sup>2</sup> (4f) <sup>4</sup>	$^5I_{g4}$	6p	5.51
Pm	61	(Xe)(6s) <sup>2</sup> (4f) <sup>5</sup>	6p	-	
Sm	62	(Xe)(6s) <sup>2</sup> (4f) <sup>6</sup>	$^7F_{g0}$	6p	5.6
Eu	63	(Xe)(6s) <sup>2</sup> (4f) <sup>7</sup>	$^8S_{u\frac{7}{2}}$	6p	5.67
Gd	64	(Xe)(6s) <sup>2</sup> (4f) <sup>7</sup> (5d)	$^9D_{u2}$	6p	6.16
Tb	65	(Xe)(6s) <sup>2</sup> (4f) <sup>9</sup>	6p	5.98	
Dy	66	(Xe)(6s) <sup>2</sup> (4f) <sup>10</sup>	6p	6.8	
Ho	67	(Xe)(6s) <sup>2</sup> (4f) <sup>11</sup>	6p	-	
Er	68	(Xe)(6s) <sup>2</sup> (4f) <sup>12</sup>	6p	6.08	
Tm	69	(Xe)(6s) <sup>2</sup> (4f) <sup>13</sup>	$^2F_{u\frac{7}{2}}$	6p	5.81
Yb	70	(Xe)(6s) <sup>2</sup> (4f) <sup>14</sup>	$^1S_{g0}$	6p	6.2
Lu	71	(Xe)(6s) <sup>2</sup> (4f) <sup>14</sup> (5d)	$^2D_{g\frac{5}{2}}$	6p	-
Hf	72	(Xe)(6s) <sup>2</sup> (4f) <sup>14</sup> (5d) <sup>2</sup>	$^3F_{g2}$	5d	7
Ta	73	(Xe)(6s) <sup>2</sup> (4f) <sup>14</sup> (5d) <sup>3</sup>	$^4F_{g\frac{3}{2}}$	6s	7.88
W	74	(Xe)(6s) <sup>2</sup> (4f) <sup>14</sup> (5d) <sup>4</sup>	$^5D_{g0}$	6s	7.96
Re	75	(Xe)(6s) <sup>2</sup> (4f) <sup>14</sup> (5d) <sup>5</sup>	$^6S_{g\frac{5}{2}}$	6s	7.87
Os	76	(Xe)(6s) <sup>2</sup> (4f) <sup>14</sup> (5d) <sup>6</sup>	$^5D_{g4}$	6s	8.5
Ir	77	(Xe)(6s) <sup>2</sup> (4f) <sup>14</sup> (5d) <sup>7</sup>	$^4F_{g\frac{3}{2}}$	6s	9
Pt	78	(Xe)(6s)(4f) <sup>14</sup> (5d) <sup>9</sup>	$^3D_{g3}$	6s	9.0
Au	79	(Xe)(6s)(4f) <sup>14</sup> (5d) <sup>10</sup>	$^2S_{g\frac{1}{2}}$	6s	9.22
Hg	80	(Xe)(6s) <sup>2</sup> (4f) <sup>14</sup> (5d) <sup>10</sup>	$^1S_{g0}$	6s	10.43
Tl	81	(Xe)(6s) <sup>2</sup> (4f) <sup>14</sup> (5d) <sup>10</sup> (6p)	$^2P_{u\frac{1}{2}}$	6p	6.106
Pb	82	(Xe)(6s) <sup>2</sup> (4f) <sup>14</sup> (5d) <sup>10</sup> (6p) <sup>2</sup>	$^3P_{g0}$	6p	7.415
Bi	83	(Xe)(6s) <sup>2</sup> (4f) <sup>14</sup> (5d) <sup>10</sup> (6p) <sup>3</sup>	$^4S_{u\frac{3}{2}}$	6p	7.287
Po	84	(Xe)(6s) <sup>2</sup> (4f) <sup>14</sup> (5d) <sup>10</sup> (6p) <sup>4</sup>	6p	9.43	
At	85	(Xe)(6s) <sup>2</sup> (4f) <sup>14</sup> (5d) <sup>10</sup> (6p) <sup>5</sup>	6p	9.5	
Rn	86	(Xe)(6s) <sup>2</sup> (4f) <sup>14</sup> (5d) <sup>10</sup> (6p) <sup>6</sup>	$^1S_{g0}$	6p	10.746

Table 5.12: The ground configurations for atoms Fr-. Also included is the term for the ground state and the ionization potential.

	Z	Configuration	Symmetry	Lowest Orb <sup>a</sup>	IP (eV) <sup>a</sup>
Fr	87	(Rn)(7s)		7p	4
Ra	88	(Rn)(7s) <sup>2</sup>	<sup>1</sup> S <sub>g0</sub>	7s	5.277
Ac	89	(Rn)(7s) <sup>2</sup> (6d)		6d	6.9
Th	90	(Rn)(7s) <sup>2</sup> (6d) <sup>2</sup>	<sup>3</sup> F <sub>g2</sub>		6.95
Pa	91	(Rn)(7s) <sup>2</sup> (5f) <sup>2</sup> (6d)			
U	92	(Rn)(7s) <sup>2</sup> (5f) <sup>3</sup> (6d)	<sup>5</sup> L <sub>u6</sub>		6.08
Np	93	(Rn)(7s) <sup>2</sup> (5f) <sup>4</sup> (6d)			-
Pu	94	(Rn)(7s) <sup>2</sup> (5f) <sup>6</sup>			5.1
Am	95	(Rn)(7s) <sup>2</sup> (5f) <sup>7</sup>			
Cm	96	(Rn)(7s) <sup>2</sup> (5f) <sup>7</sup> (6d)			
Bk	97	(Rn)(7s) <sup>2</sup> (5f) <sup>9</sup>			
Cf	98	(Rn)(7s) <sup>2</sup> (5f) <sup>10</sup>			
Ed	99	(Rn)(7s) <sup>2</sup> (5f) <sup>11</sup>			
Fm	100	(Rn)(7s) <sup>2</sup> (5f) <sup>12</sup>			
Md	101	(Rn)(7s) <sup>2</sup> (5f) <sup>13</sup>			
No	102	(Rn)(7s) <sup>2</sup> (5f) <sup>14</sup>			
Lr	103	(Rn)(7s) <sup>2</sup> (5f) <sup>14</sup> (6d)			
-	104	(Rn)(7s) <sup>2</sup> (5f) <sup>14</sup> (6d) <sup>2</sup>			

<sup>a</sup>Lowest ionizaton columns.

<sup>b</sup>The lowest state of  $V^+$  is  $(3d)^4$ , thus starting with the ground state of  $V$  we ionize one 4s and excite the other to 3d, in order to obtain the ground state of  $V^+$ .

<sup>c</sup>The lowest state of  $\text{Co}^+$  is  $(3d)^8$ .

<sup>d</sup>The lowest state of  $\text{Ni}^+$  is  $(3d)^9$ .

<sup>e</sup>The lowest state of the ion is  $(3d)^2$ .

columns, those elements with similar chemistry. The elements of each column of these tables, have a similar valence configuration, and hence, similar chemistry.

In Figures 5.14–5.20 we showed the shapes of the valence orbitals of H–Xe, arranged in the pattern dictated by the periodic table. Note that rather than writing the orbitals

$$\phi_{nlm} = R_{nl}(r)Z_{lm}(\theta, \varphi), \quad (5.74)$$

the orbitals plotted in these figures, are  $r\phi_{nlm}$ . That is, we show  $ns$ ,  $np_z$ ,  $nd_{z^2}$ , etc., and a factor of  $r$  has been included. Since the normalization integral is

$$1 = \int r^2 dr d\Omega |\phi_{nlm}|^2 = \int dr d\Omega |r\phi_{nlm}|^2, \quad (5.75)$$

the magnitude of  $(r\phi)^2$  provides the relative probability of the electron being in the spherical shell, at a distance  $r$  from the nucleus.

There are three points to note in these figures. First, the orbital always contract as we go from left to right in the same row of the periodic table. In the next section, we will see that this is due to incomplete shielding of the additional nuclear charge by the additional valence electrons. Second, the orbitals generally, but not always, get larger as we go down a column. Third, the  $3d$  orbitals are much more compact than  $4s$ , and the  $4d$  orbitals are much more compact than  $5s$ . However, the relative sizes are less disparate in the fourth Pd row, than in the third Ni row.

### 5.3.3 Shielding and Orbitals Sizes

#### Shielding

There are various ways of defining shielding. For example, we might write the experimental ionization potential, from the  $nl$  orbital, as

$$\text{IP}_{nl} = \frac{(Z^{\text{eff}})^2}{2n^2} \quad (5.76)$$

where

$$Z^{\text{eff}} = Z - \Sigma \quad (5.77)$$

and  $\Sigma$  is the shielding. There are some ambiguities with this, since the ionization potentials, from deeper orbitals, are not always known experimentally.

As an alternative, in this section, we have used the result of theoretical calculations. Optimizing the scale factor  $\zeta_{nl}$ , for Slater basis functions

$$r^n e^{-\zeta_{nl}r} \quad (5.78)$$

minimum basis set, we define the shielding  $\Sigma_{nl}$  such that

$$Z_{nl}^{\text{eff}} = n\zeta_{nl} = Z - \Sigma_{nl}. \quad (5.79)$$

The shielding  $\Sigma_{nl}$  is fitted as

$$\Sigma_{nl} = \sum_{\bar{n}\bar{l}} N_{\bar{n}\bar{l}} \sigma_{\bar{n}\bar{l},nl}, \quad (5.80)$$

Table 5.13: Shielding effects

Orbital	Shielding due to electrons of various shells
1s	$\sigma_{1s} = 0.31$
2s	$\sigma_{He} = 1.72, \sigma_{2s} = 0.36, \sigma_{2p} = 0.36$
2p	$\sigma_{He} = 2.00, \sigma_{2s} = 0.30, \sigma_{2p} = 0.33$
3s	$\sigma_{Ne} = 9.49, \sigma_{3s} = 0.20, \sigma_{3p} = 0.26$
3p	$\sigma_{Ne} = 8.89, \sigma_{3p} = 0.25, \sigma_{3p} = 0.37$
4s	$\sigma_{Ar} = 15.50, \sigma_{3d} = 0.84, \sigma_{4s} = 0.10, \sigma_{4p} = 0.11$
3d	$\sigma_{Ar} = 13.87, \sigma_{3d} = 0.25, \sigma_{4s} = 0, \sigma_{4p} = 0.13$
4p	$\sigma_{Ar} = 15.68, \sigma_{3d} = 0.89, \sigma_{4s} = 0.10, \sigma_{4p} = 0.29$

These values were deduced from Clementi and Raimondi.<sup>4</sup> Using the valence orbitals of the ground configuration, the optimum  $\zeta_{nl}$  was converted into an effective charge defined by

$$Z^* = n\zeta_{nl} = Z - \sum_i \sigma_i. \quad (5.81)$$

These  $\sigma_i$  reproduce the optimum  $Z^*$  to approximately 0.1.

where  $N_{\bar{n}\bar{l}}$  is the number of electrons in the  $\bar{n}\bar{l}$  orbital, but excluding  $nl$ , and individual contributions  $\sigma_{\bar{n}\bar{l},nl}$  are assumed independent of this atom. The results are in Table 5.13. In fact, the shielding contributions  $\sigma_{\bar{n}\bar{l},nl}$  should be allowed to depend upon the particular atom, and even upon the state of that atom. However, the fixed shielding constants are of some use for qualitative arguments.

Three important points to note are:

1. For the 2s orbital  $\sigma_{He} = 1.72$ , whereas for the 2p orbital  $\sigma_{He} = 2.00$ . Thus, the 2s orbital penetrate the He core more than the 2p orbital.
2. For the transition metals, the 3d orbitals penetrate the Ar core more than the 4s and 4p orbitals,  $\sigma_{Ar} = 13.87$  for 3d compared to 15.50 and 15.68 for 4s and 4p. This is expected, since the 3s and 3p orbitals of the Ar core have the same  $n$  as the 3d orbital.
3. The 3d orbitals are very effective in shielding the 4s and 4p orbitals,  $\sigma = 0.84$  and 0.89, respectively, but not effective in shielding each other,  $\sigma = 0.25$ .

### Orbital Sizes

The hydrogen orbitals have a size

$$\bar{r}_{nl} = \frac{n^2}{Z} \quad (5.82)$$

in atomic units. For many-electron atoms, we can estimate the size from  $Z^*$  using

$$\bar{r}_{nl} = \frac{n^2}{Z^*}. \quad (5.83)$$

Thus, for Li atom

$$\bar{r}_{1s} = \frac{1}{2.69} = 0.37a_0 = 0.20\text{\AA} \quad (5.84)$$

and

$$\bar{r}_{2s} = \frac{4}{1.28} = 3.137a_0 = 1.65\text{\AA} \quad (5.85)$$

Since the  $2s$  orbital is eight times larger than the  $1s$  orbital, it is the  $2s$  orbital that will be important in the chemistry of Li compounds. On the other hand,  $2s$  and  $2p$  orbitals are of comparable size, and both sets of orbitals must be included in analyzing bonding in first row atoms, Li–Ne. Thus, for these atoms, the  $2s$  and  $2p$  orbitals are referred to as *valence orbitals*.

Because of incomplete shielding, the effective charge seen by the valence orbitals, increases with  $Z$ . Hence, the orbitals size decreases with increasing  $Z$ . For example, the  $2s$  orbitals see effective charges of 1.28, 1.92, 2.28, 2.64, 3.00, 3.36, 4.00, and 4.64, as we go from Li to Ne. The result is a marked decrease in the size of the  $2s$  orbital. Using (5.83), we expect the  $2s$  orbital of Li to be  $\approx 4.64/1.28 = 3.6$  times as large as the  $2s$  orbital of Ne. Indeed, as shown in Figures 5.14–5.20, this is approximately the case. The same effects occur also for the  $2p$  orbitals.

The sequence Na–Ar behaves similarly to Li–Ne. The valence orbitals are  $3s$  and  $3p$ , and they also contract as we move to the right, in the periodic table.

Now consider the K atom. Adding an electron to Ar, we could put it in either a  $3d$  or a  $4s$  orbital. From Table 5.13, the  $4s$  and  $3d$  orbitals should have

$$Z_{4s}^{\text{eff}} = 19 - 15.50 = 3.50 \quad (5.86)$$

$$Z_{3d}^{\text{eff}} = 19 - 13.87 = 5.13. \quad (5.87)$$

Thus, using (5.83)

$$r_{3d} = \frac{9}{5.13} = 1.75a_0 \quad (5.88)$$

$$r_{4s} = \frac{16}{3.50} = 4.57a_0 \quad (5.89)$$

we see that the  $4s$  orbitals is approximately 2.5 times as large as the  $3d$  orbital. This trend remains valid through the transition elements. Thus, for Ni,  $s^2d^8$ , we have

$$Z_{4s}^{\text{eff}} = 28 - 22.3 = 5.7 \quad (5.90)$$

$$Z_{3d}^{\text{eff}} = 28 - 15.6 = 12.4 \quad (5.91)$$

leading to

$$r_{3d} = .73a_0 \quad (5.92)$$

$$r_{4s} = 2.80a_0. \quad (5.93)$$

Considering

$$Z^{\text{eff}} = 3.5 \quad (5.94)$$

for K with

$$Z_{4s}^{\text{eff}} = 5.7 \quad (5.95)$$

Table 5.14: IPs from various states of K, Ca, and Sc.

	Orbital <sup>c</sup>	Energy <sup>d</sup>	$Z_{\text{eff}}^a$	$\delta^b$
		eV	h	
K	4s	-4.34	-0.1595	2.26
	4p	-2.73	-0.1003	1.79
	5s	-1.73	-0.0636	1.78
	3d	-1.67	-0.0614	1.05
Ca <sup>+</sup>	4s	-11.87	-0.4362	3.74
	3d	-10.17	-0.3738	2.59
	4p	-8.73	-0.3208	3.20
Sc <sup>++</sup>	3d	-24.75	-0.9096	4.05
	4s	-21.58	-0.7931	5.04
	4p	-17.01	-0.6251	4.47
Sc <sup>+</sup>	(3d)(4s) <sup>3</sup> D	-12.89	-0.4737	3.89
	(3d) <sup>2</sup> <sup>3</sup> F	-12.28	-0.4513	2.85
	(3d)(4p) <sup>1</sup> D <sup>0</sup>	-9.66	-0.3550	3.37
Sc	(3d)(4s) <sup>2</sup> <sup>2</sup> D	-6.56	-0.2411	2.78
	(3d) <sup>2</sup> (4s) <sup>4</sup> F	-5.12	-0.1882	1.84
	(3d)(4s)(4p) <sup>4</sup> F <sup>0</sup>	-4.59	-0.1687	2.32
	(3d) <sup>3</sup> <sup>4</sup> F			

<sup>a</sup>The effective charge  $Z_{\text{eff}}$  is calculated from  $\text{IP}_{nl} = \frac{(Z_{\text{eff}})^2}{2n^2}$  in atomic units. <sup>b</sup>The quantum defect  $\delta$  is calculated from  $\text{IP}_{nl} = \frac{1}{2(n-\delta)^2}$ . <sup>c</sup>For cases with more than one electron, the orbital to be ionized (leading to the ground state of the ion) is underlined.

<sup>d</sup>All energies are relative to the lowest state of the corresponding ion.

for Ni, we see that there is not a major contraction of the 4s orbital, as we go from K through the transition metals; see Figures 5.14–5.20. The reason is that the 3d orbital is very much smaller than the 4s orbital, so that each additional 3d electron nearly completely shields the corresponding increase in nuclear charge. On the other hand, for Sc

$$Z_{3d}^{\text{eff}} = 21 - 13.87 = 7.13, \quad (5.96)$$

while for Ni

$$Z_{3d}^{\text{eff}} = 12.4, \quad (5.97)$$

leading to a decrease of  $7.13/12.40 = 58\%$  in the size of the 3d orbital from Sc to Ni.

### 5.3.4 Special Points About Transition Metals

The Aufbau principle implies the 4s orbital is filled first, and then, the 3d shell. However, for all elements K through Zn, the 4s orbital is the easiest to ionize. This apparent contradiction will be examined next.

Consider first the K atom. The low-lying states, all energies referenced with respect

to K<sup>+</sup>, are listed in Table 5.14. The effective charge  $Z_{\text{eff}}$ , is defined by

$$\text{IP}_{nl} = \frac{(Z_{\text{eff}})^2}{2n^2} \quad (5.98)$$

is also listed. In this section, the effective charge  $Z_{\text{eff}}$  is obtained from experimental ionization potentials using (5.98), whereas in the previous section, the  $Z^*$  were based on orbital sizes from theoretical calculations. The current approach is more useful for quantitative considerations.

Thus, the 3d orbital sees an effective charge of 1.05, the nucleus being essentially shielded by the core orbitals. The 4s orbital, however, has a significant penetration of the core, leading to

$$Z_{4s}^{\text{eff}} = 2.26. \quad (5.99)$$

Since

$$\text{IP}_{3d} = \frac{1}{2} \left( \frac{Z_{3d}^{\text{eff}}}{3} \right)^2, \quad (5.100)$$

and

$$\text{IP}_{4s} = \frac{1}{2} \left( \frac{Z_{4s}^{\text{eff}}}{4} \right)^2, \quad (5.101)$$

the 4s orbital will be deeper, harder to ionize, as long as

$$Z_{4s}^{\text{eff}} > \frac{4}{3} Z_{3d}^{\text{eff}}. \quad (5.102)$$

This is true for K, and the 4s orbital is 2.7 eV deeper, harder to ionize, than 3d. For Ca<sup>+</sup>, Sc<sup>++</sup>, etc., the difference between the 4s and 3d, effective charges, remains about one,

$$Z_{4s}^{\text{eff}} - Z_{3d}^{\text{eff}} \approx 1, \quad (5.103)$$

however, the total effective charges increase faster than  $Z$ , since the 4s and 3d orbitals become relatively tighter for the highly ionized cases, thereby leading to a greater penetration of the core. Using (5.102) and (5.103), the 3d orbital will be deeper when

$$Z_{3d}^{\text{eff}} > 3. \quad (5.104)$$

As a result, Sc<sup>++</sup>, Ti<sup>+++</sup>, etc., all have the valence electron in the 3d orbital, whereas K and Ca<sup>+</sup> have the valence electron in 4s.

Another illustrative case is to compare Sc, Sc<sup>+</sup>, and Sc<sup>++</sup>, Table 5.14. Again, as in (5.103), here

$$Z_{3d}^{\text{eff}} = 1.84 \quad (5.105)$$

for Sc, 2.85 for Sc<sup>+</sup>, and 4.05 for Sc<sup>++</sup>. Thus, 4s is much better than 3d for Sc, they are nearly degenerate, 4s lower, for Sc<sup>+</sup>, and 3d is much deeper for Sc<sup>++</sup>.

As a result of this effect, the lowest states of the doubly ionized ions Sc<sup>++</sup>, Ti<sup>+++</sup>, ..., Zn<sup>++</sup>, are all  $d^n$ , no valence electrons in 4s, despite the fact that for the neutral, most of these atoms have two electrons in 4s.

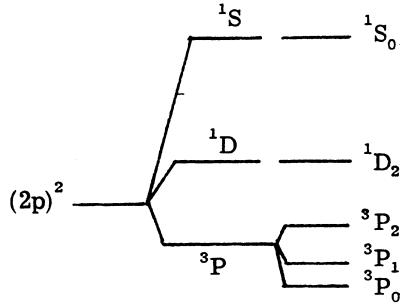


Figure 5.21:

## 5.4 LSJ States of Atoms, Hund's Rule

From the previous section, we were content to determine the ground configurations of the various atoms. For example, for C,

$$(1s)^2(2s)^2(2p)^2, \quad (5.106)$$

and for Ni

$$(1s)^2(2s)^2(2p)^6(3s)^3(3p)^6(3d)^8(4s)^2. \quad (5.107)$$

In fact, however, each such configuration may give rise to several states having energies differing by several electron volts, eV. These states are characterized by a total spatial, or orbital, angular momentum L, a total spin angular momentum S, and a total angular momentum J. Using the symbols (note that J is excluded from this sequence) S, P, D, F, G, H, I, K, ..., to denote  $L = 0, 1, 2, 3, 4, 5, 6, 7, \dots$ , the atomic states are labelled as

$$2s+1L_J. \quad (5.108)$$

Thus, the state with  $L = 1, S = 1$ , and  $J = 2$ , is denoted as  $^3P_2$ . The  $p^2$  configuration (e.g., C, Si, or Ge) leads to  $^1S$ ,  $^1D$ , and  $^3P$  states, as indicated in Figure 5.21, with  $^3P$  lowest.  $p^3$  leads to  $^4S$ ,  $^2D$ , and  $^2P$  states, as in Figure 5.22, with  $^4S$  lowest.  $p^4$  leads to the same states  $^3P$ ,  $^1D$ ,  $^1S$  as  $p^2$ , but  $^3P_2$  is lowest, rather than  $^3P_1$ . On the other hand,  $p^1$  and  $p^5$  lead only to  $^2P$ ,  $J = 3/2, 1/2$ , with  $J = 1/2$  lower for  $p^1$ , and  $J = 3/2$  lower for  $p^5$ .

Summarizing, the LS states for  $p^n$  configurations are

$$\begin{array}{ll} p^1, p^5 & : \quad ^2P \\ p^2, p^4 & : \quad ^3P, ^1D, ^1S \\ p^3 & : \quad ^4S, ^2D, ^2P. \end{array} \quad (5.109)$$

The allowed symmetries for various  $d^n$  configurations are:

$$\begin{array}{ll} d, d^9 & : \quad ^2D \\ d^2, d^3 & : \quad ^3F, ^3P, ^1G, ^2D, ^1S \end{array}$$

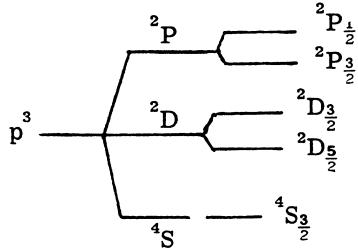


Figure 5.22:

$$\begin{aligned}
 d^3, d^7 &: {}^4F, {}^4P, {}^2H, {}^2G, {}^2F, {}^2D, {}^2D, {}^2P \\
 d^4, d^6 &: {}^5D, {}^3H, {}^3G, {}^3F, {}^3F, {}^3D, {}^3P, {}^3P, {}^1I, {}^1G, {}^1G, {}^1F, {}^1D, {}^1D, {}^1S, {}^1S \\
 d^5 &: {}^6S, {}^4G, {}^4F, {}^4D, {}^4P, {}^2I, {}^2H, {}^2G, {}^2G, {}^2F, {}^2D, {}^2D, {}^2P, {}^2S. \quad (5.110)
 \end{aligned}$$

In all cases, the ground state symmetry is listed first, but the higher states are not necessarily in the order given.

A useful rule for remembering which LS state is the ground state of an atom is *Hund's rule*. Consider the configuration of orthogonal orbitals corresponding to the ground state of an atom.

**The S rule** Of all the LS eigenstates resulting from this configuration, the lowest state is the one with the largest  $S$ .

**The L rule** If there is more than one  $L$  corresponding to this largest  $S$ , then the lowest state is the one with the largest  $L$ .

**The J rule** Of the various  $J$  states arising from the values of  $S$  and  $L$  obtained in the first two rules, the lowest state is the one of minimum  $J$ , if the configuration is less than half full, and the one of maximum  $J$ , configuration is more than half full.

We will now examine the physical basis for Hund's rules.

### 5.4.1 The $S$ Rule

High spin implies symmetric spin functions. Because of the Pauli principle, this implies antisymmetric spatial functions. Since antisymmetric spatial functions lead to exchange integrals with negative signs, we see that highest spin is good, as in the first rule. For example, the triplet state,  $S = 1$ , of the  $xy$  configuration

$$\mathcal{A}[xy\alpha\alpha] = (xy - yx)\alpha\alpha \quad (5.111)$$

leads to

$$E = h_{xx} + h_{yy} + J_{xy} - K_{xy} \quad (5.112)$$

while the single state,  $S = 0$ , for the configuration

$$\mathcal{A}[xy(\alpha\beta - \beta\alpha)] = (xy + yx)(\alpha\beta - \beta\alpha) \quad (5.113)$$

leads to an energy of

$$E = h_{xx} + h_{yy} + J_{xy} + K_{xy}, \quad (5.114)$$

$2K_{xy}$  higher than the triplet state.

The high spin state is better because the electrons in the high spin wavefunction tend to stay further apart. This can be seen by writing

$$x(1) = f(r_1\theta_1) \cos \varphi_1 \quad (5.115)$$

$$y(2) = f(r_2\theta_2) \sin \varphi_2 \quad (5.116)$$

so that the spatial wavefunction for the triplet state is

$$\begin{aligned} (xy - yx) &= f(1)f(2)[\cos \varphi_1 \sin \varphi_2 - \sin \varphi_2 \cos \varphi_1] \\ &= f(1)f(2)\sin(\varphi_2 - \varphi_1) \end{aligned} \quad (5.117)$$

whereas the spatial wavefunction for the singlet state is

$$(xy + yx) = f(1)f(2)\sin(\varphi_e + \varphi_1). \quad (5.118)$$

Thus, for the triplet state, the electrons cannot have  $\varphi_2 = \varphi_1$ , and their motions are such that  $\varphi_2$  and  $\varphi_1$  tend to be at 90 degrees, with respect to each other. On the other hand, there are no special  $\varphi$  correlations in the singlet wavefunction leading to a much larger chance of  $\varphi_1 \approx \varphi_2$ . Because the electron-electron interaction is repulsive, small  $\varphi_2 - \varphi_1$  leads to extra repulsion resulting in a higher energy for the low spin state.

### 5.4.2 The $L$ Rule

Now we consider the second rule through use of an example. Consider the wavefunctions

$$xx - yy \quad (5.119)$$

$$xx + yy \quad (5.120)$$

having angular momenta of  $M = +2$  and  $M = 0$  about the  $z$  axis, both correspond to a single state. Using (5.115)–(5.116), (5.119)–(5.120) becomes

$$xx - yy = f(1)f(2)\cos(\varphi_1 + \varphi_2) \quad (5.121)$$

$$xx + yy = f(1)f(2)\cos(\varphi_1 - \varphi_2). \quad (5.122)$$

Thus, the  $M = 0$  wavefunction has the  $\varphi$  coordinates of the electrons correlated so that  $\varphi_1$  and  $\varphi_2$  tend to be equal, while the  $M = 2$  wavefunction has no special correlation of the  $\varphi$  coordinates. Since small  $\varphi_1 - \varphi_2$  leads to bigger electron repulsion, the  $M = 2$  state is lower. A physical way of thinking about this is that maximum  $M$  corresponds to all electrons circulating in the same direction about the axis. Thus, the  $\varphi_1 - \varphi_2$  coordinates state fixed. Smaller  $M$  have the electrons circulating in opposite directions, and hence,  $\varphi_1 - \varphi_2$  must pass through zero, leading to extra repulsion.

### 5.4.3 The $J$ Rule

In the third rule, the spin orbital coupling interaction for an atom, has the form

$$\zeta(r)\mathbf{s} \cdot \mathbf{l}, \quad (5.123)$$

where  $\zeta(r) > 0$ . Thus, lower energy is obtain when  $\mathbf{s}$  and  $\mathbf{l}$  are in opposite directions and, hence, the best  $J$  should be the lowest one,

$$J = |L - S|, \quad (5.124)$$

since this has the spin and orbital momenta in opposite directions. For example, for the  $^3P_2$  state of  $p^2$ , we obtain

$$E_{ls} = \langle p_+ p_0 \alpha \alpha | \sum_i \zeta(r_i) l_i \cdot s_i | Ap_+ p_0 \alpha \alpha \rangle = \frac{1}{2} \lambda \quad (5.125)$$

where  $\lambda$  is the radical integral

$$\lambda = \langle f(r) | \zeta(r) | f(r) \rangle \quad (5.126)$$

and  $\lambda$  is positive.

To evaluate the energy of the  $^3P_1$  and  $^3P_0$  terms is a little more complicated, but can be done using

$$l \cdot s = \frac{1}{2} (\hat{l}^+ \hat{s}^- + \hat{l}^- \hat{s}^+) + \hat{l}_z \hat{s}_z \quad (5.127)$$

and the usual angular momentum properties. An alternative approach is to use the Wigner-Eckart theorem,

$$\begin{aligned} E^{LSJ} &= \langle LSJM_J | \sum_i \zeta(r_i) l_i \cdot s_i | LSJM_J \rangle \\ &= \Lambda \langle LSJM_J | L \cdot S | LSJM_J \rangle \\ &= \frac{1}{2} \Lambda [J(J+1) - S(S+1) - L(L+1)]. \end{aligned} \quad (5.128)$$

Using (5.125) in (5.128), we can evaluate  $\Lambda$  as equal to  $1/2\lambda$ . Using (5.128), we find that

$$\begin{aligned} E(^3P_2) &= \frac{1}{2} \lambda \\ E(^3P_1) &= -\Lambda = -\frac{1}{2} \lambda \\ E(^3P_0) &= -2\Lambda = -\lambda. \end{aligned} \quad (5.129)$$

Since  $\lambda > 0$ , the  $J = 0$  state is lowest.

Now consider the  $p^4$  configuration. Everything is as with  $p^2$  except that (5.125) is replaced by

$$\begin{aligned} E_{ls} &= \langle p_+ p_0 p_- p_+ \alpha \alpha \alpha \beta | \sum_i \zeta(r_i) l_i \cdot s_i | p_+ p_0 p_- p_+ \alpha \alpha \alpha \beta \rangle \\ &= \frac{1}{2} \lambda - \frac{1}{2} \lambda - \frac{1}{2} \lambda = -\frac{1}{2} \lambda. \end{aligned}$$

(5.130)

Thus,

$$\Lambda = -\frac{1}{2}\lambda \quad (5.131)$$

and the relationships in (5.127) become

$$\begin{aligned} E(^3P_2) &= -\frac{1}{2}\lambda \\ E(^3P_1) &= \frac{1}{2}\lambda \\ E(^3P_0) &= \lambda. \end{aligned} \quad (5.132)$$

Thus, the high  $J$  state is now the ground state. That is, with a greater than half-filled shell, the  $M_J = J$  state, having maximum  $M_L$  and maximum  $M_S$ , tends to make the unpaired spatial orbitals the one with most negative  $M_L$ . Thus, leading to favored spin orbit interactions with the unpaired spins.

#### 5.4.4 Comments

One should be careful to note what Hund's rule does not say. It does not tell us which configuration is lowest, rather, given the ground configuration, it tells us which  $LSJ$  is best. In addition, Hund's rule does not tell us the sequence, or order, of the state, it only tells us about the ground state. Given Hartree-Fock, or Slater determinant wavefunctions, Hund's rules are correct and can be derived, but not trivially. However, for the exact wavefunctions, interactions between configurations could conceivably lead to a ground state in disagreement with Hund's rule, I know of no such cases. For excited configurations, such interactions are often present and it is often the case that the sequence of excited state, having a given, dominant, configuration, does not satisfy Hund's rule.

### 5.5 Appendices

#### 5.5.1 Angular Momenta for Many-Electron Atoms

##### Introduction

For a many-electron atom, the Hamiltonian is

$$H = \sum_{i=1}^N h(i) + \sum_{i>j=1}^N \frac{1}{r_{ij}}. \quad (5.133)$$

Because of the  $l/r_{ij}$  term,  $l_z(i)$ , the angular momentum operator for electron  $i$ , does not commute with  $H$ . However, the  $N$  electron operator

$$\hat{L}_z = \sum_{i=1}^N l_z(i) \quad (5.134)$$

does commute with  $H$ , and similarly for  $L_x$  and  $L_y$ . Consequently,

$$\hat{L}^2 = L_x^2 + L_y^2 + L_z^2 \quad (5.135)$$

also commutes with  $H$ , and hence, the exact eigenfunctions of  $H$  can be taken as eigenstates of  $\hat{L}^2$  and  $\hat{L}_z$ . Similarly, we can define

$$\hat{S}_z = \sum_{i=1}^N s_z(i) \quad (5.136)$$

and  $\hat{S}^2$ , both of which commute with  $H$ . Consequently, all eigenfunctions of  $H$  can be taken as eigenstates of  $\hat{L}^2$ ,  $\hat{L}_z$ ,  $\hat{S}^2$ , and  $S_z$ ,

$$\begin{aligned} H\psi_{NLM_LSM_S} &= E_{NLS}\psi_{NLM_LSM_S} \\ \hat{L}^2\psi_{NLM_LSM_S} &= L(L+1)\psi_{NLM_LSM_S} \\ \hat{L}_z\psi_{NLM_LSM_S} &= M_L\psi_{NLM_LSM_S} \\ \hat{S}^2\psi_{NLM_LSM_S} &= S(S+1)\psi_{NLM_LSM_S} \\ \hat{S}_z\psi_{NLM_LSM_S} &= M_S\psi_{NLM_LSM_S}. \end{aligned} \quad (5.137)$$

In this section, we will examine how to determine the allowed values of  $L$  and  $S$ , for various configurations.

### The $(2p)^2$ Configuration

In Section 5.4, we contented ourselves with determining the ground configurations of the various atoms. For example,

$$(1s)^2(2s)^2(2p)^2 \quad (5.138)$$

for  $C$ . In this section, we will illustrate some ways of determining the possible spatial and spin symmetries for such wavefunctions.

Since there are three possibilities, for each of the  $p$  orbitals in (5.138), and two possibilities for the spin associated with each orbital, there are many possible wavefunctions corresponding to (5.138). On the other hand, the total wavefunction must satisfy Pauli's principle, restricting the possibilities. Since there is only one choice allowed for  $(1s)^2(2s)^2$ , and the essential problem here is to determine the possible states of a configuration of the form  $(2p)^2$ .

**LS Eigenstates, Complex Orbitals** Each electron is in an orbital of the form

$$\phi_m = f(r)Y_{1m}(\theta, \varphi) \quad (5.139)$$

where  $m = 0, \pm 1$  is the angular momentum along the  $z$  axis.

The Slater determinants, which can be formed from two  $p$  orbitals, are as follows:

$\Psi$	$M_L$	$M_S$
$\mathcal{A}(p_+p_0\alpha\alpha)$	+1	+1
$\mathcal{A}(p_+p_-\alpha\alpha)$	0	+1
$\mathcal{A}(p_0p_-\alpha\alpha)$	-1	+1
$\mathcal{A}(p_+p_+\alpha\beta)$	+2	0
$\mathcal{A}(p_+p_0\alpha\beta)$	+1	0
$\mathcal{A}(p_+p_-\alpha\beta)$	0	0
$\mathcal{A}(p_0p_+\alpha\beta)$	+1	0
$\mathcal{A}(p_0p_0\alpha\beta)$	0	0
$\mathcal{A}(p_0p_-\alpha\beta)$	-1	0
$\mathcal{A}(pp_-p_+\alpha\beta)$	0	0
$\mathcal{A}(pp_-p_0\alpha\beta)$	-1	0
$\mathcal{A}(pp_-p_-\alpha\beta)$	-2	0
$\mathcal{A}(p_+p_0\beta\beta)$	+1	-1
$\mathcal{A}(p_+p_-\beta\beta)$	0	-1
$\mathcal{A}(p_0p_-\beta\beta)$	-1	-1

Note that with our definition of  $\mathcal{A}$ , e.g.,  $\mathcal{A} = e - \pi$  for  $N = 2$ , each wavefunction is normalized to  $\sqrt{N!}$ . We have also left out redundant states, e.g.,

$$\mathcal{A}(p_0p_+\alpha\alpha) - \mathcal{A}(p_+p_0\alpha\alpha), \quad (5.140)$$

and zero determinants, e.g.,

$$\mathcal{A}(p_+p_+\alpha\alpha) = 0. \quad (5.141)$$

Here, we have denoted  $p_{+1}$  by  $p_+$ , and similarly for  $p - 1$ . Note that the above fifteen states are all orthogonal.

In terms of the  $M_L$  and  $M_S$  quantum numbers, these fifteen states are distributed as follows:

		$M_S$		
		+1	0	-1
$M_L$	2	0	1	0
	1	1	2	1
	0	1	3	1
	-1	1	2	1
		-2	0	1
<hr/>				

Consider, first, the states with  $M_S = 1$ . Since  $M_S$  is maximum, then  $\hat{S}^+$  operating on any of these states, leads to zero, and hence, all states with  $M_S = 1$  correspond to  $S = 1$ . Recall that

$$\hat{S}^2 = S_z^2 + \hat{S}^- \hat{S}^+ \quad (5.142)$$

thus, if

$$\hat{S}_z \psi_M = M \psi_M \quad (5.143)$$

and

$$\hat{S}^+ \psi_M = 0, \quad (5.144)$$

then

$$\hat{S}^2 \psi_M = M(M+1) \psi_M. \quad (5.145)$$

Now consider the maximum  $M_L$  with this  $M_S$ ,  $M + L = 1$ . Since  $\hat{L}^+$  operating on this state must yield zero, we have  $L = 1$ . Thus, we find a  ${}^3P$  state. Applying  $\hat{L}^-$  and  $\hat{S}^-$ , various numbers of times to the  ${}^3P$  state with  $M_S = 1$ , and  $M_L = 1$ , leads to the nine states:

	$M_S$		
	+1	0	-1
$M_L$	2	0	0
	1	1	1
	0	1	1
	-1	1	1
	-2	0	0

Comparing this with the previous table, we see that there are six states to be accounted for:

	$M_S$		
	+1	0	-1
$M_L$	2	0	0
	1	0	1
	0	0	2
	-1	0	1
	-2	0	0

The maximum  $M_S$  for these states is  $M_S = 0$ , and the maximum  $M_L$  is  $M_L = 2$ . Thus, there must be a  ${}^1D$  state. Applying  $\hat{L}^-$  successively to this  $M_L = 2$  state leads to  $M_L + 1, 0 - 1, -2$  states, and comparing with the above we see that there is one remaining state:

	$M_S$		
	+1	0	-1
$M_L$	2	0	0
	1	0	0
	0	0	1
	-1	0	0
	-2	0	0

Thus, the remaining states is  ${}^1S$ . In summary, we find  $p^2 \rightarrow {}^3P, {}^1D$ , and  ${}^1S$ . Since these states have degeneracies of 9, 5, and 1, respectively, we have accounted for all fifteen states in (??).

We will now use the  $\hat{L}^-$  and  $\hat{S}^-$  operators, to construct the many-electron wavefunctions corresponding to these states.

$\Psi$	$M_S$	$M_L$	
$\mathcal{A}[p_+\alpha p_0\alpha]$	1	1	
$\mathcal{A}[p_+\alpha p_-\alpha]$	1	0	
$\mathcal{A}[p_0\alpha p_p\alpha]$	1	-1	
${}^3P : \frac{1}{\sqrt{2}}\mathcal{A}[(p_+p_0 - p_0p_+) \alpha\beta]$	0	1	(5.146)
$\frac{1}{\sqrt{2}}\mathcal{A}[(p_+p_- - p_-p_+) \alpha\beta]$	0	0	
$\frac{1}{\sqrt{2}}\mathcal{A}[(p_0p_- - p_-p_0) \alpha\beta]$	0	-1	
$\mathcal{A}[p_-\beta p_0\beta]$	-1	+1	
$\mathcal{A}[p_+ + \alpha p_- \beta]$	-1	0	
$\mathcal{A}[p_0\alpha p_- \beta]$	-1	-1	

$\Psi$	$M_S$	$M_L$	
$\mathcal{A}[p_+\alpha p_+\beta]$	0	2	
${}^1D : \frac{1}{\sqrt{2}}\mathcal{A}[(p_+p_0 + p_0p_+) \alpha\beta]$	0	1	(5.147)
$\frac{1}{\sqrt{6}}\mathcal{A}[(2p_0p_0 + p_+p_- + p_-p_+) \alpha\beta]$	0	0	
$\frac{1}{\sqrt{2}}\mathcal{A}[(p_0p_- + p_-p_0) \alpha\beta]$	0	-1	
$\mathcal{A}[p_-\alpha p_-\beta]$	0	-2	

For  ${}^1S$ , the state must be orthogonal to the  $M_S = 0, M + L = 0$  state of  ${}^1D$  and  ${}^3P$ . (Note that the  ${}^1D$  states and the  ${}^3P$  states are automatically orthogonal.) Consequently

$${}^1S : \begin{array}{lll} \Psi & M_S & M_L \\ \frac{1}{\sqrt{3}}\mathcal{A}[(p_+p_- + p_-p_+ - p_0p_0) \alpha\beta] & 0 & 0 \end{array} \quad (5.148)$$

In deriving these expressions, we made use of the fact that  $\mathcal{A}$  commutes with  $\hat{L}^-, \hat{L}_z, \hat{S}^-, \text{ and } \hat{S}_2$ . This follows since the  $\hat{L}_i$  and  $\hat{S}_i$  treat all electrons equivalently, and hence, commute with all permutations. For  $M_S = 0$  states, we have permuted terms so that the spinfunctions are in the order  $\alpha\beta$ .

**The  $J$  States** Including spin orbital coupling, the energy eigenstates must be eigenfunctions of  $\hat{J}^2$  and  $J_z$ , where  $\hat{J}_i = \hat{L}_i + \hat{S}_i$ . For the  $p^2$  states, we obtain

$$\begin{array}{ll} {}^3P & : J = 0, 1, 2, \\ {}^1D & : J = 2, \\ {}^1S & : J = 0. \end{array} \quad (5.149)$$

We may recombine the nine  ${}^3P$  wavefunctions of (5.146) into eigenstates of  $\hat{H}^2$  and  $J_z$ , using a procedure similar to that in Chapter 10. Starting with  $J = 2$  and  $M_J = 2$ , and using the lowering operator, lead to the following

$$\begin{array}{ll} {}^3P_2 : M_J = 2 & : \mathcal{A}[p_+p_0\alpha\alpha] \\ & : M_J = 1 & : \frac{1}{2}\mathcal{A}\left[\sqrt{2}p_+p_-\alpha\alpha + (p_+p_0 - p_0p_+) \alpha\beta\right] \end{array}$$

$$\begin{aligned}
:M_J = 0 & : \frac{1}{\sqrt{6}} \mathcal{A} \left[ p_0 p_- \alpha \alpha + \sqrt{2} (p_+ p_- + p_- p_+) \alpha \beta + p_+ p_0 \beta \beta \right] \\
:M_J = -1 & : \mathcal{A} \left[ (p_0 p_- - p_- p_0) \alpha \beta + \sqrt{2} p_+ p_- \beta \beta \right] \\
:M_J = -2 & : \mathcal{A} [p_0 p_- \beta \beta]. \tag{5.150}
\end{aligned}$$

To obtain the  $J = 1$  states, we consider the  $M_J = 1$  solution orthogonal to the above case, and then apply  $\hat{J}^-$  to obtain the other two components, leading to the following

$$\begin{aligned}
^3P_1 : M_J = 1 & : \frac{1}{2} \mathcal{A} \left[ \sqrt{2} p_+ p_- \alpha \alpha - (p_+ p_0 - p_0 p_+) \alpha \beta \right] \\
M_J = 0 & : \frac{1}{\sqrt{2}} \mathcal{A} [p_0 p_- \alpha \alpha - p_+ p_0 \beta \beta] \\
M_J = -1 & : \mathcal{A} [p_0 p_- - p_- p_0 \alpha \beta - \sqrt{2} p_+ p_- \beta \beta]. \tag{5.151}
\end{aligned}$$

Constructing a third  $M + J = 0$  state orthogonal to the above two, leads to the following

$$^3P_0 : \frac{1}{\sqrt{6}} \mathcal{A} \left[ \sqrt{2} p_0 p_- \alpha \alpha - (p_+ p_- - p_- p_+) \alpha \beta + \sqrt{2} p_+ p_0 \beta \beta \right]. \tag{5.152}$$

More generally, we may write these  $J$  states as  $|LSJM_J\rangle$ , and the original  $LS$  states as  $|LSM_L M_S\rangle$ . Then

$$|LSJM_J\rangle = \sum_{M_L, M_S} C_{JM_J, M_L, M_S}^{LS} |LSM_L M_S\rangle \tag{5.153}$$

where the  $C_{JM_J, M_L, M_S}^{LS}$  are the Clebsch-Gordon coefficients, also called the vector addition, or Wigner coefficients. Tabulations are found in many references.<sup>1</sup>

**LS Eigenstates, Real Orbitals** The above analysis of  $L, S, J$  eigenstates, was greatly facilitated because the orbitals used are eigenstates of  $\hat{l}_z$

$$\hat{l}_z Y_{lm} = m Y_{lm}. \tag{5.154}$$

For molecular problems, the spherical symmetry of the atom is lost and the complex functions of (5.154) are generally not appropriate. For example, in  $D_{2h}$  symmetry, the  $p$  state is split into  $p_x, p_y$  and  $p_z$  states, each with different symmetry, and hence, generally with different energy. Thus, for molecular considerations, it is generally useful to rewrite the  $LS$  eigenstates in terms of real wavefunctions

$$f(r) Z_{lm}(\theta, \varphi). \tag{5.155}$$

Starting with the complex functions, as above, this can be done by expanding each wavefunction, using

$$\begin{aligned}
\phi_{p_{+1}} & = -\frac{1}{\sqrt{2}} (\phi_{px} + i\phi_{py}) \\
\phi_{p_{-1}} & = \frac{1}{\sqrt{2}} (\phi_{px} - i\phi_{py})
\end{aligned}$$

$$\phi_{p_0} = \phi_{pz}, \quad (5.156)$$

and recombining the resulting two-electron wavefunctions. A faster procedure is to note that the spatial part of the  ${}^3P$  state is permutationally antisymmetric

1
2

(5.157)

and hence, only

$$\begin{aligned}\Phi_x^P &= \frac{1}{\sqrt{2}} (\phi_y \phi_z - \phi_z \phi_y) \\ \Phi_y^P &= \frac{1}{\sqrt{2}} (\phi_z \phi_z - \phi_x \phi_z) \\ \Phi_z^P &= \frac{1}{\sqrt{2}} (\phi_x \phi_y - \phi_y \phi_x).\end{aligned}\quad (5.158)$$

correspond to  $L = 1$ . Combining this with the three  $S = 1$  spin functions, leads to the nine  ${}^3P$  states in (??). The  ${}^1D$  and  ${}^1S$  states have permutationally symmetric

1	2
---	---

(5.159)

spatial functions. Of these, the combination

$$\begin{aligned}\Phi^S &= \frac{1}{\sqrt{3}} [\phi_x(1)\phi_x(2) + \phi_y(1)\phi_y(2) + \phi_z(1)\phi_z(2)] \\ &= \frac{1}{\sqrt{3}} [\phi_x \phi_x + \phi_y \phi_y + \phi_z \phi_z]\end{aligned}\quad (5.160)$$

is invariant under any rotation leading to the  $L = 0$ , or  $S$ , state. Thus, the other five symmetric functions

$$\begin{aligned}\Phi_{z^2}^D &= \frac{1}{\sqrt{6}} [2\phi_z \phi_z - \phi_x \phi_x - \phi_y \phi_y] \\ \Phi_{x^2-y^2}^D &= \frac{1}{\sqrt{2}} [\phi_x \phi_x - \phi_y \phi_y] \\ \Phi_{xy}^D &= \frac{1}{\sqrt{2}} [\phi_x \phi_y + \phi_y \phi_x] \\ \Phi_{xz}^D &= \frac{1}{\sqrt{2}} [\phi_x \phi_z + \phi_z \phi_x] \\ \Phi_{yz}^D &= \frac{1}{\sqrt{2}} [\phi_y \phi_z + \phi_z \phi_y]\end{aligned}\quad (5.161)$$

describe the  $L = 2$ , or  $D$  state. Summarizing, in terms of real functions, the fifteen states of  $(p^2)$  are as follows

$$\begin{array}{ll}
{}^3P & \begin{aligned} 1 & \mathcal{A}(p_x p_y \alpha \alpha) \\ & \mathcal{A}(p_x p_z \alpha \alpha) \\ & \mathcal{A}(p_y p_z \alpha \alpha) \\ 0 & \frac{1}{\sqrt{2}} \mathcal{A}[p_x p_y (\alpha \beta + \beta \alpha)] = \frac{1}{\sqrt{2}} \mathcal{A}[(p_x p_y - p_y p_x) \alpha \beta] \\ & \frac{1}{\sqrt{2}} \mathcal{A}[p_x p_z (\alpha \beta + \beta \alpha)] = \frac{1}{\sqrt{2}} \mathcal{A}[(p_x p_z - p_z p_x) \alpha \beta] \\ & \frac{1}{\sqrt{2}} \mathcal{A}[p_y p_z (\alpha \beta + \beta \alpha)] = \frac{1}{\sqrt{2}} \mathcal{A}[(p_y p_z - p_z p_y) \alpha \beta] \\ -1 & \mathcal{A}(p_x p_y \beta \beta) \\ & \mathcal{A}(p_x p_z \beta \beta) \\ & \mathcal{A}(p_y p_z \beta \beta) \end{aligned} \\
{}^1D & \begin{aligned} \frac{1}{\sqrt{2}} \mathcal{A}[(p_x p_x - p_y p_y) \alpha \beta] \\ \frac{1}{\sqrt{2}} \mathcal{A}[(p_x p_y + p_y p_x) \alpha \beta] \\ \frac{1}{\sqrt{2}} \mathcal{A}[(p_x p_z + p_z p_x) \alpha \beta] \\ \frac{1}{\sqrt{2}} \mathcal{A}[(p_y p_z + p_z p_y) \alpha \beta] \\ \frac{1}{\sqrt{6}} \mathcal{A}[(2p_z p_z - p_x p_x - p_y p_y) \alpha \beta] \\ \frac{1}{\sqrt{3}} \mathcal{A}[(p_x p_x + p_y p_y + p_z p_z) \alpha \beta] \end{aligned} \\
{}^1S & 
\end{array} \tag{5.162}$$

Note that in terms of real orbitals, only the  $M_S = \pm 1$  components of  ${}^3P$  can be written as single Slater determinants, whereas for the complex form, the  $M_L = \pm 2$  components of  ${}^1D$  could also be written as single Slater determinants.

### Energies for $(2p)^2$ Wavefunctions

In the following appendix, we evaluate the energies of the  $p^2$  states. The result is

$$\begin{aligned}
E({}^3P) &= h_{xx} + h_{yy} + J_{xy} - K_{xy} \\
&= \frac{2}{3}h^0 + \frac{1}{6}J^0 - \frac{1}{6}K^0 \\
E({}^1D) &= h_{xx} + h_{yy} + J_{xy} + K_{xy} \\
&= h_{xx} + h_{yy} + J_{xx} - K_{xy} \\
&= \frac{2}{3}h^0 + \frac{1}{10}J^0 + \frac{1}{30}K^0 \\
E({}^1S) &= h_{xx} + h_{yy} + J_{xx} + 2K_{xy} \\
&= \frac{2}{3}h^0 + \frac{1}{3}K^0
\end{aligned} \tag{5.163}$$

where

$$\begin{aligned}
h^0 &= \sum_{i=1}^3 h_{ii} \\
J^0 &= \sum_{i,j=1}^3 J_{ij} \\
K^0 &= \sum_{i,j=1}^3 K_{ij}
\end{aligned} \tag{5.164}$$

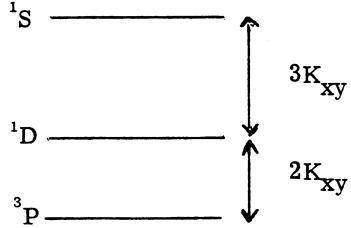


Figure 5.23:

The expressions in (5.163) are obtained directly from the wavefunctions. These qualities have been rewritten in terms of the spherical invariants, by which we mean that the quantities are each invariant under any rotation about the origin. From (5.163) we see that the general energy expression is

$$E = fh^0 + aJ^0 + bK^0 \quad (5.165)$$

and hence, the variational Hamiltonian is

$$H = fh + 2a \sum_j J_j + 2b \sum_j K_j. \quad (5.166)$$

This Hamiltonian is invariant under all rotations, and hence, its eigenstates are spherical harmonics

$$H\phi_i = \epsilon_i \phi_i \quad (5.167)$$

$$\phi_i = f_i(r) Z_{lm}(\theta, \varphi). \quad (5.168)$$

Using (5.163), or (5.164), we see that

$$\frac{E(^1S) - E(^1D)}{E(^1D) - E(^3P)} = \frac{3K_{xy}}{2K_{xy}} = \frac{3}{2} \quad (5.169)$$

with  $E(^1S) > E(^1D) > E(^3P)$ . Thus, the energy diagram is as in Figure 5.23. Figure 5.23 is the energy diagram for  $(p)^2$ .

### Other $(2p)^n$ Configurations

**More Than Half-filled Configurations** Consider a  $(p)^4$  configuration, as the O atom. There are six spin orbitals to be occupied,  $p_+\alpha, p_0\alpha, p_-\alpha, p_+\beta, p_0\beta$ , and  $p_-\beta$ , of which we will occupy four. For example,

$$\mathcal{A}(p_+p_0p_-p_+\alpha\alpha\alpha\beta). \quad (5.170)$$

All together, we find 15 such wavefunctions, each of which corresponds exactly to one of the 15  $p^2$  functions in (??). This correspondence is as follows

$$\mathcal{A}(p_+p_0p_-p_+\alpha\alpha\alpha\beta) \leftrightarrow \mathcal{A}(p_0p_-\beta\beta) \quad (5.171)$$

$$\mathcal{A}(p_+p_0p_0p_- \alpha\alpha\beta\beta) \leftrightarrow \mathcal{A}(p_-p_+\alpha\beta), \quad (5.172)$$

etc. This is, considering the  $p^4$  configuration, we identify which two spin orbitals are not occupied (that is, the *holes*) and it is the two-electron configuration with only these holes occupied that corresponds to the  $p^4$  configuration. Since the  $M_L$  for the  $p^2$  configuration has the same symmetries as a  $p^2$  configuration, that is

$$p^4 \rightarrow {}^3P, {}^1D, {}^1S. \quad (5.173)$$

**Summary** The allowed symmetries for various  $p^n$  configurations are listed as follows

$$\begin{array}{ll} p^1, p^5 & : {}^2P \\ p^2, p^4 & : {}^3P, {}^1D, {}^1S \\ p^3 & : {}^4S, {}^2D, {}^2P \end{array} \quad (5.174)$$

### The $(d)^n$ Configurations

The general procedure of obtaining the allowed  $L$  and  $S$  values, for a configuration is

1. Find the number of orthogonal determinants allowed for each  $M_S \geq 0$  and  $M_L \geq 0$ .
2. Start with the largest allowed  $M_S$  and with the largest  $M_L$  for this  $M_S$ . Since  $\hat{L}^+$  and  $\hat{S}^+$  on these states must both lead to zero, these states have  $L = M_L$  and  $S = M_S$ .
3. Considering the increases in the numbers of state for smaller  $M_L$ , we find the other  $L$  states allowed for  $S = M_S$ .
4. Consider the next largest  $M_S$ , starting with the largest allowed  $M_L$ .
5. Continue this procedure until all states are considered.

We will illustrate the process once more, for the  $(d^3)$  configuration.

**The  $(d^3)$  Configurations** We find (using an obvious shorthand notation)

$M_S$	$M_L$	State
3/2	3	$(2^\alpha 1^\alpha 0^\alpha)$
	2	$(2^\alpha 1^\alpha \bar{1}^\alpha)$
	1	$(2^\alpha 0^\alpha \bar{1}^\alpha, 2^\alpha 1^\alpha \bar{1}^\alpha)$
	0	$(1^\alpha 0^\alpha \bar{1}^\alpha), (2^\alpha 0^\alpha \bar{1}^\alpha)$
	5	$(2^\alpha 1^\alpha 2^\beta),$
1/2	4	$(2^\alpha 0^\alpha 2^\beta), (2^\alpha 1^\alpha 1^\beta),$
	3	$(2^\alpha \bar{1}^\alpha 2^\beta), (1^\alpha 0^\alpha 2^\beta), (2^\alpha 0^\alpha 1^\beta), (2^\alpha 1^\alpha 0^\beta),$
	2	$(2^\alpha \bar{2}^\alpha 2^\beta), (1^\alpha \bar{1}^\alpha 2^\beta), (2^\alpha \bar{1}^\alpha 1^\beta), (1^\alpha 0^\alpha 1^\beta), (2^\alpha 1^\alpha \bar{1}^\beta)$
	1	$(1^\alpha \bar{2}^\alpha 2^\beta), (0^\alpha \bar{1}^\alpha 2^\beta), (2^\alpha \bar{2}^\alpha 1^\beta), (1^\alpha \bar{1}^\alpha 1^\beta),$
	0	$(2^\alpha \bar{1}^\alpha 0^\beta), (1^\alpha \bar{2}^\alpha 0^\beta), (2^\alpha 0^\alpha \bar{1}^\beta), (2^\alpha 1^\alpha \bar{2}^\beta),$
0	5	$(0^\alpha \bar{2}^\alpha 2^\beta), (1^\alpha \bar{2}^\alpha 1^\beta), (0^\alpha \bar{1}^\alpha 1^\beta), (2^\alpha \bar{2}^\alpha 0^\beta),$
	4	$(1^\alpha \bar{1}^\alpha 0^\beta), (2^\alpha \bar{1}^\alpha \bar{1}^\beta), (1^\alpha 0^\alpha \bar{1}^\beta), (2^\alpha 0^\alpha \bar{2}^\beta).$

	$M_S$	States
	$3/2$	$\frac{1}{2}$
$M_L$		
5	0	H
4	0	G
3	1	F
2	1	D
1	2	P
0	2	S

Figure 5.24:

Therefore, we obtain the numbers in Figure 5.24, for  $d^3$ .

1. Consider  $M_S = 3/2$ . From  $M_L = 3$  we know that we have one  $^4F$ , since there are one fewer states after applying  $\hat{L}^+$ . Thus,

- (a)  $M_L = 3$  must have one  $^4F$ ;
- (b)  $M_L = 2$  no new states, since we obtain the same number after applying  $\hat{L}^+$ ;
- (c)  $M_L = 1$  must have one  $^4P$ ;
- (d)  $M_L = 0$  no new states.

2. Now consider  $M_S = 1/2$ :

- (a)  $M_L = 5$  we have one  $^2H$ ;
- (b)  $M_L = 4$  we have one  $^2G$ ;
- (c)  $M_L = 3$  we have  $F$  states, since there are two fewer after applying  $\hat{L}^+$ . But we already have one  $^4F$ , therefore we must also have one  $^2F$ .
- (d)  $M_L = 2$ , two  $D$  states and both are  $^2D$  since there is no  $^4D$ .
- (e)  $M_L = 1$  two  $p$  states, applying  $\hat{L}^+$ , but one is  $^4P$ , therefore one is  $^2P$ .
- (f)  $M_L = 0$ , no  $s$  states.

Therefore, the  $d^3$  configuration is  $^4F, ^4P, ^2H, ^2G, ^2F, ^2D, ^2D$ , and  $^2P$ . The check for this would be, for  $\alpha\alpha\alpha$  we have  $5 \cdot 4 \cdot 3/6 = 10$  different determinants, which checks. And for  $\alpha\alpha\beta$ , we have  $(5 \cdot 4/2)5 = 50$  different determinants, which also checks.

### Inequivalent Configurations

Earlier we considered the  $(2p)^2$  configuration and found that only  $^3P$ ,  $^1D$ , and  $^1S$  states are allowed by the Pauli principle. Consider now the case  $(2p)^1(3p)^1$  so that the two electrons are in inequivalent orbitals. This  $\phi_x\phi_x$  state can be replaced by a permutationally symmetric term

$$\phi_{2x}\phi_{3x} + \phi_{3s}\phi_{2x} \quad (5.176)$$

or an antisymmetric term

$$\phi_{2x}\phi_{3x} - \phi_{3x}\phi_{2x}. \quad (5.177)$$

Thus, we get two wavefunctions with  $S$  symmetry ( $x^2 + y^2 + z^2$ ): one using (5.176) leads to a singlet state  $^1S$ , and the other using (5.177) leads to  $^3S$ . Similarly, the  $xy - yx$  term becomes

$$(\phi_{2x}\phi_{3y} \pm \phi_{3y}\phi_{2x}) - (\phi_{2y}\phi_{3x} \pm \phi_{3x}\phi_{2y}) \quad (5.178)$$

which leads to  $^3P$  and  $^1P$ . Thus, with inequivalent orbitals, we obtain

$$(2p)(3p) \rightarrow ^3D, ^1D, ^3P, ^1P, ^3S, ^1S. \quad (5.179)$$

No states are excluded by the Pauli principle.

### 5.5.2 Energies for $(2p)^2$ Wavefunctions

We will not evaluate the energies for the wavefunctions. All energies will involve the same one-electron contributions,  $2\langle p|h|p\rangle$ , so we will just consider the two-electron terms.

#### Energies Using Real Wavefunctions

Using the real wavefunctions of equations (??) through (??), or (5.160) and (5.161), leads to the following energies:

State	Energy	
$^3P$	$J_{xy} - K_{xy} = J_{xz} - K_{xz} = J_{yz} - K_{yz}$	
$^1D$	$J_{xy} + K_{xy} - J_{xz} + K_{xz} = J_{yz} - K_{yz}$ $= \frac{1}{2}[J_{xx} + J_{yy} - 2K_{xy}]$ $= \frac{1}{6}[4J_{zz} + J_{xx} + J_{yy} - 4K_{xz} - 4K_{yz} + 2K_{xy}]$	(5.180)
$^1S$	$\frac{1}{3}[J_{zz} + J_{xx} + J_{yy} + 2K_{xy} + 2K_{xz} + 2K_{yz}]$ .	

Using symmetry, there are only three different quantities here,  $J_{xx}$ ,  $J_{xy}$ , and  $K_{xy}$  so that the above energies reduce to

$^3D$	:	$E = J_{xy} - K_{xy}$	
$^1D$	:	$E = J_{xy} + K_{xy} = J_{xx} - K_{xy}$	
$^1S$	:	$E - J_{xx} + 2K_{xy}$ .	(5.181)

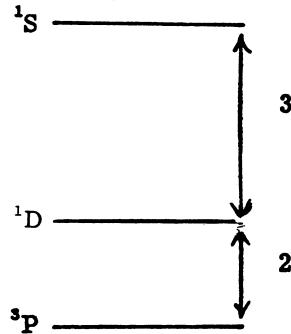


Figure 5.25: The energy diagram for  $(2p)^2$ .

Since both expressions for  $E(^1D)$  must be the same, we find that the Coulomb and exchange integrals must be related by

$$J_{xx} = J_{xy} + 2K_{xy} \quad (5.182)$$

Consequently,

$$\begin{aligned} {}^3P &: E = J_{xy} - K_{xy} \\ {}^1D &: E = J_{xy} + K_{xy} \\ {}^1S &: E = J_{xy} + 4K_{xy} \end{aligned} \quad (5.183)$$

leading to

$$\frac{E({}^1S) - E({}^1D)}{E({}^1D) - E({}^3P)} = \frac{3K_{xy}}{2K_{xy}} = \frac{3}{2}. \quad (5.184)$$

Thus, since  $K_{xy} > 0$ , we see that the states must be in the order given in Figure 5.25, with the ratio of 3 to 2 in the energy separations.

### Spherically Averaged Energies

The problem with the energy expressions of (??) through (5.181), or (5.183), is that they distinguish specific directions over others. For example, using

$$E = \langle x|h|x\rangle + \langle y|h|y\rangle + J_{xy} + K_{xy} \quad (5.185)$$

leads to variational operators

$$H_x = h + J_y + K_y \quad (5.186)$$

and

$$H_y = h + J_x + K_x. \quad (5.187)$$

Since the operators do not have spherical symmetry, the solutions are not spherical harmonics

$$\phi_u = f(r)Y_{lm}(\theta, \varphi). \quad (5.188)$$

In order to remedy this, we will average the energy expressions for different equivalent states. Thus, (??), (??), and (5.180) lead to

$$E(^3P) = \frac{1}{3} \sum_{i>j} (J_{ij} - K_{ij}) \quad (5.189)$$

$$E(^1D) = \frac{1}{3} \sum_{i>j} (J_{ij} + K_{ij}) = \frac{1}{3} \sum_i J_{ii} - \frac{1}{3} \sum_{i>j} K_{ih} \quad (5.190)$$

$$E(^1S) = \frac{1}{3} \sum_{i>j} J_{ii} + \frac{2}{3} \sum_{i>j} K_{ij}. \quad (5.191)$$

Since only equal energies were averaged together, nothing has been changed but the appearance of the energy expression. Going one step further, we add

$$\frac{1}{6} \sum_i (J_{ii} - K_{ii}) = 0, \quad (5.192)$$

to (5.191), leading to

$$E(^3P) = \frac{1}{6} (J^0 - K^0) \quad (5.193)$$

where

$$J^0 = \sum_{i,j} J_{ij} \quad (5.194)$$

and

$$K^0 = \sum_{i,j} K_{ij} \quad (5.195)$$

are spherically invariant. Similarly, using (5.192), (??) becomes

$$E(^1S) = \frac{1}{3} K^0. \quad (5.196)$$

This leads to

$$\begin{aligned} E(^1D) &= \frac{1}{5} \sum_{i>j} (J_{ij} + K_{ij}) + \frac{2}{15} \sum_{i>j} (J_{ij} - K_{ij}) \\ &= \frac{1}{10} J^0 + \frac{1}{30} K^0 \end{aligned} \quad (5.197)$$

Thus, we find that

$$E(^1S) - E(^1D) = \frac{1}{10} (3K^0 - J^0) \quad (5.198)$$

$$E(^1D) - E(^3P) = \frac{1}{15} (3K^0 - J^0) \quad (5.199)$$

leading again to (5.184). Comparing to (5.183), we see that

$$\frac{1}{15} (3K^0 - J^0) = 2K_{xy} > 0. \quad (5.200)$$

From (5.193) through (5.197), we see that for each state, the energy can be written as

$$E = f \sum_i h_{ii} + a \sum_{i,j} J_{ij} + b \sum_{i,j} K_{ij}, \quad (5.201)$$

where each sum is over the three  $p$  functions,  $f = 2/3$  for the  $p^2$  configuration. Thus, the variational Hamiltonian is

$$H = fh + 2a \sum_j J_j + 2b \sum_j K_j. \quad (5.202)$$

This operator is rotationally invariant, and hence, the eigenstates

$$H\phi_i = \epsilon_i \phi_i \quad (5.203)$$

are spherical harmonics

$$\phi_i = f_i(r) Z_{lm}(\theta, \varphi). \quad (5.204)$$

### Energies Using Complex Orbitals

Using complex orbitals  $p_+$ ,  $p_0$ , and  $p_-$ , the energies for the  $p^2$  configurations are

State	Energy
${}^3P$	$J_{+0} - K_{+0} = J_{+-} - K_{+-} = J_{0-} - K_{0-}$
${}^1D$	$J_{++} = J_{+0} + K_{+0}$
	$= \frac{1}{6}(1J_{00} + 2J_{+-} + 2K_{+-} - 4K_{+0} - 4K_{0+})$
	$= J_{-0} + K_{-0} = J_{--}$
${}^1S$	$\frac{1}{3}(2J_{+-} + J_{00} + 2K_{+-} + 2K_{+0} + 2K_{-0})$

(5.205)

where we have used  $\phi_0^* = \phi_0$ , and

$$\begin{aligned} \langle 00 | \frac{1}{r_{12}} | + - \rangle &= \int d\tau_1 \phi_0(1) \underbrace{\phi_+(1)}_{-\phi_-(1)^*} \int d\tau_2 \frac{1}{r_{12}} \phi_b(2) \phi_-(2) \\ &= -\langle -0 | \frac{1}{r_{12}} | 0 - \rangle = -K_{0-} \end{aligned} \quad (5.206)$$

Averaging over the various components, of a state, and using  $J_{++} = J_{--} = J_{+-}$ , we obtain

State	Energy
${}^3P$	$\frac{1}{6}J^0 - \frac{1}{6}K^0$
${}^1D$	$\frac{1}{10}J^0 - \frac{1}{30}K^0$
${}^1S$	$\frac{1}{3}K^0$

(5.207)

where

$$J^0 = \sum_{m,m'=-1}^{+1} J_{mm'} \quad (5.208)$$

and

$$K^0 = \sum_{m,m'=-1}^{+1} J_{mm'} \quad (5.209)$$

are the spherical invariants and are equivalent to the forms used in (??).

### 5.5.3 The Virial Theorem

To summarize, in a system of particles interacting through a Coulomb potential, the total kinetic energy  $T$ , total potential energy  $V$ , and total energy  $E$ , are related as

$$E = -T = \frac{1}{2}V. \quad (5.210)$$

This relationship is also true for approximate wavefunctions if the scale of the approximate wavefunction is optimized.

#### Coulomb Potentials

In this chapter, we found that any approximate wavefunction yields an energy greater than, or equal to, the exact energy. Hence, varying various parameters in the wavefunction to minimize the energy, should lead to better wavefunctions for the ground state. As a corollary, we know that the energy of the exact wavefunction must already be a minimum, with respect to variation of any parameters in the wavefunction. This knowledge can be used to obtain a relationship between the average kinetic and potential energies of a wavefunction.

Starting with some wavefunction  $\phi_1(r)$ , say

$$\phi_1(r) = e^{-2r} \cos(3r), \quad (5.211)$$

we will consider the scaled wavefunction

$$\phi_\alpha(r) = e^{-2\alpha r} \cos(3\alpha r), \quad (5.212)$$

obtained from  $\phi_1(r)$  by replacing  $r$  with  $\alpha r$ . This amounts to squeezing a wavefunction by a factor of  $\alpha$ , as indicated in Figure 5.26.

The energy of the new wavefunction is given by

$$E_\alpha = T_\alpha + V_\alpha \quad (5.213)$$

where

$$T_\alpha = \frac{\langle \phi_\alpha | -\frac{1}{2}\nabla^2 | \phi_\alpha \rangle}{\langle \phi_\alpha | \phi_\alpha \rangle} \quad (5.214)$$

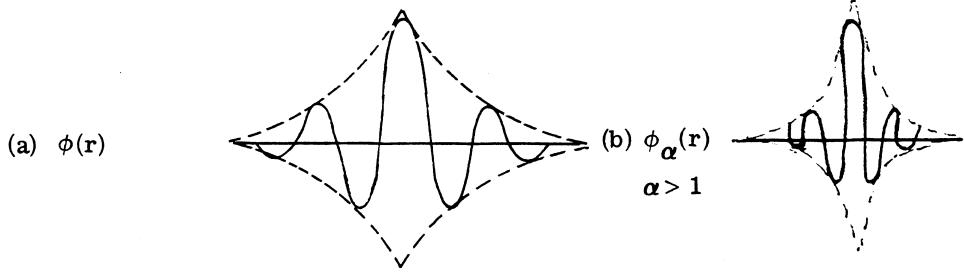


Figure 5.26: Illustration for the virial theorem.

and

$$V_\alpha = \frac{\langle \phi_\alpha | -\frac{Z}{r} | \phi_\alpha \rangle}{\langle \phi_\alpha | \phi_\alpha \rangle}. \quad (5.215)$$

But

$$\phi_\alpha(r) = \phi_1(\alpha r) \quad (5.216)$$

and  $\phi_1(r)$  are normalized,

$$\langle \phi_1 | \phi_1 \rangle = \int d^3r \phi_1^*(r) \phi_1(r) = 1, \quad (5.217)$$

so that

$$\begin{aligned} \langle \phi_\alpha | \phi_\alpha \rangle &= \int d^3r \phi_\alpha^*(r) \phi_\alpha(r) = \int d^3r \phi_1^*(\alpha r) \phi_1(\alpha r) \\ &= \frac{1}{\alpha^3} \int d^3(\alpha r) \phi_1^*(\alpha r) \phi_1(\alpha r) = \frac{1}{\alpha^3} \int d^3r' \phi_1^*(r') \phi_1(r') \\ &= \frac{1}{\alpha^3} \end{aligned} \quad (5.218)$$

Similarly

$$\begin{aligned} \langle \phi_\alpha | -\frac{Z}{r} | \phi_\alpha \rangle &= \alpha \langle \phi_\alpha(r) | -\frac{Z}{\alpha r} | \phi_\alpha(r) \rangle \\ &= \frac{\alpha}{\alpha^3} \langle \phi_1(\alpha r) | -\frac{Z}{\alpha r} | \phi_1(\alpha r) \rangle \\ &= \frac{\alpha}{\alpha^3} V_1, \end{aligned} \quad (5.219)$$

where

$$V_1 = \langle \phi_1(r) | -\frac{Z}{r} | \phi_1(r) \rangle = \langle \phi_1(\alpha r) | -\frac{Z}{\alpha r} | \phi_1(\alpha r) \rangle. \quad (5.220)$$

In (5.220) the two forms just differ by a change of variable  $r' = \alpha r$ . This does not change the boundary conditions, since the wavefunction is zero at  $t = \infty$ , and hence, at  $r' = \infty$ , and (5.220) follows. Thus,

$$V_\alpha = \alpha V_1. \quad (5.221)$$

Similarly

$$T_\alpha = \alpha^2 T_1, \quad (5.222)$$

so that the energy has the form

$$E_\alpha = \alpha^2 T_1 + \alpha V_1. \quad (5.223)$$

Requiring  $E_\alpha$  to be a minimum with respect to the  $\alpha$ , leads to

$$0 = 2\alpha T_1 + V_1 \quad (5.224)$$

or

$$\alpha = -\frac{V_1}{2T_1}. \quad (5.225)$$

Thus, from (5.221) and (5.222), we obtain

$$\begin{aligned} V^{\text{opt}} &= -\frac{(V_1)^2}{2T_1} \\ T^{\text{opt}} &= +\frac{(V_1)^2}{4T_1} \end{aligned} \quad (5.226)$$

and hence,

$$2T^{\text{opt}} + V^{\text{opt}} = 0. \quad (5.227)$$

This is called the *virial theorem*, and leads to

$$E^{\text{opt}} = -T^{\text{opt}} = +\frac{1}{2}V^{\text{opt}}. \quad (5.228)$$

Since the exact eigenfunction must already be optimum with respect to scaling, (5.227) must apply to the exact wavefunction.

### Other Potentials

If, instead of the Coulomb potential,

$$\hat{V} = -\frac{Z}{r}, \quad (5.229)$$

we consider some other homogeneous potential,

$$V = \beta r^n, \quad (5.230)$$

then the above scaling considerations, lead to

$$E_\alpha = \alpha^2 T_1 + \alpha^{-n} V_1 \quad (5.231)$$

and hence, to

$$2\alpha T_1 - n\alpha^{-n-1} V_1 = 0 \quad (5.232)$$

in place of (5.225). This results in the general form of the virial theorem

$$2T^{\text{opt}} = nV^{\text{opt}} \quad (5.233)$$

in place of (5.227). For example, a harmonic oscillator has  $n = 2$ , and hence,

$$T^{\text{opt}} = V^{\text{opt}}. \quad (5.234)$$