7.1 Electronic states of helium atom

Neutral He atom (Z=2) has 2 electrons. The electronic Hamiltonian in a.u. is (Figure 7.1)

$$\hat{H} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}} \qquad \text{eq 7.1a}$$

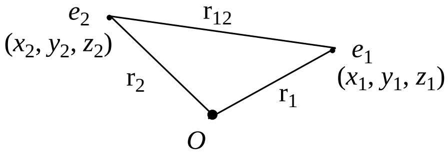

Figure 7.1 Interparticle distances in the helium atom. The nucleus is at the origin of a Cartesian coordinate system (axes not shown). The nucleus is fixed in space; only the electrons are moving.

The last term in eq 7.1a is the contribution to the potential energy arising from the repulsion between the two electrons; the value of this term depends on the coordinates of both electrons whereas the first four terms depend on coordinates of individual electrons only. We rewrite eq 7.1a in the form

$$\hat{H} = \hat{h}(1) + \hat{h}(2) + \frac{1}{r_{12}} \qquad \text{eq 7.1b}$$

where

$$\hat{h}(j) = -\frac{1}{2}\nabla_j^2 - \frac{2}{r_j}\,, \qquad j = 1, 2. \qquad \text{eq 7.2}$$

depends on the coordinates of the jth electron only. The operator $\hat{h}$ is recognized as the Hamiltonian of an electron in a hydrogenlike atom (with Z=2, in this case; see eqs 6.41-43). The two operators $\hat{h}(1)$ and $\hat{h}(2)$ trivially commute with each other because they depend on different variables. However, neither one commutes with the interaction term $1/r_{12}$. Because of this latter fact, the Schrödinger equation for the helium is not separable, and we must use approximation methods.

7.2 The Variation Method

The "variation method" is a powerful procedure that forms the basis of most quantum-mechanical calculations made on atoms and molecules. It is based on the "variation principle".

Let $\hat{H}$ be a time-independent Hamiltonian operator, and E_1 be the exact lowest eigenvalue of $\hat{H}$ (i.e. the exact ground state energy). Given a normalized wavefunction, Ψ_{trial}, we can calculate an energy by the average value expression

$$E_{trial} = \int \Psi_{trial}^* \hat{H} \Psi_{trial} d\tau \qquad \text{normalized } \Psi_{trial} \qquad \text{eq 7.3a}$$

Note that in this expression, $\hat{H}$ is the exact Hamiltonian whereas Ψ_{trial} is an approximate function that we design (i.e. we guess it). The variation principle states that E_{trial} can never be less than the true lowest energy:

$E_{trial} \geq E_1$ Variation Principle eq 7.3b

The normalized function Ψ_{trial} is called a "trial variation function", and the integral in eq 7.3a is called the "variational integral". In order to achieve a good approximation to the ground state energy, we try many different trial functions and look for the one that gives the lowest value for the variational integral. The approximate functions that we devise for this purpose must have certain characteristic properties that are known about the exact solutions of the Schrödinger equation.

7.3 Total Orbital and Spin Angular Momenta in an Atom

We can obtain very useful information about the features of the exact wavefunctions if there are available other operators that commute with the Hamiltonian of the system. This is because when $\hat{H}$ commutes with another operator $\hat{A}$, the two operators have simultaneous eigenfunctions. It is generally the case that the eigenvalues and the eigenfunctions of $\hat{A}$ can be found much more easily than solving the Schrödinger equation, $\hat{H}\Psi = E\Psi$. The fact that Ψ must also be an eigenfunction of $\hat{A}$ means that Ψ can be characterized by the eigenvalues (and eigenfunctions) of $\hat{A}$. It is thus important to search for operators that commute with $\hat{H}$. We now discuss properties of several operators of this type.

7.3.1 The total orbital angular momentum of electrons in an atom

The total orbital angular momentum of *N* electrons in an atom is a vector operator defined by

$$\vec{\hat{L}} = \vec{\hat{L}}_1 + \vec{\hat{L}}_2 + \cdots + \vec{\hat{L}}_N \qquad \text{eq 7.4}$$

where $\vec{\hat{L}}_j$ is the orbital angular momentum vector operator of the jth electron. The z-component of $\vec{\hat{L}}$ is

$$\hat{L}_z = \hat{L}_{1z} + \hat{L}_{2z} + \cdots + \hat{L}_{Nz} \qquad \text{eq 7.5}$$

As in the case for a single electron, it may be shown that $\hat{L}_z$ commutes with $\hat{L}^2$, and that both of these operators also commute with the Hamiltonian $\hat{H}$ of the atom. It follows that the exact solutions, Ψ, of the Schrödinger equation are eigenfunctions of $\hat{L}^2$ and $\hat{L}_z$. It is found that eigenvalues of the latter operators are (in a.u.) as in Table 7.1:

Table 7.1 Eigenvalues of orbital angular momentum operators (a.u.)

Operator	$\hat{L}^2$	$\hat{L}_z$
Eigenvalues	$L(L+1)$ where $L=0, 1, 2,\ldots$	M_L where $-L \leq M_L \leq L$

Thus the exact atomic functions Ψ can be classified according to the *L* and M_L values they possess. It turns out that the total electronic energy, *E*, of a many-electron atom is independent of the M_L quantum number, but it does depend on *L* (for *N*>1). The spatial degeneracy of an atomic energy level characterized by a given *L* value is 2*L*+1. For a single electron (*N*=1), it is conventional to use the lowercase symbols l and m_l for the orbital momentum quantum numbers, reserving the corresponding uppercase symbols for the totals (i.e. for *N*>1 cases). This notation is also used for the spin angular momentum discussed next.

7.3.2 The total spin angular momentum of *N* electrons

In Section 3.3, we mentioned that an electron has two "spin states" designated by α and β. In theoretical considerations, α and β are postulated to be functions of the "spin variable" of the electron. The spin variable is independent of the spatial variables of the electron. Thus an electron moving in 3D is considered to have 4 independent variables: 3 position variables to locate it in the 3D physical space plus 1 spin variable to specify its spin state. It is further postulated that an electron has a spin angular momentum vector operator, $\vec{\hat{S}}$, that is a function of the spin variable of the electron only, such that the spin functions α and β are eigenfunctions of $\hat{S}^2$ and $\hat{S}_z$:

$$\hat{S}^2\sigma = s(s+1)\sigma$$
$$\hat{S}_z\sigma = m_s\sigma$$

where *s*=1/2; σ=α or β; and m_s=1/2 for σ=α, and m_s=-1/2 for σ=β

They are assumed to satisfy the orthonormality conditions:

$$\int \sigma^*\sigma d\tau_s = 1,\ \sigma = \alpha,\beta \qquad \text{and} \qquad \int \alpha^*\beta d\tau_s = 0 \qquad \text{eq 7.6}$$

where $d\tau_s$ is the volume element for the spin variable.

For N>1 electrons, the total spin angular momentum operators of the electrons are defined similarly to those in eqs 7.4-5

$$\vec{\hat{S}} = \vec{\hat{S}}_1 + \vec{\hat{S}}_2 + \cdots + \vec{\hat{S}}_N \qquad \text{eq 7.7a}$$

$$\hat{S}_z = \hat{S}_{1z} + \hat{S}_{2z} + \cdots + \hat{S}_{Nz} \qquad \text{eq 7.7b}$$

with the eigenvalues of $\hat{S}^2$ and $\hat{S}_z$ given in Table 7.2.

Table 7.2 Eigenvalues (in a.u.) of spin angular momentum operators for *N* electrons.

Operator	$\hat{S}^2$	$\hat{S}_z$
Eigenvalues	$S(S+1)$, such that $S_{max}=N/2$	M_S where $-S \le M_S \le S$

The allowed values of the total spin quantum number *S* depend on whether there is an even or an odd number of electrons in the atom (or molecule):

S=0, 1,…, *N*/2 if *N* is even eq 7.8a

S=1/2, 3/2,…, *N*/2 if *N* is odd eq 7.8b

For a single electron (N=1), eigenvalues in Table 7.2 reduce to those given previously. Note the usage of lowercase and uppercase symbols for the quantum numbers, depending on whether we have a single electron or many electrons. This is a general convention.

The Hamiltonian operator of the atom that we are considering, e.g. eq 7.1 for He, is a function of only the spatial variables of the electrons whereas $\hat{S}^2$ and $\hat{S}_z$ are functions of the spin variables. Therefore, the latter operators trivially commute with $\hat{H}$. Hence the state functions Ψ of an atom must be eigenfunctions of $\hat{S}^2$ and $\hat{S}_z$; and as a result, Ψ can be labeled by the spin quantum numbers S and M_S, in addition to L and M_L.

Similar to the case with the orbital angular momentum, the total electronic energy of an atom does not depend on the M_S quantum number, but it does depend on the total spin quantum number S (for N>1). There are 2S+1 different values of M_S for a given S. Thus the "spin degeneracy" of an atomic energy level E is 2S+1 with the total degeneracy being (2L+1)(2S+1). The spin degeneracy, 2S+1, is also called the "spin multiplicity" or simply, the multiplicity of the atomic state.

As an example let us consider the allowed electronic states in the helium atom. Here, N=2 so that there are only two values for S: 0 and 1. For S=0, the spin multiplicity is 1 ("singlet"), and for S=1 the multiplicity is 3 ("triplet"). Thus the complete set of states can be grouped into two types as distinguished by their multiplicities: a group of "singlet states", and another group consisting of "triplet states". These states are also characterized by an L quantum number associated with each one of them. In contrast to S which takes only two values in the He atom, L may take infinitely many different values: L=0, 1, 2,… Angular momentum characteristics of a state are shown by combining the multiplicity and L in the following form:

^{2S+1}L Atomic Term Symbol eq 7.9

where a letter code is used for L. The letters employed are the uppercases of those used for the orbitals. Thus, in the He atom, the term symbols of the singlet states are ^{1}S, ^{1}P, …, and those of the triplets are ^{3}S, ^{3}P,… Note that there are infinitely many states of each of these term types; i.e. many ^{1}S states with different energies, many ^{3}S states, etc.

***Exercise* 7.1** List all possibilities of the spin multiplicities for each of the atoms: a) Li, b) Be, c) N.

7.3.3 The Pauli Exclusion Principle

In Section 3.3 we stated this principle in terms of the maximum occupation number of an orbital energy level as n_{max}=2g where g is the degeneracy of the orbital energy. Since by definition, g is the number of different orbitals having the same energy, this form of the Pauli principle means that the maximum occupation number of a single orbital is 2. Here we will give a more general definition of this principle.

Let us consider the two electrons in the He atom. We label the electrons by the integers 1 and 2, and write the wavefunction as $\Psi(1,2)$ where the arguments stand for all four independent variables (3 position+1 spin variable) for each electron. The general statement of the Pauli principle is:

The wavefunction $\Psi(1,2)$ must change sign when the labels of the two electrons are exchanged,

$\Psi(2,1) = -\Psi(1,2)$ Pauli exclusion principle eq 7.10

For the purpose of gaining a better insight about the meaning of eq 7.10, let us introduce the permutation operator $\hat{P}_{12}$ that exchanges the labels of the two electrons in any function $f(1,2)$ of their variables; i.e. $\hat{P}_{12}f(1,2) = f(2,1)$. Since applying $\hat{P}_{12}$ twice in a row to $f(1,2)$ restores the function to its original value, we have $\hat{P}_{12}^2 = 1$, i.e. the identity operator. Finding eigenvalues of $\hat{P}_{12}$ is easy. Assume that f is an eigenfunction of $\hat{P}_{12}$ with eigenvalue p:

$$\hat{P}_{12}f = pf$$

Applying $\hat{P}_{12}$ to both sides of this equation, we have

$$\hat{P}_{12}^2 f = p(\hat{P}_{12}f) = p^2 f$$

Since the squared operator on the left is the identity operator, one has $f=p^2f$, or $p=\pm1$. The eigenfunctions with $p=+1$ do not change sign in the exchange of the two electrons; they are said to be “symmetric” with respect to the exchange. Those eigenfunctions with $p=-1$ change sign in the interchange, and are said to be “antisymmetric” with respect to the exchange. We see from eq 7.10 that $\Psi(1,2)$ must be an eigenfunction of $\hat{P}_{12}$ with eigenvalue $p=-1$; i.e. it must be antisymmetric when all four variables of the two electrons are exchanged.

You should easily see that if you exchange the electron labels in eq 7.1a or b, you will obtain the same expression. Because of this property, the Hamiltonian operator of an atom commutes with the permutation operator. Note that $\hat{P}_{12}$ also commutes with the operators $\hat{L}^2$, $\hat{L}_z$, $\hat{S}^2$ and $\hat{S}_z$. It follows that $\hat{H}$ and $\hat{P}_{12}$ have simultaneous eigenfunctions; i.e. the state functions $\Psi(1,2)$ can be labeled by p. According to the Pauli principle, only those $\Psi(1,2)$ with $p=-1$ are physically acceptable.

7.4 Designing trial variation functions for the helium atom

The trial functions that are used in the variational integral (eq 7.3a) must have the properties of exact wavefunctions outlined above: a) Ψ_{trial} must be antisymmetric with respect to the exchange of the variables of the two electrons; b) Ψ_{trial} must be a simultaneous eigenfunction of the four operators: $\hat{L}^2$, $\hat{L}_z$, $\hat{S}^2$ and $\hat{S}_z$. We discuss first the antisymmetry requirement.

The exact wavefunction for a two-electron system such as the He atom can be written as the product of a space-dependent part and a spin-dependent part:

$\Psi(1,2) = \Psi_{space}(1,2)\, \Psi_{spin}(1,2)$ eq 7.11

where $\Psi_{space}(1,2)$ is a function of only the spatial variables of the two electrons, and $\Psi_{spin}(1,2)$ is a function of only the spin variables. For the total wavefunction $\Psi(1,2)$ to obey the Pauli principle, one of the factors in eq 7.11 must be symmetric while the other one antisymmetric with respect to electron exchange. There are two cases to consider as shown in Table 7.3

Table 7.3

	$\Psi_{space}(1,2)$	$\Psi_{spin}(1,2)$
a)	+1	–1
b)	–1	+1

where +1 and -1 are the two eigenvalues of $\hat{P}_{12}$.

7.4.1 Two-electron spin functions

Since the Hamiltonian operator (eq 7.1a) is independent of the spin variables, $\Psi_{spin}(1,2)$ is determined entirely by the requirements that it must be a simultaneous eigenfunction of the three commuting operators $\hat{S}^2$, $\hat{S}_z$, and $\hat{P}_{12}$. Each electron has two spin functions of its own spin variable: α(1), β(1) for electron 1, and α(2), β(2) for electron 2. The one-electron spin functions are eigenfunctions of $\hat{S}^2$ (for one electron) with *s*=1/2 (i.e. the eigenvalue is *s*(*s*+1)=3/4). α and β are also eigenfunctions of $\hat{S}_z$ with eigenvalues m_s=1/2 and -1/2, respectively. By taking a spin function for each electron we can form 2^2=4 products as shown in the first row of Table 7.4. The second and third rows of the table give the eigenvalues of $\hat{S}_z$ and $\hat{P}_{12}$when the product spin function is an eigenfunction of the corresponding operator; a "no" entry means that the particular product function is not an eigenfunction of $\hat{P}_{12}$.

Table 7.4

	α(1)α(2)	α(1)β(2)	β(1)α(2)	β(1)β(2)
$\hat{S}_z$	1	0	0	-1
$\hat{P}_{12}$	+1	no	no	+1

All of the product spin functions are eigenfunctions of $\hat{S}_z$ as can be easily shown. For two electrons, we have $\hat{S}_z = \hat{S}_{1z} + \hat{S}_{2z}$ (eq 7.7b with *N*=2). The spin variable of electron 1 is independent of that of electron 2. Let σ_1 be either α or β spin function for electron 1 (with m_s=1/2 or -1/2, respectively). Similarly, σ_2 denotes the spin function of electron 2. The product of the two spin functions is $\sigma_1\sigma_2$. We have

$$\hat{S}_z\sigma_1\sigma_2 = (\hat{S}_{1z} + \hat{S}_{2z})\sigma_1\sigma_2 = \sigma_2\hat{S}_{1z}\sigma_1 + \sigma_1\hat{S}_{2z}\sigma_2 = [m_s(1) + m_s(2)]\sigma_1\sigma_2 \qquad \text{eq 7.12}$$

Therefore, M_S=m_s(1)+m_s(2) for the two-electron case. In general, for *N* electrons there are 2^N products of spin functions of the form $\sigma_1\sigma_2 \ldots \sigma_N$, and

$$M_S = \sum_{j=1}^{N} m_s(j) \qquad \text{eq 7.13}$$

Returning to Table 7.4, we know that for two electrons, the total spin quantum number *S* can only be either 0 or 1. We also know that *S* ≥ M_S. Since the largest value of M_S in the table is 1 for the function αα (suppressing the electron labels), we conclude that the latter two-electron spin function is an eigenfunction of $\hat{S}^2$ with *S*=1 (i.e. the eigenvalue is *S*(*S*+1)=2). When there is an eigenfunction with *S*=1, we must search for all functions with -1 ≤ M_S≤1. Since the function ββ has M_S =-1, it must also belong to *S*=1. Note that these two functions are symmetric in spin exchange (i.e. eigenfunctions of $\hat{P}_{12}$ with *p*=+1). Now, there are two functions, $\alpha\beta$ and $\beta\alpha$, with M_S =0 in the table. However, they are not eigenfunctions of $\hat{P}_{12}$ as required by $\Psi_{spin}(1,2)$ of Table 7.3. When there are two or more independent functions at some stage of a problem, the actual expression for the "true" function is obtained by using extra information known about it. In this case, we know that they have to be eigenfunctions of $\hat{P}_{12}$ with an eigenvalue +1 or -1. To find them, we form the linear combination of $\alpha\beta$ and $\beta\alpha$

$\Sigma = c_1\, \alpha(1)\beta(2) + c_2\, \beta(1)\alpha(2)$

where the coefficients c_1 and c_2 are to be (partially) determined by requiring that $\hat{P}_{12}\Sigma = p\,\Sigma$ with $p=\pm1$. You should verify that for $p=1$, $c_2=c_1$, whereas for $p=-1$, $c_2=-c_1$. We thus have two spin functions with correct symmetry under the permutation operator

$\Sigma_a = c_1\,(\alpha\beta + \beta\alpha)$

$\Sigma_b = c_1\,(\alpha\beta - \beta\alpha)$

where the electron labels have been suppressed to simplify writing. The value of c_1 is found by normalizing the spin functions. The volume element for two spin variables is $d\tau_s = d\tau_s(1)d\tau_s(2)$; the integrals are factorized; using properties of spin functions in eq 7.6, one finds that $c_1=1/\sqrt{2}$. Final results for the two-electron spin functions are collected in Table 7.5.

Table 7.5 Normalized spin functions for two electrons (with electron labels suppressed).

S	Spin function	M_S	*p*
1	$\alpha\alpha$	1	+1
	$2^{-1/2}(\alpha\beta + \beta\alpha)$	0	+1
	$\beta\beta$	-1	+1
0	$2^{-1/2}(\alpha\beta - \beta\alpha)$	0	-1

The three functions with *S*=1 are called the triplet spin functions. They are symmetric with respect to spin exchange. The function $\alpha\alpha$ with the highest M_S=1 value is often referred to as the "high spin" function, and represented by two parallel up arrows in energy level diagrams. The last function in the table with *S*=0 is called a singlet spin function, and represented by one up arrow parallel to a down arrow. It is antisymmetric with respect to spin exchange.

7.4.2 Two-electron functions of spatial variables

The major problem in solving the electronic Schrödinger equation for the helium atom is the determination of the space part, $\Psi_{space}(1,2)$, of the wavefunction. According to case (a) of Table 7.3, a singlet spin function must be multiplied by a spatial function that is symmetric in the exchange of position variables of the two electrons.

$^1\Psi_{space}(1,2) = {}^1\Psi_{space}(2,1)$ for *S*=0 (singlets) eq 7.14

where the left superscript indicates the multiplicity of the overall function. On the other hand, a triplet spin function must be combined with an antisymmetric spatial function (case (b) in table 7.3).

$^3\Psi_{space}(1,2) = -\,{}^3\Psi_{space}(2,1)$ for S=1 (triplets) eq 7.15

All three triplet spin functions in Table 7.5 are multiplied by the same space function. Since the energy is eventually determined by the space part, one immediately sees that E is independent of the M_S quantum number, as stated before.

To proceed further we need to write down explicit expressions for the spatial functions. The usual starting point for this purpose is the "orbital approximation". If we omit the electron-electron repulsion term from the Hamiltonian in eq 7.1b, we obtain a separable Hamiltonian

$$\hat{H}_{core} = \hat{h}(1) + \hat{h}(2) \qquad \text{eq 7.16}$$

where the one-electron Hamiltonian is defined in eq 7.2. The Hamiltonian of eq 7.16 is called the "core" Hamiltonian. It describes the motion of two independent (i.e. noninteracting) electrons in the field of a He nucleus (Z=2). The one-electron Hamiltonian $\hat{h}$ is that of a hydrogenlike atom with Z=2 that we considered in Section 6.3. From eq 6.43, the orbital energies are (in hartree)

$$E_n = -\frac{2}{n^2}, \qquad n = 1, 2, \ldots \qquad \text{eq 7.17}$$

The corresponding orbitals are 1s, 2s, $2p_1$, $2p_0$, $2p_{-1}$, etc. For the purposes here, it is convenient to employ the complex orbitals because they have well-defined m_l values. Both electrons of eq 7.16 have the same set of energy levels and orbital functions. The only difference in the explicit expressions of the orbitals is the labels of the electrons. For example, 1s(1) and 1s(2) are the 1s orbitals of electron 1 and 2, respectively. Remember that the electron labels denote three spatial variables for each electron.

The eigenvalues of the core Hamiltonian are the sum of orbital energies, and the eigenfunctions are products of orbitals

$$E_{core} = E_{n_1} + E_{n_2} \qquad \text{eq 7.18a}$$

$$\Psi_{core}(1,2) = \psi_{n_1 l_1 m_{l_1}} \psi_{n_2 l_2 m_{l_2}} \qquad \text{eq 7.18b}$$

Note that the orbital products above are eigenfunctions of $\hat{L}_z = \hat{L}_{1z} + \hat{L}_{2z}$ with eigenvalues M_L= $m_l(1)+m_l(2)$. In general, for an orbital product containing N factors, one has

$$M_L = \sum_{j=1}^{N} m_l(j) \qquad \text{eq 7.19}$$

This is one of the required properties of approximate functions since we know that the exact solutions have the same property, as discussed in Section 7.3.1 above. The spatial parts of the trial functions to be used in the variational integral (eq 7.3a) must also be eigenfunctions of $\hat{L}^2$, and additionally, they must obey eq 7.14 for the singlet states, and eq 7.15 for the triplet states. We will illustrate how this is done by considering the ground state of the He atom, and several of its excited states. Let us first simplify the variational integral a little bit.

$$E_{trial} = \int \Psi_{trial}^* \hat{H} \Psi_{trial} d\tau = \int \Psi_{space}^* \Psi_{spin}^* \hat{H} \Psi_{space} \Psi_{spin} d\tau_{space} d\tau_{spin} = I_{space} I_{spin}$$

The variational integral is factorized because the Hamiltonian does not contain spin variables. The integral over the spin variables is equal to 1 since the spin functions are normalized (Table 7.5). Therefore, the approximate energy is given by the integral over the spatial variables[1]

$$E_{trial} = \int \Psi_{space}^* \hat{H} \Psi_{space} d\tau_{space} \qquad \text{eq 7.20}$$

In the following we will drop the subscripts “trial” and “space”, with the understanding that we will be talking about approximate energies and approximate spatial functions. Note that the Hamiltonian in eq 7.20 is the exact (nonrelativistic) Hamiltonian (eq 7.1a or b), including the electron-electron interaction term, $1/r_{12}$.

7.4.3 Ground state of He atom.

We use the lowest energy orbitals for the two electrons in eq 7.18b; i.e. the 1s orbital for both electrons. The space part of the trial function is then

$$^1\Psi_{space} = 1s(1)1s(2) \qquad \text{eq 7.21}$$

This function has M_L=0, and L=0. It is symmetric to exchange of the spatial variables of the two electrons. Thus, it can be combined only with a singlet spin function (see eq 7.14). Therefore, its term symbol is ^1S. There are many other functions belonging to this term symbol, e.g. 2s(1)2s(2). Calculations show that the function in eq 7.21 gives the lowest value for the energy, obtained by evaluating the integral in eq 7.20. The ground state of He atom is denoted by 1^1S, where the “1” in front indicates that it is the “first” singlet S state (in order of increasing energy of ^1S states). The particular selection of the orbitals in eq 7.21 is designated by the symbol: $1s^2$; it is called the “electron configuration” for the ground electronic state of the helium atom.

***Exercise* 7.2** The true electronic ground state energy of He atom is -79.01 eV. In an approximate calculation of this quantity, we try the following function for the 1s orbital in eq 7.21

$$\psi_{1s} = \frac{\zeta^{3/2}}{\sqrt{\pi}} e^{-\zeta r} \qquad \text{so that} \qquad 1s(1)1s(2) = \frac{\zeta^3}{\pi} e^{-\zeta r_1} e^{-\zeta r_2}$$

where ζ (“zeta”) is taken as a variational parameter. When this function is used in the integral of eq 7.20, one obtains (in hartree)

$$E_{trial} = \zeta^2 - \frac{27}{8}\zeta$$

Find the best choice for the value of ζ, and use it to calculate the best energy for E_{trial} in eV. What is the percent error in the calculated energy?

Ans. ζ_{best}=27/16; error by 1.9 %.

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[1] This simplification is valid only for a two-electron atom or a molecule.

7.4.4 Excited electronic states of He atom.

Let us consider the electron configuration 1s2s. It means that we have decided to take the 1s orbital for one of the electrons and the 2s orbital for the other, in eq 7.18b. We may write the product function as either 1s(1)2s(2) or 2s(1)1s(2), since we can not distinguish between the two electrons. Both have M_L=0, and L=0; however, they do not obey eq 7.14 or 7.15, required by the Pauli exclusion principle. Hence, we form linear combinations of these two functions to obtain two new functions with desired symmetry properties, as we did for the spin functions above. Suppressing the electron labels, we have

$^1\Psi_{space}$ = c (1s2s + 2s1s) for singlet (S=0) spin state eq 7.22

$^3\Psi_{space}$ = c (1s2s - 2s1s) for triplet (S=1) spin state eq 7.23

where $c=2^{-1/2}$ is a normalization constant. The term symbols of these states are ^1S and ^3S. When the integral in eq 7.20 is evaluated with the functions above, both give higher energies than that of the function in eq 7.21. They form part of the low-lying excited states of He atom.

In general, if u and v are different orbitals, the symmetric linear combination

$u(1)v(2) + v(1)u(2) \equiv uv + vu$ for S=0 eq 7.24

satisfies eq 7.14 for singlet states while the antisymmetric combination

$u(1)v(2) - v(1)u(2) \equiv uv - vu$ for S=1 eq 7.25

fulfills requirement 7.15 for triplet states. For simplicity in writing we have omitted the normalization constant c.

Closed and open subshells. The group of orbitals for a given n and a given l is called a “subshell”; there are $g_l = 2l+1$ orbitals in the group. According to the simpler statement of Pauli principle, the maximum occupation number of a single orbital is 2, and hence the maximum occupation number of a subshell is $2g_l$. If a subshell in an electron configuration has the maximum occupancy, the subshell is said to be “closed”; otherwise, it is an “open” subshell. Thus, in $1s^2$ configuration, the 1s subshell is closed, and in 1s2s, there are two open subshells. We have seen above (eq 7.21) that the orbitals in the former subshell can give only a singlet space function. Other multiplicities are possible only when there are open subshells in the electron configuration, as in 1s2s which gives both a singlet and a triplet space function (eqs 7.22-23).

There are simple rules for determining the possible values of the total L quantum number from the l values of subshells in an electron configuration. For closed subshells, L=0 (and also S=0). The next rule pertains to 2 electrons in open subshells, as in He. Let l_1 and l_2 be orbital angular momentum quantum numbers of the two subshells (which may be same, i.e. $l_1 = l_2$). Possible values of total L are integers given by

$L = L_{max}, \ldots, L_{min}$ where $L_{max} = l_1 + l_2$ and $L_{min} = |l_1 - l_2|$ eq 7.26

It is instructive to consider several examples.

a) The configuration 1s2p gives a single value for L because l_1=0, and hence L= l_2=1. Using the orbitals belonging to these subshells, 3 singlet space functions of the form in eq 7.24, and 3 triplet space functions (eq 7.25) can be constructed. The term symbols are ^{1}P and ^{3}P.The ^{1}P term has a spatial degeneracy, (2L+1), of 3; the ^{3}P term, on the other hand, has an additional three-fold spin degeneracy, so the total degeneracy of this term is 3x3=9. The total number of states of both spins is 3+9=12.

b) Consider the configuration 2p3p. Here, l_1=1 and l_2=1. From eq 7.26 we have: L=2, 1 and 0, designated by D, P, and S, respectively. The spatial degeneracies are 5, 3, and 1, in the same order. The two subshells are different because of their *n* values. As in this and the previous example; when the two subshells are different, both spin values (S=0 and S=1) are allowed for each value of L. Thus the terms are: ^{1}S, ^{1}P, ^{1}D for the singlet states, and ^{3}S, ^{3}P, ^{3}D for the triplets. They form an additional set of excited states of He atom with 6 distinct energies. The total degeneracies are 1, 3, and 5 for the singlet energies, and 3, 3x3=9, 3x5=15 for the triplets. The total number of atomic states associated with the 2p3p configuration is thus 36.

c) Next we examine the states from the 2p^2 configuration, which may be written as 2p2p. The latter notation indicates that the two subshells are the same in this case. The possible values of L are as in the previous example: 2, 1, and 0. In the 2p3p case, the orbitals u and v of eqs 7.24-25 are selected from different subshells: u from the set ($2p_1$, $2p_0$, $2p_{-1}$) and v from ($3p_1$, $3p_0$, $3p_{-1}$). Hence we can form 3x3=9 different singlet functions (eq 7.24) and 9 triplet functions (eq 7.25), leading to the remarks made in example (b). However here, both of u and v must be selected from the same set: ($2p_1$, $2p_0$, $2p_{-1}$). Two-electron functions that can be constructed for the singlet and triplet states are shown in Table 7.6. There is only one triplet term: ^{3}P. The D term is a singlet; there must be 5 functions for L=2 corresponding to the values of $-2 \le M_L \le 2$. For $M_L = \pm 1$ and ± 2, there is only one function for each value of M_L. They belong to ^{1}D term. For $M_L = 0$, however, there are two functions. The presence of an extra function with $M_L = 0$ tells us that there must be an additional term with L=0, i.e. ^{1}S. In conclusion, the allowed terms for the 2p^2 electron configuration are ^{1}D, ^{3}P, and ^{1}S, with three different energies. The total number of states of both spins is 15.[2]

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[2] All functions in Table 7.6 except for the two singlets with M_L=0 are eigenfunctions of $\hat{L}^2$ operator with eigenvalues $L(L+1)$. By forming linear combinations of the latter two functions, two new functions can be obtained such that one of them has L=2 and the other has L=0.

Table 7.6 Two-electron spatial functions for a np^2 configuration (n is omitted for simplicity in writing)

S	Two-electron space functions	M_L	Term Symbol
1	$p_1p_0 - p_0p_1$	1	^3P
	$p_1p_{-1} - p_{-1}p_1$	0	
	$p_{-1}p_0 - p_0p_{-1}$	-1	
0	p_1p_1	2	^1D
	$p_1p_0 + p_0p_1$	1	
	p_0p_0 and $p_1p_{-1} + p_{-1}p_1$	0	^1S
	$p_{-1}p_0 + p_0p_{-1}$	-1	
	$p_{-1}p_{-1}$	-2	

***Exercise* 7.3** Use similar arguments as in the np^2 configuration to show that for a nd^2 configuration, the allowed term symbols are: ^1G, ^1D, ^1S for the singlets and ^3F, ^3P for the triplets. It is easier if you consider the triplets and singlets separately, as in Table 7.6.

7.5 The term with the lowest energy: Hund's Rule

Relative energies of terms belonging to a given electron configuration must be determined by actual calculations of the integral in eq 7.3a (or eq 7.20 for a two-electron atom). Results of a large number of such numerical calculations on atoms are summarized by Hund's rule:

Among the terms of a given electron configuration, the term with the highest spin multiplicity (i.e. maximum S) is lowest in energy. In case such a term is not unique, choose the one with the highest L among the terms with the same S_{max}.

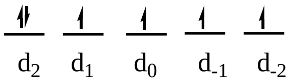
Let us apply this rule to the various electron configurations of He atom discussed above. For the 1s2s configuration, ^3S term has a lower energy than the ^1S term. For 1s2p, ^3P is lower in energy than ^1P. For 2p3p, among the six terms, ^3D should be lowest, and among the three terms of the $2p^2$ configuration, ^3P is lowest.

7.6 Atomic term symbols for *N*>2 electrons

For electron configurations with only 2 electrons in open subshells, the allowed terms are found as in the He atom discussed above, since the closed subshells do not contribute to either L or S. For configurations containing 3 or more electrons in open subshells, determination of the allowed terms is more complicated, and will not be discussed in this course. There is, however, a simple rule if there is only one open subshell in the electron configuration considered. Let l be the orbital angular momentum quantum number of such a subshell. Its maximum occupation number is, $n_{max}=2(2l+1)$. If n electrons are assigned to this subshell, the set of terms arising from the subshell configuration l^n are the same as those from $l^{n_{max}-n}$. E.g, the term symbols of p^4 are the same as those of p^2; a d^9 subshell gives the same term symbol as the one for d^1, i.e. a single ^2D term (a "doublet"); etc. Note that the term with the lowest energy can always be guessed by Hund's rule for any permissible value of n for the occupancy of the subshell.

***Example* 7.1**: What is the term symbol for the ground state of neutral Fe (Z=26) atom?

Solution: The electron configuration for N=26 electrons in the iron atom is: (closed subshells)3d^6. The 3d subshell here is an open subshell because its n_{max} =10. Hund's rule is: distribute the 6 electrons into as many different orbitals of the d subshell as possible to achieve a maximum value for M_S. There are 5 orbitals in the d subshell. We begin by assigning the first 5 valence electrons with parallel spins (i.e. each with m_s=+1/2) to these orbitals, so that the resultant M_S is 5(1/2)=5/2, and M_L due to them is 2+1+0-1-2=0. The 6th electron must be assigned to the d_2 orbital to make the total M_L largest; hence M_L becomes 2. However, the spin of the added electron must be reversed (m_s=-1/2) because of the Pauli principle, so that M_S=5/2-1/2=2.



$M_S = 2, M_L = 2$

There can be only one function of space and spin variables, with highest values for both M_S and M_L. It follows that S=2 and L=2. Hence, the term symbol with the lowest energy is ^5D (a "quintet").[3]

***Exercise* 7.4** Find the ground state term symbols for the following atoms: a) oxygen, b) nitrogen, c) bromine, d) argon, e) nickel.

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[3] You will arrive at the same result by taking a d^4 configuration.

7.7 The total angular momentum J and atomic energy levels

Energies of the “terms” are those of the solutions of the atomic Hamiltonian where the potential energy *V* takes into account only the Coulomb interactions. When these energies are compared with experimental ones, some qualitatively significant differences are found. As an example of experimental data, Figure 7.2 shows the first four energy levels of the carbon atom. Spectroscopic measurements can be extremely precise as you see from the data in the figure.[4] The first two excited levels are separated from the ground state by only 16.40 and 43.40 cm^{-1}, respectively. On the other hand, separation of the third excited level (denoted by $^1D_2$), when compared with these values, is very high.

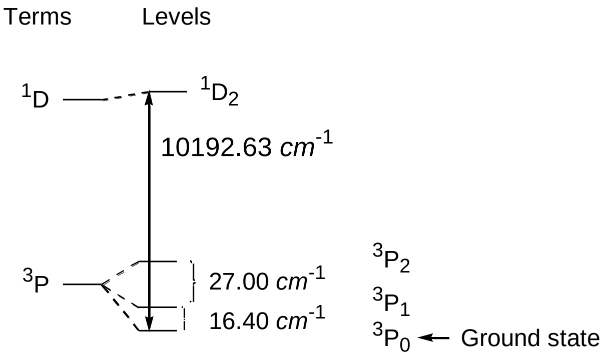

Figure 7.2 The first four experimentally observed energy levels of the carbon atom. The lowest two terms are shown on the left.

What does the theory say about the energy levels of the carbon atom (Z=6)? Its low-energy terms arise from the configuration $1s^2 2s^2 2p^2$. There is only one open shell, namely 2p, and the allowed terms are ^3P, ^1D, and ^1S.[5] We know from Hund’s rule that ^3P has the lowest energy. Numerical calculations show that the next term is ^1D with a separation from ^3P, near 10000 cm^{-1}. On the other hand; experimentally, carbon atom has several closely spaced levels with energies near to that of the ^3P term. Similar small discrepancies between theoretical energies and experimental data have been observed for many other atoms.

It has been found that this splitting of a term energy into several levels can be explained by supplementing the atomic Hamiltonian we have been using thus far by a new contribution called the spin-orbit Hamiltonian:

$$\hat{H}_{SO} = A\,\vec{\hat{L}} \cdot \vec{\hat{S}} \qquad \text{eq 7.27}$$

where *A* is a constant that depends on the particular term (i.e. on *L* and *S*) under consideration. Inclusion of this operator modifies the energy of the term by a correction, E_{SO}, called the spin-orbit interaction energy. In order to find a working expression for E_{SO}, one introduces the total angular momentum operator of the atom. It is a vector sum of spin and orbital angular momenta:

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[4] As an energy unit, 1cm^{-1}=0.0001240 eV = 0.01196 kJ/mol.

[5] See example (c) in Section 7.4.4.

$\vec{\hat{J}} = \vec{\hat{L}} + \vec{\hat{S}}$ eq 7.28

It can be shown that $\hat{J}^2$ and $\hat{J}_z$ commute with the full Hamiltonian operator of the atom. The former two operators also commute with $\hat{L}^2$ and $\hat{S}^2$. It follows that a solution Ψ of the atomic Schrödinger equation including the spin-orbit interaction is simultaneously an eigenfunction of these four operators. Eigenvalues of the total angular momentum are given in Table 7.7. Each wavefunction is labeled by four quantum numbers: Ψ_{JM_JLS}.

Table 7.7 Eigenvalues (in a.u.) of the total angular momentum operators.

Operator	$\hat{J}^2$	$\hat{J}_z$
Eigenvalues	$J(J+1)$	M_J where $-J \le M_J \le J$

The allowed values of *J* for given *L* and *S* (i.e. for a term) are (*cf*. eq 7.26)

$J = J_{max}, \ldots, J_{min}$ where $J_{max} = L+S$ and $J_{min} = |L-S|$ eq 7.29

As an example, for the ^{3}P term, *L*=1 and *S*=1. Hence there are three possibilities for *J* in this term: *J*=2, 1, 0. For the ^{1}D term, on the other hand, there is just one possibility: *J*=2.

The spin-orbit correction to the energy of an atomic term is given by

$E_{SO} = (A/2)\,[\,J(J+1) - L(L+1) - S(S+1)\,]$ eq 7.30

It is seen that energy levels belonging to the term depend on *J*, but not on M_J. Thus each level is (2*J*+1)-fold degenerate. Levels are designated by adding *J* as a right subscript on the term symbol. Thus the first three energy levels of the carbon atom have the “level symbols” shown in Figure 7.2. The spin-orbit interaction (or “coupling”) splits the 9-fold degeneracy of the ^{3}P term into 3 levels with degeneracies of 1, 3, and 5, corresponding to *J*=0, 1, and 2, respectively.

There is a useful rule for determining the order of the levels within a given term. If the open subshell is less than half filled, the level with the smallest *J* is the lowest; if it is more than half filled, the level with the highest *J* lies lowest. This rule is valid only if the electron configuration has one open subshell.

In the carbon atom, the 2p subshell is less than half filled, and hence the level with *J*=0 is lowest. The ground level of carbon atom is $^3P_0$; it is nondegenerate. According to eq 7.30, the first excited level (*J*=1) is separated from the ground level by *A*. One can obtain an estimate of this constant by reference to the experimental data given in Figure 7.2: *A*=16.4 cm^{-1} for the ^{3}P term of the carbon atom.

7.8 Selection rules for transitions between atomic energy levels in absorption or emission of light.

1. ΔS=0; i.e. spin multiplicity does not change in the transition.
2. The initial and the final levels must belong to different electron configurations such that there must be a change $\Delta l = \pm 1$ in the subshell of only one electron between the two configurations.
3. ΔL=0, ±1
4. ΔJ=0, ±1, except that J=0 to J=0 transition is forbidden.

As an example, let us consider absorption of light by ground state, $^3P_0$, carbon atoms. Transitions from this level to J=1 or J =2 levels of the same term, or to the $^1D_2$ and $^1S_0$ levels of the same electron configuration are forbidden because of rule 2 above. Transitions to triplet states (rule 1) belonging to another electron configuration such as $1s^22s2p^3$, (here, $\Delta l = 1$), are allowed within the restrictions of rules 3 and 4.

***Exercise* 7.5** The electronic configuration $1s^22s2p^3$ gives rise to 6 terms: ^1D, ^3D, ^1P, ^3P, ^3S, and ^5S.

a) For each of the 6 terms, give the level symbols associated with the term. What is the total number of distinct energy levels? Which of these levels is expected to have the lowest energy? *Ans*. 10 levels; lowest is $^5S_2$.

b) Find the allowed transitions between each of the levels $^3P_0$, $^3P_1$, and $^3P_2$ of ground configuration $1s^22s^22p^2$ and the levels of part (a).