## 1. Introduction

In these Notes we present the theory required for a basic qualitative and semi-quantitative understanding of the low-lying energy levels and energy eigenfunctions in multi-electron atoms. We concentrate mostly on the ground state configuration of low-$Z$ atoms where $LS$-coupling is applicable. The presentation in these Notes is based largely on the book *Intermediate Quantum Mechanics* by Bethe and Jackiw.

## 2. Information from Hartree-Fock Theory

At this stage we leave Hartree-Fock theory behind, apart from a limited amount of information that is passed to us. That information includes the self-consistent eigenfunctions $u_\lambda(\mathbf{r})$ of the Hartree-Fock equations (30.103) for at least the $N$ orbitals that are lowest in energy, plus their eigen-energies $\epsilon_\lambda$, plus the self-consistent direct and exchange potentials $\bar{V}_d$ and $\bar{V}_{ex}$ that appear in the the Hamiltonian of that equation. Actually, since the potentials can be expressed in terms of the orbitals, just specifying the orbitals and their eigen-energies is sufficient. In the following we write the single particle Hamiltonian in Eq. (30.103) as

$$h(\mathbf{r}, \mathbf{p}) = \frac{p^2}{2} - \frac{Z}{r} + \bar{V}_d(r) - \bar{V}_{ex}, \tag{1}$$

where we just write $\bar{V}_{ex}$ for the exchange operator, whose position-space kernel is the function $\bar{V}_{ex}(\mathbf{r}, \mathbf{r}')$. Then Eq. (30.103) is equivalent to

$$h u_\lambda(\mathbf{r}) = \epsilon_\lambda u_\lambda(\mathbf{r}). \tag{2}$$

We assume the potentials have been averaged to make them invariant under both spatial and spin rotations, as explained in Sec. 30.16. Thus the Hamiltonian $h$ is rotationally invariant, its eigenfunctions are central field eigenfunctions, and the index $\lambda$ can be identified with the usual list of central field quantum numbers $(n\ell m_\ell m_s)$. The spatial part of the orbitals has the form,

$$u_\lambda(\mathbf{r}) = R_{n\ell}(r) Y_{\ell m_\ell}(\theta, \phi), \tag{3}$$

and the spin parts are given by some assignment of magnetic spin quantum numbers $m_{s\lambda}$ for each orbital. As for the eigen-energies $\epsilon_\lambda$, they can be written as $\epsilon_{n\ell}$, since the energies do not depend on the magnetic quantum numbers $m_\ell$ and $m_s$. The solution of the Hartree-Fock problem also gives us

an electron configuration for the ground state, that is, a list of occupation numbers of the various subshells. In the ground state, all but the subshell of highest energy are filled, but the one of highest energy may be only partially filled. Notice that because of the form (2) for the wave functions, it is only necessary to specify the radial eigenfunction $R_{n\ell}(r)$ for each subshell in the configuration; for example, in the case of carbon with the configuration $1s^2 2s^2 2p^2$, the output of the Hartree-Fock theory will be three radial wave functions, $R_{1s}(r)$, $R_{2s}(r)$ and $R_{2p}(r)$, plus the associated energies $\epsilon_{1s}$, $\epsilon_{2s}$ and $\epsilon_{2p}$. These radial functions and energies can only be found numerically.

The Hartree-Fock estimate for the ground state wave function of the basic $N$-electron Hamiltonian (30.1) is the Slater determinant $|\Phi\rangle$, defined in terms of the orbitals $u_\lambda(\mathbf{r})$ and the spin assignments $m_{s\lambda}$ by Eq. (30.39). At this point we can regard that Slater determinant as being composed of central field eigenfunctions.

### 3. Limitations of the Hartree-Fock Wave Function

The main limitation of the Hartree-Fock wave function $|\Phi\rangle$ for the ground state is that it is not an eigenstate of all of the exact good quantum numbers of the Hamiltonian (30.1). As discussed in Sec. 30.2, a set of operators that commute with that Hamiltonian and with each other include $L^2$, $L_z$, $S^2$, $S_z$ and $\pi$. Thus the eigenstates of the Hamiltonian (30.1) can rigorously be characterized by their quantum numbers $(LM_LSM_S\pi)$ (using $\pi$ both for the parity operator and its eigenvalue). The Slater determinant $|\Phi\rangle$, however, is an eigenstate only of $L_z$, $S_z$ and $\pi$, and not, in general, of $L^2$ and $S^2$.

To see this consider first

$$L_z = \sum_{i=1}^{N} L_{iz}, \tag{4}$$

the $z$-component of orbital angular momentum, summed over all the electrons. When this is applied to a single term in the Slater determinant, each operator $L_{iz}$ will bring out the value $m_{\ell i}$, the $m_\ell$ value of the orbital assigned to electron $i$ in the given term. Thus $L_z$ brings out the sum of these values, $\sum_i m_{\ell i}$. There are, of course, $N!$ terms in the Slater determinant, but these consist of permuting orbitals among electrons, and this sum is invariant under such permutations. Thus the sum is the same for all the $N!$ terms of the Slater determinant, and we have

$$L_z|\Phi\rangle = \left(\sum_{i=1}^{N} m_{\ell i}\right)|\Phi\rangle. \tag{5}$$

Similarly, we have

$$S_z|\Phi\rangle = \left(\sum_{i=1}^{N} m_{si}\right)|\Phi\rangle. \tag{6}$$

As for parity, the operator $\pi$ maps all position vectors $\mathbf{r}_i$ into $-\mathbf{r}_i$, and so brings out a factor $(-1)^{\ell_i}$ from the orbital with angular momentum quantum number $\ell_i$. The product of these factors is

invariant under permutations and therefore the same for all the terms of the Slater determinant, and we have

$$\pi|\Phi\rangle = \Big[\prod_{i=1}^{N}(-1)^{\ell_i}\Big]|\Phi\rangle. \tag{7}$$

In summary, the Slater determinant composed of central field orbitals is an eigenstate of $L_z$, $S_z$ and $\pi$ with quantum numbers

$$M_L = \sum_{i=1}^{N} m_{\ell i}, \qquad M_S = \sum_{i=1}^{N} m_{si}, \qquad \pi = \prod_{i=1}^{N}(-1)^{\ell_i}. \tag{8}$$

A similar argument does not work, however, for the operators $L^2$ and $S^2$. The individual terms of the Slater determinant are not in general eigenstates of these operators, and neither is the sum. But since the energy levels of the basic $N$-electron Hamiltonian can be labeled by their $L$ and $S$ quantum numbers, we must do further work to find approximate wave functions that are eigenstates of all the conserved quantities in the system, including $L^2$ and $S^2$, and to understand how the energies depend on the associated quantum numbers. This has to be regarded as a minimum level of understanding of the structure of multielectron atoms.

## 4. Coupling Schemes

We can achieve what we want and learn quite a bit about atomic structure by building a perturbation analysis on top of the results of Hartree-Fock theory. We begin by writing the Hamiltonian for an $N$-electron atom in the form $H = H_0 + H_1 + H_2$, where

$$H_0 = \sum_{i=1}^{N} h(\mathbf{r}_i, \mathbf{p}_i) = \sum_{i=1}^{N}\Big[\frac{p_i^2}{2} - \frac{Z}{r_i} + \bar{V}_d(r_i) - \bar{V}_{ex,i}\Big], \tag{9a}$$

$$H_1 = \sum_{i<j}\frac{1}{r_{ij}} - \sum_{i=1}^{N}\Big[\bar{V}_d(r_i) - \bar{V}_{ex,i}\Big], \tag{9b}$$

$$H_2 = \sum_{i=1}^{N}\xi(r_i)\mathbf{L}_i \cdot \mathbf{S}_i, \tag{9c}$$

The sum $H_0 + H_1$ is the same as the basic $N$-electron Hamiltonian (30.1), written in a particular way (in Notes 30 that Hamiltonian was written as $H_1 + H_2$, but the notation $H_1$, $H_2$ in these Notes is different). In particular, the sum over the electrons of the direct minus exchange potentials has been added and subtracted to create the terms $H_0$ and $H_1$ above, which add up to the Hamiltonian (30.1).

The first term $H_0$ is a sum over the electrons of the self-consistent, single particle Hamiltonian $h$, of the same functional form for all the electrons, containing the kinetic energy, the potential energy of interaction with the nucleus, and a kind of rotational average of the potential energy of interaction with all the other electrons. This Hamiltonian is called the *central field approximation*

to the Hamiltonian for the atom; it is an approximation that is cruder than the basic $N$-electron
Hamiltonian (30.1) that we started with. The eigenfunctions of $H_0$ are just products of central field
eigenfunctions of $h$, one for each electron, or linear combinations of such products. Thus, the Slater
determinant $|\Phi\rangle$, the Hartree-Fock estimate to the ground state of the atom, made up out of central
field orbitals, is an eigenfunction of $H_0$,

$$H_0|\Phi\rangle = E_0|\Phi\rangle, \tag{10}$$

with a corresponding energy,

$$E_0 = \sum_\lambda \epsilon_\lambda = \sum_{n\ell} \nu_{n\ell}\, \epsilon_{n\ell}, \tag{11}$$

where in the last sum $\nu_{n\ell}$ is the occupation number of subshell $(n\ell)$, that is, the number of electrons
in that subshell. Although the ground eigenstate $|\Phi\rangle$ of $H_0$ is the Hartree-Fock estimate to the
ground state eigenfunction of the atom, $E_0$ is not the Hartree-Fock estimate to the energy, since it
double counts the direct and exchange potential energies among the electrons. See Eq. (30.97), which
shows that $E_0$ is too high. This energy will, however, be corrected by the perturbation treatment we
shall carry out below, which will also give us the dependence of the energy on the quantum numbers
$L$ and $S$.

    The term $H_1$, Eq. (9b), consists of the exact interelectron Coulomb interactions, that is, the term
$\sum_{i<j} 1/r_{ij}$, minus the rotational average of those potentials (the direct minus exchange potentials,
summed over electrons). It is sometimes called the "residual Coulomb potential." If the rotational
averaging provides a good approximation to the exact interelectron Coulomb interactions, then the
term $H_1$ should be much smaller than the exact interelectron interactions. The exact interelectron
Coulomb interactions are too big to treat by perturbation theory (apart from the case of helium,
where the results are not very satisfactory from a numerical standpoint), but with the rotational
average subtracted off, the result, the term $H_1$ above, is small enough for a successful perturbation
treatment. That is, we have $H_1 \ll H_0$. We shall outline this perturbation treatment below.

    But if $H_1$ is now a small term, the question is how it compares to other small terms we have
neglected so far, such as the fine structure terms. To take these into account as well, we have
included the spin-orbit interaction for each electron, summed over all electrons, in the term $H_2$ in
Eq. (9c). The quantity $\xi(r)$ is a function of the radius of the electron (see Eq. (23.12)) whose details
will not concern us. The spin-orbit term is only one of several fine structure terms, most of which
we are omitting for simplicity, and even the spin-orbit term is treated somewhat schematically. Our
goal will be to give a qualitative understanding of the effects of the fine structure terms without
going into detail.

    But to return to the question posed, what is the quantitative relation between $H_1$ and $H_2$? It
turns out that the answer depends on $Z$. In low $Z$ atoms near the beginning of the periodic table,
we have $H_2 \ll H_1 \ll H_0$. For such atoms, it makes sense to first treat $H_1$ as a perturbation on $H_0$,
find the eigenstates of $H_0 + H_1$, then to treat $H_2$ as a second perturbation on top of $H_0 + H_1$. This
scheme involves classifying the eigenstates of $H_0 + H_1$ by their good quantum numbers, which, as

we have indicated, include $L$ and $S$. This scheme is called *LS-* or *Russell-Saunders coupling.* For high $Z$ atoms, however, near the end of the periodic table, it turns out that $H_1 <\approx H_2 \ll H_0$. In this case it makes sense to first treat $H_2$ as a perturbation on top of $H_0$, then to treat $H_1$ as a perturbation on top of $H_0 + H_2$. This scheme is called *jj-coupling,* on account of the quantum numbers that arise in it. In these Notes we consider only *LS*-coupling.

## 5. The Unperturbed System

Let us therefore consider $H_1$ as a perturbation on top of $H_0$. As usual in perturbation theory, we must first understand the unperturbed system, its eigenstates and eigenvalues, and in particular its degeneracies, since those affect how the perturbation calculation is carried out. The ground state energy of $H_0$ is $E_0$, shown in Eq. (11), and the Slater determinant $|\Phi\rangle$ composed of central field orbitals is a ground state eigenfunction. In general, there are degeneracies, since the orbitals that go into $|\Phi\rangle$ are specified by all four quantum numbers $(n\ell m_\ell m_s)$, while the energy $E_0$ depends only on the quantum numbers $(n\ell)$. That is, the energy $E_0$ is independent of the assignment of magnetic quantum numbers $(m_\ell m_s)$ to the electrons. Each subshell contains $2(2\ell + 1)$ orbitals, the total number of possible $m_\ell$ and $m_s$ values, and if the subshell is filled, then there is only one way of assigning these magnetic quantum numbers to the electrons in that subshell. But if a subshell is "incomplete," that is, only partially filled, then there is more than one way of assigning magnetic quantum numbers, and therefore more than one Slater determinant $|\Phi\rangle$ with the same energy. To clarify which assignment of magnetic quantum numbers we mean, we will replace the notation $|\Phi\rangle$ with $|m\text{-set}\rangle$, where "$m$-set" refers to the magnetic quantum numbers in incomplete subshells only. To be even more explicit about this, we will sometimes write $|\text{cfg}; m\text{-set}\rangle$, to indicate the electron configuration we are thinking of. The electron configuration specifies the $(n\ell)$ quantum numbers of the electrons, the $m$-set the $(m_\ell m_s)$ quantum numbers in incomplete subshells, and the $(m_\ell m_s)$ quantum numbers in complete subshells take on the only values they can. In the equation,

$$H_0|\text{cfg}; m\text{-set}\rangle = E_0|\text{cfg}; m\text{-set}\rangle, \tag{12}$$

the energy $E_0$ depends on the configuration but not on the $m$-set. Therefore the order of the degeneracy is the number of possible $m$-set values.

Notice that in assigning orbitals to electrons the order of the assignment does not matter, since all electrons are permuted among all orbitals by the Slater determinant. All that matters is which orbitals are assigned, that is, the list of assigned orbitals. More precisely, if we change the order in which the orbitals are assigned to the electrons, the Slater determinant may change sign, if the rearrangement of the orbitals amounts to an odd permutation. Apart from this sign, the order does not matter, and even the sign is pinned down if we put the orbitals in a standard order when assigning them. Therefore the number of distinct assignments of $n$ electrons to orbitals in a subshell containing $s = 2(2\ell+1)$ slots is the binomial coefficient $\begin{pmatrix} s \\ n \end{pmatrix}$, which is the number of distinct unordered subsets of $n$ elements taken from a set of $s$ elements. This is the number of distinct $m$-sets possible for the

given subshell. In excited state configurations of an atom, for example, $1s^2 2s^2 2p 3s$ in carbon, there may be more than one incomplete subshell, so the total number of possible assignments of $m$-sets is the product of the binomial coefficients $\begin{pmatrix} s \\ n \end{pmatrix}$, one for each incomplete subshell. For the ground state configuration we are considering in these Notes, there is only one incomplete subshell, so the order of the degeneracy of the ground state of $H_0$, that is, the number of distinct possible $m$-sets, is the one binomial coefficient $\begin{pmatrix} s \\ n \end{pmatrix}$ for the one incomplete subshell.

**Problems**

**1.** Work out the multiplets (terms) $^{2S+1}L$ which result from 3 equivalent $d$ electrons. ("Equivalent" means that they all belong to the same subshell.) Check to make sure your answer adds up to the correct number of levels, based on the degeneracy expected in the central field approximation. In the case of vanadium, use Hund's rules to determine the ground state multiplet. When spin-orbit coupling is turned on, the multiplets split, and the resulting levels are denoted $^{2S+1}L_J$. Which of these represents the ground state of vanadium?

**2.** Write out the $^2P$ wave functions explicitly for an $(np)^3$ configuration (e.g., nitrogen), that is, as linear combinations of Slater determinants that you may identify by their $m$-sets (the set of magnetic quantum numbers for electrons in incomplete subshells). You may denote these Slater determinants simply by $|m\text{-set}\rangle$.