Physical Basis for Hund’s Rule

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It is shown that a consideration of the Coulombic and spin-orbit interactions between the electrons of a given atomic configuration is sufficient to arrive at a lowest-energy state consistent with Hund’s rule. The maximum-spin requirement of Hund’s rule is a result of minimum Coulombic energy alone, whereas maximum orbital angular momentum consistent with maximum spin is a result of minimum spin–orbit energy. It is argued that, to first order, the spin–spin interaction is not a principal factor in determining the properties of this state. The simple notions used to obtain these results are extended to excited states of the \( \pi^2 \) configuration and are shown to give results consistent with calculations based on hydrogenic wavefunctions.

I. INTRODUCTION

The empirical rule for determining the lowest-lying level of a given atomic configuration was discovered by Hund in 1925 and today bears his name.\(^1\)\(^-\)\(^3\) The rule is usually stated as follows: For a given atomic configuration, an energy level with largest total spin \( S \) lies deepest and, of these, the level with largest total orbital angular momentum \( L \) lies deepest. In his book published in 1927,\(^4\) Hund states an additional rule that applies only to configurations of equivalent electrons.\(^5\) This rule may be stated as follows: Where the number of equivalent electrons \( N \) is less than or equal to half a filled shell, the total angular momentum \( J \) of the deepest level is given by \( J = |L - S| \) and, otherwise, by \( J = L + S \).\(^6\)

Without going too far afield, it is safe to say that Hund’s rule is found to hold with but one known exception\(^9\) for ground configurations of all atoms. In those atoms (primarily those with large atomic number) where there is a breakdown

\(^1\) F. Hund, Z. Physik, 33, 345 (1925).
\(^6\) See Ref. 3., p. 126.
\(^7\) Atomic electrons are equivalent if they share single-electron states that have the same principal and orbital angular-momentum quantum numbers, or, in other words, electrons in the same shell.
\(^8\) In the jargon of spectroscopists, the former is said to be a normal fine structure whereas the latter is called inverted.
Hund's rule states that the total angular momentum is given by $J = L - S = 2$. The atomic system described by the quantum numbers $S = 1, L = 3$, and $J = 2$ is designated $^3P_2$. If the two $d$ electrons are not equivalent, i.e., in the configuration $n'd$ where $n' \neq n$, then the projections $m_i$ need not differ and $L = 4$ is possible. Hund's rule does not provide the value for $J$ in this case, and the state is designated simply by $^6C$.

In Sec. II, the physical arguments leading to a ground state consistent with Hund's rule are presented. In Sec. III, these arguments are shown to give correct results even when applied to excited states of the $n^6$ configuration, whereas a natural extension of Hund's rule fails.

II. LOWEST LEVEL

One method for handling the energy $E(r)$ due to the electrostatic repulsion between electrons in an atom is to introduce a fictitious potential energy $U(r)$ into the Hamiltonian for the system. This potential energy is adjusted to describe the major portion of the true interaction so that $E(r) - U(r)$ is small and may be treated by ordinary perturbation methods. Although this procedure is useful for obtaining quantitative results, the importance of the electrostatic energy relative to the spin-orbit and spin–spin energies is not clear when assessed from such a perspective. For our purposes, it is necessary to consider these interactions before any averaging.

An accurate, rigorous appraisal of the magnitudes of the electronic interactions in a given configuration requires machinery far too complicated to provide a simple physical picture of the situation. Let us then simply assume that the electrostatic interaction is by far the most important of the three. This assumption is not without basis. If one considers averages of the form $\langle r^{-2} \rangle$ to be approximately equal to $a^{-2}$ where $a$ is some reasonable atomic dimension, say $a = 10^{-9}$ cm, then one finds the electrostatic energy to be about $10^5$ times as large as either

of the other two. Therefore, in order to obtain the atomic state that has the least energy, it is proper first to minimize $E(r)$, and then to consider the other interactions only as they may be compatible with the results of such a minimization. The arguments that follow hinge on the validity of this statement.

Consider an atomic system of $N$ equivalent electrons, each with $l$ units of angular momentum. The electrostatic energy between two of these electrons is of the form $\langle |r_1 - r_2| \rangle^{-1}$ so that the least energy is obtained when the probability (on the average) of finding the two electrons close to each other is smallest. It is a property of wavefunctions which are antisymmetric in the spatial coordinates of the electrons that the probability of finding any two of the electrons in the same infinitesimal volume is zero. (Of course, the total wavefunction for $N$ electrons, including spin, must always be antisymmetric on the interchange of both the spatial and spin coordinates of any two electrons.) Thus, a plausible assumption is that the state with least energy will be of this type. The antisymmetrization of the spatial part of the wavefunction involving $N$ equivalent electrons is possible only when $N \leq 2l + 1$ (less than or equal to half a filled shell) so that we phrase a postulate based on the observations stated above with this consideration in mind:

**Postulate I.** The ground state wavefunction of a configuration involving $N$ equivalent electrons is as maximally antisymmetric in the spatial coordinates of the electrons as is compatible with the exclusion principle.

Necessarily associated with an antisymmetric spatial wavefunction is a symmetric spin function.
tion, in order that the product be totally anti-
symmetric. If the number of equivalent electrons
exceeds half a filled shell, then at most, the
electrons in the first half-shell can be spatially
antisymmetric (spin-wise symmetric) on inter-
changes among themselves, and similarly for
those electrons in the second half-shell. The total
wavefunction (including spin) must then
be antisymmetrized on interchanges between
the electrons occupying different half-shells. For
the symmetric spin function, the following
theorem applies:

**Theorem 1.** A necessary and sufficient con-
dition that the total spin of \( p \)-spin one-half
particles is the maximum possible, i.e., \( \frac{1}{2}p \),
is that the spin function for those particles is
symmetric on the interchange of any two.

**Proof.** The proof of this theorem is simple if
one utilizes the operator \( m_{ij} \) which interchanges
the spin projections of the \( i \)th and \( j \)th particles.\(^9\)
For spin one-half particles, the product \( s_i \cdot s_j \) is
given by

\[
s_i \cdot s_j = \frac{1}{2} (m_{ij} - \frac{1}{2} + \delta_{ij}), \tag{1}
\]

where \( s_i \) is the spin operator for the \( i \)th particle,
\( \delta_{ij} \) is the Kronecker delta, and the units are
such that \( \hbar = 1 \). The simplest check that this
relationship is valid is when \( i = j \). Then it is
known that \( s_i \cdot s_j = \frac{1}{2} (\frac{1}{2} + 1) = \frac{3}{2} \). On the other
hand, \( m_{ii} = \delta_{ii} = 1 \) so that the right hand side
is also \( \frac{3}{2} \).

(a) **Sufficiency Proof.** Assume \( x_E \) is a sym-
metric spin function involving \( p \)-spin one-half
particles. Then

\[
S^2 x_E = (\sum_{ij} s_i \cdot s_j) x_E, \tag{2}
\]

where

\[
S = \sum_i s_i. \tag{3}
\]

Using (1),

\[
S^2 x_E = \sum_{ij} \left( \frac{1}{2} (m_{ij} - \frac{1}{2} + \delta_{ij}) \right) x_E
= (\sum_{ij} \frac{1}{2} + \sum_{ij} \frac{1}{2}) x_E
= \frac{1}{2} p (\frac{1}{2} p + 1) x_E, \tag{4}
\]

since

\[
m_{ij} x_E = x_E. \tag{5}
\]

(b) **Necessity Proof.** Assume that \( \chi \) involves
\( p \)-spin one-half particles and that

\[
S^2 \chi = \frac{1}{2} p (\frac{1}{2} p + 1) \chi. \tag{6}
\]

Using (1), we obtain

\[
(\sum_{ij} m_{ij}) \chi = p^2 \chi, \tag{7}
\]

or

\[
\sum_{ij} \chi^* m_{ij} \chi = p^2, \tag{8}
\]

assuming the normalization

\[
\chi^* \chi = 1. \tag{9}
\]

In general, if the state \( \chi \) is written as the sum of
two terms, one even and the other odd on the
interchange of particles \( i \) and \( j \), it is readily shown that

\[
\langle m_{ij} \rangle = \chi^* m_{ij} \chi \leq 1, \tag{10}
\]

so that

\[
\sum_{ij} \langle m_{ij} \rangle \leq p^2, \tag{11}
\]

with equality only in the event that \( m_{ij} \chi = \chi \)
for all \( i \) and \( j \). But from (5), it is seen that the
equality does hold, hence \( \chi = x_E \).

On the basis of this theorem and the postulate
stated previously, the primary requirement of
Hund’s rule, that is, maximum \( S \), follows
directly. If \( N \leq 2l+1 \), the spatial (spin) wave-
function is antisymmetric (symmetric) and the
spin of the lowest level is given by

\[
S = \frac{1}{2} N. \tag{12}
\]

If \( 2l+1 < N \leq 2(2l+1) \), then the spatial (spin)
wavefunction describing the electrons in each
half-shell are antisymmetric (symmetric) on inter-
changes within the respective half-shells. Consequently, the spin \( S \) for the \( 2l+1 \) electrons
in the first half-shell, is \( \frac{1}{2} (2l+1) \), and the
spin associated with the remaining electrons \( S_t \) is
\( \frac{1}{2} [N - 2l - 1] \). The spins \( S_i \) and \( S_t \) are forced by the
exclusion principle to be antiparallel\(^9\) so
that the spin for the system in this case is

\[
S = S_i - S_t \tag{13}
\]

where \( N \) is the number of “holes” in the shell.

\(^9\) From the exclusion principle, the electrons in the
second half-shell must possess \( m_s \) values differing from
those in the first half-shell. Thus, if \( S_i \) is oriented to have
maximum \( z \) projection, i.e., \( S_{iz_{max}} = S_i \), each electron in
this shell has \( + \frac{1}{2} \) projection so that each electron in the
second half-shell must have \( - \frac{1}{2} \) projection.
It is, therefore, a consequence merely of minimizing the energy due to the electrostatic repulsion among the electrons that the system tends to be in a state of maximum spin $S$. What is clear is that these results do not owe their origin to the spin–orbit interactions that are known to exist in an atom!

The spin–orbit interaction, although limited to a degree by the foregoing considerations, can otherwise come into full play to further minimize the energy. This interaction is of the form $\xi \sum s_i \cdot L_i$, where $\xi$ is a positive quantity\(^{31}\) so that minimum energy is obtained for antiparallel alignments of the spins with the orbital angular momenta. If the spins of the electrons are all in the same direction, then the $L_i$ align maximally antiparallel to this direction. Thus, for $N < 2l+1$, the resultant orbital angular momentum $L$ is antiparallel to $S$ and has the magnitude\(^{32}\)

$$L = \sum_{i=1}^{N-1} (l_i - l) = \frac{1}{2}N(2l+1-N).$$

Since $L$ and $S$ are antiparallel, this suggests that the ground state has a definite total angular momentum given by $J = L - S$. In case $N = 2l+1$, then $L = 0$ and $J = S$.

The situation for $2l+1 < N \leq 2(2l+1)$ can be similarly analyzed. The total orbital angular momentum results solely from the electrons in the second half-shell (for the closed half-shell $L_1 = 0$) and is, accordingly, antiparallel to $S_2$; however, the total spin for the system is determined by the direction of $S_1$ since $S_1 \geq S_2$, thus $L$ and $S$ are parallel and $J = L + S$. In terms of $N$, we have in this case,

$$L = \frac{1}{2}N(2l+1-N).$$

It is, therefore, a consequence of minimizing the spin–orbit interaction that the ground state has maximum $L$ consistent with the requirements of minimum electrostatic energy, that is, consistent with maximum $S$. This is Hund's rule.

### III. Excited Levels

As a demonstration of the usefulness of the simple notions set forth in the previous section, let us consider the configuration $n^6$, i.e., six equivalent electrons with $l = 3$. The ground state is expected to have $S = 3$, $L = 3$ and $J = L - S = 0$, and is designated $^1F_0$. Judd\(^{33}\) gives a diagram of the energy levels of this configuration calculated on the basis of hydrogenic wavefunctions. Simply on the basis of the statement of Hund's rule, one would expect the group of excited states nearest to the ground state to be characterized by $S = 2$ (a relaxation of the primary requirement of Hund's rule), the next group by $S = 1$, and so forth. Among the states in each group, the state with maximum $L$ would be expected to be lowest. For $S = 2$, five electrons have, say, spin projection $\frac{1}{2}$ and one electron has spin projection $-\frac{1}{2}$. Thus, the maximum $L$ is the maximum for the five electrons $L_1 = 5$, plus the maximum for the one electron, $L_0 = 3$. That is, for $S = 2$, $L_1 + L_0 = 8$ is expected simply by a "rule of thumb" extension of Hund's rule. However, on the basis of the discussion in the previous section, it is clear that $L_1$ and $L_0$ are antiparallel for minimum spin–orbit energy (since the spins of the associated groups of electrons are antiparallel), and on this basis one would expect $L = L_1 - L_0 = 2$ to give the total orbital angular momentum of the lowest-lying state. The calculations based on hydrogenic wavefunctions agree with the latter prediction, i.e., the $^1D$ state is the lowest among the $S = 2$ states. Similarly, for $S = 1$ and $S = 0$, the analysis according to the previous section predicts lowest levels of $^3P$ and $^1S$, respectively, again in agreement with the hydrogenic-wavefunction calculations.

### IV. Conclusions

It has been shown that a consideration of the Coulombic and spin–orbit interactions between electrons of a given configuration is sufficient to arrive at a lowest energy state consistent with Hund's rule. It was argued that, to a first approximation, the spin–spin interaction is not a factor in determining the properties of this lowest state. The maximum-spin requirement is a result of considering the Coulombic interaction alone, whereas maximum $L$ is a result of

\(^{31}\) The word "minimizing" is used here in the context of the assumptions that were clearly stated previously. Of course no analytic minimization process has taken place.

\(^{32}\) See Ref. 4, p. 122.

minimizing the spin–orbit energy which, in
addition, provides the correct $J$ value for
configurations of equivalent electrons.

The interactions considered above do not
exhaust all of the interactions that are present
in an atom; however, in most atomic systems,
these are the most important and certainly are
adequate to provide answers that are qualita-
tively correct in many cases. The understand-
ing of the physical basis for Hund’s rule has
been shown here to be one such case.

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A Library of Experiments

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A new concept in physics laboratory instruction is described in which the experiments are
available to the student in much the same fashion as books in a library. The general nature of
the experiments is explained and the philosophy underlying the use of the laboratory for in-
struction is discussed.

THE University of Colorado is developing a
new concept of physics laboratory instruc-
tion for lower-division physics courses. We are
constructing a “library of experiments” in which
the apparatus for an experiment is nearly as
accessible as are the books in the stacks of a
university library. Our library at present contains
about sixty-five different experiments, two-thirds
of which have at least one duplicate. Eventually
we hope to have between eighty and ninety
different experiments.

These experiments are set up permanently on
metal tables which can be moved from one
location to another by means of a specially
constructed dolly. The tables containing the
experiments in most active use are located in a
single room whose area is about 3200 sq ft,
while the remainder of the tables are stored in
an adjacent room. The library-laboratory is open
regularly from 8:30 a.m. to 9:00 p.m. and the
scheduled laboratory classes meet in this room.
Moreover, individual students are encouraged to
return to perform experiments on their own.
The laboratory sections are conducted by the
regular teaching staff of the Physics Department,
and a technician who is thoroughly familiar with
the experiments is on hand during all open hours
of the library.

Under this concept of laboratory instruction
the students may be expected to do two or three
experiments in the course of a 2-h period. In
general, of course, students get more out of a
laboratory session if the experiments have been
discussed and if the procedures have been
demonstrated during a previous session. Ways
in which this may be handled are discussed
below.

THE PEDAGOGICAL PURPOSE

OF THE LABORATORY

The experiments in our library are not research
projects and we make no pretense that the
student is led to discover the laws of physics or
even to establish them firmly. Moreover, since
the setups are ready made for the student, we
cannot claim that one of the objectives of the
laboratory instruction is to teach laboratory
 technique by assembling apparatus for an
experiment.

The experiments, however, are designed to be
both exercises and demonstrations which are
closely related to the content of the course. In
It is shown that a consideration of the Coulombic and spin-orbit interactions between the electrons of a given atomic configuration is sufficient to arrive at a lowest energy state consistent with Hund’s rule. The maximum-spin requirement of Hund’s rule is a result of minimum Coulombic energy alone, whereas maximum orbital angular momentum consistent with maximum spin is a result of minimum spin-orbit energy. It is argued that, to first order, the spin-spin interaction is not a principal factor in determining the properties of this state. The simple notions used to obtain these results are extended to excited states of the $nf^6$ configuration and are shown to give results consistent with calculations based on hydrogenic wavefunctions.