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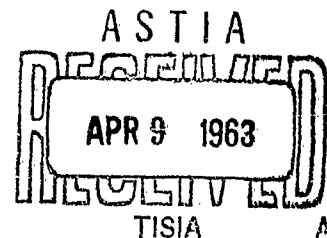
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ANGULAR MOMENTUM STATES

Nick Karayianis

Clyde A. Morrison

8 March 1963



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WASHINGTON 25, D.C.

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PREFACE

This report is intended to be the first of a series that will attempt to incorporate some of the latest theoretical techniques into a unified but concise treatment of crystal field theory and the analytical methods used therein. The series of papers assumes familiarity with the fundamentals of quantum mechanics, and a firm background in general physics and mathematics.

The book of E. U. Condon and G. H. Shortley, "The Theory of Atomic Spectra," first published in 1935 and reprinted as late as 1959, provides a solid basic reference to the field. Since the time it was first published, there has been an increased use of group theoretic methods (Bethe used these methods in a paper as early as 1929) and "Racah Algebra" in the analysis of the atomic spectra and their modification due to crystalline fields. The book by M. E. Rose, "Elementary Theory of Angular Momentum," provides an excellent account of the Clebsch-Gordan (vector coupling) coefficients and the Racah (recoupling) coefficients, the manipulation of which constitutes the so-called "Racah Algebra."

The standard reference to group theory is E. P. Wigner's book by that name, but there exist references that are more readable. Examples of these are J. S. Lomont, "Application of Finite Groups," and M. Hammermesh, "Group Theory."

Although these latest references are readily available, there are several examples in the literature where the methods employed are not quite up to date. There is failure, in some instances, to recognize the unified treatment of quantities which have been given various symbols by different authors but are simply related to C-G and Racah coefficients. As a result, some unnecessarily involved and lengthy expressions have resulted. Now with the availability of complete tables of 3-j and 6-j symbols which are proportional to the Clebsch-Gordan and Racah coefficients respectively, the expression of results entirely in these quantities is at least desirable, if not necessary.

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ABSTRACT

This paper is intended to be the first of a series that will attempt to incorporate some of the latest theoretical techniques into a unified but concise treatment of crystal field theory and the analytical methods used therein. The emphasis in this paper is on angular momentum states and the so-called Clebsch-Gordan and Racah coefficients which arise in the handling of such states.

In order to illustrate the use of the formalism introduced in connection with the angular momentum states, a simple problem in quantum mechanics is solved in detail. The problem brings out some features of atomic systems such as the Zeeman effect and spin-orbit coupling, and, in addition, it illustrates the use of first and second-order degenerate perturbation theory.

1. INTRODUCTION

In the treatment of quantum mechanical systems with bound states due to central potentials, it is convenient to describe the system in terms of angular momentum states (ref 1). Even in cases where the spherical symmetry is destroyed by the imposition, say, of an external magnetic or electric field, angular momentum states in many cases, still serve as a useful basis in which to represent the system. For this reason, the earlier sections of this paper describe the essential features of angular-momentum states and their associated properties. The later sections of this paper utilize some of these properties in the analysis of an illustrative problem and introduce, in addition, the techniques of elementary perturbation theory.

2. ROTATIONS OF ANGULAR MOMENTUM STATES

Let us denote an angular momentum state by $|jm\rangle$. The arguments associated with this state indicate that it is an eigenstate of J^2 and J_z thus,*

$$J^2 |jm\rangle = j(j+1) |jm\rangle \quad (1)$$

$$J_z |jm\rangle = m |jm\rangle \quad (2)$$

where J^2 and J_z are, respectively, the square of the total angular momentum operator and its z component.

The total angular momentum operator may be defined in terms of the three dimensional rotation operator $R(\hat{n}, \theta)$, (ref 2) where $\hat{n}$ is the unit

* The units $\hbar = c = 1$ are used throughout this report.

vector about which the rotation through an angle θ is effected. An alternative description of the rotation is provided by the Euler angles (ref 3) so that $R(\hat{n}, \theta)$ may, equivalently, be denoted $R(\alpha \beta \gamma)$. In terms of such a rotation operator, the angular momentum operator is defined by

$$R(\hat{n}, \theta) |jm\rangle = e^{-i\hat{n} \cdot J\theta} |jm\rangle \quad (3)$$

or, equivalently,

$$R(\alpha \beta \gamma) |jm\rangle = e^{-iJ_z\alpha} e^{-iJ_y\beta} e^{-iJ_z\gamma} |jm\rangle \quad (4)$$

Assuming the $|jm\rangle$ to have a normalization,*

$$\langle j'm' | jm \rangle = \delta_{jj'} \delta_{mm'} \quad (5)$$

the matrix representation of $R(\alpha \beta \gamma)$ in that basis is defined thus,

$$\langle j'm' | R(\alpha \beta \gamma) | jm \rangle = \delta_{jj'} D_{m',m}^j(\alpha \beta \gamma) \quad (6)$$

The rotation operator is diagonal in j since the angular momentum of a system is not altered if the system is viewed from a rotated frame. The projections of j , however, are obviously not conserved under such an arbitrary rotation. Using the completeness relation for the states $|jm\rangle$, i.e.

$$\sum_{jm} |jm\rangle \langle jm| = 1 \quad (7)$$

one may determine the result of rotating an arbitrary state. The result, using (6) and (7) is,

$$\begin{aligned} R(\alpha \beta \gamma) |jm\rangle &= 1 \cdot R(\alpha \beta \gamma) |jm\rangle \\ &= \sum_{j'm'} |j'm'\rangle \langle j'm' | R(\alpha \beta \gamma) | jm \rangle \\ &= \sum_{m'} D_{m',m}^j(\alpha \beta \gamma) |jm'\rangle \end{aligned} \quad (8)$$

* For those not familiar with the Dirac bra-ket notation, associate wave functions ψ_{jm} with the $|jm\rangle$ and $\oint d\Omega \psi_{j'm'}^+ P \psi_{jm}$ with $\langle j'm' | P | jm \rangle$ for the matrix element of an arbitrary operator P . Further information may be obtained in "Quantum Mechanics," E. Merzbacher, p. 306, (ref 1) or "The Principles of Quantum Mechanics," P. A. M. Dirac (ref 10).

Thus one has expanded, into the set of states that form the basis, the result of rotating the state $|jm\rangle$ (which itself is one of the "members" of the basis) through angles defined by α, β, γ . To avoid confusion, it is here emphasized that the operator $R(\alpha \beta \gamma)$ as defined above operates on the physical system described by the ket and physically rotates that system. After such a rotation, the physical system is not (in general) in a pure state insofar as the basis of states (the $|jm\rangle$) is concerned. It is in a state of impure z projection as evidenced by its description as a superposition of pure states with various m values as given by (8). In many places in the literature one will read that the coordinate system is being rotated and in many instances, it is not clear, to which coordinate system reference is being made. The interpretation given above seems to be less confusing.

It is convenient at times to write the explicit dependence of $D_{m',m}^j(\alpha \beta \gamma)$ on its arguments α and γ . That this is possible is easily seen if the expression (4) is substituted into (6). The result is

$$\begin{aligned} D_{m',m}^j(\alpha \beta \gamma) &= \langle jm' | e^{-iJ_z \alpha} e^{-iJ_y \beta} e^{-iJ_z \gamma} | jm \rangle \\ &= e^{-im' \alpha} \langle jm' | e^{-iJ_y \beta} | jm \rangle e^{-im \gamma} \end{aligned} \quad (9)$$

since the J_z can be replaced by the eigenvalues of the states on which they operate.*

The matrix element in (9) is denoted by the symbol $d_{m',m}^j(\beta)$, so that one has,

$$D_{m',m}^j(\alpha \beta \gamma) = e^{-im' \alpha} d_{m',m}^j(\beta) e^{-im \gamma} \quad (10)$$

where

$$d_{m',m}^j(\beta) \equiv \langle jm' | e^{-iJ_y \beta} | jm \rangle \quad (10a)$$

To fix some of these results and to relate the D^j to known functions, consider the rotation of a system described by a Legendre Polynomial $P_l(\cos \theta_0)$, (ref 1, 4). Now, θ_0 can be considered as the angle between two unit vectors. It is simply a function of the dot product of these two unit vectors which are purely intrinsic to the system, and, thus, independent of any external reference frame. Therefore, one must have,

*For example, such a requirement can be thought to define what is meant by $e^{-iJ_z \alpha}$, viz., $e^{-iJ_z \alpha} |jm\rangle = e^{-im \alpha} |jm\rangle$ if $J_z |jm\rangle = m |jm\rangle$.

$$R(\alpha\beta\gamma) P_\ell(\cos \theta_0) = P_\ell(\cos \theta_0) \quad (11)$$

independent of the rotation. From (A15) Appendix A, P_ℓ may be expressed in terms of the spherical harmonics, $Y_{\ell m}$ (ref 4), thus enabling a different interpretation of RP_ℓ . Since the $Y_{\ell m}$ are angular momentum states, we may apply formula (8) to obtain

$$\begin{aligned} R(\alpha\beta\gamma) P_\ell(\cos \theta_0) &= \left(\frac{4\pi}{2\ell+1} \right)^{1/2} R(\alpha\beta\gamma) Y_{\ell 0}(\theta_0, 0) \\ &= \left(\frac{4\pi}{2\ell+1} \right)^{1/2} \sum_{m'} D_{m',0}^\ell(\alpha\beta\gamma) Y_{\ell m'}(\theta, \phi) \end{aligned} \quad (12)$$

In the above, the $Y_{\ell 0}(\theta_0, 0)$ refers to a particular orientation of the physical system with one of the unit vectors in the x-z plane (hence $\phi_0 = 0$), and the other specifically along the z axis, so that the angle between the two is the θ_0 as required. The angles θ, ϕ are the spherical coordinates of the former unit vector after rotation. Using the invariance of $P_\ell(\cos \theta_0)$ as expressed by (11) and comparing the result (12) with the additional formula for the spherical harmonics given by (A15), one concludes that

$$D_{m0}^\ell(\alpha\beta\gamma) = \left(\frac{4\pi}{2\ell+1} \right)^{1/2} Y_{\ell m}^*(\beta, \alpha) \quad (13)$$

That $D_{m0}^\ell(\alpha\beta\gamma)$ is independent of γ is seen by (10). The expression (13) is an important relationship and is used later.

The D^J are thus shown to be simply related, for certain values of their arguments, to the more familiar spherical harmonics. Some of the properties of the D^J are listed in Appendix C for convenience.

3. ADDITION OF TWO ANGULAR MOMENTUM STATES

When adding two angular momentum states to obtain a combined state that has a definite total angular momentum (ref 2), one necessarily loses some information in the process. Initially, one possesses a "product" state

$$|j_1 m_1\rangle |j_2 m_2\rangle = |j_1 m_1 j_2 m_2\rangle \quad (14)$$

which is defined by four quantum numbers. It is desired to obtain (by some superposition of such states) a resultant state $|JM j_1 j_2\rangle$ that

has a well-defined total angular momentum and projection as indicated, and in which the individual angular momenta are preserved as good quantum numbers. The transformation can formally be effected thus,

$$\begin{aligned}
|JMj_1j_2\rangle &= 1 \cdot |JMj_1j_2\rangle \\
&= \sum_{j'_1m'_1j'_2m'_2} |j'_1m'_1j'_2m'_2\rangle \langle j'_1m'_1j'_2m'_2 | JMj_1j_2 \rangle
\end{aligned}
\tag{15}$$

The matrix element is proportional to $\delta_{j_1j'_1}\delta_{j_2j'_2}$ so that the final form is

$$|JMj_1j_2\rangle = \sum_{m_1m_2} \langle j_1m_1j_2m_2 | JMj_1j_2 \rangle |j_1m_1j_2m_2\rangle
\tag{16}$$

The coefficients given by the matrix element above are generally called Clebsch-Gordan (C-G), vector coupling, or Wigner coefficients and constitute an orthogonal transformation. From here on, the notation to be used for them is

$$\langle j_1(m_1) j_2(m_2) | J(M) \rangle = \langle j_1m_1j_2m_2 | JMj_1j_2 \rangle
\tag{17}$$

denoting that angular momenta j_1 and j_2 with projections m_1 and m_2 are added to produce a resultant total angular momentum J with projection M . Other useful properties of these coefficients are listed in Appendix B. In the simplest one, the coefficient vanishes unless $m_1 + m_2 = M$.

Therefore, the sum in (16) over one of the m_i can be performed to obtain, in the new notation,

$$|JMj_1j_2\rangle = \sum_m \langle j_1(m) j_2(M-m) | J(M) \rangle |j_1mj_2M-m\rangle
\tag{18}$$

In this form, the information which has been "lost" in order to gain information about the total angular momentum is made apparent. In summing over m , we have lost information regarding the individual projections m_1 and m_2 written m and $M-m$, respectively. In other words, in order to obtain a state with well defined total angular momentum J one must superimpose states of all possible projections m_1 and m_2 consistent with the requirement $m_1+m_2 = M$. The amplitude with which each such combination enters into the superposition is given by the Clebsch-Gordan coefficient as shown in (18).

An immediate application of (18) can be made to the electromagnetic field of any such vector field (ref 4). The orbital angular momentum in such a field is given by the Y_m and the intrinsic spin of that field is one, hence it is described by the χ_{j_1} , the spin-one spinors (ref 4, 5).

The $Y_{\ell m}$ is an angular momentum state of angular momentum ℓ and projection m . The $\vec{\chi}_{\mu}$ is an angular momentum state of angular momentum one and projection μ . Hence, according to (18)

$$\vec{Y}_{J\ell}^M = \sum_{\mu} \langle \ell(M-\mu) \ 1(\mu) | J(M) \rangle Y_{\ell M-\mu} \vec{\chi}_{\mu} \quad (19)$$

where the equation defines the vector spherical harmonics, the $\vec{Y}_{J\ell}^M$. These are wave functions of total angular momentum J and projection M , and are useful to describe the radiation from atomic states that are expressed in terms of total angular momentum states.

Another example that is, perhaps, more familiar is the coupling of two Pauli spinor (spin one-half) states. Let χ_{μ} represent a Pauli spinor (ref 6) where $\mu = \pm 1/2$ then,

$$\psi_{1\mu} = \sum_{\mu'} \langle \frac{1}{2}(\mu-\mu') \ \frac{1}{2}(\mu') | 1(\mu) \rangle \chi_{\mu-\mu'} \chi_{\mu'} \quad (20)$$

and

$$\psi_{00} = \sum_{\mu'} \langle \frac{1}{2}(-\mu') \ \frac{1}{2}(\mu') | 0(0) \rangle \chi_{-\mu'} \chi_{\mu'} \quad (21)$$

The states given by (20) are the familiar triplet states for two particles usually denoted χ_{μ}^t , and the state given by (21) is the singlet two-particle state, usually denoted χ^s .

The addition formula for two D^J is obtained by a consideration of (18). Rotate the physical systems related by (18) with the operator $R(\alpha\beta\gamma)$. One may write

$$R(\alpha\beta\gamma) |JMj_1j_2\rangle = \sum_m \langle j_1(m)j_2(M-m) | J(M) \rangle R(\alpha\beta\gamma) |j_1m\rangle \cdot R(\alpha\beta\gamma) |j_2M-m\rangle, \quad (22)$$

since the state $|j_1m j_2M-m\rangle$ is a product of two single system states according to (14). Taking the matrix element with the adjoint equivalent of (18) and referring to the definition of D^J given by (6), one obtains,

$$\delta_{JJ'} D_{M'M}^J(\alpha\beta\gamma) = \sum_{mm'} \langle j_1(m)j_2(M-m) | J(M) \rangle \langle j_1(m')j_2(M'-m') | J'(M') \rangle \cdot D_{m'm}^J(\alpha\beta\gamma) D_{M'-m'M-m}^{J2}(\alpha\beta\gamma) \quad (23)$$

The expression above is easily inverted if one operates on both sides with

$$\sum_{JJ'} \langle j_1(\mu) j_2(M-\mu) | J(M) \rangle \langle j_1(\mu') j_2(M'-\mu') | J'(M') \rangle \quad (24)$$

and uses the property of the C-G coefficients given by (B9) Appendix B. The result is

$$\begin{aligned} \sum_J \langle j_1(\mu) j_2(M-\mu) | J(M) \rangle \langle j_1(\mu') j_2(M'-\mu') | J(M') \rangle D_{MM'}^J(\alpha\beta\gamma) \\ = D_{\mu\mu'}^{J_1}(\alpha\beta\gamma) D_{M-\mu, M'-\mu'}^{J_2}(\alpha\beta\gamma) \end{aligned} \quad (25)$$

If, now, μ' and M' are set equal to zero, the expression above reduces (applying (13) and taking complex conjugates) to the expression (A22) Appendix A involving the spherical harmonics.

The result (25) enables one to evaluate integrals involving three (or more) D^J . The orthogonality of the D^J is expressed by

$$\oint d\omega D_{m\mu}^{J*}(\alpha\beta\gamma) D_{m'\mu'}^J(\alpha\beta\gamma) = \frac{8\pi^2}{2J+1} \delta_{JJ'} \delta_{mm'} \delta_{\mu\mu'} \quad (26)$$

where $d\omega \equiv d\alpha d(\cos \beta) d\gamma$. Therefore, using (25), it is simple to deduce

$$\begin{aligned} \oint d\omega D_{MM'}^{J*}(\alpha\beta\gamma) D_{m_1\mu_1}^{J_1}(\alpha\beta\gamma) D_{m_2\mu_2}^{J_2}(\alpha\beta\gamma) = \frac{8\pi^2}{2J+1} \langle j_1(m_1) j_2(m_2) | J(M) \rangle \\ \cdot \langle j_1(\mu_1) j_2(\mu_2) | J(M') \rangle \end{aligned} \quad (27)$$

where the Kronecker deltas involving the projections are implicit in the C-G coefficients. For $M' = \mu_1 = \mu_2 = 0$, one may obtain by the use of (13), the following expression for the integral of three spherical harmonics,

$$\begin{aligned} \oint d\Omega Y_{LM}^*(\theta, \varphi) Y_{l_1 m_1}(\theta, \varphi) Y_{l_2 m_2}(\theta, \varphi) = \left[\frac{(2l_1+1)(2l_2+1)}{4\pi(2L+1)} \right]^{1/2} \langle l_1(m_1) l_2(m_2) | L(M) \rangle \\ \cdot \langle l_1(0) l_2(0) | L(0) \rangle \end{aligned} \quad (28)$$

where $d\Omega \equiv d\varphi d(\cos \theta)$. It is an often used fact in the theory of atomic spectra that,

$$\langle l_1(0) l_2(0) | L(0) \rangle \propto [1 + (-)^{l_1+l_2+L}] \quad (29)$$

i.e., it vanishes unless l_1+l_2+L is an even integer.

In the manner demonstrated above, one may proceed to evaluate the integrals involving an arbitrary number of D^j or spherical harmonics. The integrals will, of course, be expressed in terms of the C-G coefficients.

In many ways, it is advisable to become familiar with D^j . They are referred to as the irreducible representations of the three dimensional rotation group, a three-parameter continuous group. Although their normalization (26) is not as simple as that of the spherical harmonics, in certain applications their use is to be preferred. Such matters will be considered in a later paper.

4. ADDITION OF THREE ANGULAR MOMENTUM STATES

The method of coupling three angular momentum states (ref 2) to obtain a total angular momentum state proceeds logically from expression (18). The procedure is to couple two of the states (any two) to obtain a resultant two-particle total angular momentum state, and then to couple this resultant state with the third state, again according to (18).

To illustrate, suppose the three states are $|j_1 m_1\rangle$, $|j_2 m_2\rangle$ and $|j_3 m_3\rangle$. Couple the first two to obtain

$$|j m j_1 j_2\rangle = \sum_{m_1 m_2} \langle j_1(m_1) j_2(m_2) | j(m) \rangle |j_1 m_1\rangle |j_2 m_2\rangle \quad (30)$$

remembering that the sums are restricted since $\langle j_1(m_1) j_2(m_2) | j(m) \rangle \propto \delta_{m_1+m_2, m}$. Then, couple $|j m j_1 j_2\rangle$ to $|j_3 m_3\rangle$ to obtain,

$$|J M j j_3\rangle = \sum_{m m_3} \langle j(m) j_3(m_3) | J(M) \rangle |j m j_1 j_2\rangle |j_3 m_3\rangle \quad (31)$$

If (30) is substituted into (31), then result is

$$|J M (j_1 j_2) (j j_3)\rangle = \sum_{m_1 m_2 m m_3} j_1(m_1) j_2(m_2) |j(m)\rangle \langle j(m) j_3(m_3) | J(M) \rangle |j_1 m_1\rangle |j_2 m_2\rangle |j_3 m_3\rangle \quad (32)$$

Each of the individual angular momenta as well as the intermediate j are good quantum numbers (since they have not been summed out) and are therefore included in the resultant state. Because of the nature of the C-G coefficients, the sum over projections collapses to a sum over only two indices.

$$|JM(j_1 j_2)(j j_3)\rangle = \sum_{m\mu} \langle j_1(\mu) j_2(m-\mu) | j(m) \rangle \langle j(m) j_3(M-m) | J(M) \rangle \\ |j_1 \mu\rangle |j_2^{m-\mu}\rangle |j_3^{M-m}\rangle \quad (33)$$

The order in which the individual angular momenta appear in $|JM(j_1 j_2)(j j_3)\rangle$ is very important because it indicates the order in which the states were coupled. For example, $|J'M'(j_2 j_3)(j' j_1)\rangle$ defines,

$$|J'M'(j_2 j_3)(j' j_1)\rangle = \sum_{m'\mu'} \langle j_2(\mu') j_3(m'-\mu') | j'(m') \rangle \langle j'(m') j_1(M'-m') | J'(M') \rangle \\ |j_1^{M'-m'}\rangle |j_2^{\mu'}\rangle |j_3^{m'-\mu'}\rangle \quad (34)$$

The order in which the single particle states appear in the summation is immaterial since they do not interact amongst themselves. What is important, however, is the order of the angular momenta in the C-G coefficients. It is emphasized, too, that the projections of the individual angular momenta are the same in the C-G coefficients and the states that they couple.

It is frequently of interest to express a three-particle state that has been formed by one method of coupling in terms of states coupled in a different manner. This expression is determined by obtaining the following matrix element,

$$\langle J'M'(j_2' j_3')(j' j_1') | JM(j_1 j_2)(j j_3) \rangle = \sum_{\substack{m\mu \\ m'\mu'}} \langle j_1(\mu) j_2(m-\mu) | J(m) \rangle \langle j(m) j_3(M-m) | J(M) \rangle \\ \cdot \langle j_2'(\mu') j_3'(m'-\mu') | j'(m') \rangle \langle j'(m') j_1'(M'-m') | J'(M') \rangle \delta_{j_1 j_1'} \delta_{j_2 j_2'} \delta_{j_3 j_3'} \\ \delta_{m-\mu, \mu'} \delta_{\mu, M'-m'} \delta_{M-m, m'-\mu'} \quad (35)$$

using the normalizations given by (5). The product of the three Kronecker deltas in (35) involving the projections are equivalent to $\delta_{MM'} \delta_{m-\mu, \mu'} \delta_{M-\mu, m'}$ so that the sum over m' and μ' can be performed. The result is

$$\begin{aligned}
\langle J'M'(j_2'j_3')(j_1'j_1') | JM(j_1j_2)(j_3j_3) \rangle &= \delta_{j_1j_1'} \delta_{j_2j_2'} \delta_{j_3j_3'} \delta_{MM'} \\
\cdot \sum_{\mu} \langle j_1(\mu)j_2(m-\mu) | j(m) \rangle \langle j(m)j_3(M-m) | J(M) \rangle \\
\langle j_2(m-\mu)j_3(M-m) | j'(M-\mu) \rangle \langle j'(M-\mu)j_1(\mu) | J'(M) \rangle & \quad (36)
\end{aligned}$$

In order to allow the use of (B8) Appendix B, the C-G coefficients involving j' and J' must be recoupled so that they assume the form of the first two coefficients. To effect this, the so-called Racah coefficients (ref 2), $W(a b c d; ef)$, must be used. These coefficients accomplish the task desired, as follows:

$$\begin{aligned}
\langle a(\mu)b(m-\mu) | e(m) \rangle \langle e(m)d(M-m) | c(M) \rangle &= \\
= \sum_f [(2e+1)(2f+1)]^{1/2} W(abcd; ef) \\
\cdot \langle b(m-\mu)d(M-m) | f(M-\mu) \rangle \langle a(\mu)f(M-\mu) | c(M) \rangle & \quad (37)
\end{aligned}$$

In order to apply (37) to our problem, first j_2 and j_3 must be interchanged. Using, whenever necessary, formula (B5), we obtain,

$$\begin{aligned}
\langle j_2(m-\mu)j_3(M-m) | j'(M-\mu) \rangle \langle j'(M-\mu)j_1(\mu) | J'(M) \rangle &= \\
= (-)^{j_2+j_3-j'} \langle j_3(M-m)j_2(m-\mu) | j'(M-\mu) \rangle \langle j'(M-\mu)j_1(\mu) | J'(M) \rangle &= \\
= (-)^{j_2+j_3-j'} \sum_f [2j'+1)(2f+1)]^{1/2} W(j_3j_2j'j_1; j'f) \\
\cdot \langle j_2(m-\mu)j_1(\mu) | f(m) \rangle \langle j_3(M-m)f(m) | J'(M) \rangle &= \\
= (-)^{j'-j_1-j} \sum_f [2j'+1)(2f+1)]^{1/2} W(j_3j_2j'j_1; j'f) \\
\cdot \langle j_1(\mu)j_2(m-\mu) | f(m) \rangle \langle f(m)j_3(M-m) | J'(M) \rangle & \quad (38)
\end{aligned}$$

If the result (38) is utilized in (36), then the sum over μ may be performed to yield δ_{fj} according to (B8). This, then, enables the sum over f in (38) to be performed, fixing $f=j$. Then the sum over m in (36) can be performed to yield $\delta_{JJ'}$. The final result is,

$$\langle J'M'(j_2'j_3')(j_1') | JM(j_1j_2)(jj_3) \rangle = \delta_{j_1j_1'} \delta_{j_2j_2'} \delta_{j_3j_3'} \delta_{JJ'} \delta_{MM'} \cdot (-)^{J-j_1-j'} [(2j+1)(2j'+1)]^{1/2} w(j_3j_2jj_1;j'j) \quad (39)$$

from which we deduce

$$|JM(j_1j_2)(jj_3) \rangle = \sum_{j'} (-)^{J-j_1-j'} [(2j+1)(2j'+1)]^{1/2} w(j_3j_2jj_1;j'j) \cdot |JM(j_2j_3)(j'j_1) \rangle \quad (40)$$

The Kronecker deltas in (39) could have been predicted at the start. In each of the states, the total angular momentum and its projection, and each of the individual angular momenta are good quantum numbers and, what is more essential, are independent of the mode of coupling. Thus, since the only way in which the two three-particles states differ is in this latter property, one can expect and understand the orthogonality in those discrete variables embodied in the Kronecker deltas. The intermediate angular momenta j and j' however are not on the same footing since the former is the result of j_1 and j_2 coupling in a prescribed manner, and the latter is the result of a coupling between j_2 and j_3 . Formula (4) expresses the fact that $|JM(j_1j_2)(jj_3) \rangle$ is a mixture of states $|JM(j_2j_3)(j'j_1) \rangle$ with various values for the intermediate angular momentum.

The symmetry properties of the Racah coefficients are given by Rose (ref 2, p 226). They are related to the Wigner 6-j symbols in the following manner, given by Edmonds (ref 5),

$$W(abcd;ef) = (-)^{a+b+c+d} \begin{Bmatrix} a & b & e \\ d & c & f \end{Bmatrix} \quad (41)$$

Further information regarding the 6-j symbols is available in Edmonds, and a complete table of their values for angular momenta less than or equal to 6 is given by Rotenberg, et. al. (ref 7).

5. APPLICATION OF THEORY

The foregoing general discussion shall now be utilized to calculate the energy levels of a rather simple problem. The problem is the consideration of a single electron in a coulombic potential (ref 6) with spin orbit coupling and a magnetic field. The specific Hamiltonian is

$$H = H_0 + H_1 + H_2 \quad (42)$$

where

$$\begin{aligned} H_0 &= \frac{p^2}{m} + V(r) \quad \text{with } \vec{p} = -i \nabla \\ H_1 &= \vec{\mu} \cdot \vec{H} \\ H_2 &= \lambda \vec{L} \cdot \vec{S} \end{aligned} \quad (43)$$

Although the problem is quite simple, its solution has the advantage of illustrating many general features common to more complicated cases.

The problem is treated first by perturbation theory (ref 1, 6) using states that are diagonal in $H_0 + H_1$ with H_2 being the small perturbation and carrying the calculation through to second order in H_2 . The procedure is then repeated using states that are diagonal in H_0 and H_2 with H_1 considered small. Finally the problem is solved exactly, and the result is expanded to second order in H_2 and then to second order in H_1 to show the agreement of the results obtained by perturbation theory in each case with the exact result.

When the potential is coulombic, the energy levels of H_0 depend only on the principal quantum number n (ref 6). The eigenfunctions of H_0 are then of the form $R_{nl} Y_{lm} \chi_\mu$ where l is the orbital angular momentum quantum number and m its projection, and χ_μ is a Pauli spinor representing the spin of the electron. Only the case $n = 2$ is discussed, hence $l = 1, 0$ and $m = 1, 0, -1$ and $\mu = \pm 1/2$.^{*} The energies given by H_1 and H_2 will then be relative to the energy level associated with $n = 2$ for the operator H_0 above.

6. CASE I: SMALL H_2

In this case we consider the magnetic energy much larger than the spin orbit energy and treat the latter as a perturbation. The magnetic field will be taken to point in the negative z direction, so that

$$H_1 = \mu_B H(L_z + 2S_z) \quad (44)$$

where μ_B is the Bohr magneton (ref 8). The states described by the spherical harmonics, Y_{lm} , are diagonal in L_z , i.e., $L_z Y_{lm} = m Y_{lm}$ and the Pauli spinors, χ_μ , are diagonal in S_z , i.e., $S_z \chi_\mu = \mu \chi_\mu$. For convenience we will replace m by $M - \mu$ in the Y_{lm} above. Then

$$\mu_B H[L_z + 2S_z] Y_{l, M-\mu} \chi_\mu = \mu_B H(M+\mu) Y_{l, M-\mu} \chi_\mu \quad (45)$$

^{*}The number of states giving the same energy (degeneracy) for an electron in a coulombic potential is $2n^2$ (equal to 8, in this case).

and the energy due to the magnetic field is

$$E_{M\mu} = \beta(M+\mu) \quad \text{where } \beta \equiv \mu_B H \quad (46)$$

We then obtain the energy levels listed in the column headed by $E_{M\mu}$ in table I.

TABLE I. ENERGY LEVELS TO SECOND ORDER IN H_2

ℓ	M	μ	$E_{M\mu}$	1st order	2nd order
1	3/2	1/2	2β	$\frac{\lambda}{2}$	0
1	1/2	-1/2	0	$-\frac{\lambda}{2}$	$-\frac{\lambda^2}{2\beta}$
1	1/2	1/2	β	0	$\frac{\lambda^2}{2\beta}$
1	-1/2	-1/2	$-\beta$	0	$-\frac{\lambda^2}{2\beta}$
1	-1/2	1/2	0	$-\frac{\lambda}{2}$	$\frac{\lambda^2}{2\beta}$
1	-3/2	-1/2	-2β	$\frac{\lambda}{2}$	0
0	1/2	-1/2	β	0	0
0	-1/2	-1/2	$-\beta$	0	0

We see that there are eight states, as there should be, with 3 of the energy levels two-fold degenerate.

The perturbing Hamiltonian is

$$\lambda \vec{L} \cdot \vec{S} = \lambda S_z L_z + \frac{\lambda}{2} [L^+ S^- + L^- S^+] \quad (47)$$

where

$$L^\pm = L_x \pm iL_y, \quad S^\pm = S_x \pm iS_y \quad (48)$$

We will need the relations (ref 1)

$$L^\pm Y_{\ell m} = \sqrt{(\ell \mp m)(\ell \pm m + 1)} Y_{\ell, m \pm 1} \quad (49)$$

$$S^- \chi_\mu = \chi_{-\mu} \quad S^+ \chi_{-\mu} = \chi_\mu \quad S^- \chi_{-\mu} = S^+ \chi_{+\mu} = 0 \quad (50)$$

The latter formulas are special cases of the former with $\ell = 1/2$ and $m = \mu$. In perturbation theory the energy of a given state m to second order is given by (ref 6)

$$E_m = E_m + (H_2)_{mm} + \sum_n \frac{(H_2)_{mn} (H_2)_{nm}}{E_m - E_n} \quad (51)$$

where $(H_2)_{mn} = \oint d\Omega \psi_m^+ H_2 \psi_n$ and ψ_m are eigenfunctions of the unperturbed Hamiltonian. Now

$$\lambda \vec{S} \cdot \vec{L} Y_{\ell M-\mu} \chi_\mu = \lambda S_z L_z Y_{\ell M-\mu} \chi_\mu + \frac{\lambda}{2} (L^+ S^- + L^- S^+) Y_{\ell M-\mu} \chi_\mu \quad (52)$$

$$= \lambda (M-\mu)\mu Y_{\ell M-\mu} \chi_\mu + \frac{\lambda}{2} (L^+ S^- + L^- S^+) Y_{\ell M-\mu} \chi_\mu \quad (53)$$

The last part is easier to carry through by choosing specific values for ℓ , M , and μ . For $\ell = 1$, $M = 3/2$ and $\mu = 1/2$

$$(S^+ L^- + S^- L^+) Y_{11} \chi_{1/2} = 0 \quad (54)$$

since $L^+ Y_{11} = 0$, and $S^+ \chi_{1/2} = 0$. The same result is obtained for $\ell = 1$, $M = -3/2$ and $\mu = -1/2$ or

$$\lambda \vec{S} \cdot \vec{L} Y_{1\pm 1} \chi_{\pm 1/2} = \lambda \left(\frac{1}{2}\right) Y_{1\pm 1} \chi_{\pm 1/2} \quad (55)$$

Using the formulas given above, the results of the perturbation acting on the remaining state is

$$\begin{aligned} \lambda \vec{S} \cdot \vec{L} Y_{11} \chi_{-1/2} &= H_2 Y_{11} \chi_{-1/2} = -\frac{\lambda}{2} Y_{11} \chi_{-1/2} + \frac{\lambda}{2} \sqrt{2} Y_{10} \chi_{1/2} \\ H_2 Y_{1-1} \chi_{1/2} &= -\frac{\lambda}{2} Y_{1-1} \chi_{1/2} + \frac{\lambda}{2} \sqrt{2} Y_{10} \chi_{-1/2} \\ H_2 Y_{10} \chi_{1/2} &= \frac{\lambda}{2} \sqrt{2} Y_{11} \chi_{-1/2} \\ H_2 Y_{10} \chi_{-1/2} &= \frac{\lambda}{2} \sqrt{2} Y_{1-1} \chi_{1/2} \\ H_2 Y_{00} \chi_{1/2} &= 0 \\ H_2 Y_{00} \chi_{-1/2} &= 0 \end{aligned} \quad (56)$$

We see that the perturbation in no case connects degenerate states, so that the second order energy can be calculated by the simple method. In general this is not the case when one has degenerate states, and the problem can become rather involved (ref 6, p 155 ff.) The results of the calculations for first and second order are shown in table I.

7. CASE II: H_1 SMALL

In this part we use eigenfunctions of $\vec{L}$, $\vec{S}$, $\vec{J} = \vec{L} + \vec{S}$ and J_z and call these functions y_{JM}^{LS} . Then we have

$$\begin{aligned} J_z y_{JM}^{LS} &= M y_{JM}^{LS} \\ J^2 y_{JM}^{LS} &= J(J+1) y_{JM}^{LS} \\ L^2 y_{JM}^{LS} &= l(l+1) y_{JM}^{LS} \\ S^2 y_{JM}^{LS} &= S(S+1) y_{JM}^{LS} \end{aligned} \tag{57}$$

The reason for using these eigenfunctions is that H_2 can be written

$$H_2 = \lambda \vec{L} \cdot \vec{S} = \frac{\lambda}{2} [J^2 - L^2 - S^2] \tag{58}$$

and is diagonal in the functions y_{JM}^{LS} . Further since H_0 is degenerate in the angular momentum we can also use these functions as eigenfunctions of H_0 , i.e.,

$$H_0 R_{nl} y_{JM}^{LS} = E_n R_{nl} y_{JM}^{LS} \tag{59}$$

This choice of eigenfunctions is desirable since the Hamiltonian $H_0 + H_2$ is diagonal in that basis. In case I, the eigenfunctions chosen were $Y_{lm} \chi_\mu$, because $H_0 + H_1$ (there considered as the unperturbed Hamiltonian) is diagonal in that basis. Thus, from (57) and (58)

$$\begin{aligned} \lambda \vec{L} \cdot \vec{S} y_{JM}^{LS} &= \frac{\lambda}{2} [J(J+1) - l(l+1) - S(S+1)] y_{JM}^{LS} \\ &= \frac{\lambda}{2} [J(J+1) - l(l+1) - \frac{3}{4}] y_{JM}^{LS} \end{aligned} \tag{60}$$

since $S = 1/2$. The energy levels for different l , M , and J values are given in table II, in the column headed by E .

TABLE II. ENERGY LEVELS TO SECOND ORDER IN H_1

ℓ	j	M	E	1st order	2nd order
0	1/2	1/2	0	β	0
0	1/2	-1/2	0	$-\beta$	0
1	3/2	3/2	$\frac{\lambda}{2}$	2β	0
1	3/2	1/2	$\frac{\lambda}{2}$	$\frac{2\beta}{3}$	$\frac{4}{27} \frac{\beta^2}{\lambda}$
1	3/2	-1/2	$\frac{\lambda}{2}$	$-\frac{2\beta}{3}$	$\frac{4}{27} \frac{\beta^2}{\lambda}$
1	3/2	-3/2	$\frac{\lambda}{2}$	-2β	0
1	1/2	1/2	$-\lambda$	$\frac{\beta}{3}$	$-\frac{4}{27} \frac{\beta^2}{\lambda}$
1	1/2	-1/2	$-\lambda$	$-\frac{\beta}{3}$	$-\frac{4}{27} \frac{\beta^2}{\lambda}$

Again there are eight states, as there should be, but in this case two energy levels are two-fold degenerate, and one is four-fold degenerate.

We now consider the perturbation H_1 . This can be expressed as

$$H_1 = \vec{\mu} \cdot \vec{H} = \mu_B H [L_z + 2S_z] = \beta [J_z + S_z] \quad (61)$$

Since J_z is diagonal in the above representation we have only to consider the perturbation as βS_z .

Analogous to the expression (19), we can write the following for spin one-half

$$y_{JM}^\ell = \sum_{\mu} \langle \ell(M-\mu) \frac{1}{2}(\mu) | J(M) \rangle y_{\ell M-\mu} x_{\mu} \quad (62)$$

and

$$S_z y_{JM}^\ell = \sum_{\mu} \langle \ell(M-\mu) \frac{1}{2}(\mu) | J(M) \rangle \mu y_{\ell M-\mu} x_{\mu} \quad (63)$$

We can use expression (B9, Appendix B) to invert (62) so that

$$y_{\ell M-\mu} x_{\mu} = \sum_{J'} \langle \ell(M-\mu) \frac{1}{2}(\mu) | J'(M) \rangle y_{J'M}^\ell \quad (64)$$

Since the values of μ are $\pm 1/2$ this can be expressed as

$$\mu = \frac{1}{2} (-1)^{1/2-\mu}. \text{ Then}$$

$$S_z y_{JM}^\ell = \frac{1}{2} \sum_{\mu} \sum_{J'} (-1)^{1/2-\mu} \langle \ell(M-\mu) \frac{1}{2}(\mu) | J(M) \rangle \langle \ell(M-\mu) \frac{1}{2}(\mu) | J'(M) \rangle y_{J'M}^\ell \quad (65)$$

Using the rules for manipulation of the Clebsch-Gordan coefficients (Appendix B), we have

$$\langle \ell(M-\mu) \frac{1}{2}(\mu) | J(M) \rangle = (-1)^{1/2+\mu} \sqrt{\frac{2J+1}{2\ell+1}} \langle J(-M) \frac{1}{2}(\mu) | \ell(\mu-M) \rangle \quad (66)$$

Hence

$$\begin{aligned} S_z y_{JM}^\ell &= -\frac{1}{2} \sum_{\mu} \sum_{J'} \sqrt{\frac{2J+1}{2\ell+1}} \langle J(-M) \frac{1}{2}(\mu) | \ell(\mu-M) \rangle \langle \ell(M-\mu) \frac{1}{2}(\mu) | J'(M) \rangle y_{J'M}^\ell \\ &= -\frac{(-1)^{J+\frac{1}{2}}}{2} \sqrt{\frac{2J+1}{2\ell+1}} \sum_{\mu} \sum_{J'} \langle J(M) \frac{1}{2}(-\mu) | \ell(M-\mu) \rangle \langle \ell(M-\mu) \frac{1}{2}(\mu) | J'(M) \rangle y_{J'M}^\ell \\ &= -\frac{(-1)^{J+\frac{1}{2}}}{2} \sqrt{\frac{2J+1}{2\ell+1}} \sum_{f} \sum_{J'} \sum_{\mu} \sqrt{2f+1} W(J \frac{1}{2} J' \frac{1}{2} \ell f) \langle J(M) f(0) | J'(M) \rangle \\ &\quad \langle \frac{1}{2}(-\mu) \frac{1}{2}(\mu) | f(0) \rangle y_{J'M}^\ell \end{aligned} \quad (67)$$

From table I in Rose (ref 2), we obtain

$$\sqrt{2} \langle \frac{1}{2}(-\mu) \frac{1}{2}(\mu) | 1(0) \rangle = 1 \quad (68)$$

hence

$$\sum_{\mu} \langle \frac{1}{2}(-\mu) \frac{1}{2}(\mu) | 1(0) \rangle \langle \frac{1}{2}(-\mu) \frac{1}{2}(\mu) | f(0) \rangle = \delta_{f1} \quad (69)$$

Finally we obtain

$$\begin{aligned} S_z y_{JM}^\ell &= -\frac{1}{2} \sum_{J'} \sqrt{6(2J+1)} W(1 \frac{1}{2} \ell; \frac{1}{2} J) \langle J(M) 1(0) | J'(M) \rangle y_{J'M}^\ell \\ &= -\frac{1}{2} \sum_{J'} q_M^\ell(J'; J) y_{J'M}^\ell \end{aligned} \quad (70)$$

The final result for the total perturbation is

$$\vec{\mu} \cdot \vec{H} y_{JM}^l = \beta M y_{JM}^l - \frac{\beta}{2} \sum_J g_M^l(J'; J) y_{J'M}^l \quad (71)$$

The explicit value of $g_M^l(J'; J)$ for values of J' and J of interest can be calculated by using the results given by Rose (ref 2, Appendix I) and are given in the tables below.

TABLE III. VALUES OF $g_M^l(J'; J)$

$l=1$			$l=0$		
$J' \backslash J$	$\frac{1}{2}$	$\frac{3}{2}$	$J' \backslash J$	$\frac{1}{2}$	$\frac{3}{2}$
$\frac{1}{2}$	$-\frac{2}{3} M$	$-\frac{2}{3} (\frac{9}{4} - M^2)^{1/2}$	$\frac{1}{2}$	$2M$	0
$\frac{3}{2}$	$-\frac{2}{3} (\frac{9}{4} - M^2)^{1/2}$	$\frac{2}{3} M$	$\frac{3}{2}$	0	0

The results can be written in compact form as

$$(\vec{\mu} \cdot \vec{H}) y_{JM}^l = \frac{\beta M (2J+1)}{2l+1} y_{JM}^l - \frac{\sqrt{2}}{3} \beta \delta_{l1} \delta_{M \pm 1/2} y_{J'M}^l \quad (72)$$

which holds for $l = 0$, $J = 1/2$ and for $l = 1$, $J = 1/2$, $J' = 3/2$ and $l = 1$, $J=3/2$, $J' = 1/2$. Again the perturbation connects no degenerate states, so that the energy to second order is simply proportional to the square of the off-diagonal elements, i.e. $|\frac{\sqrt{2}}{3} \beta \delta_{l1} \delta_{M \pm 1/2}|^2$. These give four elements, $\frac{4}{27} \frac{\beta^2}{\lambda}$ twice and $-\frac{4}{27} \frac{\beta^2}{\lambda}$ twice and are shown in the last column in table II.

8. EXACT CALCULATIONS

To find the exact diagonal representation we can reduce the calculations somewhat by observing that the z component of J commutes with the total Hamiltonian. To show this we have

$$H = \vec{\mu} \cdot \vec{H} + \lambda \vec{L} \cdot \vec{S} = \beta (L_z + 2S_z) + \lambda L_z S_z + \frac{\lambda}{2} (L^+ S^- + L^- S^+) \quad (73)$$

where $L^{\pm} = L_x \pm iL_y$

and $L \times L = iL$

Then $[L_z, L^{\pm}] = \pm L^{\pm}$

and $[S_z, S^{\pm}] = \pm S^{\pm}$

Hence

$$[(L_z + S_z), H] = \frac{\lambda}{2} [L^+ S^- - L^- S^+ - L^+ S^- + L^- S^+] = 0 \quad (74)$$

or $[J_z, H] = 0$, so that M is a good quantum number. To utilize this fact, we use the functions $Y_{\ell M-\mu} X_\mu$ in place of $Y_{\ell m} X_\mu$. Since the $Y_{\ell M-\mu} X_\mu$ form a complete set of functions, and since J_z commutes with H , we can form the eigenfunctions of H from a superposition of the $Y_{\ell M-\mu} X_\mu$, that is

$$\psi = \sum_{\mu} a_{\mu} Y_{\ell M-\mu} X_{\mu} \quad (75)$$

where the a_{μ} are to be determined. The Schrödinger equation becomes

$$\begin{aligned} H\psi &= E\psi = [\beta(J_z + S_z) + \lambda S_z L_z + \frac{\lambda}{2} (L^+ S^- + L^- S^+)]\psi \\ &= \sum_{\mu} a_{\mu} \{ \beta(M+\mu) + \lambda \mu(M-\mu) \} Y_{\ell M-\mu} X_{\mu} \\ &\quad + \frac{\lambda}{2} [a_{1/2}(M+\frac{1}{2}) Y_{\ell M+1/2} X_{-1/2} + a_{-1/2}(M-\frac{1}{2}) Y_{\ell M-1/2} X_{1/2}] \\ &= \sum_{\mu} a_{\mu} E Y_{\ell M-\mu} X_{\mu} \end{aligned} \quad (76)$$

Then

$$\begin{aligned} a_{1/2} E &= a_{1/2} \{ \beta(M+\frac{1}{2}) + \frac{\lambda}{2} (M-\frac{1}{2}) \} + a_{-1/2} B(M-\frac{1}{2}) \frac{\lambda}{2} \\ a_{-1/2} E &= a_{-1/2} \{ \beta(M-\frac{1}{2}) + \frac{\lambda}{2} (M+\frac{1}{2}) \} + a_{1/2} B(M+\frac{1}{2}) \frac{\lambda}{2} \end{aligned} \quad (77)$$

where

$$B(M-\frac{1}{2}) = \sqrt{(\ell + \frac{1}{2})^2 - M^2} = B(M+\frac{1}{2})$$

from

$$L^{\pm} Y_{\ell m} = \sqrt{(\ell \mp m)(\ell \pm m+1)} Y_{\ell m \pm 1}$$

Now the two equations in $a_{1/2}$ and $a_{-1/2}$ are homogeneous and the determinant of the coefficients of $a_{\pm 1/2}$ must vanish for a nontrivial solution. Hence

$$\begin{vmatrix} \beta(M + \frac{1}{2}) + \frac{\lambda}{2}(M - \frac{1}{2}) - E & B(M - \frac{1}{2}) \frac{\lambda}{2} \\ B(M + \frac{1}{2}) \frac{\lambda}{2} & \beta(M - \frac{1}{2}) + \frac{\lambda}{2}(M + \frac{1}{2}) - E \end{vmatrix} = 0$$

so that

$$E_{(\ell, M)} = \beta M - \frac{\lambda}{4} \pm \frac{1}{2} \sqrt{\beta^2 + 2\beta M \lambda + \lambda^2 (\ell + \frac{1}{2})^2} \quad (78)$$

When $\lambda = 0$ this gives the unperturbed energy found in case I and when $\beta = 0$ the unperturbed energy found in case II.

The energy can be expanded for small λ to compare with the results of perturbation given in table I. The expansion to second order in λ are

$$\begin{aligned} E(1, \frac{3}{2}) &= 2\beta + \frac{\lambda}{2} \\ E(1, \frac{1}{2}) &= -\frac{\lambda}{2} - \frac{\lambda^2}{2\beta} \\ E(1, \frac{1}{2}) &= \beta + \frac{\lambda^2}{2\beta} \\ E(1, -\frac{1}{2}) &= -\beta - \frac{\lambda^2}{2\beta} \\ E(1, -\frac{1}{2}) &= -\frac{\lambda}{2} + \frac{\lambda^2}{2\beta} \\ E(1, -\frac{3}{2}) &= -2\beta + \frac{\lambda}{2} \\ E(0, \frac{1}{2}) &= \beta \\ E(0, -\frac{1}{2}) &= -\beta \end{aligned} \quad (79)$$

which are identical with the results shown in table I.

When the exact energy is expanded for small β keeping terms through second order in β , we have

$$\begin{aligned} E(1, \pm \frac{3}{2}) &= \pm 2\beta + \frac{\lambda}{2} \\ E(1, \frac{1}{2}) &= \frac{1}{2} \beta \pm \frac{1}{6} \beta - \frac{\lambda}{4} \pm \frac{3}{4} \lambda \pm \frac{4}{27} \frac{\beta^2}{\lambda} \\ E(1, -\frac{1}{2}) &= -\frac{\beta}{2} - \frac{\lambda}{4} \pm \frac{3}{4} \lambda \mp \frac{\beta}{6} \pm \frac{4}{27} \frac{\beta^2}{\lambda} \\ E(0, \pm \frac{1}{2}) &= \pm \beta \end{aligned} \quad (80)$$

and we see that the energies agree with the result obtained by second order perturbation theory as given in table II.

The exact result can be computed for a complete range of variables by making the following substitutions: $\beta = x$ $\lambda = 2(1-x)$ $0 \leq x \leq 1$ then

$$E(1, \frac{3}{2}) = 1 + x$$

$$E(1, \frac{3}{2}) = 1 - 3x$$

$$E(1, \frac{1}{2}) = x - \frac{1}{2} \pm \{2x^2 - 4x + \frac{9}{4}\}^{1/2}$$

$$E(1, \frac{1}{2}) = -\frac{1}{2} \pm \{3x^2 - 5x + \frac{9}{4}\}^{1/2}$$

$$E(0, \pm \frac{1}{2}) = \pm x$$

Such a substitution, in effect, turns off one of the interactions as the other is turned on so that at the point $x = 0$, there is only the spin-orbit interaction, and at $x = 1$ there is only the magnetic interaction. The proportionality constants are adjusted to give integer splittings at both ends. The splittings for arbitrary x are plotted in figure 1.

It is noticed that the states which are degenerate at $x = 0$ move off at different slopes, indicating that the degeneracy is lifted in first order by a magnetic field. In contrast, at $x = 1$, the states that are degenerate move off with identical slopes, indicating that second order perturbation theory is needed to lift the degeneracy (curvature is characterized by squared or higher power terms). These observations are evident in the calculations listed in tables I and II.

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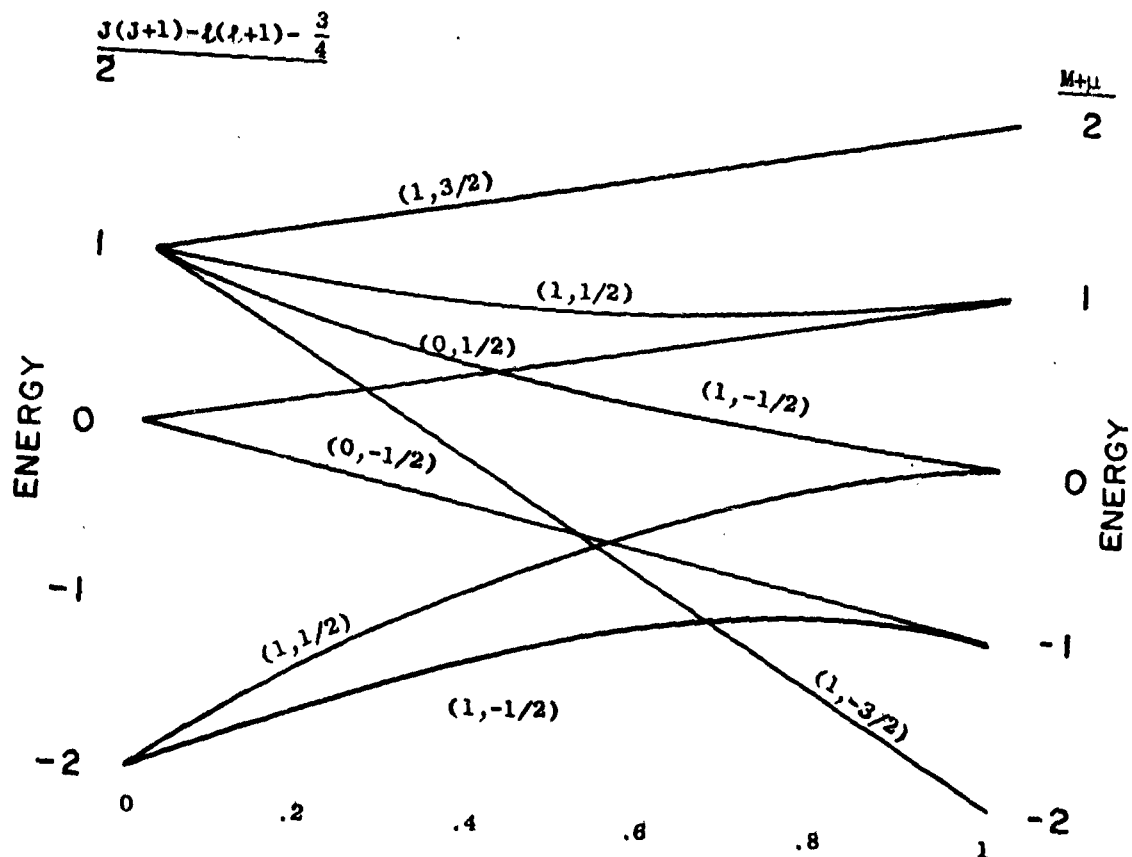


Figure 1. Relative energy levels as a function of the parameter x for the Hamiltonian.

$\frac{p^2}{2m} + V(r) + x(L_z + 2S_z) + 2(1+x) \vec{L} \cdot \vec{S}$, and for the principle quantum number $n = 2$. ($2n^2 = 8 =$ total number of states). The labels in parentheses denote the orbital angular momentum (l) and total angular momentum projection (M) for each state.

APPENDIX A

Orbital Angular Momentum Eigenfunctions

The eigenfunctions of the orbital angular momentum operator (squared) are the spherical harmonics denoted by $Y_{\ell m}(\theta, \varphi)$. We have

$$L^2 Y_{\ell m}(\theta, \varphi) = \ell(\ell+1) Y_{\ell m}(\theta, \varphi) \quad (A1)$$

$$L_z Y_{\ell m}(\theta, \varphi) = m Y_{\ell m}(\theta, \varphi) \quad (A2)$$

where

$$L^2 = - \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} \quad (A3)$$

and

$$L_z = -i \frac{\partial}{\partial \varphi} \quad (A4)$$

In the usual manner, the solutions of L^2 can be split into products of solutions, one set being functions only of θ and the other set being functions only of φ .

The functions of θ are the associated Legendre Polynomials (of the first kind), the $P_{\ell m}(\theta)$, and satisfy the equation

$$(1-\mu^2) \frac{d^2 P_{\ell m}}{d\mu^2} - 2\mu \frac{dP_{\ell m}}{d\mu} + [\ell(\ell+1) - \frac{m^2}{1-\mu^2}] P_{\ell m} = 0 \quad (A5)$$

where

$$\mu = \cos \theta$$

The functions of φ are the exponential oscillatory functions, the $\phi_m = e^{im\varphi}$ and satisfy the equation

$$\frac{d^2 \phi_m}{d\varphi^2} + m^2 \phi_m = 0 \quad (A6)$$

where the m in this equation is the same as in (A5) and

$$\ell = 0, 1, 2, \text{ etc.}, \quad -\ell \leq m \leq \ell \quad (A7)$$

if the product solution $P_{\ell m} \phi_m$ are to have physical meaning.

The solutions $P_{\ell m}(\mu)$ are given by a simple formula in terms of the solutions for $m = 0$, the $P_{\ell 0}(\mu)$. These latter solutions are denoted simply

$$P_{\ell 0}(\mu) = P_{\ell}(\mu) \quad (A8)$$

and are the so-called Legendre Polynomials. They are polynomials in μ of degree ℓ , and are given by Rodrique's formula

$$P_{\ell}(\mu) = \frac{1}{2^{\ell} \ell!} \frac{d^{\ell} (\mu^2 - 1)^{\ell}}{d\mu^{\ell}} \quad (A9)$$

For positive m the $P_{\ell m}(\mu)$ are defined by

$$P_{\ell m}(\mu) = (1 - \mu^2)^{m/2} \frac{d^m P_{\ell}(\mu)}{d\mu^m} \quad (A10)$$

The $P_{\ell - m}(\mu)$ (m positive again) are defined by

$$P_{\ell - m}(\mu) = \frac{(\ell - m)!}{(\ell + m)!} (-1)^m P_{\ell m}(\mu) \quad (A11)$$

The spherical harmonics are proportional to $P_{\ell m} \Phi_m$ with the following normalization (m position again),

$$Y_{\ell m} = (-1)^m \left\{ \frac{2\ell + 1}{4\pi} \frac{(\ell - m)!}{(\ell + m)!} \right\}^{1/2} P_{\ell m} e^{im\varphi} \quad (A12)$$

From (A12) and (A11), one can deduce that

$$Y_{\ell - m} = (-1)^m Y_{\ell m}^* \quad (A13)$$

Another useful and important property of the $Y_{\ell m}$ is their transformation under space inversion. Under such an inversion, $\theta \rightarrow \pi - \theta$ and $\varphi \rightarrow \varphi + \pi$ so that

$$PY_{\ell m}(\theta, \varphi) = Y_{\ell m}(\pi - \theta, \varphi + \pi) = (-1)^{\ell} Y_{\ell m}(\theta, \varphi) \quad (A14)$$

- where P represents the inversion operation (called the parity operator). From (A14) it is clear that the orbital angular momentum quantum number ℓ alone determines whether a state has even (positive) or odd (negative) parity, depending on whether ℓ is even or odd.

Other useful relations between the functions defined above are

$$\begin{aligned}
 P_\ell(\cos \theta) &= \sum_{m=-\ell}^{+\ell} \frac{4\pi}{2\ell+1} Y_{\ell m}(\hat{r}) Y_{\ell m}^*(\hat{k}) \\
 &= \sum_{m=-\ell}^{+\ell} \frac{4\pi}{2\ell+1} Y_{\ell m}^*(\hat{r}) Y_{\ell m}(\hat{k})
 \end{aligned} \tag{A15}$$

where $\cos \theta = \hat{r} \cdot \hat{k}$. The unit vectors used as arguments of the spherical harmonics represent the angle variables of the unit vectors, i.e., $Y_{\ell m}(\hat{r}) \equiv Y_{\ell m}(\theta, \varphi)$ where $\hat{r} = \hat{r}(\theta, \varphi)$.

We also have,

$$\frac{1}{|\vec{r}_1 - \vec{r}_2|} = \sum_{\ell} \frac{r^{<}}{r^{\ell+1}} P_\ell(\cos \theta) \tag{A16}$$

where $\cos \theta \equiv \hat{r}_1 \cdot \hat{r}_2$ and $r <$ denotes the magnitude of the lesser of $|\vec{r}_1|$ and $|\vec{r}_2|$, and $r >$ denotes the magnitude of the greater. From (A15) we have

$$\frac{1}{|\vec{r}_1 - \vec{r}_2|} = \sum_{\ell m} \frac{4\pi}{2\ell+1} \frac{r^{<}}{r^{\ell+1}} Y_{\ell m}^*(\hat{r}_1) Y_{\ell m}(\hat{r}_2) \tag{A17}$$

Another useful formula is

$$e^{i\vec{k} \cdot \vec{r}} = \sum_{\ell} (2\ell+1) (i)^\ell j_\ell(kr) P_\ell(\cos \theta) \tag{A18}$$

where $\cos \theta \equiv \hat{k} \cdot \hat{r}$, and the $j_\ell(kr)$ are the spherical Bessel functions. (ref 9). Again from (A15),

$$e^{i\vec{k} \cdot \vec{r}} = \sum_{\ell m} 4\pi (i)^\ell j_\ell(kr) Y_{\ell m}^*(\hat{r}) Y_{\ell m}(\hat{k}) \tag{A19}$$

The formulas given above are extremely useful because of the normalization of the $Y_{\ell m}$. They have the property that,

$$\oint d\Omega Y_{\ell m}^*(\theta, \varphi) Y_{\ell' m'}(\theta, \varphi) = \delta_{\ell\ell'} \delta_{mm'} \quad (\text{A20})$$

where

$$\oint d\Omega = \int_0^{2\pi} d\varphi \int_{-1}^1 d(\cos \theta)$$

The normalization of the Legendre polynomials is such that

$$\int_{-1}^1 d\mu P_\ell(\mu) P_{\ell'}(\mu) = \frac{2}{2\ell+1} \delta_{\ell\ell'} \quad (\text{A21})$$

A further property of the $Y_{\ell m}$ is

$$Y_{\ell m}(\theta, \varphi) Y_{\ell' m'}(\theta, \varphi) = \sum_L \left\{ \frac{(2\ell'+1)(2\ell+1)}{4\pi(2L+1)} \right\}^{1/2} \langle \ell(0) \ell'(0) | L(0) \rangle \\ \langle \ell(m) \ell'(m') | L(m+m') \rangle Y_{L, m+m'}(\theta, \varphi) \quad (\text{A22})$$

where the C-G coefficients are defined in Appendix B. From (A22) and (A20), one may obtain,

$$\oint d\Omega Y_{LM}^*(\theta, \varphi) Y_{\ell m}(\theta, \varphi) Y_{\ell' m'}(\theta, \varphi) = \left\{ \frac{(2\ell'+1)(2\ell+1)}{4\pi(2L+1)} \right\}^{1/2} \langle \ell(0) \ell'(0) | L(0) \rangle \\ \langle \ell(m) \ell'(m') | L(M) \rangle \quad (\text{A23})$$

APPENDIX B

Clebsch-Gordon Coefficients

Some of the useful properties of the Clebsch-Gordan (C-G) coefficients are listed here for convenient reference. The symbol used in the text is

$$\langle j_1(m_1) j_2(m_2) | j(m) \rangle \quad (B1)$$

Some other symbols for the same coefficient that are used in the literature are

$$C(j_1 j_2 j; m_1 m_2 m) \equiv \delta_{m_1+m_2, m} C(j_1 j_2 j; m-m_2 m_2)$$

$$C_{j_1 j_2}^{j_1 j_2 j} ; C_{j_1 j_2}^{j(m; m_1 m_2)} ; \langle j_1 m_1 j_2 m_2 | j m j_1 j_2 \rangle \quad (B2)$$

These coefficients are defined to be real. Their most important property is

$$\langle j_1(m_1) j_2(m_2) | j(m) \rangle \propto \delta_{m_1+m_2, m} \Delta(j_1 j_2 j) \quad (B3)$$

where $\Delta(j_1 j_2 j)$ implies that $|j_\alpha - j_\beta| \leq j_\gamma \leq |j_\alpha + j_\beta|$ for any combination of α, β, γ . This is called the triangle condition, hence the symbol $\Delta(j_1 j_2 j)$.

Other properties are

$$\langle j_1(m_1) j_2(m_2) | j(m) \rangle = (-)^{j_1+j_2-j} \langle j_1(-m_1) j_2(-m_2) | j(-m) \rangle \quad (B4)$$

$$= (-)^{j_1+j_2-j} \langle j_2(m_2) j_1(m_1) | j(m) \rangle \quad (B5)$$

$$= (-)^{j_2+m_2} \left\{ \frac{2j+1}{2j_1+1} \right\}^{1/2} \langle j(-m) j_2(m_2) | j_1(-m_1) \rangle \quad (B6)$$

$$= (-)^{j_1-m_1} \left\{ \frac{2j+1}{2j_2+1} \right\}^{1/2} \langle j_1(m_1) j(-m) | j_2(-m_2) \rangle \quad (B7)$$

$$\sum_{\mu} \langle j_1(\mu) j_2(m-\mu) | j(m) \rangle \langle j_1(\mu) j_2(m-\mu) | j'(m) \rangle = \delta_{jj'}, \quad (\text{B8})$$

$$\sum_j \langle j_1(\mu') j_2(m'-\mu') | j(m') \rangle \langle j_1(\mu) j_2(m-\mu) | j(m) \rangle = \delta_{\mu\mu'} \delta_{mm'}, \quad (\text{B9})$$

APPENDIX C

The D^J Elements

The $D^J(r)$ have the properties characteristic of unitary irreducible representations of a group, some of which are listed here.

$$D_{M'M}^{J*}(r) = D_{MM'}^J(r^{-1}) \quad (C1)$$

$$D_{M'M}^{J*}(r) = (-)^{M'-M} D_{-M'-M}^J(r) \quad (C2)$$

$$\sum_{\lambda} D_{M'\lambda}^J(r) D_{\lambda M}^J(r') = D_{M'M}^J(rr') \quad (C3)$$

$$\oint d\omega_r D_{\lambda M}^{J*}(r) D_{\lambda' M'}^{J'}(r) = \frac{8\pi^2}{2J+1} \delta_{JJ'} \delta_{MM'} \delta_{\lambda\lambda'} \quad (C4)$$

$$\text{where } \oint d\omega_r = \int_0^{2\pi} d\alpha \int_{-1}^1 d(\cos \beta) \int_0^{2\pi} d\gamma \quad \text{and } r = r(\alpha \beta \gamma).$$

If $r = r(\alpha \beta \gamma)$ and $r' = r'(\alpha' \beta' \gamma')$, then

$$\sum_{J\lambda M} \frac{2J+1}{8\pi^2} D_{\lambda M}^J(r) D_{\lambda M}^{J*}(r') = \delta(\omega - \omega') \quad (C5)$$

If $r_0 = r_0(\alpha\beta 0)$ and $r'_0 = r'_0(\alpha'\beta' 0)$, then

$$\sum_{J\lambda} \frac{2J+1}{4\pi} D_{\lambda M}^J(r_0) D_{\lambda M}^J(r'_0) = \delta(\Omega - \Omega') \quad (C6)$$

One may extract the α and γ dependence from D^J and write

$$D_{M'M}^J(r) = e^{-iM'\alpha} d_{M'M}^J(\beta) e^{-iM'\gamma} \quad (C7)$$

where the d^J are real. Hence, for $\alpha = \gamma = 0$, the formula progressing logically from (C5) and (C6) can be written

$$\sum_J \frac{2J+1}{2} d_{\lambda M}^J(\beta) d_{\lambda M}^J(\beta') = \delta(\cos \beta - \cos \beta') \quad (C8)$$

Other properties of the d^J are deduced easily from those of the D^J . Some of these are

$$d_{M'M}^{J*}(\beta) = d_{M'M}^J(\beta) = d_{MM'}^J(-\beta) = (-)^{M'-M} d_{-M'-M}^J(\beta) \quad (C9)$$

$$\int_{-1}^{+1} d(\cos \beta) d_{\lambda M}^J(\beta) d_{\lambda M}^{J'}(\beta) = \frac{2}{2J+1} \delta_{JJ'} \quad (C10)$$

Comparing (C10) with (A21), and recognizing the reality of the $d^J(\beta)$ and the $P_\ell(\mu)$, we deduce that

$$P_\ell(\cos \beta) = d_{00}^\ell(\beta) \quad (C11)$$

Similarly, comparing (C4) with (A20), it is at least consistent that

$$\left(\frac{2\ell+1}{4\pi}\right)^{1/2} D_{m0}^\ell(\alpha, \beta, 0) = Y_{\ell m}^*(\beta, \alpha) \quad (C12)$$

The generalizations of (A22) and (A23) are

$$D_{\lambda' m'}^{\ell'}(r) D_{\lambda m}^\ell(r) = \sum_L \langle \ell'(\lambda') \ell(\lambda) | L(\lambda'+\lambda) \rangle \langle \ell'(m') \ell(m) | L(m'+m) \rangle D_{\lambda'+\lambda, m'+m}^L(r) \quad (C13)$$

$$\int d\omega_r D_{\lambda m}^{L*}(r) D_{\lambda' m'}^{\ell'}(r) D_{\lambda m}^\ell(r) = \frac{8\pi^2}{2L+1} \langle \ell'(\lambda') \ell(\lambda) | L(\lambda) \rangle \langle \ell'(m') \ell(m) | L(m) \rangle \quad (C14)$$

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