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Analytic Wave Functions. III. The Spin-Orbit, Spin-Other Orbit, and Spin-Spin Interactions*

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In two earlier papers we have described our methods and programs for calculations of certain classes of atomic wave functions. In this paper we consider the application of the wave functions so obtained to the calculation of the spin-orbit, spin-other-orbit, and spin-spin interactions. As an example we consider oxygen with the electron distribution $(1s)^2(2s)^2(2p)^4$. In first approximation we suppose the spin-orbit interaction diagonal in the wave functions of the Slater diagram. These calculations then remove the horizontal degeneracy from the diagram. We assume the Coulomb potential for the spin-orbit calculation and show the relative contributions of the nucleus and various type electrons to the result. Although the order of the splitting is as observed, the observed asymmetry is not obtained. In second approximation the off-diagonal elements of the spin-orbit interaction are included. The desired asymmetry of the fine structure is obtained, and the agreement with experiment is satisfactory. The spin-other-orbit and spin-spin interactions are calculated for the diagonal first approximation.

I. INTRODUCTION

In two earlier papers of this series[1,2] we developed methods which, if not very surprising, we may hope were efficacious for the determination of atomic wave functions. In these programs the Hamiltonian does not include the spin-orbit, spin-other-orbit, and spin-spin interactions, these being considered first-order effects, and it is our intention to introduce them as perturbations here. As a first approximation we consider the Slater diagram for a given configuration of bound electrons as made up of wave functions which render the spin-orbit interaction diagonal. Then the inclusion of this interaction simply removes the horizontal degeneracy from the Slater diagram. We compute for our oxygen example the spin-orbit energies for the ^3P ground state under such an approximation. In the computation we take as the radial portion of our operator the Coulomb field of the nucleus and the remaining electrons which has been used by us in another connection. We also carry out the spin-other-orbit and spin-spin interaction calculation for this approximation. The result for oxygen is a symmetric splitting of the ground state while experiment tells us that there is an asymmetry in the splitting of about two to one.

In second approximation we include the off-diagonal elements of the spin-orbit operator. The result is a splitting which corresponds quite closely to experiment both in degree of asymmetry and in absolute separation of the levels.

II. THE TRIPLET WAVE FUNCTIONS FOR OXYGEN

The Slater diagram appropriate to oxygen $(1s)^2(2s)^2(2p)^4$ may be referred to.[3] Under our first approximation the spin-orbit interaction is diagonal in the pure wave functions of this diagram. By pure we simply mean that the linear combinations requisite to the description of some of the configurations have been obtained. Now this will mean that the triplet functions will consist of one function from each of the three positions in any given row. Since it is of no importance which horizontal set of three functions we choose, let us choose the three corresponding to the $(S,1)$ positions. The wave functions corresponding to the (1,1), (0,1), and (−1, 1) will be the $^3P_2$, $^3P_1$, and $^3P_0$, respectively.

Our wave functions will all be determinants of eight-order whose orbitals have the form:

$$\psi_{nlm}(r,\vartheta,\varphi)=[R_{nl}(r)/r]\Theta_{lm}(\vartheta)\Phi_m(\varphi), \tag{1}$$

$$R_{1s}=2Z_1^{\frac{3}{2}}r\exp[-Z_1r], \tag{2a}$$

$$R_{2s}=(1/2\sqrt{2})Z_2^{\frac{3}{2}}Z_5^{\frac{3}{2}}[Z_4-Z_2Z_5r]r \times\exp[-Z_2r/2], \tag{2b}$$

$$R_{2p}=(1/2\sqrt{6})Z_3^{\frac{5}{2}}r^2\exp[-Z_3r/2]. \tag{2c}$$

The $^3P_2$ and $^3P_0$ wave functions we have already obtained,[1] and we may represent them as:

$$\psi[(^3P_2)(-1^+0^+1^-1^+)],\quad \psi[(^3P_0)(-1^-0^-1^-1^+)].$$

The $^3P_1$ wave function is a linear combination of the two determinants appearing at the (0,1) position of the Slater diagram. It may be obtained by well-known methods as

$$\psi(^3P_1)=(1/\sqrt{2})\psi_{\mathrm{I}}(-1^-0^+1^-1^+) -(1/\sqrt{2})\psi_{\mathrm{II}}(-1^+0^-1^-1^+).$$

There would actually be a slight difference in the effective nuclear charges appearing in the two determinants immediately above and those appearing in the single determinant functions representing $^3P_2$ and $^3P_0$. However, this difference is so very slight that we will make no appreciable error in ignoring it. Therefore, the effective nuclear charges appearing in our $^3P_2$, $^3P_1$, $^3P_0$ wave functions we take to be the same.

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[1] R. G. Breene, Jr., Phys. Rev. **111**, 1111 (1958).

[2] R. G. Breene, Jr., Phys. Rev. **113**, 809 (1959).

[3] The applicable one appears as Fig. 1(c), of J. C. Slater, Phys. Rev. **34**, 1293 (1929), p. 1298.

In our second approximation to the spin-orbit interaction we shall require wave functions from other blocks of the Slater diagram. Their obtention will be presumed, however, since it precisely parallels the above. In this later consideration, we shall specify, say, a $^3P_2$ function arising from the (1,1) position as $^3P_2{}^{+1}$.

III. THE SPIN-ORBIT INTERACTION (FIRST APPROXIMATION)

The interaction of the orbital angular momentum of the electron with its own spin angular momentum give rise to a term in the Hamiltonian which has been variously derived, but which may be obtained from Condon and Shortley[4] as

$$H'=\sum_{i=1}^{Z} H_i'=\sum_{i=1}^{Z} \mathbf{L}_i\cdot\mathbf{S}_i\frac{1}{2(137)^2}\frac{1}{r}\frac{d}{dr}V(r). \tag{3}$$

Also available from these authors are the matrix elements of $\mathbf{L}\cdot\mathbf{S}$:

$$\begin{aligned}(nlsm_lm_s|\mathbf{L}\cdot\mathbf{S}|n'l'sm_l'm_s')&=\delta(nlm_l+m_s;n'l'm_l'+m_s')\{\delta(m_sm_s')m_lm_s\\&\quad+\tfrac{1}{2}\delta(m_s',m_s\pm1)[(l-m+\tfrac{1}{2})(l+m+\tfrac{1}{2})]^{\frac{1}{2}}\}.\end{aligned} \tag{4}$$

Of prime concern to us is the radial portion of the perturbing Hamiltonian, and to this we turn our attention. The point of obvious interest here is $V(r)$. This is, of course, the potential under which the electron question exists—we remark this to be a one-particle operator—due to the presence of the remaining atomic electrons. Surely, however, one must consider the Coulomb portion of this potential, and we shall assume that this potential is sufficient. We shall detail this in a moment, but let us first evaluate the angular contribution on the matrix element since this may be done in a general way.

Each of our wave functions is an eighth-order determinant. However, since the operator is a one-particle operator, the matrix element over the determinant is precisely the sum of the matrix elements over the eight individual orbitals. Next, Eq. (4) tells us that no change in any electron state goes with the first portion of this matrix element while a spin flip is accounted for by the second portion. Under our assumption the only possible nondiagonal elements arise in connection with the matrix element over the two-determinant linear combination comprising the $^3P_1$ wave function. For a matrix element to be nonzero between these two determinants would require a two particle operator, and this we do not have. Hence, we concern ourselves only with diagonal elements, that is, with the first term in Eq. (4). Now we note the m_l appears as a factor in this term which means $s0$ and $p0$ electrons contribute nothing to the matrix element. This has an important effect on the radial potential which we shall discuss in a moment, but first let us write down the angular matrix elements:

$$(^3P_2|\mathbf{L}\cdot\mathbf{S}|^3P_2)=-\tfrac{1}{2}, \tag{5a}$$

$$(^3P_1|\mathbf{L}\cdot\mathbf{S}|^3P_1)=0, \tag{5b}$$

$$(^3P_0|\mathbf{L}\cdot\mathbf{S}|^3P_0)=\tfrac{1}{2}. \tag{5c}$$

A given atomic electron exists in a $V(r)$ which is produced by the remaining $Z-1$ electrons in the atom plus the nucleus, and this potential will certainly depend on whether the electron under consideration is a $1s$, a $2s$, or a $2p$ electron, at least in the case of oxygen. Therefore, the disappearance of the $1s$ and $2s$ contributions means we shall only have to consider $2p$ electrons in this case. One $V(r)$, therefore, will suffice.

We take our remaining seven electrons as described by a seventh-order determinant obtained by simply removing those orbitals corresponding to the electron under consideration. Our potential is thus

$$V(r)=-\frac{Z}{r}+\int\frac{|\psi_{^3P}(0^+)|^2}{r_{ij}}d\tau.$$

In computing the potential[5] we have supposed that the familiar expansion of the inverse of the interparticle separation in terms of Legendre functions terminates after the first term. This is, under all conditions, true as regards the $1s$ and $2s$ contributions and very nearly so as regards the $2p$ contributions. As a result of all this we obtain

$$\begin{aligned}V(r)=&-(1/r)-(15.322+2/r)e^{-15.322r}\\&-(38.330r^2+18.368r+8.930+2/r)e^{-5.718r}\\&-(14.092r^2+19.264+13.168+4/r)e^{-4.389r}.\end{aligned} \tag{6}$$

This may be considered as four terms. The first of these—the term with no exponential—is the nuclear contribution; the second is the contribution of the $1s$ electrons. The third and fourth are the contributions from the $2s$ and $2p$ electrons, respectively. As a result we may consider separately the contributions of these various atomic components to the matrix element. Equations (5) tell us that the matrix elements of $^3P_2$ and $^3P_0$ differ only in sign, so, neglecting this for a moment, we may write for them both:

$$(^3P_2|H'|^3P_2)=\left(\frac{1}{2}\right)\left(\frac{1}{2(137)^2}\right)\int_0^\infty\frac{R_{2p}{}^2(r)}{r}\frac{dV(r)}{dr}dr. \tag{7}$$

Equation (7) may be evaluated with the help of Eqs. (1) and (5). We find the nuclear contribution to be 10.30 cm^{-1}, that of the $1s$ electrons 4.47 cm^{-1}, that of the $2s$ electrons 18.15 cm^{-1}, and that of the $2p$ electrons 27.61 cm^{-1}.

As a result of the spin-orbit interaction the ^3P ground state of oxygen is split symmetrically. The $^3P_0$ level is raised 60.52 cm^{-1}. The $^3P_1$ level corresponds to the

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[4] See E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, New York, 1935), p. 120.

[5] R. G. Breene, Jr., and M. C. Nardone, Phys. Rev. **115**, 93 (1959).

unperturbed position. The ${}^3P_2$ level is dropped 60.52 cm^{-1}. This is illustrated in Fig. 1.

IV. THE SPIN-OTHER-ORBIT INTERACTION

Since we are considering these three interactions as first order perturbations, we may deal separately with them and then simply add the three energies to obtain the total. In line with this we now take up the interaction of the spin angular momentum of one electron with the orbital angular momentum of another. Here the same atomic wave functions are, of course, used. Again, the specific problem in our oxygen example is the evaluation of certain radial integrals. The angular contributions to the matrix element have been evaluated in general form by Marvin.[6]

The spin-other-orbit operator may be written as

$$H_{\mathrm{soo}}'=[1/2(137)^2][(\mathbf{r}_1-\mathbf{r}_2)\times(\mathbf{p}_1-2\mathbf{p}_2)\cdot\mathbf{S}_1 +(\mathbf{r}_2-\mathbf{r}_1)\times(\mathbf{p}_2-2\mathbf{p}_1)\cdot\mathbf{S}_2]r_{12}^{-3}. \tag{8}$$

We have written the operator in atomic units for convenience where, of course, $c=137$. The symbols $\mathbf{r}$, $\mathbf{p}$, and $\mathbf{S}$ represent the radius vector, the linear momentum, and the spin angular momentum, respectively, for the appropriate one of the two electrons in interaction. Marvin's obtention of the specific forms for the matrix elements is basically a straightforward application of matrix algebra manipulations, albeit a very complex and necessarily lengthy one. There would not appear to be any reason for our investigation of the work. The matrix element expression is lengthy at best. Now of the three terms of which it consists, we use only one in oxygen. Therefore, the reader is advised to refer to Marvin for completeness, and we shall write down only what is appropriate to our example:

$$\begin{aligned}(ab|H_{\mathrm{soo}}'|cd)=&2(-)^{\Delta m}\delta(m_s{}^a,m_s{}^c)\delta(m_s{}^b,m_s{}^d)\\&\times\delta(m_l{}^a+m_l{}^b,\,m_l{}^c+m_l{}^d)(m_s{}^c+2m_s{}^d)\\&\times\{-4m_l{}^cC^0(ac,bd)\xi^0(ab,cd)+[\Lambda^0(ac+1,\,bd-1)\\&-\Lambda^0(ac-1,\,bd+1)]\rho^0(ab,cd)-[A^0(ac+1,\,bd-1)\\&-A^0(ac-1,\,bc+1)]\Delta^0(ab,cd)\}.\end{aligned} \tag{9}$$

The A^k, C^k, and Λ^k are the results of integration over angular coordinates and are defined as:

$$\begin{aligned}C^k(ac+j,\,bd)&\\&=(2k+1)c^k(l^am_l{}^a,\,l^cm_l{}^c+f)c^k(l^bm_l{}^b,l^dm_l{}^d),\end{aligned} \tag{10a}$$

$$\begin{aligned}\Lambda^k(ac+f,\,bd+g)&\\&=\lambda^k(l^am_l{}^a,\,l^cm_l{}^c+f)\alpha^k(l^bm_l{}^b,\,l^dm_l{}^d+g),\end{aligned} \tag{10b}$$

$$\begin{aligned}A^k(ac+f,\,bd+g)&\\&=\alpha^k(l^am_l{}^a,\,l^cm_l{}^c+f)\alpha^k(l^bm_l{}^b,\,l^dm_l{}^d+g),\end{aligned} \tag{10c}$$

$$B^k(ac+f,\,bd)=\beta^k(l^am_l{}^a,l^cm_l{}^c)c^k(l^bm_l{}^b,l^dm_l{}^d). \tag{10d}$$

We encounter the B^k in the spin-spin case, but we list it with the others for convenience. The c^k are tabulated on pages 178–179 of reference 4. The α^k, β^k, and λ^k are tabulated on pages 106–108 of reference 6.

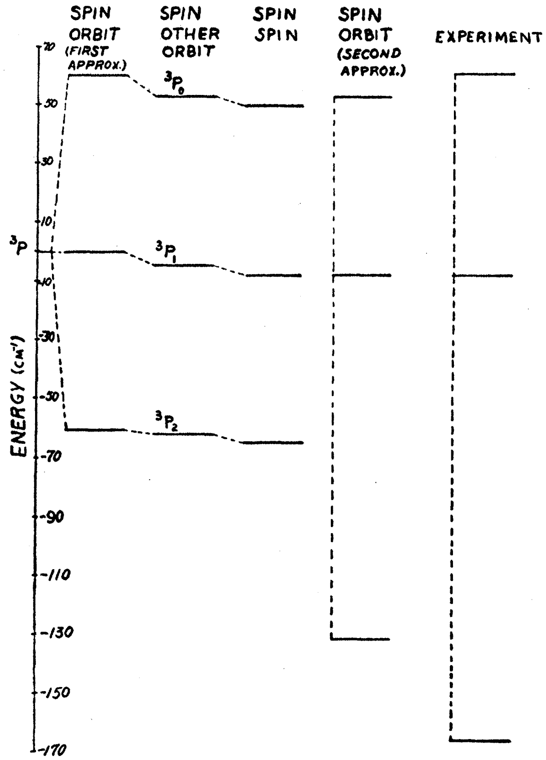

FIG. 1. The calculated energies for the three interactions. The experimental results given by Moore (reference 7) are displayed for comparison.

The ξ^k, ρ^k, Δ^k, and the σ^k which we shall encounter in the next section are functions of the radial integrals. Rather than list the general expressions we shall show the final radial integrals to which our matrix elements reduce.

In the present case we have a two particle operator which means that the matrix element over the determinant will be of the form:

$$\sum_{b>a}\sum_{a=1}^{8}[(ab|H|ab)-(ab|H|ba)].$$

We may write down the result of the rather tedious calculation in terms of the radial integrals:

$$\begin{aligned}E_{\mathrm{soo}}({}^3P_2)=8\xi^0(2p,2p;\,2p,2p)+2\rho^0(1s,2p;\,2p,1s)&\\+2\rho^0(2s,2p;\,2p,2s),&\end{aligned} \tag{11a}$$

$$E_{\mathrm{soo}}({}^3P_1)=-4\xi^0(2p,2p;\,2p,2p), \tag{11b}$$

$$E_{\mathrm{soo}}({}^3P_0)=-2\rho^0(1s,2p;\,2p,1s)-2\rho^0(2s,2p;\,2p,2s). \tag{11c}$$

It is apparent from Eqs. (11) which electrons contribute to the matrix elements over the various states. The specific radial integrals are:

$$\xi^0(2p,2p;\,2p,2p)=\frac{1}{8(137)^2}\int_0^\infty\!\!\int\frac{1}{r_>{}^3}\times R_{2p}{}^2(1)R_{2p}{}^2(2)dr_1dr_2, \tag{12a}$$

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[6] H. H. Marvin, Phys. Rev. 71, 102 (1947).

$$\rho^0(1s,2p;2p,1s)=\xi^{-1}(1s,2p;2p,1s)$$

$$=\frac{1}{8(137)^2}\int_0^\infty\!\!\int \frac{1}{r_< r_>^2}R_{1s}(1)R_{2p}(1)\times R_{1s}(2)R_{2p}(2)dr_1dr_2, \quad \text{(12b)}$$

$$\rho^0(2s,2p;2p,2s)=\frac{1}{8(137)^2}\int_0^\infty\!\!\int \frac{1}{r_< r_>^2}R_{2s}(1)R_{2p}(1)\times R_{2s}(2)R_{2p}(2)dr_1dr_2, \quad \text{(12c)}$$

and Eqs. (12a), (12b), and (12c) have the values 5.1335×10^{-6}, 10.9443×10^{-6}, and 6.3509×10^{-6}, respectively, so that:

$$E_{\text{soo}}(^3P_2)=-1.42, \quad \text{(13a)}$$

$$E_{\text{soo}}(^3P_1)=-4.51, \quad \text{(13b)}$$

$$E_{\text{soo}}(^3P_0)=-7.59. \quad \text{(13c)}$$

Thus, we have squeezed the three levels together slightly, but we have done so evenly, so that the spacing remains the same. The levels have also been lowered slightly. The effects of the spin-other-orbit interaction appear to be about an order of magnitude less than those of the spin-orbit which, it would seem, one would expect. Finally, we consider the last of three electronic interactions.

V. THE SPIN-SPIN INTERACTION

Now we shall consider the interaction between the spin angular momentum of one electron and the spin angular momentum of another. Oxygen continues to serve as our example, and we again turn to the work of Marvin[6] for the specifics of the evaluation.

The spin-spin operator may be written as:

$$H_{\text{ss}}'=[-1/(137)^2][3r_{12}^{-5}\mathbf{S}_1\cdot(\mathbf{r}_2-\mathbf{r}_1)\mathbf{S}_2\cdot(\mathbf{r}_2-\mathbf{r}_1)-r_{12}^{-3}\mathbf{S}_1\cdot\mathbf{S}_2], \quad \text{(14)}$$

where again we have written the operator in atomic units and the elements as before. The same remarks as were made concerning the Marvin matrix element evaluation may be made here. Again we shall only write down that part of the general form of the matrix element for the interaction which is applicable to oxygen and, in so doing, save quite a bit of space:

$$\begin{aligned}(ab|H_{\text{ss}}'|cd)={}&2(-)^{\Delta m}[\delta(m_s{}^a,\, m_s{}^c\mp1)\delta(m_s{}^b,\, m_s{}^d\pm1)\\&\times\delta(m_l{}^a+m_l{}^b,\, m_l{}^c+m_l{}^d)\{B^0(ac,bd)\sigma^0(ab,cd)\\&+[A^0(ac\pm1,\, bd\mp1)+A^0(ac\mp1,\, bd\pm1)]\eta^0(ab,cd)\\&+2C^0(ac,bd)\xi^0(ab,cd)\}+\delta(m_s{}^a,m_s{}^c)\delta(m_s{}^b,m_s{}^d)\\&\times\delta(m_l{}^a+m_l{}^b,\, m_l{}^c+m_l{}^d)m_s{}^cm_s{}^d\{-4[B^0(ac,bd)\\&+C^0(ac,bd)]\sigma^0(ab,cd)+8A^0(ac,bd)\eta^0(ab,cd)\\&+4C^0(ac,bd)\xi^0(ab,cd)\}]. \quad \text{(15)}\end{aligned}$$

In this case all three members of the oxygen ground state triplet have precisely the same expression for their spin-spin interaction energy, and this expression in question reduces in evaluation until we have only:

$$E_{\text{ss}}=-2\xi^0(2p,2p;2p,2p),$$

where ξ^0 is given by Eq. (12a).

The value which we have obtained for this energy is 3.08 cm^{-1}, so that all levels are depressed by that amount.

VI. THE SPIN-ORBIT INTERACTION (SECOND APPROXIMATION)

We again consider the spin-orbit interaction but this time include the off-diagonal elements of the interaction in our calculation. We introduce an approximation here which will have but small effect on our result. It is assumed that all the wave functions encountered will have the same effective nuclear charge insofar as our computation of the off-diagonal elements is concerned. The diagonal elements will, of course, contain the zeroth-order energies of the ^3P, ^1D, and ^1S configurations. We use the values for these energies computed previously.

The $^3P_2$ energy is obtained by diagonalizing the 2×2 block containing the $^3P_2{}^{+1}$ and the $^1D_1{}^2$. (We recall our definition in Sec. II.)

The $^3P_1$ energy may be obtained by diagonalizing the 3×3 block corresponding to the $^3P_2{}^0$, $^1D_1{}^{+1}$, and $^3P_1{}^{+1}$ functions.

Finally the $^3P_0$ energy is obtained by diagonalizing the 5×5 block corresponding to the $^3P_2{}^{-1}$, $^1S_0{}^0$, $^1D_2{}^0$, $^3P_1{}^0$, and $^3P_0{}^{+1}$ functions.

The result is then:

$$E_{\text{so}}(^3P_2)=-\ 63.41, \quad \text{(16a)}$$

$$E_{\text{so}}(^3P_1)=+\ 60.52, \quad \text{(16b)}$$

$$E_{\text{so}}(^3P_0)++121.04. \quad \text{(16c)}$$

In Fig. 1 we have indicated the results of these calculations.[7] For comparison of the splittings we have aligned the $^3P_1$ level of the second with that of the first approximation. We remark that the ratio of the level separations is 2:1 in agreement with the Landé interval rule.

Improvements in these results could probably be introduced by (1) including the second term in the interparticle expansion, (2) considering a potential including the effects of exchange, and (3) using the precise effective nuclear charges in the computation of the off-diagonal elements of the spin-orbit interaction.

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[7] The experimental values have been taken from *Atomic Energy Levels*, edited by C. E. Moore, National Bureau of Standards Circular No. 467 (U. S. Government Printing Office, Washington, D. C., 1948), Vol. 1.