there are $N(N-1)/2$ ΔW_{kj}'s of which only from one to five are not common for all configurations. If the common terms were also summed the calculated magnitude of the energy level separations would be greatly increased, but would have no effect in the separation of the spectrum lines. This fact that the line-separation is the small difference of two large numbers probably accounts for the variation of the calculated effect with the choice of wave function, noted by Bartlett and Gibbons, and also encountered in attempts to refine the present calculation. In any event it is not to be expected that the separation of the isotope levels would approach this high limit, since it is merely a limit and since it is so large in comparison with observed isotope separations.

The writer wishes to thank Professor Carl Eckart for suggesting the problem and discussing its solution many times with him.

Application of the Dirac Vector Model to the d^4 Configuration

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Formulae for the energies of multiplets belonging to d^4 are computed by the use of the vector model as developed by Van Vleck and Serber. Since insufficient data were available for d^4, the configuration md^4ns was used to check the formulae against experiment. Even here the data are rather meager. In order to obtain out of the above configuration the proper energies of the multiplets arising from d^4 alone, it was necessary to subtract from it the exchange energy between the s electron and the d^4 "core." The agreement with experiment is, at best, only fair, perhaps because of perturbations from neighboring levels.

INTRODUCTION

THE first calculation of the energies of multiplets was made by Slater[1] in his well-known paper on complex spectra. However, the method of diagonal sums, which he employed, does not yield the separation of multiplets occurring more than once in a given configuration; it only gives their mean energy. Slater's work was extended by Condon, Shortley and Ufford.[2] The latter two developed a method for separating multiplets occurring more than once in a given configuration. Later the problem was attacked from a somewhat different point of view by Van Vleck[3] by means of Dirac's[4] vector model. The restriction to a single configuration made by Van Vleck was removed in a subsequent paper by Serber.[5] He was able to separate multiplets occurring more than once and thus checked the results obtained previously by Ufford and Shortley[2] on the separation of the two ^2D terms in d^3. In the present paper Serber's procedure will be applied to the d^4 configuration, which apparently has not been examined previously. His method does not include spin-orbit interaction and, therefore, only the centers of gravity of the multiplets in question are calculated here.

CALCULATION OF THE FORMULAE

To begin with, the method of diagonal sums was applied to all the multiplets in d^4. This gave only the mean energies of ^3F, ^3P, ^1G, ^1D and ^1S, each of which occurs twice in d^4. In order to separate them Serber's scheme was employed. By way of illustration, the energy matrix necessary for the separation of $^3P_+$ and $^3P_-$ is given here. Vanishing matrix elements, which occur when the interacting states differ in more than two non-identical electronic orbits, are omitted.

[1] J. C. Slater, Phys. Rev. **34**, 1293 (1929).
[2] E. U. Condon, Phys. Rev. **36**, 1121 (1930); E. U. Condon and H. G. Shortley, Phys. Rev. **37**, 1025 (1931); G. H. Shortley, Phys. Rev. **40**, 185 (1932); C. W. Ufford and G. H. Shortley, Phys. Rev. **42**, 167 (1932).
[3] J. H. Van Vleck, Phys. Rev. **45**, 405 (1934).
[4] P. A. M. Dirac, *The Principles of Quantum Mechanics*, Chapter XI.
[5] Robert Serber, Phys. Rev. **45**, 461 (1934).

The states involved are:

$A: \delta\pi\sigma - \delta$ (three states); $\quad D: \sigma\sigma\delta - \pi;$
$B: \delta\delta - \pi - \delta;$ $\qquad\qquad\qquad E: \pi\pi\sigma - \pi;$
$C: -\pi - \pi\delta\pi;$

with $L = M_L = 1$; $S = 1$. The energies of the two ^3P's are now given by

$$^3P_\pm = \tfrac{1}{2}a \pm \tfrac{1}{2}(2b - a^2)^{\frac{1}{2}} \qquad (1)$$

where a is simply twice the mean value of ^3P as obtained by the method of diagonal sums while b is given by the sum of the squares of the elements in the energy matrix minus the squares of the

energies of all triplets having $L > 1$. To complete the computation it is only necessary to substitute for the elements of the energy matrix in terms of Slater's F's; no G's are involved, since, for equivalent electrons, F's and G's of the same index are equal.

The formulae for the energies of the multiplets arising from d^4 are:

$^5D = 6F_0 - 21F_2 - 189F_4$
$^3H = 6F_0 - 17F_2 - 69F_4$
$^3G = 6F_0 - 12F_2 - 94F_4$
$^3F_\pm = 6F_0 - 5F_2 - 76.5F_4$
$\qquad\qquad \pm\tfrac{1}{2}(612F_2^2 + 20025F_4^2 - 4860F_2F_4)^{\frac{1}{2}}$

	A		B	C	D	E
$H_I{}^{AA} - H_{12}{}^{AA}$ $- H_{34}{}^{AA}$	$\sqrt{\tfrac{1}{2}}[-H_{13}{}^{AA}$ $+H_{14}{}^{AA} - H_{23}{}^{AA}$ $+H_{24}{}^{AA}]$	$\sqrt{\tfrac{1}{2}}[H_{13}{}^{AA}$ $+H_{14}{}^{AA} - H_{23}{}^{AA}$ $-H_{24}{}^{AA}]$	$-H_{23}{}^{BA}$	0	$H_{13}{}^{DA}$	$H_{14}{}^{EA}$
$\sqrt{\tfrac{1}{2}}[-H_{13}{}^{AA}$ $+H_{14}{}^{AA} - H_{23}{}^{AA}$ $+H_{24}{}^{AA}]$	$H_I{}^{AA} - H_{12}{}^{AA}$ $+H_{34}{}^{AA}$ $-\tfrac{1}{2}[H_{13}{}^{AA}$ $+H_{14}{}^{AA} + H_{23}{}^{AA}$ $+H_{24}{}^{AA}]$	$\tfrac{1}{2}[-H_{13}{}^{AA}$ $+H_{14}{}^{AA} + H_{23}{}^{AA}$ $-H_{24}{}^{AA}]$	$\sqrt{\tfrac{1}{2}}H_{23}{}^{BA}$	$\sqrt{2}H^{CA}{}_{(13)(24)}$	$\sqrt{2}[-\tfrac{1}{2}H_{13}{}^{DA}$ $+H^{DA}{}_{(24)(13)}]$	$\sqrt{\tfrac{1}{2}}H_{14}{}^{EA}$
$\sqrt{\tfrac{1}{2}}[H_{13}{}^{AA}$ $+H_{14}{}^{AA} - H_{23}{}^{AA}$ $-H_{24}{}^{AA}]$	$\tfrac{1}{2}[-H_{13}{}^{AA}$ $+H_{14}{}^{AA} + H_{23}{}^{AA}$ $-H_{24}{}^{AA}]$	$H_I{}^{AA} + H_{12}{}^{AA}$ $-H_{34}{}^{AA}$ $-\tfrac{1}{2}[H_{13}{}^{AA}$ $+H_{14}{}^{AA} + H_{23}{}^{AA}$ $+H_{24}{}^{AA}]$	$\sqrt{2}[H_I{}^{BA}$ $-\tfrac{1}{2}H_{23}{}^{BA}]$		$-\sqrt{\tfrac{1}{2}}H_{13}{}^{DA}$	$\sqrt{2}[H_I{}^{EA}$ $-\tfrac{1}{2}H_{14}{}^{EA}]$
$-H_{23}{}^{BA}$	$\sqrt{\tfrac{1}{2}}H_{23}{}^{BA}$	$\sqrt{2}[H_I{}^{BA}$ $-\tfrac{1}{2}H_{23}{}^{BA}]$	$H_I{}^{BB} - H_{34}{}^{BB}$ $-\tfrac{1}{2}[H_{13}{}^{BB}$ $+H_{14}{}^{BB} + H_{23}{}^{BB}$ $+H_{24}{}^{BB}]$	$-\tfrac{1}{2}[H_{13}{}^{CB}$ $+H_{23}{}^{CB}]$	$\tfrac{1}{2}[H^{DB}{}_{(13)(34)}$ $+H^{DB}{}_{(23)(34)}]$	0
0	$\sqrt{2}H^{CA}{}_{(13)(24)}$	0	$-\tfrac{1}{2}[H_{13}{}^{CB}$ $+H_{23}{}^{CB}]$	$H_I{}^{CC} - H_{34}{}^{CC}$ $-\tfrac{1}{2}[H_{13}{}^{CC}$ $+H_{14}{}^{CC} + H_{23}{}^{CC}$ $+H_{24}{}^{CC}]$	$-\tfrac{1}{2}[H_{13}{}^{DC}$ $+H_{23}{}^{DC}]$	$-\tfrac{1}{2}[H_{14}{}^{EC}$ $+H_{24}{}^{EC}]$
$H_{13}{}^{DA}$	$\sqrt{2}[-\tfrac{1}{2}H_{13}{}^{DA}$ $+H^{DA}{}_{(24)(13)}]$	$-\sqrt{\tfrac{1}{2}}H_{13}{}^{DA}$	$\tfrac{1}{2}[H^{DB}{}_{(13)(34)}$ $+H^{DB}{}_{(23)(34)}]$	$-\tfrac{1}{2}[H_{13}{}^{DC}$ $+H_{23}{}^{DC}]$	$H_I{}^{DD} - H_{34}{}^{DD}$ $-\tfrac{1}{2}[H_{13}{}^{DD}$ $+H_{14}{}^{DD} + H_{23}{}^{ED}$ $+H_{24}{}^{DD}]$	$-\tfrac{1}{2}[H_{13}{}^{ED}$ $+H_{23}{}^{ED}]$
$H_{14}{}^{EA}$	$\sqrt{\tfrac{1}{2}}H_{14}{}^{EA}$	$\sqrt{2}[H_I{}^{EA}$ $-\tfrac{1}{2}H_{14}{}^{EA}]$	0	$-\tfrac{1}{2}[H_{14}{}^{EC}$ $+H_{24}{}^{EC}]$	$-\tfrac{1}{2}[H_{13}{}^{ED}$ $+H_{23}{}^{ED}]$	$H_I{}^{EE} - H_{34}{}^{EE}$ $-\tfrac{1}{2}[H_{13}{}^{EE}$ $+H_{14}{}^{EE} + H_{23}{}^{EE}$ $+H_{24}{}^{EE}]$

In the above matrix $H^{AA}{}_{ij}$ denotes the usual type of exchange integral wherein electrons i and j are interchanged, whereas $H^{AB}{}_{ij}$ differs from the usual type of exchange integral in that the initial wave function refers to a state of the type A and the final wave function to B. In $H_{(12)(34)}$, etc., there are two exchanges. When all the electronic orbits in a given state are different, the complete matrices P_{ij}, tabulated on page 466 of Serber's paper, are needed to represent the state in the energy matrix. Such is the case with A. When, on the other hand, orbits 1 and 2 are identical, as in states B, C, D, E, then, in considering the interactions between any of the latter and A, it must

be remembered that all the rows in P_{12} having characteristic values of -1 are not allowed; of course, the corresponding rows in all the other P matrices must be excluded also. Thus matrix elements of the type $H^{XA}{}_{ij}$, $(X = B, C, D, E)$, are given by the third row of Serber's P matrices. Similarly, in considering interactions between any two states in which orbits 1 and 2 are identical, both rows and columns of P_{12} having characteristic values of -1 are excluded. Therefore, matrix elements of the type $H^{XY}{}_{ij}$, $(X, Y, = B, C, D, E)$, are given by the element in the third row, third column of the P matrices. For more detailed discussion on this point see Serber's paper.[5]

TABLE I. *Energies of all the multiplets arising from the $3d^4$ configuration.*[6]

Terms	Calc.$3d^4<4s>$ $F_2=779.5$ $F_4=69.3$	Vanadium $F_2=790$ $F_4=62$	Obs. V I $3d^4<4s>$	Obs. V II $3d^4$	Calc. $3d^4<4s>$ $F_2=1152$ $F_4=99$	Chromium Obs. Cr II $3d^4<4s>$	Obs. Cr III $3d^4$
^5D	0 cm^{-1}	0 cm^{-1}	0 cm^{-1}	0 cm^{-1}	0 cm^{-1}	0 cm^{-1}	
^3H	11435	10600	11435		16488	16494	
$^3F_-$	13101	12197	12166	13354	18913	17370	17441 cm^{-1}
$^3P_-$	13221	12088	11848	11500	18997		
^3G	13600	13000	13600	16240	19773	19780	19780
^3D	16630	16360			24372		
^1I	17152	15900			24732		
$^1G_-$	17514	16114			25213		
$^1S_-$	19001	17684			27405		
$^1D_-$	21545	20844			31280		
^1F	23647	23100			34587		
$^3P_+$	27317	27170			40141		
$^3F_+$	27437	27059			40225		
$^1G_+$	32723	31796			47785		
$^1D_+$	40821	41240			60114		
$^1S_+$	56369	55476			82629		

[6] All the experimental values were taken out of Bacher and Goudsmith's book on *Atomic Energy States*.

$$^3D = 6F_0 - 5F_2 - 129F_4$$

$$^3P_\pm = 6F_0 - 5F_2 - 76.5F_4$$
$$\pm \tfrac{1}{2}(912F_2{}^2 + 38025F_4{}^2 - 9960F_2F_4)^{\frac{1}{2}}$$

$$^1I = 6F_0 - 15F_2 - 9F_4$$

$$^1G_\pm = 6F_0 - 5F_2 - 6.5F_4 \pm \tfrac{1}{2}(708F_2{}^2 + 30825F_4{}^2 - 6420F_2F_4)^{\frac{1}{2}}$$

$$^1F = 6F_0 - 84F_4$$

$$^1D_\pm = 6F_0 + 9F_2 - 76.5F_4$$
$$\pm \tfrac{1}{2}(1296F_2{}^2 + 30825F_4{}^2 - 10440F_2F_4)^{\frac{1}{2}}$$

$$^1S_\pm = 6F_0 + 10F_2 + 6F_4$$
$$\pm \tfrac{1}{2}(3088F_2{}^2 + 133200F_4{}^2 - 20640F_2F_4)^{\frac{1}{2}}.$$

COMPARISON WITH EXPERIMENT

Unfortunately there are very little experimental data with which to check the above computations. Obviously three multiplets are needed to determine the paremeters involved in the above equations. Only in the case of V II are there as many as four levels and even so, after the three parameters have been determined, there is but one level left to check. However, in his paper on the vector model Van Vleck[3] showed that, in case of a configuration of the form sa^k, the energy due to the addition of an s electron to the "core" a^k enters in a very simple manner, namely:

$$W = W(a^k) - \tfrac{1}{2}K_{as}\{k + 2[S(S+1) - S_k(S_k+1) - 3/4]\} + kJ_{as}, \quad (2)$$

where W is the energy of sa^k, $W(a^k)$ the energy of a^k alone, K_{as} is the exchange energy between the s electron and a^k "core," J_{as} the coulomb energy, S is the resultant spin and S_k the spin of the "core" a^k. It follows at once that the interval between two states $S = S_k \pm \tfrac{1}{2}$ originating from a given configuration L_k, S_k of a^k is:

$$h\Delta\nu = 2|K_{as}|(S_k + \tfrac{1}{2}). \quad (3)$$

Thus, if any two levels arising from such a configuration are known, it is possible, with the help of Eq. (3), to compute K_{as} and then, using Eq. (2), to determine the energy of any level arising from a^k alone. Once K_{as} has been determined, either one of any known pair of levels $S = S_k \pm \tfrac{1}{2}$ belonging to sa^k may be used to compute the energy of that particular multiplet, (belonging to a^k), from which this pair of levels originated. It is to be noted that the energies of the various multiplets computed in the above manner are obtained, except for an additive constant kJ_{as}, which, however, need not concern one here as one is interested only in the relative positions of the levels.

V I and Cr II have in their respective spectra levels belonging to the configuration $3d^44s$. In each case are found ^4D and ^6D, both arising from ^5D of d^4. The separation between ^4D and ^6D was hence used to determine K_{as} by means of (3). In accordance with the results of the previous paragraph, the energies of all the multiplets arising from $3d^4$ alone were computed and are given in Table I. In it, under the columns headed by $3d^4<4s>$, is to be understood a set of energy levels arising from $3d^4$ alone but computed from $3d^44s$. In order to obtain out of these energies those actually belonging to the multiplets of $3d^44s$, i.e., those which can be observed experimentally, it is, of course, necessary to reapply Eq. (2). The values of K_{ds} for V I and Cr II as obtained by the author are 1259 cm^{-1} and 1508.6 cm^{-1}, respectively.

In the above table the energy of ^5D is always taken as zero. There are two adjustable param-

eters F_2 and F_4 which are to be so selected as to fit the observed data as well as possible. The values of F_2 and F_4 used for the calculations in the first column were so chosen as to fit ^3H and ^3G of V I exactly. The fifth column is based on a corresponding choice for Cr II instead of V I. In the case of vanadium, $^3F_-$ and $^3P_-$ proved to be in the wrong order as compared with the observed values. However, this situation can be rectified by changing slightly the values of F_2 and F_4, as is evident from the second column of the table. The agreement for ^3H and ^3G is, of course, then to a certain extent impaired. The calculated positions of the terms not yet found experimentally should not be taken too literally, as the parameters cannot be fixed with any precision from the existing experimental data. Nevertheless it has seemed advisable to tabulate these computed positions since they at least show the general trend of the various states belonging to the configuration. Part of the

inability to fit the few observed levels very accurately may be due to perturbations by other configurations. In particular, the actual value of ^3G for V II may be abnormally high because of perturbation by the known $3d^34s$ ^3G level at 14,573 cm^{-1}. It is hard, however, to see how the displacement due to this perturbation could amount to more than 800 cm^{-1}. In the case of Cr II, the position of $^3F_-$ may be abnormally low, as the ^4F term from which it is obtained is, no doubt, strongly perturbed by the d^5 ^4F level located about 1600 cm^{-1} above the former. There is no reason why the parameters F_2 and F_4 should have exactly the same values in V I and V II, or in Cr II and Cr III, as the addition of the $4s$ electron may influence the core d^4 to a slight extent. The experimental values for Cr II and Cr III are remarkably nearly equal.

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Effect of Temperature and Pressure on the Mercury Afterglow

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Measurements have been made on the rate of escape of resonance radiation from a slab of mercury vapor 4.0 cm thick. The measurements extended over a range of pressures from 0.133 to 0.720 mm of mercury and over a range of temperature from 390°K to 585°K. Calculations have also been made of the decay constants on the basis of Kenty's theory of radiation diffusion. The variations of the disagreement between the experimental results and Kenty's theory as affected by both pressure and temperature are hence made available. Some of the difficulties for present theories in the interpretation of the experimental results are pointed out.

INTRODUCTION

DURING the last few years several studies[1] have been made on the rate of escape of resonance radiation from a slab of mercury vapor after the initial excitation has been cut off. These experiments are in agreement in showing, that for low vapor pressures, the decay constant,

β, of the exponential curve representing the decay of resonance radiation emitted by the mercury vapor, decreases as the mercury vapor pressure increases. As the mercury vapor pressure is further increased, the decay constant passes through a minimum value after which it slowly rises with increased vapor pressure.

The final interpretation of these results has not as yet been definitely fixed. In his earlier work Zemansky[2] interpreted his results on the basis of repeated atomic absorptions and re-emissions; the increase in β at higher pressures

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