

The Theory of the Magnetic Quenching of Iodine Fluorescence and of Λ -Doubling in ${}^3\Pi_0$ States

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A theoretical basis is given for Turner's proposal that the magnetic quenching of iodine fluorescence is a predissociation phenomenon. To this end it is shown that a magnetic field introduces matrix elements in the Hamiltonian function between the ${}^3\Pi_0^+$ and ${}^3\Pi_0^-$ (or possibly the ${}^3\Pi_0^+$ and ${}^3\Sigma_0^+$) states, respectively stable and unstable in I_2 . This confirms Mulliken's assignment of ${}^3\Pi_0^+$ to the upper state of the halogen visible bands. The magnetic field has a unique role for so-called 0^+ , 0^- levels because perturbations between these particular states cannot arise from rotational distortion, the cause of the usual Kronig predissociation, or from electric fields unless they are very large or else markedly inhomogeneous. The magnetic quenching should be independent of the rotational quantum number (section 5) and should depend on field strength in the form $b\mathfrak{H}^2/(a+b\mathfrak{H}^2)$. The observed mode of frequency dependence demands that in I_2 the potential curves of ${}^3\Pi_0^+$, ${}^3\Pi_0^-$ states, which are the two components of a Λ -doublet, be extremely close for certain values of r or else actually cross each other. This crossing is shown to be theoretically possible under certain conditions. The possibility of magnetic predissociation in other molecules is also discussed. The predissociation due to collision observed by Turner, Kaplan, and others probably arises because electric fields can blend u and g states, and also 0^+ and 0^- states if inhomogeneous.

Incidental points in halogen band spectra are discussed. Schlapp's intensity theory confirms Brown's assignment of ${}^3\Pi_1$ to his new level in I_2 , Br_2 . A calculation is given showing why the ${}^3\Pi_0^+$ level in ICl appears derived from ${}^2P_{3/2}(I) + {}^2P_{1/2}(Cl)$ when configuration theory (the non-crossing rule) suggests ${}^2P_{3/2} + {}^2P_{3/2}$. An explicit mechanism is thus furnished for Brown and Gibson's interpretation of the predissociation of ICl published elsewhere in this issue.

The writer's previous formulas for the width of Λ -doublets in ${}^3\Pi_0$ states are extended to include investigation of the sign of the doublet and the perturbations from ${}^1\Sigma$, ${}^3\Sigma$ states previously omitted although coordinate in importance with those from ${}^3\Sigma$. The need of considering these inter-system interactions is caused by the fact that the doubling is a second rather than first order spin-orbit effect. The structural form of the secular determinants inclusive of spin-orbit terms is exhibited for molecules arising from ${}^2P + {}^2P$, ${}^2P + {}^2P'$, and ${}^2P + {}^2S$.

1. INTRODUCTION

THE fluorescence of iodine vapor is considerably quenched by application of a magnetic field. This effect was first discovered by Steubing, and has been the subject of considerable subsequent experimentation.¹ The most recent experimental work is that of Turner.² He finds that the magnetic quenching is quite sensitive to the frequency of the exciting light. When the latter is

¹ W. Steubing, Verh. d. D. Phys. Ges. 15, 1181 (1913); Ann. der Physik 58, 55 (1919); 64, 673 (1921); R. W. Wood and G. Ribaud, Phil. Mag. 27, 1009 (1914); O. Oldenberg, Zeits. f. Physik 57, 186 (1929).

² L. A. Turner, Zeits. f. Physik 65, 464 (1930).

below $17,300\text{ cm}^{-1}$, the field is without effect, while the quenching is greatest (almost 50 percent at $12,500$ gauss) in the neighborhood of $18,500\text{ cm}^{-1}$, gradually diminishing at still greater exciting frequencies.

The theory of the effect has been suggested in bold outline by Turner.² He interprets the effect as predissociation, i.e. as dynamical interaction between stable and unstable molecular states. Such interaction causes a sort of communism in the properties of the states involved. The originally stable state partakes partially in the instability of the other state, and vice versa, because, of course, the perturbed wave functions are linear combinations of the two

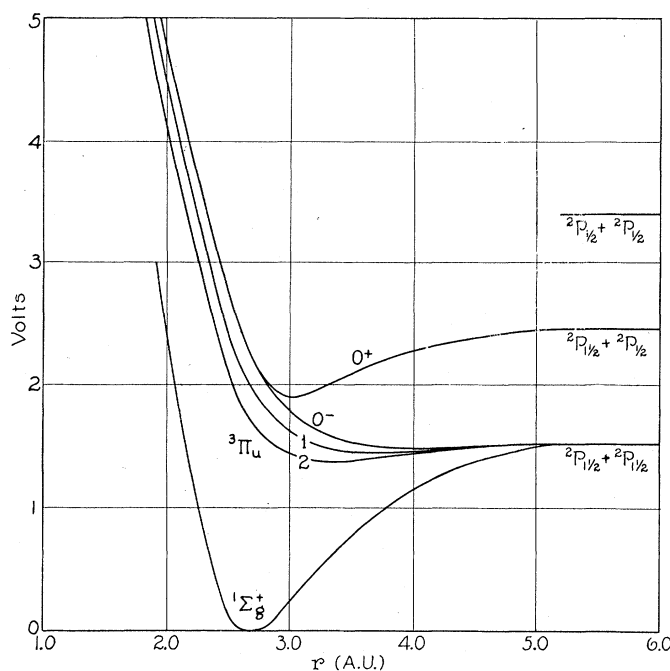


Fig. 1.

The curves marked 0^- and 0^+ in the figure are for the ${}^3\Pi_{0u}^-$ and ${}^3\Pi_{0u}^+$ states respectively. These states are often for brevity called the M and N states elsewhere in the article.

The figure shows only a very small portion of all the molecular states derived from ${}^2P+{}^2P$. We are particularly interested in the states having $\Omega=0$. There are ten states of this category; viz.

$$\begin{aligned} & {}^1\Sigma_g^+, {}^3\Pi_{0g}^+, {}^3\Sigma_g^-, {}^1\Sigma_g^+ \quad (\text{all type } 0_g^+); \quad {}^3\Pi_{0g}^- (\text{type } 0_g^-); \\ & {}^3\Pi_{0u}^-, {}^3\Sigma_u^+, {}^1\Sigma_u^-, {}^3\Sigma_u^+ \quad (\text{all type } 0_u^-); \quad {}^3\Pi_{0u}^+ (\text{type } 0_u^+). \end{aligned}$$

Of these, three are shown in Fig. 1. The derivation of these ten states must be apportioned in accordance with the following scheme:

$${}^2P_{3/2} + {}^2P_{3/2}: 0_g^+ \text{ (twice)} \quad 0_u^- \text{ (twice)}. \quad {}^2P_{3/2} + {}^2P_{1/2}: 0_g^+, 0_g^-, 0_u^+, 0_u^-. \quad {}^2P_{1/2} + {}^2P_{1/2}: 0_g^+, 0_u^-.$$

That this enumeration and apportionment of possible states is proper can be seen from the Wigner-Witmer correlation rules in the extended form given by Mulliken.⁴

unperturbed ones. There is hence a finite probability that an otherwise stable excited state will dissociate. If this probability is comparable with the proba-

bility of radiation the molecule may dissociate after optical excitation instead of reverting with radiation to the normal state. There will clearly then be a quenching of the fluorescence. For instance in Fig. 1, if the Hamiltonian function contains matrix elements connecting 0^+ and 0^- , a molecule excited to the 0^+ state may dissociate without radiation via the 0^- state instead of returning to the ${}^1\Sigma_0^+$ state.

If, following Turner, the magnetic quenching in iodine thus be ascribed to predissociation, the big theoretical problem is to show that in certain molecular configurations the predissociation is peculiarly important in magnetic fields, i.e., that such fields can introduce previously non-existent matrix components between a stable and unstable state in the Hamiltonian function. This Turner did not do, as his paper did not aim to include the necessary mathematical analysis and so incidentally could not identify correctly the character (i.e., spectroscopic nomenclature) of the unstable level which wrecks the stable one. In the present paper we shall show that the predissociation is due to the interaction between a ${}^3\Pi_0^+$ and an unstable ${}^3\Pi_0^-$ (or possibly a ${}^3\Sigma_0^+$) state, corresponding to the states labelled 0^+ , 0^- in Fig. 1, and that a magnetic field does indeed have the effect of creating an interaction between these states. In fact this is the only pair of states available in iodine for which a magnetic field can cause predissociation not otherwise present. All other pairs are either not appreciably intermixed by the magnetic field, or else intermingle and so permit predissociation even in the absence of the field (cf. p. 548). With a 0^+ , 0^- , pair we have what may be termed magnetic predissociation, to be contrasted with the usual Kronig³ predissociation due to rotational distortion, in which the molecular rotation is the agency for creating new matrix elements. The magnetic quenching phenomena thus nicely confirm Mulliken's previous assignment⁴ of a ${}^3\Pi_0^+$ configuration to the upper state of the visible iodine bands.

Rough Model. If one does not wish to wait for the more exact analysis in later sections, the following very sketchy two dimensional model may be used to illustrate roughly the *modus operandi* of the magnetic field in blending the two components of ${}^3\Pi_0$, which constitute a "Λ-type doublet". Consider two "dumb-bells" or dipoles rotating in the same plane and having a mutual potential energy $f\{\cos(\phi_1 - \phi_2)\}$. The wave equation is then of the form $d^2\psi/d\phi_1^2 + d^2\psi/d\phi_2^2 + a(W - f)\psi = 0$. If each dumb-bell has originally one quantum of angular momentum and the combined angular momentum is zero, the "zeroth approximation" wave functions for $|f| \ll W$ are $\psi^+ = \cos(\phi_1 - \phi_2)$ and $\psi^- = \sin(\phi_1 - \phi_2)$, since f will involve no matrix elements at all between states which are respectively even and odd in $\phi_2 - \phi_1$. Apply now perpendicular to the plane of rotation a magnetic field sufficiently powerful to

³ R. de L. Kronig, *Zeits. f. Physik* **50**, 347 (1928); **62**, 300 (1930).

⁴ R. S. Mulliken, *Phys. Rev.* **36**, 699, 1440 (1930); **37**, 1412 (1931). The subsequent theoretical work of R. Schlapp (*ibid.* **39**, 806, 1932) has confirmed Mulliken's conjecture that the upper state of the visible halogen bands could not be ${}^3\Sigma_{0,\pm 1}^+$ (a conceivable though unlikely alternative to ${}^3\Pi_0^+$) without contradicting observed intensities, especially the absence of a Q branch. The intensity relations would be proper, the same as for ${}^3\Pi_0^+$, if the upper state were ${}^3\Sigma_0^-$, but this configuration is not derivable from unexcited iodine atoms (cf. caption of Fig. 1).

produce Zeeman effects large compared to $W^+ - W^-$, which is of the same order as f . If one of the dumb-bells has an anomaly 2 in magnetic moment, the proper wave functions become $e^{i(\phi_1 - \phi_2)}$, $e^{-i(\phi_1 - \phi_2)}$, as exponentials rather than trigonometric functions diagonalize the operator $\partial \cdots / \partial \phi_1 + 2\partial \cdots / \partial \phi_2$ though at the expense of diagonalizing f . When the exponentials are utilized all traces of the original even and odd properties are lost, and hence the states are thoroughly intermingled, the desired result. In this model, the two dumb-bells represent symbolically spin and orbit respectively, and $\cos(\phi_1 - \phi_2)$, $\sin(\phi_1 - \phi_2)$ the ${}^3\Pi_0^+$, ${}^3\Pi_0^-$ states.

2. SYMMETRY CONSIDERATIONS

The existence or non-existence of matrix elements between different states involved in perturbations is conditioned largely by the following symmetry types⁵ and constants of the motion.

(A) A complete state inclusive of molecular rotation is called + or - by band spectroscopists according as its wave function is even or odd when the coordinates of *all* particles are reflected in the origin.

(B) In molecules of the type X_2 a state is called *g* or *u* according as there is evenness or oddness under reflections of the coordinates of all electrons in the origin, without a similar reflection for the nuclear coordinates. The origin must here be taken as the mid-point of the inter-nuclear axis.

(C) For molecules having $\Omega = 0$, there is the further classification 0^+ , 0^- (not to be confused with +, - in A) according as the wave function is even or odd as regards reflection of orbital and spin coordinates together in any plane containing the two nuclei. We follow approved⁵ spectroscopic nomenclature and so let Λ , Σ , Ω be quantum numbers determining respectively the orbital, spin, and orbital plus spin angular momentum about the figure axis. Molecules having $\Omega = 0$ we shall call 0 states. A 0 state is not necessarily a Σ state. For example, ${}^3\Pi_0$ states are 0 states, as they have $\Lambda^2 = \Sigma^2 = 1$ with $\Lambda + \Sigma = 0$. The ${}^3\Pi_0$, ${}^1\Sigma$, ${}^3\Sigma_0$ states of types 0^+ and 0^- are labelled respectively ${}^3\Pi_0^+$, ${}^1\Sigma^+$, ${}^3\Sigma_0^-$ and ${}^3\Pi_0^-$, ${}^1\Sigma^-$, ${}^3\Sigma_0^+$. The paradoxical notation ${}^3\Sigma_0^-$ for ${}^3\Sigma$ states of type 0^+ has arisen because the sign behavior is different exclusive and inclusive of spin. (See p. 559. The 0^+ , 0^- classification has a meaning only for the component of ${}^3\Sigma$ which has $\Omega = 0$ and which we denote by ${}^3\Sigma_0$ whereas the purely orbital symmetry properties envisaged in the approved notation apply to $|\Omega| = 1$ as well as $\Omega = 0$.)

(D) If the nuclei are regarded as fixed attracting centers the combined orbital plus spin angular momentum about the figure axis is a constant of the motion, *i.e.* Ω is rigorously what Mulliken calls a "good quantum number."

(E) In the absence of external fields the total angular momentum of the molecule is a constant of the motion, *i.e.* J is a good quantum number.

There is no interaction possible between states of different symmetry in (A) or in (B). This is true even in a magnetic field, as such a field does not

⁵ For further exposition of molecular symmetry types and the approved spectroscopic notation, which we use, see R. S. Mulliken Phys. Rev. **36**, 611 (1930); Rev. Modern Physics **2**, 60, 506 (1930); **3**, 90 (1931); **4**, 1 (1932).

destroy the invariance of the wave equation under the reflections (A) or (B). An electric field, however, destroys the invariance and may lead to interaction. These statements follow since $\Sigma e_i(x_i\partial/\partial y_i - y_i\partial/\partial x_i)$ is invariant under $x \rightarrow -x$, $y \rightarrow -y$, $z \rightarrow -z$, whereas $\Sigma e_i z_i$ is not. When molecular rotation is admitted, the premise (D) of fixed nuclei is not met, and interaction between states of different Ω (differing by unity in the first approximation) is possible, provided the states have the same J . This is the cause of the usual Kronig³ rotational predissociation.

Notation. To facilitate printing, we shall henceforth usually refer to the ${}^3\Pi_0^-$ and ${}^3\Pi_0^+$ levels as the M and N states respectively instead of using the Greek symbols. (Remember which is which by fact M stands for minus). It is to be further understood that if the molecule is of the symmetrical type X_2 , the M and N states here considered are odd with respect to symmetry (B), *i.e.*, are ${}^3\Pi_{0u}^-$, ${}^3\Pi_{0u}^+$.

Magnetic Field Applied to Stationary Molecule. The symmetry property (C) is not rigorously maintained under molecular rotation, and so can be used only in describing phenomena in which molecular rotation is not vital. The magnetic quenching in iodine is essentially a phenomenon of this category. The important thing to note is that a magnetic field destroys the property (C) even in a stationary molecule, since $x\partial \cdots / \partial y - y\partial \cdots / \partial x$ is not invariant under $x \rightarrow -x$, $y \rightarrow y$, $z \rightarrow z$. This situation alone is not enough to insure a new interaction due to the magnetic field. For instance, a magnetic field does not blend ${}^1\Sigma^-$, ${}^1\Sigma^+$ pairs, as such states have no Zeeman terms. The states ${}^3\Sigma^-$, ${}^3\Sigma^+$ have Zeeman terms, but not with inter-connecting elements. On the other hand Zeeman amplitudes really do exist connecting levels of the form ${}^3\Pi_0^-$, ${}^3\Pi_0^+$. This will be shown in section 5, and is also fairly obvious from the rough model at the end of section 1.

There is, however, one alternative to the above attribution of the quenching to the pair M , N which cannot be overlooked entirely, although it is somewhat unlikely. This alternative is that the new interaction due to the magnetic field be between N and a ${}^3\Sigma_0^+$ state⁶. We here use case a notation for the ${}^3\Sigma$ state (*i.e.*, subscript gives Ω), which is allowable in iodine since the multiplet structure of ${}^3\Sigma$ levels is of the same order as the Λ -doubling in ${}^3\Pi_0$ states, and hence large compared to the rotational structure in very heavy atoms. Rotational distortion does not cause interaction between the pair N , ${}^3\Sigma_0$, but does lead to interaction of N with ${}^3\Sigma_1$ (more precisely, after the molecular rotation is added, with the component of ${}^3\Sigma$ which has $|\Omega| = 1$ and is $+$ with respect to symmetry A when J is even). Usually the various components of a ${}^3\Sigma$ level are regarded as constituting virtually a single state, and if this is done, this alternative explanation of the magnetic quenching will not work, for then the predissociation due to rotational distortion via ${}^3\Sigma_1$ will completely overshadow that due to the magnetic predissociation via ${}^3\Sigma_0$. Indeed, if we neglect the difference in the shape of the potential curves for ${}^3\Sigma_1$ and ${}^3\Sigma_0$, the former predissociation is of the order $q = 4B^2J^2/\zeta^2\beta^2$ times the latter, where $B = \hbar^2/8\pi^2I$, $\beta = \hbar e/4\pi mc$. With the abnormally large moment of inertia in iodine, q is of the order $J^2/100$ in a field of 10,000 gauss, but it is found experimentally⁷ that the rotational quantum number J can be over 100 without any sign of impairing the magnetic quenching. It is just possible that in iodine the curves for ${}^3\Sigma_0$ and ${}^3\Sigma_1$ are so widely separated that the Franck-Con-

⁶ The magnetic field could also cause interaction between M and ${}^3\Sigma_0^-$, and so cause an otherwise stable ${}^3\Sigma_0^-$ state to decay, but a state of this character is not found in iodine (see end of note 4).

⁷ L. A. Turner, *Zeits. f. Physik*, **65**, 480 (1930).

don effects (crossing at a suitable r) happen to be unduly preferential to ${}^3\Sigma_0$ as compared to ${}^3\Sigma_1$, thus greatly handicapping the rotational predissociation. The whole alternative considered in this paragraph seems particularly unlikely in that the M , N curves are naturally fairly close for a large range of values of r , whereas ${}^3\Sigma_0^+$, N would be near only accidentally, and then presumably only for a particular value of r . In favor of the alternative, on the other hand, must be balanced the fact that the ${}^3\Sigma_0^+$ and N levels undoubtedly do cross, whereas we shall see that M and N can be made to cross only with rather artificial hypotheses. The crossing of ${}^3\Sigma_0^+$ and N is a consequence of the Mulliken-Hund configuration theory, which indicates that ${}^3\Sigma_0^+$ is higher than N at small r , but lower at $r = \infty$ as it is derived from ${}^2P_{3/2} + {}^2P_{3/2}$ on account of being the second lowest 0_u^- level. It appears impossible at present to determine the value of r at which this crossing takes place; if it is greater than about 5 A.U. it is clearly too large to cause appreciable predissociation (cf. Fig. 1).

It is to be noticed that in any case the magnetic quenching must be attributed to interaction between a pair of states of the form 0^- , 0^+ . In quintet spectra, for instance, ${}^5\Delta_0^+$, ${}^5\Delta_0^-$ would be a possible pair. Whether in the particular case of iodine the members of the pair are both ${}^3\Pi_0$ or one each ${}^3\Sigma_0$, ${}^3\Pi_0$ is in a certain sense a rather meaningless question, for in molecules as heavy as iodine, Λ ceases to be a good quantum number, and there is no sharp dividing line between the ${}^3\Pi_0$ and ${}^3\Sigma_0$ states.

Magnetic Field applied to Rotating Molecule. With molecular rotation, symmetry (C) is lost, and the behavior is as shown in Fig. 2, since 0^+ states are

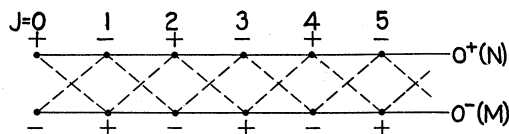


Fig. 2.

$+$ or $-$ as regards symmetry (A) according as J is even or odd, while the reverse is true of 0^- . The matrix elements proportional to the magnetic field \mathcal{H} in the Hamiltonian function are exclusively of the form $\Delta J = \pm 1$ since $\Delta J = 0$ disappears on account of $\Omega' = \Omega'' = 0$ (cf. also p. 562). These elements are shown by dotted lines in Fig. 2. Hence the field is able to blend the ${}^3\Pi^+$ and ${}^3\Pi^-$ (or ${}^3\Sigma_0^+$) states. On the other hand it is very vital that rotational distortion cannot blend this pair, for the rotational perturbative elements are by (A) and (E) exclusively of the form $+\rightarrow+$ or $-\rightarrow-$, with $\Delta J = 0$ and hence cannot appear in Fig. 2. The important thing is thus that the magnetic field breaks down the "J rule" (E), whereas the rotational effects do not.

Absence of Primary Effect in Homogeneous Electric Fields. The unique role of the magnetic field is evidenced not only by this absence of the ordinary Kronig rotational predissociation, but also by the fact that a homogeneous electric field cannot cause the predissociation in question unless exceedingly powerful. This feature seems rather necessary, for otherwise the inevitable stray electric fields might give considerable predissociation even in the absence of the magnetic field. To see that a uniform electric field cannot introduce direct interaction between the ${}^3\Pi_0$ components, in a homopolar molecule such as I_2 , we need only note that such molecules have no permanent electric moment, and so the potential due to an electric field can only introduce matrix

elements connecting two different orbital electronic configurations, whereas the two components of ${}^3\Pi_0$ belong to the same configuration. Uniform electric fields are likewise ineffective even in heteropolar molecules such as ICl. To prove this, we note that here the permanent electric moment is parallel to the figure axis and so has exclusively elements of the form $\Delta J = \pm 1$; further the potential $\sum e_i z_i$ is odd as regards reflection (A) and so there can only be elements connecting states of unlike $+$ $-$ symmetry (A). Thus the matrix elements of the permanent electric moment are represented by the solid rather than dotted lines in Fig. 2 and so do not connect the two doublet components. There can, however, be electric predissociation when we consider the secondary rather than primary effects of the field E , which means the part of the predissociation proportional to E^4 rather than E^2 . The reason is that the second approximation in any perturbation calculation introduces as new matrix elements the products of the matrix elements calculated in the unperturbed system. A product such as $a(n_+J; n'_-J \pm 1)b(n'_-J \pm 1; n_+J \pm 1)$, for instance, can then give a predissociating effect, as a , b can be elements connecting two different electron configuration n , n' , and so can be of the form $\Delta J = 0$ ($\Omega' \neq 0$) as well as $\Delta J = \pm 1$ and furthermore need not vanish in homopolar molecules. Moreover, if the electric field is not uniform the electric potential is not linear in the coordinates and so all the preceding considerations fail. Hence there can be a predissociating effect by sufficiently inhomogeneous fields even in the first approximation.

It is quite satisfactory that the predissociating effect of electric fields, especially the inhomogeneous ones, does not disappear completely. Indeed, Turner⁸ finds that the iodine fluorescence is greatly diminished by admixture of argon as a foreign gas. The first excited state of the argon atom is so high that there can be no possibility of energy transfers in which argon atoms are excited, and the results can only mean that the intense and highly inhomogeneous electric fields from the argon atoms at the time of collision introduce new matrix elements which permit predissociation. Essentially this point has been emphasized by Turner.⁸ He finds further that the critical primary frequency region in which the fluorescence is quenched is approximately the same in quenching by argon as in quenching by a magnetic field,⁹ showing that the pair of states involved in the predissociation is presumably the same in both cases.¹⁰

⁸ L. A. Turner, Phys. Rev. **38**, 574 (1931); cf. also J. Kaplan, *ibid.* **38**, 1079, 1792 (1931), F. W. Loomis and H. G. Fuller, *ibid.* **39**, 180 (1932) (abstract).

⁹ M. Eliaševich, however, apparently finds less sensitivity to the frequency of the primary source than does Turner. See Phys. Rev. **39**, 532 (1932).

¹⁰ It is not the purpose of the present paper to discuss the general subject of predissociation due to electric fields, but we may note that the important new interactions introduced by such fields are probably usually either blending of u and g states in symmetrical molecules or of 0^- and 0^+ states in symmetrical or unsymmetrical ones. Interaction between most other pairs of states can arise from rotational distortion without the necessity of external fields. It is often mentioned that external fields intermingle states of unlike J , but this effect is important only insofar as it blends electronic states not otherwise interacting (cf. dotted lines in Fig. 2). Unless we care to differentiate between different predissociation rates for different rotational members, the disturbances must be expressible in terms of a breaking down of the classifications (B), (C), (D) without invoking (A) or (E).

3. FURTHER DISCUSSION OF MAGNETIC PREDISSOCIATION

Dependence on Field Strength. The rate of predissociation is proportional to the square of the interaction matrix elements (cf. section 5). Since these are linear in the field strength \mathfrak{S} , the probability that a molecule in the N state dissociates via the M state is $b\mathfrak{S}^2$, where b is a constant, while we shall let a denote the probability factor for a radiation transition from N to the normal state. The fractional amount Q by which the resonance radiation is quenched is thus

$$Q = b\mathfrak{S}^2/(a + b\mathfrak{S}^2) \quad (1)$$

since this is merely the ratio of the number of predissociating molecules to the total number leaving the N state either by radiation or predissociation. The form of dependence predicted by (1) should be capable of experimental verification without undue difficulty.

Shape of M and N Potential Curves. Unfortunately it is impossible at present to predict except in a qualitative way how the amount of quenching should depend on the frequency of the incident light. Accurate predictions would require, for one thing, exact knowledge of the form of the potential energy curves for the M and N states. Actually the M state, which theory tells us must be not far from N , is not observed spectroscopically at all. However, this is not surprising, since a radiation transition from M to the normal state would be of the form $0^- \rightarrow 0^+$ and so is forbidden regardless of the magnitude of the spin-orbit forces.¹¹ A state discovered by Brown¹² which he thought might conceivably be M is undoubtedly ${}^3\Pi_1$. The constants of the N level are known quite well,¹³ and this level is found to arise from the union of atoms in ${}^2P_{3/2}$ and ${}^2P_{1/2}$ states, in accordance with theory, whereas the M level very probably arises from two atoms both in ${}^2P_{3/2}$ (cf. Fig. 1). The doublet width for the 2P configuration of the iodine atom is .94 volts, with ${}^2P_{3/2}$ deepest, and this width is doubtless sufficient to make N stable and M unstable at ordinary values of the inter-nuclear distance r (cf. Fig. 1). Although the separation of the M , N curves is .94 volts for $r = \infty$, it is doubtless much smaller when r is near the usual values. In fact, appreciable predissociation is possible only if the potential curves come close together. The general theory of Λ -doubling in ${}^3\Pi_0$ states (§4) shows that the separation in question should be not more than of the order $a^2/h\nu(\Pi, \Sigma)$ provided the molecular binding is large compared to the usual constant a of the atomic spin doublet. In iodine the constant a has the value 5067 cm^{-1} and so this upper limit is roughly of the order 10^3 cm^{-1} if we assume that the $\Pi - \Sigma$ separations are about 2.5×10^4

¹¹ See R. Schlapp Phys. Rev. **39**, 806 (1932). The transition $0^- - 0^+$ is no longer rigorously forbidden if the correction for rotational distortion is important, as then the classification (C) of section 2 is lost, and a Q (but not P or R) branch can appear. This correction is, however, insignificant for molecules as heavy as iodine.

¹² W. G. Brown, Phys. Rev. **38**, 1187 (1931) (I_2); *ibid.* **38**, 1179 (Br_2). Brown originally rejected the ${}^3\Pi_1$ assignment to his new level in I_2 and Br_2 because it would yield a tremendous disparity in intensity between ${}^1\Sigma - {}^3\Pi_0$ and ${}^1\Sigma - {}^3\Pi_1$. As we outline above, this disparity is, however, to be expected for inter-system combinations, and Brown himself has recently proposed the ${}^3\Pi_1$ classification (see paper by Brown and Gibson in this issue).

¹³ F. W. Loomis, Phys. Rev. **29**, 112 (1927); also W. G. Brown, *ibid.*, **38**, 709 (1931).

cm^{-1} . In Fig. 1, reproduced from one of Prof. Mulliken's papers, the M , N curves are represented as practically coincident when the inter-nuclear distance is sufficiently small. This may not be correct, as they pass over into two components of a spin multiplet when one collapses the molecule into the "united atom." However, it has not seemed advisable to redraw the curves to show the finite separation of the M , N curves at small distances, as the precise amount of the separation is so uncertain. It is quite possible, and rather necessary for our predissociation theory, that in the vicinity of some critical value of r the separation be much smaller than the above upper estimate 10^3 cm^{-1} .

Do the M and N Curves Cross? In the usual forms of predissociation one deals with levels whose potential energy curves cross. It is possible that the M and N states in iodine actually do cross. These states have different symmetries, and so this is not precluded by the "non-crossing" rule for the roots of an irreducible secular determinant. If more were known about the location of all the energy levels, both stable and unstable, of the iodine molecule, it might be possible to decide theoretically whether or not the two levels do cross. Some of the mathematical analysis connected with this point, *i.e.* the sign of the Λ -doublet, will be given in sections 4 and 6, and leads to the general conclusions stated in the next paragraph.

The two doublet components coincide when we neglect the spin-orbit interaction. The M component is unaffected by $^1\Sigma_u^+$, $^3\Sigma_u^-$, or by g levels, is depressed by higher $^1\Sigma_u^-$ or $^3\Sigma_u^+$, and elevated by lower $^1\Sigma_u^-$ or $^3\Sigma_u^+$ levels. Similar remarks apply to N if the plus and minus signs are everywhere interchanged. Even without appealing to the mathematical analysis to be given in sections 4 and 6, these statements are fairly obvious consequences of the fact that spin-orbit action exists only between states of the same Ω and (if $\Omega=0$) of like symmetry (C), section 2, and that interaction between two levels has the effect of separating them further. In this connection one must remember that $^3\Sigma_0^-$, $^3\Sigma_0^+$ are really 0^+ , 0^- states.

When one applies the foregoing rules to iodine, one is tempted to first assume that the important spin-orbit interactions are those between states which are derived from the normal atomic configurations $^2P+^2P$ inclusive of the various multiplet components. The N level is the only 0_u^+ state so derived and is hence undisplaced by such interactions. On the other hand there are three 0_u^- states so derived in addition to the M state *viz.* one $^1\Sigma_u^-$ and two $^3\Sigma_u^+$ states. If M is to cross above N when r becomes sufficiently small it is necessary that one of these three states lie below M in energy and that its interaction with M elevate M more than M is depressed by interaction with the other two of the three states, presumably because of closer proximity. These other two must be above M in energy because only two of the four 0_u^- states are derived from $^2P_{3/2}+^2P_{3/2}$, and because M is so derived by our interpretation of predissociation. The other two 0_u^- states are derived from $^2P_{1/2}+^2P_{3/2}$, $^2P_{1/2}+^2P_{1/2}$ (one each) and so must be above M by the non-crossing rule.

Existing data do not seem adequate to decide whether there really is a

0_u^- state below M . If there were such a state, it might easily escape detection, as it could not combine spectroscopically with the normal state or with the N level since $0^- - 0^+$ and $u - u$ transitions are both forbidden.¹⁴ However, the study of electron configurations in the way developed by Mulliken and Hund,¹⁵ makes it exceedingly doubtful if there is any 0^- state more firmly bound than ${}^3\Pi_0^-$.

In case M is the lowest 0^- state, one can still obtain the desired crossing if one assumes that the N level is strongly depressed by spin-orbit interaction with ${}^1\Sigma_u^+$ or ${}^3\Sigma_u^-$ levels derived from excited iodine atoms, *i.e.* from a pair of iodine atoms of more energy than ${}^2P + {}^2P$. The word strongly is inserted because N would need to be more displaced by this interaction than M is by interaction with levels derived both from ${}^2P + {}^2P$ and from excited atoms. For this reason, such an attempt to obtain crossing would appear rather forced were it not for one fact; *viz.* that the bands ${}^1\Sigma_g^+ - N$ involved in the fluorescence are inter-system combinations. Such combinations exist only in virtue of the failure of S to be a good quantum number, so that singlet and triplet states begin to share properties. Furthermore it seems altogether probable that in iodine the inter-system radiation is due to the incipient singlet characteristics of N rather than incipient triplet properties of the normal level.¹⁶

¹⁴ If the 0^- state is ${}^3\Sigma_0^+$ it must, however, be remembered that one of the other components ${}^3\Sigma_1^+$ of the same multiplet can combine with ${}^1\Sigma^+$.

¹⁵ See the most illuminating figure given by Mulliken on p. 40 of *Rev. Modern Physics*, vol. 4. In the instance of F_2 , the ten $2p$ electrons of the separated atoms undoubtedly pass over into his molecular configuration $x\sigma^2w\pi^4v\pi^4$ in the case of the ${}^1\Sigma_g$ state, and $x\sigma^2w\pi^4v\pi^3u\sigma$ in that of ${}^3\Pi_u$ (or ${}^1\Pi_u$). Reference to this figure shows that the Σ_u configurations would have to be of the form $x\sigma^2w\pi^3v\pi^3u\sigma^2$ or $x\sigma w\pi^4v\pi^4u\sigma$ both of which represent higher energies than ${}^3\Pi_u$ as they yield "more promoted" configurations of the united atom. Similarly one finds that all the Σ_g configurations except the normal state have higher energies than ${}^3\Pi_g$. Another figure (no. 44) of Mulliken's article can be used in the case of unsymmetrical molecules like ICl, and here also the indications are that ${}^1\Sigma^+$ is the lowest 0^+ state, with ${}^3\Pi_0^+$ next above, whereas ${}^3\Pi_0^-$ is the lowest 0^- state. Hence in the secular determinants of section 6, one is presumably justified in supposing that the lowest 0^+ level is derived from ${}^2P\sigma + {}^2P\sigma$, with ${}^3\Pi_0^+$ from ${}^2P\sigma + {}^2P\pi$ next above, while the lowest 0^- is ${}^3\Pi_0^-$ derived from ${}^2P\sigma + {}^2P\pi$, provided the spin-orbit corrections be neglected. Here the notation ${}^2P\sigma$ means that the isolated atom has $L=1$, $\Lambda = \Sigma\lambda=0$. It is, of course, possible for a ${}^1\Sigma^+$ configuration to arise from ${}^2P\pi + {}^2P\pi$, but it would be one of higher energy than that from ${}^2P\sigma + {}^2P\sigma$, as it would entail the electron assignment $x\sigma^2w\pi^4v\pi^2u\sigma^2$ or some still higher configuration. This is on the assumption that the atomic state is of the form p^5 , so that ${}^2P\pi$ and ${}^2P\sigma$ furnish respectively three and four π electrons. However, the result that ${}^2P\sigma + {}^2P\sigma$ is below ${}^2P\pi + {}^2P\pi$ also holds for $p+p$ as well as p^5+p^5 , for the assignment $x\sigma^2$ is lower than $w\pi^2$. Mulliken's figures are explicitly for $2p$ orbits, whereas in iodine they are $5p$, but the results on the relative positions of states are the same in both cases, as the underlying qualitative arguments are the same.

¹⁶ This does not necessarily mean that the normal state interacts less strongly with triplet states than does N with singlet levels. The reverse could even be true without contradicting Brown's results if the incipient triplet characteristics of the normal state are acquired from a triplet level which does not combine intensely with N as regards radiation transitions, and if at the same time the incipient singlet properties of N are acquired from a singlet level which radiates very intensely to the normal state. In this connection it is well to remember that in the limiting case of nearly isolated atoms, which may be a fairly good approximation in iodine, radiation is forbidden between molecular levels derived from the same dissociation products, as the Laporte rule for isolated atoms is then a good approximation, and this prohibits transi-

Particularly strong evidence to this effect is furnished by the work of Brown. He finds¹⁷ that in I_2 the transition ${}^1\Sigma_g^+ - {}^3\Sigma_{1u}$ is very much less intense than ${}^1\Sigma_g^+ - N$, the difference being greater than can be ascribed to diversity in Franck-Condon relations. If the inter-system radiation were due to incipient triplet characteristics of the normal state, one would expect these two transitions to be of the same order of magnitude in intensity, whereas they could differ greatly if this radiation is due to incipient singlet properties of ${}^3\Pi_{1u}$ and N . Namely, since spin-orbit coupling is diagonal in Ω , the singlet tendency of ${}^3\Pi_{1u}$ comes from robbing a ${}^1\Pi_u$ level, while that of N comes at the expense of ${}^1\Sigma_u^+$, and so may be entirely different from that of the former in order of magnitude, especially if ${}^1\Pi_u$ and ${}^1\Sigma_u^+$ have widely different energies or moments of inertia. If the so-called D state of the iodine molecule¹⁸ (too high to show in Fig. 1) is of the form ${}^1\Sigma_u^+$, it would have just the desired depressing effect on N , although this interaction might prove too faint on account of the wide energy separation of N and D . At any rate the great intensity of the visible iodine bands shows that there is surely some higher singlet level which strongly perturbs N . Possibly this perturbing level is unstable and so does not show up at all in the ordinary spectral analysis.

It is conceivable that the magnetic predissociation via M might be sufficiently intense even if the M , N curves do not cross but instead are very close to each other and sensibly parallel for a considerable interval of r values. It is hard to determine quantitatively how close the curves would need to be but doubtless the separation would have to be much less than the upper limit 10^3 cm^{-1} previously estimated. The Franck-Condon principle of course precludes an appreciable predissociating interaction between states whose potential energy curves are not very close to each other. It is this fact that, for instance, explains why the N state does not predissociate due to rotational distortion without a magnetic field. There are two 1_u states (*i.e.* states having $\Omega=1$ and odd with respect to symmetry B) derived from ${}^2P_{3/2} + {}^2P_{3/2}$. One of these levels, *viz.* ${}^3\Pi_1$ has already been mentioned and falls so far below N that it is unstable when its vibrational energy is sufficient to equalize its

tions within the same atomic configuration. Thus the visible halogen bands might very easily owe their intensity to spin-orbit perturbations from levels derived from excited electronic levels of iodine, too high to show in Fig. 1. In particular the D level would be apt to be an important perturber as regards the radiative but necessarily energetic properties of N , since D dissociates into one normal iodine atom and one excited atom in the upper state of the intense atomic iodine resonance line.

¹⁷ W. G. Brown, *l.c.*¹² He further informs the writer that the disparity in intensity in favor of N is less pronounced in $I\text{Br}$ and BrCl than in Br_2 and I_2 , while in ICl ${}^1\Sigma - {}^3\Pi_1$ is more intense than ${}^1\Sigma - N$. Such variations from molecule to molecule are not disquieting, as diversity in the location of states and in the multiplet constant may make the spin-orbit perturbations widely different. Also the Franck-Condon effects may vary.

¹⁸ Cf. Weizel, p. 381 of "Bandenspektren" vol. of Wien-Harms Handbuch. Weizel's energy level diagram also shows the so-called B state less than one volt above the normal level. This state was proposed by Pringsheim and Rosen (*Zeits. f. Physik*, **50**, 1, 1928) but its existence has been seriously questioned by Sponer and Watson (*ibid.* **56**, 184 (1929)). Even if there really is a B state, it is of no particular interest for us, as it is a g level, and so cannot perturb the M or N levels. On the other hand the D state is known to be of the u type.

total energy with that of the lowest vibrational member of N . Hence the N state could predissociate rotationally via ${}^3\Pi_1$ except in so far as the intensity of the effect is reduced by the separation of the potential energy curves. In general, reduction from this cause must be very important as otherwise molecules would have excessively few stable excited states.

Variation of the Magnetic Quenching With Frequency of Incident Beam. This variation can easily be understood in a qualitative way. The sharp cut-off on the low frequency side is clearly due to the fact that unless the molecule is excited to an N state with a considerable amount of vibration, it will not oscillate with sufficient amplitude to traverse the portion of the N curve near the M one (cf. Fig. 1). Turner finds that the cut-off on the high frequency side is not nearly as sharp as that on the low . (His experiments on the high side are not very comprehensive and merely show that the quenching is somewhat diminished if the frequency is raised above about 19,000 cm). This blunter cut-off on the high side is readily comprehensible if the M and N states really do cross, for, as r is diminished, they probably do not separate as rapidly after crossing as they come together before crossing. This follows from the fact that for fairly small r the separation is not more than of the order 10^3 cm⁻¹ previously estimated, whereas for $r = \infty$ the separation is the doublet interval 7.6×10^3 cm⁻¹ of the iodine atom. If the predissociation is due to close proximity rather than crossing of the curves, one at first thought might not expect the quenching to be diminished at all on the high frequency side. However, as pointed out to me by Prof. Mulliken, too much vibration might augment the time the molecule spends on the right side of the N potential curve at the expense of the left side where the predissociation effects are important. This situation is conceivable, as the left side of the curve is much steeper than the right (cf. Fig. 1).

Possibility of Magnetic Predissociation in Other Molecules. As far as I am aware this type of predissociation has not been reported or probed in other molecules than iodine.¹⁹ Clearly it should be expected whenever one of the M , N states is stable and the other unstable, provided these states cross or are very close for certain values of r . In general, the effect is less probable for lighter atoms than for I₂, as the spin-orbit interaction may easily become too feeble to be the deciding factor between stability and instability. Examination of the potential curves²⁰ for Br₂ and Cl₂ shows that only the higher vibrational members of N in Br₂, and the almost dissociated members in Cl₂, have greater energy than ${}^2P_{3/2} + {}^2P_{3/2}$, and so overlap the continuous rather

¹⁹ It is found that the band fluorescence of mercury excited by a mercury lamp is altered by application of a magnetic field (Franck and Grottrian, *Zeits. f. Physik*, **6**, 35 (1921); H. Niewodniczanski, *ibid.* **55**, 676 (1929); also unpublished thesis of F. Studer at Wisconsin). This, however, is probably a different effect than the one which we are considering. The usual interpretation of the behavior of mercury is that the Zeeman effect on the hyperfine components of 2537 affects the ability of mercury to absorb its own radiation by displacing slightly the absorption frequencies in the field relative to the emission frequencies of the lamp not situated in the field. The bands are interpreted as radiations of molecules formed by union of an unexcited mercury atom with an optically excited 3P atom.

²⁰ Cf., for instance, R. S. Mulliken, *Rev. Mod. Phys.* **4**, 17 (1932).

than discrete levels of M . Only such members should exhibit the magnetic predissociation, but no experimental data are available.

Likewise no magnetic data are available for molecules such as ICl, IBr, etc. formed from two different 2P atoms. Here the theoretical situation is particularly interesting, as one no longer has the $u-g$ distinction (B of section 2) and so symmetry considerations no longer preclude N being derived from the lowest dissociation product ${}^2P_{3/2} + {}^2P_{3/2}$. In fact it is quite probable that for ordinary values of r the N state is really one of the two lowest 0^+ states and so is derived formally from ${}^2P_{3/2} + {}^2P_{3/2}$, for the latter combination yields two 0^+ states now no longer specialized to 0_g^+ . Nevertheless according to measurements of Brown and Gibson²¹ given elsewhere in this issue, vibrational extrapolation for the N level in ICl yields a heat of dissociation corresponding to ${}^2P_{1/2}(\text{Cl}) + {}^2P_{3/2}(\text{I})$. As noted by Brown and Gibson, this paradox can be explained by supposing that the potential curve has the shape shown in our Fig. 3 or their Fig. 4. If I is the ordinary vibrational region, then

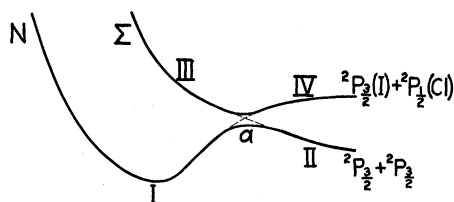


Fig. 3.

clearly the usual extrapolation will follow I+IV rather than I+II. It is not unreasonable that there should be a peak in the curve as shown in Fig. 3. Let us suppose that the secular determinant factors if certain matrix elements are neglected. If then N and Σ belong to different factors, their potential curves can cross, and be approximately of the form I-IV and II-III. If now these matrix elements are reintroduced there will no longer be any factoring, and the "non-crossing rule" will apply, making the curves of the shape I-II and III-IV. As emphasized by Hund,²² the correlation I-II and III-IV is a purely formal matter as long as the separation at a in Fig. 3 is small, for then the characteristic features of I are really continued more along IV than II. Essentially this principle is utilized in Brown and Gibson's article, but it does remain to verify, explicitly, and this is our only new contribution, that the secular determinant really does factor under reasonable simplifying assumptions. Mathematical analysis relating to this point will be given in section 6, where the secular determinant will be set up explicitly. It will there be shown that the N and Σ curves for molecules derived from ${}^2P + {}^2P'$ really do cross if we neglect certain matrix elements which would vanish were the atomic Λ 's

²¹ The writer is indebted to Dr. Brown for communication of results in advance of publication in this issue of the Physical Review. The N state in our notation is the same as the C level in Weizel's. Its dissociation products are often erroneously given in the literature (e.g. Weizel, l.c.¹⁸) as ${}^2P_{3/2}(\text{Cl}) + {}^2P_{1/2}(\text{I})$ rather than ${}^2P_{3/2}(\text{I}) + {}^2P_{1/2}(\text{Cl})$.

²² F. Hund, *Zeits. f. Physik*, **52**, 601 (1929).

rigorously good quantum numbers. It may be mentioned that when the crossing is destroyed by including all elements, molecules vibrating in the region I are unstable, in principle, because of the possibility of leakage through the peak out to the region II, giving a predissociation similar in mechanism to the well-known quantum theory of radioactive disintegration. However, both theoretically and experimentally the predissociation due to this cause is small. The experimental evidence is that Brown and Gibson find the levels of the M state do not "fuzz" unless their energy is greater than the peak a in our Fig. 3 (cf. especially their Fig. 4). The importance of all this for us is that there is thus the possibility of a magnetic predissociation effect in ICl if the M curve (not shown in Fig. 3) crosses or nearly coincides with the N one somewhere in the region I. Without the anomalous peak there could be no magnetic predissociation, as both M and N have the same formal dissociation product ${}^2P_{3/2} + {}^2P_{3/2}$ and hence the same degree of stability except for the anomaly.²³

The preceding discussion has all been for molecules derived from the atomic configuration $p^5 {}^2P + p^5 {}^2P$. For molecules derived from $p^2 P_{1/2} + p^2 P_{1/2}$ the situation is somewhat different as the atomic multiplets are regular and the lowest dissociation product is ${}^2P_{1/2} + {}^2P_{1/2}$. Now with symmetrical molecules ${}^2P_{1/2} + {}^2P_{1/2}$ and ${}^2P_{1/2} + {}^2P_{3/2}$ each yield one 0_u^- term, and ${}^2P_{3/2} + {}^2P_{3/2}$ yields two, while ${}^2P_{1/2} + {}^2P_{3/2}$ gives the sole 0_u^+ . Hence the M and N states will dissociate into different atomic multiplet components (a necessary but not sufficient condition for magnetic predissociation) provided M is not the second lowest 0_u^- state. Configuration theory shows that M is very probably usually the lowest rather than second lowest, such level.²⁴ In molecules derived from ${}^2S + {}^2P$ (HI etc.) the M and N terms will dissociate into different multiplet components provided the order of energy levels is ${}^1\Sigma^+ < {}^3\Pi < {}^3\Sigma^+$ or ${}^3\Sigma^+ < {}^3\Pi < {}^1\Sigma^+$. This follows since ${}^2S + {}^2P_{1/2}$, ${}^2S + {}^2P_{3/2}$ each yield one 0^+ and one 0^- level.

It seems impossible to say at present whether or not the iodine molecule is a fortuitous case involving closer proximity of the M and N components than usual for heavy molecules. If it is, the magnetic predissociation may not be observable in other molecules mentioned above which permit the effect in principle.

²³ Dr. Brown informs the writer that the same predissociation phenomenon is found in IBr and BrCl as in ICl and that the mode of dissociation of N and ${}^3\Pi_1$ is similar in all three molecules. He will publish details in the near future.

²⁴ See Fig. 43 of Mulliken's article.¹⁵ According to the calculations of Bartlett on $2p+2p$, the ${}^3\Sigma_u^+$ level is the lowest and M the next lowest 0_u^- state (Phys. Rev. **37**, 507; 1931; note corrections given in Phys. Rev. **38**, 211, footnote 11 and p. 225). The reason for this disparity is probably that for the actual equilibrium values of r in stable molecules Bartlett's method of approximation based on the Heitler-London method and hydrogenic $2p$ wave functions may be insufficient, while for large values of r the curve for $u\sigma$ should be drawn somewhat lower than in Mulliken's Fig. 43. Then M would still be the lowest u state at the usual values of r (about $\xi = .75$ to 1.5 in Fig. 43) in stable molecules.

4. THEORY OF Λ -DOUBLING IN ${}^3\Pi_0$ STATES

In a previous paper²⁵ the writer considered Λ -doublets in ${}^3\Pi_0$ states. These doublets are due to spin-orbit interaction in heavy atoms and hence different in origin from the usual Λ -doublets due to rotation distortion in states having $\Omega \neq 0$. We shall now extend the theory by examining the sign of the doublet separation and specially shall show that the expression for the magnitude of the separation given in the earlier paper was incomplete because it omitted the interaction of ${}^3\Pi$ with ${}^1\Sigma$, ${}^5\Sigma$ states, keeping only that with ${}^3\Sigma$ states. We shall defer until section 5 inclusion of an external magnetic field.

It will be sufficient to consider as usual the spin-orbit interaction to arise entirely from the coupling of each spin to its own orbit, yielding the well-known energy expression

$$H = \sum a_i \mathbf{l}_i \cdot \mathbf{s}_i \quad \left(a_i = \frac{e}{2m^2c^2} \frac{1}{r} \frac{dV}{dr} \right). \quad (2)$$

Our previous omission consisted in following the customary procedure of replacing (2) by $\mathbf{AL} \cdot \mathbf{S}$, which is tantamount to retaining only matrix elements connecting states of like S and L . This, however, is not allowable for our purposes, as the Λ -doubling is a second rather than first order effect in the spin-orbit couplings, so that other elements are comparable in final importance with the usual ones.

Let us start with an initial system of representation (not at all the correct final one) in which one of the two ${}^3\Pi_0$ states, say a , has $\Lambda = +1$, $\Sigma = -1$, the other, b has $\Lambda = -1$, $\Sigma = +1$. This we shall call the a, b representation. The transformation matrix for the perturbation problem associated with (2) is to a first approximation $S = 1 + S_1$ where

$$S_1(\alpha\alpha') = - \frac{H(\alpha\alpha')}{h\nu(\alpha\alpha')} \quad (3)$$

with $\alpha = a$ or b and $\alpha' = {}^1\Sigma$, ${}^3\Sigma_0$, ${}^5\Sigma_0$, ${}^3\Pi_0'$ ($\neq {}^3\Pi_0$), ${}^5\Pi_0$, or ${}^5\Delta_0$ inasmuch as the matrix elements of (2) are easily seen to be entirely of the form $\Delta\Omega = 0$, $\Delta S = 0, \pm 1$, $\Delta\Lambda = 0, \pm 1$, $\Delta\Sigma = 0, \pm 1$. The Hermitean property makes $H(\alpha'\alpha) = H(\alpha\alpha')^*$. To obtain the energy to a second approximation one must solve the secular problem connected with the transformed Hamiltonian function $H' = S^{-1}HS$. If we neglect third order terms, one finds that the determinantal equation of this is

$$\begin{vmatrix} W_0 + H'(aa) - W & H'(ab) \\ H'(ba) & W_0 + H'(bb) - W \end{vmatrix} = 0 \quad (4)$$

where

$$H'(xy) = \sum_{\alpha'} \frac{H(x\alpha')H(\alpha'y)}{h\nu(\alpha\alpha')} \quad (x, y = \text{either } a \text{ or } b).$$

The important thing to note is that $H'(ab) \neq 0$; in other words the second ap-

²⁵ J. H. Van Vleck, Phys. Rev. **33**, 467 (1929), especially section 7. See section 4 of this ref. for somewhat fuller exposition of the perturbation technique which we now use.

proximation removes the initial identity of energies for a, b and so leads to the secular equation (4). This degeneracy was not removed in the first approximation as $H(ab) \neq 0$ would require $\Delta\Lambda = -\Delta\Sigma = 2$.

Before writing down the solution of (4) explicitly it is necessary to examine the phase relations between $H'(a\alpha')$ and $H'(b\alpha')$. These are as follows

$$\begin{aligned} H(a; {}^1\Sigma^\pm) &= \pm H(b; {}^1\Sigma^\pm), & H(a; {}^3\Sigma^\pm) &= \mp H(b; {}^3\Sigma^\pm), \\ H(a; {}^5\Sigma^\pm) &= \pm H(b; {}^5\Sigma^\pm), & H(a; X_a) &= H(b; X_b), \end{aligned} \quad (5)$$

where X_a, X_b are the components of a ${}^3\Pi_0'$, ${}^5\Pi_0$, or ${}^5\Delta_0$ "Λ-type-doublet" in the a, b representation. To obtain these results one notes that reflection in a plane containing the figure axis (operation C of section 2) reverses the sense of rotation about this axis and so interchanges the wave functions ψ_a and ψ_b if the arbitrary phases in these functions be properly chosen. Furthermore the operator corresponding to (2) is even under this reflection. If α' is a Σ state one sees by making a change of variables corresponding to the above reflection that the matrix element $H(a\alpha') = \int \psi_a^* H \psi_{\alpha'} d\tau$ is identical with $H(b\alpha')$ or else the negative thereof according as $\psi_{\alpha'}$ is even or odd under the reflection. Here the integration is to be understood to include the spin summation, and it is necessary to reflect the complete wave functions inclusive of the spin parts. In the approved notation Σ^+, Σ^- the superscript gives the symmetry under a reflection of merely the orbital portion. When the spin is included the symmetry of ${}^3\Sigma$ is reversed. This is because the spin functions for the states ${}^1\Sigma, {}^5\Sigma_0$ are even, while that for ${}^3\Sigma_0$ is odd under the reflection.

These properties of the spin functions can be implicitly seen for triplets from the case (a)-case (b) correlation diagrams given by Mulliken.²⁶ It is perhaps illuminating to verify them explicitly for a two electron system, where these functions are

$$\delta(\tfrac{1}{2}; \sigma_1)\delta(\tfrac{1}{2}; \sigma_2), \quad 2^{-1/2}[\delta(-\tfrac{1}{2}, \sigma_1)\delta(\tfrac{1}{2}; \sigma_2) \pm \delta(\tfrac{1}{2}, \sigma_1)\delta(-\tfrac{1}{2}\sigma_2)], \quad \delta(-\tfrac{1}{2}, \sigma_1)\delta(-\tfrac{1}{2}, \sigma_2), \quad (6)$$

corresponding respectively to $\Sigma = +1, 0, -1$. The upper and lower signs give $S=1$, and $S=0$ respectively, and σ_1 is the component of spin of electron 1 in the direction z of the axis of figure. A reflection in a plane containing the axis of figure can be regarded as a reflection in the origin followed by a rotation through 180° about the x axis. Now reflection in the origin does not change the sign of any of the three Cartesian components of angular momentum and so may be regarded as leaving the spin wave functions invariant. On the other hand one verifies from the usual Cayley-Klein transformation scheme²⁷ obeyed by the spin that the above rotation replaces $\delta(\pm \tfrac{1}{2}, \sigma)$ by $-i\delta(\mp \tfrac{1}{2}, \sigma)$ making (6) exhibit the sign behavior noted above. The extension of the proof to include quintets and configurations with more than two electrons can be obtained from the general theory of the transformation coefficients of the rotation group.²⁸

From (5) it follows that $H'(aa) = H'(bb)$ and that the roots of (4) are

$$\begin{aligned} W({}^3\Pi_0^\pm) &= W_0' + 2 \sum \left\{ \frac{|H({}^3\Pi_0; {}^1\Sigma^\pm)|^2}{h\nu({}^3\Pi_0; {}^1\Sigma^\pm)} + \frac{|H({}^3\Pi_0; {}^3\Sigma^\mp)|^2}{h\nu({}^3\Pi_0; {}^3\Sigma^\mp)} \right. \\ &\quad \left. + \frac{|H({}^3\Pi_0; {}^5\Sigma^\pm)|^2}{h\nu({}^3\Pi_0; {}^5\Sigma^\pm)} \right\}. \end{aligned} \quad (7)$$

²⁶ R. S. Mulliken, Phys. Rev. **36**, 1444 (1930).

²⁷ Cf., for instance, Eq. (8) of ref.²⁶ with $\theta = \pi, \Omega = 0$.

²⁸ See F. Hund, Zeits. f. Physik, **63**, 722 (1930).

Here $W_0' = W_0 + \sum |H(^3\Pi_0, \cdot X)|^2 / h\nu(^3\Pi_0, \cdot X)$ (with X defined as after (5)) is a term common to both roots, and the upper or lower sign is to be read consistently. The summation is over all the electronic states of the various types indicated after each semicolon and is inclusive of the various vibrational members if we care to allow for the vibrational structure (Franck-Condon effects) which we have not done explicitly. In symmetrical molecules the elements H will vanish for $u-g$ transitions. In (7) we have classified the roots according to their symmetry under reflection (C). The correlation is as given because the transformation matrix connected with (4) has the elements

$$S(a; \text{I}) = S(b; \text{I}) = S(a; \text{II}) = -S(b; \text{II}) = 1/2^{1/2} \quad (8)$$

and with our choice of phases $\psi_a + \psi_b$, $\psi_a - \psi_b$ are respectively even and odd, so that I, II mean +, - with respect to (C). It is clearly to be understood that although (7) gives the energies in the ultimate, even-odd representation, the matrix elements on the right side are to be calculated for the initial a , b , representation.

The difference $W(^3\Pi_0^+) - W(^3\Pi_0^-)$ is, of course, the width $h\Delta\nu$ of the Λ -doublet. When one takes into account the different possible signs of the denominators, one is led to the statements regarding sign and the depressing and elevating effects on the different components given on p. 552.

Explicit Calculations. If there are only two electrons not in closed shells, one may calculate the matrix elements of s_1 , s_2 from (6) and the properties of the spin operators. Using the phase relations between l_x and l_y characteristic of an axial field, one finds that then

$$H(^3\Pi_0; ^{2\pm 1}\Sigma) = 2^{-1/2} [a_1 l_{1x} (^3\Pi; ^{2\pm 1}\Sigma) \pm a_2 l_{2x} (^3\Pi; ^{2\pm 1}\Sigma)]$$

with the z axis taken as that of figure. This relation is quite general for two electron systems, as it only supposes S , Σ , and Λ to be good quantum numbers, but is not particularly helpful, since the matrix elements of l_1 , l_2 are unknown except with special models involving in each case some rather drastic hypothesis.

One such hypothesis is that the two electrons may be considered in so nearly a central field that their individual and resultant angular momenta l_1 , l_2 , L are all good quantum numbers. The matrix elements of l_{1x} , l_{2x} for this model in the a , b , system of representation can be deduced by non-commutative algebra²⁹ or by proper adaptation³⁰ of the Kronig intensity rules (with phases inserted) and have been tabulated by Johnson.³¹ One finally finds that (7) gives

$$W = W_0' + \frac{[a_1 f(L, l_1, l_2) \pm a_2 f(L, l_1, l)]^2}{h\nu(L^3\Pi; L ^{2\pm 1}\Sigma)} + \frac{L(L+1)(a_1 \pm a_2)^2 F(L+1; l_1, l_2)}{h\nu(L^3\Pi; L+1 ^{2\mp 1}\Sigma)} + \frac{L(L+1)(a_1 \pm a_2)^2 F(L, l_1, l_2)}{h\nu(L^3\Pi; L-1 ^{2\mp 1}\Sigma)} \quad (9)$$

with the abbreviations

$$f(L, l_1, l_2) = \frac{L(L+1) + l_1(l_1+1) - l_2(l_2+1)}{4(L^2+L)^{1/2}},$$

$$F(L, l_1, l_2) = \frac{(l_2 + l_1 + 1 - L)(l_1 + l_2 + 1 + L)(L - l_1 + l_2)(L + l_2 - l_1)}{16L^2(2L-1)(2L+1)}.$$

²⁹ Güttinger and Pauli, Zeits. f. Physik **67**, 743 (1931).

³⁰ See p. 170 of the writer's "Theory of Electric and Magnetic Susceptibilities" for resumé of how this can be done.

³¹ M. H. Johnson, Jr., Phys. Rev. **38**, 1628 (1931); Eqs. (3), (4), (5), but replace J , L , S by L , l_1 , l_2 to adapt to our problem.

The first index of ν in (9) gives the value of L , and $^{2+1}\Sigma$ means $^3\Sigma$ etc. The $+$, $-$ superscripts for the Σ states have been omitted but for any given value of L , l_1 , l_2 , they can be determined from the Hund²⁸ rule that with the present model the orbital wave function for a Σ state of azimuthal quantum number L is even or odd under reflection (C) according as $L-l_1-l_2$ is even or odd. This shows that the upper choice of sign in (9) (not to be confused with the upper choice in (7)) yields $W(^3\Pi_0^+)$ or $W(^3\Pi_0^-)$ according as $L+1-l_1-l_2$ is even or odd. Eq. (9) is valid even when the electrons are equivalent; the members then representing transitions to non-existent states vanish in virtue of $a_1 = a_2$.

Another model which can be used is that in which the individual λ 's and l 's of the electrons are good quantum numbers. Let us suppose that all electrons but two are in closed shells, and that the Π state is of the type $m_1\pi m_2\sigma^3\Pi$. If the two electrons are not equivalent, i.e. $m_1 \neq m_2$, one finds from elementary construction of the wave functions that

$$W(^3\Pi_0^\pm) = W_0' + \left[\frac{a_1^2 l_1 (l_1 + 1)}{4h\nu(^3\Pi; m_1\sigma m_2\sigma^{2\mp 1}\Sigma^+)} + \frac{a_2^2 l_2 (l_2 + 1)}{8h\nu(^3\Pi; m_1\pi m_2\pi^{2\mp 1}\Sigma^+)} \right. \\ \left. + \frac{a_2^2 l_2 (l_2 + 1)}{8h\nu(^3\Pi; m_1\pi m_2\pi^{2\pm 1}\Sigma^-)} \right]. \quad (10)$$

If the two electrons are equivalent the complete bracketed expression should be multiplied by a factor 2 and the terms discarded which would involve non-existent states. The latter states are $\sigma^2\ ^3\Sigma^+$, $\pi^2\ ^1\Sigma^-$, $\pi^2\ ^3\Sigma^+$ if the "united atom" approximation is being used (i.e. l_1 , l_2 measured relative to the same center) and $\sigma^2\ ^3\Sigma_g^+$, $\pi^2\ ^1\Sigma_g^-$, $\pi^2\ ^3\Sigma_g^+$, $\sigma^2\ ^1\Sigma_u^+$, $\pi^2\ ^1\Sigma_u^+$, $\pi^2\ ^3\Sigma_u^-$ if the molecule is symmetrical and the "separated atom" approximation is used, wherein two electrons are to be considered equivalent for our purposes if their orbits are identical except for being referred to different centers of similar type.

Eqs. (8-9-10) replace (69,70) of our previous paper. We must caution that (9) and (10) apply only when the effect of L , Λ and λ_1 , λ_2 respectively upon the energy is small compared to that of the principal quantum numbers n_1 , n_2 , since in (9-10), though not in (7), we have discarded the portion of (2) not diagonal in n_1 , n_2 . In (2) a_1 , a_2 are in general functions of r_1 , r_2 , and it is only when we discard the non-diagonal matrix elements that they can be treated as ordinary numbers as in (9-10). It must be remembered that the Λ -doubling is a second order effect, and so the non-diagonal part of (2) (i.e. part of the spin-orbit interaction not diagonal in the principal quantum number) makes a contribution to (7) of the same order as the more usual diagonal part except insofar as the latter yields smaller denominators in (7).

5. EFFECT OF A MAGNETIC FIELD UPON THE Λ -DOUBLING

Stationary Molecule. Let us first neglect molecular rotation and suppose that a magnetic field is applied parallel to the axis of figure. The extra term introduced into the Hamiltonian function is then $\mathfrak{H}\beta(L_z + 2S_z)$ where β is the Bohr magneton $he/4\pi mc$. In the a , b system of representation, this expression is a diagonal matrix whose elements are $\pm\mathfrak{H}\beta$ as then one (the " a " component) has $\Lambda = 1$, $\Sigma = -1$, while the other has $\Lambda = -1$, $\Sigma = +1$. Hence the magnetic field merely has the effect of adding $-\mathfrak{H}\beta$ and $\mathfrak{H}\beta$ respectively to the two elements on the principal diagonal of (4) and so the roots of (4) become

$$W = \frac{1}{2}[W(^3\Pi_0^+) + W(^3\Pi_0^-)] \pm \frac{1}{2}(4\mathfrak{H}^2\beta^2 + h^2\Delta\nu^2)^{1/2}, \quad (11)$$

where $h\Delta\nu$ is the field-free doublet width $W(^3\Pi_0^+) - W(^3\Pi_0^-)$. Eq. (11) has the

²⁸ The small Greek letters as used here and also later in Eqs. (16) and (18) in the "separated atom model" relate to the one rather than two-center problem and hence are less specific than those in Mulliken's usage. He would, for instance, write $\sigma_u\sigma_g\Sigma_u$ in place of our $\sigma^2\Sigma_u$. In our united atom approximation, the electron is u or g according as l is odd or even.

same structure as the familiar expression for the Paschen-Back effect on doublets. The important thing to note is that after addition of the magnetic terms the transformation matrix associated with (4) no longer has the precise form (8), as (8) demands equal elements along the principal diagonal of (4) (previously secured in virtue of $H(aa) = H(bb)$). Any departure from (8), however, means loss of the even-odd property, in agreement with statements made in section 1. The analogy to the crude model at the end of section 1 is obvious. In the limit $\mathfrak{H}\beta \gg |h\Delta\nu|$ the field demands the a, b representation. In the more usual limit $\mathfrak{H}\beta \ll |h\Delta\nu|$ the roots of (11) are approximately $W({}^3\Pi_0^\pm) \pm \mathfrak{H}^2\beta^2/h\Delta\nu$.

The assumption of a stationary molecule has permitted particularly simple exhibition of the Paschen-Back effect on the doubling, but is not a good approximation to reality unless perchance the magnetic field is so extremely powerful as to align the molecular axis parallel to the field. Such an alignment would require $\mathfrak{H}^2\beta^2 \gg h|\Delta\nu|(2J+2)h^2/8\pi^2I$ as the Zeeman effect cited in the last sentence of the preceding paragraph would need to be bigger than the rotational structure. In iodine $h/8\pi^2Ic$ has the abnormally low value¹³ 0.029 cm^{-1} , but, even so, satisfaction of the above inequality at the band origin $J=0$ in a field of 20,000 Gauss would require $|\Delta\nu/c| \ll 15 \text{ cm}^{-1}$.

Effect of Molecular Rotation. This rotation profoundly modifies the Zeeman effect but will not impair the field-free theory of §4 if we suppose, as we shall, that the molecule is heavy enough so that Hund's case a is a good approximation. With the rotation, the perturbing matrix elements due to the magnetic field are

$$H_1({}^3\Pi_0^+vJ; {}^3\Pi_0^-v'J') = \frac{1}{2}\mathfrak{H}\beta \left[\frac{(J+J'+1)^2 - 4M^2}{(2J'+1)(2J+1)} \right]^{1/2} 1(v; v') \text{ with } J' = J \pm 1.$$

This can be seen by noting that in the a, b system of representation, these matrix elements are of the same structure as those of the potential energy of a rotating dipole,³³ with the moment along the axis of figure taken as β . As usual, M is the magnetic quantum number determining the component of angular momentum in the direction of the field. The factor $1(v; v')$ denotes $\int R_v^+ R_{v'}^- dr$, and has been inserted to allow for the vibrational structure;³⁴ here R_v^+ and $R_{v'}^-$ are the vibrational parts of the wave function for ${}^3\Pi_0^+$ and ${}^3\Pi_0^-$ states of vibrational quantum number v, v' respectively. Unless the field is so very strong as to give much Paschen-Back effect, one can use perturbation theory, and the energy levels in the field are, to the second order

³³ See, for instance, R. de L. Kronig, Proc. Nat. Acad. Sci. **12**, 488 (1926).

³⁴ This vibrational factor results from the fact that in calculating the matrix elements of the Hamiltonian function H , there is an integration over the radial wave function. It is possible to take H outside the integration particularly since H is a Zeeman term independent of r ; or more generally in other problems, since the variation of H with r is usually "blunt," compared to that of the radial wave functions themselves. The function $1(v; v')$ is a Kronecker delta function only in case the initial and final states have the same vibrational constants, etc. so that R^+, R^- belong to exactly the same set of orthogonal functions. In our problem the difference between $1(v; v')$ and a Kronecker delta will presumably not be great, for the potential curves for M and N are quite close for a considerable range of values of r (cf. Fig. 1).

$$W = W(^3\Pi_0^\pm) + \sum_{\nu} \sum_{J'=J\pm 1} \frac{\mathfrak{S}^2\beta^2[(J' + J + 1)^2 - 4M^2] |1(\nu; \nu')|^2}{4h\nu(^3\Pi_0^\pm \nu J; ^3\Pi_0^\mp \nu' J')(2J + 1)(2J' + 1)} \quad (12)$$

It is to be noticed that there is only a second order Zeeman effect. A first order effect³⁵ would require both $\mathfrak{S}\beta \gg |h\Delta\nu|$ and $\mathfrak{S}\beta \gg Jh^2/4\pi^2I$ (except for fortuitous near-coincidences of two states involved in the denominator ν of (12), due to counterbalancing of the stationary doublet width $\Delta\nu$ by rotational or vibrational changes). If one assumes that the effect of the rotational quantum number J on the energy is small compared to the Λ -doublet width $h\Delta\nu$, one can replace $\nu(\cdot)$ in (12) by an expression independent of J . This assumption is not an automatic consequence of Hund's case a, as the latter merely insures that the ordinary multiplet constant a_1 be $\ll Jh^2/4\pi^2I$, whereas $\Delta\nu$ is of the second order in a_1 (cf. Eq. 10). Still further simplification can be effected if we assume that both components have nearly the same potential energy curve, making $1(\nu; \nu') = \delta(\nu, \nu')$ where δ is the usual Kronecker symbol, or if, going to the other extreme, we suppose that the effect of vibration is small compared to the doublet width. The latter supposition, unlike the former, is not usually warranted, but would permit one to take ν outside the ν' summation sign and use the relation $\sum_{\nu'} |1(\nu; \nu')|^2 = 1$ proved elsewhere by the author.³⁶ If either case (12) then reduces to

$$W = W(^3\Pi_0^\pm) + \mathfrak{S}^2\beta^2 \left[\frac{2J^2 + 2J - 1 - 2M^2}{(2J - 1)(2J + 3)h\Delta\nu} \right] \quad (13)$$

provided the rotational structure is small compared to the doublet width.

Rate of Magnetic Predissociation. So far we have ostensibly supposed both doublet components to be stable. If, as in iodine, the $^3\Pi_0^-$ component is unstable, we may index and normalize its vibrational wave function with respect to the energy W . Wentzel, Dirac, and others³⁷ have shown that the rate at which a stable level 1 predissociates due to interaction matrix element $V(12)$ with a continuous level 2 is $4\pi^2 |V(12)|^2/h^2$ provided that 2 be normalized with respect to energy, and that its energy be given the same value as for the discrete level. Hence in our case the probability of predissociation of the vibrational member ν is

$$\sum_{J'=J\pm 1} \frac{\pi^2 \mathfrak{S}^2\beta^2 [(J' + J + 1)^2 - 4M^2]}{h^2(2J' + 1)(2J + 1)} |1(\nu, W)|^2 \quad (14)$$

In iodine the moment of inertia is probably so large that one is amply warranted in neglecting the rotational modulation of the vibrational potential

³⁵ It is to be emphasized that we throughout assume Hund's case (a). A linear effect, to be studied in a forthcoming paper by R. Serber, appears as soon as there is an appreciable rotational distortion, i.e., tendency towards case (b) or (d).

³⁶ J. H. Van Vleck, Proc. Nat. Acad. **15**, 754 (1929); especially pp. 757-758. Note especially that our R^+ , R^- denote different sets of orthogonal functions, so that the matrix multiplication is not of the usual type.

³⁷ G. Wentzel, Zeits. f. Physik, **43**, 524 (1927); Dirac, "The Principles of Quantum Mechanics," p. 166.

energy curves, permitting us to regard $1(v, W)$ as independent of J' . If we do this and average over the various allowed values of the magnetic quantum number, (14) becomes

$$\frac{4\pi^2 \mathfrak{S}^2 \beta^2}{3h^2} |1(v, W)|^2 \quad (15)$$

As mentioned in section 3, existing data do not permit evaluation of the factor $1(v, W)$. Different incident frequencies excite the iodine molecule to different vibrational levels v , and hence the dependence of this factor on v would be necessary in order to determine the sensitivity of the quenching to the frequency of excitation.

One point is quite clear. Experimentally the amount of magnetic predissociation does not seem to depend at all on the rotational quantum number, although Turner⁷ calculates that enormous values of J are excited in some cases. This accords nicely with the absence of J in (15).

Magnetic Susceptibility in ${}^3\Pi_0$ States. As no gas is known having a ${}^3\Pi_0$ normal level, we shall merely state the results obtained by adapting to such states the author's general quantum theory of magnetic susceptibilities.³⁸ If we assume the vibrational structure can be eliminated as in going from (12) to (13), the formula for the susceptibility is $(2N\beta^2/3h\Delta\nu) \text{tang}(h\Delta\nu/2kT)$ which reduces to $N\beta^2/3kT$ in the limit $h|\Delta\nu| \ll kT$.

6. SOME SECULAR DETERMINANTS FOR MOLECULES INCLUSIVE OF SPIN-ORBIT COUPLING

The writer has found it instructive to actually set up some of these determinants, for their structure is interesting even though insufficient data are available to permit numerical solution. Except for addition of the spin-orbit terms we shall make the usual Heitler-London approximations and so neglect any errors incurred because two wave functions belonging to different atoms are not rigorously orthogonal.

${}^2P+{}^2P$. The orbital wave functions for a molecule derived from two identical $p\ {}^2P$ atoms have been listed by Bartlett³⁹ and so need not be given here. One must, of course, multiply them by the proper spin functions (6), and in the case of the ${}^3\Pi_0$ states pass from the a, b representation to the even and odd states by using the transformation (8). The matrix elements of (2) can be calculated from the well-known properties of the angular momentum operators. We are interested primarily in the dependence of the secular structure on the spin-orbit terms, and so shall not attempt to solve the rather laborious electrostatic part of the problem, instead merely denoting the various electrostatic terms by small Greek letters. We shall use the letter a to denote the atomic multiplet constant, which is the same as $a_1 = a_2$ in (2) and is half the corresponding molecular constant.⁴⁰ The various electrostatic

³⁸ J. H. Van Vleck, "The Theory of Electric and Magnetic Susceptibilities," Chaps. VII and X.

³⁹ J. H. Bartlett, Jr., Phys. Rev. **37**, 509 (1931).

⁴⁰ For general discussion of the relation between atomic and molecular multiplet constants see R. S. Mulliken, Rev. Mod. Phys. **4**, 34 ff, (1932).

terms, and to much less extent also a , are of course functions of the internuclear distance r . The caption below Fig. 1 lists ten 0 states derived from ${}^2P+{}^2P$ but because of the symmetry properties the secular equation factors into two biquadratics and two isolated states. One of each are the following³²

$$\begin{array}{l} \sigma\pi\ {}^3\Pi_u^+ \\ \sigma\pi\ {}^3\Pi_u^- \\ \sigma^2\ {}^3\Sigma_u^+ \\ \pi^2\ {}^3\Sigma_u^+ \\ \pi^2\ {}^1\Sigma_u^- \end{array} \left| \begin{array}{ccccc} W = \alpha - \frac{1}{2}a & & & & \\ \alpha - \frac{1}{2}a - W & a & 2^{-1/2}a & 2^{-1/2}a & \\ a & \beta - W & \epsilon & 0 & \\ 2^{-1/2}a & \epsilon & \gamma - W & -a & \\ 2^{-1/2}a & 0 & -a & \delta - W & \end{array} \right| = 0 \quad (16)$$

The others are identical except that the labels are $\sigma\pi\ {}^3\Pi_g^-$; $\sigma\pi\ {}^3\Pi_g^+$, $\sigma^2\ {}^1\Sigma_g^+$, $\pi^2\ {}^1\Sigma_g^+$, $\pi^2\ {}^3\Sigma_g^-$ and that the constants $\alpha, \beta, \dots, \epsilon$ all have new values. The off-diagonal electrostatic term ϵ arises because the individual λ 's of the separate atoms are not good quantum numbers even without the spin-orbit distortion, so that certain Σ states can be part π^2 and part σ^2 .

As a check on the accuracy of the work, one may verify that (16) simplifies properly in limiting cases. When $\alpha, \beta, \dots, \epsilon$ vanish, the atoms are uncoupled, and the roots of (16) become $a, a, -\frac{1}{2}a, -2a$, in agreement with the fact that the spin-orbit energies of a 2P atom are $\frac{1}{2}a, -a$. When $\alpha, \beta, \dots, \epsilon$ are specialized appropriately for a central field,⁴¹ the problem becomes a one rather than two center one, and one can verify that then (16) yields essentially the secular determinant of the p^2 atomic configuration, studied elsewhere by Bartlett and by Goudsmit.⁴²

If one knew the numerical values of the various constants, one could solve (16) numerically for W and so determine the Λ -doubling and spin-orbit distortion even though the latter is of the same order of magnitude as the electrostatic binding, which incidentally is the case in iodine. Eqs.

⁴¹ The specialization of (16) to central fields is accomplished by setting $2(\beta - \alpha) = -2^{1/2}\epsilon = \gamma - \alpha = -(\delta - \alpha)$. This can be seen by noting that when $a=0$ the roots must agree with known electrostatic energies for p^2 or p^4 (e.g. Slater, Phys. Rev. **34**, 1293 (1929); Condon and Shortley, *ibid.* **37**, 1025 (1931)) and further with the Wigner rules for the compounding of orbital wave functions (e.g. Bartlett, *ibid.* **38**, 1623 (1931)). Making this specialization, but assuming $0 < |a| \ll |\epsilon|$ one finds that the roots of (16) become

$$F_0 + F_2 - \frac{3}{2}a, \quad F_0 + F_2 + a, \quad F_0 - 5F_2, \quad F_0 + 10F_2$$

in agreement with the energies of ${}^3D_1, {}^3D_3, {}^1P, {}^3S$ respectively in Russell-Saunders coupling. The isolated root above (16) gives 3D_2 . The notation $F_2 = (\gamma - \alpha)/6, F_0 = \alpha - F_2$ has been introduced to make our usage agree with Condon and Shortley's. The terms ${}^3D, {}^1P, {}^3S$ are not really allowed by the exclusion principle, but this discrepancy is a formal one which arises because our model is too simple to take cognizance of the "promotions" which take place when the limiting case of central fields is achieved by coalescence of two attracting centers. In the determinant for g^+ configurations which as mentioned above is similar in form to (16) the specialization appropriate to central fields is $\alpha = \delta, 4(\beta - \alpha) = 6 \times 2^{1/2}\epsilon = 3(\gamma - \alpha)$, which makes (16) factor into two quadratics, and then the roots for $0 < |a| \ll |\epsilon|$ reduce to the energies of ${}^3P_0, {}^3P_2, {}^1D, {}^1S$ in Russell-Saunders coupling. (With the g configurations, $F_2 = (\gamma - \alpha)/12, F_0 = \alpha + 5F_2$ and the isolated root gives 3P_1 .)

⁴² J. H. Bartlett, Jr., Phys. Rev. **34**, 1247 (1929); S. Goudsmit, *ibid.* **35**, 1325 (1930).

(7-9-10), on the other hand, were derived by perturbation theory and so presupposed this separation to be small. In iodine one has $p^5 + p^5$ rather than $p + p$ (used to obtain 16) but as far as the secular structure is concerned the two cases are entirely similar except for reversal of the sign of a and different numerical values of the various constants. The small Greek letters σ, π in (16), etc. then specify $\Sigma\lambda$ for an atom rather than the λ of a single electron. It may be noted that Eq. (16) may be written in the form

$$W - \alpha + \frac{1}{2}a = \frac{(\theta_1 a + 2^{-1/2}\theta_2 a)^2}{W - \beta'} + \frac{(\theta_2 a - 2^{-1/2}\theta_1 a)^2}{W - \gamma'} + \frac{a^2}{2(W - \delta)} \quad (17)$$

in which it is to be observed that unfortunately the unknown W appears on the right as well as left side. Substitution of approximate values of W on the right reduces (17) to (7), and further to (10) if $\theta_1 = 1, \theta_2 = 0$. Here β', γ' denote the characteristic values $\frac{1}{2}(\beta + \gamma) + \frac{1}{2}[(\beta - \gamma)^2 + 4\epsilon^2]^{1/2}$ of the β, γ pair of states under omission of the spin-orbit distortion, while θ_1, θ_2 are defined by $\theta_1(\beta - \beta') + \theta_2\epsilon = 0, \theta_1^2 + \theta_2^2 = 1$. If one uses the root corresponding to ${}^3\Pi_u^-$, the right side of (17) is the width of the Λ -doublet, since the isolated state above (16) is undisplaced. With this root, the right side has the value $3a/2$ for $r = \infty$ if ${}^3\Pi_u^-$ is derived from ${}^2P_{3/2} + {}^2P_{3/2}$. Let us suppose that $a < 0$, as is the case in I_2 . Then if the Λ -components cross at some intermediate value of r , it is necessary that at least one of the denominators in (17) be positive, for otherwise the right side of (17) could never be positive for any r . This means that one of the ${}^3\Sigma_u^+$ or ${}^1\Sigma_u^-$ levels, say κ , exclusive of the spin-orbit correction, must lie below the ${}^3\Pi_{0u}^-$ level, inclusive of this correction. This agrees with statements on p. 552 except that the condition $W({}^3\Pi_{0u}^-) - W_\kappa > 0$ given on that page is less severe than the more rigorous criterion $W({}^3\Pi_{0u}^-) - W_\kappa^0 > 0$, for the spin-orbit interaction terms will depress κ since κ comes from ${}^2P_{3/2} + {}^2P_{3/2}$. The purely electrostatic energy W_κ^0 of κ is, of course, the same as the least of the three quantities β', γ', δ . It is to be emphasized that all the conclusions on the size and sign of the doublets in this paragraph apply only if it is legitimate to neglect interaction with configurations derived from excited atoms not included in (16).

${}^2P + {}^2P'$. When now we turn to molecules (e.g. ICl) derived from different rather than similar 2P atoms, the $u-g$ classification is lost, and the factorization is into two quintics, one of which is

$$\begin{array}{l} \pi\sigma \quad {}^3\Pi_0^+ \\ \sigma\pi \quad {}^3\Pi_0^+ \\ \sigma\sigma \quad {}^1\Sigma^+ \\ \pi\pi \quad {}^1\Sigma^+ \\ \pi\pi \quad {}^3\Sigma_0^- \end{array} \left| \begin{array}{ccccc} \alpha - \frac{1}{2}a_1 - W & \xi & 2^{-1/2}a_1 & \frac{1}{2}a_1 & \frac{1}{2}a_1 \\ \xi & \beta - \frac{1}{2}a_2 - W & 2^{-1/2}a_2 & \frac{1}{2}a_2 & \frac{1}{2}a_2 \\ 2^{-1/2}a_1 & 2^{-1/2}a_2 & \gamma - W & \eta & 0 \\ \frac{1}{2}a_1 & \frac{1}{2}a_2 & \eta & \delta - W & -\frac{1}{2}(a_1 + a_2) \\ \frac{1}{2}a_1 & \frac{1}{2}a_2 & 0 & -\frac{1}{2}(a_1 + a_2) & \epsilon - W \end{array} \right| = 0 \quad (18)$$

The other quintic is like (18) except that the electrostatic constants γ, \dots, η (but not α, β) have different numerical values and that the labels are $\pi\sigma \quad {}^3\Pi_0^-, \sigma\pi \quad {}^3\Pi_0^-, \sigma\sigma \quad {}^3\Sigma_0^+, \pi\pi \quad {}^3\Sigma_0^+, \pi\pi \quad {}^1\Sigma^-$.

Eq. (18) suggests the following explanation of the pseudo-crossing behavior discussed in connection with Fig. 3, section 2. Application of the transformation (8) to the two $\pi\pi$ states in (18) throws Eq. (18) into a form differing from (18) in that the elements of the fourth row and column become $2^{-1/2}a_1$, $2^{-1/2}a_2$, $2^{-1/2}\eta$, $\frac{1}{2}(\delta+\epsilon) - \frac{1}{2}(a_1+a_2) - W$; $\frac{1}{2}(\delta-\epsilon)$ and those of the fifth 0, 0, $2^{-1/2}\eta$, $\frac{1}{2}(\delta-\epsilon)$, $\frac{1}{2}(\delta+\epsilon+a_1+a_2) - W$. Hence if we set $\eta = \delta - \epsilon = 0$ the determinant factors into a biquadratic and a single root $W = \frac{1}{2}(\delta + \epsilon + a_1 + a_2)$. The latter is obviously then derived from ${}^2P_{3/2} + {}^2P_{3/2}$, since the magnetic terms for ${}^2P_{3/2}$, ${}^2P_{1/2}$ are respectively $\frac{1}{2}a$, $-a$. Let us assume that at ordinary values of r the energy order is $\sigma\sigma < \sigma\pi < \pi\sigma < \pi\pi$, as seems probable in ICl, and that $a_2 < a_1 < 0$ (i.e. p^5 atoms). Then an extrapolation by means of the biquadratic will make the $\sigma\pi$ level appear derived from ${}^2P_{1/2} + {}^2P_{3/2}$ despite being the second lowest 0^+ level, for the two available 0^+ states obtained from ${}^2P_{3/2} + {}^2P_{3/2}$ will be absorbed by $\sigma\sigma^1\Sigma^+$ and the isolated root, whose potential curve will be crossed by $\sigma\pi^3\Pi_0^+$ at some large value of r . This crossing is, of course, removed when η , $\delta - \epsilon \neq 0$, and $\sigma\pi^3\Pi_0^+$ then comes from ${}^2P_{3/2} + {}^2P_{3/2}$, as explained on p. 556. Clearly the usual vibrational extrapolation will make this state appear derived from ${}^2P_{1/2} + {}^2P_{3/2}$ if the low roots of (18) are insensitive to η , $\delta - \epsilon$ at ordinary values of r . It appears quite likely that this is really the case. In the first place, η and $\delta - \epsilon$ both vanish if the λ 's (or rather $\Sigma\lambda$ over an atom) are good quantum numbers. At ordinary values of r , to be sure, it may well be that $|\delta - \epsilon| \gg |a_1 + a_2|$, meaning that the $\pi\pi$ states have a quantized resultant spin rather than much tendency towards J - J atomic coupling. Application of the transformation (8) to $\pi\pi$ is then a very bad approximation, for (8) diagonalizes spin-orbit terms at the expense of putting electrostatic exchange terms off the diagonal. Nevertheless the potential curve for $\sigma\pi^3\Pi_0^+$ would not be materially affected by η , $\delta - \epsilon$ if $|\beta - \gamma|$, $|\beta - \delta| \gg |\delta - \epsilon|$, $|\eta|$ i.e. if the $\pi\pi$ singlet-triplet separation and interaction with σ^2 is small compared to the distance between $\pi\pi$ and other configurations.⁴³ The Mulliken-Hund theory of united atoms lends considerable plausibility to this possibility, for the $\pi\pi$ configurations of $p^5 + p^5$ seem to pass into states of the united atom representing a high degree of promotion. At large values of r , on the other hand $|\delta - \epsilon|$, $|\eta|$ may be small compared to $|a_1 + a_2|$, and the above factorization into the biquadratic and isolated root is then clearly allowable except in the immediate vicinity of the crossing point.

When one considers the quintic for the five 0^- states, configuration theory suggests that $\sigma\sigma$ as well as $\pi\pi$ is higher than $\sigma\pi$ or $\pi\sigma$. Hence $\sigma\pi^3\Pi_0^-$, if less than $\pi\sigma^3\Pi_0^-$, extrapolates into ${}^2P_{3/2} + {}^2P_{3/2}$ even when a lone root is

⁴³ It is to be noted that the Π states are connected with the other states of (18) only by spin-orbit terms. Hence even if η , $\delta - \epsilon$ are not particularly small in magnitude compared to $\beta - \gamma$, $\beta - \delta$ at small values of r , the error made by setting $\eta = \delta - \epsilon = 0$ may still be quite small as far as the Π roots of (18) are concerned, for with very small r the spin-orbit terms may be subordinate to $\beta - \gamma$, $\alpha - \gamma$, etc. At larger values of r , the spin-orbit interaction cannot, of course, be considered small, for it is of the same order as the separation between the two dissociation products between which we wish to differentiate.

factored off, for $\sigma\pi^3\Pi_0^-$ is then still the lowest root of the biquadratic. If this were not so and there were a lower 0^- level of the form $\sigma\sigma$, it is hard to see how the $^3\Pi_0^-$ component in iodine could be unstable, unless perchance the corresponding "hill" in Fig. 3 is very low. Indeed, if $W(\pi^{22^+1}\Sigma_u^{\mp}) > W(^3\Pi_{0u}^-) > W(\sigma^2\ ^3\Sigma_u^+)$ the same type of argument as used in the preceding paragraph could be used to remove a root from (16) instead of (18) and make $^3\Pi_{0u}^-$ appear derived from $^2P_{3/2} + ^2P_{1/2}$. Hence in order to make the $^3\Pi_{0u}^-$ level unstable in I_2 , as needed for our theory of magnetic predissociation, it is necessary to exclude the possibility of $\sigma^2\ ^3\Sigma^+$ falling below $^3\Pi_{0u}^-$, even though such an arrangement might give the much-desired crossing of the Λ -doublet components (cf. page 552).

$^2S + ^2P$. The secular equation for $^2S + ^2P$ is formally equivalent to that of the atomic configuration s^1p^1 in an axially symmetrical electric field and hence is a generalization of Houston's⁴⁴ well-known equation for field-free atoms in this configuration. Only quadratics are involved, and the solution is

$$^3\Pi_0^-, ^3\Sigma^+: W = f(\alpha, \beta), \quad ^3\Pi_0^+, ^1\Sigma^+: W = f(\alpha, \gamma)$$

with

$$2f(x, y) = x + y - \frac{1}{2}a_2 \pm [(x - y - \frac{1}{2}a_2)^2 + 2a_2^2]^{1/2}$$

Here α, β, γ denote the energies of $^3\Pi, ^3\Sigma, ^1\Sigma$ without the spin-orbit correction.

We have given only the secular equations characteristic of $\Omega = 0$, but those appropriate to other values of Ω can be constructed without undue difficulty.

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⁴⁴ W. V. Houston, Phys. Rev. **33**, 297 (1929).