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On the Magnetic Field of a Rotating Molecule

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The space distribution and magnitude of electronic currents in a rotating molecule with a $^1\Sigma$ ground state are re-examined. An evaluation of the magnetic field set up by the rotation is attempted, and the results are used to interpret the width of radiofrequency resonance lines of some alkali halides.

I. INTRODUCTION

THE study of radiofrequency spectra of molecules in a strong magnetic field has shown that the resonance lines associated with nuclear magnetic moments are often quite wide, indicating the presence of relatively strong interactions within the molecule. In many cases the magnitude of the effect has been satisfactorily explained on the assumption that the nucleus possesses a quadrupole moment.[1] This explanation, however, does not apply to the resonance associated with the F^{19} nucleus in alkali fluorides (4000 cycles gauss sec.), as the nucleus has spin $\frac{1}{2}$ and cannot have a quadrupole moment. The widths at half-value of the resonance line are given in the second column of Table I[2]. The remaining columns in the table will be explained later. In two out of the three molecules studied so far the width was felt to be surprisingly large, considering that it could only be due to magnetic interactions. An admittedly somewhat naive evaluation of the magnitude of the interactions leads one to expect much smaller widths than found, see below. The problem, therefore, seemed to deserve further consideration.

The measurements are performed in a strong magnetic field, so that both nuclear spins in the molecule, as well as the molecular rotation, are quantized in the direction of the field; in the transitions studied here the alkali nucleus does not flip over, so that only the two following interactions are of real importance: (a) interaction between the magnetic moments of the two nuclei, and (b), interaction between the moment of the F^{19} nucleus and the molecular rotation. Interaction (a), however, is much too small to account for the effects observed and will be neglected. We are left with (b). The broadening of the line is then due to the fact that the rotation of the molecule causes a magnetic field at the nucleus, which is proportional to the component m_J of the rotational momentum along the axis of quantization. Hence molecules with different m_J's will have different frequencies, the shift being

$$\delta\nu = 4000 H_r m_J, \tag{1}$$

where H_r is the rotational magnetic field per unit rotational quantum number.

As the observed shape of the resonance line seems to fit the statistical distribution of m_J values (that follows from Boltzmann's law), one may confidently use the width at half-value of the line to compute the "experimental" value of H_r. A simple statistical consideration shows that one-half of the molecules must have an $|m_J|$ smaller than $0.674(kT/2B)^{\frac{1}{2}}$. This is listed as $m_J(\frac{1}{2})$ in the table. B is the rotational constant of the molecule $\hbar^2/2I$. Its value is not known from direct spectroscopic data;[3] it is known, however, for other alkali halides, and it is found that the internuclear distance in the molecule is from 0.1 to 0.3A smaller than the sum of the ionic radii. The internuclear distances listed in the table are derived from this rule, the uncertainty being of the order ±0.1A, which is quite accurate for our purpose. Inserting the value of $m_J(\frac{1}{2})$ in Eq. (1) and comparing the shift with the half-width of the line, the values of H_r listed in the table have been obtained.

These values are remarkable both as regards

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[1] B. T. Feld and W. E. Lamb, Phys. Rev. **67**, 15 (1944); W. A. Nierenberg, N. F. Ramsey, and S. B. Brody, Phys. Rev. **70**, 773 (1946).

[2] I am indebted to Drs. Rabi, Ramsey, and Nierenberg for communicating to me these as yet unpublished data.

[3] For CsF see, however, H. K. Hughes, Phys. Rev. **70**, 570 (1946); **72**, 614 (1947).

TABLE I. Magnitude of the magnetic field at the nucleus caused by molecular rotation computed from the width of the resonance line.

Molecule	Width of resonance line (Mc/sec.)	Internuclear distance r (A)	B		$m_J(\frac{1}{2})$	H_r (gauss)
			(10^{-16} erg)	(cm^{-1})		
LiF	0.5	1.8	2.0	1.0	13.1	±4.8
NaF	0.08	2.1	0.73	0.37	21.8	±0.46
CsF	0.5	2.6	0.3	0.15	34	±1.85

the magnitude and the trend with increasing mass of the alkali. A naive estimate of the magnitude of H_r could be made on the assumption that the magnetic field is simply caused by the rotation of the alkali ion relative to the F nucleus. One should have $H_r = 2Be/\hbar cr$, since $2B/\hbar$ is the angular velocity of the rotation per unit rotational quantum number. For LiF one finds $H_r = 0.33$ gauss, a value 14 times smaller than observed. In CsF the discrepancy is by a factor 50. As the mass of the alkali is varied, one might expect H_r to vary roughly proportionally to the angular velocity, i.e., to B. Instead, H_r drops to a very low value for NaF and rises again to a high value for CsF.

Another naive way of estimating H_r consists in the assumption that the electron cloud rotates rigidly with the molecule. The field estimated in this way[4] is indeed of the order of magnitude required by experiment. Unfortunately, the assumption of a rigid rotation of the electron cloud is wholly unjustified. Because of the slip phenomenon that was first observed and understood in the case of the H_2 molecule,[5] a rotation of the spherically symmetrical shells of the F^- ion can be induced only insofar as these shells are polarized by the neighboring ion; we shall see in Section V that the rotation of the 1s and 2s shells is quite negligible, and even the 2p shell can only yield a very small field.

It will also appear from the following discussion that the distribution of the currents induced by the rotation within the molecule is, in general, quite different from the distribution corresponding to a rigid rotation. In the next section the general formulae for these currents will be developed, and later various models will be examined.

II. GENERAL FORMULAE

For simplicity, we shall treat the rotation of the molecule classically. We consider a system of axes rigidly connected to the molecule, the z axis being the line that joins the nuclei. We assume that the rotation takes place around the x axis. One can then write, first of all, the time-dependent Schrödinger equation for the electrons, referred to non-rotating axes (one must use the time-dependent equation because the potential is time dependent). Assuming a solution that is stationary with respect to the rotating axes, and transforming the equation to these axes, one finds:

$$E\psi = H_0\psi - \omega\hbar L_x\psi, \qquad (2)$$

where H_0 is the Hamiltonian, such as it would be if the system were not rotating. The perturbation term caused by the rotation contains ω, the angular velocity, and the x component of the total orbital momentum of the electrons: $\hbar L_x$.[6] We may write: $\hbar\omega = 2BJ$, where J is the rotational quantum number. We see, therefore, that all first-order effects caused by the rotation will be proportional to J. We shall henceforth refer all such effects to unit rotational quantum number.

A simple perturbation calculation shows that the electronic current j induced by the rotation is

$$\mathbf{j} = 2B \sum_n{}' \frac{1}{E_n - E_0}[L_{0n}\mathbf{j}_{n0} + \mathbf{j}_{0n}L_{n0}], \qquad (3)$$

where L stands for L_x, and $\mathbf{j}_{0n}$ is a matrix element of the unperturbed current density, for example, in the case of one electron only: $\mathbf{j}_{0n} = (ie\hbar/2m)(\psi_0^* \operatorname{grad}\psi_n - \psi_n \operatorname{grad}\psi_0^*)$. Moreover, E_0 is the energy of the electronic ground state of

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[4] The main contribution comes from the electron shells of the F^- ion itself. In the evaluation one may assume (see Section II) that the rotation takes place around the F nucleus. A spherically symmetrical shell containing z electrons rotating with an angular velocity $2B/\hbar$ causes a field at the center: $H_r = (4zeB/3\hbar c)\overline{(1/r)}$. For the 2$p$ shell of F^-, $z=6$, and the average reciprocal distance $\overline{1/r}$ is about 2.10^8 cm^{-1}. The contribution of the 2p shell alone is $4.8B$ with B in cm^{-1}, or about the field observed in LiF. In CsF one ought to assume a partial rotation also of the inner 1s and 2s shells.

[5] R. Frisch and O. Stern, Zeits. f. Physik **85**, 4 (1933); G. C. Wick, Zeits. f. Physik **85**, 25 (1933) and Nuovo Cimento **10**, 118 (1933); N. F. Ramsey, Phys. Rev. **58**, 226 (1940).

[6] We neglect the interaction of the rotation with the electronic spins. This is permissible in light molecules in a singlet state. Inclusion of that interaction would lead to only slightly more complicated formulae, while leaving the main conclusions unchanged.

the molecule, and E_n is the energy of an excited state. Only Π-states contribute to the sum in (3) if the ground state is of the Σ type. From Eq. (3) it is found that the magnetic moment caused by the rotation, see also reference 5, is

$$M=-4B\sum_n{}'|L_{0n}|^2/(E_n-E_0) \quad \text{Bohr magnetons.} \quad (4)$$

It may be noticed that this moment has the sign that one would expect from a rigid rotation of the electron cloud together with the nuclei; the magnitude, however, may be entirely different, as we know from the case of the molecule H_2.

From Eq. (3) it is also possible to derive an expression for the average magnetic field H_r at any point within the molecule. If $\mathbf{r}$ is the radius vector from the field point to an unspecified integration point, and setting

$$H_{0n}=c^{-1}\int \mathbf{r}\times \mathbf{j}_{0n}d\mathbf{r}/r^3,$$

we have

$$H_r=2B\sum_n{}'\frac{1}{E_n-E_0}\{H_{0n}L_{n0}+L_{0n}H_{n0}\}. \quad (5)$$

Let us assume for a moment that the point at which we want the field is on the rotation axis; then the integral that yields H_{0n} is seen to be the same that yields L_{0n}, but for the presence of an additional factor r^{-3}. The value of (5) is then of the order of (4) divided by the cube of a distance, which is an average distance of the electrons from the point under question. The value of the field found by Rabi and collaborators is in accord with this evaluation in the case of the hydrogen molecule, but we shall see that the evaluation of that average distance may be quite critical.

Actually, the molecule rotates about a point which does not coincide with the F nucleus, but it can be shown that this is immaterial. In fact, the difference between the perturbation operators corresponding to two different rotation axes parallel to one another, is seen to be the operator corresponding to a uniform translation of the molecule; the magnetic field produced by this translation at a given point is related by a Lorentz transformation to the average electric field at the same point when the molecule is at rest. Now precisely at the position of a nucleus the average electric field caused by the remaining particles is zero, and the magnetic field caused by a uniform translation is also zero, as one should indeed expect.

One further remark is necessary before we proceed. If the field (5) is multiplied into the magnetic moment of the nucleus, we obtain the perturbation of the energy levels that is caused by the interaction between rotation and the magnetic moment. This formula could also be arrived at from an analogous formula derived by Hebb[7] for the interaction between the rotation and the electronic spin when this is not zero. This incidentally shows that the μ-term in Hebb's paper is exactly equivalent to the magnetic coupling between the spin of the molecule and the magnetic field set up by the molecular rotation considered by Kramers,[8] and this explains why the two computations give formulae of the same structure.

III. ORDERS OF MAGNITUDE

It is rather difficult to estimate the sums in Eqs. (4) and (5). The difficulty is best illustrated by the fact, to be discussed later, that also very high excited states may give a strong contribution to the sums. On the other hand, it is also clear that owing to the denominator E_n-E_0 the lowest excited states will be quite important. One can, however, proceed a little farther on the assumption that the various electron shells in the two ions contribute independently to the sums. The most appropriate approximation may then be applied to each shell. For the outer shells we may replace in the sums the denominator E_n-E_0 by a suitable average value, which will not be much larger than the excitation energy of the lowest Π-states. The spectroscopic evidence indicates[9] that the energy curves of these states are practically horizontal so that the minimum value of E_n-E_0 is of the order of the dissociation energy D of the molecule, or about $(1-n^{-1})e^2/r$, where n is of the order of 8 or 9. Approximate values of D for the three molecules, LiF, NaF, CsF are $D=7$ ev, 6 ev, and 5 ev,

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[7] M. H. Hebb, Phys. Rev. **49**, 610 (1936), see especially Eq. (12).

[8] Kramers, Zeits. f. Physik **53**, 422 (1929).

[9] See R. S. Mulliken, Phys. Rev. **50**, 1017 (1936) and **51**, 310 (1936).

respectively. From the structure of H_{0n} we may expect it to be of the order of the magnetic field at the nucleus caused by a $2p$ electron, when L_{0n} is of order unity, and proportionately smaller if L_{0n} is small. The field caused by a $2p$ electron in fluorine is of the order of 6.10^5 gauss.[10] Collecting all these factors together, and noticing that there are two terms in Eq. (5) that are equivalent, we get for the contribution of the outer shells the evaluation:

$$H_r \sim 4(B/D)\sum_n |L_{0n}|^2 \times 6.10^5 = 2.4\times 10^6 (B/D)(L_x^2)_{00}. \quad (6)$$

It will now be noticed at once that the values of $(L_x^2)_{00}$ that will make the field (6) equal to the experimentally observed field in Table I are fairly low (0.11, 0.03, and 0.2, respectively) and should not be very hard to explain on almost any model. But it must be pointed out that a really crucial *assumption* about the space distribution of the current $\mathbf{j}_{0n}$ has been made in estimating H_{0n} from L_{0n}.[11] Before we examine these points in more detail, let us settle a minor question.

IV. EFFECT OF THE INNER SHELLS

Some simple remarks will clarify the discussion of the inner shells. In the isolated ion these shells have spherical symmetry; because of the strong binding, the inner shells probably preserve a high degree of symmetry even in the molecule. Let us first consider a spherically symmetrical shell of the F ion; the operator L_x of Eq. (3) applied to the wave function of this shell yields zero, hence there is no perturbation, the slip is 100 percent. This result is trivial, as it is clear that a rotation of the shell will take place only as a consequence of the asymmetrical perturbation of the shell caused by the neighboring ion. Let us now consider a shell in the alkali ion; taking into account the fact that the rotation is assumed to take place with the F ion as a center (and that consequently L_x is referred to this point) it is again easy to see that the shell does not rotate about its own center, but is, of course, affected by a translational motion with a speed equal to that of the alkali nucleus. This type of velocity distribution in the shell will set up a magnetic field which outside the shell will be equivalent to the field one would obtain if the charge of the shell were concentrated at its center. We thus see that the main effect of the inner shells of the alkali ion will be to screen a large fraction of the magnetic field produced by the motion of the alkali nucleus. The value of this field is

$$H_{rn} = 2ZeB/hcr \quad (7)$$

for unit J (Z is nuclear charge of alkali). To be consistent we have, of course, assumed that the rotation takes place about the F nucleus. The field (7) should of course be added to (5) to get the complete field. It is, however, rather small compared to the observed H_r in LiF; in CsF, with $Z=55$, $H_{rn}=1.9$ gauss, which is nearly equal to the field observed. As soon as a large fraction of it is screened by the inner shells it will be negligible. This shows that we may simply omit the field (7) if at the same time we omit in the sum (5) the terms corresponding to the excitation of the inner shells of the alkali. At the same time this remark substantiates a previous statement, namely, that in the sum (5) the contribution from very high electronic levels is far from small.

V. ROTATIONAL PROPERTIES OF A FEW SIMPLE MODELS

In Section III we found that the experimental data could be explained by making some not too unreasonable assumptions about the order of magnitude of certain matrix elements. Our knowledge of the wave functions and states of the molecule is not, of course, sufficient to permit a real test of these assumptions. But a closer examination of a few strongly schematized models may perhaps contribute to a better understanding of the phenomenon. Although all the calculations may be based on the general formulae (3), (4), (5), the following remark may be useful. Since the unperturbed non-relativistic Hamiltonian H_0 is real and L_x is imaginary,

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[10] This being an average over the $P_{\frac{1}{2}}$ and the $P_{3/2}$ states estimated from the fine structure of the ground state of the F atom.

[11] Namely, in the current distribution for a p electron, the angular velocity varies as the inverse square of the distance from the rotation axis. This type of current distribution yields a much stronger field at the center than a rigid rotation, the resultant magnetic moment being the same.

the unperturbed wave function u for the Σ ground state may be assumed to be real, and the perturbed wave function, neglecting second-order terms in $\omega=2B/h$, will be of the form: $u+i\omega v$, where v is also a real function. From this it follows that the electronic density distribution relative to the nuclei is unaffected by the rotation, again neglecting second-order terms. Therefore, the time derivative of the electronic density, $\partial\rho/\partial t$, *at a space-fixed point* will be the same as for a rigidly rotating electron cloud: $\partial\rho/\partial t=-\omega\partial\rho/\partial\vartheta$, ϑ being the azimuth about the rotation axis. The electronic current induced by the rotation must hence satisfy the continuity equation

$$\operatorname{div}\mathbf{j}=\omega\partial\rho/\partial\vartheta=\operatorname{div}(\rho\boldsymbol{\omega}\times\mathbf{r}), \tag{8}$$

from which it does *not* follow, however, that j coincides with the current $\rho\boldsymbol{\omega}\times\mathbf{r}$ corresponding to a rigid rotation. This may be seen most simply for a one-electron system. One has then, with $\psi=u+i\omega v$,

$$\begin{aligned}\mathbf{j}=(ihe/2m)\{\psi^*\operatorname{grad}\psi-\psi\operatorname{grad}\psi^*\}&\\ =(2B/m)\rho\operatorname{grad}(v/u),&\end{aligned} \tag{9}$$

since $\rho=-eu^2$. For the ground state of a one-particle system u has no nodes, so that v/u is regular everywhere. Equation (9) then shows that the current is obtained by impressing on the density ρ a velocity $(2B/m)\operatorname{grad}(v/u)$, i.e., *an irrotational velocity field.* This condition together with (8) determines $\mathbf{j}$ completely and may be used instead of Eq. (3). The velocity field for rigid rotation $\boldsymbol{\omega}\times\mathbf{r}$ is not, of course, irrotational: $\operatorname{curl}(\boldsymbol{\omega}\times\mathbf{r})=2\boldsymbol{\omega}$. The actual field may be regarded as the superposition of a rigid rotation plus a velocity field $\mathbf{w}$ such that: $\operatorname{div}.\rho\mathbf{w}=0$, and $\operatorname{curl}\mathbf{w}=-2\omega$. *As the circulation of this field is contrary to the rotation, it is clear that it will lead in general to a lowering of the magnetic moment.*

An especially simple example is afforded by a one-dimensional model. An electron is constrained to move on a circle under the action of a potential $V(\vartheta-\vartheta_0)$, ϑ being the azimuth of the particle and ϑ_0 the azimuth of a massive particle symbolizing the nuclei in the actual case of a molecule. If the heavy particle rotates with an angular velocity ω, the average rotation of the light particle may be computed as follows. Equations (8) now takes the form: $\partial j/\partial\vartheta=\omega\partial\rho/\partial\vartheta$, or $j=\omega\rho-j_0$. The additive constant j_0 may be determined from condition (9) or $j=(2B/m)\rho(\partial/\partial\vartheta)(v/u)$, remembering that v/u must be a periodic function of ϑ. This gives $j_0\int d\vartheta/\rho=4\pi B/h=2\pi\omega$, or

$$j=\omega\rho-j_0=\omega\rho-\omega/\overline{\rho^{-1}}. \tag{10}$$

This shows that on the current there is superimposed a constant slip term representing a current contrary to the rotation. If the potential $V(\vartheta-\vartheta_0)$ is weak, so that ρ is nearly constant on the circle, $j_0\approx\omega\rho$; the rigid rotation, therefore, is completely cancelled by the additive term; the slip is almost 100 percent. On the other hand, if the potential is very strong so that ρ is very unevenly distributed, j_0 is much smaller than the average of $\omega\rho$, and the slip is almost negligible. This example simply illustrates the need for an asymmetry in the electron cloud in order to have an induced rotational moment.

In the actual physical case, a certain amount of asymmetry may be produced in the shells of the F^- ion by the field of the neighboring alkali ion. It is essential to ascertain not only the average amount of rotation, or the average magnetic moment induced in each shell, but also the actual distribution of the rotational currents; because of the r^{-3} factor, the field H_r depends quite strongly on the distribution (compare reference 11).

In an admittedly rough way, the electric field of the neighboring ion may be replaced by the Coulomb field of a point charge $+e$ at the center of the alkali. Considering that the distance r between the nuclei is fairly large, we may develop the potential

$$e/R=e/r+ez/r^2+e(2z^2-x^2-y^2)/2r^3+\cdots \tag{11}$$

and consider the polarization of the F^- ion by the various terms. For a simple evaluation we have used a crude model in which the electrons are treated as isotropically bound oscillators, with a suitable frequency for each shell. For the $2p$ shell of the F^- ion, a value of the frequency $\bar{\omega}=4.10^{16}$ or $h\bar{\omega}=26$ ev may be estimated from the polarizability $\alpha=Ze^2/m\bar{\omega}^2$, Z being now the number of electrons in the shell. The polarizability is about 10^{-24} cm^3. A lower limit for $h\bar{\omega}$ is certainly 5 ev.

Now consider first the second term in (11), representing a constant field $\mathcal{E}=e/r^2$. The effect of this is merely to shift the center of a shell with respect to the F nucleus by a small amount $\alpha\mathcal{E}/Ze$. The shell remains spherically symmetrical around the new center. When the system rotates about the F nucleus, the ensuing motion of the shell will be of the same type as that described in Section IV for the inner shells of the alkali. It is quite easy to compute the magnetic moment and field. The magnetic moment is, rather obviously, the same as one would find in a purely classical treatment of the elastically bound electrons:

$$M=-\omega(\alpha\mathcal{E})^2/2Zec=-\omega(Ze/2c)(e\mathcal{E}/m\bar{\omega}^2)^2. \quad (12)$$

This gives for the outer shell $(2s+2p)$ in the case of LiF, a value between 0.001 and 0.6 nuclear magneton as $\bar{\omega}$ is varied between the limits indicated above.[12] The magnetic field generated at the F nucleus depends on the charge distribution in the shell. For a shell consisting of s electrons, the field is obtained on multiplying the moment (12) by $(8/3\sqrt{\pi})(m\bar{\omega}/\hbar)^{3/2}$. The net result is a field proportional to $\bar{\omega}^{-5/2}$, so that *the contribution of the inner shells is negligible compared to that of the outer shells*, as we stated before. On the other hand, it is found that for a $2p$ shell the field at the center is much weaker than for $2s$ electrons, because of the lower density at the center. Assuming for an optimistic evaluation the formula for s electrons and applying it also to the $2p$ electrons, the ensuing field is still uncomfortably small. It may be pushed up to 2.5 gauss in LiF, or one-half the experimental value, by assuming for $\bar{\omega}$ the lower limit indicated above, but this is already an extreme assumption; since we are dealing with the perturbation caused by a homogeneous field, the higher value of $\bar{\omega}$ indicated by the polarizability should be much nearer to the truth.

Considering now the third term in Eq. (11), we may have the advantage that for this type of perturbation the average excitation energy may be closer to the lower limit of 5 ev. On the other hand, the result will be smaller by a factor $(r_0/r)^2$, r_0 being an average radius of the F$^-$ ion. This is confirmed by the detailed computation in the case of the elastically bound electrons. The effect of the perturbation is to make the frequency $\bar{\omega}_1$ in the direction of the line joining the nuclei lower than the frequency $\bar{\omega}_2$ in a perpendicular direction. We do not give the details of the calculation, which is quite elementary, as all the matrix elements needed for Eqs. (3) and (4) are known. For s electrons the result is quite simple; the stream lines instead of being circles, are equilateral hyperbolae $y^2-z^2=\text{const}$. The magnetic moment is $[(\bar{\omega}_2-\bar{\omega}_1)/(\bar{\omega}_2+\bar{\omega}_1)]^2$ times the moment for rigid rotation. This factor turns out to be 0.3. The field at the center is only 0.12 of the field for rigid rotation, assuming an optimistic value $\bar{\omega}=10^{16}$. All these data refer to LiF; in CsF the disagreement with experiment is stronger, because of the larger internuclear distance. We have also examined the case of p electrons; the current distribution is then so unfavorable that the field in the center becomes quite negligible.

The conclusion to be drawn from all this is that the polarized-ion model does not give a very satisfactory representation of the facts, although by some stretching it can be made to yield fields that are not much smaller than those observed.

It may be pointed out that the models we have considered so far do not clearly exhibit one feature that may be of importance. Let us first consider the extreme case of a molecule with a very low excited Π-state, connected to the Σ ground state by a strong L_{n0} matrix element. This will obviously make the induced momentum, Eq. (4), very strong. Physically, this means that the molecule has a nearly free angular momentum that tends to set itself parallel to the rotation axis. Now, although the alkali halides certainly do not approach this extreme case, it is clear that the kind of gyroscope-like distortion of the electronic motion we have just described will be present to a certain extent. In particular it may be noticed[13]

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[12] It may be pointed out that this result is not really dependent on the special assumption of elastically bound electrons. One may arrive at a formula perfectly similar to Eq. (12), with the sole difference that $\hbar\bar{\omega}$ is replaced by an average excitation energy of the electrons, if one replaces in Eq. (4) the energy difference in the denominator by an average value, thus expressing the magnetic moment in a form similar to Eq. (6). The average value of L_x^2 for the shell, when it is polarized by the homogeneous field, may be evaluated by perturbation theory, again introducing a suitable average value for the excitation energy.

[13] H. M. Foley, in the press. I wish to thank Dr. Foley for allowing me to see his manuscript before publication.

that the partially non-ionic character of the ground state will endow the molecule with a small component of orbital angular momentum precessing about the internuclear axis (this momentum being due to the hole in the $2p$ shell of the F atom, when it is in the neutral state). What is more important, it is not difficult to see that the currents induced by the rotation under these circumstances have just the type of space distribution that is most favorable to a strong field in the center,[11] so that the assumption made at the end of Section III about the connection between L_{n0} and H_{n0} is in this case well justified. It seems, therefore, that this model may give a satisfactory account of the data.

I wish to thank Dr. Rabi for attracting my attention to the large width of the resonance lines in LiF, CsF. Dr. Van Vleck kindly made available to me an early evaluation he had made independently by means of Hebb's formulae (unpublished). I am deeply indebted especially to Dr. Teller for his friendly interest and much helpful advice.

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Note on the Dirac Character Operators

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The Dirac character operators are evaluated for the classes of the symmetric group consisting of the triad, double interchange, tetrad, and pentad, and the corresponding group-theoretical primitive characters are listed for comparison. It is also shown that the evaluation of these and similar character operators is all that is required for the solution of the standard molecular problems in the spirit of Dirac's original program which avoids appeal to formal group theory.

I. INTRODUCTION

SOME years ago Dirac[1] established the remarkable exchange-spin identity

$$\mathbf{P}_{ij}=-\tfrac{1}{2}(1+\boldsymbol{\sigma}_i\cdot\boldsymbol{\sigma}_j), \qquad (1)$$

which expresses the simple interchanges of electron orbits in terms of the associated vector-spin operators. In the discussion of the classification of multiplets he introduced the character (class) operators

$$\chi_c=\frac{1}{n_c}\sum_{\text{class}}\mathbf{P}_c, \qquad (2)$$

defined as the average of all similar permutations, and showed that the *almost* exclusive states are characterized by the different sets of eigenvalues of these operators. These operators commute with all permutations so that in an irreducible representation of the symmetric group their matrices are scalar (Schur's lemma),[2] and it follows that the eigenvalues of the χ's are simply the corresponding primitive group characters divided by the dimension of the representation;[3] *viz.*,

$$\chi'[2^{\alpha_2}\cdots n^{\alpha_n}]=[2^{\alpha_2}\cdots n^{\alpha_n}]/[I], \qquad (3)$$

where $\{2^{\alpha_2}\cdots n^{\alpha_n}\}$ is the usual group exponent notation (omitting unary cycles) for the partition[4] of n defining the class of permutations, and the square brackets indicate the associated primitive characters; $[I]$ being that of the unit class. From the result (1) and the expression

$$\sum_{i<j}(\boldsymbol{\sigma}_i\cdot\boldsymbol{\sigma}_j)=\tfrac{1}{2}[4S(S+1)-3n]=\boldsymbol{\mu} \qquad (4)$$

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[1] Cf. P. A. M. Dirac, *Quantum Mechanics* (Clarendon Press, Oxford, 1935).

[2] Cf. F. D. Murnaghan, *Theory of Group Representations* (The Johns Hopkins University Press, Baltimore, 1938).

[3] This may be easily seen by operating on a degenerate set of eigenstates (symbolic $|\,\rangle$'s) with the χ's and taking the spur, the degree of degeneracy being, of course, the dimension of the representation.

[4] $\alpha_1+2\alpha_2+\cdots n\alpha_n=n$.