# The Rotational Stark Spectrum of Linear Molecules

HAROLD KENNETH HUGHES
*Technical Service Department, Socony-Vacuum Laboratories, Brooklyn, New York*
(Received July 20, 1949)

In the electric resonance method of radiofrequency spectroscopy various molecular and nuclear parameters of linear polar molecules may be determined from observations of the $1,0\rightarrow1,\pm1$ transition. An equation is given for the energy difference of these two states which is good to terms in $\lambda^6$ up to values of $\lambda=1.0$, where $\lambda$ is a quantity which is proportional to the electric field strength. From this equation, expressions are derived for the permanent electric dipole moment and the moment of inertia in terms of experimentally determined parameters.

## I. INTRODUCTION

IN the investigation of molecular and nuclear structure by the electric resonance method of radiofrequency spectroscopy[1-3] the practice has been, up to the present time, to interpret the experimental results with the aid of Brouwer's equation.[4] This perturbation equation describes the rotational energy levels of a linear polar molecule which is rotating in the presence of an electric field. Representing the rotational quantum number by $R$ and the electric quantum number by $p$, the energy of the $R=1$, $p=0$ state was stated by Brouwer to be

$$\epsilon=2+(1/10)\lambda^2-(73/7900)\lambda^4+\cdots, \quad (1)$$

where $\epsilon$ is in units of $\hbar^2/2I$, $I$ is the moment of inertia in g-cm$^2$, $\lambda=\mu E/(\hbar^2/2I)$, $\mu$ is the permanent electric dipole moment in e.s.u. and $E$ in the electric field strength in e.s.u.

However, there is an error[5] in Brouwer's published value for the coefficient of the $\lambda^4$-term in Eq. (1) and the correct energy of the 1,0 state, to this degree of approximation, is given by the expression

$$\epsilon=2+(1/10)\lambda^2-(73/7000)\lambda^4+\cdots. \quad (2)$$

Brouwer's equation for the $1,\pm1$ state is given correctly in reference 1.

In considering the effect of this error on the reported values for the moment of inertia and the electric dipole moment of CsF, the author discovered that Brouwer's equations are not sufficiently accurate for use with the $1,0\rightarrow1,\pm1$ transition at values of $\lambda$ as high as 0.8. It is the purpose of this paper to extend his equations by the addition of terms in $\lambda^6$. These yield values of $\Delta\epsilon$ for the transition which are good to within 0.008 percent up to $\lambda=0.8$. The error at $\lambda=1$ is only 0.04 percent. These new equations are adequate for the interpretation of all data collected up to the present and should serve well for experiments now in progress and being designed.

When there are terms in the Hamiltonian arising from a nuclear electric quadrupole moment or from an **I·R** type of coupling, the equations in this paper can still be applied. When these terms are small, it is only necessary to calculate the unperturbed center of gravity of the split lines. When the quadrupole coupling is large, this is determined at low fields and then the unperturbed position of a high field Stark line calculated.

## II. ENERGY OF THE 1,0 AND 1, ±1 STATES

To obtain values of $\Delta\epsilon$ reliable to within 0.04 percent, the exact energies of the two levels which are involved in the transition have been calculated to seven significant figures by Lamb's equation.[1] The results for values of $\lambda$ between 0 and 1.0, in steps of 0.1, are tabulated in Table I, together with the corresponding energies as calculated by Brouwer's corrected equations.

In the analysis of data from observations of the $1,0\rightarrow1,\pm1$ transition, it is desirable to have an analytic expression for the energy. Lamb's equation for the energy eigenvalues is in the form of a continued fraction which is not well suited to rapid use. Therefore, empirical equations have been prepared which fit Lamb's equation very well up to $\lambda=1.0$. For the 1,0

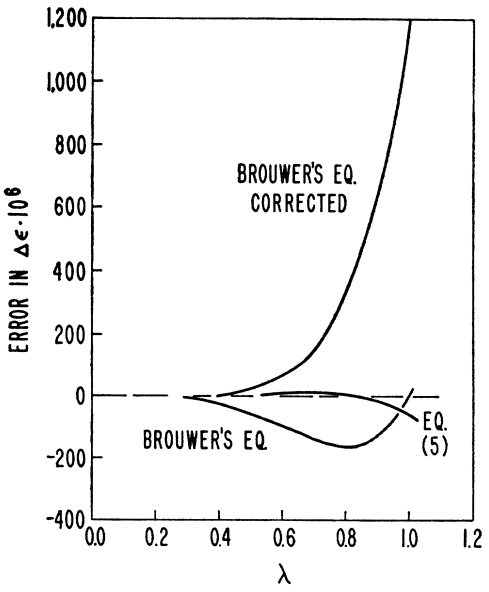


FIG. 1. Error in $\Delta\epsilon$ as a function of $\lambda$.

[1] H. K. Hughes, Phys. Rev. **72**, 614 (1947).
[2] J. W. Trischka, Phys. Rev. **74**, 718 (1948).
[3] U. Fano, J. Research Nat. Bur. of Stand. **40**, 215 (1948).
[4] F. Brouwer, Dissertation, Amsterdam, 1930.
[5] The author is indebted to Professor J. W. Trischka of Syracuse University for communicating this observation.

TABLE I. Energy of the 1,0 and 1, ±1 states in units of $\hbar^2/2I$.

| λ | 1,0 state | | | 1, ±1 state | |
|---|---|---|---|---|---|
| | Brouwer corrected | Lamb | Eq. (3) | Brouwer | Lamb and Eq. (4) |
| 0.0 | 2.0000000 | 2.0000000 | 2.0000000 | 2.0000000 | 2.0000000 |
| 0.1 | 2.0009990 | 2.0009990 | 2.0009990 | 1.999500 | 1.999500 |
| 0.2 | 2.0039833 | 2.0039834 | 2.0039834 | 1.9980005 | 1.9980005 |
| 0.3 | 2.008916 | 2.008917 | 2.008917 | 1.995503 | 1.995503 |
| 0.4 | 2.015733 | 2.015739 | 2.015738 | 1.992009 | 1.992009 |
| 0.5 | 2.024348 | 2.024369 | 2.024367 | 1.987521 | 1.987521 |
| 0.6 | 2.034648 | 2.034710 | 2.034706 | 1.982044 | 1.982044 |
| 0.7 | 2.046496 | 2.046647 | 2.046642 | 1.975582 | 1.975581 |
| 0.8 | 2.059729 | 2.060057 | 2.060054 | 1.968139 | 1.968138 |
| 0.9 | 2.074158 | 2.074807 | 2.074817 | 1.959723 | 1.959720 |
| 1.0 | 2.089571 | 2.090761 | 2.090811 | 1.950339 | 1.950334 |

state, we have

$$\epsilon=2+(1/10)\lambda^2-(73/7000)\lambda^4+0.00124\lambda^6. \quad (3)$$

Up to $\lambda=0.8$ a somewhat better fit is obtained using 0.00126 as the coefficient of the $\lambda^6$-term.

For the 1, ±1 state, values of $\epsilon$ derived from the equation,

$$\epsilon=2-(1/20)\lambda^2+(19/56{,}000)\lambda^4-5\cdot10^{-6}\lambda^6, \quad (4)$$

are identical, to seven significant figures, with those derived from Lamb's equation.

Values of $\Delta\epsilon$ are given in Table II. The last column is computed from the equation

$$\Delta\epsilon=0.15\lambda^2-0.010768\lambda^4+0.00125\lambda^6. \quad (5)$$

The error in Eq. (5) rises to a maximum of 0.0076 percent at about $\lambda=0.6$, drops to zero near $\lambda=0.8$ and thereafter increases steadily. At $\lambda=1.0$, the error is, however, still only 0.039 percent. In comparison with these figures, the error in Brouwer's corrected fourth degree equation rises steadily and is 0.85 percent at $\lambda=1.0$. Figure 1 shows the error in $\Delta\epsilon$ as a function of $\lambda$. It is seen clearly that the best value for the coefficient of the $\lambda^6$-term depends upon the range in $\lambda$ covered by any particular set of experimental data. The value 0.00125 is the best compromise for values between 0 and 0.9. Values lower than 0.00125 raise the error moderately at lower values of $\lambda$ but improve the fit at the upper end.

## III. QUADRATIC APPROXIMATION TO $\Delta\epsilon/\lambda^2$

Over a limited range of $\lambda$ or when the precision of the experimental data does not justify the labor of fitting a sixth degree equation, it is convenient to draw the best straight line through the points of a $\Delta\epsilon/\lambda^2$ *vs.* $\lambda^2$ plot. The line may also be fitted by the least-squares method.

Let two constants, $\alpha'$ and $\beta'$, be defined by the equation

$$(\Delta\epsilon/\lambda^2)=\alpha'-\beta'\lambda^2. \quad (6)$$

The least-squares method has been applied to the determination of $\alpha'$ and $\beta'$, using the data in the third column of Table II. Over the range $\lambda=0.1$ to 0.8, $\alpha'=0.1499$ and $\beta'=0.00998$. Between the limits of 0.5 and 0.8, the best fit is obtained with $\alpha'=0.1498$ and $\beta'=0.00966$. These values are to be compared with $\alpha'=0.1500$, $\beta'=0.00958$ for Brouwer's original equation and with $\alpha'=0.1500$, $\beta'=0.01077$ for the corrected version. It is readily seen that the incorrect equation actually gives the better fit to the true values. $\alpha'$ is changed but little by varying the range; $\beta'$, however, does show a significant dependence on this factor.

TABLE II. Values of $\Delta\epsilon$ for the 1,0→1, ±1 transition.

| λ | Brouwer corrected | Lamb | Eq. (5) |
|---|---|---|---|
| 0.0 | 0.000000 | 0.000000 | 0.000000 |
| 0.1 | 0.001499 | 0.0014990 | 0.001499 |
| 0.2 | 0.005983 | 0.0059829 | 0.005983 |
| 0.3 | 0.013413 | 0.013414 | 0.013414 |
| 0.4 | 0.023724 | 0.023730 | 0.023729 |
| 0.5 | 0.036827 | 0.036848 | 0.036847 |
| 0.6 | 0.052604 | 0.052666 | 0.052662 |
| 0.7 | 0.070915 | 0.071066 | 0.071062 |
| 0.8 | 0.091590 | 0.091919 | 0.091918 |
| 0.9 | 0.114435 | 0.115087 | 0.115099 |
| 1.0 | 0.139232 | 0.140427 | 0.140482 |

## IV. EQUATIONS FOR THE MOMENT OF INERTIA AND THE ELECTRIC DIPOLE MOMENT

The data in experiments based on the electric resonance method of radiofrequency spectroscopy consist of values of the electric field strength in volts per cm and the corresponding resonant frequency in cycles per second. From these, two experimentally determined constants, $\alpha$ and $\beta$, defined by the equation

$$f/E^2=\alpha-\beta E^2+\gamma E^4 \quad (7)$$

are derived by the least-squares method. From Eqs. (6) and (7) the following expressions are obtained for the electric dipole moment, $\mu$, in e.s.u. and the moment of inertia, $I$, in gm-cm$^2$.

$$\mu^2=300^2\hbar^2(\alpha/\alpha')^3(\beta'/\beta). \quad (8)$$

$$I=(\hbar/4\pi)(\beta/\beta')(\alpha'/\alpha)^2. \quad (9)$$

In reference 1 the values of $\alpha$ and $\beta$, derived from a series of experiments between $\lambda=0.1$ and 0.8, were reported as follows: $\alpha=448\pm5.4$ and $\beta=(1.91\pm0.23)\times10^{-5}$. Inserting these values and the values of $\alpha'$ and $\beta'$, derived above for this range, into Eqs. (8) and (9), there is obtained:

$$\mu=7.42\pm0.47 \text{ debye},$$

and

$$I=(180\pm22)10^{-40} \text{ g-cm}^2.$$

The inter-nuclear distance, $r$, derived from $I$ is

$$r=(2.55\pm0.16)10^{-8} \text{ cm}.$$

$B$, the rotational constant, is:

$$B=(1/hc)(\hbar^2/2I)=0.156 \text{ cm}^{-1}.$$

It is likely that these figures which are weighted averages for the unresolved vibrational states, correspond approximately to those for the $v=1$ or $v=2$ vibrational states which Trischka[2] resolved.

V. ACKNOWLEDGMENTS

I wish to thank Professor P. Kusch and Professor Charles Townes of Columbia University for suggesting improvements in this paper.

PHYSICAL REVIEW VOLUME 76, NUMBER 11 DECEMBER 1, 1949

# On the Interactions of Mesons with the Electromagnetic Field

M. NEUMAN* AND W. H. FURRY
*Harvard University, Cambridge, Massachusetts*
(Received July 11, 1949)

By means of the formalism of Duffin and Kemmer there is constructed for mesons interacting with the electromagnetic field a theory that is manifestly Lorentz invariant and also gauge invariant and invariant under charge conjugation. The transformation to an interaction representation is accomplished by a procedure necessarily somewhat more complicated than that used by Schwinger for the quantum electrodynamics of electrons. The longitudinal components of the electromagnetic field are eliminated in a covariant manner.

The resulting interaction Hamiltonian is analyzed into terms corresponding to self-energies and terms describing interactions. By a suitable interpretation of ambiguous expressions, the photon self-energy is shown to vanish. Expressions are found for the polarization of the mesic vacuum by a given electromagnetic field. In the case of mesons of spin 1, not only the term proportional to the original current, but also that proportional to its d'Alembertian has an infinite factor. A formal procedure for the unambiguous exclusion of such infinite contributions is suggested. Explicit expressions are found for the self-energies of scalar and vector mesons. These self-energies can be eliminated by renormalization of mass.

## INTRODUCTION

IN the last few years the theory of quantum electrodynamics, or the interaction of electrons and positrons with the quantized electromagnetic field, has been advanced into a rather satisfactory condition. The new developments of the theory have been found to agree well with the latest experimental results.

Although precise experimental data on electromagnetic effects are available only for electrons, there is good reason to believe in the existence of charged mesons of spin 0, and there is at least considerable speculation about similar particles of spin 1. Thus an appreciable interest attaches to the various theoretical discussions of such particles.

In the present paper the theory for mesons of spins 0 and 1 is developed throughout on the basis of Kemmer's formulation of the wave equations of these particles. In this formulation the equations of motion and the expression for the current are formally precisely like those for the Dirac electron, and charge conjugation can be defined in a very similar way. We thus have the possibility of developing the theory in the closest possible analogy to Schwinger's treatment of quantum electrodynamics.

There are a number of necessary differences in the treatment, and in all such respects the electron case is the simpler. A main source of additional complication is the fact that in the Kemmer case not all components of the wave function are dynamically independent. When properly formulated, the commutation relations involve only the dynamically independent parts of the wave function. The remaining part of the wave function is expressed by means of space-like derivatives of the dynamically independent part.

The introduction of an interaction representation, which is accomplished in the Dirac case by a unitary transformation, here requires, in addition, a redefinition of the particle wave function. Because the interaction Hamiltonian density involves space-like derivatives of the dynamically independent wave function, a more precise statement of the meaning of differential operators in various representations is necessary. The interaction Hamiltonian density in the Kemmer case is not precisely the negative of the coupling term in the Lagrangian, as it is in quantum electrodynamics.

The Kemmer case resembles the Dirac case in that it is possible, by identical physical considerations, to resolve the ambiguities inherent in the interpretation of divergent integrals in such a way that the self-energy of a photon is found to vanish. The elimination of the longitudinal components of the electromagnetic field is also accomplished in essentially the same way in both cases.

A major difference in the results appears in the polarization of the vacuum due to fluctuations in the vector meson field. The possibility of the simple procedure of charge renormalization depends on the absence of higher order derivatives in the polarization kernel, and is thus an accidental feature of fields of spins 0 and $\frac{1}{2}$. For the vector meson case an unambiguous procedure for eliminating the infinite polarization

* Now at Institute for Advanced Study, Princeton, New Jersey.