rather good considering the difference in the methods. Fig. 5 shows a similar comparison between the radial charge density for $(1s)(2p)\ ^1P$ and $(1s)(2p)\ ^3P$ as computed by Eckart[3] by the variational method and $-dZ/dr$ for this state from the self-consistent field calculations. The agreement is again seen to be very gratifying. It is interesting to note that the density for the singlet state of Eckart agrees better with the present values than does that for the triplet.

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The van der Waals Interaction of Hydrogen Atoms

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The van der Waals interaction energy of two hydrogen atoms at large internuclear distances is discussed by the use of a linear variation function. By including in the variation function, in addition to the unperturbed wave function, 26 terms for the dipole-dipole interaction, 17 for the dipole-quadrupole interaction, and 26 for the quadrupole-quadrupole interaction, the interaction energy is evaluated as

$$W'' = -\frac{6.49903\, e^2}{a_0\, \rho^6} - \frac{124.399\, e^2}{a_0\, \rho^8} - \frac{1135.21\, e^2}{a_0\, \rho^{10}} - \cdots,$$

in which $\rho = R/a_0$, with R the internuclear distance. Some properties of the functions $F_{\nu\lambda\mu}(\xi, \vartheta, \varphi)$, which are orthogonal for the volume element $\xi d\xi \sin \theta d\theta d\varphi$, are discussed, and their usefulness in atomic problems is pointed out.

INTRODUCTION

An approximate second-order perturbation treatment of the inverse sixth power interaction energy of two hydrogen atoms a large distance apart (corresponding to the so-called dipole-dipole van der Waals attraction) was given in 1930 by Eisenschitz and London.[1] This treatment led to the result $W'' = -e^2 A/a_0\rho^6$, with $\rho = r_{AB}/a_0$ (r_{AB} being the internuclear distance for the two atoms), A being evaluated as 6.47. Applications of the variation method by Hassé[2] and by Slater and Kirkwood[3] verified this result essentially, the constant A being shown to be equal to or greater than 6.4976.

As early as 1927 this problem had been attacked by Wang,[4] using the method developed by Epstein[5] for the treatment of the Stark effect. Wang claimed to have obtained an exact solution; it was, however, pointed out by Eisenschitz and London that Wang's result is necessarily in error. It seemed to us possible that Wang's work might have contained only a numerical error, and that the method might actually be capable of giving an exact solution. Because of the usefulness which a method of exact solution of problems of this sort would have, we thought it worth while to study the problem thoroughly. We have found that the method used by Wang does not give an exact solution,[6] but that it can be extended to give as closely approximate a solution as is desired. The results of the treatment are communicated in this paper.

A rough treatment of the dipole-quadrupole and quadrupole-quadrupole interactions of two hydrogen atoms has been published by Mar-

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[1] R. Eisenschitz and F. London, Zeits. f. Physik **60**, 491 (1930).

[2] H. R. Hassé, Proc. Camb. Phil. Soc. **27**, 66 (1931).

[3] J. C. Slater and J. G. Kirkwood, Phys. Rev. **37**, 682 (1931).

[4] S. C. Wang, Physik. Zeits. **28**, 663 (1927).

[5] P. S. Epstein, Phys. Rev. **28**, 695 (1926).

[6] Wang does not present the final steps in his calculation in detail, but states that he set up a sixth degree secular equation from which he obtained an accurate value for the energy. We believe that the error in his treatment occurs at this point.

genau.[7] We have applied our method to obtain reasonably accurate expressions for these interactions also.

FORMULATION OF THE PROBLEM

In the wave equation for two hydrogen atoms $H\psi=W\psi$ let us put $H=H^0+H'$, H^0 being the part of the Hamiltonian corresponding to two isolated hydrogen atoms and H' representing the interaction of the two hydrogen atoms. In order to do this we neglect the resonance phenomenon (which is unimportant at large distances), taking as the unperturbed wave function the product function $\psi_{100}(A1)\ \psi_{100}(B2)$; that is, we consider electron 1 to be attached to nucleus A and electron 2 to nucleus B. We also write $W=W^0+W''$ (W', the first-order perturbation energy, being equal to zero). We shall consider only the interaction of two normal hydrogen atoms, so that W^0 is equal to $-e^2/a_0$. Making the substitutions $\xi_1=2r_{A1}/a_0$ and $\xi_2=2r_{B2}/a_0$, the wave equation becomes

$$\left(\nabla_1{}^2+\frac{1}{\xi_1}-\frac{1}{4}\right)\psi+\left(\nabla_2{}^2+\frac{1}{\xi_2}-\frac{1}{4}\right)\psi-\frac{a_0}{2e^2}H'\psi=\lambda\psi, \quad (1)$$

in which $\lambda=-W''a_0/2e^2$.

The interaction H' is equal to

$$-e^2/r_{A2}-e^2/r_{B1}+e^2/r_{AB}+e^2/r_{12}.$$

If $R(=r_{AB})$ is large, this can be expanded[7] in inverse powers of R to give the expression

$$\begin{aligned} H'=&(e^2/R^3)(x_1x_2+y_1y_2-2z_1z_2)\\ &+(3/2)(e^2/R^4)\{r_1{}^2z_2-r_2{}^2z_1\\ &+(2x_1x_2+2y_1y_2-3z_1z_2)(z_1-z_2)\}\\ &+\tfrac{3}{4}(e^2/R^5)\{r_1{}^2r_2{}^2-5r_2{}^2z_1{}^2-5r_1{}^2z_2{}^2\\ &-15z_1{}^2z_2{}^2+2(x_1x_2+y_1y_2+4z_1z_2)^2\}+\cdots. \quad (2)\end{aligned}$$

In this expression $x_1y_1z_1$ are Cartesian coordinates of electron 1 relative to nucleus A, and $x_2y_2z_2$ those of electron 2 relative to nucleus B, the z axis for each being directed towards the other nucleus. The first term represents the mutual energy of two dipoles; this term alone is important for large values of R. The second and third terms represent the dipole-quadrupole and quadrupole-quadrupole interactions, respectively. It can be easily shown that in the calculation of the second-order perturbation energy the terms can be considered separately, their contributions being additive.

In the solution of the problem we shall make use of the functions $F_{\nu\lambda\mu}\ (\xi,\ \vartheta,\ \varphi)$ discussed in the appendix. Each of these functions can be made identical with a hydrogen-like wave function $\psi_{nlm}\ (r,\ \vartheta,\ \varphi)$ by choosing a suitable linear relation between r and ξ; the functions $F_{\nu\lambda\mu}$ all contain the same exponential function, in contradistinction to the functions ψ_{nlm}. We have defined ξ_1 and ξ_2 in such a way that $F_{100}\ (\xi_1,\ \vartheta_1,\ \varphi_1)$ and $F_{100}\ (\xi_2,\ \vartheta_2,\ \varphi_2)$ are identical with $\psi_{100}\ (r_1,\ \vartheta_1,\ \varphi_1)$ and $\psi_{100}\ (r_2,\ \vartheta_2,\ \varphi_2)$, respectively; that is, the unperturbed wave function can be written as $F_{100}\ (\xi_1)\ F_{100}\ (\xi_2)$. We now apply the variation method in treating the perturbed wave equation, using as the variation function a linear combination of the product functions $F_{\nu_1\lambda_1\mu_1}\ (\xi_1,\ \vartheta_1,\ \varphi_1)\ F_{\nu_2\lambda_2\mu_2}\ (\xi_2,\ \vartheta_2,\ \varphi_2)$, with arbitrary coefficients. It can be seen that the second-order perturbation energy for the perturbation function

$$\begin{aligned} H'=&-(2e^2/a_0)\{\alpha\xi_1\xi_2\cos\vartheta_1\cos\vartheta_2\\ &+\beta\xi_1\xi_2{}^2\cos\vartheta_1(3\cos^2\vartheta_2-1)\\ &+\gamma\xi_1{}^2\xi_2{}^2(3\cos^2\vartheta_1-1)(3\cos^2\vartheta_2-1)\\ &+\cdots\}, \quad (3)\end{aligned}$$

in which

$$\alpha=(6)^{\frac{1}{2}}a_0{}^3/8R^3,\quad \beta=(30)^{\frac{1}{2}}a_0{}^4/32R^4,\quad \text{and}\quad \gamma=(70)^{\frac{1}{2}}a_0{}^5/128R^5, \quad (4)$$

is identical with that for the function of Eq. (2), and, moreover, that to obtain the first-order perturbed wave function and the second-order perturbation energy, the variation function used need contain, in addition to the unperturbed part $F_{100}\ (\xi_1)\ F_{100}\ (\xi_2)$, only the terms $F_{\nu_1 10}\ (\xi_1,\ \vartheta_1)\ F_{\nu_2 10}\ (\xi_2,\ \vartheta_2)$ (for the dipole-dipole term in α), $F_{\nu_1 10}\ (\xi_1,\ \vartheta_1)\ F_{\nu_2 20}\ (\xi_2,\ \vartheta_2)$ (for the term in β), and $F_{\nu_1 20}\ (\xi_1,\ \vartheta_1)$. $F_{\nu_2 20}\ (\xi_2,\ \vartheta_2)$ (for the term in γ).[8]

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[7] H. Margenau, Phys. Rev. **38**, 747 (1931).

[8] On application of the ordinary methods of perturbation theory, it is seen that the first-order perturbed wave function for a normal hydrogen atom with perturbation function $f(r)T(\vartheta,\ \varphi)$, where T is a tesseral harmonic, has the form $\Psi_{100}(r)+\Phi(r)T(\vartheta,\ \varphi)$, the perturbed part involving the same tesseral harmonic as the perturbation function. The statements in the text can be verified by an extension of this argument.

For a linear variation function $\sum_l a_l \Phi_l$ (where Φ_l represents the product functions $F_{\nu_1\lambda_1\mu_1}(\xi_1, \vartheta_1, \varphi_1)\, F_{\nu_2\lambda_2\mu_2}(\xi_2, \vartheta_2, \varphi_2)$) the secular equation corresponding to the wave equation (1) is the determinantal equation[9]

$$|\mathcal{H}_{jk}{}^0 + \mathcal{H}_{jk}{}' - \Delta_{jk}\lambda| = 0, \qquad (5)$$

in which

$$\mathcal{H}_{jk}{}^0 = \int\int \Phi_j{}^*(\nabla_1{}^2 + (1/\xi_1) - \tfrac{1}{4} + \nabla_2{}^2 + (1/\xi_2) - \tfrac{1}{4})\Phi_k d\tau_1 d\tau_2,$$

$$\mathcal{H}_{jk}{}' = \int\int \Phi_j{}^*(-(a_0/2e^2)H')\Phi_k d\tau_1 d\tau_2,$$

and

$$\Delta_{jk} = \int\int \Phi_j{}^* \Phi_k d\tau_1 d\tau_2,$$

$d\tau_1$ being equal to $\xi_1{}^2 \sin \theta_1 d\xi_1 d\vartheta_1 d\varphi_1$ (with $d\tau_2$ differing only in the subscripts) and the integrals extending over the configuration space of the system. It is to be noted that the volume element $d\tau_1 d\tau_2$ is not such as to make the functions Φ mutually orthogonal. The integrals can be evaluated with the help of the relations given in the appendix. To obtain the second-order perturbation energy we need introduce the term in λ in the row and column corresponding to the wave function for the unperturbed system only.

THE DIPOLE-DIPOLE INTERACTION

The secular equation for the dipole-dipole interaction is

$$\begin{array}{c|ccccccccccc|}
\nu_1\lambda_1\mu_1\nu_2\lambda_2\mu_2 & & & & & & & & & & & \\
100100 & -4\lambda & 32\alpha & -16\alpha & -16\alpha & 8\alpha & 0 & 0 & 0 & 0 & 0 & \cdots \\
210210 & 32\alpha & -8 & 2 & 2 & 0 & 0 & 0 & 0 & 0 & 0 & \cdots \\
210310 & -16\alpha & 2 & -14 & 0 & 4 & \surd(10) & 0 & 0 & 0 & 0 & \cdots \\
310210 & -16\alpha & 2 & 0 & -14 & 4 & 0 & \surd(10) & 0 & 0 & 0 & \cdots \\
310310 & 8\alpha & 0 & 4 & 4 & -24 & 0 & 0 & 2\surd(10) & 2\surd(10) & 0 & \cdots \\
210410 & 0 & 0 & \surd(10) & 0 & 0 & -20 & 0 & 6 & 0 & 0 & \cdots \\
410210 & 0 & 0 & 0 & \surd(10) & 0 & 0 & -20 & 0 & 6 & 0 & \cdots \\
310410 & 0 & 0 & 0 & 0 & 2\surd(10) & 6 & 0 & -34 & 0 & 3\surd(10) & \cdots \\
410310 & 0 & 0 & 0 & 0 & 2\surd(10) & 0 & 6 & 0 & -34 & 3\surd(10) & \cdots \\
410410 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 3\surd(10) & 3\surd(10) & -48 & \cdots \\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot &
\end{array} = 0, \quad (6)$$

the rows and columns corresponding to the values of $\nu_1 \cdots \mu_2$ shown at the left. We obtain successive approximations to the solution of this equation by neglecting rows and columns beyond the nth. This process has been carried out for $n = 2$, 5, 10, 17 and 26. Some simplification is achieved by combining rows (and columns) with ν_1 and ν_2 interchanged, the corresponding functions having the same coefficient. The results of the calculation are given in Table I, in terms of the constant A in the expression $W'' = -Ae^2/a_0\rho^6$, with $\rho = R/a_0$ (A being equal to $3\lambda/16\alpha^2$).

TABLE I. *The dipole-dipole interaction constant A.*

Degree of approx.	Terms included		A
2	$\nu_1 \leq 2$,	$\nu_2 \leq 2$	6
5	3	3	6.4822
10	4	4	6.4984
17	5	5	6.49899
26	6	6	6.49903

TABLE II. *The dipole-quadrupole interaction constant B.*

Degree of approx.	Terms included		B
2	$\nu_1 \leq 2$,	$\nu_2 \leq 3$	115.7
5	3	4	124.10
10	4	5	124.386
17	5	6	124.399

TABLE III. *The quadrupole-quadrupole interaction constant C.*

Degree of approx.	Terms included		C
2	$\nu_1 \leq 3$,	$\nu_2 \leq 3$	1063.1
5	4	4	1132.6
10	5	5	1134.35
17	6	6	1135.12
26	7	7	1135.21

It is seen that the convergence is rapid, the final value of A, 6.49903, being trustworthy to within one unit in the last decimal place.

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[9] See, for example, L. Pauling and E. B. Wilson, Jr., *Introduction to Quantum Mechanics, with Applications to Chemistry*, McGraw-Hill Book Co., **1935**, Chap. VII.

THE DIPOLE-QUADRUPOLE INTERACTION

The secular equation for the dipole-quadrupole interaction is

$$\begin{array}{c|ccccccccccc|l}
\nu_1\lambda_1\mu_1\nu_2\lambda_2\mu_2 & & & & & & & & & & & & \\
100100 & -4\lambda & -192\surd(3)\beta & 96\surd(3)\beta & 96\sqrt{2}\beta & -48\sqrt{2}\beta & 0 & 0 & 0 & 0 & 0 & \cdots & \\
210320 & -192\surd(3)\beta & -14 & 4 & \surd(6) & 0 & 0 & 0 & 0 & 0 & 0 & \cdots & \\
310320 & 96\surd(3)\beta & 4 & -24 & 0 & 2\surd(6) & 2\surd(10) & 0 & 0 & 0 & 0 & \cdots & \\
210420 & 96\sqrt{2}\beta & \surd(6) & 0 & -20 & 6 & 0 & \surd(14) & 0 & 0 & 0 & \cdots & \\
310420 & -48\sqrt{2}\beta & 0 & 2\surd(6) & 6 & -34 & 0 & 0 & 3\surd(10) & 2\surd(14) & 0 & \cdots & \\
410320 & 0 & 0 & 2\surd(10) & 0 & 0 & -34 & 0 & 3\surd(6) & 0 & 0 & \cdots & \\
210520 & 0 & 0 & 0 & \surd(14) & 0 & 0 & -26 & 0 & 8 & 0 & \cdots & =0. \quad (7)\\
410420 & 0 & 0 & 0 & 0 & 3\surd(10) & 3\surd(6) & 0 & -48 & 0 & 3\surd(14) & \cdots & \\
310520 & 0 & 0 & 0 & 0 & 2\surd(14) & 0 & 8 & 0 & -44 & 4\surd(10) & \cdots & \\
410520 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 3\surd(14) & 4\surd(10) & -62 & \cdots & \\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & & \\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & & \\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & &
\end{array}$$

We have solved this equation approximately, the results being given in Table II in terms of the constant B in the energy expression $-Be^2/a_0\rho^8$.

The error in the final value of B we estimate to be less than one unit in the last figure quoted.

THE QUADRUPOLE-QUADRUPOLE INTERACTION

The secular equation for the quadrupole-quadrupole interaction is

$$\begin{array}{c|ccccccccccc|l}
\nu_1\lambda_1\mu_1\nu_2\lambda_2\mu_2 & & & & & & & & & & & & \\
100100 & -4\lambda & 3456\gamma & -576\surd(6)\gamma & -576\surd(6)\gamma & 576\gamma & 0 & 0 & 0 & 0 & 0 & \cdots & \\
320320 & 3456\gamma & -24 & 2\surd(6) & 2\surd(6) & 0 & 0 & 0 & 0 & 0 & 0 & \cdots & \\
320420 & -576\surd(6)\gamma & 2\surd(6) & -34 & 0 & 3\surd(6) & 2\surd(14) & 0 & 0 & 0 & 0 & \cdots & \\
420320 & -576\surd(6)\gamma & 2\surd(6) & 0 & -34 & 3\surd(6) & 0 & 2\surd(14) & 0 & 0 & 0 & \cdots & \\
420420 & 576\gamma & 0 & 3\surd(6) & 3\surd(6) & -48 & 0 & 0 & 3\surd(14) & 3\surd(14) & 0 & \cdots & \\
320520 & 0 & 0 & 2\surd(14) & 0 & 0 & -44 & 0 & 4\surd(6) & 0 & 0 & \cdots & \\
520320 & 0 & 0 & 0 & 2\surd(14) & 0 & 0 & -44 & 0 & 4\surd(6) & 0 & \cdots & =0. \quad (8)\\
420520 & 0 & 0 & 0 & 0 & 3\surd(14) & 4\surd(6) & 0 & -62 & 0 & 4\surd(14) & \cdots & \\
520420 & 0 & 0 & 0 & 0 & 3\surd(14) & 0 & 4\surd(6) & 0 & -62 & 4\surd(14) & \cdots & \\
520520 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 4\surd(14) & 4\surd(14) & -80 & \cdots & \\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & & \\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & & \\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & &
\end{array}$$

The results of the approximate solution of this equation, in terms of the constant C in the energy expression $-Ce^2/a_0\rho^{10}$, are given in Table III.

The final value, $C=1135.21$, is reliable except for the last figure.

DISCUSSION OF RESULTS

We have thus found for the interaction energy of two normal hydrogen atoms at the large distance $R=\rho a_0$ the expression

$$W''=-\frac{6.49903\ e^2}{a_0\rho^6}-\frac{124.399\ e^2}{a_0\rho^8}-\frac{1135.21\ e^2}{a_0\rho^{10}}-\cdots. \qquad (9)$$

It is interesting to note that the value $A=6.4976$ found by Hassé for the dipole-dipole coefficient by the use of a variation function $\psi_{100}\ (r_1)\ \psi_{100}\ (r_2)\ \{1+H'(A+Br_1r_2+Cr_1^2r_2^2+Dr_1^3r_2^3)\}$ is very close to our value for $\nu_1\leq 4$, $\nu_2\leq 4$, which is based on a variation function involving all terms (unsymmetric as well as symmetric) out to $r_1^3r_2^3$. This indicates that the unsymmetric terms are of minor importance.

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[10] We use here shortened symbols, such as $F_{\nu_1}F_{\nu_2}$ for $F_{\nu_1\lambda_1\mu_1}(\xi_1,\vartheta_1,\varphi_1)F_{\nu_2\lambda_2\mu_2}(\xi_2,\vartheta_2,\varphi_2)$, etc.

The approximate second-order perturbation energy $W_0'' = (H_{00}')^2/W_0^0$, with $W_0^0 = -e^2/a_0$, leads to the values $A=6$, $B=135$, and $C=1417.5$, the last two values being given by Margenau.[7] It is seen that the value of A is too low, and those of B and C are too high. This means that the dipole-dipole interaction is due more to excited states with negative energy (less than e^2/a_0 above the normal state of the system of two hydrogen atoms) than to excited states with positive energy, whereas the dipole-quadrupole and quadrupole-quadrupole interactions are due more to the latter than to the former states.

As has been pointed out by earlier authors, the van der Waals forces are more important than exchange forces for values of R greater than about $7a_0$. At this distance the dipole-quadrupole force is about one-half as large as the dipole-dipole force, and the quadrupole-quadrupole force is about one-eighth as large, the dipole-dipole attraction becoming relatively still more important at larger distances. This van der Waals calculation, based on product wave functions, is not significant for values of R much less than $7a_0$ because of neglect of the resonance phenomenon and because of failure of the expansion given in Eq. (2).

While our treatment has not led to an exact solution of our problem, the use of the functions $F_{\nu\lambda\mu}(\xi, \vartheta, \varphi)$ has permitted the reasonably accurate approximate solution to be made with considerable ease, and we feel that these functions may be found useful in the treatment of other problems of atomic and molecular structure.[11]

APPENDIX

The functions $F_{\nu\lambda\mu}(\xi, \vartheta, \varphi)$

We define

$$F_{\nu\lambda\mu}(\xi, \vartheta, \varphi) = \Lambda_{\nu\lambda}(\xi)\Theta_{\lambda\mu}(\vartheta)\Phi_\mu(\varphi),$$

with

$$\Lambda_{\nu\lambda}(\xi) = \{(\nu-\lambda-1)!/[(\nu+\lambda)!]^3\}^{\frac{1}{2}} e^{-\xi/2}\xi^\lambda L_{\nu+\lambda}{}^{2\lambda+1}(\xi),$$

L being an associated Laguerre polynomial,

$$\Theta_{\lambda\mu}(\vartheta) = \{[(2\lambda+1)(\lambda-\mu)!]/2(\lambda+\mu)!\}^{\frac{1}{2}} P_\lambda{}^{|\mu|}(\cos\vartheta),$$

P being an associated Legendre function, and

$$\Phi_\mu(\varphi) = (2\pi)^{-\frac{1}{2}} e^{i\mu\varphi}.$$

The functions are orthogonal and normalized for the weight function $\xi \sin\vartheta$, satisfying the equation

$$\int_0^\infty \int_0^\pi \int_0^{2\pi} F'_{\nu'\lambda'\mu'}(\xi, \vartheta, \varphi) F_{\nu\lambda\mu}(\xi, \vartheta, \varphi)\xi \sin\vartheta d\varphi d\vartheta d\xi = \delta_{\nu'\nu}\delta_{\lambda'\lambda}\delta_{\mu'\mu}.$$

$F_{\nu\lambda\mu}(\xi, \vartheta, \varphi)$ satisfies the differential equation

$$(\nabla^2 + 1/\xi - \tfrac{1}{4})F_{\nu\lambda\mu} = -[(\nu-1)/\xi]F_{\nu\lambda\mu}.$$

The following relations involving the Λ's can be easily derived from the properties of the associated Laguerre polynomials:

$$\xi\Lambda_{\nu\lambda} = -\{(\nu-\lambda)(\nu+\lambda+1)\}^{\frac{1}{2}}\Lambda_{\nu+1,\,\lambda} + 2\nu\Lambda_{\nu\lambda} - \{(\nu+\lambda)(\nu-\lambda-1)\}^{\frac{1}{2}}\Lambda_{\nu-1,\,\lambda}.$$

$$\begin{aligned}\xi^2\Lambda_{\nu\lambda} = &-\{(\nu-\lambda)(\nu+\lambda+1)(\nu+\lambda+2)(\nu+\lambda+3)\}^{\frac{1}{2}}\Lambda_{\nu+2,\,\lambda+1}\\ &+2(2\nu-\lambda)\{(\nu+\lambda+1)(\nu+\lambda+2)\}^{\frac{1}{2}}\Lambda_{\nu+1,\,\lambda+1} - 6\nu\{(\nu+\lambda+1)(\nu-\lambda-1)\}^{\frac{1}{2}}\Lambda_{\nu,\,\lambda+1}\\ &+2(2\nu+\lambda)\{(\nu-\lambda-1)(\nu-\lambda-2)\}^{\frac{1}{2}}\Lambda_{\nu-1,\,\lambda+1} - \{(\nu+\lambda)(\nu-\lambda-1)(\nu-\lambda-2)(\nu-\lambda-3)\}^{\frac{1}{2}}\Lambda_{\nu-2,\,\lambda+1}.\end{aligned}$$

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[11] *Added in proof:* Professor J. H. Van Vleck has pointed out to us that the functions were used in the treatment of dispersion by hydrogen-like atoms by B. Podolsky, Proc. Nat. Acad. Sci. **14**, 253 (1928).

$$\begin{aligned}\xi^3\Lambda_{\nu\lambda}= &-\{(\nu-\lambda)(\nu+\lambda+1)(\nu+\lambda+2)(\nu+\lambda+3)(\nu+\lambda+4)(\nu+\lambda+5)\}^{\frac{1}{2}}\Lambda_{\nu+3,\ \lambda+2}\\ &+2(3\nu-2\lambda)\{(\nu+\lambda+1)(\nu+\lambda+2)(\nu+\lambda+3)(\nu+\lambda+4)\}^{\frac{1}{2}}\Lambda_{\nu+2,\ \lambda+2}\\ &-5(3\nu-\lambda)\{(\nu-\lambda-1)(\nu+\lambda+1)(\nu+\lambda+2)(\nu+\lambda+3)\}^{\frac{1}{2}}\Lambda_{\nu+1,\ \lambda+2}\\ &+20\nu\{(\nu+\lambda+1)(\nu+\lambda+2)(\nu-\lambda-1)(\nu-\lambda-2)\}^{\frac{1}{2}}\Lambda_{\nu,\ \lambda+2}\\ &-5(3\nu+\lambda)\{(\nu+\lambda+1)(\nu-\lambda-1)(\nu-\lambda-2)(\nu-\lambda-3)\}^{\frac{1}{2}}\Lambda_{\nu-1,\ \lambda+2}\\ &+2(3\nu+2\lambda)\{(\nu-\lambda-1)(\nu-\lambda-2)(\nu-\lambda-3)(\nu-\lambda-4)\}^{\frac{1}{2}}\Lambda_{\nu-2,\ \lambda+2}\\ &-\{(\nu+\lambda)(\nu-\lambda-1)(\nu-\lambda-2)(\nu-\lambda-3)(\nu-\lambda-4)(\nu-\lambda-5)\}^{\frac{1}{2}}\Lambda_{\nu-3,\ \lambda+2}.\end{aligned}$$

From these we obtain similar relations in the F's. The following special cases are needed in evaluating the matrix elements in Eqs. (6), (7) and (8):

$$\begin{aligned}\xi F_{100}&=-\sqrt{2}F_{200}+2F_{100},\\ \xi^2\cos\vartheta F_{100}&=-2\sqrt{2}F_{310}+4\sqrt{2}F_{210},\\ \xi^3(3\cos^2\vartheta-1)F_{100}&=-24F_{420}+24\sqrt{(6)}F_{320}.\end{aligned}$$

The evaluation of the matrix elements

In order to illustrate the method of construction of the matrices in Eqs. (6), (7) and (8), we shall evaluate some of the integrals. Let us first consider the integral[10]

$$\mathcal{H}^0_{\nu_1'\nu_2'\nu_1\nu_2}=\int\int F^*_{\nu_1'}F^*_{\nu_2'}\{\nabla_1^2+1/\xi_1-\tfrac{1}{4}+\nabla_2^2+1/\xi_2-\tfrac{1}{4}\}F_{\nu_1}F_{\nu_2}d\tau_1 d\tau_2.$$

By using the differential equation for $F_{\nu\lambda\mu}$ (ξ, ϑ, φ), the equation becomes

$$\begin{aligned}\mathcal{H}^0_{\nu_1'\nu_2'\nu_1\nu_2}&=\int\cdots\int F^*_{\nu_1'}F^*_{\nu_2'}\{-(\nu_1-1)/\xi_1-(\nu_2-1)/\xi_2\}F_{\nu_1}F_{\nu_2}\xi_1^2\xi_2^2\sin\vartheta_1\sin\vartheta_2 d\xi_1 d\vartheta_1 d\varphi_1 d\xi_2 d\vartheta_2 d\varphi_2\\ &=\int\cdots\int F^*_{\nu_1'}F^*_{\nu_2'}\{-(\nu_1-1)\xi_2-(\nu_2-1)\xi_1\}F\nu_1 F_{\nu_2}\xi_1\xi_2\sin\theta_1\sin\theta_2 d\xi_1 d\vartheta_1 d\varphi_1 d\xi_2 d\vartheta_2 d\varphi_2.\end{aligned}$$

For Eq. (6) ($\lambda_1=\lambda_2=1$, $\mu_1=\mu_2=0$) this becomes

$$\begin{aligned}\mathcal{H}^0_{\nu_1'\nu_2'\nu_1\nu_2}=\int\cdots\int F^*_{\nu_1'}F^*_{\nu_2'}[&(\nu_2-1)\{(\nu_1-1)(\nu_1+2)\}^{\frac{1}{2}}F_{\nu_1+1}F_{\nu_2}+(\nu_1-1)\{(\nu_2-1)(\nu_2+2)\}^{\frac{1}{2}}F_{\nu_1}F_{\nu_2+1}\\ &-2(2\nu_1\nu_2-\nu_1-\nu_2)F_{\nu_1}F_{\nu_2}+(\nu_2-1)\{(\nu_1+1)(\nu_1-2)\}^{\frac{1}{2}}F_{\nu_1-1}F_{\nu_2}\\ &+(\nu_1-1)\{(\nu_2+1)(\nu_2-2)\}^{\frac{1}{2}}F_{\nu_1}F_{\nu_2-1}]\xi_1\xi_2\sin\vartheta_1\sin\vartheta_2 d\xi_1 d\vartheta_1 d\varphi_1 d\xi_2 d\vartheta_2 d\varphi_2,\end{aligned}$$

and hence we obtain

$$\begin{aligned}\mathcal{H}^0_{\nu_1+1,\ \nu_2,\ \nu_1,\ \nu_2}&=(\nu_2-1)\{(\nu_1-1)(\nu_1+2)\}^{\frac{1}{2}},\\ \mathcal{H}^0_{\nu_1,\ \nu_2+1,\ \nu_1,\ \nu_2}&=(\nu_1-1)\{(\nu_2-1)(\nu_2+2)\}^{\frac{1}{2}},\\ \mathcal{H}^0_{\nu_1-1,\ \nu_2,\ \nu_1,\ \nu_2}&=(\nu_2-1)\{(\nu_1+1)(\nu_1-2)\}^{\frac{1}{2}},\\ \mathcal{H}^0_{\nu_1,\ \nu_2-1,\ \nu_1,\ \nu_2}&=(\nu_1-1)\{(\nu_2+1)(\nu_2-2)\}^{\frac{1}{2}},\end{aligned}$$

and

$$\mathcal{H}^0_{\nu_1,\ \nu_2,\ \nu_1,\ \nu_2}=-2(2\nu_1\nu_2-\nu_1-\nu_2),$$

all others being equal to zero.

In Eq. (7) we have

$$\mathcal{H}'_{\nu_1\nu_2,\,11}=\beta\int\cdots\int F_{\nu_1}{}^*F_{\nu_2}{}^*\xi_1\xi_2{}^2\cos\vartheta_1(3\cos^2\vartheta_2-1)F_1F_1\xi_1{}^2\xi_2{}^2\sin\vartheta_1\sin\vartheta_2 d\xi_1 d\vartheta_1 d\varphi_1 d\xi_2 d\vartheta_2 d\varphi_2$$

$$=\beta\int\cdots\int F_{\nu_1}{}^*F_{\nu_2}{}^*\{48\surd 2F_{310}F_{420}-96\surd(3)F_{310}F_{320}-96\surd 2F_{210}F_{420}$$

$$+192\surd(3)F_{210}F_{320}\}\xi_1\xi_2\sin\vartheta_1\sin\vartheta_2 d\xi_1 d\vartheta_1 d\varphi_1 d\xi_2 d\vartheta_2 d\varphi_2,$$

and hence

$$\mathcal{H}'_{23,11}=192\surd(3)\beta,\qquad \mathcal{H}'_{33,11}=-96\surd(3)\beta,\qquad \mathcal{H}'_{24,11}=-96\surd 2\beta,$$

and $\mathcal{H}'_{34,\,11}=48\surd 2\beta$, all others being equal to zero.

To illustrate the evaluation of the integral Δ let us consider $\Delta_{11,\,11}$:

$$\Delta_{11,\,11}=\int\cdots\int\{F_{100}(\xi_1)F_{100}(\xi_2)\}^2\xi_1{}^2\xi_2{}^2\sin\vartheta_1\sin\vartheta_2 d\xi_1 d\vartheta_1 d\varphi_1 d\xi_2 d\vartheta_2 d\varphi_2$$

$$=\int\cdots\int F_{100}(\xi_1)F_{100}(\xi_2)\{2F_{200}(\xi_1)F_{200}(\xi_2)-2\surd 2F_{200}(\xi_1)F_{100}(\xi_2)-2\surd 2F_{100}(\xi_1)F_{200}(\xi_2)$$

$$+4F_{100}(\xi_1)F_{100}(\xi_2)\}\xi_1\xi_2\sin\vartheta_1\sin\vartheta_2 d\xi_1 d\vartheta_1 d\varphi_1 d\xi_2 d\vartheta_2 d\varphi_2,$$

or, making use of the orthogonality and normalization of the F's, $\Delta_{11,\,11}=4$.

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The Magnetic Moment of the K^{39} Nucleus

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Starting with the K^+ field given by Hartree, a $4s$ wave function has been found by numerical integration. The orthogonality correction diminishes the value of the wave function at the origin by about one-third. The experimental value of the hyperfine structure separation of the ^2S normal state is 0.015 cm^{-1}. From this is calculated a molecular magnetic moment of 1.2 nuclear magnetons, as compared with the value of 0.38 nuclear magnetons calculated by Millman, Fox and Rabi on the basis of the modified Goudsmit's formula. The disagreement seems to be due chiefly to the possibility that the single electron wave functions of Fermi and Segré are not mutually orthogonal.

THERE have recently been published two independent determinations of the h.f.s. separation of the normal state of the K^{39} atom. Jackson and Kuhn[1] have used a spectroscopic method; Millman, Fox and Rabi[2] have relied on the method of molecular beams. The numerical agreement is good, and 0.015 cm^{-1} may be taken as the value of the separation.

From this, Millman, Fox and Rabi estimate the value of the nuclear magnetic moment to be 0.38 nuclear magneton, using the semi-empirical formula due to Goudsmit[3] and Fermi and Segré.[4, 5] Since previous cases of low magnetic moments have been associated with isotopes of even mass number, the above value seemed somewhat anomalous, and we therefore thought it of interest to ascertain whether or not the "anomaly" could be removed by the use of a Hartree wave function. This we now proceed to investigate.

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