[24] J. R. Oppenheimer, Phys. Rev. 31, 349 (1928).

[25] F. W. Martin, Phys. Rev. 140, A75 (1965).

[26] G. W. F. Drake, G. A. Victor, and A. Dalgarno, Phys. Rev. 180, 25 (1969).

[27] I. A. Sellin, M. Brown, W. W. Smith, and B. Donnally, Phys. Rev. A 2, 1189 (1970); R. Marrus and R. W. Schmieder, Phys. Rev. Letters 25, 1689 (1970).

[28] R. H. Hughes, E. D. Stokes, Song-Sik Choe, and T. J. King, Phys. Rev. A 4, 1453 (1971); D. H. Crandall and D. H. Jaecks, *ibid.* 4, 2271 (1971).

[29] J. Jackson and M. Schiff, Phys. Rev. 89, 359 (1953).

[30] D. W. Marquardt, J. Soc. Ind. Appl. Math. 11, 431 (1963).

PHYSICAL REVIEW A VOLUME 6, NUMBER 4 OCTOBER 1972

Energy Levels of Hydrogenlike Atoms in a Magnetic Field

H. C. Praddaude
*Francis Bitter National Magnet Laboratory,**
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

(Received 7 April 1972)

A new expansion of the wave function in Laguerre polynomials for hydrogenlike atoms in a magnetic field has been developed. This expansion reduces the Schrödinger equation to an infinite set of algebraic equations for which a fast, accurate, and unambiguous calculation of the bound states of a hydrogen atom in a magnetic field is possible. Four quantum numbers (K, C, M, N) are used to label the energy levels of the system in cylindrical coordinates. When the magnetic field is zero, the new labeling of the states is equivalent to the standard (n, l, m) quantum numbers obtained for the Coulomb potential in spherical coordinates. Numerical results are presented for the first 14 energy levels with principal quantum number $n = 1, 2, 3$. Several energy-level crossings occur in the region $0 < \gamma < 1$, where $\gamma = \hbar\omega_c/2\mathcal{R}$ and $\mathcal{R}$ is the effective Rydberg energy.

Calculations of the energy levels of hydrogenlike atoms in a magnetic field are essential for many problems in solid-state physics involving excitons or shallow donors. This paper presents a new method of calculating the bound energy levels, the general form of the wave functions, and uniquely labels the discrete energy levels of hydrogenlike atoms in a magnetic field.

In semiconductors, with relative static dielectric constants κ from 10 to 50 and effective-mass ratios from 0.01 to 0.1, the strength of the magnetic field relative to the Coulomb energy $\gamma = \hbar\omega_c/2\mathcal{R}$ ranges between 0.5 to 1000 for $B = 10T$. Here the cyclotron frequency is $\omega_c = eB/m$ and the effective Rydberg is $\mathcal{R} = Ze^4 m/(32\pi^2\kappa^2\hbar^2)$. For values of γ between 0 and 1 the bound Coulomb energy levels lose their identity because of the strong admixture of levels necessary to satisfy the perturbed Schrödinger equation. For values of $\gamma \gg 1$ the binding effect of the magnetic field in the xy plane is so large that an adiabatic approximation is appropriate.[1–4] Larsen[5] and Pokatilov and Rusanov[6] have performed variational calculations for $0 \lesssim \gamma \lesssim 3$, for the first few lowest levels. Recently Cabib, Fabri, and Fiorio[7] have integrated the Schrödinger equation numerically and obtained very accurate values for the 1s and 2s energy levels for $\gamma \lesssim 5$. These calculations did not answer two pressing questions: (i) How does one classify and label the bound energy levels? (ii) What is the general form of the wave function? Satisfactory answers to both questions are present here. I outline the calculation here and present some of the results in tabulated and graphical form. An extensive report containing more detailed results is being prepared for publication.

The Hamiltonian for this problem is

$$H = (1/2m)(\vec{p} + \tfrac{1}{2}e\vec{B}\times\vec{r})^2 - Ze^2/(4\pi\kappa r) \quad . \tag{1}$$

It is well known that the above Hamiltonian is invariant with respect to arbitrary rotations around an axis which contains the Coulomb center and is parallel to the direction of the applied magnetic field $\vec{B}$. Therefore, the projection of the angular momentum along the direction of $\vec{B}$ is conserved. Using the cylindrical coordinates (ρ, φ, z), with the origin on the Coulomb center $+Ze$ and the z axis along the direction of the magnetic field $\vec{B}$, the angular dependence of the wave function can be separated out,

$$\Phi(\phi) = (2\pi)^{-1/2} e^{iM\phi} \quad .$$

The z component of the angular momentum is $L_z = \hbar M$, and the quantum number $M = 0, \pm 1, \pm 2, \ldots$. Defining the effective Rydberg as the unit of energy, γ as the unit of magnetic field, and $a = 8\pi\kappa\hbar^2/(Ze^2 m)$ as the unit of length, the Schrödinger equation reduces to the well-known form

$$\left[\frac{\partial^2}{\partial\rho^2} + \frac{1}{\rho}\frac{\partial}{\partial\rho} + \frac{\partial^2}{\partial z^2} - \frac{M^2}{\rho^2} - 4\gamma^2\rho^2 \right.$$

$$+\frac{4}{r}+4\left(\frac{E}{\mathcal{R}}-\gamma M\right)\Bigg]\,\xi(\rho,z)=0\,. \qquad (2)$$

The wave function for the bound states is written as

$$\xi(\rho,z)=z^{C}\rho^{|M|}e^{-|\gamma|\rho^{2}}e^{-2|\epsilon|^{1/2}r}\sum_{m=0}^{N}L_{m}^{|M|}(2|\gamma|\rho^{2})$$
$$\times\sum_{k=0}^{\infty}\sum_{n=0}^{k}A_{mkn}\,\rho^{2n}L_{k-n}^{(\alpha)}(4|\epsilon|^{1/2}r)\;, \qquad (3)$$

where

$$\epsilon=E/\mathcal{R}-\gamma M-|\gamma|(|M|+2N+1),\quad 0>\epsilon=-|\epsilon|,$$
$$\alpha=2(C+|M|+2N)+1\,,$$
$$r=(\rho^{2}+z^{2})^{1/2},$$
$$C=0,1,\quad M=0,\pm1,\pm2,\;\ldots\;,\quad N=0,1,2,\;\ldots$$

and $L_s^{(\alpha)}(x)$ is the generalized Laguerre polynomial of order s and argument x.

The rationale for the selection of Eq. (3) as the wave function is the following: (i) Equation (2) is invariant with respect to reflections along the z axis. Therefore the wave function must have a definite parity, which is selected by the term z^C with $C=0,1$. The remainder of the wave function must be a function of z^2. Terms containing $|z|$ are not allowed since $p_z\psi(x,y,z)$ must be continuous across the xy plane. At this stage we find it convenient to introduce a new set of variables (ρ, r) where $r=(\rho^2+z^2)^{1/2}\geq\rho$. (ii) The term $\rho^{|M|}$ isolates the regular behavior of the wave function as $\rho\to0$. (iii) The term $e^{-|\gamma|\rho^2}$ isolates the asymptotic behavior of the wave function as $\rho\to\infty$, $\rho/r\to1$. (iv) The term

$$e^{-2|\epsilon|^{1/2}r}L_{N}^{|M|}(2|\gamma|\rho^{2})\;,$$

where $N=0,1,2,\;\ldots$, represents the asymptotic behavior of the wave function for the bound states when $r\to\infty$, $\rho/r\to0$. However, when we attempt to separate out this form, Laguerre polynomials of order $(N-1)$ are encountered. Hence we are forced to use the expression

$$e^{-2|\epsilon|^{1/2}r}\sum_{m=0}^{N}L_{m}^{|M|}(2|\gamma|\rho^{2})g_{m}(\rho,r)\;\;.$$

The function $g_m(\rho,r)$ should approach a constant value in the limit $r\to\infty$, $\rho\to\infty$, $\rho/r\to0$. The double summation

$$g_{m}(\rho,r)=\sum_{k=0}^{\infty}\sum_{n=0}^{k}A_{mkn}\,\rho^{2n}L_{k-n}^{(\alpha)}(4|\epsilon|^{1/2}r)$$

reduces the set of coupled equations for $g_m(\rho,r)$ to an infinite set of linear algebraic equations for the coefficients A_{mkn}. For $0\leq m\leq N-1$ the coefficients A_{mkn} depend on $A_{(m+1)kn}$. For $m=N$ the equations for A_{Nkn} are homogeneous and the requirement for a nonzero solution, i.e., that the determinant of the coefficients of the equation be zero, determines the allowed values for $|\epsilon|$ and the eigenvalues E of the energy bound states.

The roots $|\epsilon|$ of the secular equation are classified in order of decreasing magnitude by an index $K=0,1,2,\;\ldots\;.$

Four discrete parameters or quantum numbers (K,C,M,N) are necessary to classify the energy levels of the bound states. Note, however, that combinations of M, N, and C occur. In order to understand this better we examine the closed form solution which we obtain for the bound levels of the Coulomb potential for $\gamma=0$. When these wave functions are compared with the standard hydrogen-atom wave functions in spherical coordinates, we find a one-to-one correspondence. The relationship between the quantum numbers (n,l,m) and (K,C,M,N) is

$$n=C+|M|+2N+K+1\;, \qquad (4a)$$
$$l=C+|M|+2N\;, \qquad (4b)$$
$$m=M\;. \qquad (4c)$$

Here, as well as in Eq. (3), the quantum number N indicates the highest power dependence $(2N)$ of the variable ρ. We can use the correspondence given by Eqs. (4) to relate the wave functions at zero magnetic field, $\gamma=0$, with those for $\gamma\neq0$. Note, however, that the limiting process $\lim(\gamma\to0^{+})\,\psi_{KCMN}(\gamma)$ does not necessarily reproduce $\psi_{KCMN}(\gamma=0)$. This effect is first noticed with the levels $3d(0)$ and $3s$. For $\gamma\to0^{+}$, first-order degenerate-level perturbation theory, applied to the $n=3$ manifold, produces a 9×9 matrix which couples the $3s$ and $3d(0)$ levels. Consequently, for $\gamma\to0^{+}$ the perturbed levels are a combination of the $3s$ and $3d(0)$ unperturbed levels. The $3s$ and $3d(0)$ levels were calculated for the values $\gamma=10^{-5}$, 10^{-4}, 10^{-3}, 10^{-2}, 0.02, 0.03, 0.04, 0.05. The ratio

$$[\tfrac{1}{9}+E(3s)]/[\tfrac{1}{9}+E(3d(0))]$$

was compared with the value resulting from the first-order perturbation calculation 3.786. We find that, for $\gamma\lesssim10^{-5}$, the numerical calculation agrees with perturbation theory. For $\gamma<10^{-2}$, the $3d(0)$ energy level is a quadratic function of γ, but the energy of the $3s$ level deviates from a quadratic dependence on γ for $\gamma\gtrsim10^{-4}$. The $3s$ and the $3d(0)$ levels cross for $0.03<\gamma<0.04$; for $\gamma>0.04$ they behave as shown in Fig. 1. For pure hydrogenic wave functions this level crossing would be forbidden. However, the present wave functions are nonhydrogenic and this accidental degeneracy is possible.

The above discussion demonstrates that we have

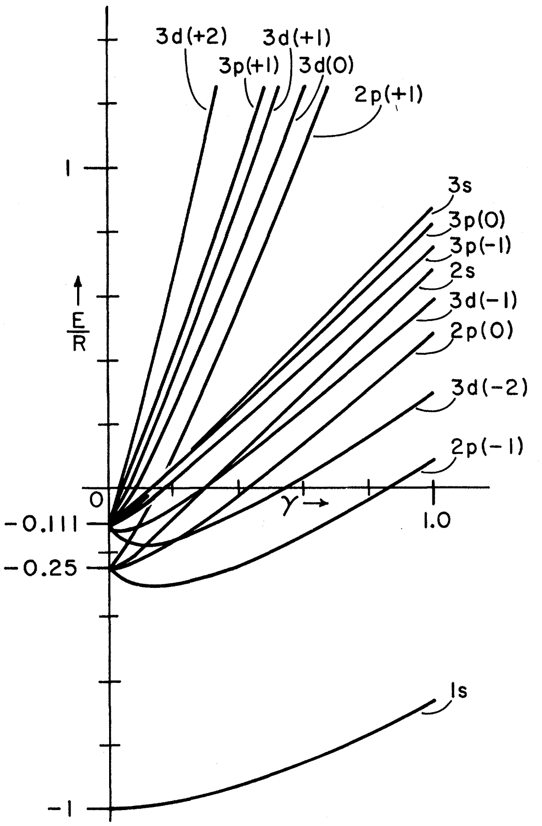

FIG. 1. Plot of the 14 energy levels with principal quantum number $n = 1, 2, 3$. The energy, measured in units of the effective Rydberg, $E/\mathcal{R}$, is plotted vs the normalized magnetic field $\gamma = \hbar\omega_c/(2\mathcal{R})$.

obtained a general expression for the wave function and a unique labeling of the energy levels.

We next evaluate the infinite determinant and obtain the roots $|\epsilon|$. At this stage we approximate the infinite summation over k by a finite number of terms with restriction $0 \le k \le k_{\max}$. This is equivalent to the use of a finite number of Coulomb wave functions to approximate the wave function Eq. (3). We have calculated the first 14 levels with principal quantum number $n = 1, 2, 3$ for $k_{\max} \le 12$. This amounts to the evaluation of determinants of order $N_D = \frac{1}{2} k_{\max}(k_{\max} + 1)$ or $N_D \le 78$. Approximately 30 to 90 sec per energy level is required with the MIT time-sharing computer. For some of the levels we have studied the convergency of the solution as a function of $k_{\max}$. As expected we find that the speed of convergency becomes poorer as $|\epsilon| \to 0$. This is so because the wave functions have a longer range and more terms are necessary to approximate the regular behavior of $\xi(\rho, z)$. The approach to the exact value is oscillatory, and error bounds can be established by studying the behavior of $\epsilon(k_{\max})$ as a function of $k_{\max}$. For $k_{\max} = 12$ all the levels studied are at least accurate to four digits. For the 1s level and for $|\gamma| < 1$ we have obtained an accuracy of 10^{-6} to 10^{-7}. Our results are compared with a few representative results of Larsen[5] and Cabib *et al.*[7] in Table I. Our energy levels are always lower than those of Larsen, as expected from a variational calculation and fall well within the error bounds set by Cabib *et al.*[7] In Table II, we present the energy levels for $\gamma = 0.1, 1, 2, 3$ for all 14 levels. Figure 1 shows the same levels for $0 \le |\gamma| \le 1$. This figure shows that there exist a number of energy-level crossings as a function of γ. This happens when the Coulomb levels lose their identity and start to resemble the pure magnetic levels. For example, the crossing of the $3d(-2)$ and the $2p(0)$ level occurs because the large magnetic moment of the $3d(-2)$ level makes the upturn due to the second-order magnetic effect more difficult. Since the $2p(0)$ level has no magnetic moment, the sec-

TABLE I. Comparison between the variational calculation of Larsen (L), the numerical solution of the Schrödinger equation of Cabib, Fabri, Fiorio (CFF), and the present calculation (P). The error bounds of E_{CFF} apply the last quoted digit.

	E_{L}	E_{CFF}	E_{P}
$\gamma = 0.1$			
1s	−0.99505	−0.99508(±5)	−0.99505
2s	−0.19614	−0.1962(±1)	−0.19617
2p(0)	−0.22476		−0.22482
2p(−1)	−0.30162		−0.30169
$\gamma = 1$			
1s	−0.662	−0.66241(±9)	−0.66233
2s	+0.683	+0.6793(±3)	+0.67897
2p(0)	+0.4807		+0.47999
2p(−1)	+0.0882		+0.08682

TABLE II. Tabulation of the 1s, 2s, 2p(0, ±1), 3s, 3p(0, ±1), and 3d(0. ±1, ±2) energies in units of the effective Rydberg $E/\mathcal{R}$, for different values of $\gamma = \hbar\omega_c/(2\mathcal{R})$.

	$\gamma = 0.1$	1.0	2.0	3.0
1s	−0.99505	−0.66233	−0.04442	0.67095
2s	−0.19617	0.67897	1.65194	2.63463
2p(0)	−0.22482	0.47999	1.40461	2.35996
2p(−1)	−0.30169	0.08682	0.80083	1.59297
2p(+1)	−0.10169	2.08682	4.80083	7.59297
3s	−0.04986	0.86727	1.86116	2.85706
3p(0)	−0.03978	0.81952	1.80612	2.78969
3p(−1)	−0.06236	0.74889	1.71492	2.69461
3p(+1)	0.13763	2.74889	5.71492	8.69461
3d(0)	0.02432	2.29389	5.05757	7.88551
3d(−1)	−0.11562	0.58686	1.50947	2.46216
3d(+1)	0.08437	2.58686	5.50947	8.46216
3d(−2)	−0.17567	0.29389	1.05757	1.88551
3d(+2)	0.22432	4.29389	9.05757	13.88551

ond-order effect of the magnetic field is the only one operative.

We expect that some of the experimental results on shallow-donor spectroscopy and exciton absorption in a magnetic field may require reanalysis in view of the present findings.

ACKNOWLEDGMENTS

The author is grateful to S. Foner and B. B. Schwartz for valuable comments and to D. M. Larsen for making available his unpublished results and for informative discussions.

---

*Supported by the National Science Foundation.

[1] R. J. Elliott and R. Loudon, J. Phys. Chem. Solids 15, 196 (1960).

[2] H. Hasegawa and R. E. Howards, J. Phys. Chem. Solids 21, 179 (1961).

[3] A. G. Zhilich and B. S. Monozon, Fiz. Tverd. Tela 8, 3559 (1966) [Sov. Phys. Solid State 8, 2846 (1967)].

[4] A. Baldereschi and F. Bassani, in *Proceedings of the Tenth International Conference on the Physics of Semiconductors, Cambridge, Massachusetts*, 1970, CONF-700801 (U. S. AEC, Oak Ridge, Tenn., 1970).

[5] D. M. Larsen, J. Phys. Chem. Solids 29, 271 (1968), and private communication.

[6] E. P. Pokatilov and M. M. Rusanov, Fiz. Tverd. Tela 10, 3117 (1968) [Sov. Phys. Solid State 10, 2458 (1969)].

[7] D. Cabib, E. Fabri and G. Fiorio, Solid State Commun. 9, 1517 (1971).

PHYSICAL REVIEW A VOLUME 6, NUMBER 4 OCTOBER 1972

Submillimeter Microwave Spectrum of $H_2{}^{18}O$†

Frank C. De Lucia, Paul Helminger,* Robert L. Cook,‡ and Walter Gordy
Department of Physics, Duke University, Durham, North Carolina 27706

(Received 18 April 1972)

The rotational spectrum of $H_2{}^{18}O$ in the ground vibrational state has been investigated by means of high-resolution microwave spectroscopy. We report the measurement of ten new rotational transitions in the 1.0- to 0.4-mm wavelength region. Among these are several low-*J* lines which are of significance in the atmospheric absorption of electromagnetic radiation in the microwave region. The frequencies of newly observed transitions are (in MHz): $5_{1,5} \leftarrow 4_{2,2}$, 322 465.17; $4_{1,4} \leftarrow 3_{2,1}$, 390 607.76; $4_{2,3} \leftarrow 3_{3,0}$, 489 054.26; $6_{2,4} \leftarrow 7_{1,7}$, 517 181.96; $6_{4,3} \leftarrow 5_{5,0}$, 520 137.32; $5_{3,3} \leftarrow 4_{4,0}$, 537 337.57; $1_{1,0} \leftarrow 1_{0,1}$, 547 676.44; $6_{4,2} \leftarrow 5_{5,1}$, 554 859.87; $5_{3,2} \leftarrow 4_{4,1}$, 692 079.14; and $2_{1,1} \leftarrow 2_{0,2}$, 745 320.20. Assignments were based on a weighted analysis of combined microwave and infrared data.

INTRODUCTION

Recently we reported microwave investigations[1,2] of the rotational spectra of $HD^{16}O$ and $H_2{}^{16}O$ in the millimeter and submillimeter wavelength regions. In the present paper we report measurements of ten previously unobserved submillimeter wave transitions of $H_2{}^{18}O$ in the region from 1.0 to 0.4 mm. Only two rotational lines of this isotopic species have been previously observed, neither of which falls in the submillimeter wave region. Among the newly observed transitions are several low-*J* lines which are of significance in the atmospheric absorption of electromagnetic radiation in the microwave region.[3] The measurement of higher-frequency transitions of $H_2{}^{18}O$ has been made possible by a recent extension of the operating range of our tunable microwave spectrometers to a wavelength of 0.368 mm and an accompanying order-of-magnitude improvement in sensitivity in the previously covered submillimeter region.[4]

Lines attributed to the isotopic species $H_2{}^{18}O$ in natural abundance have been identified in the rotation-vibration spectrum of water vapor in a number of past infrared investigations. Rao and his co-workers[5,6] have recorded several rotation-vibration bands of the infrared spectrum of $H_2{}^{18}O$ in isotopically enriched samples. One of the two previously observed microwave lines of $H_2{}^{18}O$, the $6_{1,6} \leftarrow 5_{2,3}$ transition measured by Powell and Johnson,[7] occurs in the centimeter wave region; the other, the $3_{1,3} \leftarrow 2_{2,0}$ transition reported by Steenbeckeliers and Bellet,[8] occurs in the millimeter wave region.

RESULTS

Submillimeter wave energy for this investigation was produced by a klystron-driven crystal harmonic multiplier[9] and detected by an InSb photoconducting detector[10] operated at 1.6 °K. Accurate measurements of the klystron frequency were made with a frequency multiplication chain referenced to WWVB. Typically, a klystron oscillating in the 50-GHz region was used as the fundamental source.