Hydrogen atoms in strong magnetic fields*

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We propose a variational scheme for calculating the energy eigenvalues and eigenfunctions of the hydrogen atom in the presence of a strong magnetic field. Numerical calculations were performed for several of the lowest states, and for the wavelengths of some allowed transitions. We discuss briefly the equivalence of the problems related with solid-state physics and astrophysics, and compare our results with previous calculations. Because the suggested scheme converges very fast for fields up to approximately 10^9 G this is a convenient manner in which to treat problems where the interest is concentrated in the range of variation of the magnetic field from zero up to approximately 10^9 G.

I. INTRODUCTION

In the past few years there has been a great deal of interest in the study of atoms and particularly the hydrogen atom in the presence of strong magnetic fields. As many aspects of atomic structure are affected by these fields, a detailed understanding of the behavior of the hydrogen atom in the presence of strong magnetic fields can provide a deeper insight into several problems in the fields of astrophysics, plasma physics, and solid-state physics. Much work concentrated on astrophysics-related problems[1-5] and also on problems concerning excitons, as well as donor and acceptor impurities in semiconductors.[6-10] Unfortunately, there seems to exist a certain communication gap between researchers working in both fields; very few works in astrophysics mention the solid-state papers and vice versa. We will present here a brief review of some of the work which has been done in the past in both fields, and will propose a variational calculation which we will discuss later.

Concerned basically with astrophysics problems, Cohen, Lodenquai, and Ruderman[1] discussed the implications of magnetic fields as strong as 10^2 G (characteristic fields in neutron-star models for pulsars) for the ionization energy of atoms. Smith *et al.*[2] studied the behavior of hydrogen atoms in the presence of fields in the range from about 10^6 to 10^{12} G, using a multiparameter trial wave function and a variational procedure. Also using a variational procedure but a four-parameter trial wave function, Rajagopal *et al.*[3] determined the ionization energy of a hydrogen atom in its ground state in the presence of fields of the order of those found in magnetic white dwarfs and some neutron stars. Concerned with astrophysically interesting effects such as opacities in white dwarfs and pulsars, Smith *et al.*[4] calculated bound-bound transition probabilities for a hydrogen atom in magnetic fields from 10^7 to 10^8 G.

Canuto and Kelly[5] solved the Schrödinger equation employing a combination of the variational method and perturbation theory, obtaining analytic expressions for the approximate wave functions and energy eigenvalues for fields in the range from 10^{10} to 10^{12} G. Their results were not reliable for fields below 10^{10} G.

A great amount of work has been motivated by shallow electronic states associated with impurity levels in semiconductors.[6-10] Yafet, Keyes, and Adams[6] studied the energy levels and wave functions for a hydrogen atom in a very strong magnetic field. They calculated the ionization energy for fields up to approximately 10^{11} G.

This same problem was studied by Wallis and Bowlden,[7] and some binding energies were calculated for fields ranging from approximately 10^{10} to 10^{12} G. It is interesting to note that these results for the ionization energy are in good agreement with those of Ref. 2, and are better than those presented in Ref. 1. Larsen[8] also considered in the effective-mass approximation the problem of a hydrogenic atom in a strong static magnetic field, and gave a more accurate treatment of the ground state and the lowest-lying excited states with $m=1$ and $m=-1$ for donor levels in a magnetic field.

Praddaude[9] calculated the 14 lowest-energy levels of the hydrogen atom in a semiconductor, assuming an appropriate expansion of the wave functions in terms of Laguerre polynomials, and solving the Schrödinger equation in cylindrical coordinates. His results were in very good agreement with those of Cabib, Fabri, and Fiorio,[10] who solved exactly numerically the Schrödinger equation for the ground state and for the first excited state with $m=0$ and even parity. The results of Praddaude[9] and Cabib *et al.*[10] are in good agreement with those of Ref. 2, once we define properly the ionization energy for the ground state.

Yafet *et al.*[6] and Kemp[11] have discussed the importance in analyzing the problem of a hydrogen atom in the presence of magnetic fields of strength in the range 10^8–10^9 G. In the present work we will propose a variational calculation assuming that the trial function is written as a linear combination of the eigenfunctions of the Hamiltonian for the hydrogen atom in the absence of the magnetic field. Such expansion is reliable for fields up to approximately 10^9 G. We also suggest an extension of this method for fields $B > 10^{11}$ G.

II. THEORY

First we will write the Hamiltonians of interest in astrophysics and solid-state semiconductor physics in terms of a dimensionless parameter γ. Then we discuss the variation of the energy spectrum as a function of γ, which is undoubtedly the most convenient way to look at the problem because it unifies both theoretical approaches. Finally, we will discuss the variational procedure.

Choosing the Landau gauge, the Hamiltonian for a hydrogen atom in the presence of a constant magnetic field is

$$H = (1/2m)[-i\hbar\vec{\nabla} + (e/2c)\vec{B}\times\vec{r}]^2 - e^2/r\,. \qquad (1)$$

In atomic units and spherical coordinates Eq. (1) becomes

$$H = -\nabla^2 - 2/r + \gamma L_z + \tfrac{1}{4}\gamma^2 r^2 \sin^2\theta\,. \qquad (2)$$

Energy is now measured in rydbergs and length in units of the Bohr radius. $\gamma = \mu_B B/\mathrm{Ry}$ is dimensionless, since μ_B is the Bohr magneton. For a hydrogenic atom inside a semiconductor the Hamiltonian is

$$H^* = (1/2\overline{m})[-i\hbar\vec{\nabla} + (e/2c)\vec{B}\times\vec{r}]^2 - e^2/Kr\,, \qquad (3)$$

where the electron effective mass depends on the nature of the crystal ($\overline{m} = m/\alpha$). This Hamiltonian can be immediately rewritten in the same form as Eq. (1) by defining an effective field $\vec{B}^* \equiv \vec{B}/K^2$ and redefining an effective mass by $m^* = m/(\alpha K^2)$. Therefore

$$H^* = (1/2m^*)[-i\hbar\vec{\nabla} + (e/2c)\vec{B}^*\times\vec{r}]^2 - e^2/r\,.$$

In "effective atomic units" and spherical coordinates the equivalent of Eq. (2) is

$$H^* = -\nabla^2 - (2/r) + \gamma^* L_z + \tfrac{1}{4}\gamma^{*2} r^2 \sin^2\theta\,. \qquad (4)$$

Therefore, to obtain the spectra of energy eigenvalues of the Hamiltonian (2) as a function of γ is entirely equivalent to obtaining the spectra of H^* as a function of γ^*. We note that in Eq. (4), energy is measured in units of the "effective rydberg" $R^*_\infty = m^* e^4/2\hbar^2$, and length in terms of an "effective Bohr radius" ($a_0^* = \hbar^2/m^* e^2$). The dimensionless parameter γ^* can be written as $\gamma^* = \mu_B^* B^*/R^*_\infty = (\alpha K)^2\gamma$.

It is interesting to note that because of this equivalence certain semiconducting materials naturally suggest themselves as specially suitable for simulating strong magnetic fields. For instance,[6] in InSb the value of K is 16 and the value of α approximately 77. Thus the product αK is about 1200 and for a field of 10^5 G, $\gamma^* \sim 100$. To achieve this value for γ a field of approximately 10^{11} G would be necessary. Therefore, even if the highest magnetic fields currently available in the laboratory are not much larger than 10^5 G, it would be possible to perform experiments simulating superstrong magnetic fields.

We will now present a possible variational solution for the problem of the hydrogen atom in a magnetic field. The proposed solution is good for values of γ ranging from zero to approximately 1.

Let us assume that the eigenfunctions of H have the form

$$\psi(\vec{r}) = \sum_i a_i \phi_i(\vec{r})\,, \qquad (5)$$

where

$$H_0\phi_i = (-\nabla^2 - 2/r)\phi_i = \epsilon_i^{(0)}\phi_i = -(1/n_i^2)\phi_i\,, \qquad (6)$$

where

$$\phi_i(\vec{r}) = R_{n_i l_i}(r)\, Y_{l_i}^{m_i}(\theta,\phi) = N_{n_i l_i} F_{n_i l_i}(X)\, Y_{l_i}^{m_i}(\theta,\phi)\,, \qquad (7)$$

with

$$X = \frac{2r}{n}\,, \quad N_{nl} = \frac{2}{n^2}\left(\frac{(n-l-1)!}{[(n+l)!]^3}\right)^{1/2}, \qquad (8)$$

and

$$F_{nl}(x) = x^l e^{-x/2} L_{n-l-1}^{2l+1}(x)\,. \qquad (9)$$

$L_{n-l-1}^{2l+1}(x)$ are the Laguerre polynomials.[12]

Now we will minimize the energy, imposing the normalization condition $\langle\psi|\psi\rangle = 1$.

Remembering that $\sin^2\theta$ is a linear combination of $Y_0^0(\theta,\phi)$ and $Y_2^0(\theta,\phi)$, we rewrite Eq. (2) as

$$H = -\nabla^2 - \frac{2}{r} + \gamma L_z + \frac{\gamma^2}{6} r^2\left[1 - \left(\frac{4\pi}{5}\right)^{1/2} Y_2^0\right]. \qquad (10)$$

Using the fact that[12]

$$\int Y_{l_j}^{*m_j} Y_2^0 Y_{l_i}^{m_i}\, d\Omega = (-1)^{m_j}[(2l_j+1)(2l_i+1)]^{1/2}\left(\frac{5}{4\pi}\right)^{1/2}\begin{pmatrix} l_j & l_i & 2 \\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} l_j & l_i & 2 \\ -m_j & m_i & 0\end{pmatrix}, \qquad (11)$$

and defining the quantities

$$\langle r^2\rangle_{ij} = \int_0^\infty R_{n_j l_j}(r) R_{n_i l_i}(r)\, r^4 dr\,, \tag{12}$$

which can be calculated exactly in terms of Γ functions, and

$$\epsilon_i = \epsilon_i^{(0)} + \gamma m_i\,, \tag{13}$$

we have

$$\langle\psi|H|\psi\rangle = \sum_i |a_i|^2\epsilon_i + \frac{\gamma^2}{6}\sum_{i,j} a_i a_j \langle r^2\rangle_{ij}\left[\delta_{l_i l_j}\delta_{m_i m_j} - (-1)^{m_j}[(2l_i+1)(2l_j+1)]^{1/2}\begin{pmatrix} l_i & l_j & 2\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} l_j & l_i & 2\\ -m_j & m_i & 0\end{pmatrix}\right]. \tag{14}$$

Therefore we can define a symmetric matrix C with elements

$$C_{ij} = \frac{\gamma^2}{6}\langle r^2\rangle_{ij}\left[\delta_{l_i l_j}\delta_{m_i m_j} - (-1)^{m_i}[(2l_i+1)(2l_j+1)]^{1/2}\begin{pmatrix} l_i & l_j & 2\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} l_j & l_i & 2\\ -m_i & m_i & 0\end{pmatrix}\right]. \tag{15}$$

The symmetries of the Hamiltonian are explicit in the form of the matrix elements of C. From the properties of the 3-j symbols we obtain, as expected, that the non-null elements are only those connecting states of the same parity and with the same value of m.

Regarding the coefficients a_i's as parameters to be varied, and using Eqs. (14) and (15), the variational condition is expressed as

$$\frac{\partial}{a_k}\left|\sum_i |a_i|^2\epsilon_i + \sum_{i,j} a_i a_j C_{ij} - \sum_i \lambda_i |a_i|^2\right| = 0\,. \tag{16}$$

The last term expresses the normalization constraint and the λ_i's are Lagrange multipliers. Using the fact that the matrix C is symmetric, we obtain the secular equation

$$\sum_j a_j[C_{k_j} - (\lambda_j - \epsilon_j)\delta_{k_j}] = 0\,, \tag{17}$$

and in principle the whole spectrum of eigenvalues and eigenvectors can be obtained by evaluating the infinite determinant

$$|C - (\lambda - \epsilon)I| = 0\,. \tag{18}$$

III. RESULTS AND DISCUSSION

An interesting result is that the Zeeman effect is trivially obtained from Eq. (17) if we neglect terms in γ^2 in Eq. (10), in this case $C_{ij} = 0$, and

$$\lambda_j = \epsilon_j^{(0)} + \gamma_{m_j}\,. \tag{19}$$

The Paschen-Back limit is also immediately obtained, including the term $2\gamma S_z$ in Eq. (10), and, assuming the basis functions ϕ_i to be spin dependent, $\phi_i = \phi_i(\vec{r})\chi_{ms}$, $\chi_{ms}(S)$ are the usual spin functions, eigenfunctions of S_z and S^2.

In this case

$$\lambda_j = \epsilon_j^0 + \gamma(m_j + 2m_{sj})\,. \tag{20}$$

In the present work we are primarily concerned with understanding the possible convenience of applying this scheme for a variation of the parameter γ ranging from 0 to 1.

We have restricted our basis of Eq. (5) to a finite number of functions, and diagonalized the matrix C for different sets of basis functions. The diagonalization of this matrix is simple because of the symmetries already discussed; the C matrix breaks in blocks along the diagonal. These involve only elements connecting functions of the same parity and same m. This scheme is then similar to a perturbation theory, but the results from the variational method are expected to be better than those of perturbation theory.

We checked the convergence of the calculations for the eigenvalues of C by increasing the number of basis functions and comparing the obtained eigenvalues with those from a more restricted basis.

For this range of variation of γ, we have shown that only s and d functions are important to assure convergence for the ground-state energy and also for the energy of the $2s$ state.

We have included in our basis ns and $n'd$ functions ($1 \leq n \leq 10$; $3 \leq n' \leq 10$), and we have shown that to assure convergence at least to five digits (largest value of γ) for the ground-state energy we must include in our basis only functions with $1 \leq n \leq 6$ and $3 \leq n' \leq 6$. As expected for the $2s$ level, convergence is poorer for large values of γ, when these same bases are assumed.

For the $2p$ levels we have shown that the inclusion in the basis of functions np, $2 \leq n \leq 9$, is enough to assure convergence at least to four digits (largest value of γ).

For a given value of γ we require approximately 5 msec of central-processor-unit time of an IBM 370/165 to obtain all the eigenvalues and eigenvectors for the largest basis considered here.

We would like to comment that this scheme is

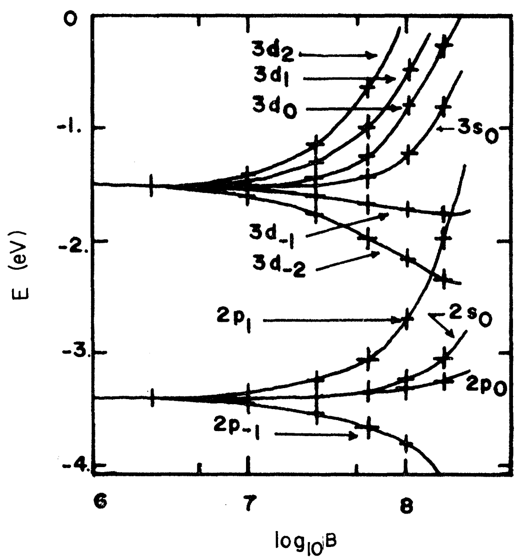

FIG. 1. Energy spectrum of the hydrogen atom in a magnetic field for some of the lowest excited states. Present calculation: crosses; Smith *et al.* (Ref. 2): solid line.

particularly convenient for fields up to $\sim 5\times10^8$ G because convergence is quite fast. To obtain all energy eigenvalues for the 14 lowest states in this region it was enough to include in our basis only ns, $n'd$, $n''p$ functions with $1\leqslant n\leqslant 6$, $2\leqslant n''\leqslant 7$, $3\leqslant n'\leqslant 8$, to assure convergence up to four digits.

In Fig. 1 we compare the present results for the energy spectrum of some lowest excited states as a function of the magnetic field with those of Ref. 2. We have also omitted the ground-state $1s$ since its value is essentially constant at -13.6 eV over the range of variation of the magnetic field considered.

The agreement is excellent except for the $3s$ and the $3d_0$ levels, which we believe were mistakenly changed for each other in Ref. 2; when we interchange these two levels the agreement is again excellent. In our calculations we have good physical arguments to distinguish between the $3s$ and the

TABLE I. Wavelengths for some allowed transitions (in angstroms, except for the rows $2s_0$, for which the units are micrometers), comparing present calculations and those of Ref. 4 for $B = 10^7$ and 10^8 G.

B (G)		λ (Present calc.)			λ (Ref. 4)		
		$2p_{-1}$	$2p_0$	$2p_1$	$2p_{-1}$	$2p_0$	$2p_1$
10^7	$1s_0$	1222	1213	1208	1217	1210	1203.9
	$2s_0$	21.35	1281	22.08	21.279	1258	21.46
	$3d_0$	6294	6484	6681	6318.6	6508.6	6715.8
	$3s_0$	6316	6505	6706	6341.4	6532.8	6741.5
10^8	$1s_0$	1280	1206	1145	1267.0	1204	1132.7
	$2s_0$	1.882	14.17	2.563	2.060	13.73	2.219
	$3d_0$	3979	4874	6283	4126.7	4973.4	6723
	$3s_0$	4713	6021	8332	4870.5	6095.1	8950

TABLE II. Comparison between the present results (P), the results of Ref. 6 (YKA), and the exact results of Ref. 10 (CFF) for the ground-state energy (units of rydbergs or effective rydbergs).

γ	YKA	CFF	P
0.1	−0.844 43	−0.995 08	−0.995 04
0.2	−0.839 56	−0.980 76	−0.980 51
0.3	−0.810 97	−0.958 41	−0.956 99
0.4	−0.783 64	−0.923 23	−0.924 82
0.5	−0.750 54	−0.894 47	−0.884 06
0.6	−0.712 52	−0.854 94	−0.834 66
0.7	−0.670 32	−0.811 42	−0.786 64
0.8	−0.624 49	−0.764 57	−0.709 88
0.9	−0.575 54	−0.714 73	−0.634 39
1.0	−0.523 86	−0.662 41	−0.551 01

$3d_0$. Because of the form of the matrix C when we include ng functions in our basis, we can expect that the $3d_0$ level will be more affected than the $3s$ level.

In Table I we compare the wavelength for some of the possible transitions with those of Ref. 4, for fields of 10^7 and 10^8 G, and the agreement is also very good. This is also a good indication of the accuracy of the energy levels.

Table II compares the energies for the ground state as a function of γ with those obtained by Refs. 6 and 10. Our results agree very well with the exact numerical calculation of Ref. 10 for small

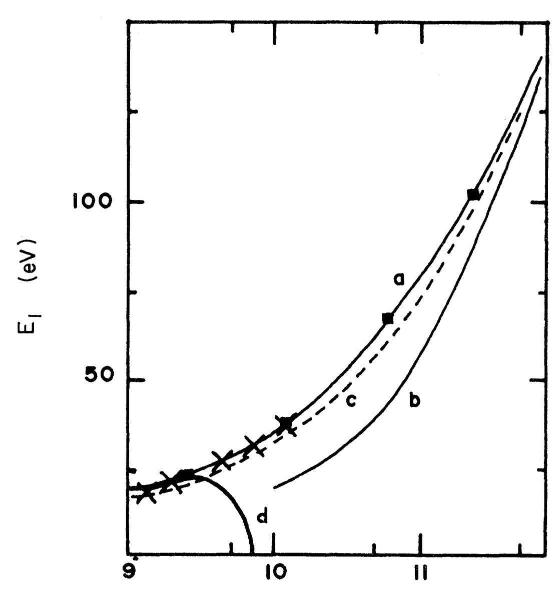

FIG. 2. Ionization energy of the ground state of hydrogen as a function of the magnetic field. Smith *et al.* (Ref. 2): a; Cohen *et al.* (Ref. 1): b; Wallis and Bowlden (Ref. 7): c; present calculations: d; Larsen (Ref. 8): ■; Cabib *et al.* (Ref. 10): ×.

values of γ, but get worse with increasing γ. They are always better in this region than those of Ref. 6.

We note that we are labeling the states as for the hydrogen energy levels in the absence of a magnetic field. This is only an extension of the notation, because it is clear from the symmetries of the Hamiltonian and from the matrix C that the good quantum numbers are m and the parity.

Now we would like to comment briefly about the ionization energy of a hydrogen atom in the ground state. The ionization energy is defined as the difference between the energies of the lowest bound state and the lowest free state. Therefore we should subtract from the energy of the first "Landau level" the energy of the ground state of the hydrogen atom,

$$E_I = \gamma - E_{1s}.$$

For the sake of comparison we present in Fig. 2 the ionization energy of the ground state of a hydrogen atom as a function of the magnetic field, obtained by several authors. We note that our results are in very good agreement up to $B \sim 10^9$ G, but are only a slight improvement over perturbation theory for larger fields. In this region the energy due to the magnetic field ($\mu_B B$) becomes much larger than the rydberg, and the basis chosen for our trial function is not appropriate.

We would also like to comment that the proposed scheme can be applied to very strong fields $\gamma \approx 100$ by changing our basis of Eq. (5) to harmonic oscillator wave functions, rewriting H_0 in Eq. (6) as the Hamiltonian of the harmonic oscillator, and redefining appropriately the matrix C. The ionization energy in the intermediate region can be obtained by interpolation.

We are presently using this scheme to calculate oscillator strengths and transition probabilities, as well applying this same idea to calculate the energy levels of the hydrogen atom in the presence of an electric field.

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