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HOMOGENEOUS MAGNETIC FIELD: A VARIATIONAL APPROACH

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ABSTRACT. We propose a variational scheme to obtain the spectrum of the hydrogen atom in the presence of an external homogeneous magnetic field. We use two different sets of basis function to diagonalize the Hamiltonian describing the system, namely: the eigenfunctions of the free hydrogen atom and of the three-dimensional harmonic oscillator; both having their radial coordinates properly scaled by a variational parameter. Because of its characteristics the present approach is suitable to describe the ground state as well as an infinite number of excited states also for a wide range of magnetic field strengths.

RESUMO. Usamos o método variacional para obter o espectro atômico do átomo de hidrogênio na presença de um campo magnético externo. Utilizemos dois conjuntos de funções de base para diagonalizar a Hamiltoniana do sistema: as autofunções das Hamiltonianas do átomo de hidrogênio livre e do oscilador harmônico isotrópico tridimensional. Ambos os conjuntos da funções tiveram suas partes radiais modificadas introduzindo-se um parâmetro variacional. As características específicas deste método tornam-no apropriado para descrever o estado fundamental bem como um número infinito de estados excitados para uma grande faixa de valores do campo magnético.

INTRODUCTION

The problem of atoms[1-9] in external magnetic
fields has been extensively studied in the last few years;
Garstang[10] presents a detailed review of this subject.
It is well known that an adequate treatment of this problem,
even for the hydrogen atom, valid for a large range of
magnetic field strengths requires, in general, elaborated
techniques and lengthy computational calculations, if one is
concerned not only with the ground state but also with
excited states.   Perturbation theory can be applied only
in the case of weak[10] or ultra strong magnetic fields[10],
and the most common approach is the use of variational
schemes.

In this work we present a variational calculation
which extends the region of validity of the method previously
proposed by one of us (HSB).[1]   The present approach
incorporates the conveniences of that method and is valid
for a much wider range of values of magnetic field strengths.

THEORY

For a hydrogen atom in the presence of an homoge-
neous magnetic field $(\vec{B} = B\hat{z})$, the Hamiltonian, in spherical
coordinates and atomic units (energy is measured in Rydbergs
(Ry)), is[1]

$$H \equiv H_0 + H_1 = -\nabla^2 - \frac{2}{r} + \gamma L_z + \frac{1}{4}\gamma^2 r^2 \sin^2\theta \qquad (1)$$

where $\gamma \equiv \mu_B B/Ry$, is dimensionless (μ_B is the Bohr magneton), and $H_0 = -\nabla^2 - 2/r$.

In Ref. 1 a simple scheme was proposed which consists of diagonalizing eq. (1) assuming a finite basis set of eigenstates of H_0, the free hydrogen atom Hamiltonian (which from now on we call Basis I). It describes adequately the ground states of the system for $\gamma \lesssim 1$ ($B \lesssim 2.35 \times 10^9 G$), as well as the 14 lowest excited states for $\gamma \lesssim 0.1$; being very fast computationally. Its limitations are intrinsically related to the choice of the set of basis functions for which the diagonalization of the Hamiltonian is performed.[2] If the diagonalization is performed in a set of eigenstates of the isotropic three dimensional harmonic oscillator[2] (from now on called Basis II), the results for the energy eigenvalues are in agreement with the best calculations for $1 \lesssim \gamma \lesssim 100$, but the use of two sets of basis functions presents problems in connecting the states in the intermediate field region. Of course the use of a single set for a broad range of field strengths is desirable.

In the present work we follow the same procedure of Ref. (1) and (2), but introduce an exponential variational parameter. In this manner the extension of the region of validity of the method is accomplished, and because of the specific characteristics of the formulation[1] the variational approach may also be applied to an infinite (but not all) number of excited states. In some aspects this treatment is similar to that of Smith et al.[5] and Callaway[9] who

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considered a basis constituted by Slater type functions and a large number of linear and exponential variational parameters. The present scheme is undoubtly much simpler, in the case of basis I it has the correct zero field limit but it is restricted to a region of field strengths smaller than that of Smith et al[5] (because of the smaller number of variational parameters).

Using the same notation as Ref. 1 we write the trial wave functions in the form (Basis I)

$$\phi(\vec{r}) = \sum_i a_i \varphi_i^\beta(\vec{r}) \tag{2}$$

where

$$\varphi_i^\beta(\vec{r}) = \beta^{3/2} R_{n_i \ell_i}(\beta r) Y_{\ell_i}^{m_i}(\theta,\varphi) \tag{3}$$

is properly normalized.

Noticing that

$$(-\nabla^2 - \frac{2\beta}{r}) \varphi_i^\beta(\vec{r}) = -\frac{\beta^2}{n_i^2} \varphi_i^\beta(\vec{r}) \tag{4}$$

we rewrite eq. (1) as

$$H = (-\nabla^2 - \frac{2\beta}{r}) + \frac{2(\beta - 1)}{r} + \gamma L_z + \frac{\gamma^2}{6} r^2 \left[1 - (\frac{4\pi}{5})^{1/2} Y_2^0(\theta,\varphi) \right] \tag{5}$$

The matrix elements of H in the basis $\{\varphi_i^\beta\}$ are

$$H_{ij} = C_{ij}^\beta + \epsilon_j^\beta \delta_{ij} \tag{6}$$

$$C_{ij}^{\beta} \equiv 2(\beta-1)\beta\langle 1/r\rangle_{ij}\ \delta_{\ell_i \ell_j}\delta_{m_i m_j} + \frac{\gamma^2}{6\beta^2}\langle r^2\rangle_{ij}\ \times$$

$$\times\ \left[\delta_{\ell_i \ell_j}\delta_{m_i m_j} - (-1)^{m_i}[(2\ell_i+1)(2\ell_j+1)]^{\frac{1}{2}}\right.$$

$$\left.\times\ \begin{pmatrix}\ell_i & \ell_j & 2 \\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}\ell_i & \ell_j & 2 \\ m_i & -m_j & 0\end{pmatrix}\right] \tag{7}$$

and

$$\epsilon_i^{\beta} = -\frac{\beta^2}{n_i^2} + \gamma m_i \tag{8}$$

As in refs. (1), (2):

$$\langle r^s\rangle_{ij} = \int_0^{\infty} R_{n_j\ell_j}(r)\ r^s R_{n_i\ell_i}(r) r^2 dr \tag{9}$$

The spectrum of eigenvalues and eigenfunctions of H can be determined by solving the eigenvalue problem:

$$H\Psi^n = \lambda^n(\beta)\Psi^n \tag{10}$$

which reproduces the one of ref. (1) when $\beta = 1$.

The symmetry of the Hamiltonian implies that the only nonzero matrix elements are those connecting functions of same quantum numbers m and π (parity), therefore in diagonalizing H we are restricted to subsets of functions with the same good quantum numbers, which must be truncated according to a given criterium. The parameter β is then

chosen to minimize the lowest eigenvalue of Eq. (10) for
each set of quantum numbers (m,π), that is:

$$\frac{\partial \lambda^0_{m,\pi}(\beta)}{\partial \beta} = 0 \qquad (11)$$

Of course, for a given pair (m,π), Eq. (11) yields a dif-
ferent value for β. If we label the states as for the
hydrogen atom in the absence of the magnetic field, the
energy of states $1s_0, 2p_0, 2p_{\pm 1}$, $3d_{\pm 1}$, $3d_{\pm 2}$ and $n\ell_m$ with
$\ell = n - 1$ and $m = \pm \ell$ for $n > 3$ are easily obtained.

We also applied this variational scheme with
Basis II. Following Ref.( ), we diagonalize the hamiltonian
using the basis of eigenfunctions of the three dimensional
isotropic oscillator, with the radial part scaled by a
variational parameter, as discussed above; this parameter
is determined from condition (11). As in Ref. (2) the non
crossing rule can be used to relate the energy levels to
the free hydrogen levels.

RESULTS AND DISCUSSIONS

In Table I, we present the results of calculations
in the same scheme of refs. (1) and (2), those obtained with
the proposed variational scheme and also results obtained
by different authors.[3,4] Basis I is known to provide a
good description of the low field region.[1] The introduc-

tion of a variational parameter $(I - 3)$ extends the validity of the scheme to a broader range of magnetic field strengths. The results in Table I correspond to the same 17 Basis I functions as in Ref. (1) and to 6 $1 - 3$ functions (n : 4, $l = 0,2$) and we see they are equivalent for $\gamma \sim 0.1$, but the $I - 3$ results are clearly superior for large values of γ. The results in the oscillator Basis (II) correspond to 35 basis functions (n $\leq$ 26, $l \leq$ n), which are different from those in Ref. (2). Keeping the same total number of basis functions, increasing n and cutting the maximum value of l improves the low field results and slightly worsens the high field region. The present variational calculation $(II - 6)$ corresponding to 6 basis functions, provides much better results in the low and intermediate field regions ($\gamma \leq 1$), and equivalent results for larger values of γ. Of course for $\gamma = 0$ the oscillator basis does not give the correct value of the energy, and our results show that in this case the inclusion of a large number of basis functions is of fundamental importance to improve the results, rather than the use of a variational technique. Since the case $\gamma = 0$ is of no interest here, we no longer discuss it.

It is most difficult to describe correctly the excited states in the intermediate field region ($\gamma \sim 1$), since perturbation theory is clearly inadequated, and except for the work of Rau and Spruch[7], the treatment for this problem is computationally rather involved.[5-10] In table II we compare the present calculations with the results of Praddaude for a few excited states for $\gamma = 1$.

As for the ground state for this value of γ the inclusion of a variational parameter improves the results for the case of Basis I and gives practically equivalent results for Basis II, with much smaller basis sets in both cases. We have done calculations for other values of γ, and these general conclusions are also valid for $1 < \gamma < 100$.

It is interesting to notice that a reduction in the number of basis functions from 6 to 2 in the variational scheme still yields reasonable results for the ground state energy. In the case of Basis II, for $\gamma = 0.1$, two variational function give a lower value for the ground state energy than the whole set of 35 oscillator function.

Because of the specific form of c^2 (Eq. (7)) and (Eq. (8), it is clear that for a given value of γ the energy associated with the set of quantum numbers $(-m, \gamma)$ is obtained from the one for (m, γ) by subtracting $2m\gamma$ from it.

Finally, we comment on the values of the variational parameter z which minimize the energy of the ground and excited states. For the case of Basis I, z mimics an effective charge due to the magnetic field, and as expected it increases with the field strength $(z = 1$ for $\gamma = 0)$. For instance, for the ground state, results presented in table I correspond to $z = 1.22$ for $\gamma = 1$ and $z = 2.84$ for $\gamma = 10$; for the $2p_z$ state $z = 2.00$ and $z = 5.70$ and for $2p_{+1}$, $z = 2.31$ and $z = 6.72$ for $\gamma = 1$ and $\gamma = 10$ respectively. In the case of Basis II, there is no direct physical interpretation for the parameter z; $z < 1$ for very high fields and $z > 1$ for lower fields.

In conclusion, the present approach is an improvement over the method suggested in Refs. 1 and 2: the introduction of a variational scaling factor, not only extends the region of validity of the method, still incorporating its conveniences, but also reduces significantly the number of basis functions needed to give equivalent results, simplifying the computational work.

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TABLE CAPTIONS

Table I - Ground state energy calculations for several values
          of magnetic field intensities: Basis I with 17
          functions and Basis II with 35 functions.
          I-* and II-* are variational calculations for
          basis I and II respectively with six functions each.

Table II - Results for some hydrogen excited states energies
           for γ = 1; P: calculations of Praddaude[*];
           I, II, I-* and II-* are the same as in Table I.

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Table I

γ	*	Basis I	Basis II	I - β	II - β
0	-1.	-1.	-0.98412	-1.	-0.945272
0.1	-0.99508	-0.99504	-0.6755	-0.99504	-0.94074
0.5	-0.89447	-0.8840	-0.7871	-0.8894	-0.8452
1	-0.66241	-0.5510	-0.5991	-0.6281	-0.6152
2	-0.04450	0.7779	-0.0058	0.1045	0.0076
3	0.67087	2.9898	0.7011	0.9793	0.7315
5	2.2392	10.067	2.2618	2.9206	2.3178
10	-	43.235	6.523	8.319	6.634
25	20.267	-	20.262	-	20.590
100	92.543	4421.59	92.959	121.638	94.937

*Values for $\gamma \leq 5$ are from Cabib et al.[3] and the others are from Larsen[4].

Table II

	P	Basis I	Basis II	I - β	II - β
$2p_0$	0.47999	2.070	0.481	0.693	0.501
$2p_1$	2.08682	3.067	2.092	2.221	2.097
$3d_1$	2.58686	23.47	2.632	2.927	2.624
$3d_2$	4.29389	24.52	4.295	4.473	4.303