

Single state variational calculations with applications to large and small magnetic fields

Brian L Burrows

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1 Introduction

Many calculations of the effects of magnetic fields on atomic and molecular systems have concentrated on small field strengths, and have usually been performed in the framework of perturbation theory. Here, we treat large fields as well as small, and so resort to variational calculations suitable for discrete bound states. Details of our calculations will be given, together with a simple example that illustrates both the theory and the method of our calculations. Essentially, our choice of basis is tailored for each state treated, and contains a set of linear and non-linear parameters appropriate to each state studied. With these parameters fixed, we undertake an $N \times N$ matrix calculation of the lowest N states of the system. As is well-known, and illustrated here, the eigenvalues of this matrix provide upper bounds to each of the states separately, and may be minimised with respect to all embedded parameters for each state separately. In the present calculations, a single nonlinear parameter suffices. We treat the atom H , and the diatomic ion H_2^+ in the latter case with the field parallel to the internuclear axis. Our results are compared with some other non-variational treatments some of which extend the traditional treatment to very large fields.

2 Variational specification of a state

For any normalised real wave function and Hermitian H we have for each eigenvalue E

$$E = \frac{\langle \psi | H \psi \rangle}{\langle \psi | \psi \rangle}, W = \frac{\langle (\psi + d\psi) | H (\psi + d\psi) \rangle}{\langle \psi + d\psi | \psi + d\psi \rangle} \quad (1)$$

so that using the normalisation and without loss of generality choosing $d\psi$ orthogonal to ψ we have

$$W = E + dE + d^2E, dE = \frac{2}{N_0} \langle d\psi | (H - E) \psi \rangle, d^2E = \frac{2}{N_0} \langle d\psi | (H - E) d\psi \rangle \quad (2)$$

with

$$N_0 = 1 + \langle d\psi | d\psi \rangle \geq 0 \quad (3)$$

We assume that we have a Hamiltonian where the eigenvectors form a complete set and $\{\psi_n\}$ and

$$H\psi_n = E_n\psi_n, n = 0, 1, \dots \quad E_n < E_{n+1} \quad (4)$$

so the stationary points can be analysed by expanding d^2E in terms of the stationary states and for each eigenstate n considering

$$\Delta m = \langle \psi_m | (H - E) \psi_n \rangle \quad (5)$$

Thus we have $\Delta(m) > 0, m > n, \Delta(m) < 0, m < n$ and we have a saddle point for all excited states whereas the ground state is a minimum. The same conclusions hold for a more general basis $\phi_n = U\psi_n$ where U is a non singular operator and d^2E is then expanded in terms of $U^{-1}\phi_m$. We may construct such a basis to depend on a set of non-linear parameters and for any fixed values of these we may solve the generalised eigenvalue problem with the first $N + 1$ basis elements.

$$(h - \lambda s)\mathbf{a} = 0, \quad h[i, j] = \langle \phi_i | H \phi_j \rangle, s[i, j] = \langle \phi_i | \phi_j \rangle \quad (6)$$

This is equivalent to a variation of W subject to the normalisation of the wave function and we obtain the eigenvalues and eigenvectors $(e_k, w_k), k = 0 \dots N$. Here e_n is a maximum in the space spanned by the set $F = \{w_k, k = 0 \dots n\}$ and simultaneously a minimum in the set $G = \{w_k, k = n \dots N\}$. We note that in the space generated by the set F , since it is of dimension $n+1$, there exists a function v orthogonal to the space generated by $\{\psi_m, m = 0 \dots (n-1)\}$ and is therefore in the space generated by $\{\psi_m, m \geq n\}$. Consequently calculating W with $\psi = v$ leads to

$$e_n \geq E(v) \geq E_n \quad (7)$$

since e_n is the maximum in F . Thus we have bounds for a general state and we can vary the non-linear parameters to improve them. To illustrate this procedure we can use the trial functions $\exp(-\alpha r), r\exp(-\alpha r), r^2\exp(-\alpha r)$ and vary α , to estimate the first excited s-state for non-relativistic atomic hydrogen. The choice of the non-linear parameter is made by constructing a sequence of values in the form

$$\alpha_i = \alpha_0 + \delta(i\sqrt{(2)} - \text{int}[i\sqrt{(2)})), i = 1 \dots M \quad (8)$$

where int denotes integer part, and choosing the minimum value of the corresponding eigenvalue. So that for example $M = 10, \alpha_0 = 0, \delta = 1$ leads to the accurate value -0.12499997 compared to the exact -0.125 but the other two states are much less accurate. Restarting the iteration with the estimate of α and a smaller $\delta = 0.02$ the after another 10 iterations we obtain the accurate value $E = -0.1250000$. But the estimates of the other two eigenstates are -0.489339 and -0.01074646 compared to the exact values -0.5 and -0.0555555 so they are much less accurate.

So it is a state dependent estimate. The $\sqrt{2}$ in the sequence can be replaced by \sqrt{P} where P is a prime; the essential required property is that the sequence is equi-distributed in the interval. The proof of this result was given in 1965 by B C Baayen and G Helmborg who established the analogous general results for any irrational number.

2.1 The Hydrogen molecule Ion with a magnetic field

The one-electron Hamiltonian for this system, with zero angular momentum and subject to a field along the molecular axis is

$$H = -\frac{1}{2}\nabla^2 - \frac{1}{r_a} - \frac{1}{r_b} + \frac{1}{R} + B(x^2 + y^2) \quad (9)$$

where the atoms are at a and b separated by R and B is the field strength. Values of B are from $10^8 G$ which is the level in a white dwarf star to $10^{12} G$ which is a typical level attained in neutron stars. Thus the field is not a small perturbation and we use a conversion factor of $2.3505 \times 10^9 G = 1 a.u.$. The coordinate system used is the spheroidal system where

$$p = \frac{r_a + r_b}{R}, q = \frac{r_a - r_b}{R} \quad (10)$$

The problem is independent of the azimuthal angle and there is an additional symmetry that the states are symmetric or antisymmetric with respect to a plane through the mid-point of the intermolecular axis. In addition we note that in these coordinates the inner product includes a weight factor proportional to $(p^2 - q^2)$

The chosen basis functions are

$$\phi_n = \bar{N}L(n_1, 2\alpha(p-1))\exp(-\alpha(p-1))P(m_1, q), 0 \leq n_1 \leq N_1, 0 \leq m_1 \leq M_1 \quad (11)$$

where for integers n_1, m_1 , $L(n_1, 2\alpha(p-1))$ is a Laguerre polynomial in the variable $(2\alpha(p-1))$, $P(m_1, q)$ is a Legendre polynomial and \bar{N} is a normalisation constant. We note that formally the specification of H by the operator in (9) which models the problem is not a sufficient definition since we need to specify the domain. We are interested in bound states so that we need to choose $\alpha > 0$ and the functions in (11) for all positive integers $N_1 < \infty, M_1 < \infty$ form the domain which at each stage also depends on a single non-linear parameter α .

For any state α can be chosen optimally. An advantage of the basis is that all integrals can be evaluated analytically as functions of α so for example

$$\langle \phi_i | (\frac{1}{r_a} + \frac{1}{r_b}) \phi_j \rangle = K_i K_j LP[1][n_1, n_2] LQ[0][m_1, m_2] \quad (12)$$

where K_i, K_j are constants depending on the normalisations, i is associated with the pair (n_1, m_1) and j is associated with the pair n_2, m_2 and

$$LP[1] = \int_1^\infty L(n_1, 2\alpha(p-1))pL(n_2, 2\alpha(p-1))\exp(-2\alpha(p-1))dp \quad (13)$$

and

$$LQ[0] = \int_{-1}^1 P(m_1, q)P(m_2, q)dq = 0, m_1 \neq m_2 \quad (14)$$

Given values of B, R the non-linear parameter α can be efficiently chosen to obtain the minimum energy. The eigenvalues are obtained using Maple and the process is fairly fast. However if large matrices are required to obtain the solution to a particular accuracy, smaller matrices may be used initially to estimate the parameters.

2.2 The Hydrogen atom in a magnetic field

The required Hamiltonian expressed in parabolic coordinates is

$$H = -\frac{1}{2}\nabla^2 - \frac{2}{u+v} + Buv \quad (15)$$

where

$$x = \sqrt{uv}\cos(\Phi), y = \sqrt{uv}\sin(\Phi), z = \frac{1}{2}(u-v) \quad (16)$$

and since the problem is independent of the azimuthal angle we may choose $\Phi = 0$ In this case the basis is taken to be

$$\phi_n = \bar{N}L(n_1, 2\alpha u)\exp(-\alpha u)L(m_1, 2\alpha v)\exp(-\alpha v), \quad 0 \leq n_1, m_1 \leq N_1 \quad (17)$$

which for fixed α is part of a complete set in a Hilbert space which defines the domain of H . The weight function for the inner product is proportional to $u+v$ and similarly all integrals can be evaluated analytically. Since we have symmetry in exchange of u and v the eigenfunctions then provided there is no degeneracy, the eigenfunctions are symmetric or antisymmetric in the interchange of u and v . (For degeneracy they can be chosen symmetric or antisymmetric and in the limit as B tends to zero we obtain the s and p states respectively.) This symmetry reduces the size of the matrices used by a factor 2.

3 Results

Table 1: The Lowest symmetric state minima

| B | R(a.u.) | α | E | Comparison |
|--------------------|---------|----------|----------|------------|
| 0 | 2.0 | 1.5738 | -0.60263 | -0.60263 |
| 1×10^8 | 2.0 | 1.5738 | -0.60234 | -0.60234 |
| 5×10^8 | 1.98 | 1.5249 | -0.59551 | - 0.59548 |
| 1×10^9 | 1.92 | 1.6206 | -0.57537 | -0.57535 |
| 1a.u. | 1.75 | 1.8953 | -0.47498 | -0.47496 |
| 5×10^9 | 1.50 | 2.1434 | -0.17478 | - |
| 1×10^{10} | 1.25 | 2.2360 | 0.54489 | 0.54522 |
| 1×10^{11} | 0.58 | 2.6135 | 17.52081 | 17.5216 |
| 1×10^{12} | 0.283 | 3.4965 | 204.1499 | 204.1947 |

Table 2: The first excited symmetric state minima

| B | R(a.u.) | α | E | Comparison |
|--------------------|---------|----------|-----------|------------|
| 0 | 8.8 | 3.1661 | -0.17505 | -0.17505 |
| 1×10^8 | 8.8 | 3.0619 | -0.17272 | -0.17270 |
| 5×10^8 | 8.2 | 2.5218 | -0.13384 | - 0.12939 |
| 1×10^9 | 7.6 | 5.0604 | -0.060792 | -0.06052 |
| 1a.u. | 6.6 | 5.3946 | 0.174487 | 0.17456 |
| 5×10^9 | 5.8 | 6.4229 | 0.685415 | - |
| 1×10^{10} | 5.2 | 8.0545 | 1.699210 | 1.69969 |
| 1×10^{11} | 3.9 | 17.7582 | 20.70149 | 20.7045 |
| 1×10^{12} | 3.55 | 80.6912 | 212.1062 | 212.11385 |

Table 3: The lowest antisymmetric state minima

| B | R(a.u.) | α | E | Comparison |
|--------------------|---------|-----------|------------|------------|
| 0 | 12.55 | 6.24654 | -0.500061 | -0.500061 |
| 1×10^8 | 12.55 | 6.24654 | -0.499610 | -0.49961 |
| 5×10^8 | 12.00 | 7.68703 | -0.489251 | - 0.489050 |
| 1×10^9 | 11.50 | 7.6031 | -0.460563 | -0.460515 |
| 1a.u. | 9.58 | 10.43018 | -0.3314365 | -0.3314365 |
| 5×10^9 | 8.4 | 10.5749 | 0.020852 | 0.10097 |
| 1×10^{10} | 7.0 | 11.72655 | 0.8191167 | 0.81995 |
| 1×10^{11} | 5.0 | 28.47712 | 18.41176 | 18.41835 |
| 1×10^{12} | 3.2 | 50.051336 | 206.7727 | 206.8038 |

Table 4: The lowest symmetric state minima for hydrogen

| B | α | E | Comparison |
|--------------------|----------|------------|-------------|
| 1×10^8 | 5.12409 | -0.499548 | -0.499548 |
| 0.1 a.u | 2.4655 | -0.4975265 | -0.49752665 |
| 1×10^9 | 1.9685 | -0.460427 | - 0.4604113 |
| 1 a.u | 1.95252 | -0.3311689 | -0.331166 |
| 1×10^9 | 1.76349 | 0.819733 | 0.820181 |
| 10 a.u | 1.637226 | 3.252203 | 3.25261 |
| 1×10^{11} | 1.49617 | 18.41261 | 18.4199 |
| 100 a.u | 1.4439 | 46.211 | 46.2178 |
| 1×10^{12} | 1.389027 | 206.814439 | 206.831 |

Table 5: The lowest antisymmetric state minima for hydrogen

| B | α | E | Comparison |
|--------------------|-----------|------------|------------|
| 1×10^8 | 4.1246 | -0.122403 | -0.12237 |
| 0.1 a.u | 2.96190 | -0.1224100 | -0.1224099 |
| 1×10^9 | 1.860171 | -0.0043598 | - 0.004351 |
| 1 a.u | 1.6833996 | 0.23999339 | 0.24004 |
| 1×10^9 | 1.64 | 1.7881937 | 1.78895 |
| 10 a.u | 1.63 | 4.61735 | 4.61795 |
| 1×10^{11} | 1.63 | 20.83136 | 20.837 |
| 100 a.u | 1.63 | 49.5367 | 49.537 |
| 1×10^{12} | 1.63 | 212.28 | 212.28 |

Table 6: The first excited symmetric state minima for hydrogen

| B | α | E | Comparison |
|--------------------|----------|-----------|------------|
| 1×10^8 | 2.682 | -0.119091 | -0.1207 |
| 0.1 a.u | 1.999 | -0.098089 | - |
| 1×10^9 | 1.53 | 0.063190 | 0.06080 |
| 1 a.u | 1.39 | 0.339642 | - |
| 1×10^9 | 1.40 | 1.938609 | - |
| 10 a.u | 1.36 | 4.80949 | - |
| 1×10^{11} | 1.33 | 21.3254 | - |
| 100 a.u | 1.31 | 162.4052 | - |
| 1×10^{12} | 1.31 | 218.9834 | - |

4 Conclusion

We have adapted a well known variational method so as to obtain bounds for each state independently of the other states and applied this to the problems of hydrogen and the hydrogen molecular ion in weak and strong magnetic fields. To do this we use a basis set of functions in the space. Each of these sets contains an arbitrary positive parameter, α . The basis is chosen by truncating the expansion in a particular set and choosing α as a variational parameter for one particular state. The variational estimate of the energy is then found by optimising the appropriate eigenstate of the secular equation in this basis. In each case we have chosen a separable basis which reduces the number of matrix element calculations required and all integrations may be evaluated analytically in terms of α , B and R so that the same elements can be used for different problems. For weak fields the secular equation calculation converges for small-sized matrices but for the stronger fields larger matrices are required in order to obtain at least 5 digit accuracy in the comparisons. More qualitative results to less than 1 percent accuracy can be obtained with much smaller matrices but for all the calculations carried out here the Maple routines were sufficient. In general a more sophisticated choice of basis with more variational parameters may result in smaller matrices for a given accuracy, but this will almost certainly require numerical integration for which there will be additional problems of accuracy and the time taken for each calculation.