Pseudo-spectral methods for atoms in strong magnetic fields

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ABSTRACT

We present a new pseudo-spectral algorithm for the calculation of the structure of atoms in strong magnetic fields. We have verified this technique for one-, two- and three-electron atoms in zero magnetic fields against laboratory results and find typically better than 1 per cent accuracy. We further verify this technique against the state-of-the-art calculations of hydrogen, helium and lithium in strong magnetic fields (up to about $2 \times 10^6$ T) and find a similar level of agreement. The key enabling advantages of the algorithm are its simplicity (about 130 lines of commented code) and its speed (about $10^2$–$10^5$ times faster than finite-element methods to achieve similar accuracy).

Key words: atomic data – magnetic fields – methods: numerical – stars: magnetic field – stars: neutron – white dwarfs.

1 INTRODUCTION

A hydrogen atom in a magnetic field is arguably the simplest Hamiltonian without an analytic solution – it is a combination of a harmonic oscillator with a Coulomb potential. The problem of atoms in magnetic fields is also a vexing challenge in the study of neutron stars and white dwarfs. A sufficiently intense magnetic field cannot be treated perturbatively. If the magnetic field completely dominates over the nucleus, one can understand the atomic structure as a one-dimensional (1D) atom (Loudon 1959; Haines & Roberts 1969). A non-trivial relaxation of the 1D assumption is the adiabatic approximation that assumes that the wave function of the electron perpendicular to the magnetic field is simply the ground Landau level of the electron without the nucleus (e.g. Heyl & Hernquist 1998).

The most challenging regime is of course where the nucleus and the magnetic field compete for the electron’s attention. This lies around $10^6$–$10^7$ T for hydrogen and is known as the strong-field regime. For such field strengths, one cannot assume that the electron lies in the lowest Landau level. For a detailed bibliography of the vast literature of atomic calculations in strong magnetic fields, we encourage the reader to consult our recent work (Thirumalai & Heyl 2009).

In the strong-field regime, one can assume that the wave function is a sum of Landau levels or spherical harmonics (e.g. Ruder et al. 1994) or solve the two-dimensional (2D) partial differential equation without this assumption (e.g. Thirumalai & Heyl 2009). This work takes the second approach and solves the differential equations for the electronic wave functions and the interelectron potentials numerically. The main goal of this paper is not to present more accurate calculations of atoms in strong magnetic fields (although the calculations rival the current state of the art), but rather the purpose is to provide a new, much faster algorithm to perform these calculations and verify its results against previous work.

This new algorithm is straightforward to implement and compact; the 30-line program for single-electron atoms and the 130-line program for multiple-electron atoms are presented in the appendices. With this simplicity comes a dramatic speed-up of the calculation of a factor of $10^2$–$10^5$ relative to finite-element techniques (Thirumalai & Heyl 2009) while achieving similar accuracy. This pseudo-spectral algorithm interpolates the approximate solution to the differential equations as a polynomial over an irregular mesh. Because the approximate solution is a polynomial, it is also analytic over the mesh. Even if the actual solution oscillates on a scale of a couple of mesh points, the analytic interpolant still provides an accurate approximation to the solution. On the other hand, if the actual solution develops discontinuities (i.e. it is not analytic), the pseudo-spectral method is less useful (however see Boyd 2001). In the case of magnetized atoms, the solution to the Schroedinger equation is analytic everywhere except at the origin where we can set a boundary condition, so the pseudo-spectral method yields great returns.

In the following sections, we will present the partial differential equations for the electronic wave functions (Section 2.1), the inter-electron potential (Section 2.2), an introduction to pseudo-spectral methods (Section 2.3), the application of boundary conditions (Section 2.4), our results (Section 3) and source code (Appendices A and B).

2 CALCULATIONS

2.1 The Hamiltonian

Rather than examining the Hamiltonian of an atom in a magnetic field in detail, we will simply recap the relevant equations here and
refer the reader to Thirumalai & Heyl (2009) for further details. We use the Hartree–Fock equations to describe the wave function of a multiple-equation system, this yields a coupled set of Schrödinger-like equations for an approximation to the wave function of each electron:

\[
\left[-\nabla^2 - \frac{2}{r_i} + \beta_z R_i + \frac{2}{Z} \sum_{j \neq i} V_{ij} - E_i\right] \psi_i = 0, \tag{1}
\]

where \(i, j = 1, 2, 3, \ldots, N\). Here, \(N\) is the number of electrons, \(Z\) is the charge of the nucleus located at the origin, \(V_{ij}\) is the interelectron potential operator and \(\beta_z\) measures the strength of the magnetic field, \(\beta_z = B\hbar/(2Z^2 e^2 m_i c^2) = B/(4.72 \times 10^5 \text{T})\). The variable \(r_i\) is the distance from the origin and \(R_i = r_i \sin \theta\), the distance from the axis defined by the direction of the magnetic field; this notation is consistent with the software in the appendices. The functions \(\psi_i\) must be finite at the origin and approach zero as \(r \to \infty\).

The total binding energy of the atom is given by

\[
E = \sum_i \left[ E_i + 2\beta_z \left( m_i + s_i - \frac{1}{2} \right) - \frac{1}{Z} \sum_{j \neq i} \langle \psi_j | V_{ij} | \psi_i \rangle \right] \tag{2}
\]

in units of \(Z^2 2^7 m_i c^2/2\).

Although the Hamiltonian is no longer spherically symmetric, it is still symmetric about the magnetic axis, so we expect the azimuthal or magnetic quantum number \(\ell = m_i\) to be good. We will label the solutions to equation (1) by \(v_i, s_i\) and \(m_i\) where \(s_i\) is the spin of the electron and \(v_i\) equals 1 for the most bound state with a particular value of \(s_i\) and \(m_i\) and 2 for the next most bound state and so on.

The first step is to specify the precise differential equations to solve. Specifically, we will take

\[
\psi_i = \frac{u_i(r, \mu)}{r} e^{im_i \phi}. \tag{3}
\]

The parameter \(\mu = \cos \theta\), where \(\theta\) is the angle from the z-axis. For the radial dependence, the domain is \([0, \infty)\), so we would like to compactify the domain to \([-1, 1]\). Let

\[
r = 2 \tanh \frac{r_z}{r_Z} - 1, \tag{4}
\]

where \(r_z\) ranges from zero to infinity while \(r\) now ranges from \(-1\) to 1. The quantity \(r_Z\) is the ‘zoom radius’ that determines at what value of \(r\) the relationship between \(r\) and \(r_z\) goes from linear to exponential,

\[
r \approx \frac{2r_z}{r_Z} - 1, \quad r \ll r_Z; \quad r \approx 1 - 4 \exp(-2r_z/r_Z), \quad r \gg r_Z. \tag{5}
\]

Because 2 tanh \(1 - 1 \approx 0.5\), about one third of the points lie at \(r > r_Z\). Because the domain is compactified, we can easily apply boundary conditions both at infinity and at the origin as appropriate for solving the Schrödinger equation: \(u_i(-1, \mu) = u_i(+1, \mu) = 0\) and the additional condition for \(m_i \neq 0\) that \(u_i(r, -1) = u_i(r, +1) = 0\).

Using the substitution of equations (3) into (1), yields

\[
\left[-\frac{\partial^2}{\partial r_i^2} - \frac{1}{r_i^2} (1 - \mu^2) \frac{\partial^2}{\partial \mu^2} + \frac{2\mu}{r_i^2} \frac{\partial}{\partial \mu} + m_i^2 + \frac{2}{r_i^2} \right] + \beta_z R_i + \frac{2}{Z} r_i e^{-im_i \phi} \sum_{j \neq i} \langle \psi_j | V_{ij} | \psi_i \rangle u_i = 0 \tag{6}
\]

where

\[
\frac{\partial^2}{\partial r_i^2} = 4 \left(1 - r_i^2\right) \left[\frac{\partial^2}{\partial r_i^2} - r_i^2 \frac{\partial}{\partial r_i}\right] \tag{7}
\]

where \(r_p = (r + 1)/2\).

### 2.2 Interelectron potential

Using the results of Section 2.3, we can convert this partial differential equation into a matrix equation, specifically an eigenvalue equation. However, before doing this in Section 2.4, we must discuss the interelectron potential \(V_{ij}\).

The interelectron potential consists of two terms, the direct and exchange interactions where

\[
V_{ij} = V_{\text{direct},ij} - V_{\text{exchange},ij}, \tag{8}
\]

if the spins of electrons \(i\) and \(j\) are aligned and \(V_{ij} = V_{\text{direct},ij}\) otherwise. The direct interaction satisfies

\[
V_{\text{direct},ij} \psi_i = \phi_j(r) \psi_i \tag{9}
\]

where

\[
\nabla^2 \phi_j = -4\pi \psi_j^* \psi_j \tag{10}
\]

which we can solve, knowing the values of \(\psi_j\), by inverting the Laplacian to yield

\[
\phi_j = (\nabla^2)^{-1}[-4\pi \psi_j^* \psi_j], \tag{11}
\]

where \((\nabla^2)^{-1}\) is the inverse of the Laplacian with the appropriate boundary conditions supplied. Therefore, the direct interaction is a diagonal operator, essentially a function.

On the other hand the exchange interaction is more complicated. We have

\[
V_{\text{exchange},ij} \psi_i = \tilde{\phi}_{ij}(r) \psi_j \tag{12}
\]

where

\[
\nabla^2 \tilde{\phi}_{ij} = -4\pi \psi_i^* \psi_j. \tag{13}
\]

Therefore, we have

\[
V_{\text{exchange},ij} \psi_i = \tilde{\phi}_{ij}(r) \psi_j = \psi_j (\nabla^2)^{-1}[-4\pi \psi_j^* \psi_i]. \tag{14}
\]

Thinking of the different components of the right-hand sides of equations (12) and (14) as matrices, we can write the potentials due to the direct and exchange interactions in matrix notation as

\[
V_{\text{exchange},ij} \psi_i = -4\pi \left( \psi_j (\nabla^2)^{-1} \right) \psi_i, \tag{15}
\]

where we have dropped the index \(i\) because the exchange interaction operator only depends on the wave function of the electron \(j\). Both the direct and exchange potentials must go to zero as \(r \to \infty\) and be finite at the origin.

The set of coupled equations is of course non-linear and difficult to solve directly; however, we can approach the solution iteratively, by first solving the equation (1) ignoring the interelectron terms and then on subsequent iterations using the wave functions from the previous iteration to calculate the interaction operator using equations (11) and (15). At each iteration, the equations are decoupled, so the time to calculate a single iteration scales as the number of electrons, making the calculation of even large atoms tractable. If the equations were coupled through the exchange term, then each dimension of the matrix to diagonalize would scale with the number of electrons, so the time to complete an iteration would scale as the cube of the number of electrons.

Let us evaluate for the exchange potential operator using the substitution of equation (3). We have

\[
V_{\text{exchange},ij} \left( \frac{e^{im_i \phi}}{r_j} \right) = \tilde{\phi}_{ij}(r) \frac{e^{im_i \phi}}{r_j}, \tag{16}
\]

and

\[
r_j e^{-im_i \phi} V_{\text{exchange},ij} \left( \frac{e^{im_i \phi}}{r_j} \right) = \tilde{\phi}_{ij}(r) \frac{e^{-\Delta \phi \phi}}{r_j}, \tag{17}
\]
where $\Delta m = m_i - m_j$. Because none of the other terms in the Hamiltonian depend on $\phi$, neither side of equation (17) can depend on $\phi$ so let us define
\[ \phi_{ij}(r) = \phi_{ij}^\text{int}(r_i, \mu) e^{i\Delta m \phi}. \] (18)

where
\[ \nabla^2 \left[ \phi_{ij}^\text{int}(r_i, \mu) e^{i\Delta m \phi} \right] = -4\pi \frac{\partial^2 u_{ij}}{r_{ij}^2} e^{i\Delta m \phi}. \] (19)

Simplifying this result yields
\[ \left( \nabla^2 - \frac{\Delta m^2}{r_{ij}^2} \right) \tilde{\phi}_{ij}(r_i, \mu) = -4\pi \frac{\partial^2 u_{ij}}{r_{ij}^2} \] (20)

and
\[ r_s e^{-i\mu \phi} V_{\text{exchange}, i j} \frac{e^{i\mu \phi}}{r_s} = -4\pi \text{diag}(u_{ij}) \left( \nabla^2 - \frac{\Delta m^2}{r_{ij}^2} \right)^{-1} \text{diag} \left( \frac{u_{ij}}{r_{ij}^2} \right) \] (21)

where
\[ \nabla^2 = \frac{\partial^2}{\partial r_i^2} + \frac{1}{r_i} \frac{\partial}{\partial r_i} \left( 1 - \mu^2 \right) \frac{\partial^2}{\partial \mu^2} - \frac{2\mu}{r_i^2} \frac{\partial}{\partial \mu}. \] (22)

The result for the direct interaction is nearly trivial because it is a function rather than an operator. We have
\[ r_s e^{-i\mu \phi} V_{\text{direct}, i j} \frac{e^{i\mu \phi}}{r_s} \equiv -4\pi (\nabla^2)^{-1} \left[ \frac{u_{ij}^2}{r_{ij}^2} \right]. \] (23)

We must specify the boundary conditions on the inverse operators in equations (21) and (23). Both the direct and exchange potentials must go to zero at $r \to \infty$ and be finite at the origin. Furthermore, for $\Delta m \neq 0$, the exchange potential must vanish along the magnetic axis.

In principle, one could solve for all of the electronic wave functions at the same time, but this would render the differential equations non-linear; therefore, we first neglect the electronic contribution to the potential to find a first guess at the electronic wave functions. These wave functions become the input into equations (21) and (23) for the second iteration. This process is repeated until the total energy of the state is constant to one part in $10^5$ between successive iterations.

### 2.3 Pseudo-spectral methods

The basic idea behind interpolating spectral (or pseudo-spectral) methods is to approximate functions by their values at a set of points and a set of smooth functions to interpolate between these points for the purpose of calculating derivatives and integrals. An example is useful to make this concrete. A function $f(x)$ takes the values $f_i$ at the points $x_i$. We could construct an interpolation scheme by linearly interpolating between the points or using a cubic spline. This is the basis of finite difference schemes with successively higher accuracy. However, if we wanted an analytic function through the points, we could use the polynomial that passes through all of the points. This polynomial interpolant is given by
\[ f_i(x) = \sum_i f_i^p(x) = \sum_i f_i \prod_{j \neq i} (x - x_j) \prod_{j \neq i} (x_i - x_j). \] (24)

where we have used the notation of Trefethen (2000). The polynomial $p_i(x)$ has the property that it takes the value of unity at $x_i$ and it vanishes at all of the other points where the function values are given. We can take the derivative of the basic polynomial to yield
\[ p_i'(x) = p_i(x) \sum_{j \neq i} (x - x_j)^{-1} \] (25)

and evaluate it at one of the points $x_i$ to yield
\[ p_i'(x_i) = p_i(x_i) \sum_{j \neq i} (x_i - x_j)^{-1} = D_{ii} \] (26)

where
\[ D_{ii} = \prod_{j \neq i} (x_i - x_j). \] (27)

This domain is well suited for the angular dependence in spherical coordinates where we define $\mu = \cos \theta = z/r$ and use the Chebyshev points $x_i = \cos(i\pi/N), \ i = 0 \ldots N$. (28)

The choice of the points $x_i$ is completely arbitrary but for finite domains it is more stable to pick the points to be bunched towards the ends of the domain and more sparse in the middle (Trefethen 2000). A convenient set of points over the domain $[-1, 1]$ are the Chebyshev points
\[ x_i = \cos(i\pi/N), \ i = 0 \ldots N. \] (29)

This domain is well suited for the angular dependence in spherical coordinates where we define $\mu = \cos \theta = z/r$ and use the Chebyshev points to sample $\mu$. Thus, the angular dependence is evenly sampled in $\theta$.

### 2.4 Discrete equations

The octave programs given in the appendices for the single and multiple-electron problems convert the partial differential equations of Section 2.1 and Section 2.2 to matrix equations using the pseudo-spectral methods outlined in Section 2.3. We encourage readers that are familiar with octave or matlab to look under the hood and dissect the routines.

The previous section outlined how to construct a differentiation matrix using a pseudo-spectral method in one dimension. The second derivative is simply the square of this matrix and an integration operator is the inverse of the differentiation matrix with some boundary condition supplied. The remaining subtleties are how to apply boundary conditions and how to move to more than one dimension. The techniques outlined here are presented in Trefethen (2000) in greater detail, clarity and generality.

Supplying the boundary conditions for the eigenvalue equations is rather straightforward and most easily illustrated by an example. Let us find the eigenvalues of the matrix $M$ with the solution $f$ vanishing at the end points. We have
\[ Mf = \lambda f. \] (30)

Let us define the diagonal matrix, $B$.
\[ B = \begin{bmatrix} 0 & 0 & 0 & \cdots & 0 \\ 0 & 1 & 0 & \cdots & 0 \\ 0 & 0 & 1 & \cdots & 0 \\ \vdots & \ddots & \ddots & \ddots & \vdots \\ 0 & 0 & 0 & \cdots & 1 \\ 0 & 0 & 0 & \cdots & 0 \end{bmatrix} \] (31)

\[ B = \begin{bmatrix} 0 & 0 & 0 & \cdots & 0 \\ 0 & 1 & 0 & \cdots & 0 \\ 0 & 0 & 1 & \cdots & 0 \\ \vdots & \ddots & \ddots & \ddots & \vdots \\ 0 & 0 & 0 & \cdots & 1 \\ 0 & 0 & 0 & \cdots & 0 \end{bmatrix} \] (32)
with all of the diagonal elements being unity except for the first and last that vanish. Multiplying the vector \( f \) by \( B \) has the effect of setting the endpoints to zero, so let us look at the following eigenvalue equation

\[
\text{BMB} f = \lambda f. 
\]

(31)

The matrix \( B \) that precedes \( M \) ensures that the resulting output vector satisfies the boundary conditions, and the matrix that follows \( M \) ensures that the input vector satisfies the boundary conditions as well, so the eigenvectors of the matrix \( \text{BMB} \) except for two are guaranteed to satisfy the boundary conditions. The two remaining eigenvectors are linear combinations of \([1 0 \cdots 0] \) and \([0 0 \cdots 0 1]\) and have zero eigenvalues. We can either ignore these eigenvectors or define a new matrix \( \tilde{M} \) that lacks the first and last columns and the first and last rows of the original matrix \( M \). The eigenvectors of \( \tilde{M} \) are the same at those of \( \text{BMB} \) but with the first and last entries omitted.

In summary, to obtain the set of eigenvectors of \( M \) that satisfy the boundary conditions we construct \( \tilde{M} \) and add the first and last entries if needed. For the potential calculation, it is often more useful to work with \( \text{BMB} + (I - B) \), so that the resulting matrix can be inverted before setting the boundary conditions. In the potential calculation, we set the boundary condition at infinity because the Laplacian matrix vanishes for the row and column corresponding to infinity, so we drop the row and column before inverting the Laplacian. However, we would also like to set a boundary condition at the origin, so we must include the origin in the calculation. At the origin the angular terms in the Laplacian diverge, but this is a coordinate singularity that we address by including only a single entry for the origin and drop the angular derivatives there. In this way, we address the divergent terms at the origin and the vanishing terms at infinity.

The second issue is how to build the various operators in more than one dimension. Let us say that we have obtained a vector of points \( x \) of dimension \( N \) and a pseudo-spectral derivative \( D_\nu \) and similarly a vector of points \( y \) of dimension \( M \) and its derivative \( D_\gamma \). If we construct

\[
x' = x \otimes I_M, \quad y' = I_N \otimes y, 
\]

(32)

where \( I_N \) is a vector of \( N \) ones and \( \otimes \) denotes the Kronecker product, we obtain a 2D mesh \( (x', y') \) of points in two vectors of dimension \( N \times M \). Finally, we would like to construct the Laplacian over this mesh (this example is Cartesian). We have

\[
\nabla^2 = (D_\nu)^2 \otimes I_M + I_N \otimes (D_\gamma)^2, 
\]

(33)

where \( I_N \) is the \( N \times N \) identity matrix. The resulting matrix \( \nabla^2 \) has dimensions \( (N \times M) \times (N \times M) \) and calculates the Laplacian over the mesh specified by \( (x', y') \).

These techniques allow us to discretize the equations outlined in Section 2.1 and Section 2.2 to obtain the software in the appendices.

3 RESULTS

3.1 Hydrogen

As a first test of the algorithm, we examined hydrogen in a strong magnetic field and in zero field. The \texttt{octave} program is presented in Appendix A. This is one case where the program is shorter than the tables it calculates and replaces. In zero field with 30 radial points \( (N = 31, \) excluding \(-1 \) and \(1 \) in the compactified domain, corresponding to the origin and infinity, respectively, in the real domain) and with 12 angular points \( (M = 11) \), it calculates the eigenvalues up to principal quantum number, \( n = 12 \) to at least three digits of accuracy (a total of 650 states). Up to \( \beta \sim 10 \), it determines the low-lying states of hydrogen (again with \( N = 31 \) and \( M = 11 \)) to at least three digits of accuracy (Ruder et al. 1994; Thirumalai & Heyl 2009); for \( \beta \lesssim 1 \), the accuracy is typically two orders of magnitude better. The distinct advantage of the pseudo-spectral algorithm is the speed to achieve accurate results. The fine mesh calculations of Thirumalai & Heyl (2009) took up to 2 d or \( 1.7 \times 10^8 \) s – the pseudo-spectral algorithm takes about \( 1.4 \) s to get the same accuracy on the same processors. The algorithm uses spherical coordinates, so it is not well suited to fields much stronger than \( \beta = 10 \). At \( \beta = 100 \), a finer mesh \( (M = 31 \) and \( N = 51) \) and 150 s of computation time are required to obtain three digits of agreement with Ruder et al. (1994); however, in this regime, cylindrical coordinates may be more appropriate and one can use the adiabatic approximation to obtain accurate results (Heyl & Hernquist 1998).

3.2 Helium and lithium

The problem of multi-electron atoms (Appendix B) is of course much more complicated than hydrogen. Again we begin with the zero-field case, but we have many states to examine that test the direct and exchange interactions separately. In this case, some validation for a vanishing magnetic field is useful. Table 1 compares the zero-field results for some low-lying states of helium and lithium with the experimentally determined values from Ralchenko et al.

| Conf. | Term | \( J \) | \( E_{\text{exp}} \) | \( E_{\text{spe}} \) | \( \Delta \) (per cent) |
|-------|------|------|----------------|----------------|----------------------|
| Helium I | \( 1s^2 \) | \( 1S \) | 1.451 692 958 | 1.431 89 | -1.364 |
| | \( 1s^2 \) | \( 3S \) | 1.087 514 256 | 1.089 96 | 0.225 |
| | \( 1s^2 \) | \( 1S \) | 1.072 885 081 | 1.079 29 | 0.598 |
| | \( 1s^2 \) | \( 3P^\circ \) | 1.066 484 964 | 1.068 56 | 0.195 |
| | | | 1.066 484 790 | 1.068 57 | 0.196 |
| | | | 1.066 482 539 | 1.068 56 | 0.195 |
| | \( 1s^2 \) | \( 1P^\circ \) | 1.061 818 980 | 1.065 93 | 0.387 |
| | \( 1s^2 \) | \( 1S \) | 1.034 248 834 | 1.037 19 | 0.284 |
| | \( 1s^2 \) | \( 1S \) | 1.030 539 891 | 1.034 56 | 0.391 |
| | \( 1s^2 \) | \( 3P^\circ \) | 1.028 945 784 | 1.031 74 | 0.272 |
| | | | 1.028 945 735 | 1.031 74 | 0.271 |
| | | | 1.028 945 117 | 1.031 74 | 0.272 |
| | \( 1s^2 \) | \( 3D \) | 1.027 722 445 | 1.030 73 | 0.293 |
| | \( 1s^2 \) | \( 3P^\circ \) | 1.027 722 439 | 1.030 73 | 0.293 |
| | \( 1s^2 \) | \( 3D \) | 1.027 722 338 | 1.030 73 | 0.293 |
| | \( 1s^2 \) | \( 3P^\circ \) | 1.027 714 652 | 1.030 73 | 0.294 |
| | \( 1s^2 \) | \( 1P^\circ \) | 1.027 476 815 | 1.030 92 | 0.335 |
| Lithium I | \( 1s^2 2s \) | \( 2S \) | 1.661 773 620 | 1.655 95 | -0.350 |
| | \( 1s^2 2p \) | \( 2P \) | 1.646 683 387 | 1.640 97 | -0.347 |
| | \( 1s^2 2p \) | \( 2P \) | 1.646 683 042 | 1.640 97 | -0.347 |
| | \( 1s^2 2s \) | \( 2S \) | 1.634 226 909 | 1.628 83 | -0.330 |

Note. Energies are in units of Rydberg energies in the Coulomb potential of nuclear charge \( Z e \), where \( Z = 2 \) for helium and \( Z = 3 \) for lithium. We use \( M = 7, N = 31 \) and \( r_2 = 58 \). The value of \( r_2 \) is chosen to provide close agreement for the ground state of helium and held fixed. Individual calculations take about 10 s for helium and 20 s for lithium. The primary source for the helium data is Drake & Martin (1998) and Moore (1971) for the lithium data.
Table 2. Table listing the binding energies of the most tightly bound states of helium in moderate to large magnetic fields; $M_z = -1$ or $M_z = -2$ and $S_z = -1$, $\pi_z = +1$.

| $\beta_Z$ | $M_z = -1$ | R94 | $M_z = -2$ | R94 |
|-----------|------------|-----|------------|-----|
| 0.01      | 1.1221     | 1.1183 | 1.1182     | 1.0871 | 1.0852 | 1.0828 |
| 0.02      | 1.1656     | 1.1612 | 1.1609     | 1.1265 | 1.1234 | 1.1207 |
| 0.05      | 1.2734     | 1.2691 | 1.2658     | 1.2215 | 1.2175 | 1.2097 |
| 0.07      | 1.3359     | 1.3319 | 1.3258     | 1.2764 | 1.2732 | 1.2596 |
| 0.10      | 1.4211     | 1.4189 | 1.4069     | 1.3515 | 1.3510 | 1.3266 |
| 0.20      | 1.6586     | 1.6585 | 1.6270     | 1.5653 | 1.5598 | 1.5073 |
| 0.50      | 2.1603     | 2.1550 | 2.0508     | 2.0415 | 2.0009 | 1.8508 |
| 0.70      | 2.4584     | 2.4029 | 2.2329     | 2.2902 | 2.2246 | 1.9935 |
| 1.00      | 3.2165     | 2.7026 | 2.4675     | 3.0102 | 2.4981 | 2.2572 |
|           | 2.7115     |       |            |       |       | 2.6668 |

Note. Energies are in units of Rydberg energies in the Coulomb potential of nuclear charge $Ze$, where $Z = 2$ for helium. The results from the current work can be compared readily with previous work (Ruder et al. 1994; Thirumalai & Heyl 2009). The first row for $\beta_Z = 1$ is for $M = 11$ like the other rows; the second row gives the results from $M = 41$. TH08 indicates results from Thirumalai & Heyl (2009), and R94 indicates results from Ruder et al. (1994).

Table 3. Table listing the binding energies of three tightly bound states of lithium in moderate to large magnetic fields.

| $\gamma$    | $2^0\!+\!\gamma$ | $4(-1)^+\!+\!\gamma$ | $4(-3)^+\!+\!\gamma$ |
|-------------|-------------------|------------------------|------------------------|
| 18$\beta_Z$ | Here              | Other                  | Here                   | Other                  |
| 0.00        | 1.6560            | 1.6618                 | 1.1968                 | 1.1925                 |
| 0.01        | 1.6590            | 1.6629                 | 1.2017                 | 1.1969                 |
| 0.05        | 1.6681            | 1.6673                 | 1.2192                 | –                      |
| 0.10        | 1.6775            | 1.6705                 | 1.2390                 | 1.2334                 |
| 0.20        | 1.6928            | 1.6741                 | 1.2736                 | 1.2674                 |
| 0.50        | 1.7255            | 1.6729                 | 1.3533                 | 1.3463                 |
| 1.00        | 1.8256            | 1.6575                 | 1.4821                 | 1.4432                 |

Note. At the top of each pair of columns is the symmetry subspace $2^\pm\!+\!\gamma (M_z)^{\mp\!+\!\gamma}$. We take the dominant configuration for the ground state within each subspace. The column ‘Other’ gives the values from Ralchenko et al. (2008) for zero field and from Al-Hujaj & Schmelcher (2004) elsewhere.

4 DISCUSSION

One of the primary goals of the current work was to provide a computational method that would be rather economical with regard to computation time, without having to compromise on accuracy. As can be seen in Table 1, the desired level of accuracy can be achieved with computation times on the order of seconds. The calculated values therein can conceivably have better agreement with experimentally determined values if effects of spin-orbit coupling, relativistic corrections and the effects of mixing of configurations were to be included. Similarly, upon examining Table 2, it is immediately apparent that the estimates of the binding energies of the state of helium corresponding to $M_z = -1$; $S_z = -1$ are more bound than the previous estimates. The average improvement with respect to the values reported in our previous study (Thirumalai & Heyl 2009) is about 0.5 per cent, while the average improvement over the values reported in Ruder et al. (1994) is about 3.4 per cent over the entire range of magnetic field strengths reported therein. Similarly, upon comparing the results from the present calculation for the state of helium corresponding to $M_z = -2$; $S_z = -1$ we see that they are more bound on average by about 1.5 and 5.8 per cent, respectively, with respect to the calculations of Thirumalai & Heyl (2009) and Ruder et al. (1994). Finally, when comparing with the results of other authors in Table 3, we see that the current single-configuration calculation using spectral methods provides binding energies that are an improvement on previous estimates for three tightly bound states of lithium. It can be seen that the average range of improvements for the estimates of the binding energies of the three states, relative to the calculations of other work, is about 1 per cent.

In carrying out the calculations in the current study, as was noted earlier, the domain was compactified according to equation (4). This has the distinct advantage that one can set a boundary condition at true infinity rather than at a large value of the radial distance $r$. Typically, such a procedure renders the partial differential equations highly non-linear, making their solution with finite-element techniques more involved and computationally demanding, thus requiring a greater amount of computation time. In the current study, the compactification effectively changes the operators in equations (6), (21) and (23).

Since the algorithm presented here is essentially a simple prototype, several avenues for further development are apparent. They address the stability, accuracy and robustness of the calculation.
First, from a physical point of view, it does not make sense to use the same zoom radius (the value of $r_Z$) for all of the electrons in an atom. The zoom radius is essentially the scale within which the radial mesh is fine; therefore, it should reflect the expected or calculated extent of the electronic wave functions. It would be quite natural to adaptively change the value of $r_Z$ to some constant factor times $r$ or $\sqrt{r^2}$ as the Hartree–Fock iteration proceeds. Because the interelectron potential is smoother than the underlying wave functions, it would be more effective to calculate the potentials for each electron using its own value of $r_Z$ and then interpolate these results on to the meshes of the other electrons. In this manner, the value of $r_Z$ would adapt for the particular orbital that the electron occupies, achieving higher accuracy without increasing the number of radial mesh points. For the direct interaction, this is straightforward because it is essentially a function; however, the exchange interaction is an operator or a matrix, as in equation (15), so the interpolation of the final result is a bit problematic. Rather it is expedient to interpolate the wave functions of the other electrons on to each other’s mesh and calculate the exchange interaction one pair at a time. Although this interpolation would necessarily make the code more cumbersome, it need not increase the processing time significantly. The inverse Laplacians for different values of $r_Z$ are related to each other through simple scalings, so the costly matrix inversions would still only happen once at the beginning, and the results would scale for the appropriate values of $r_Z$.

A similar adaptation can be performed in the angular direction to focus grid points along the magnetic axis for strong magnetic fields. In this way, we can achieve high accuracy for all of the electrons without including more grid points. A simple way to achieve this is the ‘Arctan/Tan’ mapping (Boyd 2001) where the original angular variable $\theta$ is mapped on to $\theta'$ using

$$\theta' = \arctan(L \tan \theta).$$  

(34)

The parameter $L$ can change to reflect the actual physical extent of the wave function in the angular direction for each electron in the atom as the iterative process proceeds. This adaptation would add little additional overhead above the radial adaptive scheme outline in the last paragraph.

A second issue that we encountered is the appearance of spurious eigenvalues among the physical ones, especially for intense magnetic fields. The current software eliminates these eigenvalues by looking at the structure of the eigenfunctions. Essentially, many of the spurious eigenfunctions have significant support along the magnetic axis at large radii. Unfortunately, the current set of criteria are not sufficiently robust to exclude all of the spurious eigenfunctions. There are two clear paths to address this issue. The first is to develop a more sophisticated filtering technique to check the eigenfunctions during the iterative process. The second technique would be to use cylindrical coordinates that are better adapted to the intense-field limit where the wave functions essentially are well approximated by the product of Landau orbitals and a function of the coordinate along the magnetic field (the so-called adiabatic approximation). The use of cylindrical coordinates is of course not equivalent to the adiabatic approximation but it does fit better with the dominant symmetry of the intense-field problem. For this work, we did not employ cylindrical coordinates because we wanted to verify our results against the zero-field limit where the binding energies of the various species are known precisely.

From a mathematical point of view, we have chosen to use Chebyshev points to sample in both the angular and radial directions. In this particular case, it is possible to express the spectral derivatives using a fast-Fourier transform (Trefethen 2000; Boyd 2001).

The most obvious application for the problem at hand would be to speed up the calculation of the direct component of the interelectron potential; because this only makes a modest contribution to the workload, we decided to forego the added complexity and use matrix multiplication to determine the interelectron potential. On the other hand, given some additional work, it may be possible to speed up other parts of the calculation using FFTs.

A final improvement would be to include several electronic configurations for each state (e.g. Al-Hujaj & Schmelcher 2004), not just the dominant one as we did here. Given the excellent agreement with the observed atomic properties that we found for the zero-field limit, we expect the improvement of a multiconfiguration calculation to be modest at least for small atoms. However, recent theoretical results indicate that the atmospheres of neutron stars may be composed of elements near silicon (Hoffman & Heyl 2009), so including many configurations may be crucial at least to verify the algorithm in the weak-field limit.

5 CONCLUSION

The amount of literature available regarding atoms in strong magnetic fields is quite extensive. Since the 1970s with improvements in both computing infrastructure and numerical methods, the problem of atoms in strong magnetic fields has become increasingly tractable. However, the current state-of-the-art calculations still take on the order of hours, if not days, to obtain results of reasonable accuracy. To address this situation, we have, in this study, presented a new pseudo-spectral method for the calculation of the structure of atoms in strong magnetic fields. The key enabling advantages of the algorithm are its simplicity (about 130 lines of commented code) and its speed (about $10^2$–$10^3$ times faster than finite-element methods to achieve similar accuracy). For hydrogen, helium and lithium, it gives results that agree with the previous work at the few per cent level or better for fields weaker than about $2 \times 10^8\text{T}$.

For the purpose of analysing the spectra of magnetized white dwarfs and neutron stars, it becomes crucial to have accurate data for the energy levels of different atoms in strong magnetic fields. With the ability to perform atomic structure calculations with a significant reduction in computation time, as with the pseudo-spectral methods described in this study, it becomes possible to amalgamate atomic structure calculation software with atmosphere models of neutron stars and white dwarf stars. This is a direct advantage of the software provided in the appendices to this paper. We have additionally presented several avenues for further research with the software including larger atoms, multiconfiguration Hartree–Fock and full configuration-interaction calculations.

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APPENDIX A: MAGNETIZED HYDROGEN

Both the single-electron and multiple-electron codes are self-contained OCTAVE programs with the exception of the eight-line function CHEB that Trefethen published previously in Trefethen (2000) and is available online at http://www.comlab.ox.ac.uk/nick.trefethen/cheb.m. This function calculates the differentiation matrix in equation (27). Both programs are also compatible with MATLAB with some minor modifications in the output statements in the multielectron program. However, after experimentation we concluded that the OCTAVE version ran faster with our setup.

The hydrogen code is written as a function to be called from the OCTAVE command line that returns the eigenfunctions, eigenvalues, angular and radial points, a list of the eigenfunctions that pass a rudimentary test and the ‘zoom’ factor. For values of $M$ and $N$ on the order of 10, the vast majority of the computation time is devoted to calculating the eigenvalues, so the total execution time depends on the efficiency of the eigenvalue routine (eig); consequently, porting this algorithm to C does not result in a substantial speed up – in fact in our experience, OCTAVE runs faster.

% HYDROGEN_S -- calculate hydrogen in spherical coordinates
% beta is B/Be, M is number of mu, N is number of radial
% the wavefunction is phi=f(r, mu=cos(theta))/r exp(i m phi)
% eigenfunctions in V, e = val in Lam, coords in (w, rs)
function [V, Lam, w, rs, igood, zoom] = hydrogen_s(beta, M, N, mphi)

% w coordinate, ranging from -1 to 1
[Vw, w] = cheb(M); D2w = Dw^2;
if (mphi == 0) w = w(1:M); Dw = Dw(1:M); D2w = D2w(1:M); end

Vw = diag(1-w.\*w)\*D2w + diag(2.\*w)\*Dw;

% r coordinate, ranging from 1 to -1, rp from 1 to 0
[Dr, r] = cheb(N); rp = 0.5*(r+1); D = 2*Dr; D2 = D^2;
hh = diag(1-rp.\*rp); D2 = hh*(hh+D2); D = hh*D;
D = D2/2; N; D = D(2:N, 2:N); rp = r(2:N);

% zoom factor: set by coulomb and larmor radius; rs from inf to 0
zoom = 1./(1/110+sqrt(beta)/41); rs = zoom * atan(rp); R = diag(1./rs); R2 = diag(1./rs.\*rs);

[V, Lam] = eig(H); Lam = diag(Lam); [Lam, ii] = sort(Lam); Lam = Lam+2*beta*(mphi-1); V = V(:, ii);

% check outer B.C. and for bound states
igood = find((V(1,:)\*V(1,:))' < (M+N)'\*(-2)*1e-4 & Lam<0);

APPENDIX B: MAGNETIZED ATOMS

The atomic code is written as a script to be called from the OCTAVE command line because it has many parameters and diagnostics that one might like to examine and the script format encourages the user to choose what he or she wants to use.

Similar to the case of hydrogen, for values of $M$ and $N$ on the order of 10, the vast majority of the computation time is devoted to calculating the eigenvalues and inverting the Laplacians, so the total execution time depends on the efficiency of the eigenvalue and matrix inversion routines (eig and inv); consequently, we do not expect that porting this algorithm to a lower-level language (e.g. C) will result in a substantial speed up. In fact, the computational effort is dominated by the diagonalization that is performed for each electron at each iteration. The inversion of the Laplacian is performed before the iterations begin.

%THREEDATOM -- calculate an atom in three -- D
% the wavefunction is phi=f(r, mu=cos(theta))/r
% r coordinate, ranging from -1 to 1
% Examples for Helium I
% Examples for Lithium

nu=[1, 1, 2]; spin=[1:2]; mphi=[0, 0]; Z=2; % 1s^2 2s 2S J=1/2 : 1.65595
% nu=[1, 1, 3]; spin=[1:2]; mphi=[0, 0]; Z=3; % 1s^2 2p 2P J=1/2 : 1.64097
% nu=[1, 1, 1]; spin=[1:2]; mphi=[0, 0]; Z=3; % 1s^2 2p 3P J=3/2 : 1.64087
% nu=[1, 1, 4]; spin=[1:2]; mphi=[0, 0]; Z=3; % 1s^2 3s 2S J=1/2 : 1.62883

M=7; N=31; MAXITER = 100; beta = 0;

% add zero weight to last term so we always use the same - sized vectors
w_w=[inv(Dw(1:M, 1:M))(1, :)];
% r coordinate, ranging from 1 to -1
[r, r] = cheb(N); rp=0.5*(r+1); D = 2*s*D; D2 = D^2;

% drop infinite weight at infinity (i.e. 1) since w.w. goes to zero quickly

% now multiply by hh so we didn’t have zero for inversion above
D=hh*D;

% Radial Laplacian minus r=inf (for potential calcuations)
D2inf = D2(2:N+1, 2 : N+1);
% Construct Laplacian minus r=0 and r=inf

% (set diriclet b.c. in radial direction for eigenvalue equations) 
D2 = D2(2:N, 2:N); D = D(2:N, 2:N); rp=rp(2:N);
zoom=1/(1/116+sqrt(beta)/41)*0.5; rs=zoom*atanh(rp); wr=zoom*wr;
R = diag(1./rs); R2 = diag(1./(rs.*rs));
% Hamilton for radial coordinate

% Full single electron Hamiltonian
H=kron(Hr, eye(M+1))+kron(R2, Hw)+diag(beta*beta*rperp2);
mmmax=0;
for e1cnt=1:numel(mphi)-1
  for e2cnt=e1cnt+1:numel(mphi)
    if (spin(e1cnt)==spin(e2cnt))
      dum=abs(mphi(e1cnt)-mphi(e2cnt));
      if (dum > mmmax) mmmax=dum; end
    end
  end
end
% Construct Laplacians for electron potential calculation
Lin==zeros(DIMEN, DIMEN, mmmax+1);
for i=0:mmmax
  % set the denominator equal to one, if it goes to zero (don’t want an infinity)
  % we will drop rperp2=0 later
  L=kron(1/(zoom*zoom)+D2, eye(M+1))-kron(R2, Hw)-diag(i./(rperp2+(rperp2==0)));
  % set the BC for rperp2=0 but add in identity so can be inverted
  % an infinity in the last step would have given an NaN here
  if (i == 0) L=diag(rperp2==0)+L+diag(rperp2==0); end
  % add in the origin as a single point
  L=[[L, kron(D2inf(1:N-1, N), ones(M+1, 1))]; kron(D2inf(N, 1:N-1), ones(1, M+1)), D2inf(N, N)];
% invert Laplacian and set boundary condition at origin

Linhold = (eye(DIMEN+1)−[zeros(DIMEN+1, DIMEN), ones(DIMEN+1, 1)])\textbackslash inv(L);
% divide by R before and after and remove origin!
% don’t need to set B.C. again because the solutions for mphi \approx 0 are already zero in the
% right places, and the e \approx val equation sets them to zero when needed
Linv(:, :, i+1) = −4*pi*RR*Linhold(1:DIMEN, 1:DIMEN)*RR;
end

if needed

v(1) = zeros(DIMEN, numel(nu));
direct_old = zeros(DIMEN, DIMEN, numel(nu)); exchange_old = zeros(DIMEN, DIMEN, numel(nu), mmax + 1);
direct_new = zeros(DIMEN, DIMEN, numel(nu)); exchange_new = zeros(DIMEN, DIMEN, numel(nu), mmax + 1);
interact = zeros(DIMEN, DIMEN);

% begin iterations
etotold = etot = 1; j = 1;
while (abs((etot − etotold)/etot) > 1e−5 & j < MAXITER)

% calculate each electron wf
etotold = etot = 0;
for e1cnt = 1:numel(nu)
    interact = zeros(DIMEN, DIMEN);
    for e2cnt = 1:numel(nu)
        if (e2cnt = = e1cnt)
            if (spin(e1cnt) = = spin(e2cnt))
                interact = interact + direct_old(:, :, e2cnt) ... − exchange_old(:, :, e2cnt, abs(mphi(e1cnt)−mphi(e2cnt))) + 1);
            else
                interact = interact + direct_old(:, :, e2cnt);
            end
        end
        end
    end
    if (mphi(e1cnt) = = 0)
        [V, Lam] = eig(H + 2/Z*interact);
    else
        Htmp = H + 2/Z*interact + diag(mphi(e1cnt), mphi(e1cnt), /rperp2);
        [V, Lam] = eig(reshape(Htmp(find(rperp2 = = 0)), (M − 1)*(M − 1)));
    end
    Lam = diag(Lam); [Lam, ii] = sort(real(Lam));
    igood = find((V(:, i) > (M*N)’(−2*1e−4);
    V = V(:, i); uu = V(:, igood(nn(e1cnt))));

% add in boundary condition for angular direction (along z − axis), if needed
if (mphi(e1cnt) = = 0)
    uu = [zeros(1, N, 1); reshape(uu, M − 1, N − 1); zeros(1, N − 1)](:,);
end
l(e1cnt) = Lam(igood(nu(e1cnt)))+2+beta*(mphi(e1cnt)+sin(e1cnt))−0.5;
u2 = uu.*uu; norm = wewu2; u2 = uu/sqrt(norm); u(:, e1cnt) = uu; % normalize

een(e1cnt) = 1/2*z*we*(uu.*(interact*uu)); etot = etot + l(e1cnt)−een(e1cnt)/(2);
printf(‘%f d e1=%d E − val: %18.2f EE: %18.2f Etot: %18.2f \n ’, j, e1cnt, l(e1cnt), eeen(e1cnt), etot);
direct_new(:, :, e1cnt) = diag(Linv(:, :, 1))*uu2;
for i = 1:mmax + 1 exchange_new(:, :, e1cnt, i) = diag(uu)*Linv(:, :, i)*diag(uu);
end
end
j = j + 1; direct_old = direct_new; exchange_old = exchange_new;
end
if (j = = MAXITER)
    printf(‘Did not converge \n’);
end

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