

Assignment 5: Eigenvalue problems with B-splines

deadline Thursday April 28 2022

B-Splines are piecewise polynomial functions defined on a given interval that contains a certain number of points, t_i , referred to as a *knot sequence*, where $t_i \leq t_{i+1}$. The B-Splines of order k (polynomial order $k - 1$) are recursively defined as

$$B_{i,k=1} = 1 \text{ if } t_i \leq x < t_{i+1}, \quad B_{i,k=1} = 0 \text{ else} \quad (1)$$

and

$$B_{i,k}(x) = \frac{x - t_i}{t_{i+k-1} - t_i} B_{i,k-1}(x) + \frac{t_{i+k} - x}{t_{i+k} - t_{i+1}} B_{i+1,k-1}(x). \quad (2)$$

The B-splines will be non-zero only in a limited region of space. If the numbering is such that t_1 is the first knot point and $B_{1,k}$ is the first B-splines, then a B-spline $B_{i,k}$ is non-zero only between t_i and t_{i+k} . The B-splines form a complete set on the knot sequence and one manifestation of this is that

$$\sum_i B_{i,k}(x) = 1 \quad (3)$$

for points between t_1 and t_{last} . If the first and last knot is multiple, such that k knots are placed in the same physical point, the B-splines will be confined to the region $t_1 \leq x \leq t_{last}$. This is a common approach.

The idea is to expand the physical solution in B-splines

$$\Psi(x) = \sum_i c_i B_{i,k}(x). \quad (4)$$

This is an alternative to other approaches such as a direct representation on a grid or an expansion in global basis states. Compared to grid methods fewer knot-points (B-splines) are needed. This can be very important for large problems. In addition the knot sequence can be designed in any way as long as $t_i \leq t_{i+1}$. It is also possible to use multiple knots to represent discontinuities. The price to pay for these advantages is mainly that the B-spline approach is less simple and transparent. Compared to an expansion in global basis states the locality of B-splines is often an advantage. It gives a greater flexibility since a linear combination chosen to fit one region in space is not directly affecting that of another region. Concerning the numerical accuracy when differentiating and integrating, differentiation of the B-splines is done analytically and integration can be performed with more or less machine accuracy with Gauss (Legendre) quadrature. This is of course superior to finite difference formulas and any version of the trapezoidal formula (used with grid based methods). It has to be admitted though that global analytical basis sets often allow both analytical integration and differentiation, which is hard to beat in speed and numerical accuracy.

A common boundary condition is that the solution shall vanish at the boundary. Such a condition is easily implemented in Eq. 4. With the multiple knot scheme mentioned above only the first and last B-splines are non-zero at the boundary and these B-splines are then removed from the sum.

Let us now focus on an eigenvalue problem:

$$H\Psi(x) = E\Psi(x). \quad (5)$$

With the B-spline expansion above it can be written:

$$H \sum_i c_i B_{i,k}(x) = E \sum_i c_i B_{i,k}(x). \quad (6)$$

Multiplying with $B_{j,k}(x)$ from the left and integrating we get

$$\sum_i c_i \int_{t_{first}}^{t_{last}} B_{j,k}(x) H B_{i,k}(x) dx = E \sum_i c_i \int_{t_{first}}^{t_{last}} B_{j,k}(x) B_{i,k}(x) dx. \quad (7)$$

Note that the B-splines are not orthogonal and thus the integral on the right-hand side is non-zero as long as $|i - j| \leq k - 1$. Eq. 7 can be written in matrix form as

$$\mathbf{H}\mathbf{c} = E\mathbf{B}\mathbf{c}, \quad (8)$$

where the column vector, \mathbf{c} , is an eigenvector with eigenvalue E . The elements of the matrix \mathbf{H} are

$$H_{ij} = \int_{t_{first}}^{t_{last}} B_{j,k}(x) H B_{i,k}(x) dx, \quad (9)$$

and those of \mathbf{B}

$$B_{ij} = \int_{t_{first}}^{t_{last}} B_{j,k}(x) B_{i,k}(x) dx. \quad (10)$$

These matrices will be banded and each row will contain $2k - 1$ elements. Eq. 8 is a so called *generalized* eigenvalue problem.

• **Task** We will now use the B-spline approach to get the radial wave functions for hydrogen-like ions. We use the usual approach (discussed in most textbooks on Quantum Mechanics) and write the full three-dimensional wave function

$$\Psi(r, \theta, \phi) = R_{n\ell}(r) Y_{\ell m}(\theta, \phi) = \frac{P_{n\ell}(r)}{r} Y_{\ell m}(\theta, \phi). \quad (11)$$

The separation into radial and angular wave functions is possible since we have a central symmetric potential. The functions $Y_{\ell m}(\theta, \phi)$ are Spherical Harmonics (see e.g. Arfken and Weber). The Hamiltonian is

$$H = \frac{\mathbf{p}^2}{2m_e} - \frac{Ze^2}{4\pi\epsilon_0} \frac{1}{r} = -\frac{\hbar^2 \nabla^2}{2m_e} - \frac{Ze^2}{4\pi\epsilon_0} \frac{1}{r}. \quad (12)$$

We can now use the relation

$$\nabla^2 \left(\frac{P_{n\ell}(r)}{r} Y_{\ell m}(\theta, \phi) \right) = \frac{1}{r} \left(\frac{d^2}{dr^2} - \frac{\ell(\ell+1)}{r^2} \right) P_{n\ell}(r) Y_{\ell m}(\theta, \phi) \quad (13)$$

to write the equation for the radial part of the wave function

$$\left(-\frac{\hbar^2}{2m_e} \frac{d^2}{dr^2} + \frac{\hbar^2 \ell(\ell+1)}{2m_e r^2} - \frac{Ze^2}{4\pi\epsilon_0} \frac{1}{r} \right) P_{n\ell}(r) = E P_{n\ell}(r). \quad (14)$$

This is effectively a one-dimensional equation. The boundary conditions are that $P_{n\ell}(r)$ has to vanish in the origin, and all bound states go to zero when $r \rightarrow \infty$.

• Construct a knot sequence. Use $k = 4 - 7$ (your choice). Put the first knot point in $r = 0$. Put k knots here. Put the last knot in $R_{max} = 10$ Bohr radii (this is a suggestion, perhaps you want to investigate different choices so make this a parameter). Put k knots in R_{max} . As a starting point you can use a linear knot sequence. Another possibility is a linear knot sequence in the beginning and then some other scheme further out (exponential, quadratic). You can start to try 30 – 50 knot points (how many do you need for good performance and how is that affected by your choice of knot-sequence?). N points (counting also the equivalent ones) gives $N - k$ B-splines. Since you will disregard the first and the last B-spline to implement the boundary conditions you will get $N - k - 2$ B-splines.

• Construct the matrices \mathbf{H} and \mathbf{B} . For \mathbf{H} you use Eq. 14 for a given ℓ -value. Use the ℓ -value as a parameter so that you can test different angular momenta. Note that

$$\int_0^\infty B_{j,k}(r) \left(-\frac{d^2}{dr^2} \right) B_{i,k}(r) dr = \int_0^\infty \frac{dB_{j,k}(r)}{dr} \frac{dB_{i,k}(r)}{dr} dr, \quad (15)$$

as can be shown by partial integration. The derivative of the splines are given by:

$$\frac{\partial}{\partial r} B_{i,k}(r) = (k-1) \left(\frac{B_{i,k-1}(r)}{t_{i+k-1} - t_i} - \frac{B_{i+1,k-1}(r)}{t_{i+k} - t_{i+1}} \right) \quad (16)$$

All integrals are preferably calculated with Gaussian quadrature (see more below)

$$\int_{t_n}^{t_{n+1}} B_{j,k}(r) f(r) B_{i,k}(r) dr \approx \sum_{m=1}^k w_m B_{j,k}(r_m) f(r_m) B_{i,k}(r_m). \quad (17)$$

Since the order of the polynomial to integrate is decided by k it is natural to use around k Gaussian points in every interval.

- Use a ready made routine to solve the generalized eigenvalue problem, these are available with Lapack or Eigen for example. Remember that you need a routine for a *generalized eigenvalue* problem.
- Investigate the spectrum of eigenvalues for a few different ℓ -values. Compare with the known values. How many bound states of hydrogen can you find? How is this affected by the choice of knot-sequence?
- Plot also some eigenfunctions and compare with the wave functions you can find in most books on Quantum Mechanics.
- If you have time use a spherical charge distribution instead of a pure Coulomb potential and check for the qualitative difference. The potential energy for an electron in the potential from the charge $+Ze$, uniformly distributed in a sphere of radius R_0 is

$$\begin{aligned} V(r) &= \frac{-Ze^2}{4\pi\epsilon_0} \frac{1}{2R_0} \left(3 - \left(\frac{r}{R_0} \right)^2 \right), \quad r < R_0 \\ &= \frac{-Ze^2}{4\pi\epsilon_0} \frac{1}{r}, \quad r > R_0. \end{aligned} \quad (18)$$

Use this for

1. The effect of the true nucleus on high Z elements

Try for example hydrogenlike uranium (one electron around an uranium nucleus). Use the R_0 we discussed in Assignment 1. ($R_0 \approx 1.2A^{1/3}$ fermi) **Note:** When you increase Z you will need to change R_{max} and the distance between the knots!

2. The qualitative effect of an electron core

Compare the Coulomb case (point charge) with a spherical charge distribution in a sphere of $R_0 = 1.5$ Bohr radii, in both cases with $Z = 1$, for a few angular momenta. This can give you a feeling for some *qualitative* changes that is to be expected for many-electron atoms. To describe a real atom you need of course both a nucleus and other electrons. We will return to that question next week.

Units

For calculations on atomic systems it is practical to write programs in Hartree units. The base units are then:

$$\begin{aligned} \text{lenght : } a_0 &= \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} \approx 0.5 \cdot 10^{-10} \text{ m} \\ \text{mass} &= m_e \approx 9.1 \cdot 10^{-31} \text{ kg} \\ \text{energy : 1Hartree} &= \frac{m_e e^4}{(4\pi\epsilon_0)^2 \hbar^2} = \frac{\hbar^2}{a_0^2 m_e} \approx 27.2114 \text{ eV} \\ \text{time} &= \frac{(4\pi\epsilon_0)^2 \hbar^3}{m_e e^4} = \frac{a_0^2 m_e}{\hbar} \approx 2.42 \cdot 10^{-17} \text{ s.} \end{aligned}$$

The energy unit is twice the binding energy in the ground state of hydrogen. The time unit is the classical orbiting time for a particle with the kinetic energy of the ground state electron in an orbit with radius a_0 . With these units the natural constants is not needed in the calculation itself, but you can of course chose to display results in some other unit which you are more comfortable with (for example eV for energies).

Gaussian quadrature

A quadrature rule is an approximation of the definite integral of a function, usually a weighted sum of function values at specified points (abscissas) within the domain of integration. An n -point Gaussian quadrature rule is constructed to give an exact result for polynomials of degree $2n - 1$ or less by a suitable choice of the abscissas

x_i and weights w_i for $i = 1, \dots, n$;

$$\int_a^b W(x)f(x) dx \approx \sum_{i=1}^n w_i f(x_i). \quad (19)$$

The approximation is exact if $f(x)$ is a polynomial. Different $W(x)$ naturally require different weights. The different choices are named after the class of orthogonal polynomials whose roots define the abscissas. $W(x) = 1$ are integrated with Gauss-Legendre quadrature (sometimes just called Gauss). Since the B-splines are polynomials, that is what we will use here. You find several other possibilities in *Numerical Recipes*, for example with $W(x) = e^{-x^2}$, called Gauss-Hermite quadrature.

Abscissas and weights are available for example in Abramowitz and Stegun: Handbook of Mathematical Functions. There is an online version: <http://www.convertit.com/Go/Convertit/Reference/AMS55.ASP>, where integrations formulas of Gaussian type are discussed on page 887 and onwards. Weights and abscissas for Gauss-Legendre integration are listed on page 916 and onwards. There is also at least one calculator available on the net: http://www.efunda.com/math/num_integration/num_int_gauss.cfm. The listed abscissas are for a fixed integration interval, typically for integration from -1 to 1

$$\int_{-1}^1 f(x) dx \approx \sum_{i=1}^n w_i f(x_i). \quad (20)$$

To use these abscissas on an other interval the integral has to be slightly transformed:

$$\begin{aligned} \int_a^b f(x) dx &= \\ &\left[z = \frac{x-a}{b-a} - \frac{b-x}{b-a} \rightarrow x = z \frac{b-a}{2} + \frac{a+b}{2}, \quad dx = \frac{b-a}{2} dz \right] \\ &= \frac{(b-a)}{2} \int_{-1}^1 f\left(z \frac{b-a}{2} + \frac{a+b}{2}\right) dz \approx \frac{(b-a)}{2} \sum_{i=1}^n w_i f\left(z_i \frac{b-a}{2} + \frac{a+b}{2}\right) \end{aligned} \quad (21)$$

The B-splines with the smallest extension will be non-zero over just one interval, from one knot-point to the next. It is thus natural to divide up the integration region as a sum over small intervals extending from one knot point to the next. Looking at the abscissas needed to integrate from a to b you will notice that they all fall in the interval between a and b and never exactly on the integration limits.