Exercise sessions 8–9: Diagonalization algorithms and eigenvalue problems

Exercise 1: Power methods [4 pts]

Files: `test_power.m`, `test_ipower.m`, `test_rq.m`, `rmg.m`

The power methods for solving eigenvalue problems are very straightforward to implement: in order to obtain the eigenvector corresponding to a certain (smallest, largest, closest) eigenvalue of a matrix, one has to multiply an initial vector by a specific matrix multiple times.

Your task is to implement the power method, the inverse power method with shift and the Rayleigh quotient algorithm. The following is the template for the Rayleigh quotient function:

Listing 1: 'eig_rq.m'

```
function [vec,val] = eig_rq(input_matrix, target)

% eig_rq computes the closest eigenvector and eigenvalue
% of a given matrix.
%
% Arguments:
%
%     input_matrix (2D complex Hermitian matrix): matrix
%     for the eigenvalue problem;
%
%     target (real scalar): an estimation to the eigenvalue;
%
% Returns: a right eigenvector and the corresponding eigenvalue
% of a matrix.

% Replace these lines with your own implementation
vec = zeros(length(input_matrix),1);
val = 0;

end
```

For your convenience, we provide the test scripts your code has to pass, see the **Files** section.
Submit: Matlab functions `eig_power.m`, `eig_ipower.m` and `eig_rq.m` with the your implementations.

Exercise 2: Tight-binding model for a loop of atoms [4 pts]

One simple approach to modeling the electronic structure of molecular compounds and crystalline materials is the tight-binding approximation. Below, we will consider a molecular system representing a loop of N identical atoms, that is atom i is connected by chemical bond to atom $i + 1$ and atom N is connected to atom 1. (NB for physics students: There is no periodic lattice associated with this system, hence no k dependence and the spectrum is discrete. It's a molecule, a zero-dimensional system.) In the simplest form of the tight-binding approximation, the $N \times N$ matrix of the Hamiltonian of this system is written in the following way: matrix element $H(i, j) = \gamma$ if atoms with indices i and j are connected by a chemical bond (line); $H(i, j) = 0$ otherwise. For simplicity, lets assume the value of the hopping integral $\gamma = -1$. Finding the eigenvalues and eigenvectors of matrix $\mathbf{H}$ is equivalent to solving the Schrödinger equation. The eigenvalues correspond to discrete energy levels ϵ_i, while the corresponding eigenvectors ψ_i represent the eigenstates (one-electron wavefunctions). Each vector element corresponds to wavefunction amplitude on the corresponding atom.

1. Use your diagonalization subroutines to find the smallest (ϵ_1) and the largest (ϵ_N) eigenvalues for $N = 20$. Plot the two corresponding eigenstates and comment on the differences. Finally, plot the probability densities $\rho_i = \psi_i^\star \psi_i$ for these two states. Discuss your results.

2. Repeat the previous point for N=21. Explain the observed difference.

Submit: your report as a PDF file as well as your scripts. The points are distributed in the following way:

- [2 pts] for correct answers to point 1;

- [2 pts] for correct answers to point 2.

Exercise 3: Band structures of one-dimensional periodic graphene nanoribbons [8 pts]

As previous exercise demonstrates, numerical diagonalization provides an easy access to modeling the electronic properties of systems composed of a large number of atoms using the tight-binding approximation. In this exercise we will consider one-dimensional nanometer-wide stripes cut from the two-dimensional honeycomb lattice of graphene. Such periodic systems are called graphene nanoribbons, and are currently considered as potential components of future electronics devices. The figure below shows two examples of such graphene nanoribbons. These systems are periodic along the x direction, with the periodicity fined by the lattice constant a (approximately 0.4 nm). The rectangles denote unit cells (repeat units). Their width is defined by parameter N as shown below. The smallest $N = 2$ system corresponds to the trivial case of a chain of carbon atoms, and the unit cells of such graphene nanoribbons contain $2N$ atoms.

As these systems are periodic in one dimension, the crystalline momentum k in the first Brillouin zone ($k \in [-\pi/a, \pi/a]$) needs to be considered when describing their electronic properties. The matrix elements of the Hamiltonian matrix $\mathbf{H}_k$ for a given k can be written as

$$\mathbf{H}_k(i,j) = \gamma \sum_{j \in \text{n.n.of} i} e^{ikR}. \tag{1}$$

This notation means that only atoms j that are connected (n.n., stands for "nearest neighbor") to atoms i contribute to the matrix elements. If both atoms are located within the same unit cell (rectangle in the figure below), then $R = 0$. Connections with atoms belonging to the right or the left periodic replicas correspond to $R = a$ and $R = -a$, respectively. Below, assume the nearest-neighbor hopping integral $\gamma = -2.7$ eV.
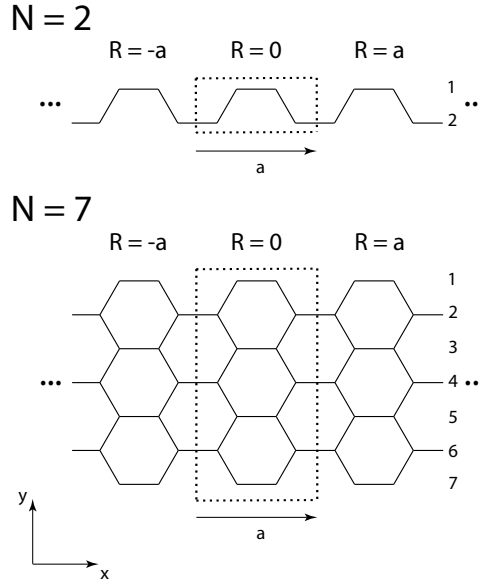

Figure 1: Two examples of the atomic structures of graphene nanoribbons described by $N = 2$ and $N = 7$. The nanoribbons are periodic along the x axis. The dotted-line rectangles denote the unit cell.

1. Plot the band structures, that is the dependences of eigenvalues $\epsilon_i(k)$ on momentum k for $k \in [-\pi/a, \pi/a]$ for several values of N (e.g. $N = 2...7$). Each value of N should correspond to a separate plot, but all $2N$ eigenvalues $\epsilon_i(k)$ (bands) for a given N should be plotted as lines in one plot. We recommend to use Matlab's diagonalization routine `eig`.

2. In this particular system, N lowest bands are populated by electrons, while the remaining N bands remain unpopulated. The energy difference between the highest occupied and lowest unoccupied states is called the band gap E_g, that is

$$E_g = \min_{k,i=N+1,..,2N} \epsilon_i(k) - \max_{k,i=1,..,N} \epsilon_i(k). \tag{2}$$

This expression assumes the eigenvalues are sorted in ascending order. Zero values of E_g corresponds to metals, while positive E_g corresponds to insulators (semiconductors). Plot the magnitude of band gap $E_g(N)$ for a series of values of N and discuss the results in terms of classification of the discussed systems as metals or insulators.

Submit: your report as a PDF file as well as your scripts. The points are distributed in the following way:

- [5 pts] for the band structure plots of graphene nanoribbons;

- [3 pts] for the band gap plot and the corresponding discussion.

Exercise 4: Jacobi method [6 pts]

Files: `test_j.m`, `rmg.m`

1. Implement the classic Jacobi method for calculating eigenvalues and eigenvectors of symmetric real matrices. Following is the function signature:

Listing 2: 'eig_j.m'

```
function val = eig_j(input_matrix)

% eig_j computes the eigenvalues of a matrix.
%
% Arguments:
%
%     input_matrix (2D real symmetric matrix): matrix
%     for the eigenvalue problem;
%
% Returns: an array with eigenvalues.

% Following is a stub
val = zeros(length(input_matrix),1);

end
```

Test your implementation with the test cases provided.
Hint: Efficiency of your Jacobi method code can be significantly improved by avoiding matrix multiplications in favor of vector operations.

2. Implement the cyclic Jacobi method. Test it. Compare the performance of classic and cyclic algorithms by studying the following two quantities – computer time and the number of Jacobi rotations required for performing diagonalization – for a broad range of matrix sizes. Compare and explain the observed quantities.

Submit: your implementations of Jacobi and cyclic Jacobi methods in Matlab functions `eig_j.m` and `eig_cj.m` as well as a PDF file with computer time and number of operations data and explanation. The points are distributed in the following way:

- [2 pts] classic Jacobi;

- [2 pts] cyclic Jacobi;

- [2 pts] plots and discussion.

Exercise 5: Two-dimensional quantum well [8 pts]

In solid-state systems, potential profiles can be tailored by means of varying chemical composition in order to spatially localize electrons. Consider a 2D quantum well. Electrons in such a system are subjected to the following potential profile:

$$V(x,y) = \begin{cases} V_0 < 0, & x^2 + \frac{y^2}{c^2} < r^2 \\ 0, & \text{otherwise} \end{cases}$$

where $V_0 = -1.5$ eV is the width of the potential and $r = 1$ nm. Parameter $c = 1$ corresponds to the circular shape quantum well, while $c > 1$ makes it elliptic.

Compute the matrix representation of the Hamiltonian operator by discretizing space in 2D :

$$H = -\frac{\hbar^2}{2m_{\mathrm{el}}}\Delta + V(x)$$

where m_{el} is the free electron mass and $\hbar$ is the reduced Planck's constant. The free electron mass is $m_{\mathrm{el}} = 9.10938291 \cdot 10^{-31}$ kg. Other constants needed are: $\hbar = 1.05457172647 \cdot 10^{-34}$ J $\cdot$ s, 1 eV $= 1.60217656535 \cdot 10^{-19}$ J. Use a grid of $N \times N$ points in a square region defined by the range parameter a.
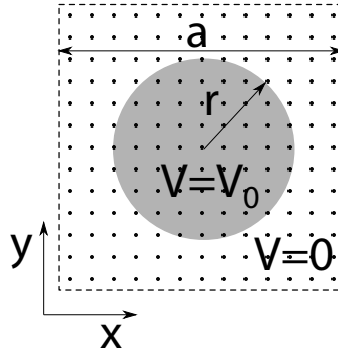
In the following, assume $N = 100$ and $a = 5r$.

1. Consider the case of $c = 1$, which correspond to the potential sketched in the figure. Find the number of bound solutions of this problem (i.e. negative eigenvalues). We recommend you to use Matlab's diagonalization routine `eigs` specially designed to deal with sparse matrices. Find the three lowest energy states, list their eigenvalues ϵ_i (in eV) and visualize the wavefunctions $\psi_i(\vec{r})$ as well as the probability densities $\psi_i^\star(\vec{r})\psi_i(\vec{r})$. You can use Matlab's function `pcolor` for this purpose. Comment on the results obtained.

2. Investigate one of the scattering solutions at a positive energy of approximately 1 eV. Visualize the wavefunction and the probability density. Calculate the probability of finding particle inside the quantum well for this state and compare this value with the one obtained for three bound solutions.

3. Consider the case of $c > 1$. Find the number of bound states as a function of c. Explain the observed trend.

4. Compare the wavefunctions and the eigenvalues corresponding to the three lowest energy states for $c = 1$ and some value $c > 1$ considered above. Explain the observed result.

Submit: your report as a PDF file as well as your scripts. The points are distributed in the following way:

- [3 pts] for the number of bound solutions, plots of the wavefunctions, probability densities and the discussion of results;

- [2 pts] for the calculation of the probability for (i) the three lowest states and (ii) the scattering state;

- [1 pt] for the plot of the number of bound states as a function of parameter c;

- [2 pt] discussion of the $c = 1$ and $c > 1$ cases.

Submit: your report as a PDF file as well as your scripts.