Homework I : Variational Principle and Concepts in Solid State

Question I (40 pnts.) : The variational solution for the double well

Consider the double-well potential given by
\[ V = (x^2 - 1)^2 \]
which is plotted in the graph to the right.

**a.** Using the basis
\[ \chi_1 = e^{-(x-1)^2} \]
\[ \chi_2 = e^{-(x+1)^2} \]
which includes the superposition of two possible wavefunction forms that are centered on either of the two wells,

i. form the $2 \times 2$ Hamiltonian and overlap operators. (10 pnts.)

ii. diagonalize the resulting generalized eigenvalue equation as discussed in class and find the ground state energy. (5 pnts.)

iii. plot the ground state and the other excited state wavefunctions using some sort of software and discuss these wavefunctions in the context of bonding and anti-bonding states you will remember from chemistry. (5 pnts.)

**b.** Enlarge your basis by including the wavefunctions
\[ \chi_3 = (x - 1)e^{-(x-1)^2} \]
\[ \chi_4 = (x + 1)e^{-(x+1)^2} \]
Using this new basis

i. download the codes entitled `integrate.m` and `differentiate.m` from the web site. Using Octave or Matlab and these codes, form the $4 \times 4$ Hamiltonian and overlap matrices. (10 pnts.)

Example usage from Octave:
```
octave:1> x=-5:0.01:5;
octave:2> chi1=exp( (x-1).^2 );
octave:3> chi1p=differentiate(x,chi1);
octave:4> T(1,1)=integrate(x,0.5*chi1p.*chi1p);
octave:5> V(1,1)=integrate(x,(x.^2-1).^2*chi1p.*chi1p);
octave:6> S(1,1)=integrate(x,chi1p.*chi1p);
```

Here the last line solves the generalized eigenvalue equation. \( v \) and \( w \) contain the eigenvectors (they should be equal when all the matrices involved are Hermitian, which is the case in our problem) and \( \lambda \) contains the eigenvalues.

ii. find the ground state energy and compare with the energy from the previous part. Is the ground state energy as expected? What can you say the symmetry of the wavefunction that is allowed by this new, extended basis? (10 pnts.)

**NOTE** that you are of course free to use any software you want or solve it analytically. If you are going to do it analytically, I suggest that you make use of the parity (even/odd) of the wavefunctions to reduce some matrix elements to zero.
c. **Bonus : 10 pnts.** Write a code to generalize this problem to a basis set that has the expression

\[ \chi_n = \frac{(x-1)^{(n-1)/2}e^{-(x-1)^2}}{\sqrt{2}} \]

\[ \chi_{n+1} = \frac{(x+1)^{(n-1)/2}e^{-(x-1)^2}}{\sqrt{2}} \]

where \( n = 1, \cdots, N \) for an arbitrary \( N \). Describe how the ground state and the wavefunctions evolve.

**Question II (30 pnts.) : The BZ of graphene**

![Graphene BZ diagram](image)

a. Looking at the representation of a two-dimensional graphene sheet above, write down the primitive unit cell lattice vectors and basis vectors. **(5 pnts.)**

b. Show (with a sketch) that the first BZ of graphene is a hexagon which is rotated with respect to the real space arrangement of hexagons. **(10 pnts.)**

c. Now find a larger unit cell in real space. Show (again with a sketch) that the first BZ of this new unit cell is included in the first BZ of the primitive unit cell. **(15 pnts.)**

**Question III (30 pnts.): Bloch’s theorem**

Assume that we have a very simple system made of \( N \) units of two different kinds of atoms, \( A \) and \( B \), that are arranged around a ring as seen in the figure. In this case, obviously, there are two atoms in the unit cell and the system obeys Born-von Karman boundary conditions. Assume that there is only nearest neighbor interaction.

Now, let’s form a variational problem, proposing two kinds of wavefunctions: a single state centered on each atom residing on site \( A \), \( \chi_{A,n} \) and a single state for atoms residing on site \( B \), \( \chi_{B,n} \) where \( n \) ranges from 1 to \( N \).

As discussed in class, there are two ways of solving this problem: one is to write a Hamiltonian and overlap operators with the elements

\[
\langle \chi_{A,n} | \chi_{A,m} \rangle = \langle \chi_{B,n} | \chi_{B,m} \rangle = \delta_{nm} \\
\langle \chi_{A,n} | \chi_{B,m} \rangle = 0 \\
\langle \chi_{A,n} | H | \chi_{A,m} \rangle = \varepsilon_A \delta_{nm} \\
\langle \chi_{B,n} | H | \chi_{B,m} \rangle = \varepsilon_B \delta_{nm} \\
\langle \chi_{A,n} | H | \chi_{B,m} \rangle = \begin{cases} t & \text{if } A \text{ and } B \text{ are nearest neighbors} \\ 0 & \text{otherwise} \end{cases}
\]

and the other is to make use of Bloch’s theorem to reduce the dimensionality of the problem.

a. For the set of localized functions above, write down (no need to diagonalize) the Hamiltonian matrix for \( N = 5 \). **(5 pnts.)** One can imagine diagonalizing the Hamiltonian for any given \( N \) (this time we just have a regular diagonalization problem since the overlap matrix is identity) and finding the eigenfunctions.
b. Show that a general, *delocalized*, $k$-dependent wavefunction that has the form

\[
\chi^k_A = \frac{1}{\sqrt{N}} \sum_{n=1}^{N} e^{i n k} \chi_{A,n} \\
\chi^k_B = \frac{1}{\sqrt{N}} \sum_{n=1}^{N} e^{i n k} \chi_{B,n}
\]

satisfies Bloch’s theorem. (10 pts.)

c. Using this new basis, the Hamiltonian reduces to a $2 \times 2$ matrix, but which now must be solved at every $k$. Write down this $2 \times 2$ matrix and solve for a general $k$. Draw the band structure, which has two branches. (15 pts.)