CHM 548 PROGRAMMING HOMEWORK 3

(1) **Hückel for molecules**: Write a general Hückel MO program applicable to the π electronic structures of polycyclic aromatic hydrocarbon (PAH) molecules. Use "jacobi.f" subprogram available in the instuctor's directory (see below) for diagonalization of symmetric matrices. Interpret the photoelectron spectra of PAH's [Boschi, Clar, and Schmidt, J. Chem. Phys. **60**, 4406 (1974)] with this program.

```
On LOP: cp /home/sohirata/CHEM548/project3/jacobi.f .
```

```
        integer maxatm                                  ! Maximum number of atoms
        parameter (maxatm=100)                          ! Maximum number of atoms
        double precision h(maxatm,maxatm)               ! Hamiltonian matrix
        double precision e(maxatm)                      ! Orbital energies
        double precision wf(maxatm,maxatm)              ! Orbital coefficients
        integer natm                                    ! Number of atoms
        integer nrot

        call jacob1(h,natm,maxatm,e,wf,nrot)     ! Diagonalizes h(natm,natm)
        call jacob2(e,wf,natm,maxatm)            ! Reorders e and wf
```

The logical dimension of h is natm × natm, but its physical (declared) dimension is maxatm × maxatm. Eigenvalues and eigenvectors will be stored in e and wf, respectively. The integer, nrot, reports the number of 2 × 2 unitary (Jacobi) transformations performed.

```
$ cat benzene
6
1 2
2 3
3 4
4 5
5 6
6 1
$ huckel
 Input connectivity file name
benzene
 natm =               6
         1           2
         2           3
         3           4
         4           5
         5           6
         6           1
 Orbital energies
   2.00000000000000       4.899978637695312E-002   eV
   1.00000000000000       2.99299979209900         eV
   1.00000000000000       2.99299979209900         eV
  -1.00000000000000       8.88099980354309         eV
  -1.00000000000000       8.88099980354309         eV
  -2.00000000000000       11.8249998092651         eV
```

Since the value of α in the Hückel model only determines the zero of energy and is insignificant. The value of β only determines the spread of energy levels and again immaterial as long as it is negative. The matrix for benzene is

$$\mathbf{H} = \begin{pmatrix} 0 & -1 & 0 & 0 & 0 & -1 \\ -1 & 0 & -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 & 0 & -1 \\ -1 & 0 & 0 & 0 & -1 & 0 \end{pmatrix}$$

(2) **Hückel 1D band structure**: Write a general one-dimensional Hückel band structure program and apply it to π bands of polyacetylene and single-wall carbon nanotubes (SWNT). Plot energy bands. Use "hhbs.f" available in the instructor's directory for diagonalization of complex, Hermitian matrices.

On LOP: cp /home/sohirata/CHEM548/project3/hhbs.f .

```
      integer maxatm                          ! Maximum number of atoms
      parameter (maxatm=100)                  ! Maximum number of atoms
      double precision e(maxatm)              ! Orbital energies
      double complex   wf(maxatm,maxatm)      ! Orbital coefficients
      double complex   dh(maxatm,maxatm)      ! Dynamical (k-dependent) H matrix
      integer natm                            ! Number of atoms

      call hhbs(maxatm,natm,dh,e,wf)          ! Diagonalizes dh(natm,natm)
```

The logical dimension of `dh` (double precision complex) is `natm` × `natm`, but its physical (declared) dimension is `maxatm` × `maxatm`. Eigenvalues (double precision real) and eigenvectors (double precision complex) will be stored in `e` and `wf`, respectively.

(2-1) Trans-polyacetylene has the alternating short C=C ($\beta = -1.1$) and long C–C ($\beta = -0.9$) bonds at $T = 0$ and is semiconductor. Its synthesis and characterization led to Nobel Prize in Chemistry in 2000 (Shirakawa, Heeger, and MacDiarmid).
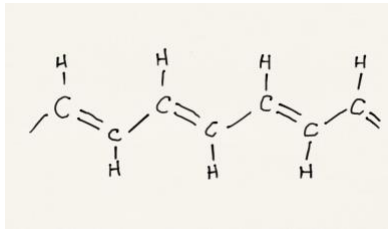
The dynamical (k-dependent) Hamiltonian matrix in the Hückel model for the bond alternating structure may be given by

$$\mathbf{H}(k) = \begin{pmatrix} 0 & -0.9 \\ 0 & 0 \end{pmatrix} e^{-ik} + \begin{pmatrix} 0 & -1.1 \\ -1.1 & 0 \end{pmatrix} + \begin{pmatrix} 0 & 0 \\ -0.9 & 0 \end{pmatrix} e^{ik}$$

The eigenvalues as a function of k are energy bands. One should observe nonzero fundamental band gap.
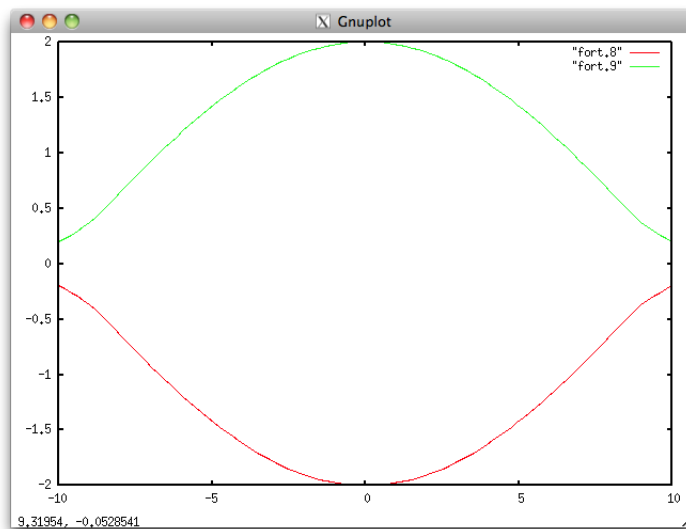
(2-2) Trans-polyacetylene should become metallic with equidistant CC ($\beta = -1.0$) bond structure. The dynamical Hamiltonian matrix may in this case be given by

$$\mathbf{H}(k) = \begin{pmatrix} 0 & -1 \\ 0 & 0 \end{pmatrix} e^{-ik} + \begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix} + \begin{pmatrix} 0 & 0 \\ -1 & 0 \end{pmatrix} e^{ik}$$

with energy bands with zero band gap. In Subproject 5, we shall confirm that the metallic structure is less stable than the semiconducting structure.
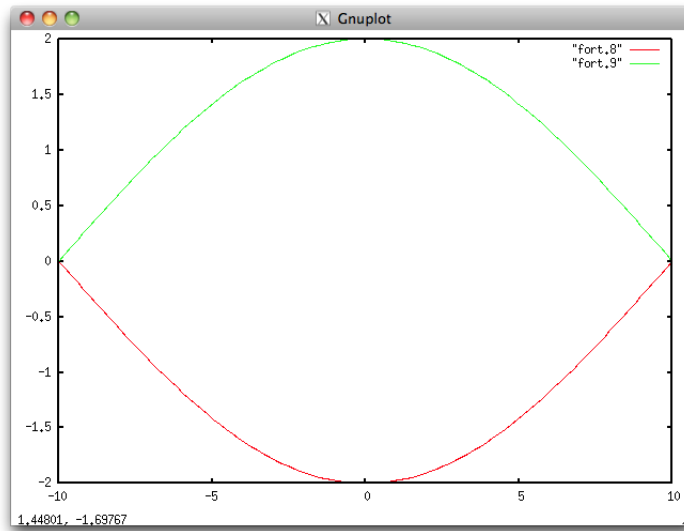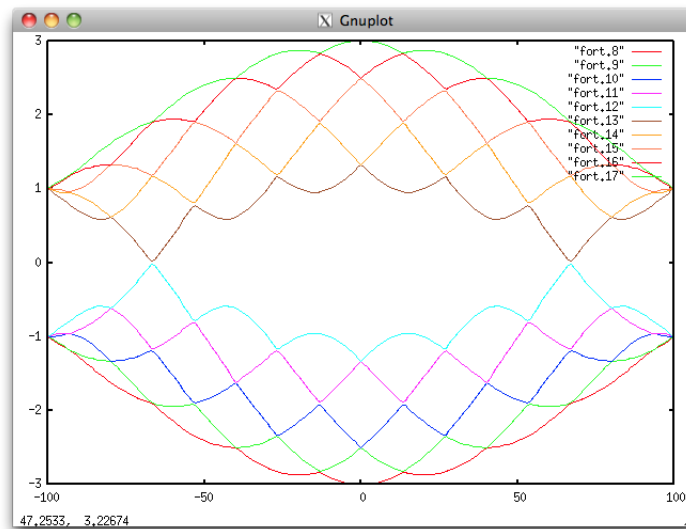

(2-3) Apply the program to SWNT. The dynamical Hamiltonian matrix for a very narrow (probably nonexistent) SWNT with only 4 carbons on a circumference is given by
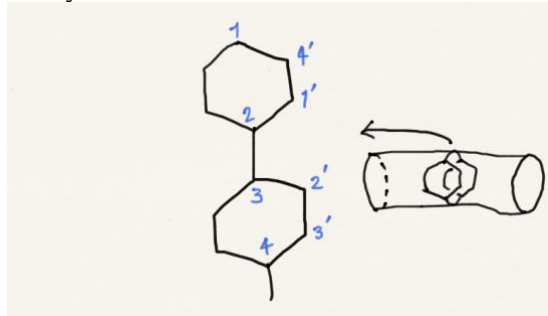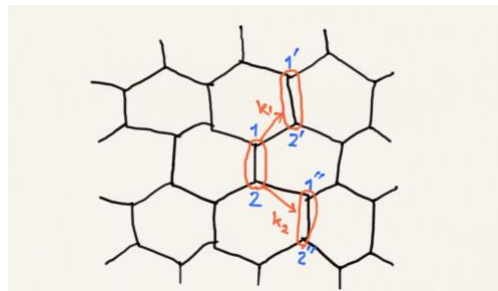

$$\mathbf{H}(k) = \begin{pmatrix} 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \\ -1 & 0 & 0 & 0 \end{pmatrix} e^{-ik} + \begin{pmatrix} 0 & 0 & 0 & -1 \\ 0 & 0 & -1 & 0 \\ 0 & -1 & 0 & 0 \\ -1 & 0 & 0 & 0 \end{pmatrix} + \begin{pmatrix} 0 & 0 & 0 & -1 \\ -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \end{pmatrix} e^{ik}$$
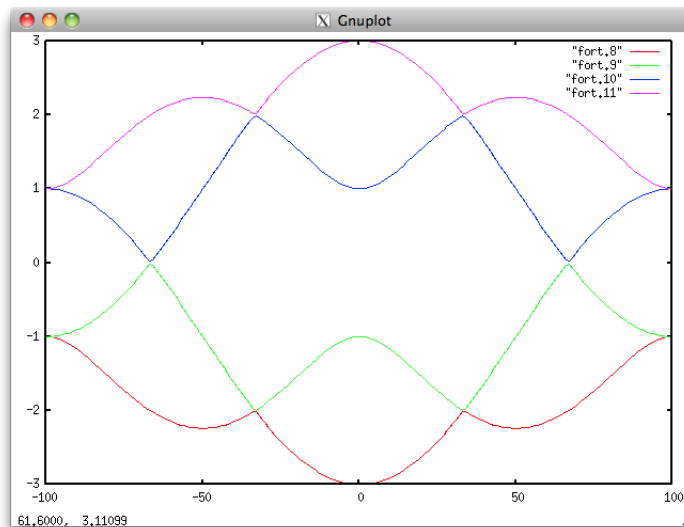
(2-4) This is the energy bands for a wider SWNT having 10 carbons on a circumference.


(3) **Hückel 2D band structure**: Write a general two-dimensional Hückel band calculation program and apply it to π bands of graphene. Plot energy bands. The pioneering studies on graphene led to Nobel Prize in Physics in 2010 (Geim and Novoselov).

The dynamical Hamiltonian matrix in the Hückel model and the corresponding energy bands are now functions of two k vectors.

$$\mathbf{H}(k) = \begin{pmatrix} 0 & 0 \\ -1 & 0 \end{pmatrix} e^{-ik_1} + \begin{pmatrix} 0 & -1 \\ 0 & 0 \end{pmatrix} e^{-ik_2} + \begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix} + \begin{pmatrix} 0 & -1 \\ 0 & 0 \end{pmatrix} e^{ik_1} + \begin{pmatrix} 0 & 0 \\ -1 & 0 \end{pmatrix} e^{ik_2}$$

The valence and conduction bands should exhibit the famous pointwise degeneracy.
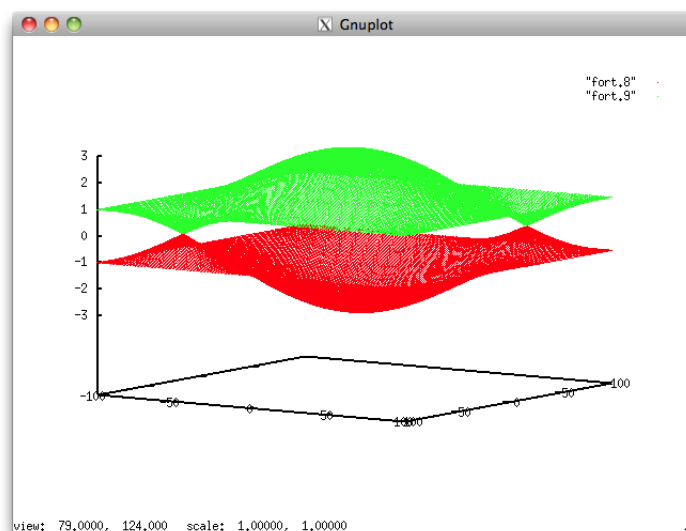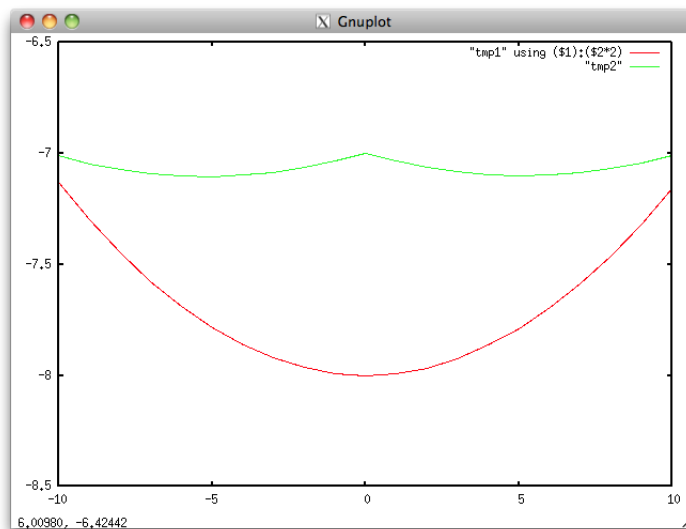
(4) **SSH and Jahn–Teller theorem**: Modify the Hückel program for PAH's in Subproject 1 to include the effect of bond length variations on both π and σ energies according to the Su–Schrieffer–Heeger model. Apply this program to benzene and benzene cation and plot their energies (the sum of π and σ energies) as a function of symmetry breaking geometry changes. Discuss the result in relation to the Jahn–Teller theorem.

$$\mathbf{H}(\Delta) = \begin{pmatrix} 0 & -1+\Delta & 0 & 0 & 0 & -1+\Delta \\ -1+\Delta & 0 & -1-2\Delta & 0 & 0 & 0 \\ 0 & -1-2\Delta & 0 & -1+\Delta & 0 & 0 \\ 0 & 0 & -1+\Delta & 0 & -1+\Delta & 0 \\ 0 & 0 & 0 & -1+\Delta & 0 & -1-2\Delta \\ -1+\Delta & 0 & 0 & 0 & -1-2\Delta & 0 \end{pmatrix}$$

where Δ denotes the change in the resonance integral in the Hückel model due to the bond length variation. The total energy of benzene is

$$E(\Delta) = 2e_1 + 2e_2 + 2e_3 + \frac{1}{2}k(\Delta^2 + \Delta^2 + \Delta^2 + \Delta^2 + 4\Delta^2 + 4\Delta^2)$$

where e_1, e_2, and e_3 are the three lowest-lying eigenvalues of $\mathbf{H}(\Delta)$ and k (not to be confused with the wave vector) is a force constant of σ bond. For the benzene cation, the coefficient multiplying e_3 should be one.

Energies of benzene (red) and benzene cation (green) as a function of symmetry breaking geometry change (Zero of the horizontal axis corresponds to the D6h geometry, while nonzero to the D2h geometries).

(5) **SSH and Peierls theorem**: Modify the Hückel program for one-dimensional solids in Subproject 2 to include the effect of bond length variations on the energy bands and total energy according to the SSH model. Apply this to polyacetylene and plot the energy with respect to the bond length alternation. Discuss the result in relation to the Peierls theorem.

$$\mathbf{H}(k;\Delta) = \begin{pmatrix} 0 & -1-\Delta \\ 0 & 0 \end{pmatrix} e^{-ik} + \begin{pmatrix} 0 & -1+\Delta \\ -1+\Delta & 0 \end{pmatrix} + \begin{pmatrix} 0 & 0 \\ -1-\Delta & 0 \end{pmatrix} e^{ik}$$

where Δ denotes the change in the resonance integral in the Hückel model due to the bond length variation. The total energy per unit cell of polyacetylene is

$$E(\Delta) = \frac{1}{K} \sum_{k=0}^{K} e_1(k;\Delta) + \frac{1}{2} k(\Delta^2 + \Delta^2)$$

where K is the number of wave vectors one sampled in the first Brillouin zone and e_1 is the valence (occupied) band energy.
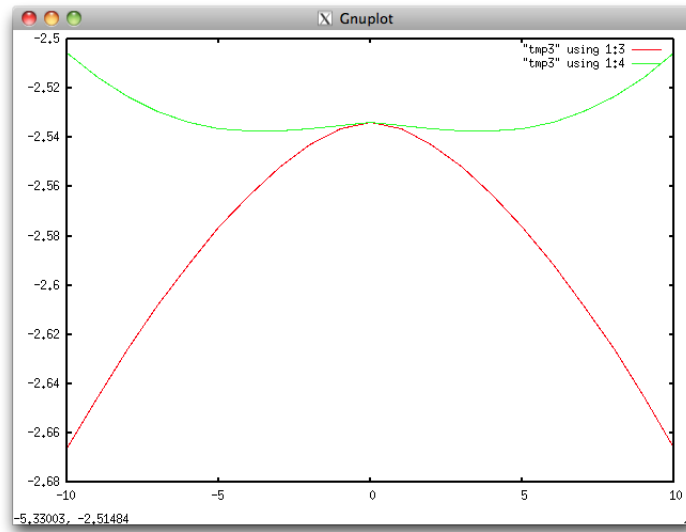
Total energy (green) and π electron energy (red) of polyacetylene as a function of bond length alternation.

Short sample programs used to generate above figures are available upon request. However, a student is strongly encouraged to write a program from scratch by taking advantage of the instructor's office hours for assistance. One can perform all these calculations more easily and interactively using Mathematica, etc., which a student is most welcome to try and include in the report. However, a student must write Fortran77/95 or C/C++ code to receive credit for this course because we ultimately have to go beyond the Hückel or SSH model.