

HOMEWORK 4

Hartree-Fock and Tight Binding Method

Due: Monday February 23, 4:30 p.m.

Problem 1: A tight binding program for carbon systems

In this problem you will write a program to calculate the total energy of a system composed of N carbon atoms for a given atomic arrangement. To do this, employ the tight binding method described in class. You will need to learn about the Slater-Koster method for building the Hamiltonian.

In this model, the total energy of the system is, as usual in the TB approach, the sum of electronic energy E_{el} and the short-ranged repulsive energy E_{rep} given by

$$E_{el} = 2 \sum_k^{occup} \varepsilon_k$$

$$E_{el} = \sum_i f \left(\sum_j \phi(r_{ij}) \right)$$

where $\phi(r_{ij})$ is a pairwise potential between atoms i and j , and f is a function expressed as a 4th order polynomial with argument $\sum_j \phi(r_{ij})$:

$$f(x) = \sum_{n=0}^4 c_n x^n$$

$$\phi(r) = \phi_0 (d_0 / r)^m \exp \left\{ n \left[- (r / r_c)^{n_c} + (r / r_0)^{n_c} \right] \right\}$$

All the parameters are listed below, and were taken directly from the original work of [Xu et al.](#) (A transferable tight-binding potential for carbon) to avoid any typos. They are:

$E_s = -2.99 \text{ eV}$, $E_p = 3.71 \text{ eV}$, $V_{ss\sigma} = -5.0 \text{ eV}$, $V_{sp\sigma} = 4.7 \text{ eV}$, $V_{pp\sigma} = 5.5 \text{ eV}$ and $V_{pp\pi} = -1.55 \text{ eV}$.

Table 1. Parameters for the functions $s(r)$ and $\phi(r)$. See equations (3), (4) and the text for details.

n	n_c	r_c (Å)	r_0 (Å)	r_1 (Å)	
2.0	6.5	2.18	1.536 329	2.45	
ϕ_0 (eV)	m	m_c	d_c (Å)	d_0 (Å)	d_1 (Å)
8.185 55	3.303 04	8.6655	2.1052	1.64	2.57

$$s(r) = (r_0/r)^n \exp\{n[-(r/r_c)^{n_c} + (r_0/r_c)^{n_c}]\} \quad (3)$$

$$\phi(r) = \phi_0(d_0/r)^m \exp\{m[-(r/d_c)^{m_c} + (d_0/d_c)^{m_c}]\} \quad (4)$$

Table 2. Coefficients of the polynomial functions $t_s(r - r_1)$, $t_\phi(r - d_1)$, and $f(x)$. See also the text for details.

	$t_s(r - r_1)$	$t_\phi(r - d_1)$	$f(x)$
c_0	$6.739\,262\,007\,431\,4 \times 10^{-3}$	$2.250\,429\,010\,9 \times 10^{-8}$	$-2.590\,976\,511\,819\,1$
c_1	$-8.188\,535\,951\,789\,8 \times 10^{-2}$	$-1.440\,864\,056\,1 \times 10^{-6}$	$0.572\,115\,149\,861\,9$
c_2	$0.193\,236\,525\,914\,4$	$2.104\,330\,337\,4 \times 10^{-5}$	$-1.789\,634\,990\,399\,6 \times 10^{-3}$
c_3	$0.354\,287\,433\,238\,0$	$6.602\,439\,022\,6 \times 10^{-5}$	$2.353\,922\,151\,675\,7 \times 10^{-5}$
c_4			$-1.242\,511\,695\,515\,87 \times 10^{-7}$

Using Matlab, C++, or a programming language with the ability to solve eigenvalue problems, write the tight binding code described, by following these steps.

1. Read in the atom coordinates for the 3 carbon systems (dimer, fullerene and nanotube).
2. Visualize each of the arrangement using [VMD](#).
3. Calculate the repulsive energy.
4. Construct the Hamiltonian matrix using the Slater-Koster method (as described in the pdf) and function $s(r)$
5. Find eigenvalues of the matrix.
6. Calculate, for all carbon arrangements given, the electronic energy, repulsive energy, E_{total} , and the binding energy per atom $E_b = E_{\text{tot}}(N)/N - E_{\text{tot}}(1)$ where $E_{\text{tot}}(1)$ is the energy of a single carbon atom.

Problem 2: Improving a Hartree program for the hydrogen molecule

Given along with this homework is a matlab file called hartree.m, written by A. Palaria¹ or alternatively a C++ version (using the GSL library) written by Adam Shai. In this problem, we will update this program to convert it from a Hartree to a Hartree-Fock program, and improve the computation time by exploiting the symmetries of our matrices. Most likely, you will need to look at [chapter 4](#) of Thijssen's "Computational Physics" in order to gain understanding of the program. Some clarification is given below:

In this program, a Gaussian basis set is used with the basis functions of the form $\chi_p(r) = \exp(-\alpha_p r^2)$. Using this type of basis allows analytical solutions for the integrals we need to compute (discussed in section 4.8 of Thijssen). Namely we have the overlap integral, the kinetic integral, the nuclear attraction integral, and the two electron integral.

¹ Palaria, Amritanshu (2006), "A MATLAB code for Hartree Fock calculation of H-H ground state bondlength and energy using STO-4G," <http://nanohub.org/resources/1718>.

The following shows the analytical solutions of the integrals with basis vectors of the form $\langle 1s, \alpha, A |$ for a basis that corresponds to the 1s orbital on atom A with exponent alpha.

The overlap integral:

$$\langle 1s, \alpha, A | 1s, \beta, B \rangle = \left(\frac{\pi}{\alpha + \beta} \right)^{3/2} \exp \left[-\frac{\alpha\beta}{\alpha + \beta} |R_A - R_B|^2 \right]$$

The kinetic integral:

$$\langle 1s, \alpha, A | -\nabla^2 | 1s, \beta, B \rangle = \frac{\alpha\beta}{\alpha + \beta} \left[6 - 4 \frac{\alpha\beta}{\alpha + \beta} |R_A - R_B|^2 \right] \left(\frac{\pi}{\alpha + \beta} \right)^{3/2} \exp \left[-\frac{\alpha\beta}{\alpha + \beta} |R_A - R_B|^2 \right]$$

The nuclear attraction integral:

$$\langle 1s, \alpha, A | \frac{-Z}{r_c} | 1s, \beta, B \rangle = -\frac{2\pi Z}{\alpha + \beta} \exp \left[-\frac{\alpha\beta}{\alpha + \beta} |R_A - R_B|^2 \right] F_0 \left((\alpha + \beta) |R_P - R_C|^2 \right)$$

$$\text{where } F_0(t) = t^{-1/2} \int_0^{t^{1/2}} dy e^{-y^2} \text{ and can be computed using the error function}$$

The two electron integrals:

$$\langle 1s, \alpha, A; 1s, \beta, B | \frac{-Z}{r_c} | 1s, \gamma, C; 1s, \delta, D \rangle = \frac{2\pi^{5/2}}{(\alpha + \gamma)(\beta + \delta)(\alpha + \beta + \gamma + \delta)^{1/2}} \\ \times \exp \left[-\frac{\alpha\gamma}{\alpha + \gamma} |R_A - R_C|^2 - \frac{\beta\delta}{\beta + \delta} |R_B - R_D|^2 \right] F_0 \left(\frac{(\alpha + \gamma)(\beta + \delta)}{(\alpha + \beta + \gamma + \delta)} |R_P - R_Q|^2 \right)$$

Because these equations can be longwinded and there are terms which are used multiple times, the program uses these substitutions:

$$as = \alpha_i + \alpha_j$$

$$ap = \alpha_i \alpha_j$$

$$rat = \frac{\alpha_i \alpha_j}{\alpha_i + \alpha_j}$$

$$rp = \frac{\alpha_i r_i + \alpha_j r_j}{\alpha_i + \alpha_j}$$

The program given to you uses this general scheme:

- 1) Input data on the basis set (in our case the exponents) and the position and type of each atom. For us, since we are only using this program for H-H it is essentially a

1D problem, and we need only to specify the distance between the two hydrogen atoms.

- 2) Determine the overlap matrix S , the kinetic matrix T , and the nuclear attraction integral A , using the analytical forms for the integrals given above.
- 3) In order to solve the generalized eigenvalue problem, the matrix S must be brought to unit form. (You do not need to worry about this step, as generally you will not be programming a generalized eigenvalue solver). Just know that the steps using the matrix V in the program are for use in converting the generalized eigenvalue problem to a normal eigenvalue problem. Try not to mess with these parts.
- 4) Compute the two electron integrals using the above equations. In the program g is used to denote the two electron matrix (notice it is 8 by 8 by 8 by 8).
- 5) Make an initial guess for the solution. Actually, although we are indeed interested in the vector which is the solution (C), in practice we generally use a density matrix, P , which is constructed from the vector C .
- 6) Loop until convergence:
 - a. Calculate Coulomb and exchange contributions to the Fock matrix (called J in the program), this is a function of the two electron integrals and the density matrix:

$$J_{pq} = \sum_{rs} P_{rs} \left[\langle pr | g | qs \rangle - \frac{1}{2} \langle pr | g | sq \rangle \right]$$
 - b. Add the uncoupled one electron matrices to the coulomb and exchange contributions to get the Fock matrix.
 - c. Perform the eigenvalue problem in order to get a new vector $C \rightarrow$ a new density matrix P
 - d. Repeat
- 7) Calculate the energy given as:

$$E = \frac{1}{2} \left[\sum_{rs} h_{rs} P_{rs} + \sum_k \epsilon_k \right] + E_{nuclei}$$

where ϵ_k are the Fock levels.

The Hartree approach is good enough for the ground state of a two-electron system because the two electrons are described by the *same* orbital: antisymmetry is taken into account via the spins which are opposite. The program you will end up with at the end of this exercise should therefore give you the same results as before, but will have the structure of a program that deals with more electrons and excited states.

To improve the program, **do the following**:

- a) Exploit the symmetry of the overlap, kinetic, and nuclear attraction integrals so as to only calculate the upper or lower triangular elements.

- b) Exploit the symmetry of the two electron matrix, g , by restricting the indices to $p \geq q$, $q \geq r$, and if $p=r$, $q \geq s$, otherwise $r \geq s$. See section 4.7 of Thijsen. For each set of p,q,r,s in these ranges, seven other g matrix elements have the same values: $qrps$, $psqr$, $qspr$, $rpsq$, $sprq$, $rqsp$, and $sqrp$.
- c) Remember the difference between Hartree and Hartree-Fock is the introduction of the Slater determinant for the wavefunction. This fixes the lack of exchange in the Hartree method, and introduces antisymmetry into the wavefunction. Now, instead of the g matrix in the original program, use the new G matrix given as (keep track of indices!):

$$G_{pqrs} = 2g_{prqs} - g_{prsq}$$

- d) Now, run both the old program and the new program moving the Hydrogen atoms closer to each other, starting at a distance of 0.5 to 2.5 a.u. (use intervals of .05 a.u.). Plot the energy as a function of distance for both cases. What is the bond length for H molecule you find? Compare this to real values.
- e) Run the programs at a distance of 1 a.u. You should be getting the same energy value. What is it? Print out the Fock matrix in both cases. Are they the same?

In submitting this problem, be sure to comment the code clearly where you have changed things. Submit the changed code, the 2 graphs asked for as well as the calculated bond lengths, energies at 1 a. u. and the Fock matrices.