

PHY 381C: Computational Physics

Final Project

Due 5 p.m. December 16, 2019

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Consider a model problem: A one dimensional hydrogen dimer (H_2), each atom has one s-state and one electron. Let's use the independent electron approximation, and assume the orthogonal basis of linear combination of atomic orbitals (LCAO).

- Construct a Hamiltonian matrix** of this problem using the LCAO basis.
- Find the eigenvalues and eigenvectors** of the dimer Hamiltonian analytically with the following matrix elements: $\langle 1|H|1\rangle = \varepsilon_0$, $\langle 1|H|2\rangle = -V$. Make a sketch of the energy levels (spectrum). Because the electrons are independent, you can simply distribute them over the just found spectrum. Remember, that electrons have spin, it is not included in the Hamiltonian, but you have to use the Pauli principle.
- The electronic contribution to the total energy of a molecule is given by $E_e = 2 \sum_i^{occ} \varepsilon_i$ where the sum runs over all occupied states. Set $\varepsilon_0 = 0$ and $|V| = 2eV$ (these are parameters in (b)), and **calculate the electronic contribution to the total energy**.
- Now, assume that the matrix element V has the following dependence on the inter-atomic distance d : $V = \frac{A}{d^2}$. Note that the electronic total energy provides attraction, it gets lower if the distance between the atoms gets smaller. Then, for the molecule not to collapse, in addition to the electronic energy there should be a purely repulsive term say of the form: $E_{rep} = \frac{B}{d^4}$. **Find analytically the total energy of a dimer as a function of d , and the equilibrium inter-atomic distance d_0** . Take $A=2 \text{ eV}\text{\AA}^2$ and $B=2 \text{ eV}\text{\AA}^4$ and sketch this energy function.
- Now, use an **appropriate numeric technique** to find the equilibrium inter-atomic distance, which corresponds to the total energy minimum. Compare with the analytic solution.
- Find the Taylor expansion of the total energy about the minimum up to second order (harmonic approximation) analytically.

- g) Assuming this total energy expression governs the dimer dynamics, *find the frequency of the dimer vibration* (make sure you are using the right mass) *analytically*.
- h) *Calculate and code up the force acting on each atom* in your model using the energy expression you found as the potential.
- i) *Write a Molecular Dynamics program* to study the dynamics of your molecule. **Hint:** what should be the time step in your program?
- j) Stretch your dimer a little, and let it vibrate while collecting the velocity data during the run. *Compute the velocity-velocity autocorrelation function:*

$$g(t) = \sum_{n=1}^N \frac{\langle v_n(t) v_n(0) \rangle}{\langle v_n(0) v_n(0) \rangle},$$

where the brackets indicate the “ensemble average” over two atoms:

$$\langle f(t_i) f(0) \rangle = \frac{1}{M-i+1} \sum_m^{M-1} f(t_{i+m}) f(t_m),$$

where t_j is the time at the j^{th} stem, and M is the total number of steps.

- k) *Calculate the Fourier cosine transform of $g(t)$:*

$$g(\omega) = \frac{1}{T} \int_0^T g(t) W(t) \cos(\omega t) dt$$

$$W(t) = 0.42 - 0.5 \cos\left(\frac{\pi t}{t_{\max}}\right) + 0.08 \cos\left(\frac{2\pi t}{t_{\max}}\right)$$

- l) *Plot it and describe how many peaks you have and what they correspond to.* What is the temperature of your simulation (**Hint:** one degree of freedom gives 0.5 kT)?