MSE 102, Fall 2006 Midterm #2

Write your name here: Solutions

Instructions:

- Answer all questions to the best of your abilities. Be sure to write legibly and state your answers clearly.
- The point values for each question are indicated.
- You are not allowed to use notes, friends, phones, etc.
- You can use calculators.
- There are a total of 100 points.
- Feel free to ask me questions, but only for clarification purposes.

This exam can contribute up to 20% of the points accrued toward your final grade, as stated in the syllabus. Good luck. I sincerely hope you all do really well.

-Prof. Chrzan

1. An electron bound to a hydrogen atom is described by the wavefunction:

$$\Psi(\mathbf{r},t) = \frac{i}{4}\exp\left(\frac{-iE_1 t}{\hbar}\right)\psi_{100}(\mathbf{r}) - \frac{\sqrt{15}}{4}\exp\left(\frac{-iE_4 t}{\hbar}\right)\psi_{431}(\mathbf{r}),$$

with $\psi_{nlm}(\mathbf{r})$ an eigenfunction of the Hamiltonian, $\hat{H}$, squared angular momentum, $\hat{L}^2$, and z-component of the angular momentum, $\hat{L}_z$.

(a) [10 points] Give the expectation value of the z-component of the angular momentum, $\hat{L}_z$, for the electron?

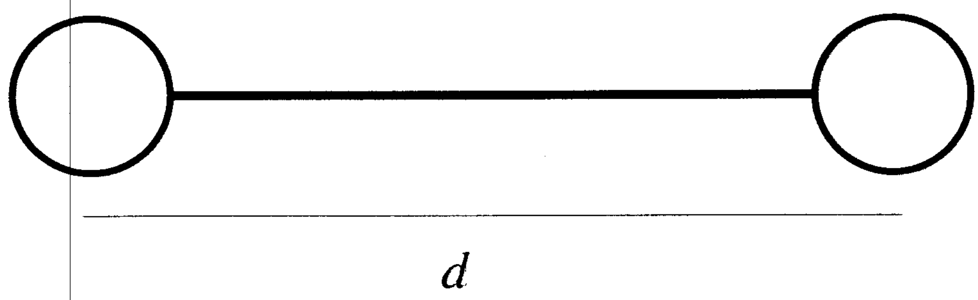
$$\langle \hat{L}_z \rangle = \frac{15}{16}\hbar \quad \left(= \sum_{n,l,m} |b_{nlm}|^2 \hbar m \right)$$

(b) [10 points] Give the expectation value of the total energy. (You can express this in terms of the energies E_1 and E_4.

$$\langle \hat{H} \rangle \equiv \langle E \rangle = \frac{1}{16} E_1 + \frac{15}{16} E_4 \quad \left(= \sum_{nlm} |b_{nlm}|^2 E_n \right)$$

(c) [10 points] Give the expectation value of the angular momentum squared, $\hat{L}^2$?

$$\langle \hat{L}^2 \rangle = \frac{15}{16}\hbar^2 \cdot 3 \cdot 4 = \frac{45}{4}\hbar^2 \quad \left(= \sum_{nlm} |b_{nlm}|^2 \hbar^2 l(l+1) \right)$$



(2) The Hamiltonian matrix for an electron bound to a dimer with bond length d, determined using a basis composed of the S states of the bare atoms, is given by:

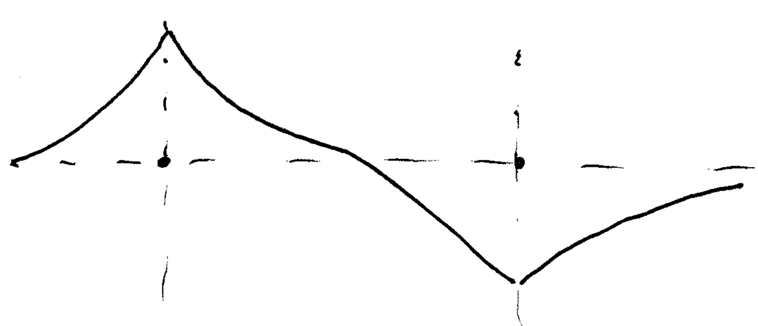
$$\mathbf{H} = \begin{pmatrix} E_o & -V_o/d \\ -V_o/d & E_o \end{pmatrix}$$

Here, E_o is the energy level for an electron in a bare atom. All energies are measured in eV, and all distances are measured in Ångstroms.

(a) [20 points] What energies may one measure for an electron bound to the dimer? (Give your answer as a function of d.)

$$\begin{vmatrix} E_0 - E & -V_0/d \\ -V_0/d & E_0 - E \end{vmatrix} = 0 \quad \Rightarrow \quad E = E_0 \pm V_0/d$$

(b) [10 points] Plot the eigenfunction associated with the *antibonding* state. (Assume the atomic basis states are $\psi_{100}(\mathbf{r})$ states.) Plot this along the line connecting the dimer.



(c) [10 points] The driving force for bond formation is given by the reduction in electron energy upon formation of the dimer. This is counteracted by a repulsive energy. Suppose that this repulsive energy is given by a form similar to that for the Lennard-Jones potential, but with a smaller exponent (2 instead of 12), and no factor of 4:

$$V_{repulsive} = \varepsilon\left(\frac{\sigma}{d}\right)^2$$

Compute the zero temperature equilibrium bond length of the dimer in terms of V_o, ε, and σ. Assume that there are two electrons bound to the dimer. Also assume that the electron-electron interactions are already included in the definition of V_o. Using this bond length, compute the cohesive energy of the dimer. That is, compute the amount the energy is reduced upon bringing the atoms from $d = \infty$ to $d =$ equilibrium bond length.

$$E(d) = \underbrace{-\frac{2V_0}{d}}_{\text{from electrons}} + \underbrace{\varepsilon\left(\frac{\sigma}{d}\right)^2}_{\text{repulsive part}}$$

$$\left.\frac{dE}{dd}\right|_{d=d_0} = 0 = \frac{2V_0}{d_0^2} - \frac{2\varepsilon}{d_0}\left(\frac{\sigma}{d_0}\right)^2$$

$$\Rightarrow \frac{V_0}{\cancel{d_0^2}} = \frac{\varepsilon}{d_0}\frac{\sigma^2}{\cancel{d_0^2}}$$

$$\boxed{d_0 = \frac{\varepsilon\sigma^2}{V_0}}$$

equilibrium bond length

$$E(d_0) = \frac{-2V_0}{(\varepsilon\sigma^2/V_0)} + \frac{\varepsilon\sigma^2}{\left(\frac{\varepsilon\sigma^2}{V_0}\right)^2} = \frac{-2V_0^2}{\varepsilon\sigma^2} + \frac{V_0^2}{\varepsilon\sigma^2} = -\frac{V_0^2}{\varepsilon\sigma^2}$$

(3) Suppose that the interaction between two atoms is given by the Lennard-Jones potential:

$$V(d) = 4\varepsilon\left[\left(\frac{\sigma}{d}\right)^{12} - \left(\frac{\sigma}{d}\right)^{6}\right] .$$

In this problem, you will consider an infinite one-dimensional lattice with one atom per site. You may need the sums:

$$\sum_{n=-\infty}^{\infty}{}' \left(\frac{1}{n}\right)^{12} = \frac{1382\pi^{12}}{638512875} = 2.00049 \quad = A_{12}$$

$$\sum_{n=-\infty}^{\infty}{}' \left(\frac{1}{n}\right)^{6} = \frac{2\pi^{6}}{945} = 2.03469 \quad = A_6$$

The primes on the sums indicate that they excluded the $n = 0$ term. Choose $\varepsilon = 4.0$ eV, and $\sigma = 2.0$ Å.

(a) [15 points] Find the equilibrium lattice parameter for the chain of atoms.

$$V(a) = \cancel{4\varepsilon \sum_u \sum_{u'} \left(\frac{\sigma}{au}\right)^{12}}$$

$$= \frac{4\varepsilon}{2} \sum_u \sum_{u'} \left[\left(\frac{\sigma}{a(u-u')}\right)^{12} - \left(\frac{\sigma}{a(u-u')}\right)^{6}\right]$$

$$= 2\varepsilon N \sum_{u'} \left[\left(\frac{\sigma}{a}\right)^{12}\left(\frac{1}{u'}\right)^{12} - \left(\frac{\sigma}{a}\right)^{6}\left(\frac{1}{u'}\right)^{6}\right]$$

$$= 2\varepsilon N \left[A_{12}\left(\frac{\sigma}{a}\right)^{12} - A_6\left(\frac{\sigma}{a}\right)^{6}\right]$$

$$\left.\frac{dV}{da}\right|_{a=a_0} = 2\varepsilon N \left[-\frac{12 A_{12}}{a_0}\left(\frac{\sigma}{a_0}\right)^{12} + \frac{6A_6}{a_0}\left(\frac{\sigma}{a_0}\right)^{6}\right] = 0$$

$$\Rightarrow \quad 2A_{12}\left(\frac{\sigma}{a_0}\right)^{6} = A_6$$

$$a_0 = \left(\frac{2A_{12}}{A_6}\right)^{1/6} \sigma = 2.23859 \text{ Å}$$

(b) [15 points] Find the cohesive energy per atom of the chain of atoms.

$$\frac{V(a_0)}{N} = 2\varepsilon\left(A_{12}\left(\frac{\sigma}{a_0}\right)^{12} - A_6\left(\frac{\sigma}{a_0}\right)^{6}\right)$$

$$= 2\varepsilon\left(A_{12}\left(\frac{A_6}{2A_{12}}\right)^{2} - A_6\left(\frac{A_6}{2A_{12}}\right)\right)$$

$$= 2\varepsilon\left(\frac{A_6^2}{A_{12}}\right)\left[\frac{1}{4} - \frac{1}{2}\right]$$

$$= -\frac{\varepsilon}{2}\frac{A_6^2}{A_{12}} = -4.13895\ \text{eV}$$