MATRL 218/CHEM277: Assignment 4

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1. For the Lennard-Jones potential:

\[ U(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] \]

Determine by setting \( \frac{\partial U(r)}{\partial r} = 0 \), the value of \( r/\sigma \) for which the potential is minimum. Also, plot the potential, by plotting \( U/\epsilon \) as a function of \( r/\sigma \). Typically how many molecular diameters away is the potential effectively 0 (say 0.1% of the well depth)?

2. Why do you expect the dispersion (van der Waals) attraction between larger noble gas atoms to be larger than for smaller ones.

3. Can a solid be held together purely through electrostatics? Consider the equation for the lattice energy, and use this to show that electrostatics (the Coulombic attraction between unlike charges) does not lead to a stable lattice and that the (Pauli) repulsion between the electron cores is essential.

4. Sketch a square lattice and decorate the vertices alternately with cations and anions of unit charge (a “2D NaCl). Write out the first few terms of the geometric Madelung constant for the above lattice. Does it look like you can sum it up to \( \infty \).

5. Write out the first four terms in the summation for the geometric Madelung constant of fluorite CaF\(_2\) (Vesta could help).

6. Sketch the \( E vs. k \) dispersion relation for a square lattice of \( p_x \) and \( p_y \) orbitals, and pay attention to \( \sigma \) and \( \pi \) interactions. The points defining the Brillouin zone boundaries are \( \Gamma(0,0) \), \( X(\pi/a,0) \), \( Y(0,\pi/a) \), and \( M(\pi/a,\pi/a) \). Sketch the densities of state alongside.

7. Now stretch the above the lattice in the \( y \) direction so that it is rectangular, with \( a < b \). How does this modify the band structure. Remember that the BZ boundaries are \( \Gamma(0,0) \), \( X(\pi/a,0) \), \( Y(0,\pi/b) \), and \( M(\pi/a,\pi/b) \). Show that if there is one electron per orbital, such a distortion can result in a gap between filled and unfilled states.
8. (Extra credit) Write a computer program to determine the geometric Madelung constant for rock salt, by considering finite cubes that are formed from $2N \times 2N \times 2N$ cation-anion pairs. Compare the data with the following image: