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Assignment 2: Bonding and harmonic chains

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Exercise 1 *Bonding: not LCAO* (9 points)

(i) In you own words, explain why ionic bonds occur, and what properties one would expect from and ionic solid.

(ii) The (first) ionisation energy of sodium is roughly $5.14\,\mathrm{eV}$, and the electron affinity of chlorine is roughly 3.62, and the bond length between the two atoms when a sodium chloride molecule is formed is roughly $0.236\,\mathrm{nm}$. Assuming that *all* of the cohesive energy is due to the Coulomb interaction, calculate the bonding energy.

(iii) The measured value of the bonding energy of sodium chloride is $4.26\,\mathrm{eV}$. How does this compare to your value above? Justify your response.

(iv) In our discussion of bonding, we did not explicitly discuss van der Waals bonding. Research what is the nature of the van der Waals bond, explicitly describing the origin of the attractive force formation and reason as to why the force is of the form R^{-7}

Exercise 2 *Bonding: LCAO* (8 points)

In our formulation of the LCAO formulation we assumed that orbitals were orthogonal, with the justification that the qualitative behaviour was still going to be fine.
Assume that we introduce a trial wavefunction:

$$|\psi\rangle = \sum_{i=1}^{N} \phi_i |i\rangle$$

however, we are not going to enforce that the state be orthogonal. Rather, we define an overlap matrix $\mathcal{S}$ with elements

$$\mathcal{S}_{i,j} = \langle i|j\rangle$$

(i) Show that with the above conditions, one arrives at an *effective* Schrödinger equation

$$\mathcal{H}\phi = E\mathcal{S}\phi$$

where

$$\mathcal{H}_{i,j} = \langle i|\hat{H}|j\rangle$$

and ϕ is the vector of the coefficients for the ϕ_i.

(ii) Consider the case where N=2 (i.e. the diatomic case) and the orbitals are s ($l=0$) orbitals. Use the above equation to solve for the energy eigenvalues of the system.

A neat treat is available for a person that can identify why we consider s states.

Exercise 3 *Quantum thermal expansion* (10 points)

In a *content unpacking* session, we discussed thermal expansion arising from the anharmonic term in the interatomic potential. Assume masses m_1 and m_2 for the interacting particles and let's consider an anharmonic perturbation δV

$$\delta V = -\frac{\kappa_3}{6}(x - x_0)^3$$

to the one-dimensional quantum harmonic oscillator H_0:

$$H_0 = \frac{p^2}{2m} + \frac{\kappa}{2}(x - x_0)^2.$$

To first order in κ_3, it can be shown that

$$\langle n|x|n \rangle = x_0 + \frac{E_n \kappa_3}{2\kappa^2}$$

where $|n\rangle$ is the eigenstate of the harmonic oscillator with

$$E_n = \hbar\omega \left(n + \frac{1}{2} \right)$$

(i) What is the value of ω in terms of m_1 and m_2?

(ii) What is the interpretation of the $|0\rangle$ state?

(iii) The expectation value of x as a function of temperature is written as

$$\langle x \rangle_\beta = \frac{\sum_n \langle n|x|n \rangle e^{-\beta E_n}}{\sum_n e^{-\beta E_n}}$$

    (a) Find the coefficient of thermal expansion

    (b) What is the behaviour of the coefficient at both high and low temperature, and comment on the physical significance of these results.

Exercise 4 *One-dimensional oscillations* (19 points)

(i) Explain what is meant by a *normal mode* and a *phonon*

(ii) Derive the dispersion relation for longitudinal oscillations of an infinite one-dimensional chain of identical atoms, assuming mass m, spring constant κ, and lattice spacing a

(iii) Show that a the mode with wavevector k is equivalent to the mode $k + 2\pi/a$

(iv) Assuming periodic boundary conditions, how many different modes are there?

(v) Find expressions for and plot both the group and phase velocities

(vi) Find an expression for the density of states $g(\omega)$ and plot $g(\omega)$

(vii) Using $g(\omega)$, find an expression for the heat capacity and use any tools at your disposal to plot the heat capacity versus temperature