

PROBLEM SET #1
"General properties of crystals"
due on 4/12/2021

Physics-172 / Applied Physics-272
Introduction to Solid State Physics
Spring quarter, 2021

Instructor: *Aharon Kapitulnik* — aharonk@stanford.edu
Class Assistant: *David Saykin* — saykind@stanford.edu
Departments of Applied Physics and of Physics

Comment. *Note that since these lecture notes are part of a manuscript, much of the language used here follows that of a book, with reference to chapters, sections, etc. In addition, some material in the notes may be more advanced, or will not directly be related to discussions in class. Please view these parts as stimulating extensions, where you are welcome to contact us about questions and relevant references.*

Problem 1.1 (Specific heat — **1 point**). The specific heat of a solid, at low temperatures, generally depends on a power of the temperature,

$$C \propto (T/T_0)^{x_c} \text{ for } T \ll T_0.$$

In a metal or an insulating glass, $x_c = 1$ while in a crystalline insulator, $x_c = 3$. Prove that the third law of thermodynamics implies that $x_c > 0$.

Remark. As a point of mathematical nicety, the third law actually permits C to vanish more slowly than any power law; for instance, $C \propto \log^{-\alpha}[T_0/T]$ with $\alpha > 1$.)

Problem 1.2 (Bulk modulus — **2 points**). The bulk modulus of a crystal is given by

$$B = -V \left(\frac{\partial P}{\partial V} \right)_T$$

where V is the volume and P is the pressure. The pressure is given as the first derivative of the free energy with respect to volume. However, at zero temperature, it is given purely in terms of the total energy of the solid $P = -dU/dV$.

Let us consider again an ionic crystal with NaCl structure as in Fig. 1. Define $u_i = U_i/N$ and $v = V/N$ as the energy and volume per particle. Show that the bulk modulus for such a crystal is given by

$$B = \frac{1}{9R_0} \left. \frac{d^2 u}{dR^2} \right|_{R=R_0},$$

where R_0 is the equilibrium nearest-neighbor separation.

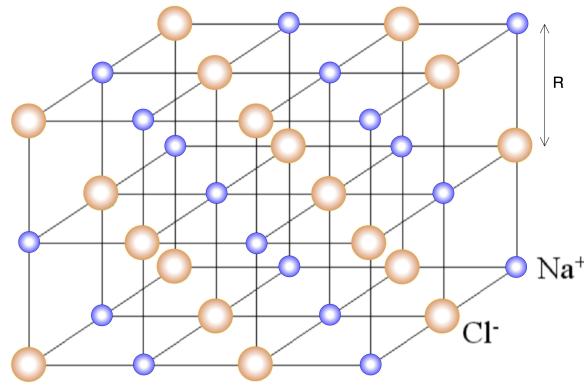


Figure 1: Crystal structure of NaCl.

Problem 1.3 (Madelung constant — **3 points**). NaCl is an ionic crystal which is a type of crystal made up of positive and negative ions, such that the Coulomb attraction between ions of opposite sign is stronger than the Coulomb repulsion between ions of the same sign. Obviously, charge neutrality is maintained in each unit cell.

While “attraction wins” within a unit cell, there is also short-range repulsion so that ions do not collapse into each other. Ion-ion interaction can be written as

$$U_{ij} = U_0 e^{-r_{ij}/\lambda} + (-)^{i-j} \frac{e^2}{r_{ij}}, \quad r_{ij} \equiv |\mathbf{r}_j - \mathbf{r}_i|$$

Since $\lambda \lesssim R$ — distance between the nearest neighbors, repulsion term is only relevant for neighboring ions. Hence, energy that includes interaction with i -th ion is given by the sum

$$\begin{aligned} U_i &\approx zU_0 e^{-R/\lambda} + \sum_{j \neq i} (-)^{i-j} \frac{e^2}{r_{ij}} \\ &= zU_0 e^{-R/\lambda} + \alpha_i \frac{e^2}{R}, \quad \alpha_i \equiv \sum_{j \neq i} \frac{(-)^{i-j} R}{|\mathbf{r}_i - \mathbf{r}_j|} \end{aligned}$$

Here z is a coordination number (number of closest neighbors) and $\alpha_i = \alpha$ is a dimensionless number called *Madelung constant*.

1. **(1 point)** Find an expression for the equilibrium separation R in terms of the potential parameters U_0 , λ and α (no need to solve for R).
2. **(1 point)** Calculate α for a one dimensional NaCl crystal.
3. **(1 point)** Calculate the first few terms in α for the 3-dimensional case. What can you say about the convergence of the sum (rigorous mathematical answer is not required)?

Problem 1.4 (Valence bonding — **3 points**). In this problem we will explain the quantum nature of valence bonding using the simplest example of a hydrogen molecule. Following the calculation of W. Heitler and H. London (1927) we would use an adiabatic approximation and a first-order perturbation theory to calculate the energy of a H_2 molecule as a function of the distance between the atoms.

Consider the Hamiltonian of the hydrogen molecule.

$$\begin{aligned}\hat{H} &= \hat{H}_1 + \hat{H}_2 + \hat{V}, \\ \hat{H}_1 &= \frac{\hat{p}_1^2}{2m} - \frac{e^2}{r_{1A}}, \\ \hat{H}_2 &= \frac{\hat{p}_2^2}{2m} - \frac{e^2}{r_{2B}}, \\ \hat{V} &= -\frac{e^2}{r_{1B}} - \frac{e^2}{r_{2A}} + \frac{e^2}{r_{12}} + \frac{e^2}{R}.\end{aligned}$$

Here m is the electron mass and we have neglected the kinetic energy of the Hydrogen nuclei exploiting the fact that $m_e \ll M_{\text{nucl}}$ (adiabatic approximation). The distance between the atoms $R \equiv r_{AB}$ enters the Hamiltonian as a parameter. We have divided our Hamiltonian in three parts such that \hat{V} could be considered as perturbation to $\hat{H}_{1,2}$ when the distance between the atoms is large $R \gg r_{1A}, r_{1B}$.

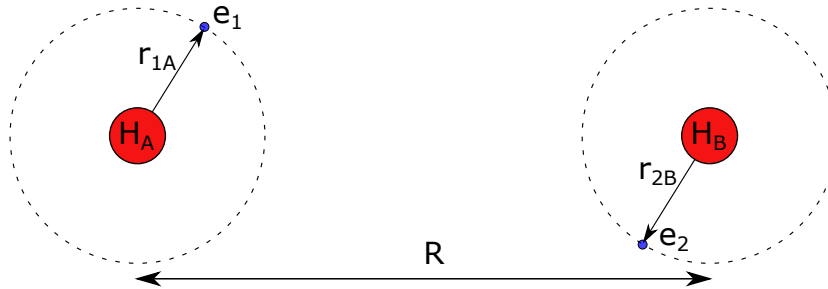


Figure 2: Notation used in the problem 1.4.

We are interested in calculating the ground state energy E satisfying Schrodinger eigenproblem

$$\hat{H}\Psi(\mathbf{r}_1, \mathbf{r}_2) = E\Psi(\mathbf{r}_1, \mathbf{r}_2).$$

In zeroth order approximation each electron is orbiting around separate atoms in $1s$ state (what is an expression for $1s$ orbital?). We know that the total wavefunction (including spin) of fermions has to be anti-symmetric. Two spins could form a singlet $S = 0$ or a triplet $S = 1$, which corresponds to symmetric and anti-symmetric orbital wavefunctions respectively.

$$\begin{aligned}\Psi_s(\mathbf{r}_1, \mathbf{r}_2) &= C_s [\psi_A(\mathbf{r}_1)\psi_B(\mathbf{r}_2) + \psi_A(\mathbf{r}_2)\psi_B(\mathbf{r}_1)], \\ \Psi_a(\mathbf{r}_1, \mathbf{r}_2) &= C_a [\psi_A(\mathbf{r}_1)\psi_B(\mathbf{r}_2) - \psi_A(\mathbf{r}_2)\psi_B(\mathbf{r}_1)],\end{aligned}$$

Wavefunction $\psi_A(\mathbf{r}_1)\psi_B(\mathbf{r}_2)$ corresponds to the picture represented on Figure 2 and $\psi_A(\mathbf{r}_2)\psi_B(\mathbf{r}_1)$ describes the state with electrons swapped between the atoms.

Using these functions as correct zeroth-order states, calculate first-order corrections to the energies of the symmetric and anti-symmetric states following the steps outlined below. Please express your answer in terms of integrals

$$\begin{aligned}S &= |\langle \psi_A | \psi_B \rangle|^2 = \left| \int \psi_A^*(\mathbf{r})\psi_B(\mathbf{r})d\mathbf{r} \right|^2, \\ W &= \int \psi_A^*(\mathbf{r}_1)\psi_B^*(\mathbf{r}_2)V(\mathbf{r}_1, \mathbf{r}_2, R)\psi_A(\mathbf{r}_1)\psi_B(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2, \\ Y &= \int \psi_A^*(\mathbf{r}_2)\psi_B^*(\mathbf{r}_1)V(\mathbf{r}_1, \mathbf{r}_2, R)\psi_A(\mathbf{r}_1)\psi_B(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2.\end{aligned}$$

What is the classical meaning of W ? Is there a classical analogue of S ?

1. (**1 point**) Calculate normalization constants C_s and C_a in terms of S .
2. (**2 points**) Calculate first-order energy corrections ΔE_s and ΔE_a in terms of S , W and Y .
3. (**BONUS — 0 points**) Using explicit expressions for integrals S , W , Y given below, plot (sketch) expressions for ΔE_s and ΔE_a as a function of interatomic distance R . Find the distance R_* that corresponds to the minimum of ΔE_s in terms of Bohr's radius a_B .

$$\begin{aligned} S &= \Delta^2, \quad \Delta = e^{-R} \left(1 + R + \frac{R^2}{3} \right), \quad \delta = e^R \left(1 - R + \frac{R^2}{3} \right), \\ W &= -\frac{1}{R} + e^{-2R} \left(\frac{1}{R} + \frac{5}{8} - \frac{3}{4}R - \frac{R^2}{6} \right), \\ Y &= -2\Delta e^{-R} (1 + R) - \frac{e^{-2R}}{5} \left[-\frac{25}{8} + \frac{23}{4}R + 3R^2 + \frac{R^3}{3} \right] + \\ &\quad + \frac{6}{5R} \left[\Delta^2(\gamma + \ln R) + \delta^2 \text{Ei}(-4R) - 2\Delta\delta \text{Ei}(-2R) \right] \end{aligned}$$

Energies and distances are given in atomic units $E_a = e^2/a_B = 2 \text{ Ry}$, $a_B = \hbar^2/me^2$.

Remark. Interestingly, such calculation gives wrong asymptotic expression for $\Delta E_s(R)$, $R \rightarrow \infty$, see [Phys. Rev. 134, A362, 1964](#) for more information.