PROBLEM SET #1
"Crystalline bond"
due on 4/11/2022

Physics–172 / Applied Physics–272
Introduction to Solid State Physics
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Problem 1.1 (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

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

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).

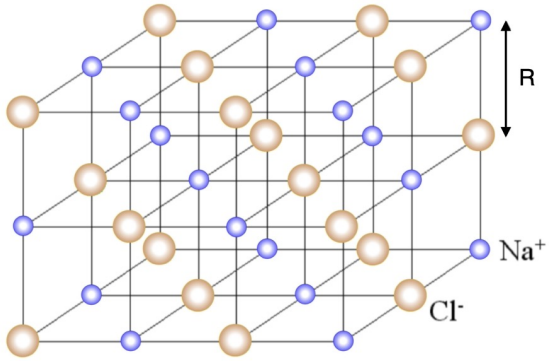

Figure 1: Crystal structure of NaCl.

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 1.2 (Toy bonding model — **4 points**)**.** In order to see how electron shared between atoms result in attracting force between the atoms, consider a particle on a line in a potential of two δ–wells located on a distance $2a$ from each other (see Fig. 2).

$$\hat{H} = \frac{\hat{p}^2}{2m} - \frac{\hbar^2\varkappa}{m}\delta(x-a) - \frac{\hbar^2\varkappa}{m}\delta(x+a). \tag{1.2.1}$$

1. (**2 points**) Find localized eigenstate ψ_0 of a single δ–well

$$\hat{H}_0 = \frac{\hat{p}^2}{2m} - \frac{\hbar^2\varkappa}{m}\delta(x), \qquad \hat{H}_0\psi_0 = E_0\psi_0, \quad E_0 < 0.$$

   Use it to find zeroth–order localized states $\psi_{1,2}$ and energies $E_{1,2}$ up to the first order of Hamiltonian H in the limit of large separation between the wells $a \gg \varkappa^{-1}$.

   Hint. One of the methods is described in solution of problem 3 in [1, §50].

2. (**2 points**) Solve eigenproblem (1.2.1) exactly and compare to the approximate solution.

Show that in the ground state, there is an attraction force between wells.

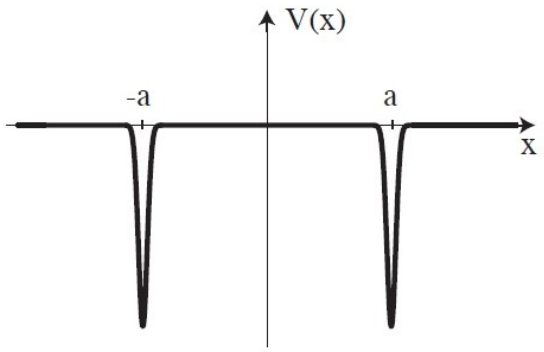

Figure 2: Potential of two δ–wells.

Problem 1.3 (Ion bonding— **4 points**)**.** Let us consider a hydrogen molecule ion H_2^+ as a hydrogen atom H and a hydrogen nucleus H^+ far away (see Fig. 3).

$$\hat{H} = \frac{\hat{p}^2}{2m} - \frac{e^2}{r} - \frac{e^2}{|\mathbf{r}-\mathbf{R}|} + \frac{e^2}{R}.$$

In the leading approximation in $R \gg a_B$ second Coulomb's potential could expanded in $r \ll R$, hence action of the second ion could be reduced to the electric field $\boldsymbol{\mathcal{E}}$ it produces.

$$\hat{H} \approx \hat{H}_0 - |e|(\boldsymbol{\mathcal{E}}, \mathbf{r}), \qquad \hat{H}_0 = \frac{\hat{p}^2}{2m} - \frac{e^2}{r}, \quad \boldsymbol{\mathcal{E}} = -\frac{|e|}{R^2}\frac{\mathbf{R}}{R}.$$

Consider electric field term as perturbation $\hat{V} = -|e|(\boldsymbol{\mathcal{E}}, \mathbf{r})$ and compute energy correction to the round state. Do hydrogen nuclei attract or repulse?

Hint. Second–order energy correction $E^{(2)} = \left\langle \psi^{(0)} \right| \hat{V} \left| \psi^{(1)} \right\rangle$ could be found by solving equation for first–order wavefunction correction

$$\left[E_0 - \hat{H}_0 \right] \psi^{(1)} = \left[\hat{V} - E^{(1)} \right] \psi^{(0)}.$$

This equation allows for separation of variables, hence $\psi^{(1)}(r, \theta, \varphi) = r^{-1}\chi(r)Y_{lm}(\theta, \varphi)$, where spherical function should be chosen such that it fits spherical part on the r.h.s.

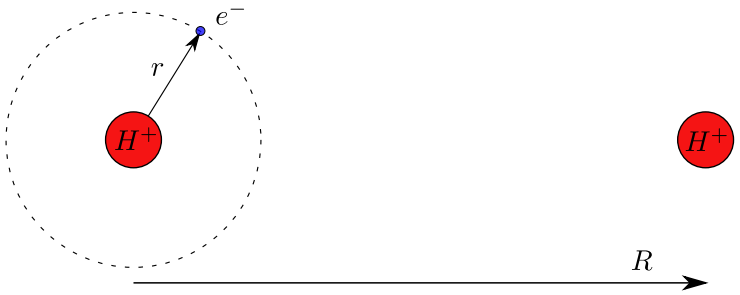

Figure 3: Hydrogen molecule ion.

Remark. We only found leading term of $E(R)$, $R \to \infty$ expansion, it does not allow us to see that stable configuration of hydrogen ion. It turns out that (as it usually happens) there are also exponentially small corrections [2], which could be viewed as valence bonding contribution and begin to play a role for distances $R < 10a_B$ [1, §81].

References

[1] L. D. Landau and E. M. Lifshitz. *Quantum Mechanics: Non-relativistic Theory*, volume 3. Elsevier, 2013.

[2] J. Cížek, R. Damburg, and *et al.* 1/R expansion for H_2^+: Calculation of exponentially small terms and asymptotics. *Phys. Rev. A*, 33:12–54, Jan 1986.

[3] C. Herring and M. Flicker. Asymptotic exchange coupling of two hydrogen atoms. *Phys. Rev.*, 134:A362–A366, Apr 1964.