Institut für Theoretische Festkörperphysik
Karlsruher Institut für Technologie

Prof. Dr. M. Garst
Dr. J. Masell
Dr. S. Sorn

Condensed Matter Theory 1 — Exercise 3

Winter term 2023/24

https://ilias.studium.kit.edu/goto.php?target=crs_2219528
To be discussed on: *Thursday 2023/11/16*

1. An application of the Born-Oppenheimer approximation

Consider a quantum mechanical oscillator with two masses, m and M, at positions r and R, respectively, connected by a spring with the spring constant γ, see Fig. 1. The Hamiltonian $\hat{H}$ for this system is given as

$$\hat{H}\Psi(r,R) = \left[-\frac{\partial_r^2}{2m} - \frac{\partial_R^2}{2M} + \frac{1}{2}\gamma(r-R)^2\right]\Psi(r,R) \qquad (1)$$

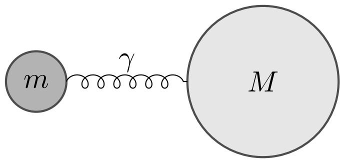


Figure 1: Quantum oscillator consisting of a spring and two masses.

where we set $\hbar = 1$.
The eigenvectors and eigenvalues of this Hamiltonian can be obtained exactly by a change of variables into the center of mass $R_0 = \frac{mr+MR}{M_0}$ and the relative position $\rho = r - R$. $M_0 = m + M$ is the total mass and $\mu = \frac{mM}{M_0}$ is the reduced mass. With the new variables, the Hamiltonian is decoupled:

$$\hat{H}\Psi(R_0,\rho) = \left[-\frac{\partial_{R_0}^2}{2M_0} - \frac{\partial_\rho^2}{2\mu} + \frac{1}{2}\gamma\rho^2\right]\Psi(R_0,\rho)\ . \qquad (2)$$

Consequently, the system is effectively described by a free particle, corresponding to the free motion of the center of mass (mass M_0), and a simple harmonic oscillator with the mass μ. The eigenvector is given by $\Psi_n(R_0,\rho) \propto e^{iKR_0}\Phi_n(\rho)$, where $\Phi_n(\rho)$ are the eigenvectors corresponding to the n-th level of a simple harmonic oscillator. The eigenvalues (energies) are given by

$$E_n(K) = \frac{K^2}{2M_0} + \omega_{\text{eff}}\left(n + \frac{1}{2}\right)\ , \qquad (3)$$

with K the linear momentum of the motion of the center of mass, $\omega_{\text{eff}} = \sqrt{\gamma/\mu}$ the oscillation frequency, and $n = 0, 1, 2, ...$ the energy levels of the harmonic oscillator.
In this exercise, we apply the Born-Oppenheimer approximation to this problem in the limit of $m \ll M$ and compare the approximated eigenvalues to the exact results.

a) For the Born-Oppenheimer approximation, the original Hamiltonian in Eq. 1 is decomposed into a fast (instantaneous) part $\hat{H}_0$ and a slow part $\hat{T}$,

$$\hat{H}_0 = -\frac{\partial_r^2}{2m} + \frac{1}{2}\gamma(r-R)^2 \quad \text{and} \quad \hat{T} = -\frac{\partial_R^2}{2M}\ , \qquad (4)$$

such that $\hat{H} = \hat{H}_0 + \hat{T}$. The instantanous eigenvalue problem $\hat{H}_0\phi_n(r-R) = \varepsilon_n\phi_n(r-R)$

is a simple harmonic oscillator problem with $\varepsilon_n = \omega(n + 1/2)$, $\omega = \sqrt{\gamma/m}$, and the exact expressions for the wavefuntion ϕ_n are known. [1]
The full eigenvalue problem is given by $E\Psi = (\hat{H}_0+\hat{T})\Psi$. By expressing the wavefunction in the basis of the instantaneous eigvenvectors, $\Psi(r, R) = \sum_{n=0}^{\infty} \varphi_n(R)\phi_n(r - R)$, show that the coefficients satisfy

$$E\varphi_l = \varepsilon_l\varphi_l - \frac{1}{2M}\partial_R^2\varphi_l - \frac{1}{M}\sum_{n=0}^{\infty}\langle\phi_l|\partial_R\phi_n\rangle\partial_R\varphi_n - \frac{1}{2M}\sum_{n=0}^{\infty}\langle\phi_l|\partial_R^2\phi_n\rangle\varphi_n, \tag{5}$$

where the Dirac notation implies the usual inner product, $\langle\phi_l|\phi_n\rangle = \int dr\, \phi_l^*\phi_n$.
Show that the Fourier component of $\varphi_l(R)$ satisfy

$$E\varphi_{ql} = \varepsilon_l\varphi_{ql} + \frac{q^2}{2M}\varphi_{ql} - \frac{iq}{M}\sum_n\langle\phi_l|\partial_R\phi_n\rangle\varphi_{qn} - \frac{1}{2M}\sum_n\langle\phi_l|\partial_R^2\phi_n\rangle\varphi_{qn}, \tag{6}$$

where $\varphi_n(R) = \int\frac{dq}{2\pi}\,\varphi_{qn}e^{iqR}$.

[1] Note: ε_n for the instantaneous problem here does not depend on R, in contrast with that of the lecture notes. There are some parallel features between the problem here and the formulation in the lecture notes, but they are not identical.

b) Equation (6) can be expressed in a matrix form using the infinite dimensional vector $\vec{\varphi}_q = (\varphi_{q0}, \varphi_{q1}, \cdots)^T$ as

$$E\vec{\varphi}_q = \begin{pmatrix} \varepsilon_0 & & & \\ & \varepsilon_1 & & \\ & & \varepsilon_2 & \\ & & & \ddots \end{pmatrix}\vec{\varphi}_q + V_q\vec{\varphi}_q\ , \tag{7}$$

where the matrix V_q has elements $(V_q)_{ln} = \frac{q^2}{2M}\delta_{ln} + \frac{iq}{M}\langle\phi_l|\partial_r\phi_n\rangle - \frac{1}{2M}\langle\phi_l|\partial_r^2\phi_n\rangle$, and δ_{ln} is the Kronecker delta.
Show that the matrix elements are explicitly given by

$$\begin{aligned}(V_q)_{ln} = {} & \frac{q^2}{2M}\delta_{ln} - \frac{iq}{M}\sqrt{\frac{m\omega}{2}}\left(\delta_{l,n+1}\sqrt{n+1} - \delta_{l,n-1}\sqrt{n}\right) \\ & - \frac{m\omega}{4M}\left[\delta_{l,n+2}\sqrt{(n+1)(n+2)} - \delta_{ln}(2n+1) + \delta_{l,n-2}\sqrt{n(n-1)}\right]\ .\end{aligned} \tag{8}$$

Hint 1: The operator $-i\partial_r$ can be viewed as a momentum operator, which can be written in terms of the ladder operators $\hat{a}^\dagger$ and $\hat{a}$ as $\hat{p} = i\sqrt{\frac{m\omega}{2}}(\hat{a}^\dagger - \hat{a})$.
Hint 2: The action of the ladder operators is $\hat{a}^\dagger|\phi_n\rangle = \sqrt{n+1}\,|\phi_{n+1}\rangle$ and $\hat{a}|\phi_n\rangle = \sqrt{n}\,|\phi_{n-1}\rangle$.

c) We can now compute the eigenvalue E perturbatively by viewing V_q as the perturbation. To second order, the correction from V_q on the eigenvalue ε_n is given by

$$E_n \approx \varepsilon_n + (V_q)_{nn} + \sum_{l\neq n}\frac{(V_q)_{nl}(V_q)_{ln}}{\varepsilon_n - \varepsilon_l}\ . \tag{9}$$

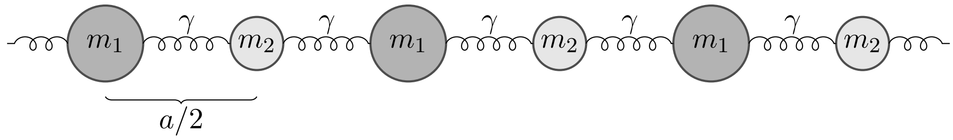
Show that this yields

$$E_n \approx \left(1 - \frac{m}{M}\right)\frac{q^2}{2M} + \left(1 + \frac{1}{2}\frac{m}{M} - \frac{1}{8}\frac{m^2}{M^2}\right)\left(n + \frac{1}{2}\right)\omega\ . \tag{10}$$

Moreover, use a Taylor expansion for $m/M \ll 1$ to show that the exact result is indeed identical to the perturbative Born-Oppenheimer result in Eq. (10). This demonstrates an explicit application of the Born-Oppenheimer approximation, whose full power is even more appreciated when the problem at hand does not have any exact solution.

2. Diatomic Chain

Consider an infinite diatomic chain as shown in the figure below. It is given by a one-dimensional chain of alternating masses m_1 and m_2 connected by springs with spring constant γ. In equilibrium, they are equally separated by a distance of $a/2$.



a) What is the primitive unit cell in the cases $m_1 \neq m_2$ and $m_1 = m_2$, respectively? What is the volume of the unit cell V_{UC} and what is the volume of the 1$^{\mathrm{st}}$ Brillouin zone in both cases? How many phonon branches do you expect in the two cases?

In the following, we choose a Bravais lattice whose lattice points coincide with the equilibrium positions, $x_{j,1}^{(0)} = ja$, of the atoms with mass m_1 and a unit cell with two atoms.
The Hamiltonian of the chain reads

$$H = \sum_{j=-\infty}^{\infty} \left[\frac{p_{j,1}^2}{2m_1} + \frac{p_{j,2}^2}{2m_2} + V_j(\{x_{m,\mu}\}) \right] \tag{11}$$

where the index j labels the unit cell and $p_{j,1}$ and $p_{j,2}$ are the momenta and $x_{j,1}$ and $x_{j,2}$ are the positions of the atoms with masses m_1 and m_2, respectively. Note that in contrast to the lecture, we are not using atomic units! In the harmonic approximation, the effective potential is given by

$$V_j(\{x_{m,\mu}\}) = \frac{\gamma}{2}\left((\delta x_{j,2} - \delta x_{j,1})^2 + (\delta x_{j-1,2} - \delta x_{j,1})^2\right) , \tag{12}$$

where $\delta x_{j,1} = x_{j,1} - x_{j,1}^{(0)}$ and $\delta x_{j,2} = x_{j,2} - x_{j,2}^{(0)}$ are the deviations from the equilibrium positions $x_{j,1}^{(0)}$ and $x_{j,2}^{(0)}$ of the two atoms with mass m_1 and m_2, respectively, within the j^{th} unit cell.

b) Use the transformations

$$\delta x_{j,\mu} = \sqrt{a} \int_{-\pi/a}^{\pi/a} \frac{dk}{2\pi} \frac{1}{\sqrt{m_\mu}} e^{ikx_{j,1}^{(0)}} q_\mu(k) \quad \text{and} \quad p_{j,\mu} = \sqrt{a} \int_{-\pi/a}^{\pi/a} \frac{dk}{2\pi} \sqrt{m_\mu} e^{-ikx_{j,1}^{(0)}} p_\mu(k) \,. \tag{13}$$

to show that the Hamiltonian can be put into the form

$$H = \int_{-\pi/a}^{\pi/a} \frac{dk}{2\pi} \frac{1}{2} \left[\sum_\mu p_\mu(k) p_\mu(-k) + \sum_{\mu,\nu} q_\mu(k) \tilde{D}_{\mu,\nu}(k) q_\nu(-k) \right] . \tag{14}$$

with the hermitian matrix

$$\tilde{D}(k) = 2\gamma \begin{pmatrix} \frac{1}{m_1} & -\frac{1}{\sqrt{m_1 m_2}} e^{ika/2} \cos\frac{ka}{2} \\ -\frac{1}{\sqrt{m_1 m_2}} e^{-ika/2} \cos\frac{ka}{2} & \frac{1}{m_2} \end{pmatrix} . \tag{15}$$

c) Determine the positive eigenvalues $d_n(k)$ with $n = 1, 2$ of the matrix $\tilde{D}(k)$, Eq. (15), from which follow the phonon dispersions $\omega_n(k) = \sqrt{d_n(k)}$. Identify which n belongs to the acoustic and optical branch. Calculate the sound velocity.

d) Sketch the dispersion relations $\omega_n(k)$ for the general case $m_1 \neq m_2$ for momenta within the first Brillouin zone ($k \in (-\frac{\pi}{a}, \frac{\pi}{a})$). The use of computer programs such as *Mathematica* or *Python* is explicitly recommended to generate a set of plots with various values for m_1/m_2. Discuss the limit $m_1 = m_2$. How is the result related to question 1(a)?

e) Consider the adiabatic limit $m_1 \gg m_2$. Show that in leading order in m_2/m_1, the masses m_1 and m_2 behave as independent oscillators with frequencies $\omega_1 \approx \omega_{01} |\sin(ak/2)|$ and $\omega_2 \approx \omega_{02}$, respectively. Here, $\omega_{0\mu} = \sqrt{2\gamma/m_\mu}$.

f) Consider oscillations for $m_1 > m_2$ at the edge of the Brillouin zone, i.e., with wavevectors $k = \pm\pi/a$. Using the eigenvectors of the dynamical matrix $\tilde{D}$, show that for the acoustic branch the masses m_2 remain immobile and the masses m_1 of adjacent unit cells oscillate in anti-phase, and vice versa for the optical branch.

g) *(not graded) Use a computer program, e.g., Mathematica or Python, to visualize the dynamics of the chain with tunable control parameters m_1, m_2, γ, and k.*