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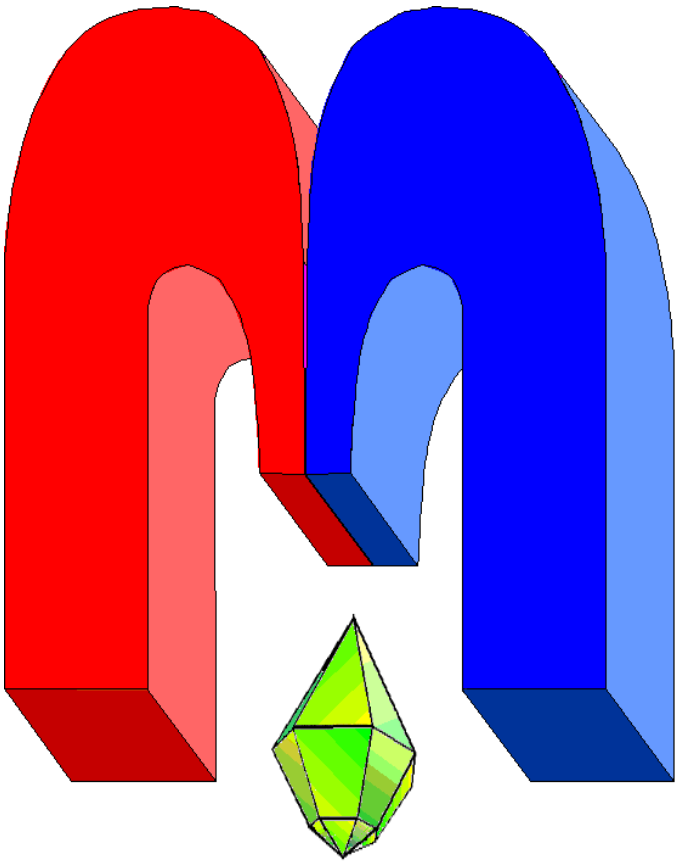

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‡ Dedicated to Professor Boris Z. Malkin on the occasion of his 85th birthday

Small polaron in linear atomic chain: perturbation theory approach†

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Using the stationary perturbation theory the equations for small polaron energies are obtained. This polaron has small spatial dimensions - only three equal atoms of a linear chain. The initial Hamiltonian has the contributions related to electron hoppings between the atoms, interaction of electron of the central atom with its oscillations and anharmonic contributions to the energy of its oscillations of the third and the fourth orders. The obtained analytical expressions give evidence that the polaron states with the fully filled (or significantly filled) atomic orbitals have the lowest energies that is in agreement with the results of numerical calculations available in the literature.

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1. Introduction

A linear chain of atoms with significant interaction of electron hoppings between neighboring atoms with vibrational degrees of freedom is a traditional model of polaron states [1, 2]. Often the studies of the properties of these polaron states are carried out using numerical methods, (see, e.g. [3]).

We will consider the problem by using the simplest model of a linear chain of identical atoms with linear interaction between electron hoppings of atoms and their vibrations to solve the problem of the energy spectrum of polaron states in an analytical form using stationary perturbation theory. In order to subsequently compare the obtained results, we used the Hamiltonian close or similar to that used in [3]. Bearing in mind the nature of small polaron, we will consider the three neighboring atoms $(n-1, n, n+1)$, where only n-th of these oscillates. The fact is that a monoatomic linear chain of atoms has the most short wavelength oscillations with the wavelength $\lambda_{\min} = 2a$, where a is the distance between the nearest atoms in the chain, for which corresponds the wave vector $q = \pi/a$ and the maximum frequency $\omega_{\text{osc}} = \omega_{\max} = 2\sqrt{\beta/\mu}$, where β is the elastic constant and μ is the mass of the atom participating in this oscillation. The central atom moves in antiphase with its nearest neighbors $n-1$ and $n+1$, that qualitatively corresponds to the oscillation of only the atom n. The group velocity $V_{\text{gr}} = a\sqrt{\beta/\mu}|\cos(qa/2)| = 0$ for oscillation with the wavelength $\lambda_{\min} = 2a$ and the wave vector $q = \pi/a$ with which the oscillation energy is transferred, is equal to zero [4].

2. Calculation details and results

For the purpose of the simplest comparison of our results we will use the Hamiltonian similar to [3]:

$$\hat{H} = \hat{H}^0 + \hat{H}^{\text{int}}, \tag{1}$$

†This paper is dedicated to Professor Boris Z. Malkin, who made a significant contribution to the field of magnetic radio spectroscopy in Kazan University, on the occasion of his 85th birthday.

where

$$\hat{H}^0 = \hat{H}^0_{\rm el} + \hat{H}^0_{\rm osc}, \qquad \hat{H}^{int} = \hat{H}^{int}_{\rm el-el} + \hat{H}^{int}_{\rm el-osc}. \tag{2}$$

$$\hat{H}^0_{\rm el} = \hbar\omega_{\rm el}\left(a^+_{n-1}a_{n-1} + a^+_n a_n + a^+_{n+1}a_{n+1}\right), \tag{3}$$

where a^+_n and a_n are the creation and annihilation operators of electron in atom n, respectively. We introduce the wave functions of electron in representation of electron filling factor $|1_k\}$ and $|0_k\}$ existing or absent on atom k, respectively. Here, for the electronic functions we will use the special brackets $|1_k\}$ and $|0_k\}$ in contrast to oscillation wave functions $|m_n\rangle$. At that $a^+_k|1_k\} = 0$, $a^+_k|0_k\} = |1_k\}$, $a_k|1_k\} = |0_k\}$, $a_k|0_k\} = 0$, $a^+_k a_k|1_k\} = |1_k\}$, and $a^+_k a_k|0_k\} = 0$ for $k = n-1,n,n+1$.

$$\hat{H}^0_{\rm osc} = \hbar\omega_{\rm osc}\left(b^+_n b_n + \frac{1}{2}\right), \tag{4}$$

where b^+_n and b_n are the creation and annihilation operators of oscillation quantum for atom n. The oscillator wave functions in the representation of filling factors $|m_n\rangle$ are subject to action of operators b^+_n and b_n, and satisfy the standard relations: $b_n|m_n\rangle = \sqrt{m_n}|m_n - 1\rangle$, $b^+_n|m_n\rangle = \sqrt{m_n+1}|m_n+1\rangle$, and $b^+_n b_n|m_n\rangle = m_n|m_n\rangle$ and

$$\hat{H}^0_{\rm osc}|m_n\rangle = \hbar\omega_{\rm osc}\left(m_n + \frac{1}{2}\right)|m_n\rangle. \tag{5}$$

The oscillator coordinate - the displacement x_n of atom n from the equilibrium position is related to b^+_n and b_n as

$$x_n = l\left(b^+_n + b_n\right), \tag{6}$$

where

$$l = \sqrt{\frac{\hbar}{\mu\omega_{\rm osc}}}. \tag{7}$$

The electron hopping Hamiltonian is

$$\hat{H}^{\rm int}_{\rm el-el} = -J\left(a^+_n a_{n+1} + a^+_n a_{n-1} + a^+_{n+1}a_n + a^+_{n-1}a_n\right), \tag{8}$$

and the electron-oscillation interaction Hamiltonian has the following form

$$\hat{H}^{\rm int}_{\rm el-osc} = -\chi l\, a^+_n a_n\left(b^+_n + b_n\right). \tag{9}$$

Since the anharmonic contributions to the oscillation energy of atom n in the chain affect the energy structure of the polaron states and in order to reduce the number of independent parameters of the model we introduce, following [3], the unique single-atomic Morse potential

$$V(x_n) = V_0\left[exp(-\alpha x_n) - 1\right]^2, \tag{10}$$

and its expansion to the anharmonic contributions of the 4-th order has the form

$$V(x_n) = V_0\left(\alpha^2 x_n^2 - \alpha^3 x_n^3 + K\alpha^4 x_n^4\right). \tag{11}$$

where $K = 7/12$. The quadratic contribution to $V(x_n)$ in (4) is related to oscillation frequency of atom n as

$$V_0\alpha^2 = \frac{\mu\omega^2_{\rm osc}}{2}. \tag{12}$$

Table 1. The matrix of operator $\hat{H}^{\rm int}_{el-el}$ constructed on the products of electron functions $|p_{n-1}\}|q_n\}|r_{n+1}\} \equiv |pqr\}$. The table columns have the same order as for the rows. Zero matrix elements are leaved blank.

	$\|000\}$	$\|100\}$	$\|010\}$	$\|001\}$	$\|011\}$	$\|101\}$	$\|110\}$	$\|111\}$
$\{000\|$								
$\{100\|$			$-J$					
$\{010\|$		$-J$		$-J$				
$\{001\|$			$-J$					
$\{011\|$						$-J$		
$\{101\|$					$-J$		$-J$	
$\{110\|$						$-J$		
$\{111\|$								

Table 2. The matrix of operator $\hat{W}(x_n)$ constructed on the functions that diagonalize the matrix of operator $\hat{H}_{\rm el-el}$. Here $V = V_{\rm anh}(x_n)$. The abbreviations for these functions are as follows: $\Psi_1 = |000\}$, $\Psi_2 = \frac{1}{\sqrt{2}}(|100\} - |001\})$, $\Psi_3 = \frac{1}{2}\left(|100\} + \sqrt{2}|010\} + |001\}\right)$, $\Psi_4 = \frac{1}{2}\left(|100\} - \sqrt{2}|010\} + |001\}\right)$, $\Psi_5 = \frac{1}{\sqrt{2}}(|011\} - |110\})$, $\Psi_6 = \frac{1}{2}\left(|011\} + \sqrt{2}|101\} + |110\}\right)$, $\Psi_7 = \frac{1}{2}\left(|011\} - \sqrt{2}|101\} + |110\}\right)$, $\Psi_8 = |111\}$. Zero matrix elements are leaved blank.

	Ψ_1	Ψ_2	Ψ_3	Ψ_4	Ψ_5	Ψ_6	Ψ_7	Ψ_8
Ψ_1	V							
Ψ_2		V						
Ψ_3			$V - J\sqrt{2}$ $-\frac{1}{2}\chi x_n$	$+\frac{1}{2}\chi x_n$				
Ψ_4			$\frac{1}{2}\chi x_n$	$V + J\sqrt{2}$ $-\frac{1}{2}\chi x_n$				
Ψ_5					$V - \chi x_n$			
Ψ_6						$V - J\sqrt{2}$ $-\frac{1}{2}\chi x_n$	$-\frac{1}{2}\chi x_n$	
Ψ_7						$-\frac{1}{2}\chi x_n$	$V + J\sqrt{2}$ $-\frac{1}{2}\chi x_n$	
Ψ_8								$V - \chi x_n$

The anharmonic contribution in $V(x_n)$ has the form

$$V_{anh}(x_n) = V_0\left(-\alpha^3 x_n^3 + K\alpha^4 x_n^4\right). \tag{13}$$

To solve the problem of energy levels of small polaron according to the perturbation theory for the degenerate levels [5] we first diagonalize the matrix of operator $\hat{H}^{\rm int}_{el-el}$ constructed on the products of electron functions $|p_{n-1}\}|q_n\}|r_{n+1}\} \equiv |pqr\}$ where $\{p;q;r\} = \{0;1\}$ (see Table 1).

Using the wave functions that diagonalize the matrix (Table 1) we construct the matrix of operator

$$\hat{W} = \hat{H}^{\rm int} + V_{\rm anh}(x_n), \tag{14}$$

see Table 2. The twofold degenerate matrix eigenvalues $\varepsilon_{I,II,III,IV}$ have the form

$$\varepsilon_{I,II} = V_{\text{anh}}(x_n) - \chi x_n + JG_{+,-}, \tag{15}$$

$$\varepsilon_{III} = V_{\text{anh}}(x_n) - \chi x_n; \qquad \varepsilon_{IV} = V_{\text{anh}}(x_n), \tag{16}$$

where

$$G_{+,-} = \frac{1}{2J}\left(\chi x_n \pm \sqrt{(\chi x_n)^2 + 8J^2}\right), \tag{17}$$

and the eigenfunctions have the form

$$\Psi_{\varepsilon Ia} = \frac{1}{\sqrt{2+G_-^2}}\left(|100\} + G_-|010\} + |001\}\right), \tag{18}$$

$$\Psi_{\varepsilon IIa} = \frac{1}{\sqrt{2+G_+^2}}\left(|100\} + G_+|010\} + |001\}\right), \tag{19}$$

$$\Psi_{\varepsilon IIIa} = |111\}, \tag{20}$$

$$\Psi_{\varepsilon IVa} = \frac{1}{\sqrt{2}}\left(|100\} - |001\}\right), \tag{21}$$

$$\Psi_{\varepsilon Ib} = \frac{1}{\sqrt{2+G_+^2}}\left(|011\} - G_+|101\} + |110\}\right), \tag{22}$$

$$\Psi_{\varepsilon IIb} = \frac{1}{\sqrt{2+G_-^2}}\left(|011\} - G_-|101\} + |100\}\right), \tag{23}$$

$$\Psi_{\varepsilon IIIb} = \frac{1}{\sqrt{2}}\left(|011\} - |110\}\right), \tag{24}$$

$$\Psi_{\varepsilon IVb} = |000\}. \tag{25}$$

Now we consider the x_n dependent contributions to ε_I, ε_{II}, ε_{III}, ε_{IV} as perturbations and obtain the corrections to the energy of the oscillator vacuum state in the first and second order of stationary perturbation theory.

For this purpose we present these expansions with accuracy up to $\chi^4 x_n^4$:

$$\varepsilon_{I,II} = V_{\text{anh}}(x_n) - \frac{1}{2}\chi x_n \pm J\sqrt{2}\left[1 + \frac{1}{2^4}\left(\frac{\chi}{J}\right)^2 x_n^2 - \frac{1}{2^9}\left(\frac{\chi}{J}\right)^4 x_n^4\right], \tag{26}$$

and obtain

$$\begin{aligned} E_{I,II} = {} & \frac{3}{4}V_0 K\alpha^4\langle 0|x_n^4|0\rangle \pm J\sqrt{2}\left[1 + \frac{1}{2^4}\left(\frac{\chi}{J}\right)^2\langle 0|x_n^2|0\rangle - \frac{1}{2^9}\left(\frac{\chi}{J}\right)^4\langle 0|x_n^4|0\rangle\right] \\ & -\frac{1}{\hbar\omega_{\text{osc}}}\left[\left|\langle 0|\frac{1}{2}\chi x_n + V_0\alpha^3 x_n^3|1\rangle\right|^2 + \frac{1}{3}\left|\langle 0|\frac{1}{2}\chi x_n + V_0\alpha^3 x_n^3|3\rangle\right|^2\right. \\ & +\frac{1}{2}\left|\langle 0|KV_0\alpha^4 x_n^4 + J\sqrt{2}\left[\frac{1}{2^4}\left(\frac{\chi}{J}\right)^2 x_n^2 - \frac{1}{2^9}\left(\frac{\chi}{J}\right)^4 x_n^4\right]|2\rangle\right|^2 \\ & \left. + \frac{1}{4}\left|\langle 0|KV_0\alpha^4 x_n^4 + J\sqrt{2}\left[\frac{1}{2^4}\left(\frac{\chi}{J}\right)^2 x_n^2 - \frac{1}{2^9}\left(\frac{\chi}{J}\right)^4 x_n^4\right]|4\rangle\right|^2\right], \end{aligned} \tag{27}$$

$$E_{III} = \frac{3}{4}V_0 K\alpha^4\langle 0|x_n^4|0\rangle - \frac{1}{\hbar\omega_{\rm osc}}\left[\left|\langle 0|\chi x_n + V_0\alpha^3 x_n^3|1\rangle\right|^2 + \frac{1}{3}\left|\langle 0|\chi x_n + V_0\alpha^3 x_n^3|3\rangle\right|^2 + \frac{1}{2}\left|\langle 0|KV_0\alpha^4 x_n^4|2\rangle\right|^2 + \frac{1}{4}\left|\langle 0|KV_0\alpha^4 x_n^4|4\rangle\right|^2\right], \tag{28}$$

$$E_{IV} = \frac{3}{4}V_0 K\alpha^4\langle 0|x_n^4|0\rangle - \frac{1}{\hbar\omega_{\rm osc}}\left[\left|\langle 0|V_0\alpha^3 x_n^3|1\rangle\right|^2 + \frac{1}{3}\left|\langle 0|V_0\alpha^3 x_n^3|3\rangle\right|^2 + \frac{1}{2}\left|\langle 0|KV_0\alpha^4 x_n^4|2\rangle\right|^2 + \frac{1}{4}\left|\langle 0|KV_0\alpha^4 x_n^4|4\rangle\right|^2\right], \tag{29}$$

written in terms of the matrix elements

$$\begin{gathered}\langle 0_n|x_n^2|0_n\rangle = \frac{1}{2}l^2, \quad \langle 0_n|x_n^4|0_n\rangle = \frac{3}{4}l^4 \quad \langle 0_n|x_n|1_n\rangle = \frac{1}{\sqrt{2}}l, \quad \langle 0_n|x_n^3|1_n\rangle = \frac{3}{2\sqrt{2}}l^3, \\ \langle 0_n|x_n^3|3_n\rangle = \frac{\sqrt{3}}{2}l^3, \quad \langle 0_n|x_n^2|2_n\rangle = \frac{1}{\sqrt{2}}l^2, \quad \langle 0_n|x_n^4|2_n\rangle = \frac{3}{\sqrt{2}}l^4, \quad \langle 0_n|x_n^4|4_n\rangle = \sqrt{\frac{1}{2}}l^4.\end{gathered} \tag{30}$$

The general contribution to the energies of all states and of only anharmonic origin is

$$\Delta E_{\rm anh} = \frac{3}{2^2}KV_0(\alpha l)^4 - \frac{V_0^2}{\hbar\omega_{\rm osc}}\left\{\frac{11}{2^3}(\alpha l)^6 + \frac{3\cdot 7}{2^3}K^2(\alpha l)^8\right\}, \tag{31}$$

and is subtracted from all polaron state energies

$$E_{I,II} - \Delta E_{\rm anh} = -\left(\Lambda_1 + \Lambda_2 + \Lambda_3\right) \pm \Lambda_4, \quad E_{III} - \Delta E_{\rm anh} = -\Lambda_5, \quad E_{IV} - \Delta E_{\rm anh} = 0, \tag{32}$$

where

$$\Lambda_1 = \frac{1}{\hbar\omega_{\rm osc}}\left[\frac{1}{2^3}\left(\chi l\right)^2 + \frac{3}{2^2}V_0\left(\alpha l\right)^3\left(\chi l\right)\right], \tag{33}$$

$$\Lambda_2 = \frac{J^2}{\hbar\omega_{\rm osc}}\left[\frac{1}{2^9}\left(\frac{\chi l}{J}\right)^4 - \frac{3}{2^{13}}\left(\frac{\chi l}{J}\right)^6 + \frac{3\cdot 7}{2^{20}}\left(\frac{\chi l}{J}\right)^8\right], \tag{34}$$

$$\Lambda_3 = \frac{J\sqrt{2}KV_0}{\hbar\omega_{\rm osc}}\left[\frac{3}{2^5}\left(\frac{\chi l}{J}\right)^2(\alpha l)^4 - \frac{3\cdot 7}{2^{11}}\left(\frac{\chi l}{J}\right)^4(\alpha l)^4\right], \tag{35}$$

$$\Lambda_4 = J\sqrt{2}\left[1 + \frac{1}{2^5}\left(\frac{\chi l}{J}\right)^2 - \frac{3}{2^8}\left(\frac{\chi l}{J}\right)^4\right], \tag{36}$$

$$\Lambda_5 = \frac{1}{\hbar\omega_{\rm osc}}\left[\frac{1}{2}\left(\chi l\right)^2 + \frac{3}{2}V_0\left(\alpha l\right)^3\left(\chi l\right)\right]. \tag{37}$$

3. Discussion and Summary

Use of the stationary perturbation theory allowed to obtain the expressions for the small polaron energies in the analytical form that contains all the parameters of the initial Hamiltonian. Since the Hamiltonian parameters may have, in general, arbitrary values, all expressions are given up to l^8, where l is the characteristic oscillation length. At the same time in the very rough approximation, when interaction of the electron with the oscillation of atom and the anharmonism of the third order are taken into account in the second perturbation order, in view of initially coincident signs of these contributions into the Hamiltonian, there appears

a strong dependence of polaron states *versus* the parameter χ, in agreement with numerical calculations [3]. All energy levels of polaron states appear twofold degenerate. For strong enough coupling constants χ the lowest energy levels appear to belong to the maximum possible filled atomic orbits.

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