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Cyclic-periodic ZRP structures. Scattering problem for generalized Bloch functions and conductivity

S. Leble

Immanuel Kant BFU, Al. Nevsky st.14, Kaliningrad, 236016, Russia

lebleu@mail.ru

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Problems of quantum description of nanostructures transport properties is investigated in a framework of the structure symmetry group. Corresponding states of conductivity electrons are defined as irreducible representations of the group. The right/left Bloch functions are written and the Floquet theorem is formulated. The results are used for formulating the zero range potential (ZRP) conditions for arbitrary orbital quantum number whose construction is presented via Darboux dressing chain built in a space of distributions. The electron spin variables are taken into account. A spectrum of the non-relativistic Hamiltonian with a system of a nanostructure ZRPs is found from the matrix eigenvalue problem. The scattering problem on an extra ZRP is formulated in terms of the right/left Bloch functions. As an example, the discrete spectrum and scattering on N-ZRP-centers is solved and compared with experimental data for benzene molecule.

Keywords: Nanostructures, zero-range potential, Bloch wave, scattering problem, charge transport.

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1. Introduction

1.1. General remarks

Problems of quantum description of nanostructures transport properties are directly connected with geometry of the object and corresponding electron states in a field of atomic systems. The conventional quantum mechanics of an electrons pure state is derived from the mathematical results of Floquet [1] from which grows the fundamental notion of the Bloch function. Thus, the quantum state is defined as an eigenfunction of commuting translational symmetric Hamiltonian and shift operators. It is well-known that the quantum mechanical description based on pure state cannot explain transport phenomenon because the discrete spectrum of energy does not allow to be accelerated in weak electric field. Only account of extra energy originated from atoms heat motion give such a possibility to move through a crystal. It means that we should apply quantum statistics method that allow to introduce a nano-object temperature and its impact on conductivity. Moreover, having a non-equilibrium system in external field we should go up to kinetic equations. As fundamental basis for such purposes, the Bogolubov chain equation is used, which, upon reduction, leads to either Boltzmann or Kolmogorov one-particle equations depending on the statement of the problem [2].

The zero-range potential (ZRP) method has proven to be an efficient tool in describing quantum structures with arbitrary geometry at sufficiently low energies (large de Broglie wavelength) such that detailed structure of atomic potential can be neglected [3–5]. Important understanding of its mathematical nature was found in theory of extensions [6, 7]. Speaking mainly either about one-dimensional spectral and scattering problems over the whole x-axis domain or half-axis r-domain for a radial Shrödinger equation, several interesting models demonstrate excellent results for many-particle systems.

This has been further developed into generalized zero-range potential (gZRP) method that takes into account effects of higher order partial waves in describing scattering properties [8–10]. Application of the regular ZRP method can be extended to describe not only small, typically atomic, structures but also larger molecular systems [12]. By definition, the method is focused on scattering problem, i.e. the continuous spectrum. For molecular systems, this also works well for discrete spectrum [5, 14]. The spectral properties for such extended systems as nanotubes demonstrate waveguide properties [13]. In the case of finite extended systems as wire crystals or nanotubes, one may use boundary or von Karman periodic conditions.

In our previous papers [14] and in the Master thesis of Ponomarev [Leble supervision], we studied stationary states of electron in the field of ZRPs that are positioned on a ring and cylinder surface in points that form a system with finite-group rotational symmetry with respect to the cylinder axis. We would mention here the important development of the theory with magnetic field account [15] and a development of computational techniques for complex ZRP systems with symmetry [16]. We also studied a scattering of a free electron on benzene-like ring systems of s-ZRP, comparing it with experiment.

In the present work, we develop these results, pose and solve a scattering problem of electrons in a tube Bloch states on a defect or a deformation potential that is modeled also by a ZRP. The main concept in such a problem is the *irreducible representation of the tube symmetry group*, formulated as a main theorem. Such functions form automatically an eigenset of complete set of commuting observables (Sec. 2.1). Both finite and infinite tubes electron spectrum are studied and compared. We introduce Hamiltonians with ZRPs eigenvalue problems for arbitrary angular momentum (orbital quantum number). In the next section (Sec 3) we reformulate the Darboux theorem that link ZRP with different values of the orbital quantum number and open a transition to nonzero range localized potentials. Further, the electron spin variable is taken into account in the same line of ZRP conditions. Next , in the Sec. 4 a normalization of the Bloch functions via electron flux is used to pose a scattering problem for such functions as a basis. The discrete and continuous spectra in a frame of scattering problem are studied for a degenerate case of N-ZRP-centers (Sec. 5). In this section, some calculations are presented for benzene molecule configuration that was compared with both experimental and calculated data.

1.2. Method of zero-range potentials

The idea of the ZRP method is to replace a real potential with potential presented by a distribution, placed at a given point that mimics the physical scattering behavior of the far zone. The behavior in the case of a point potential placed at the origin is conventionally studied via the radial Schrödinger equation at $r \in [0, \infty)$ for the free space ($r > 0$) [5]:

$$-\frac{d^2R}{dr^2} + \frac{2}{r}\frac{dR}{dr} + \frac{l\,(l+1)}{r^2}R = k^2R, \tag{1}$$

where $k^2 = \dfrac{2mE}{\hbar^2}$, k is the wave number, m, E are mass and energy of a particle (electron), respectively, $\hbar$ is Planck's constant, $R(r)$ is the radial part of the wave function.

It is well-known that the general solution can be formed as a linear combination of spherical Bessel and Neumann functions, $j_l(kr)$ and $y_l(kr)$, respectively:

$$R(r) = C_l\left(j_l(kr) - \tan\eta_l \cdot y_l(kr)\right), \tag{2}$$

with $s_l = \exp\left(2i\eta_l\right)$ being a scattering matrix.

Taking into account the following asymptotic behavior at $kr \to 0$:

$$j_l(kr) \approx \frac{(kr)^l}{(2l+1)!!}, \tag{3}$$

$$y_l(kr) \approx -\frac{(2l-1)!!}{(kr)^{l+1}}, \tag{4}$$

written with notion of the odd factorial $(2l+1)!! = (2l+1)\cdot(2l-1)\cdot\ldots\cdot 3\cdot 1$, $(-1)!! = 1$, we obtain asymptotic behavior of finite-energy solution at the origin:

$$R(r) \approx C_l \tan\eta_l \frac{(2l-1)!!}{(kr)^{l+1}}. \tag{5}$$

From the Eq. (2), the constant C_l can be expressed as:

$$C_l = \frac{(2l+1)!!}{k^l\,(2l+1)!}\,\frac{d^{2l+1}}{dr^{2l+1}}\left(r^{l+1}\psi\right)\bigg|_{r=0}. \tag{6}$$

Elimination of C_l from (6), and the equality corresponding to (5), yields:

$$\frac{1}{r^{l+1}\psi}\frac{d^{2l+1}}{dr^{2l+1}}\left(r^{l+1}\psi\right)\bigg|_{r=0} = \frac{(2l+1)!}{(2l+1)!!}\cdot\frac{1}{(2l-1)!!}\cdot\frac{k^{2l+1}}{\tan\eta_l}, \tag{7}$$

leads to the condition in the origin:

Proposition 1.1 (Zero range potential, l-ZRP). *The solution of Shrödinger equation with zero potential, that feeds the boundary condition:*

$$\frac{1}{r^{l+1}\psi}\frac{d^{2l+1}}{dr^{2l+1}}\left(r^{l+1}\psi\right)\bigg|_{r=0} = -\frac{2^l l!}{(2l-1)!!}1/a_l^{2l+1}, \tag{8}$$

with

$$a_l^{2l+1} = -\frac{\tan\eta_l}{k^{2l+1}} \tag{9}$$

results in the desired physical behavior of solution at a significant distance from the point-center.

Quantity a_l is termed as the partial wave scattering length and it is independent of particular energy value at low energies [5], see also (2) by which we conclude that

Proposition 1.2 (Scattering length)**.** *The scattering length* a_l *is defined by:*

$$\tan \eta_l \approx -\frac{A_2}{A_1\,(2l+1)!!\,(2l-1)!!} k^{2l+1},$$

that demonstrates the r.h.s. of (8) *energy independence.*

At low energies, it is often enough to consider the ZRP as a spherical point, thus neglecting higher partial waves. The solution to the (1) should be a subject to the simple boundary condition:

$$\left. \frac{d \log (r\psi)}{dr} \right|_{r=0} = -\beta, \tag{10}$$

where $\beta = 1/a_0$ is the s-wave inverse scattering length. Such ZRP we will mark as s-ZRP.

In the next section, we enhance the standard ZRP approach by means of application of a dressing procedure [10,20]. We notice and make use of the fact that a certain class of *Darboux transformations* DT of spherically symmetric ZRPs yields also a potential of zero range but, in general, with different effective characteristic (scattering length of the original ZRP is altered), including l-ZRP. Transformation parameters of a single atomic potential can be chosen based on solution of conventional bounded state problem solved for a system of ZRPs (molecule) such that resulting solution mimics the scattering behavior for the molecule as a whole.

2. Cylindrical tube with surface-centered point potentials

An interesting structure, related to mesoscopic physics, is the long tube with cross-sections periodically filled with point-centers forming symmetrical structures.

We focus on bounded state solutions for finite and an infinitely long tube made of plane N-fold symmetrical structures considered by means of unidirectional translation (Fig. 1). We also formulate a general approach to electron-impurity scattering of directed Bloch waves.

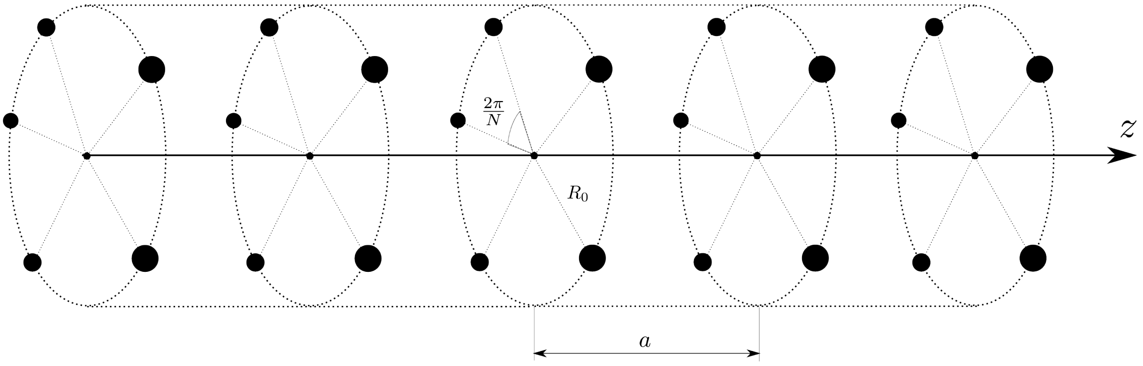

FIG. 1. The tube geometry

2.1. Bloch function

We start from general remarks, taking a spectral 3D problem based on stationary Shrödinger equation (SE):

$$\hat{H}\psi = E\psi. \tag{11}$$

Let $A \in G$ be a group of the point-centers set symmetry and the finite group $R_j \in G_c$ be a subgroup of rotations on angles $\theta_j = \frac{2\pi j}{N}$, $j = 0, ..., N-1$ in a plane, orthogonal to the z-axis. Let also the translations along z-axis be denoted as t_{na}, $n = 0, ..., M$ and form the cyclic group $t_{na} \in G_T$, hence the group elements are the pairs $A = (R_j, t_{na})$. The case of infinite group will be studied separately in Sec. 2.4. The particular case relates to the structure of Fig. 1 is described by the direct product:

$$G = G_c \star G_T, \tag{12}$$

therefore the sum by the group reads:

$$\sum_G = \sum_{G_c} \sum_{G_T} . \tag{13}$$

Let the group be represented by transformations in the position space $\vec{r} \in R^3$. It is straightforward to see that A is equivalent to the combined operations of a rotation:

$$R_j = \begin{pmatrix} \cos\theta_j & \sin\theta_j & 0 \\ -\sin\theta_j & \cos\theta_j & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{14}$$

and translation:

$$t_a \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} x \\ y \\ z+a \end{pmatrix} . \tag{15}$$

The representation of the elements A is written as:

$$A\vec{r} = R_j\vec{r} + t_a^n\vec{r} = \begin{pmatrix} \cos\theta_j x + \sin\theta_j y \\ -\sin\theta_j y + cos\theta_j \\ z + na \end{pmatrix} . \tag{16}$$

The transformations form an Abelian group, $R_j t_a = t_a R_j$.

The principal element of the construction is the function:

$$g_\pm(r_0, k) = \frac{e^{\pm ikr_0}}{r_0}, \tag{17}$$

where $\vec{r}_0 = \vec{r} - \vec{R}$, $\vec{R} = (0, -R, 0)$, that is a solution of the e.v. problem equation (11) with zero potential at $(r_0 = (\vec{r} - \vec{R}, \vec{r} - \vec{R})^{1/2} > 0)$, corresponding to the energy (Hamiltonian eigenvalue) $E = \dfrac{\hbar^2 k^2}{2m}$. Note that the origin is placed at symmetry axis of the centers positions (Fig. 1). The basic idea: it is convenient to define a class of solutions via summation by a group of symmetry.

Proposition 2.1. *The operator T_A defines the sum:*

$$\sum_{A \in G} C_A T_A g_\pm(r_0, k), \tag{18}$$

its action is given by:

$$T_A g_\pm(r_0, k) = g_\pm(r_A, k), \tag{19}$$

$$r_A = \sqrt{(\vec{R} - A\vec{r}, \vec{R} - A\vec{r})}.$$

The function (18) *is a solution of the SE* (11) *at $r_A > 0$.*

Let the irreducible representations of the symmetry group is denoted as $D^{\vec{\mu}}(A)$, where:

$$\vec{\mu} = \{\mu_1, \mu_2\}, \tag{20}$$

the integers, numerating irreducible representations run the values $j_1 = 0, ..., N-1; j_2 = 0, ..., M-1$. Hence, the following lemma holds:

Lemma 2.2 (Irreducible representations)**.** *The pair of functions, defined by:*

$$\phi_\pm^{\vec{\mu}} = C_\pm \sum_{A \in G} D^{\vec{\mu}}(A) T_A g_\pm(\vec{r}, k) \tag{21}$$

transforms as irreducible representation of G.

Proof: Action of the operator T_A yields:

$$T_B \phi_\pm^{\vec{\mu}}(\vec{r}, k) = A_\pm \sum_{A \in G} D^{\vec{\mu}}(A) T_B T_A g_\pm(\vec{r}, k) = D^{\vec{\mu}}(B^{-1}) \phi_\pm^{\vec{\mu}}, \tag{22}$$

we change the summation by A to summation by C as follows:

$$T_B T_A = T_{BA} = T_C, \quad A = B^{-1}C, \quad D^{\vec{\mu}}(A) = D^{\vec{\mu}}(B^{-1}C) = D^{\vec{\mu}}(B^{-1}) D^{\vec{\mu}}(C).$$

It is convenient to choose alternative parametrization of the group, using the cylindrical coordinate system ρ, ϕ, z, having in mind that all centers in a plane xy are lying on a circumference of a radii R. We also introduce a vector $\vec{p} = \{\phi, z\}$ in a ϕz plane, hence the rotations are equivalent to a shifts in ϕ, so:

$$T_A g_\pm \left(\rho, \phi, z,\, k\right) = g_\pm \left(\rho, \phi + \frac{2\pi j}{N}, z + na,\, k\right). \tag{23}$$

Moving to a realistic geometry of the tube and using periodic von Karman conditions we restrict the natural n variable change so as $|n| \leq M$, i.e. $g_\pm \left(\rho, \phi, z + Ma,\, k\right) = g_\pm \left(\rho, \phi, z,\, k\right)$. The group element, or the transformation is parametrized by the vector:

$$\vec{s} = \{s_1, s_2\} = \{\frac{2\pi j}{N}, na\}. \tag{24}$$

The transformation $A \in G$ is written as $A\vec{p} = \vec{p} + \vec{s}$. Next, we denote:

$$g_\pm \left(\rho, \phi, z,\, k\right) = g_\pm \left(\rho, \vec{p},\, k\right). \tag{25}$$

For the symmetry group is Abelian and subgroups are cyclic, the irreducible representations are one-dimensional. Conventionally choosing it as unitary, we write:

$$D^{\vec{\mu}}(A) = \exp[i(\vec{\mu}, \vec{s})], \tag{26}$$

the integers, numerating irreducible representations run the values $j_1 = 0, ..., N-1; j_2 = 0, ..., M-1$ as in (20):

$$\vec{\mu} = \{\mu_1, \mu_2\} = \{j_1, \frac{2\pi j_2}{aM}\}. \tag{27}$$

.

Corollary 2.3 (Bloch function)**.** *The functions* $\phi^{\vec{\mu}}_\pm$ (21) *are eigenvectors of the Hamilton operator* $\hat{H}$ *and symmetry transformations* T_B *operators.*

This statement is also valid for the subgroup of translation $B \in G_T$. We take the joint eigenfunctions (21) of the operators $\hat{H}$ as a definition of *"generalized Bloch function" (GBF).*

2.2. Floquet and Wigner theorems

The result leads directly to analog of Floquet theorem [1].

Theorem 2.4 (Floquet theorem)**.** *The function:*

$$\exp[i(\vec{\mu}, \vec{p})]\phi^{\mu}_\pm \left(\rho, \vec{p},\, k\right)$$

is invariant with respect to action:

$$T_A \exp[i(\vec{\mu}, \vec{p})]\phi^{\mu}_\pm \left(\rho, \vec{p},\, k\right) = \exp[i(\vec{\mu}, \vec{p})]\phi^{\mu}_\pm \left(\rho, \vec{p},\, k\right). \tag{28}$$

The **proof** follows directly from equality:

$$\begin{gathered} T_A \exp[i(\vec{\mu}, \vec{p})]\phi^{\vec{\mu}}_\pm \left(\rho, \vec{p},\, k\right) = \\ A_\pm \exp[i(\vec{\mu}, \vec{p} + \vec{s})] \sum_{B \in G} D^{\vec{\mu}}(B) T_A T_B g_\pm \left(\rho, \vec{p},\, k\right) = \\ \exp[i(\vec{\mu}, \vec{p} + \vec{s})] D^{\vec{\mu}}(A) \phi^{\vec{\mu}}_\pm \left(\vec{r},\, k\right) \end{gathered} \tag{29}$$

and the lemma 2.2.

The direct Wigner theorem application leads to the statement

Proposition 2.5 (Wigner theorem)**.** *The transition to the irreducible representation of symmetry transformations basis* $\phi^{\vec{\mu}}_\pm$ (21) *diagonalize the Hamilton operator* $\hat{H}$ *with natural numeration of energy levels by* $\vec{\mu}$*.*

The s-ZRP potential conditions for the Bloch functions (21):

$$\phi^{\vec{\mu}}_\pm = C_\pm \sum_{A \in G} \exp[i(\vec{\mu}, \vec{s})] T_A g_\pm \left(\vec{r},\, k\right) \tag{30}$$

are given by:

$$\left.\frac{\partial \left(\left|\vec{r} - A\vec{R}\right| \cdot \phi^{\vec{\mu}}_\pm\right)}{\partial \left|\vec{r} - A\vec{R}\right|}\right|_{\left|\vec{r} - A\vec{R}\right| = 0} = -\beta \left.\left(\left|\vec{r} - A\vec{R}\right| \phi^{\vec{\mu}}_\pm\right)\right|_{\left|\vec{r} - A\vec{R}\right| = 0}, \tag{31}$$

that for arbitrary $A \in G$ results in the eigenvalue, corresponding to the irreducible representation $\vec{\mu}$. Plugging the basic solution (35), transformed as:

$$T_A g_\pm \left(\vec{r} - \vec{R},\, k\right) = \frac{e^{\pm ikr_A}}{r_A}, \tag{32}$$

into (31) with real $\kappa_{\vec{\mu}}$: $k = i\kappa_{\vec{\mu}}$ in the limit $\left|\vec{r} - A\vec{R}\right| = r_A = 0$, calculation yields:

$$\begin{aligned}
&\left.\frac{\partial \left(r_A \sum'_{B\in G} \exp[i(\vec{\mu}, \vec{s}_B)] g_\pm \left(\vec{r} - B\vec{R},\, i\kappa_{\vec{\mu}}\right)\right)}{\partial r_A}\right|_{r_A=0} = \\
&\sum_{B\in G}{}' \exp[i(\vec{\mu}, \vec{s}_B)] g_\pm \left(\vec{r} - B\vec{R},\, k\right)\Big|_{r_A=0} - \kappa_{\vec{\mu}} \exp[i(\vec{\mu}, \vec{s}_B)] + \\
&r_A \left.\frac{\partial \left(\sum'_{B\in G} \exp[i(\vec{\mu}, \vec{s}_B)] g_\pm \left(\vec{r} - B\vec{R},\, i\kappa_{\vec{\mu}}\right)\right)}{\partial r_A}\right|_{r_A=0} = \\
&-\beta \left.\left(r_A \sum_{B\in G} \exp[i(\vec{\mu}, \vec{s}_B)] g_\pm \left(\vec{r} - B\vec{R},\, i\kappa_{\vec{\mu}}\right)\right)\right|_{r_A=0} .
\end{aligned} \tag{33}$$

The sum marked by "prime" $\sum'$ do not include the term A. Continuing to reach the limit, we change $\vec{r} = A\vec{R}$, arriving at:

$$\sum_{B\in G}{}' \exp[i(\vec{\mu}, \vec{s}_B)] g_+ \left(A\vec{R} - B\vec{R},\, i\kappa_{\vec{\mu}}\right) = (\kappa_{\vec{\mu}} - \beta) \exp[i(\vec{\mu}, \vec{s}_A)]. \tag{34}$$

Plugging the parameters s_B, and

$$g_+ \left(A\vec{R} - B\vec{R},\, -\kappa_{\vec{\mu}}\right) = \frac{e^{-\kappa_{\vec{\mu}} r_{AB}}}{r_{AB}}, \tag{35}$$

where the vector $A\vec{R} - B\vec{R} = (R_j - R_i)\vec{R} + (n - m)a\vec{e}_z$ and:

$$r_{AB} = \sqrt{(A\vec{R} - B\vec{R}, A\vec{R} - B\vec{R})}, \tag{36}$$

are the distances between atoms, arriving at equation for evaluation of $\kappa_{\vec{\mu}}$:

$$\sum_{B\in G}{}' \exp[i(\vec{\mu}, \vec{s}_B - \vec{s}_A)] \frac{e^{-\kappa_{\vec{\mu}} r_{AB}}}{r_{AB}} = \kappa_{\vec{\mu}} - \beta. \tag{37}$$

It is convenient to denote the group parameters as:

$$\vec{s}_A = \{s_{1A}, s_{2A}\} = \{\frac{2\pi j_A}{N}, n_A a\}. \tag{38}$$

.

Remark 2.6 (Sum by neighbors). This equation is the working formula for the discrete spectrum calculation. The exponent in the nominators decays at distances of closest neighbors, so we can account only such terms to estimate the result.

By the result of the Floquet theorem, denoting group invariants as:

$$\varphi_\pm^{\vec{\mu}} (\rho, \vec{p},\, k) = \exp[i(\vec{\mu}, \vec{p})] \phi_\pm^{\vec{\mu}} (\rho, \vec{p},\, k)\,, \tag{39}$$

we express the Bloch functions in terms of the group invariants as:

$$\phi_\pm^{\vec{\mu}} (\rho, \vec{p},\, k) = \exp[-i(\vec{\mu}, \vec{p})] \varphi_\pm^{\vec{\mu}} (\rho, \vec{p},\, k)\,, \tag{40}$$

or:

$$\begin{aligned}
\phi_\pm^{\vec{\mu}} (\rho, \vec{p},\, k) = \phi_\pm^{\vec{\mu}} = C_\pm \sum_{B\in G} \exp[i(\vec{\mu}, \vec{s})] T_B g_\pm (\vec{r},\, k) = \\
C_\pm \sum_{B\in G}{}' \exp[i(\vec{\mu}, \vec{s}_B)] T_B g_\pm (\vec{r},\, k) + C_\pm \exp[i(\vec{\mu}, \vec{s}_A)] T_A g_\pm (\vec{r},\, k) = \\
\exp[-i(\vec{\mu}, \vec{p})] \varphi_\pm^{\vec{\mu}} (\rho, \vec{p},\, k)\,.
\end{aligned} \tag{41}$$

2.3. On spectrum for finite tube

Plugging the vectors $\vec{\mu}$ (20) and $\vec{s}_A - \vec{s}_B$, one arrives at:

$$\sum_{B\in G}{}' \exp\Big[i\Big(j_1\frac{2\pi(j_A-j_B)}{N} + (n_A-n_B)\frac{2\pi j_2}{M}\Big)\Big]\frac{e^{-\kappa_{\vec{\mu}}r_{AB}}}{r_{AB}} = \kappa_{\vec{\mu}} - \beta. \tag{42}$$

The vector $A\vec{R} - B\vec{R} = (R_j - R_i)\vec{R} + (n-m)a\vec{e}_z$ in matrix form is written as:

$$(R_j - R_i)\vec{R} + (n-m)a\vec{e}_z = \begin{pmatrix} -R(\sin\theta_j - \sin\theta_i) \\ -R(\cos\theta_j - \cos\theta_i) \\ (n-m)a \end{pmatrix}, \tag{43}$$

and, hence:

$$r_{AB} = R\sqrt{2}\sqrt{1 - \cos(\theta_j - \theta_i) + \frac{(n-m)^2a^2}{2R^2}}. \tag{44}$$

Plugging $\theta_j = 2\pi\frac{j}{N}$ and $a = 2R\sin\frac{\pi}{N}$, we arrive at the expression, convenient for numeric solution of (42):

$$r_{AB} = R\sqrt{2}\sqrt{1 - \cos\Big(2\pi\frac{j-i}{N}\Big) + 2(n-m)^2\sin^2\frac{\pi}{N}}. \tag{45}$$

Recall that the label of an irreducible representation is $\{j_1, \frac{2\pi j_2}{aM}\}$ and by choosing the element A as unit, we formulate the proposition:

Proposition 2.7 (Discrete spectrum)**.** *The Hamiltonian of the multiatom ZRP system (Fig. 1), has the discrete spectrum, the eigenvalues of it are numerated by the irreducible representations numbers $j_{1,2}$ written as:*

$$E_{\vec{\mu}} = -\frac{\hbar^2\kappa_{\vec{\mu}}^2}{2m}, \qquad n = 0, \ldots, [M/2], \tag{46}$$

by treating transcendental equation with respect to $\kappa_{\vec{\mu}}$ (by means of numerical methods, e.g. the Newton–Raphson algorithm):

$$\sum_{j=0}^{N-1}\sum_{n=1}^{M} \exp\Big[-i\Big(j_1\frac{2\pi j}{N} + j_2\frac{2\pi n}{M}\Big)\Big]\frac{e^{-\kappa_{\vec{\mu}}r_{1B}}}{r_{1B}} = \kappa_{\vec{\mu}} - \beta, \tag{47}$$

where $r_{1B} = R\sqrt{2}\sqrt{1 - \cos(2\pi\frac{j}{N}) + 2n^2\sin^2\frac{\pi}{N}}$. The corresponding eigenfunctions are:

$$\phi^{\vec{\mu}} = C_{j_1j_2}\sum_{j=0}^{N-1}\sum_{n=1}^{M} \exp\Big[-i\Big(j_1\frac{2\pi j}{N} + j_2\frac{2\pi n}{M}\Big)\Big]\frac{e^{-\kappa_{\vec{\mu}}r_A}}{r_A}, \tag{48}$$

where $r_A = \Big|\vec{r} - R_j\vec{R} - na\vec{e}_z\Big|$, the constant $C_{j_1j_2}$ can be found from the normalization condition.

The spectrum is naturally discrete but the eigenvalues are collected in groups, that in a sense inherits the continuous spectrum of the Hamiltonian for infinite tube of the next section. It can be understood attending the Remark 2.6. Ground state $j_1 = j_2 = 0$ is non-degenerate:

$$\phi^{00} = C_{00}\sum_{j=0}^{N-1}\sum_{n=1}^{M}\frac{e^{-\kappa_{00}r_A}}{r_A}. \tag{49}$$

with energy determined via κ_{00} by the equation:

$$\sum_{j=0}^{N-1}\sum_{n=1}^{M}\frac{e^{-\kappa_{00}r_{1B}}}{r_{1B}} = \kappa_{00} - \beta. \tag{50}$$

Some alternative technique details of the spectrum calculations are described in [14] and for details see [29].

2.4. Infinite tube. Bands

Let us take the case of integer n, say $M = \infty$, then, using the Floquet theorem we write similar to (49) the complete set of bounded solutions:

$$\phi^{k,j_1} = C_0 \sum_{j=1}^{N} \sum_{n=-\infty}^{+\infty} \exp\Big[-i\Big(j_1 \frac{2\pi j}{N} + kna\Big)\Big] \frac{e^{-\kappa_{j_1} r_A}}{r_A}, \tag{51}$$

where $r_A = \left|\vec{r} - R_j\vec{R} - na\vec{e}_z\right|$, the constant C_0 can be found from the normalization condition for continuous spectrum. The first sum (index n) is carried over cross-section planes with centers while the second sum (index j) is over centers in a plane numerated, as before, from 1 to N, and positions of centers are:

$$\vec{R}_{nj} = R_j\vec{R} + na\vec{e}_z, \tag{52}$$

with $a\vec{e}_z$ being a shift vector corresponding to distances between the nearest cross-section planes with centers and $\vec{R}_j$ denoting positions of centers in a plane orthogonal to z-axis.

The corresponding energy $E_k^{(j_1)}$ can be found from the general equation (31) rewritten as (47), dividing the sum into two parts:

$$\sum_{j=1}^{N-1} \sum_{n=-\infty}^{'\infty} \exp\Big[-i\Big(j_1 \frac{2\pi j}{N} + kna\Big)\Big] \frac{e^{-\kappa_{\vec{\mu}} r_{1B}}}{r_{1B}} + \sum_{n=-\infty}^{'\infty} \exp[-ikna] \frac{e^{-\kappa_{j_1} 2nR\sin\frac{\pi}{N}}}{2nR\sin\frac{\pi}{N}} = \kappa_{j_1} - \beta, \tag{53}$$

where $r_{1B} = 2R\sqrt{\sin^2\left(\pi\frac{j}{N}\right) + n^2\sin^2\frac{\pi}{N}}$.

The series in the second term is summed up as follows ($\kappa_{j_1} = \kappa$):

$$\sum_{n=-\infty}^{\infty\prime} e^{ikna} \frac{e^{-\kappa|n|a}}{|n|\,a} = \sum_{n=1}^{+\infty} \frac{e^{-(\kappa-ik)na}}{ma} + \sum_{n=1}^{+\infty} \frac{e^{-(\kappa+ik)na}}{na}. \tag{54}$$

Denoting $\lambda_\pm = e^{-(\kappa\pm ik)a}$, we notice that $|\lambda_\pm| < 1$. This allows us to write:

$$\sum_{n=1}^{+\infty} \frac{\lambda^n}{n} = \sum_{n=1}^{+\infty} \int_0^{\lambda} \tilde{\lambda}^{n-1} d\tilde{\lambda} = \int_0^{\lambda} \underbrace{\sum_{n=0}^{\infty} \tilde{\lambda}^n}_{=\frac{1}{1-\tilde{\lambda}}} d\tilde{\lambda} = -\log(1-\lambda).$$

$$\begin{aligned} \sum_{m=-\infty}^{+\infty\prime} e^{ikma} \frac{e^{-\kappa|m|a}}{|m|\,a} &= -\frac{1}{a}\log\left[(1-\lambda_-)(1-\lambda_+)\right] = \\ &= -\frac{1}{a}\log\left[2e^{-\kappa a}(\cosh\kappa a - \cos ka)\right] = \\ &= -\frac{1}{a}\log\left[2(\cosh\kappa a - \cos ka)\right] + \kappa. \end{aligned}$$

The result of substitution leads to the theorem:

Proposition 2.8. *Given the irreducible representation j_1 of the group G_c and the infinite set of point potentials forming the tube along the symmetry group G, we state that the spectrum of energy is continuous, the dependence $E_k^{(j_1)}(k)$ for the j_1-th band state is found as solution of the transcendental equation:*

$$\sum_{j=1}^{N-1} \sum_{n=-\infty}^{'\infty} \exp\Big[-i\Big(j_1 \frac{2\pi j}{N} + kna\Big)\Big] \frac{e^{-\kappa_{j_1} r_{1B}}}{r_{1B}} + \Big(\beta - \frac{1}{a}\log\Big[2(\cosh\kappa_{j_1} a - \cos ka)\Big]\Big) = 0, \tag{55}$$

with respect to $\kappa_{j_1} = \sqrt{-\left(2m/\hbar^2\right)E_k^{(j_1)}}$.

3. Back to zero-range potentials for $l \neq 0$ and spin account

3.1. Darboux transformation and its application

Following mainly [14], consider one-dimensional Sturm–Liouville equation:

$$L\psi = \lambda\psi, \tag{56}$$

where:

$$L = -\frac{d^2}{dx^2} + u(x). \tag{57}$$

We apply algebraic-differential transformation, referred as Darboux transformation (DT):

$$D = \frac{d}{dx} - \sigma(x). \tag{58}$$

The following theorem takes place:

Theorem 3.1 (Darboux Theorem)**.** *The transformed equation preserve the same form and eigenvalue:*

$$L^{[1]}\psi^{[1]} = \lambda\psi^{[1]}, \tag{59}$$

where $\psi^{[1]} = D\psi$, $L^{[1]} = -\dfrac{d^2}{dx^2} + u^{[1]}(x)$ *and the transformed potential is:*

$$u^{[1]}(x) = u(x) - 2\sigma'(x). \tag{60}$$

where:

$$\sigma(x) = \frac{\Phi_1'}{\Phi_1} \tag{61}$$

with Φ_1 *being a particular solution to the original equation with* λ_1*:*

$$-\Phi_1'' + u(x)\Phi_1 = \lambda_1\Phi_1$$

.

In case of multiple application of the DT, the expression (61) is generalized into Crum formulas:

Theorem 3.2 (Crum observation)**.** *Let:*

$$\psi^{[N]} = D^{[N]}\psi = \frac{W(\Phi_1, \ldots, \Phi_N, \psi)}{W(\Phi_1, \ldots, \Phi_N)}, \tag{62}$$

where W *denote determinants of the Wronskian matrices. resulting in the following transformation of the potential:*

$$u^{[N]}(x) = u(x) - 2\frac{d^2}{dx^2}\Big[\log W(\Phi_1, \ldots, \Phi_N)\Big]. \tag{63}$$

We move towards the radial Schrödinger equation (1) and notice that it can be brought to the form (56) eligible for direct application of obtained transformation formulas. Namely, performing substitution $\psi = \chi/r$, one readily obtains:

$$-\chi'' + \frac{l\,(l+1)}{r^2}\chi = k^2\chi, \tag{64}$$

that contains only the centrifugal term originating from the orbital moment operator.

That is to say, having in mind to save zero potentials, that we can apply DT to equation (1), meaning that all original wave functions ψ should be multiplied by r, whereas the potential term

$$u(r) = \frac{l\,(l+1)}{r^2} \tag{65}$$

remains unchanged.

Thus, the formulas (62), (63) in spherical coordinates should be replaced with:

$$u^{[N]}(r) = u(r) - 2\frac{d^2}{dr^2}\Big[\log W(r\Phi_1, \ldots, r\Phi_N)\Big] \tag{66}$$

and:

$$\psi^{[N]} = D^{[N]}\psi = \frac{W(r\Phi_1, \ldots, r\Phi_N, r\psi)}{rW(r\Phi_1, \ldots, r\Phi_N)}. \tag{67}$$

Following an idea of the previous works [10,20], we first show how gZRP can be induced by application of DT.

We start by choosing a spherical Bessel function as the seed solution:

$$\psi_l(r) = Cj_l\left(kr\right) \tag{68}$$

and apply N-th order Darboux transformation taking spherical Hankel functions with specific parameters κ_m as prop functions:

$$\Phi_m(r) = Ch_l^{(1)}(-i\kappa_m r), \qquad m = 1, \ldots, N. \tag{69}$$

Note that we represent here and later on generic constant as C without prescribing any specific value, such that it can absorb constant multipliers (where their meaning is not important) without changing notation.

We can employ Crum's formula (62) and consider the asymptotic behavior of spherical functions at $r \to \infty$:

$$j_l(kr) \approx \frac{\sin\left(kr - l\pi/2\right)}{kr}, \tag{70}$$

$$y_l(kr) \approx -\frac{\cos\left(kr - l\pi/2\right)}{kr}, \tag{71}$$

$$h_l^{(1)}(kr) = j_l(kr) + iy_l(kr) \approx (-i)^{l+1}\,\frac{\exp\left(ikr\right)}{kr}, \tag{72}$$

$$h_l^{(2)}(kr) = j_l(kr) - iy_l(kr) \approx i^{l+1}\frac{\exp\left(-ikr\right)}{kr}. \tag{73}$$

Then, the Wronskians are transformed into Vandermonde determinants.

The asymptotic of the potential (66) and the solution (67) are expressed in terms of Vandermonde determinants:

$$\Delta\left(\kappa_1, \ldots, \kappa_N, ik\right) = \begin{vmatrix} 1 & \kappa_1 & \kappa_1^2 & \ldots & \kappa_1^N \\ 1 & \kappa_2 & \kappa_2 & \ldots & \kappa_2^N \\ \ldots & \ldots & \ldots & \ldots & \ldots \\ 1 & \kappa_N & \kappa_N^2 & \ldots & \kappa_N^N \\ 1 & ik & (ik)^2 & \ldots & (ik)^N \end{vmatrix} = C\prod_{m=1}^{N}\left(\kappa_m - ik\right).$$

$$\psi_l^{[N]}(r) = C\left[(-i)^l\,\frac{\exp\left(ikr\right)}{kr}\,\frac{\Delta\left(\kappa_1, \ldots, \kappa_N, ik\right)}{\Delta\left(\kappa_1, \ldots, \kappa_N\right)} - i^l\frac{\exp\left(-ikr\right)}{kr}\,\frac{\Delta\left(\kappa_1, \ldots, \kappa_N, -ik\right)}{\Delta\left(\kappa_1, \ldots, \kappa_N\right)}\right]. \tag{74}$$

Theorem 3.3 (ZRP by DT)**.** *Given a seed solution* (68) ***for arbitrary choice of*** N ***and parameters*** κ_m**,** $m = 1, \ldots, N$ *of prop functions* (69) *provides DT-invariance of the ZRP.*

This leads to the following:

Corollary 3.4 (s-states)**.** *For* $l = 0$*:*

$$\log W(r\Phi_1, \ldots, r\Phi_N) = \sum_{m=1}^{N}\kappa_m r + C,$$

according to ***dressed potential*** (66)*:*

$$u^{[N]}(r) \equiv 0, \qquad r > 0.$$

The scattering length is:

$$a_0 = \sum_{m=1}^{N}\kappa_m^{-1} = \beta^{-1}. \tag{75}$$

For arbitrary l, denoting:

$$s_l = \prod_{m=1}^{N}\frac{(\kappa_m - ik)}{(\kappa_m + ik)} = -\prod_{m=1}^{N}\frac{(k + i\kappa_m)}{(k - i\kappa_m)}, \tag{76}$$

we recognize in the expression (74) the asymptotes of spherical Hankel functions, hence:

$$\psi_l^{[N]}(r) = C\left[s_l h_l^{(1)}(kr) - h_l^{(2)}(kr)\right]. \tag{77}$$

The final expression (77), being alternative form of radial function coincides with (2) if:

Proposition 3.5 (S-matrix)**.**

$$s_l = \exp\left(2i\eta_l\right) = \prod_{m=1}^{N}\frac{(\kappa_m - ik)}{(\kappa_m + ik)}. \tag{78}$$

So, the DT technique reproduces the result of introduction obtained in a systematic way.

Now, alternatively to gZRP, instead of taking into account the impact of higher harmonics, we consider the transformation of spherically symmetric solution (i.e. $l = 0$) with the parameters κ_m to be chosen according to spectral data of the entire molecule obtained, for example, from the discrete spectrum of molecule modeled by regular ZRP method.

We return to:

$$a_l^{2l+1}k^{2l+1} = -i\frac{ik\sum_{n=1}^{N}\prod_{\substack{m=1\\ m\neq n}}^{N}\kappa_m + \ldots + (ik)^N}{\prod_{m=1}^{N}\kappa_m + \ldots + (ik)^{N-1}\sum_{n=1}^{N}\kappa_n}. \tag{79}$$

The conditions may be directly applied to the Bloch functions of the Sec. 2.1.

Freedom of choice of transformation parameters gives the possibility of inducing *desired poles of scattering matrix* (76) and, thereby, perform transition from atomic to molecular ZRP by choosing κ_m, $m = 1, \ldots, M$ such that the new potential allows M bounded states obtained by solving conventional formulation of the discrete spectrum problem for the set of M standard ZRPs making up the molecule. Molecular ZRP can be qualitatively characterized by *effective scattering length computed according to* (75) and thus used in such simplified scattering calculations in complicated problems involving, for example, a chain of molecules and give a model for conductivity.

3.2. Spin variable account

The Pauli equation for zero external field [24] is the equation for two-component spinor that is eigenvector of commuting operators M and M_z having in cylindrical coordinates the form:

$$\begin{gathered} M_z = -i\hbar\frac{\partial}{\partial\varphi} + \frac{\hbar}{2}\sigma_z, \\ M = \sigma_i M_i - \hbar/2, \end{gathered} \tag{80}$$

with eigenvalues $\hbar(m + \frac{1}{2})$, k'. The components ψ_i are expressed in terms of spherical functions as follows:

$$\begin{gathered} \frac{1}{\sin\theta}\frac{\partial Z}{\partial\phi} - \frac{\partial Z}{\partial\theta} = k'Y, \\ \frac{1}{\sin\theta}\frac{\partial Y}{\partial\phi} + \frac{\partial Y}{\partial\theta} = k'Z, \end{gathered} \tag{81}$$

so, that:

$$\begin{gathered} \psi_1 = f(r)Y, \\ \psi_2 = g(r)Z. \end{gathered} \tag{82}$$

The equations coincide with ones of Dirac theory (we use notations from [24]) in the nonrelativistic limit. A transition to real auxiliary functions is performed by:

$$\begin{gathered} f(r) = \frac{f_1 + if_2}{\sqrt{2}}, \\ g(r) = \frac{f_1 - if_2}{\sqrt{2}}. \end{gathered} \tag{83}$$

The radial functions f_i in nonrelativistic limit f_i^0, $|f_2| \ll |f_1|$, $f_1^0 = rR$ are defined by the equation that coincides by form with radial Shrödinger equation:

$$\frac{d^2R}{dr^2} + \frac{2}{r}\frac{dR}{dr} - \frac{k'(k'-1)}{r^2}R + \frac{2m}{\hbar^2}(E - U(r)) = 0, \tag{84}$$

where the quantum number k' is expressed in terms of the nonrelativistic quantum number l:

$$k'(k'-1) = l(l+1). \tag{85}$$

The minimal value of k' is $k' = 1$, that corresponds to $l = 0$, otherwise $k' = -l, l+1$. The system of equations for f_i^0:

$$\begin{gathered} -\frac{\hbar}{2mc}\left(\frac{df_1^0}{dr} - \frac{k'}{r}f_1^0\right) = f_2^0, \\ \frac{df_2^0}{dr} + \frac{k'}{r}f_2^0 = \frac{E-U}{2mc}f_1^0, \end{gathered} \tag{86}$$

leads to (84) for f_1^0, while the first of (86) reads as expression of f_2^0 via f_1^0. We can start from ZRP theory for (84), expressing the Pauli theory solutions (82) in nonrelativistic limit in terms of R as the solution of (84).

The general form of the solution is:

$$\begin{gathered} f_2^0 = -\frac{\hbar}{2mc}\Big(\frac{df_1^0}{dr} - \frac{k'}{r} f_1^0\Big), \\ f_1^0 = rR, \end{gathered} \tag{87}$$

while:

$$\begin{aligned} f(r) &= \frac{1}{\sqrt{2}}\Big(1 - i\frac{\hbar}{2mc}\Big(\frac{d}{dr} - \frac{k'}{r}\Big)\Big) rR = \frac{1}{\sqrt{2}}(1 - i\hat{a}) rR, \\ g(r) &= \frac{1}{\sqrt{2}}\Big(1 + i\frac{\hbar}{2mc}\Big(\frac{d}{dr} - \frac{k'}{r}\Big)\Big) rR = \frac{1}{\sqrt{2}}(1 + i\hat{a}) rR, \end{aligned} \tag{88}$$

where:

$$\hat{a} = \frac{\hbar}{2mc}\Big(\frac{d}{dr} - \frac{k'}{r}\Big) = \frac{\hbar}{2mc} r^{k'} \frac{d}{dr} r^{-k'}. \tag{89}$$

Next, such identity holds:

$$\begin{gathered} \begin{pmatrix} 1+i\hat{a} & 0 \\ 0 & 1-i\hat{a} \end{pmatrix} \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} = \begin{pmatrix} 1+i\hat{a} & 0 \\ 0 & 1-i\hat{a} \end{pmatrix} \begin{pmatrix} f(r)Y \\ g(r)Z \end{pmatrix} = \\ \begin{pmatrix} (1+\hat{a}^2)rRY \\ (1+\hat{a}^2)rRZ \end{pmatrix} = (1+\hat{a}^2)rR \begin{pmatrix} Y \\ Z \end{pmatrix}, \end{gathered} \tag{90}$$

where:

$$\hat{a}^2 = \frac{\hbar^2}{4m^2c^2} r^{k'} \frac{d^2}{dr^2} r^{-k'}. \tag{91}$$

The ZRP potential in this case is defined by asymptotic behavior of R (2) as in (4) and (5) within the algorithm shown in introduction, Eqs. (7–9). A constants $C_\pm$ in these cases are defined from:

$$\frac{1}{\sqrt{2}}(1 \pm i\hat{a}) rR(r) \approx C_\pm \frac{1}{\sqrt{2}}(1 \pm i\hat{a}) r \left(\frac{(kr)^l}{(2l+1)!!} - \frac{(2l-1)!!}{(kr)^{l+1}} \tan \eta_{l\pm} \right), \tag{92}$$

with $s_{l\pm} = \exp(2i\eta_{l\pm})$ being a scattering matrices (having in mind the link between k' and l). The sign "–" stands for f and "+" marks g. We designate next $f_+ = g$, $f_- = f$ for brevity. The leading singularity terms at $r \to 0$ are given by:

$$k^{l+1} r^{l+1} f_\pm|_{r=0} = \pm \frac{(2l-1)!!}{\sqrt{2}} C_\pm \tan \eta_{l\pm} \frac{\hbar}{2mc}(l + k'), \tag{93}$$

and:

$$C_\pm = \frac{\sqrt{2}\,(2l+1)!!}{k^l (2l+1)!} \frac{d^{2l+1}}{dr^{2l+1}} r^l f_\pm|_{r=0}. \tag{94}$$

Combining yields:

$$r^{l+1} f_\pm|_{r=0} = \pm \tan \eta_{l\pm} \frac{\hbar}{2mc}(l + k')\,(2l-1)!! \frac{(2l+1)!!}{k^{2l+1}(2l+1)!} \frac{d^{2l+1}}{dr^{2l+1}} r^l f_\pm|_{r=0}. \tag{95}$$

This gives the general ZRP conditions for the spinor wave function components taking into account the spin variable. The case of s-wave $l = 0, k' = 1$ leads to:

$$krf_\pm|_{r=0} = \pm \tan \eta_{0\pm} \frac{\hbar}{mc} \frac{d}{dr} f_\pm|_{r=0}. \tag{96}$$

Some alternative condition is formulated in [28].

4. Bloch wave scattering problem by a ZRP

4.1. Flux normalization

It is essential to note that for every allowed energy we will have two Bloch functions marked by the sign as index ±. Bloch functions for k and $-k$ will give us appropriate flux in opposite directions. We shall name such Bloch functions as "left" and "right". We consider the tube as quasi-one-dimensional structure; therefore, let us differentiate the basic solutions with respect to the variable z, which is the axis of symmetry:

$$\frac{\partial}{\partial z} g_\pm(r, k) = \Big(\pm ik - \frac{1}{r} \Big) \frac{z}{r} \frac{e^{\pm ikr}}{r}. \tag{97}$$

The flux component can be calculated by the definition:

$$j_z(\psi) = -i\frac{\hbar}{2m}\left(\psi^*\frac{d}{dz}\psi - \psi\frac{d}{dz}\psi^*\right). \tag{98}$$

Direct substitution (21) into (98) yields at $r \to \infty$:

$$j_z(\phi_\pm) = \pm 2A_\pm^* A_\pm \frac{\hbar k}{m}\sum_{A,B} D^{\vec{\mu}*}(A)D^{\vec{\mu}}(B)g_\pm^*\left(r_A,\, k\right)g_\pm\left(r_A,\, k\right). \tag{99}$$

Lemma 4.1 (Flux)**.** *Let the transverse to the tube axis plane be denoted as S. The flux through S along z is constant:*

$$\partial_z \int\limits_S j_z(\phi_\pm)dS = 0.$$

Proof: Differentiation of j_z by z and use the Hermicity of Δ_{tr} ($\Delta = \partial_z^2 + \Delta_{tr}$) yields the Statement of the Lemma.

A normalization of the left/right Bloch functions $\phi_\pm$ is defined via

Definition 4.2 (Normalization)**.** The normalization constants $A_\pm$ for the right and left Bloch waves are defined by the conditions for the stream:

$$\begin{gathered}\int\limits_S j_z(\phi_\pm)dS = \\ \pm|A_\pm|^2\frac{2\hbar k}{m}\sum_{A,B}\exp[i\vec{\mu}(\vec{s}_B - \vec{s}_A)]\int\limits_S g_\pm^*\left(r_B,\, k\right)g_\pm\left(r_A,\, k\right)dS = \pm 1,\end{gathered} \tag{100}$$

with (26) account.

4.2. Scattering problem for Bloch electron formulation

A scattering problem may be formulated by means of left and right Bloch waves:

$$\phi = \phi_+^{\vec{\mu}} + f_-\phi_-^{\vec{\mu}} = \sum_{a\in G} D^{\vec{\mu}}(a)T_a(g_+ + f_-g_-), \tag{101}$$

represents incoming and reflected wave at $z < 0$, while at $z > 0$ it is:

$$f_+\phi_+^{\mu}.$$

Let a ZRP scatterer is placed at $z = 0$. As an aim of future development, it is chosen as a defect of displacement (deformation potential) positioned at $\vec{r}_0$.

According to the idea of **ZRP method**, we write the solution to the scattering problem as:

$$\phi = \phi_+^{\mu} + f_-\phi_-^{\mu} = \sum_{a\in G} D^{\mu}(a)T_a(g_+ + fg_-), \tag{102}$$

subject to the conditions (10) at the appropriate point $\vec{R}_0$ with some other scattering length:

$$\left.\frac{\partial\log\left(\left|\vec{r} - \vec{R}_0\right|\cdot\phi(\vec{r})\right)}{\partial\left|\vec{r} - \vec{R}_0\right|}\right|_{\left|\vec{r}-\vec{R}_0\right|=0} = -\beta_0, \qquad i = 1,\,\ldots,\,M. \tag{103}$$

A one-dimensional scattering problem by ZRP for Dirac comb Bloch functions was considered in [17]. Condition of nonzero solution (zero determinant of the matrix of coefficients) gives the energy spectrum structure:

$$\cos(Ka) = \cos(ka) + \frac{m\beta}{\hbar^2}\frac{\sin(ka)}{k}. \tag{104}$$

Equation (99) is true for any x. Substitution of solution into (99) gives:

$$j(\psi_{\rightleftarrows}) = \frac{\hbar k}{m}|A_\pm|^2\frac{\pm\sin(Ka)\sin(ka)}{1 - \cos(\pm Ka + ka)}. \tag{105}$$

Next, equation (105) is used for flux normalization:

$$j(\psi_{\rightleftarrows}) = \pm 1. \tag{106}$$

Corollary 4.3 (Conduction)**.** *A conductivity of the tube with defects, modeled by s-ZRPs may be calculated directly on basis of the scattering amplitude* f_- *evaluated as a solution of* (103). *More complicated models with* $l \neq 0$ *account may be used within the prescribed algorithm.*

Below, we demonstrate the presented approach by applying it to a general cyclic molecule with eventual focus on a **benzene molecule**.

5. Case study: $M = 1$, a cyclic molecule

We here consider a molecular system as a degenerate case of the tube with $M = 1$ of N point-centers, typically atoms or groups, modeled by ZRPs which fixed positions in the xy-plane, see Fig. 1. Obviously, the group of symmetry in the plane is the cyclic $G_c = C_N$.

5.1. Bounded states problem

For discrete spectrum as in the Sec. 2.3 we chose a real κ, with the fundamental solution of the Schrödinger equation with zero potential:

$$g\,(r,\,\kappa) = \frac{e^{-\kappa r}}{r}. \tag{107}$$

According to the general idea, we write solution to the bounded state problem as subject to the particular case of conditions (31):

$$\sum_{B\in G_c}{}' \exp\left[i\mu\frac{2\pi(j_A - j_B)}{N}\right]\frac{e^{-\kappa_\mu r_{AB}}}{r_{AB}} = \kappa_\mu - \beta, \tag{108}$$

where $\mu = j_1 = 0, ..., N-1$ is an irreducible representation number. The distances between atoms are found from (45), after choice of A as unit element, that now simplifies as:

$$r_{IB} = 2R\sin\left(\frac{\pi j}{N}\right). \tag{109}$$

The equations then reads:

$$\sum_{j=0}^{N-1} \exp\left[-i\mu\frac{2\pi j}{N}\right]\frac{e^{-\kappa_\mu 2R\sin(\frac{\pi j}{N})}}{2R\sin(\frac{\pi j}{N})} = \kappa_\mu - \beta. \tag{110}$$

We note that the expression is formally valid for $\mu = 0, \ldots, N-1$, however we note that there is only $[N/2]$ different values κ_μ because equations differ only by the factors $\exp\left[-i\mu\frac{2\pi j}{N}\right]$, which coincides with $\exp\left[-i(N-\mu)\frac{2\pi j}{N}\right]$, where $[\cdot]$, here and subsequently, marks integer part of an argument (i.e. the floor function).

Theorem 5.1 (Bound states)**.** *The eigenvalue problem for n ZRP is equivalent to the algebraic system* (110). *Energy levels are numerated by an irreducible representation number, such that:*

$$E_\mu = -\frac{\hbar^2\kappa_\mu^2}{2m}, \qquad \mu = 0, \ldots, [N/2], \tag{111}$$

by treating transcendental equation with respect to κ_μ. *In case of even number of atoms N) the only non-degenerate eigenvalues are the ground state* $\mu = 0$*:*

$$\psi_0(\vec{r}) = C_0\sum_{j=0}^{N-1}\frac{e^{-\kappa_0 r_A}}{r_A}, \tag{112}$$

where $r_A = \left|\vec{r} - R_j\vec{R}\right|$ *and the state with the highest energy* $\mu = N/2$*:*

$$\psi_{N/2}(\vec{r}) = C_{M/2}\sum_{j=0}^{N-1}(-1)^j\frac{e^{-\kappa_{N/2} r_A}}{r_A}, \tag{113}$$

other states are doubly-degenerate:

$$\psi_\mu(\vec{r}) = C_\mu\sum_{j=0}^{N-1}\exp\left[-i\mu\frac{2\pi j}{N}\right]\frac{e^{-\kappa_\mu r_A}}{r_A}. \tag{114}$$

For odd number of atoms, the classification of states and levels is similar.

5.2. Continuous spectrum. Scattering problem

Let incident free particle fly axially on N-atom potential, centered in transverse xy plane symmetric structure as in previous section. A Schrödinger equation solution with energy $E = \dfrac{\hbar^2 k^2}{2\mu}$ is now taken as the superposition that accounts for the s-waves corresponding the identity irreducible representation:

$$\psi(\vec{r}) = e^{ikz} + \sum_{j=0}^{N-1} g\left(\left|\vec{r} - \vec{R}_j\right|, \, -ik\right), \tag{115}$$

at $r \to \infty$, the solution (115) tends to:

$$\psi(\vec{r}) = e^{ikz} + f(\theta, \, \phi)\frac{e^{ikr}}{r}. \tag{116}$$

Theorem 5.2 (Scattering amplitude). *Let the positions of the cyclic molecule atoms are determined as* $\vec{R}_j = R_j \vec{R}$. *The scattering amplitude at long distances in direction* $\vec{n} = \vec{r}/r = (\sin\theta\cos\phi, \, \sin\theta\sin\phi, \, \cos\theta)^T$ *is given by:*

$$f(\theta, \, \phi) = C_0 \sum_{j=0}^{N-1} e^{-ik\vec{n}\cdot\vec{R}_j}. \tag{117}$$

where

$$C_0 = \frac{-1}{\beta + ik + 2\sum_{j=1}^{(N+\chi_N)/2-1} g\left(r_j, \, -ik\right) + \chi_{N-1} \cdot g\left(r_{N/2}, \, -ik\right)}, \tag{118}$$

where $\chi_N = \dfrac{N/2 - [N/2]}{N/2 - [(N-1)/2]}$ *is an indicator of parity of the number of atoms* N.

Proof. The ZRP conditions (50) are modified as:

$$C_0 \sum_{j=0}^{N-1} \frac{e^{-ikr_{1B}}}{r_{1B}} = ik - \beta. \tag{119}$$

recall also that (109) is written as:

$$r_{1B} = r_j = 2R\sqrt{\sin(\frac{\pi j}{N})}. \tag{120}$$

The asymptotic at infinity is based on one term of the expansion $\left|\vec{r} - \vec{R}_j\right| \approx r - \dfrac{\vec{r}}{r} \cdot \vec{R}_j$. From the equation, it follows that:

$$C_0 = \begin{cases} \dfrac{-1}{\beta + ik + 2\sum_{j=1}^{(N-1)/2} g\left(r_j, \, -ik\right)}, & \text{odd}\, N, \\ \dfrac{-1}{\beta + ik + 2\sum_{j=1}^{N/2-1} g\left(r_j, \, -ik\right) + g\left(r_{N/2}, \, -ik\right)}, & \text{even}\, N. \end{cases}$$

This can be unified as in the theorem formulation. It is also useful to recall the relation (120) and rewrite the sum explicitly:

$$\sum_{j=1}^{(N+\chi_N)/2-1} g\left(r_j, \, -ik\right) = \frac{1}{2R} \sum_{j=2}^{(N+\chi_N)/2} \frac{\exp\left(2ikR\sin\left(\frac{\pi j}{N}\right)\right)}{\sin\left(\frac{\pi j}{N}\right)} \tag{121}$$

The differential cross-section is determined by:

$$\frac{d\sigma}{d\Omega} = \left|f(\theta, \, \phi)\right|^2, \tag{122}$$

as well as the total scattering cross-section:

$$\sigma = \int_0^{2\pi}\int_0^{\pi} \left|f(\theta, \, \phi)\right|^2 \sin\theta d\theta d\phi. \tag{123}$$

This also can be expressed according to the optical theorem:

$$\sigma = \frac{4\pi}{k}\operatorname{Im}\left\{f(0, \, \phi)\right\}. \tag{124}$$

Therefore:

$$\sigma \;=\; \frac{4\pi N}{k}\mathrm{Im}\left\{C_0\right\} = \frac{4\pi N}{k}\frac{k+P}{\left(k+P\right)^2+\left(\beta+Q\right)^2}, \tag{125}$$

where we denote:

$$P \equiv \frac{1}{R}\left\{\sum_{j=1}^{(M+\chi_N)/2-1}\frac{\sin\left(2kR\sin\left(\pi j/N\right)\right)}{\sin\left(\pi j/N\right)}+\frac{\chi_{N-1}}{2}\sin\left(2kR\right)\right\}, \tag{126}$$

$$Q \equiv \frac{1}{R}\left\{\sum_{j=1}^{(N+\chi_N)/2-1}\frac{\cos\left(2kR\sin\left(\pi j/N\right)\right)}{\sin\left(\pi j/N\right)}+\frac{\chi_{N-1}}{2}\cos\left(2kR\right)\right\}. \tag{127}$$

We note that for the case of a single ZRP scatterer (i.e. $N = 1$) characterized by:

$$\left.\frac{d\log\left(r\psi(r)\right)}{dr}\right|_{r=0} = -\beta_0, \tag{128}$$

the formula (118) should be obviously replaced with:

$$C_0 = -\frac{1}{\beta_0+ik}, \tag{129}$$

resulting in the very simple formula for total scattering cross-section:

$$\sigma = \frac{4\pi}{k}\mathrm{Im}\left\{C_0\right\} = \frac{4\pi}{k^2+\beta_0^2}. \tag{130}$$

As it was announced, we believe that a simplified theoretical model of molecular structures can be built by replacing each multiatomic molecule with some ZRP once its spectrum is known. Indeed, in particular for scattering on one molecule instead of (125), one would attempt to use (130) with β_0 to be chosen from the discrete spectrum levels κ_m according to the obtained formula (75).

5.3. Results for benzene molecule

It is important to verify the method of ZRP addressing a relatively simple atomic system, e.g., molecule. Focusing on particular case of a benzene molecule C_6H_6 which can be considered as a cyclic structures formed by $C-H$ constituents described by ZRPs, we set $N = 6$ and start with the bounded state problem solution.

The structure of the discrete spectrum is as it described by the Theorem 5.1 for the even number of centers, i.e. there are 4 energy levels with 2 middle ones being doubly degenerate. Numerical solution of the transcendental equations (110) yields the values of energy levels which are compared with those obtained by the well-known Hückel method on the Fig. 2. The spectrum, namely distances between the energy levels, reveals good correspondence of ZRP approach to the qualitative Hückel calculations dictating energies from the ground to the highest level to be E_0-2A, E_0-A, E_0+A, E_0+2A, respectively [18,25].

To analyze continuous spectrum, we consider total scattering cross-section dependence on energy.

We compare the results given by the standard (atomic) ZRP model of the molecule (125) and those followed from single ZRP description of the molecule, i.e. (130) using the inverse of effective scattering length for β_0 evaluation. As one can observe on the plots given below (Fig. 3), for differently estimated values of radius of benzene molecule (e.g. see the introduction of [27]), there is moderate coincidence between conventional set of atomic ZRPs model and proposed single molecular ZRP approach.

Also, we notice that better correspondence of the molecular ZRP results to those obtained with the set of standard ZRPs can be achieved if in the dressing procedure one includes only the ground state and the state with maximal energy, i.e. $E_j = -\dfrac{\hbar^2\kappa_j^2}{2\mu}$, $j = 0, 3$. This can be viewed as if we follow the described general procedure of application DT for every level, but for each doubly degenerate level with $E_j = -\dfrac{\hbar^2\kappa_j^2}{2\mu}$, $j = 1, 2$ we perform an additional DT again with the prop function of type (69) but choosing a negative transformation parameter $\kappa = -\kappa_j$, $j = 1, 2$ (corresponding to the same energy level). This results in cancellation of consecutive contributions of the DTs with opposite to each other spectral parameters gives:

$$\beta = \left(\kappa_0^{-1}+\kappa_3^{-1}\right)^{-1}, \tag{131}$$

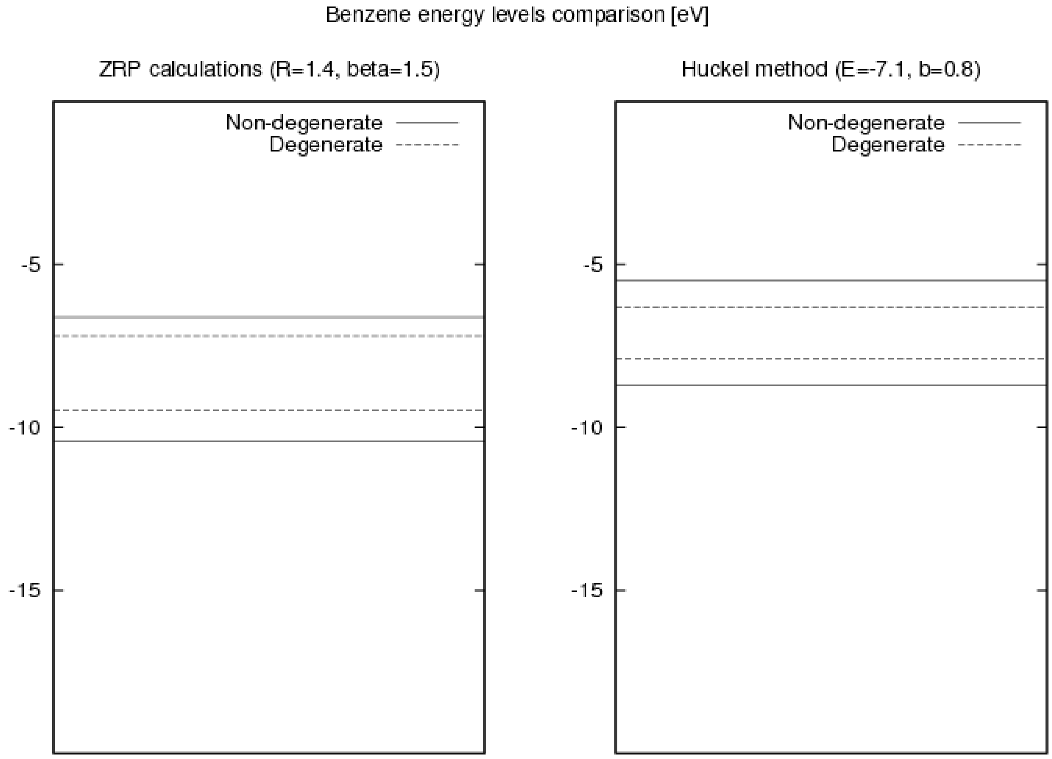

FIG. 2. The energy levels of benzene molecule. The ZRP calculations against Hückel model

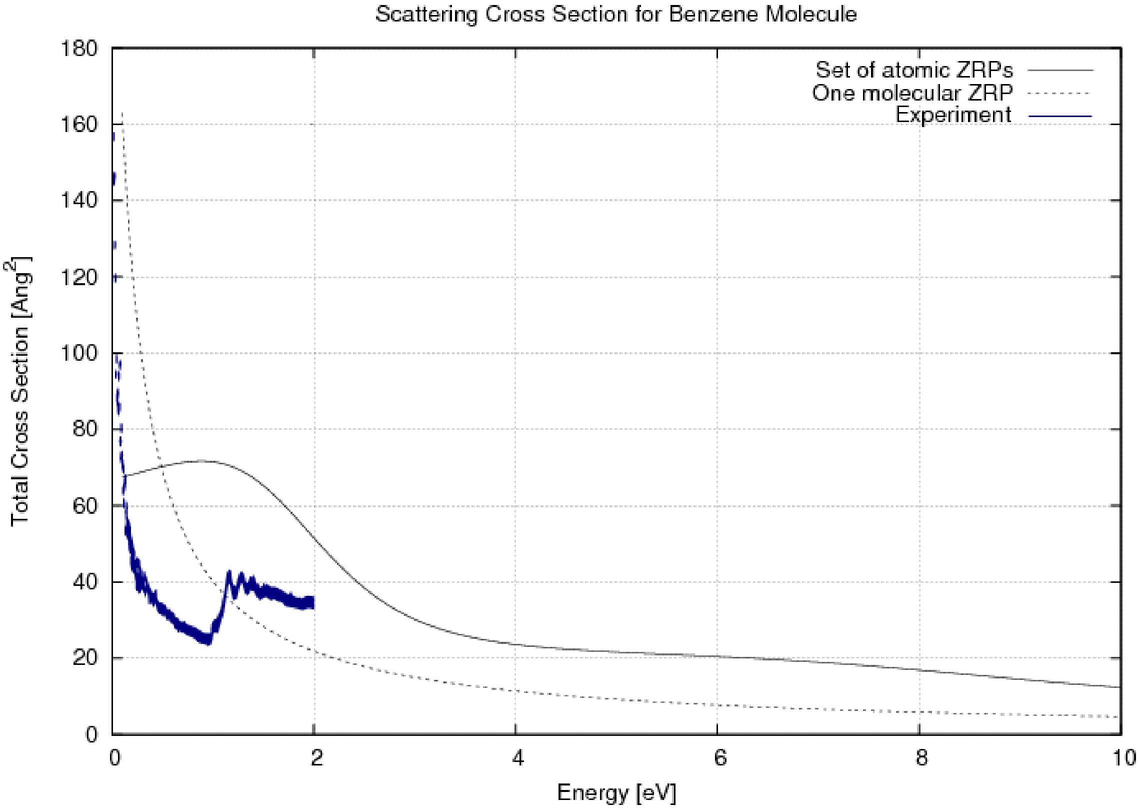

FIG. 3. The cross-section of scattering by $N = 6$ benzene molecule, lying in xy plane. The theory against experiment

This result is not surprising since, as it can be seen from the scattering matrix formalism, such pair of DTs yields consecutive adding and removal of a pole on the imaginary positive k half-axis (which corresponds to a bounded state) of (76): $s_0 \cdot \dfrac{k+i\kappa_j}{k-i\kappa_j} \cdot \dfrac{k-i\kappa_j}{k+i\kappa_j} = s_0$, $j = 1, 2$.

That is effective characteristic involves only the lowest and the highest energy level parameters. In case of odd number of atoms this would involve only the ground state energy parameter κ_0. Refined in this way, the molecular potential gives results are demonstrated by plots at [29].

6. Conclusions

The main results:

1. For arbitrary discrete symmetry, a generalization of Floquet theorem is formulated and proved. The Floquet–Bloch functions are constructed in terms of covariant summation by the symmetry group. The obtained formulas are valid as for scattering problem as for bounded states for the cases of quantum ring and quantum wire, respectively. The results are formulated for Abelian group but the proofs are based only on group-theoretical formalism, hence they may be generalized in straightforward manner.
2. Energy corresponding to the given states can be calculated numerically by solving the transcendent equations that were obtained with account of arbitrary angular momentum and electron spin.
3. In case of the quantum ring, solution to scattering problem can be further simplified depending on the range of interest in terms of energy of incident wave: either the stationary phase method can be used to estimate the resulting integral in high-energy range or simply small-argument direct series expansion for the case of large wavelengths in comparison to the size of the ring.
4. Eventually computed scattering cross-section might be used in estimates of electrical conductivity for solids that contain these quantum rings structures as inclusions or surface additions.
5. The presented method of extension of conventional atomic ZRP approach is made to describe molecular structures based on their discrete spectrum. Bounded state energies, either found from conventional ZRP calculations or in whatever alternative way, determine effective characteristic of newly introduced single ZRP that is expected to adequately describe properties of a molecule.
6. Certainly, replacement of arbitrary molecules with spherically symmetric point-centers is a crude approximation valid only in low-energy limit, however, as was demonstrated, even in case of highly anisotropic molecules, like benzene, the model gives not perfect but reasonable quality results while at the same time allowing significant simplification in formulation of more complicated molecular structures problems with molecules instead of atoms as ZRP constituents.
7. Although we believe that the molecular ZRP method should be tested on more examples in order to prove its quantitative merit, it seems to be a beneficial tool at least to obtain estimates of results on physically reasonable analytical grounds.

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