Bound states of tunneling electrons in molecular chains

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We have studied the bound states of the extra electron in a molecular chain corresponding to the physical situation of the electron tunneling through the system. The bound-state spectrum is obtained using the formalism of the multiple scattering theory (MST). The subbarrier scattering operators, the fundamental building blocks of MST, are evaluated within the variational asymptotic method which explicitly takes into account the many-electron interactions of the tunneling electron with the electrons of the scattering center. We have shown that the energy spectrum of the bound states of the tunneling electron in a linear chain of three-dimensional scattering centers substantially deviates from the spectrum of independent single-electron states of Bloch electrons in a system described by a single-electron effective potential. In particular, the number of states in the band can be less than the number of centers of the chain. These states form two bands instead of a single band and the bands exhibit nonanalytical, square root dispersion $E \sim e_{m} \times \sqrt{k_{m}}$ in the vicinity of the point $k_{m}$ where both bands come together. These findings are important for developing a physically viable theory of electron tunneling in single molecular systems.

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I. INTRODUCTION

In recent years, one-dimensional molecular structures have been actively studied both theoretically and experimentally due to their potential applications in nanoelectronics. Various device concepts are continuing to be explored including rectifying diodes, field effect transistors, and switches built from such materials as semiconductor and metal nanowires, nanotubes, small organic molecules, and large biomolecules. In order to fully utilize the unique properties of these one-dimensional nanostructures, a fundamental understanding of conduction mechanisms has to be achieved.

Recent experiments investigated conductivity in organic molecules, including DNA strands, and showed threshold or nonthreshold behavior of conductance as a function of applied voltage. Surprisingly, the absolute values of the conductance were found to be very high, approaching those observed in metallic wires. These experimental facts can be consistently rationalized by introducing a conduction mechanism based on resonant tunneling through the energy levels of the extra electron in the molecular bridge or, in chemical language, the energy levels of a negative molecular ion. Obviously, the electronic properties of the system under study including its energy spectrum are of fundamental importance for understanding the electron transport mechanisms in molecular chains.

Numerous experiments indicate that electron tunneling is the major mechanism of electron transfer through a molecule. The tunneling electron is an extra electron that interacts with the neutral molecule including its electrons and nuclei in the course of electron transition. Therefore, the states that are relevant to this mechanism of electron transfer are the states from the bound-state energy spectrum of the negative molecular ion, i.e., the system consisting of one electron plus a neutral molecular chain. The bound-state energy spectrum comprises the states of the tunneling electron with negative energies because they lie below the vacuum level which is chosen as the zero of the energy scale.

The importance of the states from the bound-state energy spectrum is in their dominant contribution to the resonant electron transfer: the resonant transitions are realized via the resonant states from the energy interval $\sim |e|V$, where $V$ is applied bias. In single molecular devices the molecule is attached to metallic electrodes. The influence of electrodes results in a shift and broadening of the states of the bound-state energy spectrum. These effects are taken into account by introducing a complex self-energy added to the molecular Green’s function. Due to exponential decay of the wave functions of the metallic electrodes inside the molecule, the electrode-molecule electronic interaction is relatively weak and can not substantially modify the fundamental features of the bound energy spectrum of the tunneling electron. In this paper we concentrate on the fundamental properties of the bound-state energy spectrum and do not consider the specifics of electron transport through the molecule. The application of the theory of bound states has been recently presented in our paper on the molecular diode and a detailed description of the transport calculations is the subject of future publication.

From a traditional viewpoint, the bound-state energy spectrum of the tunneling electron in a molecular chain can be easily determined using the independent electron approximation which describes electron-electron interactions in a mean-field framework, i.e., via an effective one-electron potential $U(r)$. In the case of molecular chains, $U(r)$ possesses one-dimensional periodicity and the application of the Bloch theorem results in the well-known linear combination of atomic orbitals (LCAO) type tight-binding solution for the energy spectrum of the tunneling electron. In this paper, we are concerned with the conceptually interesting question: would this tight-binding solution still be valid if the exchange interaction of the tunneling electron with the electrons of the chain is explicitly taken into account? To answer
of $N$ equally spaced, three-dimensional effective potential centers with one electronic state per center. The Bloch theorem allows the wave function of an extra electron to be expressed in the tight-binding representation as a linear combination of the electron wave functions of the individual centers $\varphi(r - R_i)$

$$\psi_l = \frac{1}{\sqrt{N}} \sum_l \sin(k R_i) \varphi(r - R_i),$$

(1)

where $l$ is the index of each center in the chain and $R_i$ is its coordinate. The interaction of the extra electron with the individual centers produces the splitting of $N$ identical energy levels $e_0$ into a band of $N$ collectivized states:

$$\varepsilon(k) = e_0 - 2V \cos(kd),$$

(2)

where the wave number is $k = (\pi/d)[s/(N+1)]$, $s$ is the index numbering the states in the band, and $V$ is the hopping integral of the extra electron between the centers separated by distance $d$, see Fig. 1(b). According to this standard picture, the number of states in the band is equal to number of centers in the chain, $s = 1, \ldots, N$, see Fig. 1(b).

The basic assumption used to derive the tight-binding dispersion law (2) is the notion of a single electron interacting with the molecular chain via a one-electron effective potential which is periodic with period $d$, see Fig. 1(a). However, this effective-medium type approach does not explicitly take into account the exchange interactions of the tunneling electron with the electrons in the chain. Therefore, it is expected that the substantial dependence of this interaction on the tunneling energy may result in drastically different properties of the bound-state energy spectrum of the tunneling electron. In order to address this problem, we have developed a theory of subbarrier electron scattering that specifically takes into account the many-electron effects including exchange interaction. For completeness of discussion, we outline the basics of a subbarrier scattering technique in the next section.

II. BOUND-STATE ENERGY SPECTRUM WITHIN INDEPENDENT-ELECTRON APPROXIMATION

Let us consider an elemental model of a one-dimensional linear chain of individual centers separated by distance $d$, see Fig. 1(a). The centers might represent the functional groups or structural building blocks of the molecule.

For completeness of presentation, we briefly outline here the well-known single-electron effective potential solution for the energy spectrum of a one-dimensional periodic system. According to the Bloch theorem, the electronic states of a system with a periodic Hamiltonian are described by the Bloch waves: the plane wave $\exp(ikr)$ multiplied by a function $\psi_l$ with the period of the crystalline lattice. The energies of the states constituting a band structure of a one-dimensional linear chain are functions of crystalline momentum $k$ which spans the first Brillouin zone: $-\pi/d \leq k \leq \pi/d$ in the case of a system with periodic boundary conditions, or $0 \leq k \leq \pi/d$ in the case of a chain with free-standing ends. The crystalline momentum is the quantum number to account for translational invariance of the system, and the number of quasidiscrete values of $k$ is equal to $N$, the number of centers in the system.

Let us review the results of the standard independent-electron approximation applied to a one-dimensional system
(or scattering operator, or $t$ operator) and the single-particle Green’s function of the total system is obtained by solving the secular equation of the MST. The method automatically gives the band structure and the corresponding wave functions in addition to the total Green’s function of the system which is the main object of MST.\textsuperscript{17}

We also use the fundamental principles of MST theory, i.e., we dissect a molecular chain into small parts, each piece constituting a scattering center that scatters the tunneling electron. The electronic properties of each individual scattering center are described by its corresponding scattering operator $t$. Therefore, our approach is very similar to the KKR method.\textsuperscript{17} However, unlike the KKR theory, we calculate the electronic properties of the tunneling electron, i.e., the electron with negative energy. In addition, the vacuum Green’s functions that connect the individual scatterers are exponentially decaying functions of the distance between scatterers.

Importantly, we do not use the standard one-electron effective potential approach in determining the scattering operators of the individual scatterers as is done in the KKR theory.\textsuperscript{17} In order to take explicitly into account the many-electron interactions of the tunneling electron with a scatterer, we developed a special technique, the variational-asymptotic method (VAM), which allows an efficient evaluation of the $t$ operator at the center with negative energies. As it will be shown below, the appreciable energy dependence of the exchange interaction of the tunneling electron with the electrons of the scattering center results in unique features of the energy spectrum of the tunneling electron which are very different from the properties described by the traditional one-electron effective potential approach as discussed above in Sec. II.

IV. VAM for evaluation of the subbarrier scattering operators

Let us briefly outline the main ideas of VAM (Refs. 10 and 15) before providing details of the method. As is known from quantum mechanics, the scattering properties of a quantum-mechanical system are determined by the asymptotic behavior of the wave function. The VAM is the method used for a calculation of the asymptotic wave function $\psi_{\infty}^t$ of the tunneling electron at negative energies. The method explicitly takes into account individual interactions of the incoming electron with all the electrons and nuclei of the scatterer. Once the asymptotic wave function $\psi_{\infty}^t$ is known, the $t$ operator is obtained by using the standard expression of the scattering theory for $\psi_{\infty}^t$ (which is sometimes called the Lippman-Schwinger equation) and the relationship between the total Green’s function $G$ and scattering operator $t$

\[
|\psi_{\infty}^t\rangle = GU_1|\psi_0\rangle, \tag{3}
\]

\[
G = G_0 + G_0tG_0, \tag{4}
\]

where $|\psi_0\rangle$ and $U_1$ are the wave function and the electronic potential of the source of the tunneling electron, respectively, and $G_0$ is the vacuum Green’s function.

In order to obtain the explicit expression for the $t$ operator, let us consider a system consisting of the source of the tunneling electron and the scatterer, see Fig. 2. The source is described by a short-range potential $U_s(r - R_s)$ positioned at point $R_s$, $U_s(r - R_s) = \epsilon$ is introduced to produce a bound state of the tunneling electron with tunneling energy $\epsilon$ and wave function $\psi_0^t(r)$. We investigate the propagation of the tunneling electron wave function from a source into vacuum, i.e., we are looking for the asymptote of $\psi_t$ in the presence of the scatterer. Later, we will find that the characteristics of the source itself do not enter into the final expression for the scattering operator [see Eq. (13)], i.e., the source plays an auxiliary role and is needed for the purpose of derivation. We are not interested in many-electron aspects of the source, but rather pay attention to many-electron interactions of the tunneling electron with the scatterer and its influence on the asymptote of $\psi_t$.

The scatterer positioned at the point $R$, has the ground-state many-electron wave function $\Psi_s(r_s)$, where $\{r_s\}$ denotes the coordinates of all the electrons of the scatterer including their spins. We assume that the scatterer itself is a neutral system which has ionization potential larger than $|\epsilon|$: $I_s > |\epsilon|$. This is usually the case for tunneling through organic molecules. The tunneling electron interacts with the scatterer via a many-electron potential $U_t(r,\{r_s\})$ which explicitly includes Coulomb interactions of the tunneling electron with both electrons and nuclei of the scatterer. Importantly, the potential $U_t(r,\{r_s\})$ is also short-ranged as a function of the distance between the tunneling electron and the scatterer. Therefore, we can introduce the notion of a main region of electron interaction (MREI), i.e., the region in space where there is a substantial probability of interaction of the tunneling electron with other particles (electrons and nuclei). In our case, MREI includes the regions around short-range potentials $U_s(r - R_s)$ of the source and $U_t(r,\{r_s\})$ of the scatterer, MREI, and MREI, respectively, see Fig. 2. The outer space of MREI, and MREI, is referred to as the asymptotic region (AR). Our goal is to find the values of $\psi_t$ in AR, i.e., its asymptote $\psi^t_{\infty}$.
The calculation of the scattering operator within VAM proceeds through three well-defined steps. At the first step, given the wave function \( \psi^0_t \) in MREI, (i.e., in MREI of the source), we find \( \psi_t \) in MREI, (i.e., in MREI of scatterer) by minimizing an additional contribution to the total energy due to the interaction of the tunneling electron with the scatterer referred to as interaction functional \( \delta E_{\text{int}} \). Once \( \psi_t \) in both MREI and MREI is known, the asymptote \( \psi^\infty_t \) is determined at the second step using the many-electron version of the Lippman-Schwinger equation\(^{18} \) which connects the values of the tunneling wave function \( \psi_t \) in MREIs and \( \psi^\infty_t \) in AR, and includes explicitly the many-electron interactions of the tunneling electron with the scatterer. The third step involves the extraction of the total Green’s function \( G \) of the tunneling electron from the expression for \( \psi^\infty_t \) using relationship (3), and factoring \( G \) using (4) to obtain the final expression (13) for the scattering operator \( t \).

We start the derivation by writing the standard expression for the asymptote of the tunneling wave function of the source in vacuum, i.e., when the scatterer is absent:

\[
\psi^\infty_t(a_vac, r) = \int_{MREI} \! \! dr' G_0(r, r'; e) U_t(r') \psi^0_t(r'),
\]

where \( G_0(r, r'; e) = \) the vacuum Green’s function at negative tunneling energy \( e \)

\[
G_0(r, r'; e) = G_0(|r - r'|; e) = - \frac{1}{2\pi |r - r'|} \exp(-\kappa |r - r'|),
\]

where \( \kappa = \sqrt{2|e|} \). In this paper, we use atomic units, \( e = \hbar = m_e = 1 \). The integration in (5) is over MREI, where the wave function \( \psi^0_t \) is obtained by solving a standard electronic structure problem for the source, i.e., solving Schrödinger equations for the Hamiltonian with the potential \( U_t(r - R_s) \).

When the scatterer is introduced to the system at point \( R_s \), a new MREI is formed. Therefore, \( \psi_t^{\text{vac}} \) in MREI, which was in AR before the scatterer is introduced, is modified to include the effects of many-electron interaction of the tunneling electron with the scatterer described by the potential \( U_t(r, \{r_s\}) \). The modified wave function is \( \psi_t^{MREI} \) and has to be determined by VAM. We need to explicitly include the electronic degrees of freedom of the scatterer, we will work with \( \psi_t^{MREI} \) as if it is the wave function of the total system—tunneling electron plus electrons of the scatterer which corresponds to the total Hamiltonian

\[
H_{tot} = H_s(r) + H_t(\{r_s\}) + U_t(r, \{r_s\}),
\]

Then, the wave function \( \psi_t^{MREI} \) in MREIs is written as

\[
\psi_t^{MREI}(r, \{r_s\}) = \begin{cases} \psi_t^0(\{r_s\}), & r \in \text{MREI}, \\ \psi_t^{MREI}(r, \{r_s\}), & r \in \text{MREI}, \\ \psi_t^{MREI}(r, \{r_s\}), & r \in \text{MREI}, \end{cases}
\]

where \( \psi_t^{MREI}(r, \{r_s\}) \) is the ground-state wave function of the scatterer described by the Hamiltonian \( H_s(\{r_s\}) \) and the electrons of the scatterer are always in MREI. The \( \psi_t^{MREI} \) is factorized in MREI, because of negligible interaction of the source with the scatterer. However, due to the strong exchange interaction of the tunneling electron with the scatterer’s electrons in the MREI, \( \psi_t^{MREI} \) cannot be represented in separable form. In the simplest Hartree-Fock approximation, \( \psi_t^{MREI} \) is written as

\[
\psi_t^{MREI}(r, \{r_s\}) = \hat{P}_{r, \{r_s\}}(\psi_t^{\text{vac}}(r)[1 + \varphi_{\text{car}}(r - R_s(\{r_s\}))]) \Psi_s(\{r_s\}),
\]

where \( \hat{P}_{r, \{r_s\}} \) is the normalized antisymmetrization operator with respect to electron coordinates \( r \) and \( \{r_s\} \). We introduced \( \varphi_{\text{car}}(r - R_s(\{r_s\})) \) as an additional contribution to the tunneling wave function due to its interaction with the scatterer.

The variational contribution \( \varphi_{\text{var}}(r - R_s(\{r_s\})) \) is determined by optimizing the variational parameters \( (\lambda_{\text{var}}) \) to achieve the minimum of the interaction functional, which is defined as

\[
\delta E_{\text{int}}(\lambda_{\text{var}}) = \langle \psi_t^{MREI} | \hat{H}_{\text{pol}} | \psi_t^{MREI} \rangle - E_t - E_s,
\]

where \( \psi_t^{MREI} \) is the wave function (8) and (9), and \( E_t \) and \( E_s \) are the ground-state energies of the source and the scatterer, respectively. Within VAM, the variational contribution \( \varphi_{\text{var}}(r - R_s(\{r_s\})) \) is expanded over the orbitals of the scatterer, and the variational parameters \( (\lambda_{\text{var}}) \) are the corresponding expansion coefficients. The interaction functional \( \delta E_{\text{int}} \) is due to the interaction of the tunneling electron with the scatterer described by the potential \( U_t(r, \{r_s\}) \). Because of dominant contribution of the source (positioned at \( R_s \)) to \( \psi_t^{MREI} \) and the localization of \( U_t(r, \{r_s\}) \) at \( R_s \), \( \delta E_{\text{int}} \approx \exp(-2\kappa|\text{R_s} - \text{R}_t|) \).

Once the minimum of the interaction functional (10) is found, the wave function \( \psi_t^{MREI} \) in both MREIs is known. Then, we can proceed with the calculation of the asymptote of \( \psi_t \). Using the general expression of the asymptote of many-electron wave function derived in Ref. 18 and expression (8) for \( \psi_t^{MREI} \), we obtain

\[
\psi_t(r, e) = \int_{MREI} \! \! dr' \left( G_0(r, r'; e) + \int_{MREI} \! \! d(r_s')dr' \hat{P}_{r', \{r_s\}} \right) \times \{G_0(r', r''; e)[1 + \varphi(r'' - R_s(\{r_s\}))]\} \Psi_s(\{r_s\}) \times U_t(r''(\{r_s\})) G_0(r'', r; e) \psi_t^{\text{vac}}(r') U_t(r').
\]

The expression for asymptote \( \psi_t^\infty \) can be mapped into a general expression of the scattering theory (3) which allows us to extract the expression for the total Green’s function of the system [expression in the first level of round brackets in (11)]. In order to find the final expression for the scattering operator, we expand the exponents of vacuum Green’s functions \( G_0(r, r'; e) \) and \( G_0(r', r; e) \) in the vicinity of source at \( R_s \) and the scatterer \( R_s \). This can be done because the distance between the source and the scatterer \( R_s = |R_s - R_s| \) is much larger than the radii of electronic interactions \( r_t \) and \( r_s \) in MREI and MREIs, respectively, i.e., \( r_t / R_s \ll 1, r_s / R_s \ll R_s, r_t / |R_s - R_s| \), see Fig. 2. Then, we obtain the following expres-
sion for the Green’s function of the tunneling electron interacting with the scatterer:

\[ G(\mathbf{r}, \mathbf{r}'; \varepsilon) = G_0(\mathbf{r}, \mathbf{r}'; \varepsilon) + G_0(\mathbf{R}_s, \mathbf{r}; \varepsilon) t(\varepsilon, \theta) G_0(\mathbf{R}_s, \mathbf{r}' ; \varepsilon) \]  

(12)

and the scattering operator \( t \) is

\[ t(\varepsilon, \theta) = \int_{\text{MREI}_i} d\mathbf{p} \int_{\text{MREI}_i} d\mathbf{p}_s \hat{P}_{\mathbf{p}, \mathbf{p}_s} (\exp(-\kappa \rho_{\mathbf{p}_s}) \Psi_s(\mathbf{p}_s) \times [1 + \varphi(\mathbf{p}; \lambda_{\text{min}})]) \\
\times |\Psi(\mathbf{p})| \Psi(\mathbf{p}_s) \exp(\kappa \rho_{\mathbf{p}}). \]  

(13)

In (13) the origin of the coordinate system is placed at \( \mathbf{R}_s \) and \( \mathbf{n}_{\mathbf{p}}, \mathbf{n}_{\mathbf{p}_s} \) are the unit vectors along \( \mathbf{R}_s - \mathbf{R}_i \) and \( \mathbf{r} - \mathbf{R}_i \), respectively, see Fig. 2. The expression (12) for the tunneling Green’s function has clear physical meaning: the first term describes pure vacuum tunneling, the second—the electron scattering off the center located at \( \mathbf{R}_s \) in the course of tunneling.

In general, the scattering operator may be represented in the following form:

\[ t(\varepsilon, \theta) = \frac{2\pi b(\theta)}{\varepsilon - \varepsilon_0} + t_{\text{pol}}(\varepsilon, \theta), \]

(14)

where \( \varepsilon_0 \) is the energy of the bound state of the scatterer, while \( \varepsilon \) and \( \theta \) are the energy and scattering angle of the tunneling electron. The first and second terms in (14) represent the pole and potential terms of the scattering operator, respectively.\(^{19}\) The sign of \( t(\varepsilon, \theta) \) is the indicator of the character of the effective interaction between the extra electron and the scattering center: \( t(\varepsilon, \theta) < 0 \) corresponds to an effective attraction that might produce a bound state, while the positive sign is characteristic of an effective repulsion and the absence of the bound states.\(^{19}\) A general feature of the scattering operator is the rapid increase of the potential part \( t_{\text{pol}}(\varepsilon, \theta) \) with the decrease of \( \varepsilon \) (or increase of \( |\varepsilon| \)), because \( \varepsilon < 0 \) which is due to the enhancement of the exchange interaction of the tunneling electron with the electrons of the scattering center when the energy \( \varepsilon \) approaches the energies of the electronic states of the scatterer.\(^{10}\) The expression (13) for the scattering operator is the main result of the VAM which is used for the evaluation of \( t \) operators for specific systems.

V. BOUND-STATE ENERGY SPECTRUM OF THE TUNNELING ELECTRON IN A MOLECULAR CHAIN

The formulation of the quantum mechanics based on the formalism of scattering operators allows an easy determination of the bound states of the extra electron: the poles of the scattering operator are the energies of the bound states.\(^{19}\) For a single scattering center, the pole term in (14) indicates the existence of a bound state at the isolated center. In the case of a molecular chain that consists of an ensemble of scattering centers, the total scattering operator \( T \) of the entire system is obtained using the standard formalism of MST (Ref. 17) which expresses \( T \) via scattering operators of individual scattering centers \( t_i \). Then, bound states of the chain are found as the poles of \( T \).

Within MST, the total scattering operator is easily found as a solution of the system of linear equations:

\[ T_n = t_n + \sum_{k+n} t_k G_0(|\mathbf{R}_n - \mathbf{R}_k|; \varepsilon) T_k(\varepsilon), \quad n = 1, \ldots, N, \]  

(15)

\[ T = \sum_{n=1}^N T_n. \]  

(16)

The solution of the system of linear equations may be obtained using Cramer’s rule which expresses the components of the solution vector \( (T_1, T_2, \ldots, T_N) \) as ratios of two determinants, the denominator being the determinant of the system (15). Therefore, the poles of the total scattering operator (16) are the roots of the determinant of the system of equations (15) for \( T \). Therefore, the energies of the bound states are determined from the following secular equation:

\[ \det[\delta_{ik} - t_i(\varepsilon, \theta) G_0(|\mathbf{R}_i - \mathbf{R}_k|; \varepsilon)] = 0, \quad i, k = 1, \ldots, N, \]

(17)

and they form the band of energy levels. The angles of scattering, \( \theta \), in secular equation (17) are chosen according to the paths of the scattering, and in the case of a one-dimensional molecular chain they take the values of 0 or \( \pi \).

The wave function \( \psi_i \) of the tunneling electron corresponding to the \( i \)th root of secular equation (17), \( \epsilon_i \), is written as

\[ \psi_i(\mathbf{r}) = \sum_{l} \tilde{T}_l(s) \varphi(\mathbf{r} - \mathbf{R}_i, \epsilon_i), \]

(18)

where \( \varphi(\mathbf{r} - \mathbf{R}_i, \epsilon_i) \) represent additional contributions to the exponential tail of the electronic wave function of the tunneling electron due to its interaction with the scattering center \( l \) at the position \( \mathbf{R}_i \), see Eq. (9). As it was shown above, VAM allows the determination of \( \tilde{T}_l(s) \) for each individual scattering center by optimizing the interaction energy functional (10). The role of these localized functions in forming the wave function of the tunneling electron is similar to the role the atomic wave functions play in building an independent electron tight-binding wave function (1). The components of the \( l \)th eigenvector \( \tilde{T}_l(s) \) are obtained as a normalized solution of the homogeneous system (15) and they are similar to the Bloch wave phase factors \( \sin(k R_y) \) in the tight-binding Bloch wave function (1).

In accordance with the Bloch theorem, the spatial behavior of \( \tilde{T}_l(s) \), i.e., the dependence of \( \tilde{T}_l(s) \) on the position of the centers \( R_y \), is obtained as

\[ \tilde{T}_l(s) = A_k \sin(k R_y), \]

(19)

where the quasi-wave-vector \( k \) corresponds to the number of nodes of the envelope function \( \tilde{T}_l(s) \). By examining the
spatial behavior, the number of nodes is counted and associated with the appropriate wave vector \( k \). In particular, for the case of the negative scattering operator, \( t < 0 \), we found that the wave vector \( k_m = (\pi/d) [s/(N+1)] \), and in the opposite case of \( t > 0 \), \( k_m = (\pi/d) [N+1-s/(N+1)] \). In order to clarify the general features of the spectrum, we will ignore the pole term in (14). Then, a whole set of solutions (18) can be grouped into pairs with identical \( T_l(s) \) or the same quasi-wave-vectors \( k \). Because each solution in the pair has a different eigenvalue, the two states are attributed to two different energy bands that constitute the structure of the energy spectrum of the chain.

In order to show the qualitative picture of the bound-state energy spectrum, we will consider the case of a sufficiently large intercenter distance \( d \), when \( t(e, \theta)G_0(2d; \epsilon) \ll 1 \) (so-called nearest neighbor scattering). Then, the determinant (17) becomes tridiagonal:

\[
\det[k - \beta \delta_{ks}] = 0, \quad \beta = t(e, \pi)G_0(d; \epsilon),
\]

and can be solved analytically to yield an implicit equation of band energies \( \epsilon \) as a function of the wave vector \( k \):

\[
\beta(e, d) = t(e, \pi)G_0(d; \epsilon) = \frac{t(e, \pi) \exp(-\sqrt{2} \epsilon d)}{2 \pi d} = \frac{1}{2 \cos(kd)}.
\]

The scattering operator \( t \) consists of two contributions, pole and potentials terms, see (14). Therefore, at even larger distances \( d \) between the centers such that \( t_{pol}(e, \theta)G_0(d; \epsilon) \ll 1 \), only the pole term of the scattering operator is appreciable. This limit corresponds to the one-electron effective potential tight-binding approximation. In this case, the dispersion (21) becomes identical to tight-binding dispersion (2) with the hopping integral \( V = \langle \hbar \pi d \rangle \exp(-\sqrt{2} \epsilon d) \). This nicely demonstrates the capability of the method to develop a more general picture while establishing connections with previous results.

VI. EXAMPLE: MOLECULAR CHAIN CONSISTING OF HYDROGEN ATOMS

We illustrate the simple physics of the bound-state energy spectrum by considering a prototypical example: a chain of hydrogen atoms with spin on each H atom oriented in the same direction. This in an important yet simple example because the scattering operator for individual scattering centers (hydrogen atoms) is easily determined within VAM without substantial computational effort. Moreover, it is frequently used to illustrate general features of one-dimensional systems.20 Depending on the spin of the tunneling electron there will be two cases: (i) triplet subbarrier scattering with the spin of the tunneling electron oriented in the same direction as the spins of H atoms of the chain, and (ii) singlet subbarrier scattering with the spin of tunneling electron oriented in the opposite direction. The energy dependence of the scattering operator for triplet scattering was calculated using VAM in Ref. 10: \( t(e, \pi)/2 \pi = 0.2 \pm 1.4 \). The accuracy of this calculation was checked by extrapolation to zero scattering energy and comparing the scattering amplitude \( a = -t/2 \pi \) to the value obtained in experiments on triplet scattering at small positive energies. We found a very good agreement between calculated and experimental values. In the case of triplet scattering, the scattering operator \( t > 0 \). Therefore, the electronic interaction between the tunneling electron and the scatterer (hydrogen atom) is repulsive which results in the absence of the bound state and the absence of the pole term in \( t \). This correlates with the experimental fact that there are no bound states of \( H^- \) with \( S=1 \). The spectrum of the chain in the triplet states is described by the wave vector \( k = (\pi/d) [s/(N+1-s)/(N+1)] \).

It is easy to show that Eq. (21) for band energies \( \epsilon \) has a solution only for intercenter distances \( d < 4.45 \). We calculated the energy spectrum for a particular value of \( d = 4 \) in the nearest-neighbor scattering approximation by solving Eq. (21) and solving the secular equation (17) exactly, see Fig. 3. For each value of \( K \), there are two solutions of secular equations (17) or (21) which result in two energy bands: the upper band \( e_u(k) \) and the lower band \( e_l(k) \), see Fig. 3. We also plotted solutions for the case of a negative scattering operator \( t(e, \pi)/2 \pi = -2 + 140 \epsilon + 0.22/\epsilon + 0.0277 \) which corresponds to singlet subbarrier scattering. For the singlet state of \( H^- \), there exists a bound state with energy \( \epsilon = -0.0277 \) a.u.

In the case of an infinite number of centers \( N \to \infty \) and \( t > 0 \), both bands come together at the energy \( \epsilon = \epsilon_m \) and the wave vector \( k_m \), corresponding to the minimum of the secular curve \( t(e, \pi)G_0(d; \epsilon) \) [middle expression in (21)]. The dispersion relationship in the vicinity of \( \epsilon_m \) is nonanalytic (i.e. \( d\epsilon/dk \) is singular at \( k = k_m \): \( \epsilon_u(k) = 2a \sqrt{k - k_m} \) where \( a = 2[\partial^2 \beta(\epsilon_m, d)/\partial \epsilon^2]^{-1} \). The gap between the upper (u)
the lower \((l)\) bands at \(k_m\) in Fig. 3 is due to the finite number of centers in the chain. This dispersion relationship is quite different from the analytic, quadratic dependence of energy on the \(k\) vector that is characteristic of the one-electron effective potential model at the top and the bottom of the tight-binding bands. Moreover, the number of states in each band \(N_b\) is less than the number of centers \(N: N_b=\left(N-\pi k_m d\right)/\pi\) which is also in contrast to the one-electron effective potential picture of the electron spectrum where the number of energy levels is equal to the number of the centers.

For both negative and positive scattering operators, the topology of the dispersion curves is very similar. The only differences are that in the case of negative \(t\), the secular curve \(\beta(\varepsilon)=\pi(c, \varepsilon)G(d, \varepsilon)\) will lie above the energy axis, the wave vectors will be in the interval \(0<k<k_m<\pi/2d\) and the number of the states in both bands will be \(N_b/N=\pi k_m/\pi\), see Fig. 3. It is worth noting that for both positive and negative scattering operators, the number of bound states in the upper \(e_u(k)\) and lower \(e_l(k)\) bands will be less than half of the number of the scattering centers.

The complexity of solutions of the secular equation (17) beyond nearest-neighbor scattering does not allow an analytical solution but can be solved numerically. We found that the major features of the bound energy bands remain the same. We can explore in detail the specific features of the energy spectra in the general case and contrast the differences for the systems with negative and positive scattering operators \(t\). As mentioned above, the secular equation includes scattering operators at both 0 and \(\pi\) scattering angles, but for the purpose of comparison we consider the averaged angle independent expressions \(t(\varepsilon)=2-140\varepsilon\) for \(t>0\) and \(t(\varepsilon)=-2+140\varepsilon\) for \(t<0\) and \(d=4\).

The numerical solution of the secular equation for both positive and negative \(t\) is shown in Fig. 3. We see the reduction of the bandwidth in the case of a positive scattering operator \(t>0\) and an increase of the bandwidth in the case of \(t<0\) as compared to the nearest-neighbor scattering approximation, Eq. (21). In addition, an asymmetry of the energy spectrum is observed in the case of \(t<0\): the number of states in the upper band is less than that in lower band, see Fig. 3. The upper band has fewer states because the states at the top of the upper band close to zero energy are pushed into the continuum spectrum \(\varepsilon>0\) and become resonant levels there. If the parameters of the interactions in the chain are changed in such a way as to reduce the bandwidth [for example, if \(b=0\) in (14) and \(t=140\varepsilon\)], the symmetry of the spectrum is restored because all of the states are in the negative energy interval.

As we have already shown, the sign of the scattering operator \(t\) determines the region in quasimomentum space \(k\) where the energy levels of the bound states exist. Then, substituting parametrization of \(k\) at the beginning and the end of Brillouin zone, we obtain

\[
\bar{T}_{ls}(t) = \begin{cases} 
A^s_{l}\sin\left(\frac{\pi s R_l}{(N+1)d}\right), & t < 0 \\
(-1)^tA^s_{l}\sin\left(\frac{\pi s R_l}{(N+1)d}\right), & t > 0 
\end{cases}
\]

where \(s\) is the index counting energy levels from the bottom of the lowest band \((t<0)\) or from the top of the highest band \((t>0)\) and the coefficient \(A^s_{l}\) depends not only on the wave vector \(k_s\) but also on the band index \(\nu\).

VII. DISCUSSION AND CONCLUSIONS

In this paper we have studied the bound states of the tunneling electron in a molecular chain which are the states of the tunneling electron with negative energies. In order to take explicitly into account the many-electron interactions of the tunneling electron with a scatterer, we developed and applied a special technique, the VAM, which allows an efficient evaluation of the \(t\) operator of the centers. The appreciable energy dependence of the exchange interaction of the tunneling electron with the electrons of the scattering center results in unique features of the energy spectrum of the tunneling electron scattering off a linear chain of three-dimensional scattering centers. These features are very different from the properties described by the traditional one-electron effective potential approach.

The general features of the bound states were illustrated using a very simple and physically transparent one-dimensional system: a chain of hydrogen atoms. We found that the number of states in the band can be less than the number of centers of the chain. These states form two bands instead of a single band and the bands exhibit nonanalytical, square root dispersion \(\varepsilon \sim \sqrt{1-k_m^2}\) in the vicinity of the point \(k_m\) where both bands come together.

Having discovered such unusual properties, one might ask a reasonable question: why is the bound-state spectrum of the tunneling electron in the molecular chain so different from the electron energy spectrum in solids as described by band theory? The origin of the differences lies in the specificities of the electronic interactions between an external electron with all other electrons of the system. In the case of a molecular wire, an extra electron interacts with internal and neutral scatterers. In contrast, there is a sea of collective electrons in a solid which interact among themselves and with nuclei. Therefore, the one-electron band energy spectrum in solids is adequately described within the one-electron effective potential approach which takes into account the electronic correlations within a self-consistent, mean-field framework. Obviously, metals, semiconductors or insulators cannot be represented as a system of independent electron scatterers and this is the reason why the energy spectrum of a tunneling electron spectrum in a molecular wire exhibits fundamentally different physics. It is worth noting, however, that the multiple subbarrier scattering theory with the energy-dependent scattering operators of individual molecules can be applied to calculate the conductance bands of the molecular solids such as benzene crystals.

In conclusion, the developed theory of the bound states is important from a fundamental point of view because it demonstrates substantial deviations from the single-electron effective potential picture of an extra electron in a system with
geometrical periodicity. These findings are important for developing a physically viable theory of electron tunneling in single molecular systems which will be presented in future publications.

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