On Oscillation Theorem for Two-Component Schrödinger Equation

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Conventional one-dimensional oscillation theory is found to be violated for multi-component Schrödinger equations in a general case while for two-component eigenstates coupled by the sign-constant potential operator the following statements are valid: (1) the ground state ($v = 0$) is not degenerate; and (2) the arithmetic mean of nodes $n_1$, $n_2$ for the two-component wavefunction never exceeds the ordering number $v$ of eigenstate: $(n_1 + n_2)/2 \leq v$.

I. INTRODUCTION

For a large number of physical applications there are useful the so called oscillation theorems [1, 2] that describe some remarkable properties of solutions of the one-dimensional (1D) Schrödinger equation. As for 1D problems the bonded states are nondegenerate one may enumerate the wave functions of stationary states by their numbers $v$ in increasing energy order ($v = 0, 1, 2, \ldots$). It is known (see [1], Ch.XIII.3 in [3] or Ch.VI, §6 in [4]) that the eigenfunction $\varphi^v$ corresponding to the $v$-th eigenvalue $E^v$ vanishes exactly $v$ times (another words, the $\varphi^v$ possesses exactly $v$ internal nodes). These statements may be clarified within the quasi-classical (WKB) approximate mass (see [1, 2]). For the many-dimensional problems these statements are not so simple [2].

In present study we consider the nodal properties of multi-component wave functions for the Schrödinger equation being interesting within the physical problems, where adiabatic approximation shell be used in modified forms (see e.g. [6]). For example, the spin-orbit coupling effects also are resulted in a multi-component diatomic vibrational Schrödinger equation [6, 7, 8].

Let us consider the two-component Schrödinger equation for the $2 \times 2$ matrix Hamiltonian $H$:

$$H\varphi^v = \begin{bmatrix} h_1 & V_{12} \\ V_{21} & h_2 \end{bmatrix} \begin{bmatrix} \varphi_1^v \\ \varphi_2^v \end{bmatrix} = E^v \begin{bmatrix} \varphi_1^v \\ \varphi_2^v \end{bmatrix} = E^v \varphi^v.$$ (A1)

The components $h_{1,2}$ of $H$ in Eq. (A1) have the traditional form $h_k = -\frac{1}{2\mu} \frac{\partial^2}{\partial x^2} + U_k(x)$ with some effective mass $\mu$ and real-valued potentials $U_k$ (here the rotational part of energy is included in $U_k$). The interaction operators are supposed to be some real-valued potentials $V_{21}(x) = V_{12}(x)$, and the energy levels $E^v$ are enumerated in increasing order, taking degeneracy into account, by traditional vibrational quantum number $v = 0, 1, 2, \ldots$.

For molecular problems one may suppose the components $\varphi_{1,2}^v(x)$ of a vector-function $\varphi^v$ to be real-valued functions defined for some region $\Omega$, being the same for both components. It is supposed here $\Omega = [\alpha, \beta] \subseteq \mathbb{R}$ for some finite (or infinite) $\alpha$ and $\beta$. When one of the ends of the interval $[\alpha, \beta]$, for example, $\alpha$, is finite, one supposes that both components of solution $\varphi^v$ obey the Dirichlet boundary condition at this point: $\varphi^v_{1,2}(\alpha) = 0$.

A.1 In any case only bound states are considered and solution $\varphi^v$ is supposed to be normalized by condition

$$\langle \varphi^v_1 | \varphi^v_1 \rangle + \langle \varphi^v_2 | \varphi^v_2 \rangle = 1.$$ (A2)

The analysis of the problem in the WKB- or/and ”adiabatic” approximations (of course, being modified for the systems considered) and by the perturbation theory (for small enough $V_{12}$) gives a wide range of possibilities. In particular, it is easy to find some special situations when the problems under consideration differ essentially from the traditional one-component ones. So it seems to be interesting to describe some general statements, that are valid for a large part of practical applications.

II. SOME EXAMPLES AND GENERAL NOTES

In general the problems of the form (A1,A2) seems to be not essentially differs from the one-component Schrödinger 1D-equation. It may be rewritten as a system of two equations with the same normalization condition (A2):

$$h_1 \varphi_1^v + V_{12} \varphi_2^v = E^v \varphi_1^v$$
$$V_{21} \varphi_1^v + h_2 \varphi_2^v = E^v \varphi_2^v.$$ (A3)

It is clear, that when interaction potential vanish ($V_{12}(x) = 0$ for any $x$) the problem (A3) is reduced to some one-component eigenvalue problems for Hamiltonians $h_{1,2}$. In this situation the Hamiltonians $h_1$ and $h_2$ with essentially different densities of the bond states shows it clearly, that the number of nodal points for one-component functions does not define the number (that is, the $v$ value) of the corresponding energy level.
If the spectra of $h_1$ and $h_2$ are identical and $V_{12} = 0$, any energy level is degenerate one, including the ground state level. One may also give a simple example of the situation, when degeneracy of all the states in the two-component problem Eq. (A1) appears for nontrivial situation, when degeneracy of all the states in the two-energy level is degenerate one, including the ground state. Really, when Hamiltonian on the $\mathbb{R}$ axis and $V_{12}(x) = x$, it easy to transform Eq. (A1) to a system of two eigenvalue problems for 1D-Hamiltonians $h + V_{12}$ and $h - V_{12}$, that describe the two equivalent oscillators with shifted centers. Hence, all the energy levels of the problem considered are doubly degenerate ones. Note also, that the small perturbation of the problem above allows one to construct the two-component problems, where the components of the ground state have nodes.

The simple examples above described demonstrate it clearly, that the nodal structure of the many-component wavefunctions is a much more difficult problem, than that one for one-component 1D-system. Nevertheless, one may note, that in all the examples presented the interaction potentials $V_{12}$ vanish, at least, in some points. If one exclude the situations, when $V_{12}$ change its sign or vanishes, that is, when the interaction potential $V_{12}$ is invertible, the situation changes drastically and one may prove some interesting statements on nodal structure of the multi-component wavefunctions.

For invertible potential $V_{12}(x)$ one may use the system Eq. (A3) to find $\varphi_1^v$ as a solution of the 4-th order differential equation (similar relation holds for $\varphi_2^v$):

$$[(h_2 - E^v)V_{12}^{-1}(h_1 - E^v) + V_{12}]\varphi_1^v = 0.$$  \hspace{1cm} (A4)

In particular, the most of statements below use the following idea, being the result of the well known property of the Cauchy problem:

**Lemma.** For invertible potential $V_{12}(x)$ the components of any nontrivial solution $\tilde{\varphi}^v$ of the problem (A1) cannot be identically zero into some open subregion of $\Omega$.

For the 1D one-component problems it is impossible that the wave function and its gradient vanish simultaneously at some point. In particular, near the nodal points the wavefunction changes the sign. For the multi-component problems situation is not so simple. In principle, for solutions of Eq. (A4) it is possible that at some point some component of the wave function only touches the axis. When the interaction potential does not vanish at this point, it follows from Eq. (A4) that both components $\varphi_{1,2}^v(x)$ vanish along with their second derivatives. This special situation is not stable with respect to small perturbations and we ignore it here. That is, we consider as the nodal points only the ones for which functions change their signs. Similar issues for one component problems for $\Omega = \mathbb{R}^n (n > 1)$ enforce to analyze the regions of a constant sign for wave functions [2].

### III. USEFUL STATEMENTS

Here we prove three useful statements that gives the background for discussions of the nodal properties of wavefunctions in the next Section. The notations introduced in this Section are used here and in the next Section without special comments. In particular, we use the symbol $[n/2]$ for the integer part of the $n/2$ value. The following relation is important for our discussions in this text:

$$n = \left[\frac{n}{2}\right] + \left[\frac{n + 1}{2}\right].$$  \hspace{1cm} (A5)

An other construction is typical for the problem under consideration (see, e.g. [2]). Let $\tilde{\varphi}^v$ be an eigenvector of the two-component matrix Hamiltonian $H$ with energy $E^v$ and components $\varphi_1^v$ and $\varphi_2^v$. Let us analyze the regions of a constant sign for the function $\varphi_1^v$ (or for $\varphi_2^v$), that is, the intervals on $\mathbb{R}$ where the function has a definite sign and changes it at the ends. The number $K_j$ of such regions corresponds to $n_j = K_j - 1$ nodal points of $\varphi_j^v$ ($j = 1, 2$).

Let us suppose that $\varphi_1^v$ has $K_1$ regions $\Omega_j^{(1)}$ ($j = 1, 2, \ldots, K_1$) of a constant sign. One may define for each of regions $\Omega_j^{(1)}$ the function $\varphi_j^{(1)}$ that equals to $\varphi_j^v$ on $\Omega_j^{(1)}$ and equals to zero out of $\Omega_j^{(1)}$. Let us suppose that $\varphi_2^v$ has $K_2$ regions $\Omega_k^{(2)}$ ($k = 1, 2, \ldots, K_2$) of a constant sign and $\varphi_k^{(2)}$ are the functions similar to the ones for the first component of $\varphi^v$. Hence the two-component function $\tilde{\varphi}^v$ gives rise to construct the linear space $K$ of $(K_1 + K_2)$-dimensional vectors $C$ defined by any set of $K_1$ coefficients $c_j$ and set of $K_2$ coefficients $d_k$ and corresponding vector-functions $\chi$ with components of the form

$$\chi_1 = \sum_{j=1}^{K_1} c_j \varphi_j^{(1)}, \quad \chi_2 = \sum_{k=1}^{K_2} d_k \varphi_k^{(2)}.$$  \hspace{1cm} (A6)

In particular, $\chi = \tilde{\varphi}^v$ when $d_k = c_j = 1$ for any $k$ and $j$ values. Note also, that $\chi_{1,2}$ and their gradients have to be the square integrable functions on $\Omega$ as $\varphi_{1,2}^v$ fulfill these requirements (the sets of a zero measure have no importance here).

Now we consider the properties of the matrix $M$, defined for the above mentioned space $K$ by the vector-function $\tilde{\chi}$ in the following way:

$$(C, MC) = \sum_{j,k} (c_j - d_k)^2 \langle \varphi_j^{(1)} | V_{12} | \varphi_k^{(2)} \rangle.$$  \hspace{1cm} (A7)

Our attention to the matrix $M$ is explained by the following reason. The further discussion is based on the simple expression of energy functional $E(\tilde{\chi})$ associated
with the Hamiltonian $H$, for the vector-function $\chi$ with components of the form $\langle A6 \rangle$.

**Statement 1.** If $\varphi^\dagger$ is a solution of Eq. (A11), then for any vector $C \in K$ one may write

$$E(\chi) = E^v(\chi|\chi) - (C, MC)$$  \hspace{1cm} (A8)

*Proof.* The use of a standard form for the energy functional (with kinetic energy expressed as squared gradient of wavefunction) and integration by parts enables to write, due to Eq. (A6), the following relation:

$$E(\chi) = \sum_{j=1}^{K_1} c_j^2 \langle \varphi_j^{(1)} | h_1 | \varphi_j^{(1)} \rangle + \sum_{k=1}^{K_2} d_k^2 \langle \varphi_k^{(2)} | h_2 | \varphi_k^{(2)} \rangle + 2 \sum_{j,k} c_j d_k \langle \varphi_j^{(1)} | V_12 | \varphi_k^{(2)} \rangle$$  \hspace{1cm} (A9)

where integration in each of integral in the sums is done over the regions $\Omega_j^{(1)}$, $\Omega_k^{(2)}$, or $\Omega_j^{(1)} \cap \Omega_k^{(2)}$, respectively. The use of Eq. (A3) gives immediately

$$E(\chi) = E^v \left[ \sum_{j=1}^{K_1} c_j^2 \langle \varphi_j^{(1)} | h_1 | \varphi_j^{(1)} \rangle + \sum_{k=1}^{K_2} d_k^2 \langle \varphi_k^{(2)} | h_2 | \varphi_k^{(2)} \rangle \right]$$

$$- \sum_{j,k} c_j^2 \langle \varphi_j^{(1)} | V_12 | \varphi_k^{(2)} \rangle - \sum_{j,k} d_k^2 \langle \varphi_k^{(2)} | V_21 | \varphi_j^{(1)} \rangle$$

$$+ 2 \sum_{j,k} c_j d_k \langle \varphi_j^{(1)} | V_12 | \varphi_k^{(2)} \rangle$$  \hspace{1cm} (A10)

The use of definition Eq. (A7) shows it clearly, that this is exactly expression (A8).  \hspace{1cm} ■

It is interesting, that the number of positive/negative eigenvalues of the matrix $M$ is closely connected with numbers $n_{1,2}$ of nodes for components of the vector-function $\varphi^\dagger$. To prove it one shall note the following simple statement.

**Statement 2.** There are no more than $(K_1 + K_2 - 1)$ regions $\Omega_j^{(1)} \cap \Omega_k^{(2)} \subset \Omega$, where the product $\varphi_j^{(1)} \varphi_k^{(2)}$ conserves its sign.

*Proof.* In general there are no more than $n_1 + n_2$ internal points of the region $\Omega$ where $\varphi_j^{(1)} \varphi_k^{(2)}$ changes the sign. As $n_j = K_j - 1$, there are no more than $(K_1 - 1) + (K_2 - 1)$ nodes for $\varphi_j^{(1)} \varphi_k^{(2)}$, and, hence, there is not more then $(K_1 - 1) + (K_2 - 1) + 1 = (K_1 + K_2 - 1)$ non-empty regions of the type $\Omega_j^{(1)} \cap \Omega_k^{(2)}$ where the function $\varphi_j^{(1)} \varphi_k^{(2)}$ conserves the sign.  \hspace{1cm} ■

The most important result of this Section is the following statement.

**Statement 3.** If the sign of the potential $V_{12}(x)$ is fixed, then the matrix $M$ defined by Eq. (A7) has no less than $[\frac{K_1 + K_2 + 1}{2}]$ non-negative eigenvalues.

*Proof.* According to definition (see Eq. (A7)), the quadratic form $(C, MC)$ is determined by a sum of matrices of rank 1, each of which has only one nonzero eigenvalue $2(\varphi_j^{(1)} | V_{12} | \varphi_k^{(2)})$, if any. According to the Statement 2, among those eigenvalues there are no more than $(K_1 + K_2 - 1)$ non-zero values. A half of them is negative, while another half is positive. In any case, according to the Eq. (A5) the largest number of strictly negative integrals is no more than $\left[\frac{K_1 + K_2}{2}\right]$.

According to the minimax principle (see, e.g., Ch. VI, of [3] or Sect. XIII.1 of [3]), this means that no more than $\left[\frac{K_1 + K_2}{2}\right]$ eigenvalues of matrix $M$ are strictly negative. Hence, the remaining eigenvalues of $M$ are non-negative and their number is no less than

$$(K_1 + K_2) - \left[\frac{K_1 + K_2}{2}\right] = \left[\frac{K_1 + K_2 + 1}{2}\right]$$  \hspace{1cm} (A11)

as follows from Eq. (A5).  \hspace{1cm} ■

## IV. THE NODAL POINTS IN TWO-COMPONENT PROBLEM

For 1D problems the wavefunction of the state with vibrational number $v = 0, 1, 2, \ldots$ has exactly $v$ nodes [1] [3] [4]. When $\text{dim}(\Omega) > 1$, for the one-component problem one may only prove that, for a given state, the number of regions of a definite sign is not too large [2]. For the two-component system considered here one may prove some analogue of these statements. The proof is similar to the one in the one-component case, but it requires some special modifications.

**Theorem.** For the $v$-th stationary state of the problem Eq. (A1) with the interaction potential $V_{12}(x)$ of a definite sign the number of points $n_1$ and $n_2$, where the components $\varphi_1^\dagger$ and $\varphi_2^\dagger$ of the vector eigenfunction $\varphi^\dagger$ change their signs, the following inequality holds:

$$\left\lfloor \frac{n_1 + n_2 + 1}{2} \right\rfloor \leq v,$$  \hspace{1cm} (A12)

and, hence,

$$\left\lfloor \frac{n_1 + n_2}{2} \right\rfloor \leq v.$$  \hspace{1cm} (A13)

*Proof.* Let us consider the space $K$ associated with regions of constant sign for components of the wavefunction $\varphi^\dagger$ with energy $E^v$, as was described in Section II. Each vector $C \in K$ may define some vector-function $\chi$ (see Eq. (A6)). Due to Statement 1 the corresponding energy functional value can be written as

$$E(\chi) = E^v(\chi|\chi) - (C, MC).$$  \hspace{1cm} (A14)
According to the Statement 3 (remember, that $K_j = n_j + 1$), the matrix $\mathbf{M}$ has no less than

$$T = \left[ \frac{K_1 + K_2 + 1}{2} \right] = \left[ \frac{n_1 + n_2 + 3}{2} \right] = \left[ \frac{n_1 + n_2 + 1}{2} \right] + 1 \quad \text{(A15)}$$

non-negative eigenvalues, each of them being associated with some vector $\mathbf{C}$ and corresponding vector-function $\chi$.

Let us suppose $T \geq v + 2$. Then one may find at least two independent normalized vectors $\chi^{(1,2)}$ (or, equivalently, $\mathbf{C}^{(1,2)} \in \mathcal{K}$ being orthogonal to $v$ exact solutions $\varphi^0, \varphi^1, \ldots, \varphi^{v_0}$ of Eq.(A1) with lowest energies.

For these vectors ($\mathbf{C}^{(1,2)}, \mathbf{M}^{(1,2)}$) $\geq 0$ ($j = 1,2$) and, hence, $E(\chi^{(1,2)}) \leq E^v$. It follows from the variational principle (see, e.g. Ch.VI. of [6] or Sect.XIII.1 of [3]) that both functions $\chi^{(1)}$ and $\chi^{(2)}$ are solutions of Eq.(A1) with energy $E^v$ and one may construct, as a linear combination of these vector-functions, a non-zero solution $\chi$ of the Schrödinger equation, for which, at least for one of regions $\Omega^{(1)}_j$ or $\Omega^{(2)}_l$, the corresponding component of the solution ($\chi_1$ or $\chi_2$) identically equals to zero. This is however impossible, according to the Lemma of Section 4. Hence, $T < v + 2$, or, equivalently, $T \leq v + 1$. Hence, one may write

$$\left[ \frac{n_1 + n_2}{2} \right] \leq \left[ \frac{n_1 + n_2 + 1}{2} \right] \leq v. \quad \text{(A16)}$$

due to Eq.(A15). The usage of Eq.(A16) proves the statement. □

It is clear, that $(n_1 + n_2)/2$ is the arithmetic mean of number of nodes for components of the two-component solution. Hence, the Theorem statement Eq.(A13) is an analogue to the usual one-component statement for the case of the Schrödinger Equation in $\mathbb{R}^n (n > 1)$ (see Ref. 2).

**Corollary 1.** For the Theorem’s conditions, the components of the function $\varphi = 0$ conserve their signs into $\Omega$.

[Indeed, for $v = 0$ inequality Eq.(A12) means $n_1 = n_2 = 0$.]

**Corollary 2.** For the Theorem’s conditions for the ground state and $V_{12}(x) \leq 0$ the signs of $\varphi^1_1$ and $\varphi^2_2$ coincide, while for $V_{12}(x) > 0$ the signs mentioned are opposite.

**Proof.** Let $\varphi^1_1, \varphi^2_2$ be the components of the ground state vector-function $\varphi^1$. According to the Corollary 1, the signs of $\varphi^1_1, \varphi^2_2$ are fixed. Hence, for the potential $V_{12}$ of fixed sign one may conclude that $\langle \varphi^1_1 | V_{12} | \varphi^2_2 \rangle \neq 0$. The mean value of the Hamiltonian has the form

$$\langle \varphi^1 | \mathbf{H} | \varphi^2 \rangle = \langle \varphi^1_1 | h_1 | \varphi^1_1 \rangle + \langle \varphi^2_2 | h_2 | \varphi^2_2 \rangle + 2 \langle \varphi^1_1 | V_{12} | \varphi^2_2 \rangle. \quad \text{(A17)}$$

If one replaces $\varphi^2_2$ by $-\varphi^2_2$ and calculates the mean value of the Hamiltonian $\mathbf{H}$, the variational principle yields immediately $\langle \varphi^1_1 | V_{12} | \varphi^2_2 \rangle < 0$. Hence, the signs of the product $\varphi^1_1 \varphi^2_2$ and $V_{12}(x)$ are opposite. □

**Corollary 3.** For the Theorem’s conditions the ground state is not degenerate.

[The proof is the same as in one-component case, see Ref. 2. Indeed, two vector-functions with components which conserve their signs and the sign of the product $\varphi^1_1 \varphi^2_2$ cannot be orthogonal. Hence, the ground state is not degenerate.]

**Note.** If dim$(\Omega) > 1$ one has no rights to insist on the validity of the Theorem. However, for the interaction potential $V_{12}(x)$ of a fixed sign one may prove Corollaries 1 - 3 by similar arguments.

**V. CONCLUSION**

For eigenvalue problems with matrix Hamiltonians the structure of nodal points is much more complex than for an one-component 1D-problem, and the nodal structure of multi-component problems is of less importance than for one-component ones. Nevertheless, for the interaction potential of a fixed sign there are some analogues of the oscillation theorems. In particular, for a two-component problems for $\mathbb{R}^1$ axis (or a half-axis, or a finite segment) one may prove the following statements:

(1) the ground state is not a degenerate one, and the components of the ground-state wavefunction conserve their sign, defined by the sign of interaction potential;

(2) for the state number $v$ (for energies in increasing order $v = 0, 1, 2, \ldots$) the wavefunction components $\varphi^1_1$ and $\varphi^2_2$ have the arithmetic mean of the number of nodal points $(n_1 + n_2)/2$ not larger than $v$. (For a more precise form, see Eq.(A12)).

We suppose it to be sufficient for practical applications. Though the condition of a constant sign for $V_{12}$ seems to be too restrictive, one may note, that in practice it is sufficient to be sure in a constant sign of $V_{12}(x)$ for the region of localization of the wavefunction components only.

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Analogue of Oscillation Theorem for Nonadiabatic Diatomic States

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Relative intensity measurements in the high resolution $A^1\Sigma^+ \rightarrow b^3\Pi$ laser induced fluorescence spectra of KCs molecule highlighted a breakdown of the conventional one-dimensional oscillation theorem [L.D. Landau and E.M. Lifshitz, Quantum Mechanics, Pergamon, New York, 1965]. For strongly coupled $A^1\Sigma^+$ and $b^3\Pi$ states the number of nodes $n_A$ and $n_B$ of the non-adiabatic vibrational eigenfunctions $\varphi^A_v$ and $\varphi^B_v$ corresponding to the $v$-th eigenstate differs essentially from their adiabatic counterparts. It is found, however, that in general case of two-component states with wave functions $\varphi^A_v$ and $\varphi^B_v$ coupled by the sign-constant potential operator $V_{12} \neq 0$: (1) the lowest state $v = 0$ is not degenerate; and (2) the arithmetic mean of the number of nodes $n_A$ and $n_B$ of $\varphi^A_v$ and $\varphi^B_v$ never exceeds the ordering number $v$ of eigenstate: $(n_A + n_B)/2 \leq v$.

The conventional oscillation theorem [1, 2] states the remarkable properties of bound solutions of the one-dimensional (1D) Schrödinger equation: (1) none of the bound states is a degenerate one and (2) the eigenfunction $\varphi^v$ corresponding to the $v$-th eigenvalue $E^v$ vanishes exactly $v$ times (possesses $v$ internal nodes). Harmonic and Morse oscillators, being the basic models for approximation of vibrational motion in diatomic molecules, are the most famous examples of exact solution of the 1D equation leading to analytical dependence of eigenvalues $E^v$ and eigenfunctions $\varphi^v$ on $v$-values [1, 2]. A shape of rovibrational (radial) wavefunction (WF) of a diatomic state can be recognized experimentally from the relative intensity distribution $I_v'(v')$ in emission spectrum originating from a singly excited rovibronic level $v'(J')$. Nodal structure of the upper state WF $|\varphi^v|^2$ then appears in the laser induced fluorescence (LIF) spectra as intensity $I_v'(v'')$ oscillation in full progression of vibrational bands stretching from $(v', v'' = 0)$ to $(v', v'' = m)$. This takes place in the case of so-called strongly non-diagonal electronic transitions, when equilibrium distances $r_m$ and $r_m''$ of the upper and lower states are markedly shifted, see Fig. 1. Since the vibrational quantum number $v'$ is equal to the number of nodes of $\varphi^{v'}$, the full vibrational LIF progression yields absolute vibrational assignment of the excited electronic state $A$. The situation becomes more subtle when an upper electronic state is subject to pronounced perturbations and the adiabatic approximation is apparently not valid [3]. In particular, for the first excited $A^1\Sigma^+$ and $b^3\Pi$ states of Rb-containing alkali diatomics, strong spin-orbit (SO) interaction matrix element $\zeta_{Ab}^{SO}$ leads to apparent disorder in vibrational spacing observed in $A$ for Rb$_2$ and $B$ for NaRb. Though in such a situation vibrational numbering becomes a complicated task, unambiguous $v''$-assignment of NaRb A-state was achieved in $[4, 8]$ by analyzing LIF intensity distribution $I_v'(v'')$ in long $A \sim b \rightarrow X$ progressions. This became possible since the number of maxima in observed intensity $I_v'(v'')$ precisely follows the conventional 1D oscillation theorem. In case of alkali diatomics containing heavy Cs atom the situation becomes more complicated [4, 11] because of the adiabaticity parameter $\zeta_{Ab}^{SO}/\sqrt{\omega_A\omega_B}$ is close to one for the $A \sim b$ complex, $\omega_A$, $\omega_B$ being harmonic frequencies. A significant mixing of adiabatic (or
diabatic) vibrational WFs should inevitably affect the shape of the non-adibatic WFs; indeed, peculiarities in the $A \sim b \rightarrow X$ intensity distribution have been already observed for NaRb \[12\] and NaCs \[10\] molecules.

In present study we report on the breakdown of oscillation theorem in the $A \sim b \rightarrow X$ LIF of the KCs molecule unambiguously observed even for the lowest vibrational level of the $A$-state, and suggest, basing on the model study, a non-adiaibatic analogue of oscillation theorem which is valid for two-component states coupled by the sign-constant potential operator $V_{12} \neq 0$. It should be noted that polar alkali diatomics are of fundamental interest due to recent progress in the production and trapping of ultracold species \[13\] leading to their possible applications in quantum information devices controlled by an external electric field \[13\]. Favorably for the above applications, the singlet-triplet $A \sim b$ complex can provide with intermediate levels for efficient absorption-emission cycles into "absolute" ground state $a^3\Sigma^+ (E_a'', J'' = 0) \rightarrow A \sim b (E''; J' = 1) \rightarrow X^3\Sigma^+ (v'' = 0, J'' = 0)$ for formation of stable ultracold molecules \[16\].

The experimental setup and details of measurements can be found elsewhere \[10, 17\]. Briefly, KCs molecules were produced in a stainless steel heat pipe and kept at about 280°C temperature. The scanned diode lasers with 850 nm, 980 nm and 1020 nm laser diodes were employed for $A \sim b \leftarrow X$ excitation. Backward LIF was collected on the input aperture of the Fourier transform spectrometer Bruker IFS 125HR with the resolution 0.03 cm$^{-1}$ leading to the uncertainty of the line positions about 0.003 cm$^{-1}$. Relative intensity distributions were determined with about 5% uncertainty taking into account the spectral sensitivity of the InGaAs detector. Fig. 2 presents $A \sim b \rightarrow X$ LIF intensities from the levels with $J' = 50, 109$ and 128 with respective term values 10188.33, 10401.79 and 10508.09 cm$^{-1}$ related to the minimum of the ground state potential energy curve \[17\]. These levels belong to the lowest vibrational level $v_A^{dii} = 0$ of the diabatic $A$-state with predominant singlet fraction $P_A^b = \langle \varphi_A^b | \varphi_A^b \rangle_r$ being 88.6%, 81.0% and

![FIG. 2: (color online) Relative intensity distributions in the $A \sim b (E''; J' = 1) \rightarrow X(v'' = 0, J'' = J' \pm 1)$ LIF spectra of KCs originated from the $J' = 50, 109$ and 128 levels with predominant fraction of the $v_A^{dii} = 0$ state. Numbers over bars denote vibrational quantum number of the ground X-state $v_X^\prime$. The inset zooms additional maximum for $J' = 50$.](image)

![FIG. 3: (color online) The two-component non-adibatic wavefunctions $\varphi_A^b (r)$ and $\varphi_b^s (r)$ calculated for the rovibronic levels of the KCs $A^3\Sigma^+ \sim b^3\Pi$ complex presented in Fig. 2. $\chi_A (r)$ is diabatic WF of the deperturbed $A$-state for $v_A^{dii} = 0$. Insets enlarge a nodal structure of the non-adibatic $\varphi_A^b (r)$ wavefunctions in the region $r \in [3.5, 4.5]$ Å.](image)
79.6%, respectively. This was determined by a de-perturbation analysis of the experimental term values of the KCs $A \sim b$ complex in the framework of the inverted channel-coupling approach by means of the 4 × 4 model Hamiltonian constructed on Hund’s coupling case (a) basis functions similar to allow constructing diabatic $A^1\Sigma^+$ and $b^3\Pi_\Omega$ potentials and relevant SO coupling function (see Fig. 1) and to reproduce term values with experimental accuracy of about 0.005 cm$^{-1}$. Indeed, a single maximum of intensity distribution in the LIF spectrum originating from the level with $J' = 128$ confirms the energy based $v_A^{di} = 0$ assignment. However, manifestation of a smaller second maximum observed in the region of 8900 cm$^{-1}$ for the levels $J' = 50$ and 109 unambiguously highlights the presence of at least one additional oscillation in a relevant upper state WF, thus, at least for the $J' = 50$ and 109 there is an apparent contradiction between the observed intensity distribution and the vibrational assignment based on the deperturbation arguments.

To elucidate such a discrepancy the $A \sim b(E^{v'}; J') \rightarrow X(v''; J'' = J' \pm 1)$ intensities $I_{A\sim b \rightarrow X}^{v''}$ were simulated as

$$I_{A\sim b \rightarrow X}^{v''} \sim \nu_{A\sim b \rightarrow X}^{v''} \sum_{\nu} \left| \langle \varphi_{A}^{v''} | d_{AX} | \chi_{X}^{v''} \rangle \right|^2,$$  

where $d_{AX}(r)$ is the spin-allowed $A^1\Sigma^+ - X^1\Sigma^+$ transition dipole moment, $\nu_{A\sim b \rightarrow X}$ is the transition wave number, $E_{A\sim b}^{v''}$ is the energy of the rovibronic level $v'(J')$ of the $A \sim b$ complex, $\varphi_{A}^{v''}(r)$ is the singlet $A$-state fraction of non-adiabatic WF, while $E_{X}^{v''}$ and $\chi_{X}^{v''}(r)$ are the adiabatic energy and WF of the $X$-state, respectively. As follows from Eq. (1), the intensities provide information essentially about the singlet $A$-state WF since the $b^3\Pi \rightarrow X^1\Sigma^+$ transition is strictly forbidden, i.e. $d_{AX} = 0$. To obtain the required non-adiabatic WF the simplified two-channel form of Hamiltonian was used.

$$\left[ \begin{array}{cc} h_1 & V_{12} \\ V_{21} & h_2 \end{array} \right] \begin{pmatrix} \varphi_1^{v'} \\ \varphi_2^{v'} \end{pmatrix} = E^{v'} \begin{pmatrix} \varphi_1^{v'} \\ \varphi_2^{v'} \end{pmatrix}$$  

was used. Here, $v \in [0, N]$ is the ordering number of the eigenvalue $E^{v'}$, $h_i$ are the ordinary 1D radial Hamiltonians

$$h_i = \frac{1}{2\mu} \frac{d^2}{dr^2} + U_i(r) + \frac{J(J+1)}{2\mu r^2}; \quad i \in [1, 2]$$  

coupled by Hermitian operator $V_{12}(r)$, $\mu$ is the reduced mass, $U_i$ are diabatic rotationless potentials while bound state eigenfunctions $\varphi_i^{v'}$ obey the conventional boundary $\varphi_i^{v'}(0) = 0; \varphi_i^{v'}(r \rightarrow \infty) \rightarrow 0$ and normalization $P_i^{v'} = \int \varphi_i^{v'}(r) \varphi_i^{v'}(r) \, dr = 1$ conditions, where $P_i^{v'} = \langle \varphi_i^{v'} | \varphi_i^{v'} \rangle$. Inserting into Eq. (2) the deperturbed diabatic potentials $U_i \equiv U_A(r), U_2 \equiv U_b(r)$ and SO coupling function $V_{12} \equiv \sqrt{\Delta E_{so}}(r)$, see Fig. 1, the non-adiabatic eigenvalues $E^{v'} = E_{A\sim b}^{v'}$ and eigenfunctions $\varphi_1^{v'} = \varphi_b^{v'}(r)$ and $\varphi_2^{v'} = \varphi_a^{v'}(r)$ of the $A \sim b$ complex were obtained. The obtained WFs are presented in Fig. 3 along with the diabatic $A$-state WFs $\chi_A(r)$ corresponding to $v_A^{di} = 0$ level. The present deperturbation model accounts only for the SO interaction between $A^1\Sigma^+$ state and $b^3\Pi_{\Omega = 0}$ component of the triplet state as applied in and adiabatic eigenvalues $E_{X}^{v''}$ and eigenfunctions $\chi_{X}^{v''}(r)$ of the ground state from yielded the intensity distributions shown in Fig. 2. Remarkable agreement of the predicted intensities with their experimental counterparts justifies the applicability of the simplified 2 × 2 deperturbation model. As can be seen from Fig. 3 for $J' = 128$ the shape of non-adiabatic WF $\varphi_b^{v'}(r)$ in the classically allowed region of motion $r \in [4.5, 5.5]$ Å is similar to a diabatic one, thus confirming the $v_A^{di} = 0$ assignment, see Fig. 2. Additional WFs minimum at $r = 5.33$ Å has a very small amplitude of 0.006 and can not be seen in the scale of Fig. 3. In contrast, WFs $\varphi_b^{v'}(r)$ for $J' = 109$ and 50 have a pronounced additional minimum and a respective node located at $r \approx 5.1$ Å which is responsible for the second maximum in the respective intensity distributions in Fig. 2 thus explaining the observed breaking.
of the oscillation theorem. Careful analysis (see insets in Fig. 3) reveals that the full number of nodes \( n_A \) of the non-adiabatic WF \( \psi_A^{\nu} \) for \( J' = 50, 109 \) and 128 levels possessing respective ordering numbers of eigenvalues \( \nu' = 20, 19 \) and 19, is equal to \( n_A = 14, 13 \) and 13 respectively. However, most “additional” nodes of \( \psi_A^{\nu} \) apparently could not be observed in the LIF spectra since they are located in the classically forbidden region of motion of the deperturbed A-state where the amplitude of WF is very small, see insets in Fig. 3. The non-adiabatic \( \psi_B^{\nu} \) in Fig. 3 for \( J' = 50, 109 \) and 128 possesses the respective number of nodes \( n_B = 16, 15 \) and 15 which is close to the diabatic \( b \)-state vibrational number \( v_B^0 = 16, 15 \) and 14 as discovered from rigorous deperturbation analysis [18].

To find an analogue of oscillation theorem for a two-component system \( \psi_1^{\nu}, \psi_2^{\nu} \) it is necessary to establish a connection between the respective number of nodes \( n_1, n_2 \) and the ordering number of the eigenstate \( \nu \). For this purpose it is useful to trace such a connection for the KCs \( A \sim b \) system under study at different strength of the SO interaction \( V_{12} = \lambda \times \sqrt{2} \xi_{\alpha} \xi_{\beta} \) which is varied by a factor \( \lambda \). To get rid of the influence of a particular \( J' \) value determining the effective potential, the simulation of \( \psi_A^{\nu} \) and \( \psi_B^{\nu} \) yielding the respective number of nodes \( n_A \) and \( n_B \) was performed for the rotationalless case \( J' = 0 \). The resulting \( \nu' \)-dependencies of \( n_A \) and \( n_B \) values are presented on Fig. 3 for different \( \lambda \) values.

It can be seen that, at fixed \( \lambda, \) for all \( \nu' \) below some particular \( v_{\text{max}}^{\nu} \), the number of nodes coincides with \( \nu' \): \( n_a = n_b = \nu' \leq v_{\text{max}}^{\nu} \), where \( v_{\text{max}}^{\nu} \) monotonically increases with \( \lambda \) being \( v_{\text{max}}^{\nu} = 19, 33 \) and 57 for \( \lambda = 1, 5 \) and 10, respectively. The smallest number \( v_{\text{max}}^{\nu} = 17 \) corresponds to vanishing perturbation \( \lambda \to 0 \). The cases \( n_A = n_B < \nu' \) and \( n_A \neq n_B \ll \nu' \) take place for high levels \( \nu' > v_{\text{max}}^{\nu} \). The quasi-periodic alterations of \( n_A \) and \( n_B \) observed at \( \nu' > v_{\text{max}}^{\nu} \) is attributed to accidental degeneration of deperturbed levels of diabatic \( A \) and \( b \) states [18].

The most important feature is that in all cases the arithmetic mean of the number of nodes \( n_A \) and \( n_B \) never exceeds the ordering number \( \nu' \). This general property allowed us to formulate a non-adiabatic analogue of the oscillation theorem valid for two-component states mutually perturbed by a sign-constant potential operator \( V_{12}(r) \neq 0 \): (1) the lowest bound \( \nu = 0 \) state is not a degenerate one and the respective two-component WFs \( \varphi_1^{\nu=0}, \varphi_2^{\nu=0} \) do not have nodes; (2) the number of nodes \( n_1 \) and \( n_2 \) of the wavefunctions \( \varphi_1^{\nu} \) and \( \varphi_2^{\nu} \) corresponding to the \( \nu \)-th non-adiabatic eigenvalue obeys the inequality \( n_1 + n_2 < 2 \nu \). Rigorous mathematical proof of the theorem is obtained basing on minimax principle [20] and is presented in the Appendix. In practical implementation of the theorem a constant sign of the coupling operator is important only for the limited region where the WFs are localized. In particular, it is easy to verify that the theorem is valid for the rovibronic \( J' = 50, 109 \) and 128 levels of the KCs \( A \sim b \) complex studied above since \( n_A + n_B < 2 \nu' \) (see Fig. 3).

Thus, the spin-orbit coupling effect can affect the nodal structure of a multi-component diatomic vibrational WF leading to a breakdown of the conventional 1D oscillation theorem. Nevertheless, for two-component states coupled by the sign-constant potential operator non-adiabatic analogue of the oscillation theorem has been formulated and proved.

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**APPENDIX: Proof of Oscillation Theorem for Nonadiabatic Diatomic States**

I. NOTATIONS AND GENERAL NOTES

Here we consider the two-component Schrödinger equation (see Eq.(2) of the Main Text) for the \( 2 \times 2 \) matrix Hamiltonian \( \mathbf{H} \):

\[
\mathbf{H} \varphi^\nu = \begin{bmatrix} h_1 & V_{21} \\ V_{21} & h_2 \end{bmatrix} \begin{bmatrix} \varphi_1^\nu \\ \varphi_2^\nu \end{bmatrix} = E^\nu \begin{bmatrix} \varphi_1^\nu \\ \varphi_2^\nu \end{bmatrix} = E^\nu \varphi^\nu. \tag{A1}
\]

The components \( h_{1,2} \) of \( \mathbf{H} \) in Eq.(A1) have the traditional form \( h_k = -\frac{1}{2m}\frac{\partial^2}{\partial x^2} + U_k(x) \) with some effective mass \( \mu \) and real-valued potentials \( U_k \) (here the rotational part of energy is included in \( U_k \)). The interaction operators are supposed to be some real-valued potentials \( V_{21}(x) = V_{12}(x) \), and the energy levels \( E^\nu \) are enumerated in increasing order, taking degeneracy into account, by traditional vibrational quantum number \( \nu = 0, 1, 2, \cdots \). The matrix form of Eq.(A1) is equivalent to the following system of equations:

\[
\begin{align*}
&h_1 \varphi_1^\nu + V_{21} \varphi_2^\nu = E^\nu \varphi_1^\nu \\
&V_{21} \varphi_1^\nu + h_2 \varphi_2^\nu = E^\nu \varphi_2^\nu.
\end{align*} \tag{A2}
\]

For molecular problems one may suppose the components \( \varphi_{1,2}^\nu(\alpha) \) of a vector-function \( \varphi^\nu \) to be real-valued functions defined for some region \( \Omega \), being the same for both components. It is supposed here \( \Omega = [\alpha, \beta] \subset \mathbb{R}^1 \) for some finite (or infinite) \( \alpha \) and \( \beta \). When one of the ends of the interval \([\alpha, \beta]\), for example, \(\alpha\), is finite, one supposes that both components of solution \( \varphi^\nu \) obey the Dirichlet boundary condition at this point: \( \varphi_{1,2}^\nu(\alpha) = 0 \).
In any case only bound states are considered and solution \( \psi^n \) is supposed to be normalized by condition
\[
\langle \psi^n | \psi^n \rangle = \langle \psi^n_1 | \psi^n_1 \rangle + \langle \psi^n_2 | \psi^n_2 \rangle = 1. \tag{A3}
\]
It is worth to note that for invertible potential \( V_{12}(x) \) one may use the system Eq.(A2) to find \( \psi^n_1 \) as a solution of the 4-th order differential equation (similar relation holds for \( \psi^n_2 \)):
\[
[(h_2 - E^n)V_{12}^{-1}(h_1 - E^n) + V_{12}]\psi^n_1 = 0. \tag{A4}
\]
In particular, as a result of a well known property of the Cauchy problem, the following Lemma is useful for analysis of Eq.(A2):

**Lemma.** For invertible potential \( V_{12}(x) \) the components of any nontrivial solution \( \psi^n \) of the problem (A1) cannot be identically zero into some open subregion of \( \Omega \).

For the 1D one-component problems it is impossible that the wave function and its gradient vanish simultaneously at some point. In particular, near the nodal points the wavefunction changes the sign. For the multi-component problems situation is not so simple. It is possible that at some point some component of the wave function only touches the axes. When the interaction potential does not vanish at this point, it follows from Eq.(A2) that both components \( \psi^n_{i,2}(x) \) vanish along with their second derivatives. This special situation is not stable with respect to small perturbations and we ignore it here. That is, we consider as the nodal points only the ones for which functions change the sign. Similar issues for one component problems for \( \Omega = \mathbb{R}^n(n > 1) \) enforce to analyze the regions of a constant sign for wave functions [2].

## II. SOME STATEMENTS

For one-component one-dimensional problems it is well known that the vibrational state number \( v \) coincides with the number of nodal points (see Ch.XIII.3 in [21] or Ch.VI, §6 in [21]). For matrix equation (A1) the problem is much more difficult.

Let \( \psi^n \) be an eigenvector of the two-component matrix Hamiltonian \( H \) with energy \( E^n \) and components \( \psi^n_1 \) and \( \psi^n_2 \). Let us analyze the regions of a constant sign for functions \( \psi^n_{i,2} \), that is, the intervals where the function has a definite sign and changes it at the ends. The number \( K_j \) of such regions corresponds to \( n_j = K_j - 1 \) nodal points of \( \psi^n_j \) \((j = 1, 2)\). Let us suppose that \( \psi^n_1 \) has \( K_1 \) regions \( \Omega_1^{(1)} \) \((j = 1, 2, \ldots, K_1)\) of a constant sign. One may define for each of regions \( \Omega_1^{(1)} \) the function \( \psi^{(1)}_j \) that equals to \( \psi^n_1 \) on \( \Omega_1^{(1)} \) and equals to zero out of \( \Omega_1^{(1)} \). Let us suppose that \( \psi^n_2 \) has \( K_2 \) regions \( \Omega_2^{(2)} \) \((k = 1, 2, \ldots, K_2)\) of a constant sign and \( \psi^{(2)}_k \) are the functions similar to the ones for the first component of \( \psi^n \). Hence \( \psi^n \) defines the linear space \( \mathcal{K} \) of \( (K_1 + K_2) \)-dimensional vectors \( C \) defined by any set of \( K_1 \) coefficients \( c_j \) and set of \( K_2 \) coefficients \( d_k \) and corresponding vector-functions \( \chi \) with components defined by the relation
\[
\chi_1 = \sum_{j=1}^{K_1} c_j \varphi^{(1)}_j \quad \chi_2 = \sum_{k=1}^{K_2} d_k \varphi^{(2)}_k. \tag{A5}
\]

Note that \( \chi_1,2 \) and their gradients have to be the square integrable functions on \( \Omega \).

Here we will study some properties of the matrix \( M \), defined for the above mentioned space \( \mathcal{K} \) by the vector-function \( \chi \) in the following way:
\[
(C, MC) = \sum_{j,k} (c_j - d_k)^2 \langle \varphi^{(1)}_j | V_{12} | \varphi^{(2)}_k \rangle. \tag{A6}
\]

The described notations are used in all statements of this section. We use also the symbol \( [n/2] \) for the integer part of the \( n/2 \) value. The following relation is important for our discussions:
\[
n = \left[ \frac{n}{2} \right] + \left[ \frac{n + 1}{2} \right]. \tag{A7}
\]

Our further discussion is based on the simple expression of energy functional \( E(\chi) \) associated with the Hamiltonian \( H \), for the vector-function \( \chi \) with components of the form (A5).

**Statement 1.** If \( \psi^n \) is a solution of Eq.(A1), then for any vector \( C \in \mathcal{K} \) one may write
\[
E(\chi) = E^n \langle \chi | \chi \rangle - \sum_{j,k} (c_j - d_k)^2 \langle \varphi^{(1)}_j | V_{12} | \varphi^{(2)}_k \rangle. \tag{A8}
\]

**Proof.** The use of a standard form for the energy functional (with kinetic energy expressed as squared gradient of wavefunction) and integration by parts enables to write, due to Eq.(A5),
\[
E(\chi) = \sum_{j=1}^{K_1} c_j^2 \langle \varphi^{(1)}_j | h_1 | \varphi^{(1)}_j \rangle + \sum_{k=1}^{K_2} d_k^2 \langle \varphi^{(2)}_k | h_2 | \varphi^{(2)}_k \rangle + 2 \sum_{j,k} c_j d_k \langle \varphi^{(1)}_j | V_{12} | \varphi^{(2)}_k \rangle, \tag{A9}
\]

where integration in each of integral in the sums is done over the regions \( \Omega_1^{(1)} \), \( \Omega_2^{(2)} \) or \( \Omega_1^{(1)} \cap \Omega_2^{(2)} \), respectively. The use of Eq.(A2) gives immediately
\[
E(\chi) = E^n \left[ \sum_{j=1}^{K_1} c_j^2 \langle \varphi^{(1)}_j | \varphi^{(1)}_j \rangle + \sum_{k=1}^{K_2} d_k^2 \langle \varphi^{(2)}_k | \varphi^{(2)}_k \rangle \right] - \sum_{j=1}^{K_1} c_j^2 \langle \varphi^{(1)}_j | V_{12} | \varphi^{(1)}_j \rangle - \sum_{k=1}^{K_2} d_k^2 \langle \varphi^{(2)}_k | V_{12} | \varphi^{(2)}_k \rangle + 2 \sum_{j,k} c_j d_k \langle \varphi^{(1)}_j | \varphi^{(2)}_k \rangle. \tag{A10}
\]
This is exactly expression (A8). ■

**Statement 2.** There are no more than \((K_1 + K_2 - 1)\) regions \(\Omega_j^{(1)} \cap \Omega_k^{(2)} \subset \Omega\), where the product \(\varphi_j^v \varphi_k^v\) differs from zero and conserves the sign.

**Proof.** Let us suppose that there exist \(K_j\) regions of a constant sign for \(\varphi_j^v\). There are no more than \(n_j = K_j - 1\) internal points of \(\Omega\) where \(\varphi_j^v\) changes the sign. Hence, there are no more than \(n_1 + n_2\) points where \(\varphi_1^v \varphi_2^v\) changes the sign. That is, there exist no more than \((K_1 - 1) + (K_2 - 1) + 1 = (K_1 + K_2 - 1)\) non-empty regions of the type \(\Omega_j^{(1)} \cap \Omega_k^{(2)}\) where \(\varphi_j^v \varphi_k^v\) conserves the sign. ■

**Statement 3.** Let us suppose that the sign of the potential \(V_{12}(x)\) is fixed. Then the matrix \(M\) defined by Eq.(A6) has no less than \(\left[\frac{K_1 + K_2 + 1}{2}\right]\) non-negative eigenvalues.

**Proof.** According to definition, the quadratic form \((C,M)\) is determined by a system of matrices of rank 1, each of which has only one nonzero eigenvalue \(2\langle \varphi_j^{(1)} | V_{12} | \varphi_k^{(2)} \rangle\). According to Statement 2, among those eigenvalues there are no more than \((K_1 + K_2 - 1)\) nonzero values; half of them is negative, while another half is positive. In any case the largest number of strictly negative integrals is no more than \(\langle \varphi_j^{(1)} | V_{12} | \varphi_k^{(2)} \rangle\). According to the minimax principle (see, e.g. Ch.VI. of [22] or Sect.XIII.1 of [20]), this means that no more than \(\left[\frac{K_1 + K_2 + 1}{2}\right]\) eigenvalues of matrix \(M\) are strictly negative. Hence, the remaining eigenvalues of \(M\) are non-negative and their number is no less than

\[
(K_1 + K_2) - \left[\frac{K_1 + K_2}{2}\right] = \left[\frac{K_1 + K_2 + 1}{2}\right]. \tag{A11}
\]

■

### III. THE NODAL POINTS IN TWO-COMPONENT PROBLEM

For 1D problems the wavefunction of the state with vibrational number \(v = 0,1,2,\ldots\) has exactly \(v\) nodes [20, 21]. When \(\text{dim}(\Omega) > 1\), for one-component problem one may only prove that, for a given state, the number of regions of a definite sign is not too large [2]. For the two-component system considered here one may prove some analogue of these statements. The proof is similar to the one in the one-component case, but it requires some special modifications.

**Theorem.** For the stationary state \(E^v, \varphi^v\) of the problem \((\ref{A1})\) with the interaction potential \(V_{12}\) of a definite sign the number of points \(n_1\) and \(n_2\), where the respective components \(\varphi_1^v\) and \(\varphi_2^v\) change their signs, the following inequalities hold:

\[
\frac{n_1 + n_2 + 1}{2} \leq v. \tag{A12}
\]

and, hence,

\[
\frac{n_1 + n_2}{2} \leq v. \tag{A13}
\]

**Proof.** Let us consider the space \(\mathcal{K}\) associated with regions of constant sign for components of the wavefunction \(\varphi^v\), as was described in Section [11]. Each vector \(C \in \mathcal{K}\) may define some vector-function \(\tilde{\chi}\) (see Eq.(A5)), due to Statement 1 the corresponding energy functional value can be written as

\[
E(\tilde{\chi}) = E^v(\tilde{\chi}|\tilde{\chi}) - (C,MC). \tag{A14}
\]

According to Statement 3 (note that, \(K_j = n_j + 1\)), the matrix \(M\) has no less than

\[
T = \left[\frac{K_1 + K_2 + 1}{2}\right] = \left[\frac{n_1 + n_2 + 3}{2}\right] = \left[\frac{n_1 + n_2 + 1}{2}\right] + 1 \tag{A15}
\]

non-negative eigenvalues, each of them being associated with some vector \(C\) and corresponding vector-function \(\tilde{\chi}\).

Let us suppose \(T \geq v + 2\). Then one may find at least two independent normalized vectors \(\tilde{\chi}_1^{(1,2)}\) (or, equivalently, \(C^{(1,2)}\)) \(\in\mathcal{K}\) being orthogonal to \(v\) exact solutions \(\varphi_0^v, \varphi_1^v, \ldots, \varphi_{v-1}^v\) of Eq.(A1) with lowest energies. For these vectors \((C^{(1,2)},MC^{(1,2)}) \geq 0\) \((j = 1,2)\), and, hence, \(E(\tilde{\chi}_1^{(1,2)}) \leq E^v\). It follows from the variational principle (see, e.g. Ch.VI. of [22] or Sect.XIII.1 of [20]) that both functions \(\tilde{\chi}_1^{(1)}\) and \(\tilde{\chi}_2^{(2)}\) are solutions of Eq.(A1) with energy \(E^v\) and one may construct, as a linear combination of these vector-functions, a non-zero solution \(\tilde{\chi}\) of Schrödinger equation, for which, at least for one of regions \(\Omega_j^{(1)}\) or \(\Omega_k^{(2)}\), the corresponding component of the solution \((\chi_1\text{ or }\chi_2)\) identically equals to zero. This is however impossible, according to the Lemma of Section [1]. Hence, \(T < v + 2\), or, equivalently, \(T \leq v + 1\), and one may write

\[
\frac{n_1 + n_2}{2} \leq \frac{n_1 + n_2 + 1}{2} \leq v. \tag{A16}
\]

The use of Eq.(A17) proves the statement. ■

**Corollary 1.** For the Theorem’s conditions, the components of the function \(\varphi^{v=0}\) conserve their signs into \(\Omega\). Indeed, for \(v = 0\) inequality \((A13)\) means \(n_1 = n_2 = 0\).

**Corollary 2.** For the Theorem’s conditions for the ground state and \(V_{12}(x) \leq 0\) the signs of \(\varphi_1^v\) and \(\varphi_2^v\) coincide, while for \(V_{12}(x) > 0\) the signs are opposite.

**Proof.** Let \(\varphi_{1,2}^v\) be the components of the ground state vector-function \(\varphi^v\). According to the Corollary 1, the signs of \(\varphi_{1,2}^v\) are fixed. Hence, for the potential \(V_{12}\) of fixed sign one may conclude that \(\langle \varphi_1^v | V_{12} | \varphi_2^v \rangle \neq 0\). The mean value of the Hamiltonian has the form

\[
\langle \varphi_1^v | H | \varphi_2^v \rangle = \langle \varphi_1^v | h_1 | \varphi_1^v \rangle + \langle \varphi_1^v | h_2 | \varphi_2^v \rangle + 2\langle \varphi_1^v | V_{12} | \varphi_2^v \rangle. \tag{A17}
\]
If one replaces $\varphi_v^2$ by $-\varphi_v^2$ and calculates the mean value of the Hamiltonian $H$, the variational principle yields immediately $\langle \varphi_1^v | V_{12} | \varphi_2^v \rangle < 0$. Hence, the signs of $\varphi_1^v$, $\varphi_2^v$, and $V_{12}$ are opposite.

**Corollary 3.** For the Theorem’s conditions the ground state is not degenerate. Indeed, two vector-functions with components which conserve their signs and the sign of the product $\varphi_1^v \varphi_2^v$ cannot be orthogonal. Hence, the ground state is not degenerate. See also Ref. [2].

**Note.** If $\dim(\Omega) > 1$ one has no rights to insist on the validity of the Theorem. However, for the interaction potential $V_{12}(x)$ of a fixed sign one may prove Corollaries 1 - 3 by similar arguments.

**IV. CONCLUSION**

For eigenvalue problems with matrix Hamiltonians the structure of nodal points is much more complex than for a one-component 1D problem, and the nodal structure of multi-component problems is of less importance than for one-component ones. Nevertheless, for the interaction potential of a fixed sign there are some analogues of the oscillation theorems. In particular, for a two-component problems for $\mathbb{R}^1$ axes (or a half-axes) one may prove the following statements: (1) the ground state is not a degenerate one, and the components of the ground-state wavefunction conserve their sign, defined by the sign of interaction potential; (2) for the state number $v$ (for energies in increasing order $v = 0, 1, 2, \ldots$) the wavefunction components $\varphi_1^v$ and $\varphi_2^v$ have the arithmetic mean of the number of nodal points $(n_1 + n_2)/2$ not larger than $v$. We suppose it to be sufficient for practical applications.

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