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ATOMS, MOLECULES, OPTICS

Decay of a Negative Molecular Ion in a Constant Electric Field

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Abstract—The problem of the shift and broadening of the electron energy levels in the field of two 3D short-range potentials (e.g., the model of a negative molecular ion) by a constant electric field **F** is considered. The interaction of an electron with attraction centers is taken into account in the effective range approximation. We analyze the cases when both centers maintain weakly bound *s* states and when the electron state in the field of one of the centers is a *p* state. Exact numerical results for the shift and the width of the energy levels of a quasi-molecule as functions of field **F**, distance *R* between atomic centers, and the orientation of the quasi-molecule axis relative to vector **F** are presented, as well as the results of analytic treatment for a number of limiting cases. The exact values of complex energies of the quasi-molecule are compared with analytic results for a weak field in the case of identical *s* centers [26], as well as nonequivalent *s* centers and *s*–*p* centers; the applicability boundaries of the weak field approximation are established. It is shown that for large values of *R*, the position and width of the levels in a strong field are correctly described in perturbation theory in the exchange interaction. We analyze the field-induced quasi-intersection of molecular energy levels of the system with nonequivalent atomic centers and peculiarities in the energy level widths associated with this intersection. The results make it possible to qualitatively interpret the results of numerical calculations of the probability of homo- and heteronuclear molecules being ionized by a low-frequency laser field.

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1. INTRODUCTION

The interaction of a molecular system with a constant electric field **F** has attracted the attention of researchers in recent years due to its close relation to phenomena in strong low-frequency laser fields. In particular, qualitative description of the high-energy plateau in the higher-harmonic generation spectrum of laser radiation emitted by gases [1] and above-threshold ionization of atoms and molecules [2] is based on the well-known rescattering model [3]. In this model, ionization of a quantum system in the effective constant electric field is a source of low-energy electrons that are accelerated in the laser field and that recombine with the emission of high-energy radiation; or they are scattered from the atomic–molecular core and form an angular distribution of electrons in the region of the high-energy plateau upon ionization. It is well known that the probability of an atom being ionized by a strong low-frequency field is determined to a high degree of accuracy by the probability of ionization by a constant field *F* averaged over the period and determined by the instantaneous value of the laser field amplitude [4–7]. An analogous result for molecules was obtained quite recently [8]. Even for a diatomic molecule, the problem is complicated as compared to the case of an atom due to an additional parameter (internuclear distance vector **R**) appearing in the problem. This leads to the orientation dependence (on angle θ between **R** and **F**) and the spatial dependence (on distance *R* between the nuclei) of the ionization probability of the molecule. The dependence on *R* is essentially nonlinear, which does not permit us to obtain simple approximations for ionization probabilities in a wide range of *R* values. For this reason, analytic results for the ionization probability of molecules are limited to the tunnelling regime and small internuclear distances [8].

A strong field may noticeably change the distance *R* between the nuclei; therefore, the dependence of the shift and field broadening of the molecular term on *R* is of special interest. The shifts and widths of the electron molecular terms in a constant field were calculated numerically in [9] for the simplest molecule (H_2^+ ion) by direct numerical integration of the Schrödinger equation. Analogous but more detailed numerical analysis was carried out in [10, 11] (see also [12]). These numerical results confirmed the linear field dependence of the position of the ground (ϵ_+) and first excited (ϵ_-) states of H_2^+ with increasing *R*, which was predicted earlier in [13]:

$$\epsilon_\pm(F) \approx \epsilon_\pm(F = 0) \mp |e| FR/2.$$

Such a dependence of energy on the field strength and internuclear separation is due to localization of an electron at one of the centers, which leads to the emergence of a dipole moment $\pm |e|\,\mathbf{R}/2$ interacting with the field [10, 11, 13]. Another interesting feature of the

interaction of the H_2^+ ion with constant field **F** is the nonmonotonic dependence of width Γ^- of the excited state on the internuclear spacing upon an increase in R. The physical origin of such a dependence is disputable, and three different hypotheses exist concerning this dependence [9, 10, 14]. In [9], the nonmonotonic dependence $\Gamma^-(R)$ is explained by charge resonance[1] existing between the ground state and the first excited state of H_2^+ (the wavefunctions of these states for **F** = 0 exhibit opposite symmetries relative to transposition of nuclei) and by the lowering of the barrier for tunneling from the excited state for certain values of R and F. Conversely, the nonmonotonic behavior of the width is explained in [10] by the involvement of intermediate resonances associated with highly excited levels of H_2^+ into tunneling of a particle through the barrier formed by the field of the two centers and the constant field. Finally, the nonmonotonic dependence of Γ^- on R is attributed in [14] (based on analysis of the 2D model of the H_2^+ ion in field **F** parallel to **R**) to the interference of two waves emerging during tunneling from the excited state; one of these waves is determined by direct tunneling, while the other is determined by tunneling with rescattering from the neighboring atomic center followed by the reflection from the barrier formed by field **F**. (It should be noted that this interpretation is confirmed in our study by the results of an exactly solvable 3D model.) The orientation dependence of widths $\Gamma^\pm(\theta)$ of H_2^+ terms was calculated numerically in [16], in which it is shown that the positions of maxima and minima of width $\Gamma^-(\theta)$ considerably depend on the orientation of the H_2^+ ion, while the width $\Gamma^+(\theta)$ of the ground state is a smooth function of θ. (Analogous results were also obtained for the terms of multielectron molecules modified by an electric field [17]. In this case, the existence of two states in charge resonance is also of fundamental importance.)

Although the contemporary level of the computational technique permits direct numerical analysis of the Schrödinger equation for simple molecules in an electric field, this approach does not give results in a wide range of parameters of the problem due to significant technical difficulties; in some cases (e.g., for H_2^+), this approach even fails to give an unambiguous physical interpretation of the numerical results. For this reason, it is expedient to use simplified models for explaining the qualitative features of interaction of a strong electric field with multicenter (molecular) systems. For example, it was shown in [18] that some patterns in the shifts and widths of energy levels of the H_2^+ ion aligned with field **F** can be described qualitatively using the 1D model with two Coulomb potentials, although the Schrödinger equation was also solved numerically in [18]. Numerical analysis of ionization of H_2^+ in the 2D model was carried out in [19]. Exactly solvable analytic models are known only for the case of short-range atomic centers, which corresponds, for example, to the interaction of a negative molecular ion with an electric field. Detailed analysis of the simplest 1D model (electron in the field of two 1D zero-range (δ) potentials in a constant electric field) was carried out in [20–22]; in recent publication [23], this model was used for a qualitative description of photodetachment of an electron from the O_2^- negative molecular ion in parallel geometry (**F** ∥ **R**). More realistic results should be expected in simulating atomic centers by 3D δ potentials whose action is equivalent to imposition of appropriate boundary conditions on the wavefunction near the centers [24]. It is well known that in zero electric field, an electron in the field of two attracting zero-range potentials has two bound states [25]. These states precisely form a pair of charge-resonant states [15] which, as noted above, play an important role in the description of molecules in an electric field. The system of short-range atomic centers was considered for the first time in [26], where equations for molecular terms of a multicenter systems, as well as analytic expression for the shifts and widths of the ground state and the excited state of an electron in the field of two identical 2D δ potentials, were derived in the weak electric field approximation (in which the shift of a level is described by the quadratic Stark effect, and the width is determined by the semiclassical tunneling probability).

In this study, we derived general relations for calculating the shift and width of bound states of an electron in the field of several atomic centers taking into account the interaction of the electron with each center ($i = 1, 2, ..., N$) in the effective range approximation. These results are applicable to the case of short-range potentials sustaining (in zero field) the bound states with zero orbital angular momentum l_i (s centers), as well as to the case with $l_i > 0$; e.g., for $l_i = 1$ (p centers). If all atomic centers are s centers, our model coincides with the model of δ potentials [26] in the approximation $r_0^{(i)} = 0$, where $r_0^{(i)}$ is the effective range [27] corresponding to the ith s center. For a two-center system with s centers, as well as with s and p centers, exact (with the model used here) numerical results for the shift and width of the energy levels of the quasi-molecule are given as functions of the electric field F, separation R between the centers, and orientation of the quasi-molecule axis relative to vector **F**. The analytic expressions are obtained for the shift and

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[1] Two energy levels are in charge resonance if the distance between them becomes negligibly small upon an increase in R, while the dipole matrix element of the transition becomes anomalously large ($\sim R$) [15].

width of the levels using perturbation theory in the exchange interaction (i.e., in the small ratio of the overlap integral of one-center wavefunctions of an electron localized at different centers to the energy difference between the ground state and the excited state of the quasi-molecule in field $\mathbf{F}$), as well as analytic formulas for the shift and width of the electron energy levels in the field of two nonequivalent ($s-s$ and $s-p$) centers in the weak field approximation, in which the expansion of the level shift begins with the terms of order F (linear Stark effect).

As in all publications on the interaction of a molecule with electric field $\mathbf{F}$ mentioned above, angle θ between the direction of the molecular axis and vector $\mathbf{F}$ in our model is treated as a parameter of the problem; i.e., we assume that the predicted angular dependences can be observed only in experiments with ensembles of molecules aligned (in the case of identical centers) or oriented (in the case of nonequivalent centers) in a fixed direction. (Corresponding results for an ensemble of freely rotating molecules can be obtained by averaging over θ.) In recent years, a number of effective methods have been developed for the alignment of molecules by relatively weak laser radiation (laser alignment), which are described, in particular, in reviews [28, 29] and are used in most contemporary experiments on observing angular distributions during ionization of molecules by a high-intensity femtosecond laser radiation. Recently, first experiments [30] on orientation of asymmetric molecules by two-frequency laser radiation have been carried out; the orientation is preserved for several rotational periods of the molecule after an abrupt interaction with a laser pulse.

In Section 2 of this paper, the formalism of the effective range theory for a multicenter system is briefly described. In Sections 3−5, the shift and width of the energy levels of two-center systems with identical (Section 3) and nonequivalent (Section 4) ss centers, as well as s and p centers (Section 5), are analyzed. In Section 6, the main results are summarized and a qualitative interpretation is given of some results of numerical calculations of the ionization probability for homo- and heteronuclear molecules by a low-frequency laser field. The Appendix contains a number of required analytical formulas.

In this article, we will use atomic units: $\hbar = m = |e| = 1$.

2. BASIC RELATIONS OF THE EFFECTIVE RANGE THEORY FOR A MULTICENTER SYSTEM IN AN EXTERNAL FIELD

We first consider the relations in effective range theory, which are essential for calculating energy ϵ of the quasi-stationary state appearing when interaction $V(\mathbf{r})$ with an external static field is superimposed on an electron in a weakly bound state $\psi_{\kappa l m_l}^{(0)}(\mathbf{r})$ with orbital

angular momentum l and energy $E_0 = -\kappa^2/2$ in the short-range potential $U(r)$ of the atomic center ($U(r) = 0$ for $r \gtrsim r_c$, where $r_c \kappa \ll 1$) [31, 32]. According to [32], to determine ϵ, it is sufficient to find the solution $\psi_{\epsilon l m_l}(\mathbf{r})$ to the Schrödinger equation for the electron in the external field (for $U(r) \equiv 0$), which has an asymptotic form of diverging spherical waves for $r \longrightarrow \infty$ and satisfies the following boundary condition for $r_c \lesssim r \ll \kappa^{-1}$:

$$\int \psi_{\epsilon l m_l}(\mathbf{r}) Y_{l m_l}^*(\hat{\mathbf{r}}) d\Omega_{\mathbf{r}}$$
$$\sim \frac{1}{r^{l+1}} + \ldots + B_l(\epsilon) r^l + \ldots, \tag{1}$$

where $Y_{l m_l}(\hat{\mathbf{r}})$ is a spherical function and coefficient $B_l(\epsilon)$ can be formally expressed in terms of phase $\delta_l(k)$ ($k = \sqrt{2E}$) of scattering from potential $U(r)$:

$$\frac{[(2l+1)!!]^2}{2l+1} B_l(E) = \mathscr{B}_l(E) = k^{2l+1} \cot \delta_l(k). \tag{2}$$

Since $B_l(\epsilon)$ is an analytic function of energy, which is complex-valued in the general case (if the external field leads to the decay of bound state $\psi_{\kappa l m_l}^{(0)}(\mathbf{r})$), expression (2) can be treated as an analytic continuation of scattering phases to complex plane k. Assuming that ϵ differs from unperturbed energy E_0 only slightly ($|\epsilon - E_0|/|E_0| \ll 1$), we can limit the parameterization of $B_l(\epsilon)$ to only the first two terms in the expansion in ϵ in accordance with the effective range approximation for scattering phases in collision theory [27]:

$$\mathscr{B}_l(\epsilon) = -\frac{1}{a_l} + r_l \epsilon, \tag{3}$$

where a_l and r_l are the scattering length and the effective range, which are parameters of the problem. Note that we can also use as parameters of the problem the binding energy $|E_0| = \kappa^2/2$ and coefficient $C_{\kappa l}$ in the asymptotic form,

$$\psi_{\kappa l m_l}^{(0)}(\mathbf{r}) \approx C_{\kappa l} r^{-1} \exp(-\kappa r) Y_{l m_l}(\hat{\mathbf{r}})$$

of the wavefunction of the bound state at large distances because [33]

$$a_l^{-1} = (-1)^l \kappa^{2l+1} - r_l \kappa^2/2,$$
$$2 C_{\kappa l}^{-2} = (-1)^l (2l+1) \kappa^{-1} - r_l \kappa^{-2l}. \tag{4}$$

Solutions $\psi_{\epsilon l m_l}(\mathbf{r})$, which are singular at zero, can be written in terms of the spatial derivatives of the time-independent Green function $G_\epsilon(\mathbf{r}, \mathbf{r}')$ of an electron in an external field [31, 32]:

$$\psi_{\epsilon l m_l}(\mathbf{r}) = 2\pi \mathscr{Y}_{l m_l}(\nabla_{\mathbf{r}'}) G_\epsilon(\mathbf{r}, \mathbf{r}')|_{\mathbf{r}'=0}, \tag{5}$$

where the differential operator is written in terms of spherical function $\mathscr{Y}_{l m_l}(\nabla_{\mathbf{r}})$ of gradient operator $\nabla_{\mathbf{r}}$

$[\mathcal{Y}_{lm_l}(\mathbf{r}) = r^l Y_{lm_l}(\hat{\mathbf{r}})]$, and the Green function satisfies the following equation:

$$\left(-\frac{1}{2}\nabla^2 + V(\mathbf{r}) - \epsilon\right)G_\epsilon(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}').$$

The transcendental equation for energy ϵ can be obtained by joining the projection of solution (5) onto spherical function $Y_{lm_l}(\hat{\mathbf{r}})$ with boundary condition (1) (details and analysis of some of the most important cases for applications for the one-center problem are given in [32, 34]; a generalization to the case of monochromatic perturbation $V(\mathbf{r}, t)$ can be found in [35, 36]).

Considering an electron in the field of N atomic centers located at points $\mathbf{R}_j$, $j = 1, ..., N$, we assume that $|\mathbf{R}_i - \mathbf{R}_j| \gg r_i^{(c)} + r_j^{(c)}$ for $i \neq j$ ($r_k^{(c)}$ is the range of action of the potential of the kth center) and that each center sustains a weakly bound state with energy $E_0^{(j)} = -\kappa_j^2/2$ and orbital angular momentum l_j. In this case, under perturbation $V(\mathbf{r})$, electron wavefunction $\psi_\epsilon(\mathbf{r})$ is mainly determined by the action of the external field except in the neighborhoods of points $\mathbf{r} = \mathbf{R}_j$ at which boundary conditions analogous to (1) must be satisfied for $\psi_\epsilon(\mathbf{r})$:

$$\psi_\epsilon(\mathbf{r})|_{\mathbf{r} \to \mathbf{R}_j} \approx \left[\frac{1}{r_j^{l_j+1}}\right.$$
$$\left. + ... + B_{l_j}(\epsilon - V(\mathbf{R}_j))r_j^{l_j}\right]f_{l_j, m_j}Y_{l_jm_j}(\hat{\mathbf{r}}_j).$$

(6)

Here, $\mathbf{r}_j = \mathbf{r} - \mathbf{R}_j$, $m_j \equiv m_{l_j}$, and $f_{l_j, m_j} \equiv f_{l_j, m_j}(\epsilon)$ are constant coefficients. Since potential energy $V(\mathbf{R}_j)$ at points $\mathbf{r} = \mathbf{R}_j$ is generally not small as compared to characteristic variations of ϵ, the external field in the vicinity of these points is taken into account in Eq. (6) by the relevant shift of energy ϵ in B_{l_j} (we assume that $V(0) = 0$).

The general expression for wavefunction $\psi_\epsilon(\mathbf{r})$ of the electron in the external field and the field of N atomic centers can be written as a superposition on one-center functions (5):

$$\psi_\epsilon(\mathbf{r}) = \sum_{i=1}^{N} \sum_{m_i=-l_i}^{l_i} f_{l_im_i}\psi_{l_im_i}(\mathbf{r}, \mathbf{R}_i), \quad (7)$$

$$\psi_{l_im_i}(\mathbf{r}, \mathbf{R}_i) = 2\pi\mathcal{Y}_{l_im_i}(\nabla_{\mathbf{R}_i})G_\epsilon(\mathbf{r}, \mathbf{R}_i), \quad (8)$$

where $f_{l_im_i}$ are the coefficients appearing in boundary condition (6). Since wavefunction $\psi_{l_im_i}(\mathbf{r}, \mathbf{R}_i)$ of the ith center is singular only for $\mathbf{r} = \mathbf{R}_i$, its expansion in the vicinity of the jth center (in $r_j = |\mathbf{r} - \mathbf{R}_j|$) taking into

account only the principal terms in r_j can be written in the form

$$\psi_{l_im_i}(\mathbf{r}, \mathbf{R}_i) \sim \frac{(2l_j - 1)!!}{r_j^{l_j+1}} Y_{l_jm_j}(\hat{\mathbf{r}}_j)\delta_{i,j}\delta_{m_i, m_j}$$
$$+ ... + \sum_l \sum_{m_l=-l}^{l} \frac{A_{l_im_i; lm_l}^{(i,j)}(\epsilon)}{(2l+1)!!}\mathcal{Y}_{lm_l}(\mathbf{r}_j),$$

(9)

where only the regular part is left for $i \neq j$ (in particular, the term with $l = 0$ in expression (9) is $\psi_{l_im_i}(\mathbf{R}_j, \mathbf{R}_i)$).

The explicit form of matrix elements $A_{l_im_i; lm_l}^{(i,j)}(\epsilon)$ is given by the relations

$$A_{l_im_i; lm_l}^{(i,j)}(\epsilon) = 8\pi^2\mathcal{Y}_{lm_l}(\nabla_{\mathbf{R}_j})$$
$$\times \mathcal{Y}_{l_im_i}(\nabla_{\mathbf{R}_i})G_\epsilon(\mathbf{R}_j, \mathbf{R}_i), \quad i \neq j,$$

(10)

$$A_{l_im_i; lm_l}^{(i,i)}(\epsilon) = 8\pi^2\mathcal{Y}_{lm_l}(\nabla_{\mathbf{R}_i})\min_{R_j \to R_i}\mathcal{Y}_{l_im_i}(\nabla_{\mathbf{R}_i})$$
$$\times \left[G_\epsilon(\mathbf{R}_j, \mathbf{R}_i) - \frac{1}{2\pi|\mathbf{R}_j - \mathbf{R}_i|}\right], \quad i = j,$$

(11)

in deriving these expressions, we used formula (6) from [37] for the expansion of the irreducible rank J tensor depending on vector $\mathbf{r}_j + \mathbf{R}_j$ into a series in spherical harmonics $\mathcal{Y}_{lm_l}(\mathbf{r}_j)$ taking into account only the zero-order terms in r_j in the expansion coefficients. Formulas (10) and (11) obviously lead to the following symmetry relations:

$$A_{l_im_i; lm_l}^{(i,j)}(\epsilon) = A_{lm_l; l_im_i}^{(j,i)}(\epsilon).$$

Projecting $\psi_\epsilon(\mathbf{r})$ onto $Y_{l_jm_j}(\hat{\mathbf{r}}_j)$ in the vicinity of point $\mathbf{r} = \mathbf{R}_j$ with the help of (9) and comparing the result with boundary condition (6), we obtain the following equation for coefficients f_{lm}:

$$\mathcal{B}_{l_j}(\epsilon - V(\mathbf{R}_j))f_{l_jm_j}$$
$$= \sum_{i=1}^{N} \sum_{m_i=-l_i}^{l_i} A_{l_im_i; l_jm_j}^{(i,j)}(\epsilon)f_{l_im_i}.$$

(12)

In the general case, the dimensionality of system of linear equations (12) is $\sum_i (2l_i + 1)$, and the energy of the electron in the external field and the field of N atomic centers (or quasi-molecule terms) is determined by the roots of the transcendental equation

$$\det\left\|A_{l_im_i; l_jm_j}^{(i,j)}(\epsilon) - \mathcal{B}_{l_j}(\epsilon - V(\mathbf{R}_j))\delta_{i,j}\delta_{m_i, m_j}\right\| = 0. \quad (13)$$

In the approximation of the scattering length for scattering phases [27], i.e., for

$$a_{l_i} = (-1)^{l_i}\kappa_i^{-(2l_i+1)}, \quad r_{l_i} = 0$$

(r_{l_i} is the effective range for the ith center), the dependence of $\mathscr{B}_{l_i}$ on energy ϵ disappears:

$$\mathscr{B}_{l_i}(\epsilon - V(\mathbf{R}_i)) = (-1)^{l_i+1}\kappa_i^{2l_i+1}.$$

In particular, for a system of s centers ($l_i = 0$, $i = 1, ..., N$), boundary conditions (6) and Eqs. (12) and (13) in the scattering length approximation are transformed into the corresponding results for the electron wavefunction in the field of N δ potentials [24].

Matrix elements (10) and (11) are generally quite cumbersome and can be expressed directly in terms of G_ϵ only for a system with s centers:

$$A^{(i,j)}_{0,0;0,0} = 2\pi G_\epsilon(\mathbf{R}_i, \mathbf{R}_j), \quad i \neq j,$$

$$A^{(i,i)}_{0,0;0,0} = 2\pi \lim_{\mathbf{R}_i \to \mathbf{R}_j}\left[G_\epsilon(\mathbf{R}_i, \mathbf{R}_j) - \frac{1}{2\pi|\mathbf{R}_i - \mathbf{R}_j|}\right].$$

If operator $V(\mathbf{r})$ describes the interaction with uniform electric field $\mathbf{F}$, matrix elements $A^{(i,j)}_{l_i m_i; l_j m_j}(\epsilon)$ can be expressed in terms of combinations of the Airy functions and their derivatives. For a two-center system (with ss and sp centers), these matrix elements are given in the Appendix.

3. ELECTRON ENERGY LEVELS FOR A SYSTEM WITH IDENTICAL s CENTERS

3.1. Exact Results for Complex Energy $\epsilon(F, R, \theta)$ and Comparison with the Results for a Weak Field

We consider an electron in the field of two identical s centers located at points $\mathbf{r} = \mathbf{R}_1 = \mathbf{R}/2$ and $\mathbf{R}_2 = -\mathbf{R}/2$ and in an electric field $\mathbf{F}$ forming an angle θ with the line connecting the centers. For $F = 0$ and $R = |\mathbf{R}_1 - \mathbf{R}_2| \longrightarrow \infty$, each center can be described by effective range r_0 and it sustains the s state with energy $E_0 = -\kappa_0^2/2$. In this case, system of equations (12) for complex energy $\epsilon = \mathrm{Re}\,\epsilon - i\Gamma/2$ and coefficients $f_{l_1=0, m_1=0} \equiv f_1$, $f_{l_2=0, m_2=0} \equiv f_2$ in Eq. (7) contains two equations,

$$\begin{pmatrix} A_+ & A_0 \\ A_0 & A_- \end{pmatrix}\begin{pmatrix} f_1 \\ f_2 \end{pmatrix} = 0, \tag{14}$$

where

$$A_0 = \mathscr{G}_\epsilon(R),$$

$$A_\pm = J(\xi_\pm) + \kappa_0 - r_0(\epsilon - E_0 \pm \mathbf{F}\cdot\mathbf{R}/2),$$

and the explicit form of $J(\xi_\pm)$ and $\mathscr{G}_\epsilon(R)$ in terms of Airy functions is given by formulas (A.6) and (A.7).

Writing determinant $A_+A_- - A_0^2$ of system (14) in the form

$$\frac{1}{4}(A_+ + A_- - \sqrt{(A_+ - A_-)^2 + 4A_0^2})$$

$$\times (A_+ + A_- + \sqrt{(A_+ - A_-)^2 + 4A_0^2}),$$

we obtain two independent equations for ϵ:

$$A_+ + A_- + \sqrt{(A_+ - A_-)^2 + 4A_0^2} = 0, \tag{15}$$

$$A_+ + A_- - \sqrt{(A_+ - A_-)^2 + 4A_0^2} = 0. \tag{16}$$

For $r_0 = 0$, Eqs. (15) and (16) follow from the results obtained in [26] as equations for the poles of the exact Green function for an electron in the field of two δ potentials and in a constant electric field. For $\mathbf{F} = 0$, Eqs. (15) and (16) lead to equations for unperturbed energies $E_\pm$ of two electron energy levels corresponding to symmetric (+) and antisymmetric (−) (relative to the transposition of the centers) states of the system,

$$(k_\pm - \kappa_0)\left[1 - \frac{1}{2}r_0(k_\pm + \kappa_0)\right] = \pm\frac{\exp(-k_\pm R)}{R}, \tag{17}$$

where $k_\pm = \sqrt{-2E_\pm}$. For $r_0 = 0$ (we will confine our analysis to this case for comparing exact numerical results for $\epsilon_\pm$ with the results obtained in [26] for a weak field), relation (17) gives the familiar result for splitting of energy levels of the electron in the field of two δ potentials, which is associated with the exchange interaction [25]. For $\mathbf{F} \neq 0$, relations (15) and (16) are exact transcendental equations for complex energies ϵ_+ and ϵ_- (which are transformed to $E_\pm$, respectively, for $F = 0$) for arbitrary F, R, and orientation of $\mathbf{F}$ relative to $\mathbf{R}$,

$$\epsilon_\pm = \mathrm{Re}\,\epsilon_\pm - \frac{i}{2}\Gamma_\pm = E_\pm + \Delta\epsilon_\pm - \frac{i}{2}\Gamma_\pm, \tag{18}$$

where $\Delta\epsilon_\pm$ in the limit of weak field F gives the Stark shift of energy levels $E_\pm$, which is quadratic in the field:

$$\Delta\epsilon_\pm = \mathrm{Re}\,\epsilon_\pm - E_\pm = -\frac{1}{2}\beta_\pm F^2.$$

For the one-center problem (negative atomic ion), the shift and broadening of energy E_0 of the bound s state in the model of a δ potential were obtained in [38] in the approximation of weak field F (in the tunnel regime). The results for a strong field (including analytic approximations for $\mathrm{Re}\,\epsilon$ and Γ) are given in [39]. The formulas for the shift and broadening of energies $E_\pm$ of the bound states of a system with two identical s centers in the regime of a weak field [$F \ll \tilde{F}$, where $\tilde{F} = (|E_\pm| - FR)^{3/2}$] were obtained in [26] [see formulas (29) for $\Gamma_\pm$ and (28) for polarizability $\beta_\pm$]. For fur-
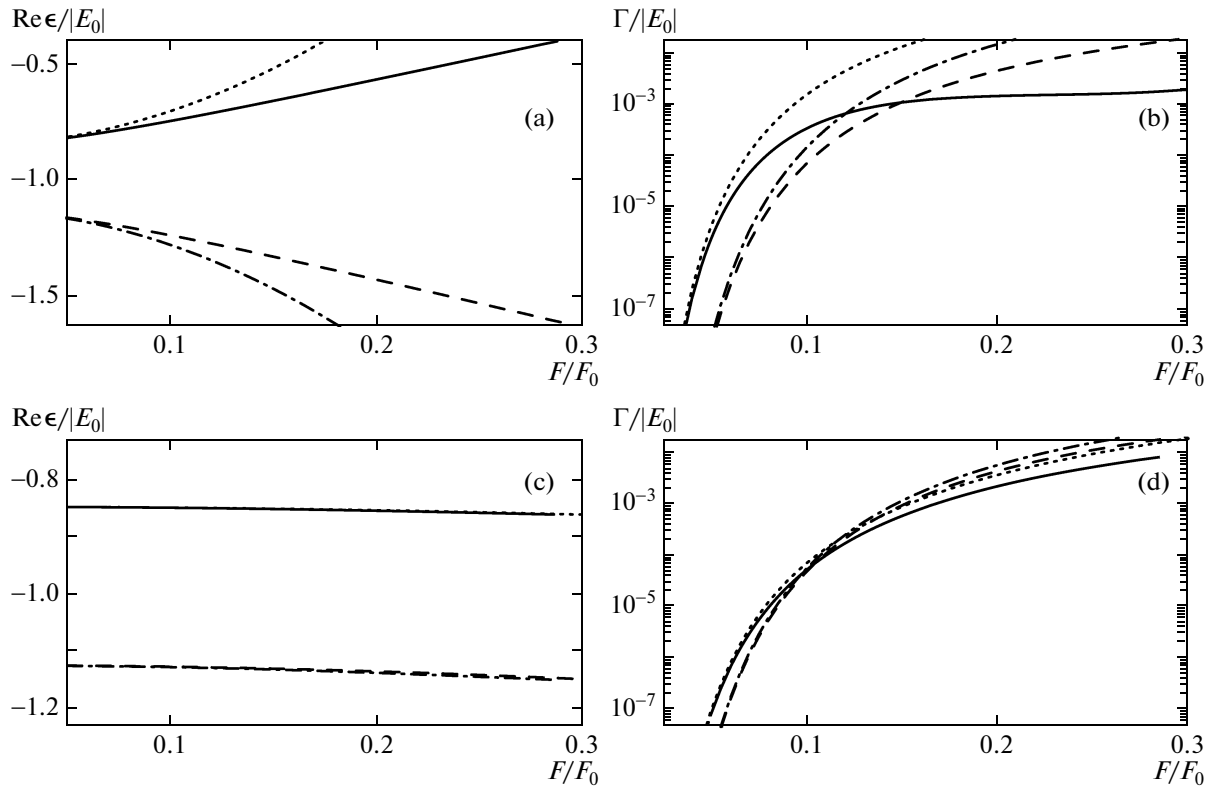
Fig. 1. Electric field dependences of the position ($\mathrm{Re}\,\epsilon_\pm$) and width ($\Gamma_\pm = -2\,\mathrm{Im}\,\epsilon_\pm$) of electron energy levels in the field of two identical s centers for $R = 2\kappa_0^{-1}$ and $\theta = 0$ (a, b) and 90° (c, d). Solid (dashed) curves correspond to exact results for ϵ_- (ϵ_+), while dotted (dot-and-dash) curves are the results obtained by Dalidchik and Slomin [26] for ϵ_- (ϵ_+); $F_0 = \kappa_0^3$ and $E_0 = -\kappa_0^2/2$.

ther comparison, we will use only the formula for $\Gamma_\pm$ from [26], writing it in the form

$$\Gamma_\pm = \frac{F}{2k_\pm}\exp\left(-\frac{2}{3}\frac{k_\pm^3}{F}\right)g(F, R, \theta),$$

$$g(F, R, \theta) = \frac{\cosh(k_\pm R\cos\theta) \pm (1 - FR^2/4k_\pm)}{1 \pm \exp(-k_\pm R)},$$

(19)

where $\cosh x = (e_x + e^{-x})/2$, and the term proportional to F in the expression for $g(F, R, \theta)$ must be retained only for Γ_- as $\theta \longrightarrow \pi/2$, when $g \sim F$ and the dependence of the preexponential factor on F changes to a quadratic dependence.

To illustrate the behavior of function $\epsilon_\pm(F, R, \theta)$ in a wide range of values of F and R and the range of applicability of analytic results obtained in [26], Figs. 1 and 2 show the dependence of real and imaginary parts of complex energies ϵ_+ and ϵ_- on F and R in parallel ($\theta = 0$) and perpendicular ($\theta = 90°$) geometry. It can be seen from Fig. 1 that for $\theta = 90°$, the position of the level excellently correlates with the results for a weak field even in the range of strong fields ($F \lesssim k_\pm^3$), and exact widths $\Gamma_\pm$ exceed the values given by formulas (19) only slightly. (This is due to the fact that for $\theta =$

90°, diagonal matrix elements $A_\pm$ from formula (14) are independent of R and remain the same as for an isolated atomic center, for which the results obtained for a weak field in [38] are applicable up to $F \sim \kappa_0^3$ [39].) However, for $\theta = 0$, the results obtained in [26] considerably exceed the exact results even at $F \approx 0.1 k_\pm^3$ (Figs. 1a and 1b). For $\theta = 90°$, the conformity between the exact and analytic results [26] is also observed for the dependences of the position and width of energy levels on R in a weak field (Figs. 1c and 1d). However, for $\theta = 0$, when the electric field caused complete breaking of the symmetry of the problem, it can be seen from Figs. 2a and 2b that the behavior of $\mathrm{Re}\,\epsilon_\pm$ and $\Gamma_\pm$ upon an increase in R beginning from $R \approx 3\kappa_0^{-1}$ sharply differs from the behavior predicted in the weak field approximation even in weak field ($F = 0.015\kappa_0^3$) [26]. The most interesting effect of a strong field is a peculiar minimum appearing on the curve describing the dependence of Γ_- on R in Fig. 2b, which can be explained taking into account A_0 in formula (14) in perturbation theory (see below).
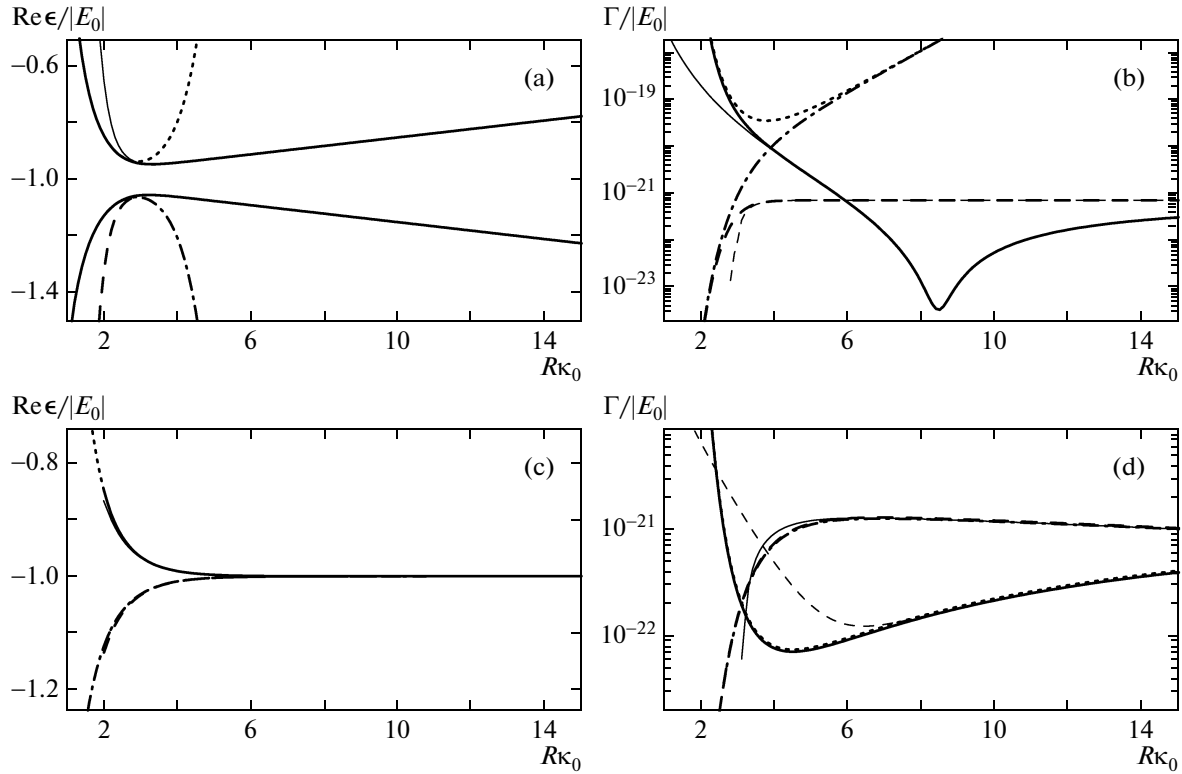
Fig. 2. Same as in Fig. 1, but for the dependence on R for $F = 0.015\,\kappa_0^3$. Thin solid and dashed curves are the results obtained in perturbation theory in the exchange interaction (see Section 3.2).

3.2. Perturbation Theory in Exchange Interaction

Although the nondiagonal matrix element A_0 responsible for the exchange interaction is generally not small, its value rapidly decreases with increasing R; therefore, starting from a certain value of R, we can use an iterative procedure for taking into account A_0 in the determination of complex energies $\epsilon_\pm$. The choice of this procedure depends on the ratio of A_0 to the difference $A_+ - A_-$. If the condition

$$\Delta = \left| \frac{A_0}{A_+ - A_-} \right| \ll 1 \qquad (20)$$

is satisfied, the expansion of radicands in formulas (15) and (16) gives

$$A_+ = -A_0^2/(A_+ - A_-), \qquad (21)$$

$$A_- = A_0^2/(A_+ - A_-). \qquad (22)$$

Treating the right-hand sides of formulas (21) and (22) as perturbations, we obtain

$$\epsilon_\pm \approx \epsilon_\pm^{(0)} + \delta_\pm(\epsilon_\pm^{(0)}), \qquad (23)$$

where $\epsilon_\pm^{(0)}$ are the roots of transcendental equations

$$A_-(\epsilon_+^{(0)}) = 0, \quad A_+(\epsilon_-^{(0)}) = 0, \qquad (24)$$

and corrections $\delta_\pm(\epsilon_\pm^{(0)})$ are defined by the relations

$$\delta_+ = \left. \frac{A_0^2}{A_+ A_-'} \right|_{\epsilon = \epsilon_+^{(0)}}, \quad \delta_- = \left. \frac{A_0^2}{A_+' A_-} \right|_{\epsilon = \epsilon_-^{(0)}}, \qquad (25)$$

where $A_\pm' \equiv \partial A_\pm(\epsilon)/\partial\epsilon$. As follows from the definition of $J(\xi_\pm)$ (see (A.5) and (A.6)), A_+ and A_- differ only in sing in the combinations $\epsilon \pm \mathbf{F} \cdot \mathbf{R}/2$ containing the entire dependence of $A_\pm$ on ϵ and R. If we denote $\epsilon \pm \mathbf{F} \cdot \mathbf{R}/2$ by $\epsilon^{(DC)}$, both equations in (24) become identical and give the equation for complex energy $\epsilon^{(DC)}$ of the negative atomic ion in field $\mathbf{F}$, whose solution is well known both for weak and strong fields $\mathbf{F}$ [38, 39]. As a result, the expression for $\epsilon_\pm$ in approximation (20) assumes the form

$$\epsilon_\pm = \epsilon^{(DC)} + \delta_\pm \mp \frac{\mathbf{F} \cdot \mathbf{R}}{2}. \qquad (26)$$

The solution to system (14) for coefficients f_1 and f_2, which determine the degree of localization of the electron near the first and second centers ($f_1 = \pm f_2$ in zero field), gives

$$\frac{f_1}{f_2} = \left. -\frac{A_0}{A_+} \right|_{\epsilon = \epsilon_+^{(0)}} \quad \text{for } \epsilon = \epsilon_+^{(0)}, \qquad (27)$$
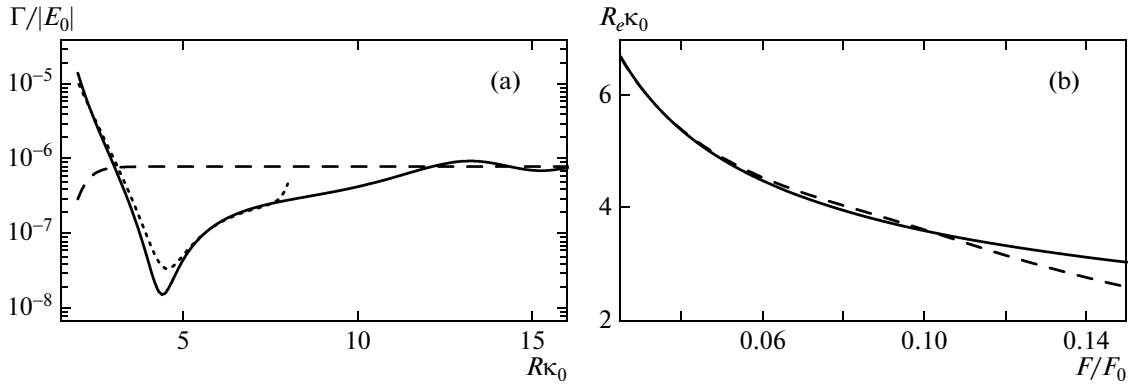
Fig. 3. (a) Dependences of widths $\Gamma_{\pm}$ of a two-center ss system on R for $F = 0.06\,\kappa_0^3$. Solid (dashed) curves are the exact results for $\Gamma_-(\Gamma_+)$; dotted curve corresponds to the result obtained from expression (34). (b) Dependences of the position of the minimum ($R = R_e(F)$) on the electric field. Solid curve is the exact result; dashed curve is the result obtained from formula (34); $F_0 = \kappa_0^3$ and $E_0 = -\kappa_0^2/2$.

$$\frac{f_2}{f_1} = -\frac{A_0}{A_-}\bigg|_{\epsilon\,=\,\epsilon_-^{(0)}} \quad \text{for } \epsilon = \epsilon_-^{(0)}. \tag{28}$$

Thus, with increasing R, the electron in the state with energy $\epsilon = \epsilon_+$ is mainly localized near the second center (at point $\mathbf{R}_2 = -\mathbf{R}/2$), while in the state with energy $\epsilon = \epsilon_-$, it is localized in the vicinity of the first center ($\mathbf{R}_1 = \mathbf{R}/2$).

Expressions (26)–(28) are inapplicable in orthogonal geometry ($\mathbf{F} \cdot \mathbf{R} = 0$) when $A_+ = A_- \equiv A(\epsilon)$ and condition (20) does not hold. In this case, the iterative inclusion of the exchange interaction involves the solution of system (16), which can be reduced to the equations

$$A(\epsilon) = \pm A_0,$$

in this case, the right-hand side is treated as a perturbation. This gives

$$\epsilon_{\pm} = \epsilon^{(DC)} \mp \delta(\epsilon^{(DC)}),$$
$$\delta(\epsilon^{(DC)}) = \frac{A_0}{A'(\epsilon)}\bigg|_{\epsilon\,=\,\epsilon^{(DC)}}. \tag{29}$$

It can easily be seen that for $\theta = \pi/2$, we have ratio $|f_1/f_2| = 1$ for both states (because the transposition symmetry is preserved in orthogonal geometry in the presence of the field also).

The results depicted in Fig. 2 show that iterative inclusion of the exchange interaction is valid for $R \gtrsim 3\kappa_0^{-1}$. It was noted above that with increasing R, the electron is localized in the vicinity of one of the centers and, hence, the main contribution to the energy shift is determined by the potential difference produced by the electric field between the origin (at which $V(\mathbf{r}) = 0$) and the point of location of the center (i.e., by the terms $\pm\mathbf{F} \cdot \mathbf{R}/2$ in relation (26)). It should be noted that the linear dependence of the position of the

level on R cannot be obtained in perturbation theory in F because, in addition to the smallness of F, it is also required that product $\mathbf{F} \cdot \mathbf{R}$ be much smaller than the energy difference $|\epsilon_+ - \epsilon_-|$ [26]. Therefore, for $\mathbf{F} \cdot \mathbf{R} = 0$, the Stark shift is quadratic in F and is correctly described in perturbation theory (see Fig. 2c), while for angles θ close to zero, the condition $|\mathbf{F} \cdot \mathbf{R}/(\epsilon_+ - \epsilon_-)| \ll 1$ is violated upon an increase in R, and the dependence of the level shift on F becomes close to linear (i.e., the quadratic Stark effect is transformed into the linear effect).

The dependence of the electron energy level widths on R is most interesting in parallel geometry ($\theta = 0$) (see Fig. 2b as well as the results for a stronger field $F = 0.06\kappa_0^3$ in Fig. 3a). Upon an increase in R, the width Γ_+ of the ground state assumes the limiting value (for a given F), which is determined by the imaginary part of energy $\epsilon^{(DC)}$ of the one-center problem, exponentially rapidly. Conversely, the width Γ_- of the upper level first decreases, attains its minimum in a narrow interval of R, and then approaches it asymptotically, oscillating about the limiting value of $\epsilon^{(DC)}$ (see Fig. 3a). Such a behavior of $\Gamma_{\pm}(R)$ can be explained taking into account the above-mentioned localization of the electron in the ground state and the excited state at different centers upon an increase in R. In the ground state, the electron is localized at the second center (at point $-\mathbf{R}/2$) and, hence, tunnels in the direction of $-\mathbf{F}$ without an appreciable interaction with the first center. The ratio of coefficients f_1/f_2 for the upper state decreases exponentially upon an increase in R to its value $R = R_0 \approx \kappa_0^2/2F$, after which it decreases much more slowly (in proportion to $R^{-3/2}$). Point R_0 is distinguished by the fact that for $R > R_0$, the electron cannot be localized near point $-\mathbf{R}/2$ any longer (because

$\mathbf{F} \cdot \mathbf{R} + \epsilon_- > 0$); in this case, the regime is referred to as the "above-barrier decay" [12–14]. In this regime, the electron localized in the excited state near the first center (at point $\mathbf{r} = \mathbf{R}/2$) is partly scattered from the potential of the second center when it passes through the barrier. Therefore, oscillations in $\Gamma_-(R)$ are determined by the interference of two waves: the wave scattered in the direction of $-\mathbf{F}$ and the wave emerging as a result of scattering in the $\mathbf{F}$ direction and subsequently reflected from the potential barrier formed by the electric field. Period ΔR of Γ_- oscillations upon a change in R can be estimated in terms of phase difference $\Delta\phi$ between the forward and reflected waves, which is determined by classical action $\mathscr{S}$ accumulated by the electron moving from the point at which it emerges from under the barrier to the scattering center (in absolute units):

$$\Delta\phi(R) = \frac{2\mathscr{S}}{\hbar} = \frac{2}{\hbar} \int\limits_{-R/2}^{\mathrm{Re}\,\epsilon_-/|e|F} p\,dr \qquad (30)$$

$$= \frac{2\sqrt{2m}}{3|e|F\hbar}(|e|FR - |E_0|)^{3/2},$$

where we have used for ϵ_- the approximate relation $\epsilon_- \approx |e|FR/2 - |E_0|$. Having determined ΔR from the equation

$$\Delta\phi(R + \Delta R) - \Delta\phi(R) = 2\pi,$$

in the limit of large R, we obtain

$$\Delta R \approx 2\pi\hbar[2m(|e|FR - |E_0|)]^{-1/2}.$$

An analogous result can also be obtained for ΔR more rigorously using the asymptotic expansion for A_0 and $A_\pm$ in expression (25) for δ_-. Obviously, the anomalous behavior of $\Gamma_-(R)$ mentioned above is sensitive to the geometry of the problem; for $\theta = 90°$, oscillations in $\Gamma_-(R)$ disappear because there is no barrier along the axis of the molecule.

Expressions (25) and (26) are exact in field F. Using the asymptotic forms of the Airy function, we can obtain the analytic forms of $\mathrm{Re}\,\epsilon_\pm$ and $\Gamma_\pm$ for small F. In particular, the expression for Γ_- can be written in the form

$$\Gamma_- = \Gamma^{(DC)} - f_-(F, R, \theta), \qquad (31)$$

where $\Gamma^{(DC)}$ is the level width in the one-center problem [38, 40]:

$$\Gamma^{(DC)} = \frac{C_{\kappa_0 0}^2 F}{4\kappa_0^2} \exp\left(-\frac{2\kappa_0^3}{3F}\right), \qquad (32)$$

$$f_-(F, R, \theta) = \frac{C_{\kappa_0 0}^2 F}{2\kappa_0 R N \sqrt{z_+ z_-}} \exp\left(-\frac{2z_+^{3/2}}{3F}\right)$$

$$\times \left[1 - \frac{(\sqrt{z_+} + \sqrt{z_-})^2}{8RNz}\right]$$

$$\times \exp\left(-\frac{2[z^{3/2} - z_-^{3/2}]}{3F}\right)\bigg], \qquad (33)$$

$$z = \kappa_0^2 - 2\mathbf{F} \cdot \mathbf{R}, \quad z_\pm = \kappa_0^2 - \mathbf{F} \cdot \mathbf{R} \pm FR,$$

$$N = a_0^{-1} - \sqrt{z} + \frac{r_0 z}{2}.$$

Since $z_+ = \kappa_0^2$ and $z_- = z$ for $\theta = 0$, term $f_-(F, R, \theta)$ in formula (31) in this case changes only the preexponential factor in formula (32). Expressions (31)–(33) for $r_0 = 0$, $a_0 = \kappa_0^{-1}$, and $\theta = 0$ make it possible to describe analytically the dependence of Γ_- on R in Figs. 2b and 3a in the region of the minimum. In this case, formula (31) is simplified:

$$\Gamma_-(\theta = 0) = \frac{F}{2\kappa_0} \exp\left(-\frac{2\kappa_0^3}{3F}\right)$$

$$\times \left[1 - \frac{\kappa_0^2(1 + \mathscr{E})}{FR^2\mathscr{E}}\left(1 - \frac{\kappa_0(1 + \mathscr{E})^3}{16FR^2\mathscr{E}^2}\right)\right], \qquad (34)$$

where

$$\mathscr{E} = \sqrt{1 - \frac{2FR}{\kappa_0^2}}$$

and we consider that $C_{\kappa_0 0} = \sqrt{2\kappa_0}$ for $r_0 = 0$ (see relation (4)). Analysis of the dependence of the preexponential factor in formula (34) on R shows that in the range of $R < \kappa_0^2/(2F)$, it has the single minimum at point $R = R_e(F)$, whose position is determined by the root of the fifth-order polynomial. Figure 3b demonstrates the conformity of the dependence of R_e on F obtained from analysis of relation (34) to the results of solution of the exact equation for $\epsilon_-(\theta = 0)$.

The orientation dependence of complex energies $\epsilon_\pm$ of the electron in the field of two s centers is shown in Fig. 4 for two values of R. For small values of R (see Fig. 4b), width Γ_- of the upper state considerably exceed Γ_+, and both widths have a maximum at $\theta = 0$ and a minimum at $\theta = 90°$. Such a dependence is in qualitative agreement with the results for a weak field because the entire dependence of widths on θ is determined by the imaginary parts of the diagonal matrix elements $A_\pm$, i.e., by exponential terms of the type

$$\exp\left[-\frac{2}{3}\frac{(-2E_\pm \pm \mathbf{F} \cdot \mathbf{R})^{3/2}}{F}\right]$$

$$\approx \exp\left(-\frac{2}{3}\frac{|2E_\pm|^{3/2}}{F}\right)\exp(\pm\sqrt{2|E_\pm|}\,R\cos\theta), \qquad (35)$$

where $E_\pm = \epsilon_\pm(F = 0)$. It can be seen from formula (35) that the dependence of $\Gamma_\pm$ on θ is determined by rapidly varying coefficient $\exp(\sqrt{2|E_\pm|}\,R|\cos\theta|)$ in accordance with Fig. 4b. With increasing R or F, the weak
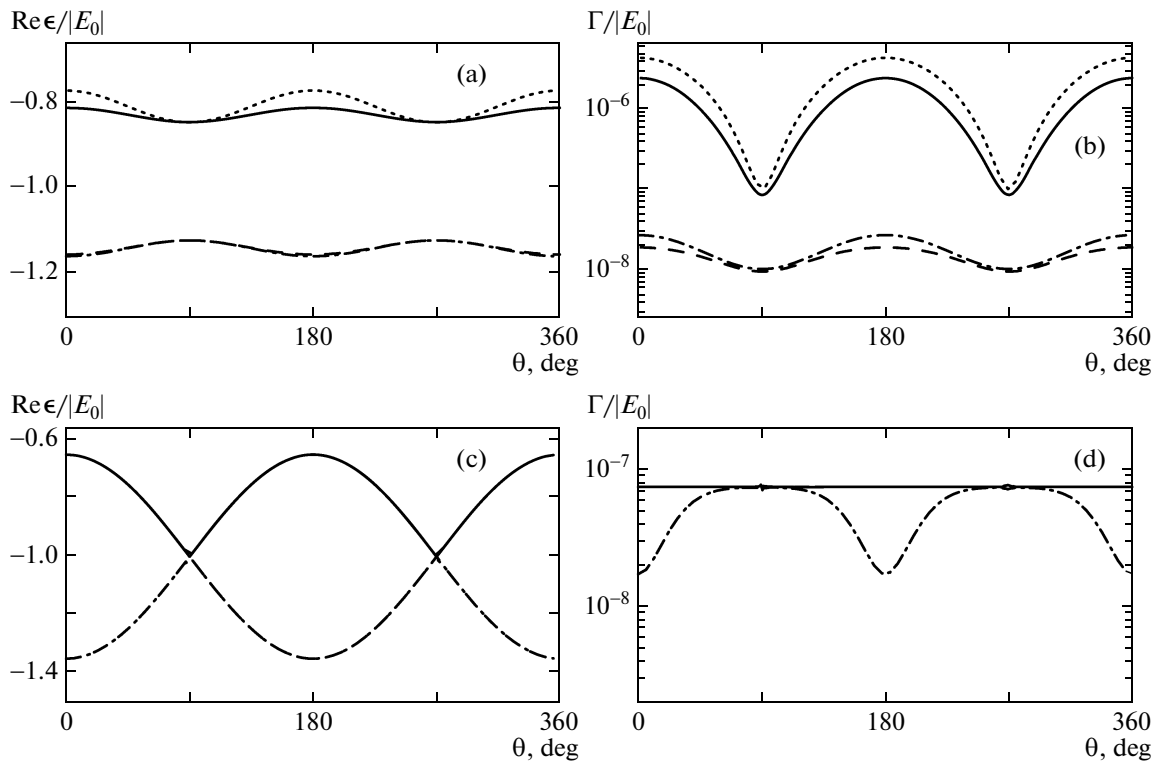
Fig. 4. Dependences of (a, c) the position and (b, d) the width of electron energy levels in the field of two s centers on angle θ between $\mathbf{R}$ and $\mathbf{F}$ for $F = 0.05\kappa_0^3$ and $R = 2\kappa_0^{-1}$ (a, b) and $7\kappa_0^{-1}$ (c, d). Solid and dashed curves are exact results for ϵ_- and ϵ_+; dotted and dot-and-dash curves in (a, b) are the results from [26]; dotted and dot-and-dash curves in (c, d) are the results obtained in perturbation theory in the exchange interaction (which almost coincide with the exact results); $E_0 = -\kappa_0^2/2$.

field approximation (together with expansions of type (35)) becomes inapplicable, and the orientation dependence becomes more complicated; in particular, the positions of the maxima and minima of Γ_- now depend on R (see Fig. 4d), and the angular dependence of Γ_+ disappears.

4. TWO-CENTER SYSTEM WITH NONEQUIVALENT s CENTERS

A system with nonequivalent s centers ($\kappa_1 \neq \kappa_2$; for definiteness, we assume that $\kappa_1 < \kappa_2$) basically differs from the system with identical centers in that the molecular system possesses a nonzero dipole moment $\mathbf{d}_{ss} \sim \mathbf{R}$ for $\mathbf{F} = 0$ due to different effects of the centers on a weakly bound electron and different electron density distributions in the regions of the first and second centers, which is associated with these effects. Therefore, for $F \longrightarrow 0$, the power expansion of the level shifts in F begins with a term of order F (linear Stark effect), and the energies of the ground state and the excited state become closer up to the quasi-intersection point. For a unified description of the positions of energy levels for small values of F (including the region of quasi-intersection of molecular terms), it

is convenient to use an iterative procedure for solving system of equations (12) (with $N = 2$ and $l_i = l_j = 0$) based on the field-modified "zeroth" approximation, in which the linear Stark effect is contained even for energies $E = E(\mathbf{F})$ of the zeroth approximation. To this end, using the asymptotic expansion of the Airy functions for $|\xi_{\pm}| \gg 1$, we expand matrix elements $A_{0,0;0,0}^{(i,j)}$ in (A.3) and (A.4) into asymptotic series taking into account lower-order terms in the field for real ($\sim F^2$) and imaginary ($\sim F$) parts:

$$J(\xi_{\pm}) = -\kappa_{\pm} + \frac{iF}{4\kappa_{\pm}^2}\exp\left(-\frac{2\kappa_{\pm}^3}{3F}\right) + \frac{F^2}{8\kappa_{\pm}^5}, \qquad (36)$$

$$\begin{aligned} G_{\epsilon}(R) &= \frac{\exp(-\kappa R)}{R} + i\frac{F}{4\kappa^2}\exp\left(-\frac{2\kappa^3}{3F}\right) \\ &+ \frac{F^2\exp(-\kappa R)}{8\kappa^2}\left(\frac{R^2}{3} + \frac{R}{\kappa} + \frac{1}{\kappa^2}\right), \end{aligned} \qquad (37)$$

where

$$\kappa = \sqrt{-2\epsilon}, \quad \kappa_{\pm} = \sqrt{-(2\epsilon \pm \mathbf{F} \cdot \mathbf{R})}.$$

Taking into account only the principal (first) terms in expansions (36) and (37) and replacing exact energy

$\epsilon(\mathbf{F})$ by $E(\mathbf{F}) = -k^2/2$, we can write system of equations (12) in the zeroth approximation in the form

$$\begin{pmatrix} \mathcal{L}_0^{(1)}(k_+) & \dfrac{e^{-kR}}{R} \\[2mm] \dfrac{e^{-kR}}{R} & \mathcal{L}_0^{(2)}(k_-) \end{pmatrix} \begin{pmatrix} f_1 \\ f_2 \end{pmatrix} = 0, \qquad (38)$$

$$\mathcal{L}_0^{(i)}(k) = (\kappa_i - k)\left[1 - \frac{r_0^{(i)}}{2}(\kappa_i + k)\right], \qquad (39)$$

where

$$k = \sqrt{-2E}, \quad k_\pm = \sqrt{-(2E \pm \mathbf{F} \cdot \mathbf{R})}$$

and $r_0^{(1)}$ and $r_0^{(2)}$ are the effective radii for the first and second centers. The entire dependence of system (38) and, accordingly, of energy E on $\mathbf{F}$ is associated only with terms $\pm \mathbf{F} \cdot \mathbf{R}$ in the expressions for $k_\pm$ in diagonal matrix elements $\mathcal{L}_0^{(i)}$. The two real values of energy $E = E^\pm(\mathbf{F})$ obtained from the solution of system of equations (38) determine the zeroth approximations for the energies of the ground (E^+) and excited (E^-) molecular terms in the field, which are transformed for $\mathbf{F} = 0$ into unperturbed energies $E_0^\pm$ following from (38) upon the substitution of $k_0^\pm = \sqrt{-2E_0^\pm}$ for $k_\pm$ and k. The contribution from the terms of order F and F^2 in expansions (36) and (37) for the matrix elements appearing in the solution of Eq. (13) for ϵ will be taken into account in perturbation theory based on the solution of system (38). For this purpose, we write ϵ in the form

$$\epsilon^\pm = E^\pm(\mathbf{F}) + \Delta\epsilon^\pm$$

and confine the solution of transcendental equation (13) to the term linear in $\Delta\epsilon$ and the terms on the order of F and F^2, which appear from expansions (36) and (37) for matrix elements $A_{0,0;0,0}^{(i,j)}$ in Eq. (13). It turns out that the expansion for the level shift in F begins with terms on the order of F^2 as in the case of the quadratic Stark effect; therefore, the resultant expression for $\Delta\epsilon^\pm$ can be written in the form

$$\Delta\epsilon^\pm = -\frac{1}{2}\alpha^\pm(\mathbf{F})F^2 - i\frac{\Gamma^\pm}{2}, \qquad (40)$$

$$\alpha^\pm(\mathbf{F}) = \frac{1}{4N}\left[\frac{k_+^{-5}}{\mathcal{L}_0^{(1)}(k_+)} + \frac{k_-^{-5}}{\mathcal{L}_0^{(2)}(k_-)}\right.$$
$$\left. - 2Rk^{-5}\left(1 + kR + \frac{1}{3}(kR)^2\right)\right], \qquad (41)$$

$$\Gamma^\pm = \frac{F}{2N}\left[\frac{k_+^{-2}}{\mathcal{L}_0^{(1)}(k_+)}\exp\left(-\frac{2k_+^3}{3F}\right)\right.$$

$$\left. + \frac{k_-^{-2}}{\mathcal{L}_0^{(2)}(k_-)}\exp\left(-\frac{2k_-^3}{3F}\right) - 2Rk^{-2}\right. \qquad (42)$$

$$\left. \times \exp\left(kR - \frac{2k^3}{3F}\right)\right],$$

where

$$N = \frac{\mathcal{C}_0^{(1)}(k_+)}{\mathcal{L}_0^{(1)}(k_+)} + \frac{\mathcal{C}_0^{(2)}(k_-)}{\mathcal{L}_0^{(2)}(k_-)} - \frac{2R}{k}, \qquad (43)$$

$$\mathcal{C}_0^{(i)}(k) = k^{-1} - r_0^{(i)}. \qquad (44)$$

The result for $\alpha^\pm(F = 0)$ (weak field approximation) follows from formulas (41), (43) for $k_\pm = k = k_0$, $k_0^\pm = \sqrt{-2E_0^\pm}$:

$$\alpha^\pm(0) = \frac{R}{4k_0^5 N(k_0)}\left[(\mathcal{L}_0^{(1)}(k_0) + \mathcal{L}_0^{(2)}(k_0))\right.$$
$$\left. \times R\exp(2k_0R) - 2\left(1 + k_0R + \frac{1}{3}(k_0R)^2\right)\right], \qquad (45)$$

where $k_0 = \sqrt{-2E_0^+}$ for $\alpha^+(0)$, $k_0 = \sqrt{-2E_0^-}$ for $\alpha^-(0)$, and $N(k_0)$ is given by expression (43) with $k_\pm = k = k_0$. However, expression (45) gives polarizabilities $\beta^\pm$ of unperturbed terms $E_0^\pm$ independent of $\mathbf{F}$ only in orthogonal geometry $(\theta = \pi/2)$ because additional terms on the order of $(F\cos\theta)^2$ appear in the expansion of energies $E^\pm(\mathbf{F})$ in the zeroth approximation into a power series in F. This expansion can be obtained using the iterative solution of Eq. (38) and representing $E^\pm(\mathbf{F})$ in the form $E^\pm(F) = E_0^\pm + \Delta E^\pm$. Expanding $k_\pm$ in the diagonal matrix elements in expression (38) up to terms of order F^2, we obtain the following expression for $\Delta E^\pm$:

$$\Delta E^\pm(\mathbf{F}) = -\mathbf{d}_{ss}^\pm \cdot \mathbf{F} - \frac{1}{2}\alpha_0^\pm F^2, \qquad (46)$$

where $\mathbf{d}_{ss}^\pm$ is the above-mentioned dipole moment

$$\mathbf{d}_{ss}^\pm = d_0^\pm \mathbf{R},$$

$$d_0^\pm = \frac{1}{2N(k_0)}\left[\frac{\mathcal{C}_0^{(1)}(k_0)}{\mathcal{L}_0^{(1)}(k_0)} - \frac{\mathcal{C}_0^{(2)}(k_0)}{\mathcal{L}_0^{(2)}(k_0)}\right]. \qquad (47)$$

(It should be noted that expression (47) can also be obtained by calculating $\mathbf{d}_{ss}^\pm$ directly as the mean value of vector $\mathbf{r}$ with unperturbed two-center wavefunctions.) It can be seen from expression (47) that $\mathbf{d}_{ss}^\pm$ vanishes in the case of identical s centers (when $\mathcal{C}_0^{(1)} =$
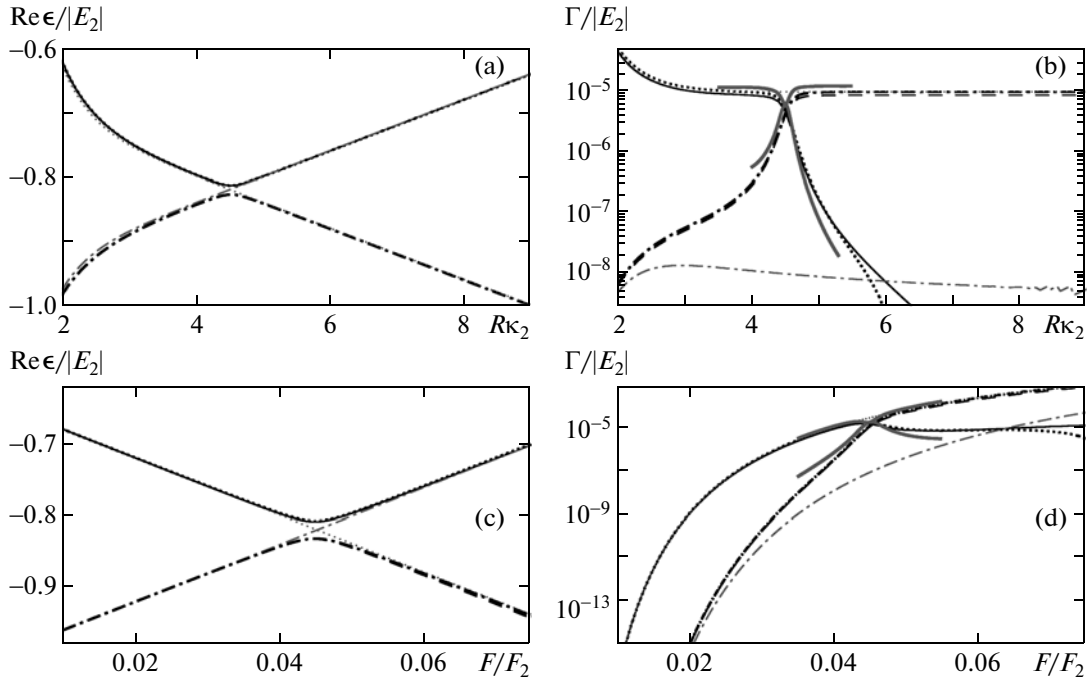
Fig. 5. Dependences of the position and width of the levels of a two-center ss system with $\kappa_1 = 0.8\kappa_2$, which is oriented along field $\mathbf{F}$ ($\theta = 0$) on R (a, b; $F = 0.04\kappa_2^3$) and F (c, d; $R = 4\kappa_2^{-1}$). Solid and dashed curves are exact results for ϵ_- and ϵ_+, respectively; dotted and dot-and-dash curves are the results of calculations based on formulas (40)–(42); gray dotted and dot-and-dash curves are the results for a weak field calculated by formula (49) (for $\Gamma^\pm$) and (50) (for $\mathrm{Re}\,\epsilon^\pm$); gray solid curves in (b) and (d) are the results of calculations by formulas (58) and (58), (61); $E_0 = -\kappa_2^2/2$ and $F_2 = \kappa_2^3$.

$\mathscr{C}_0^{(2)}$ and $\mathscr{L}_0^{(1)} = \mathscr{L}_0^{(2)}$). Coefficient $\alpha_0^\pm$ defining the term quadratic in F in expansion (46) has the form

$$
\begin{aligned}
\alpha_0^\pm = {} & \frac{R^2\cos^2\theta}{2k_0^3 N(k_0)}\left[\frac{(2d_0^\pm - 1)^2}{\mathscr{L}_0^{(1)}(k_0)} + \frac{(2d_0^\pm + 1)^2}{\mathscr{L}_0^{(2)}(k_0)}\right. \\
& + 2k_0^3\frac{\mathscr{C}_0^{(1)}(k_0)\mathscr{C}_0^{(2)}(k_0)}{\mathscr{L}_0^{(1)}(k_0)\mathscr{L}_0^{(2)}(k_0)}[(2d_0^\pm)^2 - 1] \qquad (48) \\
& \left. - 8(d_0^\pm)^2 R(1 + 2k_0 R)\right],
\end{aligned}
$$

and its sum with $\alpha^\pm(\mathbf{F} = 0)$ from (45) gives the total polarizability of a heteropolar ion with $\kappa_1 \neq \kappa_2$:

$$
\beta^\pm(R, \theta) = \alpha^\pm(0) + \alpha_0^\pm.
$$

The expression for $\beta^\pm$ is considerably simplified in the case of a homeopolar ion ($\kappa_1 = \kappa_2$) and coincides with the expression obtained in [26] in the model of δ potentials for $r_0^{(1)} = r_0^{(2)} = 0$. (It should be noted that the expression for polarizability $\beta^\pm(R, \theta = 0)$ of an ion with two s centers with $\kappa_1 \neq \kappa_2$ was obtained in [41] in the model of δ potential using a different method. However, the expression given in [41] is extremely

cumbersome and does not follow from our result for $r_0^{(1)} = r_0^{(2)} = 0$. Numerical comparison also shows a considerable difference between our results for $\beta^\pm(R, 0)$ and the results obtained in [41].)

Widths $\Gamma^\pm$ from formula (42) in the limit of a weak field ($\Gamma_{F\to0}^\pm \equiv \Gamma_0^\pm$) and $r_0^{(1)} = r_0^{(2)} = 0$ have the form

$$
\begin{aligned}
\Gamma_0^\pm = {} & \frac{F}{2k_0(\kappa_1 + \kappa_2 - 2k_0 - 2R^{-1}\exp(-2k_0 R))} \\
& \times \exp\left(-\frac{2k_0^3}{3F} - 2d_0^\pm k_0 R\cos\theta\right)[(\kappa_2 - k_0) \\
& \times \exp(k_0 R\cos\theta) + (\kappa_1 - k_0)\exp(-k_0 R\cos\theta) \\
& - 2R^{-1}\exp(-k_0 R)].
\end{aligned} \qquad (49)
$$

It is interesting that in orthogonal geometry ($\theta = \pi/2$), the preexponential factor on the right-hand side of expression (49) for the upper level (in Γ_0^-) has a minimum, but does not vanish as in formula (19) for $\kappa_1 = \kappa_2 = \kappa_0$ (vanishing of Γ_0^- in formula (49) in the latter case obviously follows from the relation

$$
k_0^\pm - \kappa_0 = \pm\exp(-k_0^\pm R)/R,
$$

which is a consequence of relation (17) for $r_0 = 0$ and is associated with an additional factor of order F in the probability of tunneling from the antisymmetric state in the direction perpendicular to the axial symmetry axis analogously to the probability of tunneling from the one-center p state with $|m| = 1$ [40].)

Figure 5 shows the positions and widths of terms ϵ^+ and ϵ^- of the ss system with $\kappa_2 = 0.8\kappa_1$ and $r_0^{(1)} = r_0^{(2)} = 0$ in a wide range of values of R and fields F. It can be seen that analytic results (41) and (42) are in excellent agreement with the exact results for $\mathrm{Re}\epsilon$ and Γ obtained from the numerical solution of Eq. (13). The results for $\mathrm{Re}\epsilon$ in Figs. 5a and 5c were obtained using the formula for the conventional Stark effect (with quantities $\mathbf{d}_{ss}^{\pm}$ and $\beta^{\pm}$ independent of F),

$$\mathrm{Re}\epsilon^{\pm} = E_0^{\pm} - \mathbf{d}_{ss}^{\pm} \cdot \mathbf{F} - \frac{1}{2}\beta^{\pm}F^2, \tag{50}$$

correctly describe the level shift up to the region of quasi-intersection of terms ($\mathrm{Re}\epsilon^+ \approx \mathrm{Re}\epsilon^-$), starting from with which the description of the position of energy levels in perturbation theory for isolated level is not applicable any longer.

A characteristic feature of Figs. 5b and 5d is the sharp variation in the behavior of the level width in the region of quasi-intersection of terms ϵ^+ and ϵ^- upon an increase in R or F. To explain such a behavior, let us analyze the system of equations (38) in the limit of a strong field $\mathbf{F}$. Considering that the diagonal matrix elements in (38) are functions of energy $E(\mathbf{F})$, we expand them in the vicinity pf the points

$$E_1 = -\frac{\kappa_1^2}{2} - \frac{\mathbf{F} \cdot \mathbf{R}}{2}, \quad E_2 = -\frac{\kappa_2^2}{2} + \frac{\mathbf{F} \cdot \mathbf{R}}{2}:$$

$$\kappa_1 - k_+ - \frac{r_0^{(1)}}{2}(\kappa_1^2 - k_+^2) \approx \frac{2(E - E_1)}{C_{\kappa_1 0}^2}, \tag{51}$$

$$\kappa_2 - k_- + -\frac{r_0^{(2)}}{2}(\kappa_2^2 - k_-^2) \approx \frac{2(E - E_2)}{C_{\kappa_2 0}^2}. \tag{52}$$

Here, we have introduced the asymptotic coefficients

$$C_{\kappa_i 0} = \sqrt{\frac{2\kappa_i}{1 - \kappa_i r_0^{(i)}}}$$

of one-center wavefunctions in accordance with formula (4). The determinant of system (38) with diagonal matrix elements (51) and (52) gives the transcendental equation for energy E, which can be written in the form

$$2E = E_1 + E_2$$
$$\pm \sqrt{\Delta_{12}^2 + C_{\kappa_1 0}^2 C_{\kappa_2 0}^2 R^{-2} e^{-2\sqrt{-2ER}}}, \tag{53}$$

where

$$\Delta_{12} = E_1 - E_2 = \frac{\kappa_2^2 - \kappa_1^2}{2} - \mathbf{F} \cdot \mathbf{R}.$$

Taking into account the exchange term ($\sim e^{-2\sqrt{-2ER}}$) in Eq. (53) by the iterative method on the basis of the zeroth approximation,

$$E_0^{\pm} = (E_1 + E_2 \pm |\Delta_{12}|)/2,$$

we obtain

$$E^{\pm} = E_0^{\pm} \pm \Delta_{\pm}/2, \tag{54}$$

where

$$\Delta_{\pm} = C_{\kappa_1 0}^2 C_{\kappa_2 0}^2 R^{-2} \exp(-2\sqrt{-2E_0^{\pm}R})$$

$$\times \left\{ |\Delta_{12}| + \sqrt{\Delta_{12}^2 + C_{\kappa_1 0}^2 C_{\kappa_2 0}^2 R^{-2} \exp(-2\sqrt{-2E_0^{\pm}R})} \right\}^{-1}. \tag{55}$$

Analysis of relation (54) shows that for $\mathbf{F} \cdot \mathbf{R} > 0$, with increasing R or F, terms $E^{\pm}$ come closer to each other up to a certain minimal distance, after which they diverge.

We first consider the case when the field strength is fixed and R is a free parameter. The values of $R = R_0$ for which the terms $E^{\pm}$ converge to the minimal distance follows from the equality $E_1 = E_2$ ($\Delta_{12} = 0$):

$$R_0 = \frac{\kappa_2^2 - \kappa_1^2}{2F\cos\theta}. \tag{56}$$

It can be seen from this relation that R_0 has a minimum in parallel geometry ($\theta = 0$); we will confine our further analysis to this case only. The minimal distance $\Delta_{\min}$ between the terms for $R = R_0$ is determined by the exchange interaction,

$$\Delta_{\min} = E^+ - E^- = C_{\kappa_1 0} C_{\kappa_2 0} \frac{1}{R_0}$$

$$\times \exp\left(-\sqrt{\frac{\kappa_1^2 + \kappa_2^2}{2}} R_0\right), \tag{57}$$

and coefficients f_1 and f_2 determining the contribution of one-center states to the two-center wavefunction at the point of quasi-intersection are identical (in absolute value) for the "+" as well as the "−" term (with energies E^+ and E^-, respectively). For the "+" term, we have $|f_1| > |f_2|$ for $R < R_0$ and $|f_1| < |f_2|$ for $R > R_0$, while for the "−" term, these inequalities are inverted: $|f_1| < |f_2|$ for $R < R_0$ and $|f_1| < |f_2|$ for $R > R_0$. This means that during the passage through point R_0, a resonant transition of the electron from one center to another takes place, which leads to an almost abrupt variation of the dependence of the level width (or decay probability) of the ion on R (see Fig. 5b). We prove this for width Γ^+ of the "+" term, substituting E^+ from Eq. (54) into (42) and using expansions (51) and

(52) (in this case, we can omit the last term ($\sim R$) in Eq. (42)). As a result, we obtain the following expression for Γ^+ in the region of quasi-intersection of the terms:

$$\Gamma^+ = [1 + f(R)]^{-1}$$

$$\times \begin{cases} \Gamma_1 + \Gamma_2 f(R), & R \le R_0 \\ \Gamma_2 + \Gamma_1 f(R), & R \ge R_0, \end{cases} \quad (58)$$

where function $f(R)$ and the widths Γ_i of one-center states in field $\mathbf{F}$ have the form

$$f(R) = \frac{\Delta_+}{F|R - R_0| + \Delta_+}, \quad (59)$$

$$\Gamma_i = \frac{C_{\kappa_i,0}^2 F}{4\kappa_i^2} \exp\left(-\frac{2\kappa_i^3}{3F}\right). \quad (60)$$

An analogous result for the "$-$" term can be obtained from expression (58) by substitutions $\Delta_+ \longrightarrow \Delta_-$ and $\Gamma_1 \rightleftharpoons \Gamma_2$.

The case when R is fixed and the field strength is a free parameter can be analyzed analogously to the case of a fixed F. In particular, an analog of formula (58) for this case can be obtained by substituting function $f(R)$ for $f(F)$ into (58):

$$f(F) = \frac{\Delta_+}{R|F - F_0| + \Delta_+}, \quad (61)$$

where $F_0 = (\kappa_2^2 - \kappa_1^2)/2R$. Figures 5b and 5d demonstrate the high accuracy of asymptotic formulas of type (58) for $\Gamma^\pm(R)$ and $\Gamma^\pm(F)$ in the region of quasi-intersection of the terms.

5. ELECTRON ENERGY LEVELS IN THE FIELD OF s AND p CENTERS

Modification of the results for two s centers upon a change in the orbital symmetry of one-center states can be seen even from a simple example of a heteropolar ion of the AB^- type, in which A and B centers sustain, respectively, weakly bound s and p states ψ_0 and ψ_{1m} with energies $E_1^{(0)} = -\kappa_1^2/2$ and $E_2^{(0)} = -\kappa_2^2/2$ (e.g., the OH^- ion). Although the basis set required for constructing the two-center function (7) contains four one-center states, system of equations (12) for $\mathbf{F} = 0$ and for the quantization axis directed along the axis of the quasi-molecule contains only two equations for coefficients $f_1^{(0)} \equiv f_{l_1 = 0, m_1 = 0}$ and $f_2^{(0)} \equiv f_{l_2 = 1, m_2 = 0}$ for the mixture of states $\psi_{l_1 = 0, m_1 = 0}$ and $\psi_{l_2 = 1, m_2 = 0}$ corresponding to two two-center states of an electron with zero projection of the angular momentum onto the interatomic axis with energies $E_0 = E_0^\pm$: $E_0^+ =$

$-(k_0^+)^2/2$ and $E_0^- = -(k_0^-)^2/2$. These equations have the form

$$\begin{pmatrix} \mathcal{L}_0^{(1)}(k_0) & Q(k_0) \\ Q(k_0) & -\mathcal{L}_1^{(2)}(k_0) \end{pmatrix} \begin{pmatrix} f_1^{(0)} \\ f_2^{(0)} \end{pmatrix} = 0, \quad (62)$$

where

$$k_0 = \sqrt{-2E_0}, \quad Q(k_0) = \frac{\sqrt{3}e^{-k_0 R}(1 + k_0 R)}{R^2},$$

and the explicit form of function $\mathcal{L}_0^{(1)}(k_0)$ is given by formula (39),

$$\mathcal{L}_1^{(2)}(k) = \kappa_2^3 - k^3 + \frac{r_1^{(2)}}{2}(\kappa_2^2 - k^2). \quad (63)$$

Since the electron densities of two-center states are different in the regions of the first and second centers, the system with s and p centers has a constant dipole moment $\mathbf{d}_{sp}^\pm \approx \mathbf{R}$ like for a system with nonequivalent s centers.

When an electric field is applied, it is convenient to choose the quantization axis along vector $\mathbf{F}$ so that system of equations (12) can be written in the form

$$\begin{pmatrix} \hat{A}_{0,0;0,0}^{(1,1)} & A_{0,0;1,0}^{(1,2)} & A_{0,0;1,1}^{(1,2)} & A_{0,0;1,1}^{(1,2)} \\ A_{0,0;1,0}^{(1,2)} & \hat{A}_{1,0;1,0}^{(2,2)} & 0 & 0 \\ A_{0,0;1,1}^{(1,2)} & 0 & \hat{A}_{1,1;1,1}^{(2,2)} & 0 \\ A_{0,0;1,1}^{(1,2)} & 0 & 0 & \hat{A}_{1,1;1,1}^{(2,2)} \end{pmatrix} \begin{pmatrix} f_{0,0} \\ f_{1,0} \\ f_{1,1} \\ f_{1,-1} \end{pmatrix} = 0, \quad (64)$$

where

$$\hat{A}_{lm;lm}^{(j,j)} = A_{lm;lm}^{(j,j)} - \mathcal{B}_l\left(\epsilon + (-1)^j \frac{\mathbf{F} \cdot \mathbf{R}}{2}\right),$$

and the explicit form of matrix elements $A_{l_1 m_1; l_2 m_2}^{(i,j)}(\epsilon)$ is given in the Appendix (see formulas (A.8)–(A.13)). Equating the determinant of system (64) to zero, we obtain the following transcendental equation for complex energies ϵ:

$$\hat{A}_{1,1;1,1}^{(2,2)}[\hat{A}_{1,1;1,1}^{(2,2)}\hat{A}_{1,0;1,0}^{(2,2)}\hat{A}_{0,0;0,0}^{(1,1)} $$
$$- \hat{A}_{1,1;1,1}^{(2,2)}(A_{0,0;1,0}^{(1,2)})^2 - 2\hat{A}_{1,0;1,0}^{(2,2)}(A_{0,0;1,1}^{(1,2)})^2] = 0. \quad (65)$$

In accordance with formulas (64) and (65), three quasi-stationary two-center (molecular) states are formed in the field $\mathbf{F}$, forming an angle θ with the axis of the molecule. One of these states appears only for $\theta \ne 0$ because, in accordance with formula (A.12), $A_{0,0;1,1}^{(1,2)} = 0$ for $\theta = 0$, and the two-center system sustains, in accordance with formulas (64) and (65), only two molecular states formed from the wavefunction of the s center and the state of the p center with zero projection m of the angular momentum onto the direction

of $\mathbf{F}$. The deviation of vector $\mathbf{F}$ from the molecular axis leads to the exchange interaction (i.e., nonzero overlap integral) between the wavefunctions of the s center and the states of the p center with angular momentum projections $m = \pm 1$. As a result, the third two-center state appears in the form of a superposition of the wavefunction of the s center and a symmetric combination of states with $m = +1$ and $m = -1$ localized at the p center (because in the case of an antisymmetric combination, the terms in the matrix elements responsible for the exchange interaction are mutually compensated, and no molecular state is formed).

In the case of arbitrary geometry, analytic calculations of complex energy ϵ are quite cumbersome; for this reason, we confine our analysis to the most important case of parallel geometry ($\theta = 0, \pi$). It was mentioned above that the wavefunctions of two molecular states are determined in this case by a superposition of the wavefunctions for the s and p centers with projections $m = 0$ so that system (64) can be reduced to the following two equations:

$$\begin{pmatrix} \hat{A}_{0,0;0,0}^{(1,1)} & \hat{A}_{0,0;1,0}^{(1,2)} \\ \hat{A}_{0,0;1,0}^{(1,2)} & \hat{A}_{1,0;1,0}^{(2,2)} \end{pmatrix} \begin{pmatrix} f_{0,0} \\ f_{1,0} \end{pmatrix} = 0, \qquad (66)$$

while the transcendental equation for complex energies $\epsilon = \epsilon^{\pm}$, which are transformed onto unperturbed energies E_0^{+} and E_0^{-} following from Eq. (62) for $F = 0$, has the form

$$\hat{A}_{0,0;0,0}^{(1,1)}(\epsilon, F)\hat{A}_{1,0;1,0}^{(2,2)}(\epsilon, F) - [A_{0,0;1,0}^{(1,2)}(\epsilon, F)]^2 = 0. \quad (67)$$

Analysis of system (66) by the methods of perturbation theory in the exchange interaction is completely analogous to the case of ss centers considered in Section 3.2.

We will now consider the results of analysis of Eq. (67) based on the approach used in Section 4. The equation for energies $E = E^{\pm}(\mathbf{F})$ of the sp system in the zeroth approximation, which is analogous to Eq. (38), can be derived from Eq. (62) using the substitution $k_0 \longrightarrow k = \sqrt{-2E(\mathbf{F})}$ in the exchange term $Q(k_0)$,

$$k_0 \longrightarrow k_+ = \sqrt{-[2E(\mathbf{F}) + \mathbf{F} \cdot \mathbf{R}]}$$

in $\mathscr{L}_0^{(1)}(k_0)$, and

$$k_0 \longrightarrow k_- = \sqrt{-[2E(\mathbf{F}) + \mathbf{F} \cdot \mathbf{R}]}$$

in $\mathscr{L}_1^{(2)}(k_0)$. Writing now ϵ in formula (67) in the form $\epsilon^{\pm} = E^{\pm}(\mathbf{F}) + \Delta\epsilon^{\pm}$ and taking into account the terms on the order of F appearing in expansions of type (36), (37) for matrix elements $A_{l_1 m_1; l_2 m_2}^{(i,j)}$ in (67), we obtain complex correction $\Delta\epsilon^{\pm}$ to $E^{\pm}(\mathbf{F})$:

$$\Delta\epsilon^{\pm} = -\mathbf{d}^{\pm}(\mathbf{F}) \cdot \mathbf{F} - i\Gamma^{\pm}/2, \qquad (68)$$

where

$$\mathbf{d}^{\pm}(\mathbf{F}) = \frac{R}{Nk(1 + kR)}\mathbf{R}, \qquad (69)$$

$$\Gamma^{\pm} = \frac{F}{2N}\left(\frac{k_+^{-2}}{\mathscr{L}_0^{(1)}(k_+)}\exp\left(-\frac{2k_+^3}{3F}\right)\right.$$

$$- \frac{3}{\mathscr{L}_1^{(2)}(k_-)}\exp\left(-\frac{2k_-^3}{3F}\right) \qquad (70)$$

$$\left.+ \frac{2R^2}{k(1 + kR)}\exp\left(\frac{kR - 2k^3}{3F}\right)\right),$$

$$N = \frac{\mathscr{C}_0^{(1)}(k_+)}{\mathscr{L}_0^{(1)}(k_+)} + \frac{\mathscr{C}_1^{(2)}(k_-)}{\mathscr{L}_1^{(2)}(k_-)} - \frac{2R^2}{1 + kR}, \qquad (71)$$

$$\mathscr{C}_1^{(2)}(k_-) = 3k_- + r_1^{(2)},$$

and $\mathscr{L}_0^{(1)}(k_+)$, $\mathscr{C}_0^{(1)}(k_+)$, and $\mathscr{L}_1^{(2)}(k_-)$ are defined in formulas (39), (44), and (63). It can be seen from formula (68) that in contrast to expansion (40) for the s centers, the principal term in the expansion of $\Delta\epsilon^{\pm}$ is linear in F so that the real correction of order F^2 to energies $E^{\pm}(\mathbf{F})$ is small. It should be noted that the inclusion of this correction as well as the terms of order F^2 in the expansion of $E^{\pm}(\mathbf{F})$ in F makes it possible to obtain an analytic expression for polarizability $\beta_{sp}^{\pm}(R, \theta = 0)$ of the sp system, which is rather cumbersome and is not given here.

Constant dipole moment $\mathbf{d}_{sp}^{\pm}$ of the sp system, which describes the linear Stark effect in the unperturbed terms with energies $E_0^{\pm}$: $\Delta E_0^{\pm} = -\mathbf{d}_{sp}^{\pm} \cdot \mathbf{F}$, is given by the sum of $\mathbf{d}^{\pm}(\mathbf{F} = 0)$ and dipole moment $\mathbf{d}_0^{\pm}$ that determines the principal term in the series expansion of $E^{\pm}(\mathbf{F})$ in F:

$$E^{\pm}(\mathbf{F}) = E_0^{\pm} - \mathbf{d}_0^{\pm} \cdot \mathbf{F}.$$

The expression for $\mathbf{d}_{sp}^{\pm}$ has the form

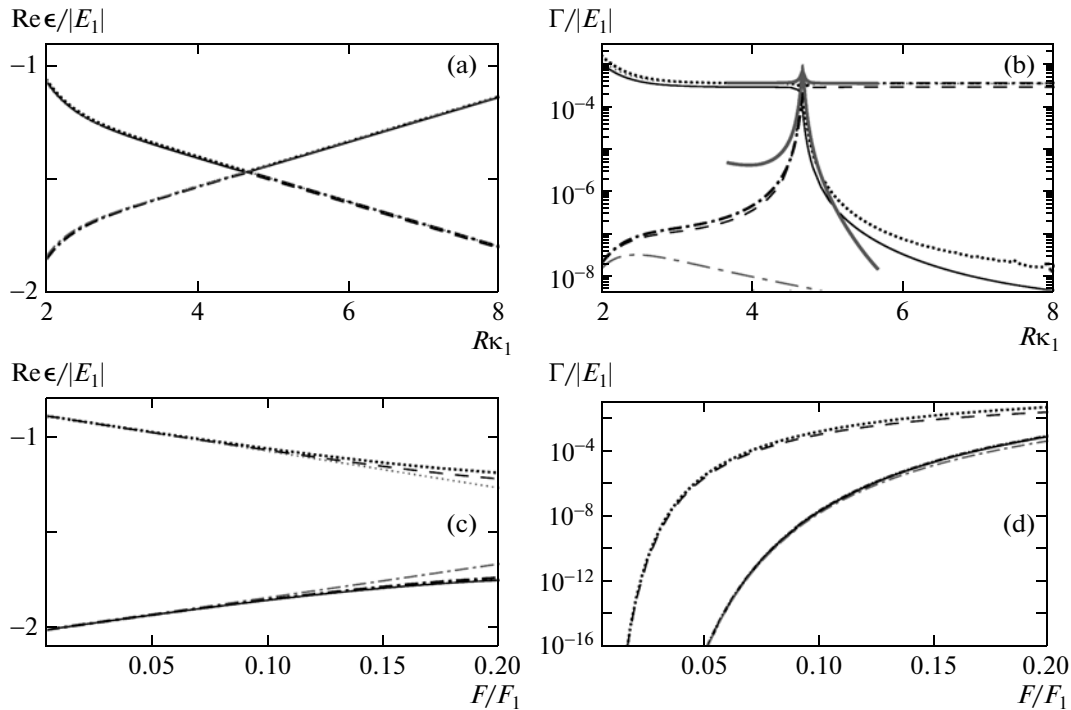$$\mathbf{d}_{sp}^{\pm} = \mathbf{d}^{\pm}(\mathbf{F} = 0) + \mathbf{d}_0^{\pm},$$

$$\mathbf{d}^{\pm}(0) = \frac{R}{N(k_0)k_0(1 + k_0R)}\mathbf{R}, \qquad (72)$$

$$\mathbf{d}_0^{\pm} = \frac{1}{2N(k_0)}\left[\frac{\mathscr{C}_0^{(1)}(k_0)}{\mathscr{L}_0^{(1)}(k_0)} - \frac{\mathscr{C}_1^{(2)}(k_0)}{\mathscr{L}_1^{(2)}(k_0)}\right]\mathbf{R},$$

where $N(k_0) \equiv N(k_0^{\pm})$ follows from expression (71) for N after the substitution of $k_0^{\pm} = \sqrt{-2E_0^{\pm}}$ for k, k_+, and k_-. We can also write expression (70) for widths $\Gamma^{\pm}$ in the limit of a weak field ($F \longrightarrow 0$):

$$\Gamma_0^{\pm} = \frac{F}{2N(k_0)}\exp\left(-\frac{2k_0^3}{3F} - 2d_{sp}^{\pm}k_0\cos\theta\right)$$

Fig. 6. Dependences of the position and width of the levels of a two-center *sp* system with $\kappa_2 = 1.4\kappa_1$, which is oriented along field **F**, on R (a, b; $F = 0.05\kappa_1^3$) and F (c, d; $R = 2\kappa_1^{-1}$). Solid and dashed curves are exact results for ϵ_- and ϵ_+, respectively; dotted and dot-and-dash curves are the results of calculations based on formulas (68)−(70); gray dotted and dot-and dashed curves are the results for a weak field calculated by formulas $\mathrm{Re}\,\epsilon_\pm = E_0^\pm - \mathbf{d}_{sp}^\pm \cdot \mathbf{F}$ and (73) (for $\Gamma^\pm$); gray solid curves in (b) are the results of calculations by formula (58) taking into account (74) and (75); $E_1 = -\kappa_1^2/2$ and $F_1 = \kappa_1^3$.

$$\times \left(\frac{k_0^{-2} \exp(k_0 R \cos\theta)}{\mathcal{L}_0^{(1)}(k_0)} \right. \tag{73}$$

$$\left. - \frac{3 \exp(-k_0 R \cos\theta)}{\mathcal{L}_1^{(2)}(k_0)} + \frac{2R^2 \exp(k_0 R)}{(1 + k_0 R)k_0} \right).$$

The high accuracy of formulas (68)−(70) for the shift and width of the energy levels of the *sp* system in an electric field follows from comparison with the results of numerical analysis of system (66) for $\kappa_2 = 1.4\kappa_1$, $\kappa_1 = 0.236$, $r_0^{(1)} = 2.64$, and $r_1^{(2)} = -1.49$ (as for the OH⁻ ion); see Fig. 6. It can be seen from Fig. 6 that as in the case of nonequivalent *s* centers, quasi-intersection of energy levels upon a change in R and peculiarities in widths $\Gamma^\pm$ associated with it are also observed for a quasi-molecule with *s* and *p* centers, while no quasi-intersection takes place upon a change in F for parameters κ_1 and κ_2 considered here. All results obtained in Section 4 for the region of the quasi-intersection of energy levels in the *ss* system are also valid for an *sp* system to within notation. In particular, analogs of formulas (55) and (58) for *sp* centers can be obtained from these formulas using the follow-

ing substitution of coefficients describing the exchange interaction:

$$\frac{C_{\kappa_1 0} C_{\kappa_2 0} \exp(-k_0^\pm R)}{R}$$

$$\longrightarrow \sqrt{3} C_{\kappa_1 0} C_{\kappa_2 1} \frac{\exp(-k_0^\pm R)(1 + k_0^\pm R)}{\kappa_2 R^2}. \tag{74}$$

In addition, decay probability Γ_2 for the one-center state in expression (58) for width Γ^+ and in an analogous expression for Γ^- should be replaced by probability $\Gamma_2^{(p)}$ of the decay of a weakly bound *p* state with angular momentum projection $m = 0$ in field **F** [40]:

$$\Gamma_2 \longrightarrow \Gamma_2^{(p)} = 3 \frac{C_{\kappa_2 1}^2 F}{4\kappa_2^2} \exp\left(-\frac{2\kappa_2^3}{3F}\right). \tag{75}$$

It can be seen from Fig. 6b that widths $\Gamma^\pm$ of the *sp* system in the region of quasi-intersection of terms, which were obtained using the above method, are in good agreement with the exact results as well as with the results obtained by formula (70).

6. CONCLUSIONS

We have considered the simplest exactly solvable model of interaction of a molecular system with a constant electric field $\mathbf{F}$, which generalizes the effective range approximation for describing the interaction of a weakly bound electron with field $\mathbf{F}$ [32] to the case of several atomic centers. As in the method of effective range for the one-center problem, the short-range potentials of the centers are taken into account in boundary conditions (6) for the wavefunction of the multicenter problem near each of N centers, which are determined by the spatial symmetry of the bound state sustained by the field of the ith center. For a system with s centers, transcendental equation (13) for molecular terms ϵ in the model considered here in the approximation of the scattering length for scattering phases is equivalent to the equation for the poles of the exact Green function for an electron in field $\mathbf{F}$ and in the field of N 3D δ potentials [26]. Since the equation for ϵ contains only Green function $G_\epsilon(\mathbf{R}_i, \mathbf{R}_j)$ for a free electron in field $\mathbf{F}$ and its spatial derivatives, a convenient analytic representation for $G_\epsilon(\mathbf{r}, \mathbf{r}')$ [26] makes it possible to obtain exact numerical results for complex energies $\epsilon = \epsilon(F, R, \theta)$ of the two-center system considered here, as well as analytic approximations for a number of limiting cases. In spite of the simplicity of the model used here, the results of analytic calculations give a visual qualitative interpretation of some features of the probabilities of ionization of homo- and heteronuclear molecules by a strong low-frequency laser field, which follow from direct numerical calculations.

For two identical s centers, analytic expressions for $\epsilon(F, R, \theta)$ were obtained in the limit of weak field ($F \longrightarrow 0$), in which our results are in conformity with the data from [26], as well as using perturbation theory in the exchange interaction without assumption of the smallness of F. These results make it possible to analytically calculate the width and shift of the level both in the tunneling regime (for $\mathbf{F} \cdot \mathbf{R} + \epsilon_0 < 0$, where ϵ_0 is the characteristic energy of the molecular term under investigation for $F = 0$) and in the above-barrier mode of the decay (when $\mathbf{F} \cdot \mathbf{R} + \epsilon_0 > 0$). Comparison of these results with the results of exact calculations of ϵ demonstrates good agreement even beginning with interatomic distances $R \gtrsim R_{cr} \approx 3\sqrt{2|\epsilon_0|}$, for which the expansions for the shift and width of energy levels in a weak field become inapplicable. For $R \gtrsim R_{cr}$, the position of the levels in a strong field changes insignificantly when the exchange interaction is taken into account and is successfully approximated by the formula $\operatorname{Re}\epsilon_{\pm}(\mathbf{F}) \approx \epsilon_0 \mp \mathbf{F} \cdot \mathbf{R}/2$ of the zeroth approximation. This result confirms the linear dependence of the real part of the molecular term energy on R, which was obtained in numerical calculations for one- [18], two- [14], and three-dimensional [12, 17] problems. Conversely, modification of the exchange interaction by a

strong electric field is of fundamental importance for the width of the levels. In particular, for a molecule oriented along field $\mathbf{F}$, the probability of ionization in the above-barrier mode exhibits an oscillatory dependence on R. Since an electron in a strong field is localized in the vicinity of one of atomic centers, such oscillations appear due to the interference of two waves, one of which is determined by direct tunneling of the electron in the $-\mathbf{F}$ direction, while the other is determined by tunneling with rescattering from the neighboring center followed by reflection from the barrier formed by the electric field. This result is confirmed by the analysis carried out in [14] in the 2D model and is in qualitative agreement with the results of numerical calculations for molecular systems with two Coulomb centers [11, 12, 16, 17]. The results obtained in Section 3.2 also provide a qualitative explanation of the dependence of the probability of ionization of the H_2^+ ion on its orientation relative to vector $\mathbf{F}$ in the weak and strong field regimes. Numerical calculations performed in [16] show that the probability of ionization of H_2^+ from the excited state in the tunnel regime is higher than from the ground state, and the maxima (minima) of the ionization probability are observed for the orientation of the molecule along (across) the field. Conversely, in the above-barrier regime, the probability of ionization from the excited state can be lower than from the ground state, and the orientation dependence is inverted (i.e., the ionization probability maximum is observed for $\mathbf{F} \cdot \mathbf{R} = 0$). An analogous result also follows from analysis based on the model developed here (see Fig. 4).

For a system with nonequivalent atomic centers, the position and width of energy levels in field $\mathbf{F}$ are essentially determined by the effects of a constant dipole moment; explicit expressions (47) and (72) were derived for dipole moments $\mathbf{d}_{ss}^{\pm}$ and $\mathbf{d}_{sp}^{\pm}$ of systems with ss and sp centers. In particular, the position of energy levels up to a strong field is mainly determined by the linear Stark effect. In a strong field, a constant dipole moment leads to quasi-intersection of energy levels, which substantially changes their field widths: the smooth dependence of the width on R or F can abruptly change in narrow intervals of R or F, which are determined by the exchange interaction (see Figs. 5 and 6). Such a variation is associated with a change in the spatial localization of an electron in the system of two centers in the region of quasi-intersection of energy levels. These results permit a clear physical interpretation of the results of numerical calculations [42] of the dependence of the probability of ionization of asymmetric molecules on the internuclear spacing. It was demonstrated numerically in [42] that the probability of ionization of a molecule by a low-frequency laser field as a function R has a sharp peak corresponding to the region of R in which quasi-intersection of molecular terms takes place. Obviously, a

slowly varying laser field induces in this region a non-adiabatic transition (of the Landau–Zener type [27]) between the ground and excited molecular terms. Thus, the molecule is in the ground state up to the point of quasi-intersection of energy levels, and the probability of its ionization increases with R; in the vicinity of the point of quasi-intersection, a nonadiabatic transition to the excited state takes place and a further increase in R leads to a decrease in the ionization probability, thus forming a peak in the dependence of the probability on R.

It can be noted in conclusion that the model considered here permits direct generalization to the case of a monochromatic perturbation $V(\mathbf{r}, t)$ with frequency ω also. As in the theory of effective range for the one-center problem [35, 36], a complication is due to the fact that coefficients $f_{l_i m_i}$ in boundary condition (6) are periodic functions of time in this case, while the homogeneous system of linear algebraic equations (12) changes for a homogeneous system of 1D integrodifferential equations for $f_{l_i m_i}(\omega t)$ and complex quasi-energy $\epsilon(\mathbf{R}, \mathbf{F}, \omega)$. The application of this model to molecular photo-induced processes in a strong optical field requires special analysis.

ACKNOWLEDGMENTS

APPENDIX

Analytic Expressions for Matrix Elements $A_{l_i m_i;\, l_j m_j}^{(i,j)}(\epsilon)$

We write below matrix elements $A_{l_i m_i;\, l_j m_j}^{(i,j)}$ for a two-center system with *ss* centers ($l_1 = 0, l_2 = 0$) and *sp* centers ($l_1 = 0, l_2 = 1$) in a constant electric field.

The Green function for an electron in a constant electric field has the form [26]

$$G_\epsilon(\mathbf{r}, \mathbf{r}') = \frac{\text{Ai}(Z_+)\text{Ci}'(Z_-) - \text{Ai}'(Z_+)\text{Ci}(Z_-)}{2|\mathbf{r} - \mathbf{r}'|}, \quad (\text{A.1})$$

where

$$Z_\pm = -\frac{1}{(2F)^{2/3}}[2\epsilon - F(z + z' \pm |\mathbf{r} - \mathbf{r}'|)], \quad (\text{A.2})$$

$\text{Ci}(x) = \text{Bi}(x) + i\text{Ai}(x)$, $\text{Ai}(x)$ and $\text{Bi}(x)$ being the regular and irregular Airy functions [43]. We write the analytic expressions for matrix elements $A_{l_i m_i;\, l_j m_j}^{(i,j)}$ obtained from formula (A.1) and definitions (10) and (11). For

ss centers ($l_1 = 0, l_2 = 0$), these expressions have the form

$$A_{0,0;\,0,0}^{(1,1)} = J(\xi_+), \quad A_{0,0;\,0,0}^{(2,2)} = J(\xi_-), \quad (\text{A.3})$$

$$A_{0,0;\,0,0}^{(1,2)} = A_{0,0;\,0,0}^{(2,1)} = \mathcal{G}_\epsilon(R), \quad (\text{A.4})$$

where we have introduced the notation

$$\xi_\pm \equiv \xi_\pm(\theta) = -\frac{2\epsilon \pm \mathbf{F} \cdot \mathbf{R}}{(2F)^{2/3}}, \quad (\text{A.5})$$

$$J(\xi) = \pi(2F)^{1/3}[\text{Ai}'(\xi)\text{Ci}'(\xi) - \xi\text{Ai}(\xi)\text{Ci}(\xi)], \quad (\text{A.6})$$

$$\mathcal{G}_\epsilon(R) \equiv G_\epsilon\left(\frac{\mathbf{R}}{2}, -\frac{\mathbf{R}}{2}\right)$$

$$= \frac{\pi}{R}[\text{Ai}(\xi_-(0))\text{Ci}'(\xi_+(0)) \quad (\text{A.7})$$

$$- \text{Ai}'(\xi_-(0))\text{Ci}(\xi_+(0))],$$

while for the *sp* centers ($l_1 = 0, l_2 = 0$), we have

$$A_{0,0;\,0,0}^{(1,1)} = J(\xi_+), \quad (\text{A.8})$$

$$A_{1,0;\,1,0}^{(2,2)} = (2F)^{2/3}[J''(\xi_-) - \xi_- J(\xi_-)], \quad (\text{A.9})$$

$$A_{1,\pm 1;\,1,\pm 1}^{(2,2)} = (2F)^{2/3}[J''(\xi_-)/4 - \xi_- J(\xi_-)], \quad (\text{A.10})$$

$$A_{1, m_i;\, 1, m_j}^{(2,2)} = 0, \quad i \neq j, \quad (\text{A.11})$$

$$A_{0,0;\,1,\pm 1}^{(1,2)} = \sqrt{\frac{3}{2}}\sin\theta\frac{\partial\mathcal{G}_\epsilon(R)}{\partial R}, \quad (\text{A.12})$$

$$A_{0,0;\,1,0}^{(1,2)} = -\sqrt{3}\left[\cos\theta\frac{\partial\mathcal{G}_\epsilon(R)}{\partial R} + \frac{F}{2}\frac{\partial\mathcal{G}_\epsilon(R)}{\partial\epsilon}\right], \quad (\text{A.13})$$

where

$$J''(x) = -\pi(2F)^{1/3}[\text{Ai}'(x)\text{Ci}(x) + \text{Ai}(x)\text{Ci}'(x)].$$

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