Quasistationary and virtual states in the problem of two Coulomb centers. The electron energy spectrum

S. Yu. Ovchinnikov and E. A. Solov'ev

A. F. Ioffe Physicotechnical Institute, Academy of Sciences of the USSR, Leningrad

(Submitted 12 February 1986)
Zh. Eksp. Teor. Fiz. **91**, 477–484 (August 1986)

Antibonding (quasistationary and virtual) states are found. The dependence of their energy and width on the internuclear distance R and the charges Z_1 and Z_2 is investigated. A general expression is obtained for the energy spectrum of the electrons produced upon ionization, and a calculation of this spectrum for the reaction $\mathrm{H}(1s) + \mathrm{H}^+ \rightarrow \mathrm{H}^+ + \mathrm{H}^+ + e$ is given.

1. INTRODUCTION

Antibonding (quasistationary and virtual) states in the problem of two Coulomb centers Z_1eZ_2 have not been investigated until now. This is explained primarily by the fact the problem does not contain an obvious effective barrier of the type with which a quasistationary state is usually associated. However, in the study of the ionization process in the adiabatic approximation the question of the existence of such states inevitably arises. The ionization of a quasimolecular system with long-range Coulomb interaction is connected with the superpromotion of a diabatic term, through the Rydberg bunching of levels, into the continuous spectrum.[1] Such diabatic terms for the problem of two Coulomb centers were discovered in Ref. 2 and were studied there below the boundary of the continuous spectrum. The behavior of the diabatic terms above the boundary of the continuous spectrum depends on the structure of the quasistationary levels, and it is this behavior which determines the energy spectrum of the electrons produced upon ionization. In view of this it becomes necessary to seek and investigate the antibonding states in the region in which the diabatic term emerges into the continuous spectrum. Such an investigation is also of general theoretical interest, since because of the long-range Coulomb interaction the existing theory of antibonding levels as poles of the S-matrix[3] is inapplicable here, and the situation is not even qualitatively clear.

In this paper we find quasistationary and virtual states in the problem of two Coulomb centers, investigate the dependence of their energy and width on the internuclear distance R and the nuclear charges Z_1 and Z_2, and also obtain a general expression for the energy spectrum of the electrons produced upon ionization and give the calculation of this spectrum for the reaction $\mathrm{H}(1s) + \mathrm{H}^+ \rightarrow \mathrm{H}^+ + \mathrm{H}^+ + e$. Various methods can be used for seeking and calculating the quasistationary and virtual terms. Our method consisted in the following. Adibatic terms $E_i(R)$ of the same symmetry are different branches of one analytic function $E(R)$. Two terms $E_1(R)$ and $E_2(R)$ are joined into a single analytic function by a common branch point R_C ($\operatorname{Im} R_C \neq 0$), in the neighborhood of which the difference of the terms has the form[4]

$$E_1(R)-E_2(R)=\text{const}\,(R-R_C)^{1/2}, \qquad (1)$$

and, therefore, starting for real values of R from the term $E_1(R)$, after passing around the point R_C and returning to the real R axis we find ourselves on the second term $E_2(R)$. If $E_1(R)$ is an adiabatic bound-state term, and $E_2(R)$ is an adiabatic antibonding-state term, we thereby have a comparatively simple method of calculating antibonding terms that uses the already existing program for calculating discrete terms in the complex R plane.[2] Here one must first find the corresponding branch points R_C. The search for the branch points was carried out automatically in our program from the condition, which follows from the expression (1), that the derivative $dE_i(R)/dR$ becomes infinite at R_C.

For the classification of the bound states, below we shall use the spherical quantum numbers nlm of the united atom ($R = 0$) and their spectroscopic notation: $l = s, p, d, \ldots$, $m = \sigma, \pi, \delta, \ldots$. To a quasistationary or virtual term we shall assign the quantum numbers of the discrete term with which it is conected by the branch point R_C (with a bar over the quantum numbers: $\overline{nlm}$). By a quasistationary state, as usual, we mean a state with $\operatorname{Re} E(R) > 0$, and by a virtual state we mean a state with $\operatorname{Re} E(R) < 0$. In the article we use the atomic system of units.

2. QUASISTATIONARY AND VIRTUAL TERMS ASSOCIATED WITH SUPERPROMOTION OF A DIABATIC TERM

The phenomenon of superpromotion was discovered in the problem of two Coulomb centers and consists in an infinite chain of close quasi-intersections between pairs of adiabatic terms, $E_{nlm}(R)$ and $E_{n+1,lm}(R)$, for all $n \geqslant l+1$ (Ref. 2). Replacing the quasi-intersections by exact intersections, we obtain a system of diabatic terms, in which one term (W_{lm}) emerges into the continuous spectrum. Associated with each quasi-intersection there is in the upper half-plane of R a branch point[1] R_{nlm}, in the neighborhood of which

$$E_{n+1,\,lm}(R)-E_{nlm}(R)=\text{const}\,(R-R_{nlm})^{1/2}.$$

The set of all branch points R_{nlm} with a fixed choice of l and m forms an infinite series S_{n_0lm} of points ($n_0 = l + 1$ is the principal quantum number of the lowest adiabatic term in the given series), localized in a small region Ω of the complex R plane and converging to a certain limit point

$$R_{lm}=\lim_{n\to\infty} R_{nlm}.$$

The branch points R_{nlm} successively connect all the terms of the given $\{lm\}$ series into a single analytic function $E_{lm}(R)$. In the neighborhood of the region Ω the energy surface $E_{lm}(R)$ has the form of an infinite "spiral staircase," climbing which, i.e., moving toward the boundary of the contin-

0038-5646/86/080280-04$04.00

uous spectrum, we cross increasingly excited terms (higher "floors"). The boundary of the continuous spectrum is reached after an infinite number of clockwise turns around the region Ω. By passing around Ω in the anticlockwise direction we pass to the lower-lying terms, until we reach the ground term $E_{l+1,lm}(R)$ in the given series S_{n_0lm}.

As a result of a calculation using the scheme described in the Introduction, we have found a new branch point on the ground term $E_{l+1,lm}(R)$—a branch point that is common with a certain antibonding term $E_{\overline{l+1,lm}}(R)$. This branch point is located near the branch point $R_{l+1,lm}$ (the first point in the series $S_{l+1,lm}$). Then, on the antibonding term $E_{\overline{l+1,lm}}(R)$, we found a further branch point, which coincides with the limit point R_{lm} and connects the term $E_{l+1,lm}(R)$ with the limiting Rydberg term

$$E_{lm}{}^{\infty}(R)=\lim_{n\to\infty}E_{nlm}(R).$$

Thus, the infinite "spiral staircase" closes on itself through the antibonding term $E_{\overline{l+1,lm}}(R)$, i.e., turns into a ring. In Fig. 1 we give the results of a numerical calculation of the antibonding terms of the molecular ion H_2^+, in the form of a standard pattern of poles of the S-matrix in the complex plane of the wave number $k=(2E)^{1/2}$. The position of the poles depends parametrically on the internuclear distance. The pattern of the poles is symmetric about the imaginary k axis. The poles in the left half-plane of k correspond to the antibonding terms $E^*_{\overline{l+1,lm}}(R)$ that are obtained when one passes around the branch points in the lower half-plane of R. With change of R the poles move along a trajectory similar in shape to a hyperbola with vertex on the imaginary axis at the point $k_t\cong 2[l(l+1)]^{-1/2}$. The internuclear distance at which two symmetric poles coalesce at the vertex of the hyperbola corresponds to the minimum of the diabatic term W_{lm}, the position of which, for $m=0$, is approximately equal to[2] $R_0\approx l(l+1)$. With decrease of the internuclear distance from the value $R=R_0$ the two poles move to opposite sides, and, as $R\to 0$, move away to infinity. As a result, when $R=0$ the lower half-plane of k is completely cleared of poles, as it should be for a one-center Coulomb potential.[3,4] As can be seen from Fig. 1, with increase of R, for $l\geqslant 3$, the trajectories of the poles intersect the bisectrix and the state is transformed from a virtual into a quasistationary state.

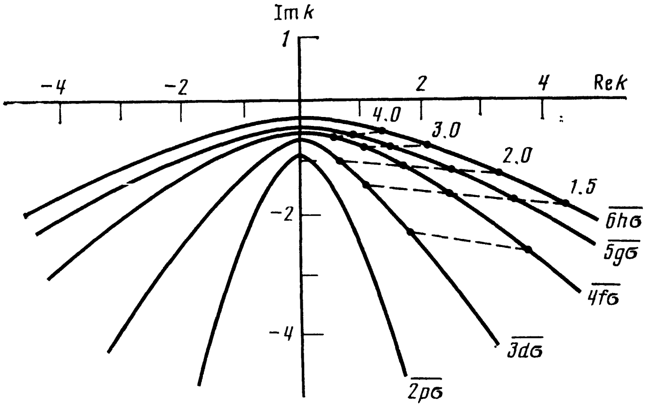

FIG. 1. Trajectories of poles of the S-matrix in the complex plane of the wave number $k=(2E)^{1/2}$ for the antibonding states $\overline{2p\sigma}$, $\overline{3d\sigma}$, $\overline{4f\sigma}$, and $\overline{5g\sigma}$ of the molecular ion H_2^+. The values of the internuclear distance R are indicated.

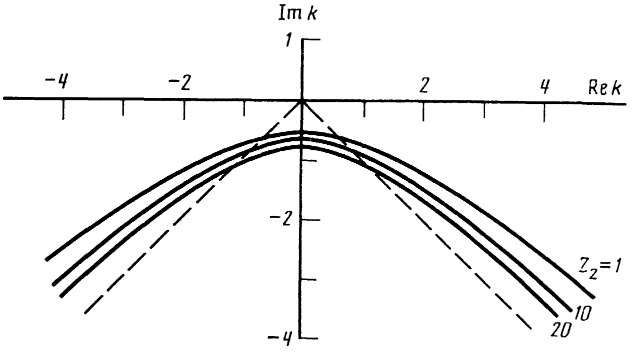

FIG. 2. The same for the antibonding state $\overline{4f\sigma}$ of the system (Z_1,eZ_2) for different values of the charge $Z_2=1$, 10, 20; $Z_1=1$.

The effect of the charges Z_1 and Z_2 on the described pattern of the poles of the S-matrix reduces mainly to a change of the characteristic scale in the R plane and k plane. With increase of the total charge $Z=Z_1+Z_2$ the distances in the R plane decrease in proportion of Z^{-1}, while the distances in the k plane increase in proportion to Z. The dependence on the charge ratio Z_1/Z_2 is weak. In Fig. 2 we give the trajectories of the poles of the $\overline{4f\sigma}$ state for the charges $Z_1=1$, $Z_2=1$, 10, 20.

A qualitative feature of the behavior of the poles of the S matrix in the presence of long-range Coulomb interaction is the fact that the symmetric poles coalesce on the imaginary axis at $k\neq 0$ (see Fig. 1). In the case of a short-range potential such a situation is possible only for an s-state, and for $l\neq 0$ the poles always coalesce at the point $k=0$ (Ref. 5). This difference from the previously known behavior is explained by the fact that the S-matrix has at $k=0$ an essential singularity associated with the Rydberg bunching of the levels toward the continuum boundary, from which an isolated pole cannot split off on change of the parameters of the Hamiltonian.

The results given above pertain to the region of internuclear distances $0<R<R_0$. For $R>R_0$ it is not possible to calculate the antibonding terms by the method that we have used, because of the divergence of the continued fraction corresponding to the radial equation. However, it should be noted that in this calculation there is no particular need for this, since the energy spectrum of the electrons produced upon ionization depends on the behavior of the antibonding terms only for $R<R_0/2$, when the diabatic term W_{lm} has already emerged into the continuum.

In the problem of two Coulomb centers there are also other antibonding terms besides those discussed above. In particular, we have found new series S_{n_0lm} with $n_0>l+1$, which are located in the complex R plane at approximately the same value of the real part of the internuclear distance as the series with $n_0=l+1$, but further from the real R axis. These series are analogous in their structure to the series $S_{l+1,lm}$ and differ from these latter only in the fact that terms $E_{nlm}(R)$ with $l+1<n<n_0$ are not involved in them.

Each new series S_{n_0lm} also has its own antibonding term $E_{\overline{n_0lm}}(R)$, through which it closes on itself. However, the S-matrix poles corresponding to these terms are situated far from the real k axis, and therefore are of no physical interest. This also applies to the other antibonding terms not mentioned here.

3. ENERGY SPECTRUM OF THE ELECTRONS

In the study of ionization the aim of the theory is to calculate the ionization cross section and the energy spectrum of the electrons. As already noted, the ionization process $Z_1e + Z_2 \to Z_1 + Z_2 + e$ is explained in the adiabatic approximation by the passage of the quasimolecular system Z_1eZ_2 through an infinite sequence of quasi-intersections that are bunched toward the boundary of the continuous spectrum, this sequence being induced by the piercing of the Rydberg series of levels by the diabatic term W_{lm}. To calculate the ionization cross section it is sufficient to know the characteristics of these quasi-intersections.[2] The problem of calculating the specturm of the electrons, which we shall consider below, is more complicated.

The general expression for a nonstationary wavefunction in the adiabatic approximation has the form[6]

$$\psi(r,t)=(2\pi v)^{-1/2}\int_{-\infty}^{\infty} dE\left[\frac{dR_i(E)}{dE}\right]^{1/2}\varphi_i(r,E)$$

$$\times\exp\left\{\frac{i}{v}\int_{E_i^\infty}^{E} R_i(E')\,dE'-iEt\right\}, \qquad (2)$$

where

$$E_i^\infty=\lim_{R\to\infty} E_i(R),$$

$R_i(E)$ is the inverse function to $E_i(R)$, and

$$\varphi_i(r,E)\equiv\varphi_i(r,R_i(E))$$

is the adiabatic wave function, in which the variable R has been replaced by E. In (2) the functions $R_i(E)$ and $\varphi_i(R,E)$ are to be regarded as the analytic continuation, into the entire complex E plane, of the solution of the stationary Schrödinger equation

$$H(R_i(E))\varphi_i(r,E)=E\varphi_i(r,E),$$

and in fact describe not only the initial ith adiabatic term but also the entire set of the terms connected with this term by branch points in the complex R plane. As $t\to-\infty$ one can displace the ends of the contour of integration over E in (2) into the upper half plane and calculate the integral by the method of steepest descent; this leads to the initial condition

$$\psi(r,t)\xrightarrow[t\to-\infty]{}\varphi_i(r,E_i^\infty)\exp(-iE_i^\infty t).$$

As $t\to+\infty$ the ends of the contour must be displaced into the lower half-plane of E. In this case the contour will link with the standard cut on the boundary of the continuous spectrum ($E=0$) and, as a result, besides the saddle points there appears an integral taken along the cut $0\leqslant E<\infty$ and describing the wave packet of the ionized particles:

$$\psi_{ion}(r,t)=(2\pi v)^{-1/2}\int_{0}^{\infty} dE\left[\frac{dR_i(E)}{dE}\right]^{1/2}\varphi_i(r,E)$$

$$\times\exp\left\{\frac{i}{v}\int_{E_i^\infty}^{E} R_i(E')\,dE'-iEt\right\}. \qquad (3)$$

The adiabatic wave function $\varphi_i(r,E)$ for $E<0$ is normalized to unity. For $E>0$ it describes a particle moving away to infinity with momentum k

$$\varphi_i\sim\exp(ikr)$$

and can be represented in the form

$$\varphi_i(r,E)=C_i(E)\chi_i(r,E), \qquad (4)$$

where $\chi_i(r,E)$ is the adiabatic wave function, normalized to unit flux. Substituting (4) into (3), we obtain $\psi_{\rm ion}(r,t)$ in the form of an expansion in the continuum function $\chi_i(r,t)$ with normalized flux, whence, for the probability density of the energy distribution of the particles, we obtain

$$P(E)=\frac{1}{2\pi v}\left|\frac{dR_i(E)}{dE}C_i^2(E)\exp\left\{\frac{2i}{v}\int_{E_i^\infty}^{E} R_i(E')\,dE'\right\}\right|. \qquad (5)$$

This expression was obtained in Ref. 6 for short-range potentials by another method. In fact, the presence of the long-range Coulomb interaction and the associated Rydberg bunching of levels is unimportant for the above derivation of the expression (5). This becomes clear even without a special investigation if we note that expressions (2) and (5) are exact for the Demkov-Osherov model,[6] which contains, in particular, the variant with a long-range Coulomb interaction. In the framework of this variant of the Demkov-Osherov model the ionization process has already been considered in the paper by Demkov and Komarov.[1]

The expression for the nonstationary wave function $\psi(r,t)$ (2) has been taken, for simplicity, for a head-on, uniform collision of the nuclei, when $R=vt$. In the case of an arbitrary trajectory of the nuclei, in place of $R(t)$ one must introduce the variable $\tau=vt$ (v is the velocity of the nuclei at $t\to-\infty$), which has the meaning of the internuclear coordinate along which the nuclei are moving, and replace $R_i(E)$ by $\tau_i(E)$ in (2)–(5).[6]

As can be seen from (5), to calculate the electron spectrum it is necessary to know $R_i(E)$ for $E>0$. In discussions of the ionization process it is more usual to use the inverse function $E_i(R)$, which gives the position and width of the quasistationary state as the term emerges into the continuous spectrum. As a whole, both functions carry equivalent information about the system. However, the electron spectrum is determined not by values of $E_i(R)$ for real R, but by values of $R_i(E)$ for real $E>0$. Since $\operatorname{Im} R_i(E)\neq 0$ for $E>0$,[2] these two functionally related sets $\{E,R\}$ differ from each other.

In Fig. 3 we give curves of $\operatorname{Re} R_i(E)$ and $\operatorname{Im} R_i(E)$ for several channels W_{lm} of ionization of the molecular ion H_2^+. The calculation was performed using the same program as in the determination of the antibonding terms $E_{\overline{nlm}}(R)$. The only difference was that, after passage around the branch point R_C, the calculation was then performed along the real

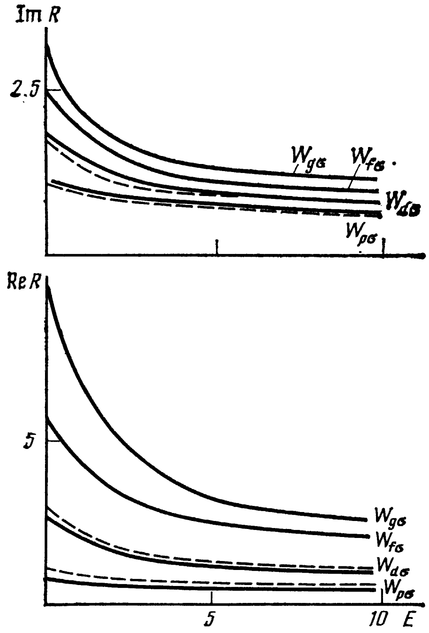

FIG. 3. Dependences Re $R_i(E)$ and Im $R_i(E)$ for several channels W_{lm} of ionization of the molecular ion. The dashed lines are calculated using formula (6), and the scales of the energy axes in the two figures are the same.

axis of E, not of R. The curves obtained for Re $R_i(E)$ and Im $R_i(E)$ can be approximated with good accuracy by the simple expressions

$$\begin{aligned} \operatorname{Re} R_i(E) &= 2 \operatorname{Re} R_{lm} / \{1 + [1 + 4 \operatorname{Re} R_{lm} E/(Zl)]^{1/2}\}, \\ \operatorname{Im} R_i(E) &= 2 \operatorname{Im} R_{lm} / \{1 + (1 + 2 \operatorname{Im} R_{lm} E/Z)^{1/2}\}. \end{aligned} \qquad (6)$$

In Fig. 3 the results of the calculation using formula (6) are given by dashed lines. It can be seen that there is an appreciable discrepancy with the exact calculation only for $l = 1, 2$; for $l \geqslant 3$ the exact and approximate curves coalesce on the scale used in the figure.

To calculate the electron spectrum it is necessary to know not only the function $R_i(E)$ but also the function $C_i(E)$. In principle, the latter can also be calculated exactly for the problem of two Coulomb centers. However, taking into account that it appears only in the pre-exponential factors, it is fully justified to replace $C_i(E)$ by its analog $C_i^{\text{Coul}}(E)$ for the one-center (hydrogen-like) system. Here we keep the long range Coulomb interaction, which has the greatest influence on the analytic properties and form of the function $C_i(E)$. If we compare the Coulomb-wavefunction asymptotic forms (36.15) and (36.23) in Ref. 4, it is not difficult to obtain for $C_i^{\text{Coul}}(E)$ the following expressions:

$$C_i^{\text{Coul}}(E) = (k^3/Z)^{1/2} [1 - \exp(-2\pi Z/k)]^{1/2}. \qquad (7)$$

In Fig. 4 we give differential (with respect to the energy) cross sections for production of electrons for the reaction

$$\text{H}(1s) + \text{H}^+ \rightarrow \text{H}^+ + \text{H}^+ + e \qquad (8)$$

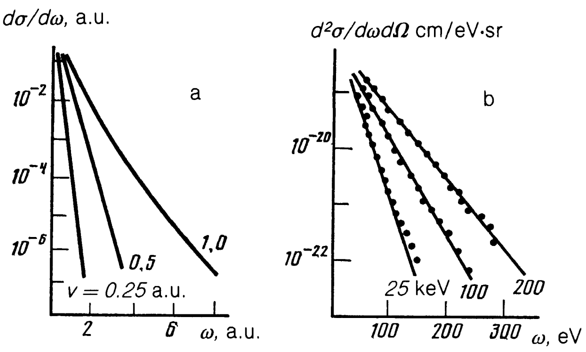

FIG. 4. Differential (with respect to the energy) cross sections for production of electrons for several values of the collision velocity: a) calculation for the system H(1s) + H$^+$ for the ionization channel $W_{p\sigma}$; b) experimental data for the system Ne$^+$ + Ne (Ref. 7).

for several values of the collision velocity v. These cross sections are obtained by integrating $P(E)$ (5) over the impact parameters ρ in the approximation of rectilinear flight ($R^2(t) = \rho^2 + v^2 t^2$). Here we used exact numerical values of $R_i(E)$, and $C_i(E)$ was taken in the form (7). In the calculation we also took into account the double passage through the region of ionization as the nuclei came together and flew apart. In the literature there are no experimental data on the electron spectra for the reaction (8). From a comparison of the curves given in Fig. 4a with the available experimental spectra for other colliding partners[7] (Fig. 4b) it can be seen that they explain at least qualitatively the dependence of the cross section both on the electron energy and on the collision velocity v.

The authors are grateful to Yu. S. Gordeev, Yu. N. Demkov, I. V. Komarov, E. E. Nikitin, V. I. Osherov, and L. I. Ponomarev for useful discussions.

[1)] The terms possess the obvious symmetry property $E_i(R) = E_i^*(R^*)$, and therefore to each branch point R_C in the upper half-plane there corresponds a conjugate branch point R_C^* in the lower half-plane.

[2)] A zero value of Im $R_i(E)$ for $E > 0$ would imply the existence of a bound state above the boundary of the continuous spectrum.

---

[1] Yu. N. Demkov and I. V. Komarov, Zh. Eksp. Teor. Fiz. **50**, 286 (1966) [Sov. Phys. JETP **23**, 189 (1966)].

[2] E. A. Solov'ev, Zh. Eksp. Teor. Fiz. **81**, 1681 (1981) [Sov. Phys. JETP **54**, 893 (1981)].

[3] R. G. Newton, Scattering Theory of Waves and Particles, McGraw-Hill, New York (1966) [Russ. Transl., Mir, Moscow (1969)].

[4] L. D. Landau and E. M. Lifshitz, Kvantovaya mekhanika (Quantum Mechanics), Nauka, Moscow (1974) [English translation published by Pergamon Press, Oxford (1977)].

[5] Yu. N. Demkov and G. F. Drukarev, Zh. Eksp. Teor. Fiz. **49**, 691 (1965) [Sov. Phys. JETP **22**, 479 (1966)].

[6] E. A. Solov'ev, Zh. Eksp. Teor. Fiz. **70**, 872 (1976) [Sov. Phys. JETP **43**, 453 (1976)].

[7] P. H. Woerlee, Yu. S. Gordeev, H. de Waard, and F. W. Saris, J. Phys. B **14**, 527 (1982).

Translated by P. J. Shepherd