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ZERO-RADIUS-POTENTIAL APPROXIMATION AND INELASTIC SCATTERING OF ELECTRONS BY A MOLECULE. THE $e + H_2$ SCATTERING

Yu. N. DEMKOV and V. N. OSTROVSKIĬ

Leningrad State University

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We consider a generalization of the zero-radius-potential approximation to include a multichannel case. A phenomenological account of the splitting of the singlet and triplet terms of the molecule makes it possible to calculate in this approximation the cross section for the excitation of the triplet state of the molecule by electron impact. The calculations are made for the case of the $e + H_2$ system. The energies and widths of the terms of the molecular ion H_2^- are calculated. The trajectories of the S-matrix poles on the complex-energy plane are investigated as functions of the internuclear distance.

1. INTRODUCTION

THE zero-radius-potential approximation has recently been used in a number of problems in the theory of atomic collisions.[1-6] In particular, this approximation was used to consider scattering of electrons by a hydrogen molecule.[5] However, if we confine ourselves to the simplest variant of the approximation, wherein we seek the solution of the equation for the free particle, and each atom in the molecule is replaced by one zero-radius potential (i.e., by the boundary condition), then we can consider only elastic scattering, thereby greatly limiting the capabilities of the approximation. We consider here a natural generalization of this approximation, whereby a multicomponent wave function of the electron is introduced. This makes it possible, in principle, to take a more detailed account (phenomenologically) of the structure of each center—its spin, the possible excited states, etc. For nuclear problems, such an approach (but only for the case of one force center, i.e., for the case of spherical symmetry) has been considered in Dalitz's book.[7] For the simplest problem of two centers, the system $e + H_2$, such an approach was used in implicit form in [2,5]. In these papers, however, the splitting of the singlet and triplet terms of the hydrogen molecule was neglected, a procedure which is valid only at large internuclear distances and which leads in the analysis of scattering to misunderstandings connected with the presence of exchange scattering.

The zero-radius-potential is attractive because it makes it possible to describe the interaction of a bound state with a continuous spectrum of the system. We can therefore trace the transformation of the bound states into quasistationary states, the transition of the S-matrix poles from one energy sheet to another, the meanings of different types of resonances, etc. In the present paper all this is done with the simplest system $e + H_2$ as an example. We were able to calculate the elastic scattering with excitation of the ${}^3\Sigma_u^+$ state of H_2 and subsequent dissociation, the influence of the inelastic channel on the elastic one, threshold singularities, etc.

2. ZERO-RADIUS POTENTIALS FOR A MULTICOMPONENT WAVE FUNCTION

Assume that in a multicomponent wave function

$$\Psi = (\psi_1, \psi_2, \dots, \psi_N) \tag{1}$$

each component ψ_s satisfies the equation

$$[\nabla^2 - 2V_s(\mathbf{r}) + k_s^2]\psi_s(\mathbf{r}) = 0. \tag{2}$$

At the point $\mathbf{r}_0$ we specify the boundary condition

$$\psi_s(\mathbf{r})\,|_{|\mathbf{r}-\mathbf{r}_0|\to 0} \sim \frac{A_s}{|\mathbf{r}-\mathbf{r}_0|} + B_s + O(|\mathbf{r}-\mathbf{r}_0|), \tag{3}$$

$$B_s = \sum_{t=1}^{N} \alpha_{st} A_t, \tag{4}$$

and assume that the potentials $V_s(\mathbf{r})$ have no singularities at $\mathbf{r} = \mathbf{r}_0$. The solution of Eq. (2) with singularity (3) is the Green's function for the potential V_s; if it is known, then the scattering problem becomes algebraic. In particular, if $V_s(\mathbf{r}) \equiv 0$ and there is an incident wave in the j-th channel, then

$$\psi_s = e^{i\mathbf{k}_s\mathbf{r}}\delta_{sj} + A_s \frac{\exp\{ik_s|\mathbf{r}-\mathbf{r}_0|\}}{|\mathbf{r}-\mathbf{r}_0|}. \tag{5}$$

From the boundary conditions follows a system for the determination of the coefficients A_s:

$$ik_s A_s + \delta_{sj} = \sum_{t=1}^{N} \alpha_{st} A_t. \tag{6}$$

The multichannel problem can be reduced to such a model by using the method of equivalent boundary conditions,[7] provided only s-waves are present in all the channels. The model wave function (5) then coincides with the asymptotic form of the exact wave function at large r, and the matrix α depends on the momentum and is expressed in terms of the matrix $\alpha = K^{-1}$ of the reactions of the initial multichannel problem K. Both matrices are self-adjoint and real, this being the consequence of the self-adjoint nature of the problem and the invariance against time reversal. The method of equivalent boundary conditions is convenient when there are several potential centers whose dimensions are small compared with the distance between them and with the electron wavelength.

In the problem of electron-atom scattering, we arrive at the described model if we replace the potentials in the equations of the strong-coupling method by equivalent boundary conditions. Let us consider by this method the exchange scattering of an electron by a hydrogen atom. The results can also be used for other atoms (with nonzero spin) by regarding them as valence electrons situated in the field of the atomic core. In the static-field approximation, with allowance for exchange, the coordinate wave function, which has no definite symmetry with respect to permutation of the electron coordinates, is

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_1(\mathbf{r}_1)\varphi_a(\mathbf{r}_2) + \psi_2(\mathbf{r}_2)\varphi_a(\mathbf{r}_1).$$

Here φ_a is the wave function of the atom, and the functions ψ_1 and ψ_2 satisfy the equations

$$(\nabla^2 + k^2)\psi_1 = 2V_{11}\psi_1 + 2\hat{V}_{12}\psi_2, \quad (\nabla^2 + k^2)\psi_2 = 2V_{22}\psi_2 + 2\hat{V}_{21}\psi_1,$$

where

$$V_{11}(\mathbf{r}) = V_{22}(\mathbf{r}) = -\frac{1}{r} + \int \frac{\varphi_a(\mathbf{r}_1)^2}{|\mathbf{r} - \mathbf{r}_1|} d\mathbf{r}_1,$$

$$[\hat{V}_{12}\psi](\mathbf{r}) = [\hat{V}_{21}\psi](\mathbf{r}) = \varphi_a(\mathbf{r}) \int \left(\frac{1}{|\mathbf{r} - \mathbf{r}_1|} - \frac{1}{2} - \frac{k^2}{2}\right)\varphi_a(\mathbf{r}_1)\psi(\mathbf{r}_1) d\mathbf{r}_1.$$

By replacing the potentials V_{st} by the boundary conditions, we obtain for the functions ψ_s the equations

$$(\nabla^2 + k^2)\psi_s = 0, \tag{7}$$

and from the equality $V_{11}(\mathbf{r}) = V_{22}(\mathbf{r})$ there follows an additional condition $\alpha_{11} = \alpha_{22}$ for the elements of the matrix α. By solving (6) we obtain the connection of α_{11} and α_{12} with the singlet and triplet scattering lengths a_+ and a_-:

$$\alpha_{11} = -\frac{a_+ + a_-}{2a_+a_-}, \quad \alpha_{12} = \frac{a_+ - a_-}{2a_+a_-}. \tag{8}$$

Let us now consider the scattering of an electron in the field of two atoms a and b. We denote by φ_a and φ_b the wave functions of the valence electrons. The wave function of the system is sought approximately in the form

$$\begin{aligned}\psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = {}& \psi_1(\mathbf{r}_1)\varphi_a(\mathbf{r}_2)\varphi_b(\mathbf{r}_3) + \psi_2(\mathbf{r}_2)\varphi_a(\mathbf{r}_1)\varphi_b(\mathbf{r}_3) \\ &+ \psi_3(\mathbf{r}_3)\varphi_a(\mathbf{r}_1)\varphi_b(\mathbf{r}_2) + \psi_4(\mathbf{r}_1)\varphi_a(\mathbf{r}_3)\varphi_b(\mathbf{r}_2) \\ &+ \psi_5(\mathbf{r}_2)\varphi_a(\mathbf{r}_3)\varphi_b(\mathbf{r}_1) + \psi_6(\mathbf{r}_3)\varphi_a(\mathbf{r}_2)\varphi_b(\mathbf{r}_1).\end{aligned} \tag{9}$$

Assuming that the functions φ_a and φ_b do not overlap and disregarding their distortions when the atoms come close together, we replace the potentials by boundary conditions and obtain Eqs. (7) for the functions ψ_s. At the points $\mathbf{r}_a$ and $\mathbf{r}_b$ we specify boundary conditions of the form (3) and (4) with respective matrices $\tilde{\alpha}^a$ and $\tilde{\alpha}^b$ having a dimensionality 6 × 6. The nonzero elements of these matrices are expressed in the following manner in terms of the quantities $\alpha_{11}^{a', b}$ and $\alpha_{12}^{a, b}$, which characterize the individual atoms:

$$\tilde{\alpha}_{ss}^a = \alpha_{11}^a, \quad \overset{a}{\tilde{\alpha}}_{2n-1\,2n} = \overset{a}{\tilde{\alpha}}_{2n\,2n-1} = \alpha_{12}^a;$$

$$\tilde{\alpha}_{ss}^b = \alpha_{11}^b, \quad \overset{b}{\tilde{\alpha}}_{2n\,2n+1} = \overset{b}{\tilde{\alpha}}_{2n+1\,2n} = \alpha_{12}^b, \quad \tilde{\alpha}_{16}^b = \tilde{\alpha}_{61}^b = \alpha_{12}^b.$$

The unitary transformation of the vector $\Psi(1)$

$$\Psi' = U\Psi$$

transforms the matrices of the boundary conditions as follows:

$$\tilde{\alpha}^{a'} = U^{-1}\tilde{\alpha}^a U, \quad \tilde{\alpha}^{b'} = U^{-1}\tilde{\alpha}^b U.$$

Using the symmetry of the problem against permutation of the electrons, we can find the unitary transformation U that transforms the matrices $\tilde{\alpha}^a$ and $\tilde{\alpha}^b$ simultaneously into the cellular-diagonal form:

$$U = \begin{pmatrix} 1/2 & -1/2 & 0 & 1/2 & -1/2 & 0 \\ -1/2 & 1/2 & 1/2 & 0 & 0 & -1/2 \\ 1/2 & 1/2 & -1/2 & 0 & 0 & -1/2 \\ 1/2 & 1/2 & 0 & -1/2 & -1/2 & 0 \\ 1/\sqrt{6} & -1/\sqrt{6} & 1/\sqrt{6} & -1/\sqrt{6} & 1/\sqrt{6} & -1/\sqrt{6} \\ 1/\sqrt{6} & 1/\sqrt{6} & 1/\sqrt{6} & 1/\sqrt{6} & 1/\sqrt{6} & 1/\sqrt{6} \end{pmatrix},$$

$$\tilde{\alpha}^{a'} = \{M_a,\ M_a,\ \alpha_{11}^a - \alpha_{12}^a,\ \alpha_{11}^a + \alpha_{12}^a\},$$
$$\tilde{\alpha}^{b'} = \{M_b,\ M_b,\ \alpha_{11}^b - \alpha_{12}^b,\ \alpha_{11}^b + \alpha_{12}^b\};$$

$$M_a = \begin{pmatrix} \alpha_{11}^a - \frac{1}{2}\alpha_{12}^a & \frac{\sqrt{3}}{2}\alpha_{12}^a \\ \frac{\sqrt{3}}{2}\alpha_{12}^a & \alpha_{11}^a + \frac{1}{2}\alpha_{12}^a \end{pmatrix},$$

$$M_b = \begin{pmatrix} \alpha_{11}^b - \frac{1}{2}\alpha_{12}^b & -\frac{\sqrt{3}}{2}\alpha_{12}^b \\ -\frac{\sqrt{3}}{2}\alpha_{12}^b & \alpha_{11}^b + \frac{1}{2}\alpha_{12}^b \end{pmatrix}.$$

The curly brackets give here the cells of the transformed matrices $\tilde{\alpha}^{a'}$ and $\tilde{\alpha}^{b'}$ in the diagonals; all the other matrix elements are equal to zero.

We can now satisfy the boundary conditions if only ψ_1' and ψ_2' in Ψ' are different from zero. The wave function of the system is then

$$\begin{aligned}\psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \frac{1}{2}\Big\{&\psi_1'(\mathbf{r}_1)[\varphi_a(\mathbf{r}_2)\varphi_b(\mathbf{r}_3) + \varphi_a(\mathbf{r}_3)\varphi_b(\mathbf{r}_2)] \\ &- \psi_1'(\mathbf{r}_3)[\varphi_a(\mathbf{r}_1)\varphi_b(\mathbf{r}_2) + \varphi_a(\mathbf{r}_2)\varphi_b(\mathbf{r}_3)] + \frac{1}{\sqrt{3}}\psi_2'(\mathbf{r}_1)[\varphi_a(\mathbf{r}_2)\varphi_b(\mathbf{r}_3) \\ &- \varphi_a(\mathbf{r}_3)\varphi_b(\mathbf{r}_2)] + \frac{2}{\sqrt{3}}\psi_2'(\mathbf{r}_2)[\varphi_a(\mathbf{r}_1)\varphi_b(\mathbf{r}_3) - \varphi_a(\mathbf{r}_3)\varphi_b(\mathbf{r}_1)] \\ &+ \frac{1}{\sqrt{3}}\psi_2'(\mathbf{r}_3)[\varphi_a(\mathbf{r}_1)\varphi_b(\mathbf{r}_2) - \varphi_a(\mathbf{r}_2)\varphi_b(\mathbf{r}_1)]\Big\}\end{aligned}$$

and corresponds to a spin $S = 1/2$.[8] It is a superposition of two configurations: a weakly-bound electron described by a function ψ_1' in the field of the singlet state of the quasimolecule, and a weakly-bound electron described by the function ψ_2' in the field of the triplet state of the quasimolecule. The case when only ψ_3' and ψ_4' differ from zero also leads to $S = 1/2$. If only ψ_5' differs from zero, then $S = 3/2$; finally, if only ψ_6' is not equal to zero, then the coordinate wave function of the system (9) turns out to be symmetrical in the coordinates of all the electrons, which is forbidden by the Pauli principle.

3. SINGLET-TRIPLET SPLITTING AND ELASTIC-AND INELASTIC-SCATTERING CROSS SECTIONS

The equations (7) for ψ_1' and ψ_2' do not take into account the quasimolecule-energy difference $\epsilon(R)$ between the triplet and singlet states ($R = \mathbf{r}_a - \mathbf{r}_b$) is the internuclear distance). This splitting can be taken into account phenomenologically within the framework of the employed model, if it is assumed that the functions ψ_1' and ψ_2' satisfy the equations

$$(\nabla^2 + k_1^2)\psi_1' = 0, \quad (\nabla^2 + k_2^2)\psi_2' = 0; \quad k_1^2 - k_2^2 = 2\varepsilon(R)$$

with the same boundary conditions as before. $\epsilon(R)$ is an external quantity with respect to the model and should be obtained from an exact calculation of the terms of the molecule or from experiment.

Let us consider the scattering of an electron with momentum $\mathbf{k}_1$ by a molecule in the ground state, assumed to be singlet. The total spin of the system is $S = 1/2$, and the functions ψ_1' and ψ_2' are given by

$$\psi_1' = e^{i\mathbf{k}_1\mathbf{r}} + A_1^a \frac{\exp\{ik_1|\mathbf{r}-\mathbf{r}_a|\}}{|\mathbf{r}-\mathbf{r}_a|} + A_1^b \frac{\exp\{ik_1|\mathbf{r}-\mathbf{r}_b|\}}{|\mathbf{r}-\mathbf{r}_b|},$$

$$\psi_2' = A_2^a \frac{\exp\{ik_2|\mathbf{r}-\mathbf{r}_a|\}}{|\mathbf{r}-\mathbf{r}_a|} + A_2^b \frac{\exp\{ik_2|\mathbf{r}-\mathbf{r}_b|\}}{|\mathbf{r}-\mathbf{r}_b|}.$$

The elastic-scattering amplitude (at a fixed position of the nuclei) is

$$f_e(\theta) = A_1^a \exp\{i{}^1/{}_2 k_1 R \cos\theta\} + A_1^b \exp\{-i{}^1/{}_2 k_1 R \cos\theta\},$$

where θ is the angle between the momentum vector of the scattered electron and R. When $k_1 > \sqrt{2\epsilon}$, there is also inelastic scattering accompanied by a transition of the molecule into the triplet state, with an amplitude

$$f_i(\theta) = A_2^a \exp\{i{}^1/{}_2 k_2 R \cos\theta\} + A_2^b \exp\{-i{}^1/{}_2 k_2 R \cos\theta\}.$$

$A_s^{a,b}$ is determined from an inhomogeneous system of four linear equations; this system follows from the boundary conditions

$$\begin{gathered}
ik_1A_1^b + \gamma_1A_1^a + \exp\left\{-i\frac{1}{2}\mathrm{k}_1\mathrm{R}\right\} = \left(\alpha_{11}^b - \frac{1}{2}\alpha_{12}^b\right)A_1^b + \frac{\sqrt{3}}{2}\alpha_{12}^bA_2^b,\\
ik_2A_2^a + \gamma_2A_2^b = \left(\alpha_{11}^a + \frac{1}{2}\alpha_{12}^a\right)A_2^a - \frac{\sqrt{3}}{2}\alpha_{12}^aA_1^a,\\
ik_1A_1^a + \gamma_1A_1^b + \exp\left\{i\frac{1}{2}\mathrm{k}_1\mathrm{R}\right\} = \left(\alpha_{11}^a - \frac{1}{2}\alpha_{12}^a\right)A_1^a - \frac{\sqrt{3}}{2}\alpha_{12}^aA_2^a,\\
ik_2A_2^b + \gamma_2A_2^a = \left(\alpha_{11}^b + \frac{1}{2}\alpha_{12}^b\right)A_2^b + \frac{\sqrt{3}}{2}\alpha_{12}^bA_1^b,
\end{gathered} \tag{10}$$

where $\gamma_s = \exp(ik_sR)/R$.

In the case when the atoms a and b are identical, we can use the classification with respect to parity to break up the system (10) into two systems of two equations. We put

$$A_1^\pm = A_1^a \pm A_1^b, \quad A_2^\pm = A_2^a \mp A_2^b;$$

and then, solving these systems, we obtain

$$A_s^\pm = \Phi_s^\pm[\exp(i{}^1/{}_2 k_1 R) \pm \exp(-i{}^1/{}_2 k_1 R)],$$

where

$$\Phi_1^\pm = -\frac{ik_2 \pm \gamma_2 - (\alpha_{11} + {}^1/{}_2\alpha_{12})}{\Delta_\pm}, \quad \Phi_2^\pm = -\frac{\sqrt{3}\,\alpha_{12}}{2\Delta_\pm},$$

$$\Delta_\pm = [ik_1 \pm \gamma_1 - (\alpha_{11} - {}^1/{}_2\alpha_{12})][ik_2 \mp \gamma_2 - (\alpha_{11} + {}^1/{}_2\alpha_{12})] - {}^3/{}_4\alpha_{12}^2.$$

The total elastic- and inelastic-scattering cross sections averaged over the molecule orientations are, respectively,

$$\sigma_e = 4\pi\left\{|\Phi_1^+|^2\left(1 + \frac{\sin k_1R}{k_1R}\right)^2 + |\Phi_1^-|^2\left(1 - \frac{\sin k_1R}{k_1R}\right)^2\right\}, \tag{11}$$

$$\begin{aligned}
\sigma_i = 4\pi\frac{k_2}{k_1}\Big\{&|\Phi_2^+|^2\left(1 + \frac{\sin k_2R}{k_2R}\right)\left(1 - \frac{\sin k_1R}{k_1R}\right)\\
&+ |\Phi_2^-|^2\left(1 - \frac{\sin k_2R}{k_2R}\right)\left(1 + \frac{\sin k_1R}{k_1R}\right)\Big\}.
\end{aligned} \tag{12}$$

A discussion of the region of validity of the approximation of the zero-radius wells in the theory of scattering of electrons by molecules can be found in Subramanyan's paper.[5] On the low-energy side it is determined by the fact that no account is taken of the polarization effect; on the high-energy side it is determined by the fact that no account is taken of the possibility of electron excitations. When the multicomponent-function model is used, the latter limitation is partly lifted.

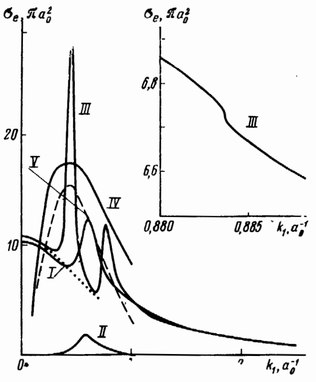

FIG. 1

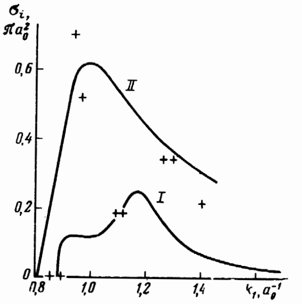

FIG. 2

FIG. 1. Cross section for the elastic scattering of electrons by a hydrogen molecule.

FIG. 2. Cross section for the excitation of a hydrogen molecule by electron impact in the state $^3\Sigma_u^+$: I—results of present work, II—calculation by the Ochkur-Rudge method [16]; +—variational calculation [15].

Subramanyan[5] disregarded the splitting $\epsilon(R)$ of the singlet and triplet terms of the molecule. The elastic-scattering cross section obtained by him (formula (22) of his paper) is actually equal to the total cross section $\sigma_e + \sigma_i$; his result for this quantity coincides with that obtained from our formulas (12) at $\epsilon = 0$. Figure 1 allows us to evaluate the relation between σ_e and σ_i at $\epsilon = 0$ (curves I and II) with the scattering of an electron by a hydrogen molecule as an example. The values of α_{11} and α_{12} were determined from the calculated scattering lengths[9] $a_+ = 5.7a_0$ and $a_- = 1.768a_0$; the internuclear distance is $R = 1.4a_0$. Introducing $\epsilon(1.4) = 0.3903$ at.un.,[10] we obtain the curve III for σ_e. At the inelastic-scattering threshold it has a vertical tangent.[11] This section is shown separately in an enlarged scale. The maxima on curves I and III are due to the antisymmetrical part of the scattering, i.e., to the second term in (12). To illustrate this, the dotted curve shows the contribution of the first term of (12) to the curve III. A discussion of these maxima will be presented below in the analysis of the quasistationary states. Curves IV and V[12, 13] represent the results of theoretical calculations of the cross section, and the dashed line represents the experimental data.[14]

Curve I on Fig. 2 shows the cross section for the excitation of the lower triplet state $^3\Sigma_u^+$ of the H_2 molecule, calculated from formula (13). There is a variational calculation of this process,[15] which is accompanied by the dissociation of the molecule in accord with the repulsive $^3\Sigma_u^+$ term. There are no details of the calculation in [15], so that it is impossible to assess its reliability. All the other calculations of σ_i are based on various modifications of perturbation theory. Curve II gives the results of the most reliable of these calculations, in which the Ochkur-Rudge method is used.[16][1]

It can be concluded from Figs. 1 and 2 that the model of zero-radius potentials yields somewhat undervalued

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[1] Since the motion of the nuclei is taken into account in the cited paper, the threshold is shifted towards lower energies.

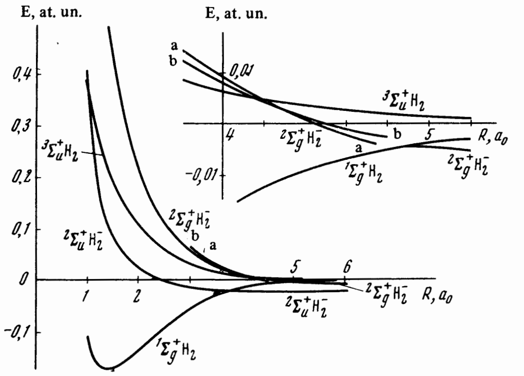

FIG. 3. Terms of the molecule H_2 and of the molecular ion H_2^-.

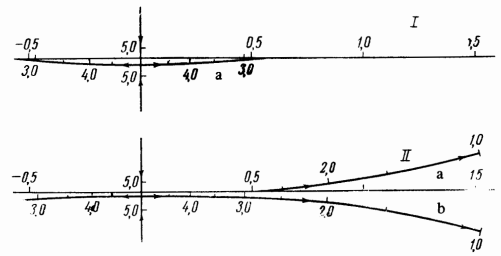

FIG. 4. Trajectories of the S-matrix poles for the $^2\Sigma_g^+$ states of H_2^- on the two-sheeted surface of the complex momentum in the first channel k_1. The values of R are indicated. The cuts are not shown, since the positions of the branch points $k_1 = \pm\sqrt{2\epsilon(R)}$ depend on the parameter R.

results for both σ_e and σ_i. This is natural, since real potentials with finite radii of action lead to a wave function with a larger effective radius and this in turn increases the cross section. It is well known that perturbation-theory calculations overestimate the scattering cross sections; our model underestimates them, so both methods supplement each other to some degree.

4. TERMS OF THE SYSTEM e + H_2

The energies of the bound and quasistationary states of the molecule, corresponding to a total spin $S = ^1\!/_2$, are the roots of the determinant of the system (10). The transcendental equation from which they are determined breaks up in the case of a molecule made up of identical atoms into two independent equations for the states u and g, respectively; when $\epsilon(R) \equiv 0$, this equation coincides with that obtained by Smirnov and Firsov[2] (Eq. (16) of their paper; Eq. (13), contains, in addition, a factor that describes states with $S = ^3\!/_2$).

Using $\epsilon(R)$ from [10], we calculated numerically the terms of H_2^- shown in Fig. 3, and their energies were reckoned from the terms of H_2,[10] which are also shown. The term $^1\Sigma_g^+$ of the molecule H_2 is the boundary of the continuous spectrum for H_2^-; above this term, the energies of the terms of H_2^- become complex, and Fig. 3 shows their real parts. At the point where the spectrum becomes continuous, the term $^2\Sigma_g^+$ is tangent to the boundary of the continuous spectrum (the vicinity of this point is shown in Fig. 3 separately in an enlarged scale), and the term $^2\Sigma_u^+$ crosses it, as required by the theory.[1,3] We note that if we put $\epsilon(R) \equiv 0$, then both terms are tangent to the boundary of the continuous spectrum, for in this case the expansion of the wave function of the outgoing electron in partial waves will always contain an s-component, which becomes predominant at the instant of tangency.

Since we determined α_{11} and α_{12} from the scattering lengths, and since a_+, $a_- > 0$ for hydrogen, two bound states of H^-, singlet and triplet, are obtained in the zero-radius potential model. Actually, the state $H^-(^3S)$ does not exist, but its appearance in the model can be understood from the following considerations. It is known that the equation with the static and exchange potentials for the triplet state has a solution that coincides with the atomic wave function.[17] The total two-electron wave function then vanishes identically because of the antisymmetrization. Our small-radius potential is an approximation of the static potential with exchange, and also has a corresponding solution (but with a different energy and a different wave function). This state should be regarded as forbidden by the Pauli principle. It generates in our model two states of the H_2^- molecule with symmetries $^2\Sigma_g^+$ and $^2\Sigma_u^+$; these states lie below the real terms of H_2 and are not shown in Fig. 3. One of these states (antisymmetrical) goes into the continuous spectrum at $R = 1.8a_0$ and produces a sharp maximum of σ_e at $k_1 = 0.44a_0^{-1}$.[2] Actually, such resonances do not exist and the curve III of Fig. 1 should be replaced in the region of the first maximum by the dotted curve. The other maximum of σ_e (at $k_1 = 0.76a_0^{-1}$) is due to the S-matrix pole corresponding to the physical $^2\Sigma_u^+$ state, which in our model goes into the continuous spectrum at $R = 3.8a_0$.

Introduction of the splitting $\epsilon(R)$ reveals clearly the two-channel character of the problem; this character was not considered in detail in earlier investigations.[2,5] The S matrix of the two-channel problem is specified on a four-sheeted complex-energy plane. We shall map the results of the calculations on the complex-momentum sheet in the first channel k_1. This is a two-sheet surface with cuts along the real axis from $-\infty$ to $-\sqrt{2\epsilon(R)}$ and from $\sqrt{2\epsilon(R)}$ to $+\infty$; on the first sheet $\operatorname{Im}(k_2) > 0$ and on the second $\operatorname{Im}(k_2) < 0$, where k_2 is the momentum in the second channel. Figure 4 shows the trajectories of the S-matrix poles corresponding to the states of H_2^- with symmetry $^2\Sigma_g^+$ as functions of R. At large R, a pole corresponding to the bound state is located on the upper imaginary semiaxis of the first sheet. With decreasing R, this pole moves downward and merges with the pole corresponding to the virtual state, after which the poles go off the imaginary axis, become complex-conjugate,[19] and move along the real axis, which they gradually approach (curve a of Fig. 4). At $R = 2.8a_0$, they cross the cut and go upward from under it to the second sheet.[3] In sheet II, a similar motion is executed by the pair of so-called shadow poles,[20] which, however, cannot go under the cut (this

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[2] A similar "ghost" resonance connected with a state forbidden by the Pauli principle was obtained by Herzenberg and Law [18] in a calculation of the cross section for elastic scattering of an electron by an He atom.

[3] As a result, there exists at $R = 2.8a_0$ a continuous-spectrum function (for $k_1 = 0.502a_0^{-1}$) having only a converging wave in one channel and only a diverging one in the other.

would contradict the unitarity of the S matrix) and remain on the second sheet all the time. The real parts of the complex energies of these two pairs of poles are given by curves a and b of Fig. 3, respectively.

When the real ${}^2\Sigma_g^+$ term of H_2^- lies under the ${}^3\Sigma_u^+$ term of H_2 (but above the ${}^1\Sigma_g^+$ term of H_2), H_2^- can decay only to the ground state of H_2. The wave function of the corresponding quasistationary state at large r has an exponentially growing asymptotic form only in the first channel and corresponds to the first pair of poles (curve a). If the ${}^2\Sigma_g^+$ term lies above the ${}^3\Sigma_u^+$ term of H_2, then two decay channels are open—to the ground state ${}^1\Sigma_g^+$ and to the excited state ${}^3\Sigma_u^+$. The asymptotic form of the corresponding solution increases with increasing r in both channels. This resonance is described by the second pair of poles (curve b) and leads to a peak in the excitation cross section σ_1 (curve I, Fig. 2). Thus, out of the two pairs of S-matrix poles connected with the ${}^2\Sigma_g^+$ states of the system, each describes resonances in a different region of the parameter R.[11] In the intermediate region there is a sort of quasiintersection in the complex plane. This circumstance may be of interest in the theory of dissociative capture.[21]

The H_2^- terms (Fig. 4) and the widths of the quasistationary states given by the model in question differ from noticeably from those obtained by the variational method.[22] However, the results of [22] are not perfectly reliable and deviate just as strongly from the semiempirical relations obtained from the experimental data on dissociative capture.[23] It should be noted that the singularities of the motion of the S-matrix poles corresponding to the ${}^2\Sigma_g^+$ states, which were considered here, were not taken into account in the variational calculation.[22]

5. CONCLUSION

The model of zero-radius potentials can also be applied without fundamental complications to more complicated systems, in the analysis of several excited states, of scattering by a polyatomic molecule, etc. The main problem here is the development of a method for selecting the semiempirical parameters characterizing each atom. It is obvious that the choice of these parameters from the data for the free atoms is a rather crude approximation. With a suitable choice of the parameters, the results of the calculation of the $e + H_2$ scattering can be improved even within the framework of the present approximation. However, the development of semiempirical selection rules calls for a large volume of systematic calculations for different molecules.

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