Angular distribution of saddle-point electrons in slow $H^+ + H$ collisions

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The production of the saddle-point electrons in slow $H+H^+$ collisions is discussed in the framework of the quantum adiabatic approach. An analytical expression for the angular distribution of the ejected electrons is obtained.

Recently, a new channel of ionization was revealed in calculations of $H^+ + H$ collisions using the three-body classical trajectory Monte Carlo method.[1] It is due to the "stranding" of electron on the transitory saddle region of the electric potential between the two protons. These "saddle-point" electrons have velocities that are nearly one-half the velocity of the projectile and are called $v/2$ electrons in Ref. 1. Here we present a quantum calculation of this phenomena in the framework of an adiabatic approach.

In the adiabatic approach the collision of two atomic particles A and B is divided into regions of elastic scattering along adiabatic potential-energy curves $E_j(R)$ and into small regions of nonadiabatic transitions between potential curves in the vicinity of their avoided crossings. Every avoided crossing of two potential curves $E_1(R)$ and $E_2(R)$ reflects their exact crossing at a complex branch-point R_c and near R_c the difference $\Delta E(R)=E_1(R)-E_2(R)$ takes the form

$$\Delta E(R)=\text{const}\times\sqrt{R-R_c}\ .$$

At low relative velocities v of the nuclei the probability of a transition is expressed through the contour integral of the energy difference around the branch point[2]

$$P=\exp(-2\Delta/v)\ , \tag{1}$$

where

$$\Delta=\left|\mathrm{Im}\int_{\mathrm{Re}(t_c)}^{t_c}\Delta E(R(t))v\,dt\right| \tag{2}$$

is the Massey parameter, t_c is the complex root of the equation $R(t_c)=R_c$, and $R(t)$ is the time-dependent internuclear distance. The above expression underlies the calculation of the probability of ionization when one or both atomic particles are positive ions. In this case the electronic Hamiltonian of the quasimolecule contains the Coulomb attraction and there is an infinite number of bound Rydberg states, which prevents, according to the Neumann-Wigner theorem,[3] the merging of the initial energy potential curves with the continuous spectrum. Thus in the adiabatic approach the ionization process occurs only if there is an infinite chain of avoided crossings, which becomes denser at the boundary of the continuous spectrum. Passing sequentially and inelastically through all these avoided crossings with probability (1) results in ionization. This type of infinite series of avoided crossings (the so-called S series) was revealed for the first time in the two-Coulomb-center problem using direct numerical calculation of the branch points of the potential curves in the complex R plane.[4] These avoided crossings are not manifested in the pattern of the potential curves at real R and can be considered as "hidden" avoided crossings (a similar situation exists in the Rozen-Zener-Demkov model). The ionization due to the S-series occurs during the approach stage of the collision, because the avoided crossings of a given S-series approach the boundary of the continuum with decreasing values of the internuclear distance R. Later, in the same problem[5] a second type of infinite series of hidden avoided crossings was revealed, which was named the T series (recently this was rediscovered in Ref. 6). These series lead to ionization during the separation stage of collision and results in the production of saddle-point electrons.[7,8] A quantal treatment of this ionization mechanism using a different method was reported earlier.[9,10]

Before we consider the ionization process, we will briefly review the results found in Ref. 5. The Schrödinger equation of the two–Coulomb-center problem

$$\left[-\frac{1}{2}\Delta-\frac{Z_1}{r_1}-\frac{Z_2}{r_2}\right]\Psi(\mathbf{r})=E(R)\Psi(\mathbf{r})\ , \tag{3}$$

admits, as it is well known, a separation of variables in prolate spheroidal coordinates $(r_1=|\mathbf{r}-\mathbf{R}/2|, r_2=|\mathbf{r}+\mathbf{R}/2|)$

$$\xi=\frac{r_1+r_2}{R},\quad \eta=\frac{r_1-r_2}{R},\quad \phi=\text{arctang}(x/y)\ .$$

Substitution of the wave function

$$\Psi(\mathbf{r})=[(\xi^2-1)(1-\eta^2)]^{-1/2}F(\xi)G(\eta)\exp(im\phi)$$

in Eq. (3) yields the following equations for the functions $F(\xi)$ and $G(\eta)$:

$$\frac{d^2F(\xi)}{d\xi^2}+\left[-p^2+\frac{a\xi-\lambda}{\xi^2-1}+\frac{1-m^2}{(\xi^2-1)^2}\right]F(\xi)=0\ , \tag{4}$$

$$\frac{d^2G(\eta)}{d\eta^2}+\left[-p^2+\frac{b\eta-\lambda}{1-\eta^2}+\frac{1-m^2}{(1-\eta^2)^2}\right]G(\eta)=0\ , \tag{5}$$

where $p=(-2E)^{1/2}R/2$, $a=(Z_1+Z_2)R$, $b=(Z_2$

$-Z_1)R$, and λ is the separation constant. In the classification of levels it is usual to employ spherical quantum numbers (n,l,m) of a united hydrogenlike atom at $R=0$. They are related to the number of zeros (k,q,m) of the wave function $\Psi(\mathbf{r})$ in the variables ξ,η,ϕ: $n=k+q+m+1$, $l=q+m$. In the case of l and m we shall employ also the spectroscopic notation: $l=s,p,d,\ldots$ instead of $l=0,1,2,\ldots$ and $m=\sigma,\pi,\delta,\ldots$ instead of $m=01,2,\ldots$.

In the problem of two Coulomb centers there are two nontrivial parameters, the internuclear distance R and the ratio of the nuclear charges Z_1/Z_2. We shall consider the symmetric problem $Z_1=Z_2$. In this case there is the additional symmetry—the parity relative to inversion in the reference frame with the origin at the midpoint of the nuclei. Owing to this symmetry all the states are divided into even (g states) and odd (u states). The potential curves with different values of m or different parity do not have common branch points, since the exact symmetry of a state cannot change as a result of variation of R. Figure 1 shows the branch points of the potential curves $1s\sigma_g$ and $2p\sigma_u$ of molecular ion H_2^+. These branch points were shown in Ref. 5 as belonging to the S and T series. From the point of view of our problem, only the branch points of the T series are important. These are located in the region of $\mathrm{Re}(R)=5$ a.u. as shown in Fig. 1. Merging of the branch points of the $1s\sigma_g$ and $2p\sigma_u$ potential curves into a common T series is related to the degeneracy of these potential curves in the limit $R\to\infty$. In the symmetric case ($Z_1=Z_2$) all levels split into such (g,u) pairs to that in the limit $R\to\infty$ one of them becomes a sum and the other a difference between two hydrogen states of separated atoms (Z_1e) and (Z_2e) having the same set of parabolic quantum numbers (n_1,n_2,m). The quantum numbers q and k introduced above are related to the latter by

$$q=2n_2-\tfrac{1}{2}[(-1)^m-1],\quad k=n_1\quad (g\text{ states})$$

$$q=2n_2+\tfrac{1}{2}[(-1)^m+1],\quad k=n_1\quad (u\text{ states}).$$

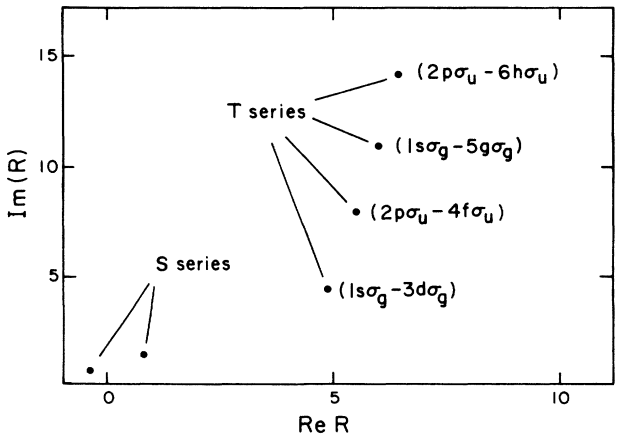

FIG. 1. Branch points of the adiabatic potential curves $1s\sigma_g$ and $2p\sigma_u$ in the complex R plane for the H_2^+ quasimolecule (Ref. 5). The expressions in parentheses give the quantum numbers of the adiabatic states associated with a given branch point.

As was reported in Ref. 5 for each pair of (g,u) potential curves there is a T series of branch points shared with higher potential curves. These series are described by the approximate relationships illustrated in Fig. 1. All the points of a given series are located on a straight line which is almost orthogonal to the real R axis. They are separated by steps $\Delta R\approx\pi i n_\infty$, where $n_\infty=n_1+n_2+m+1$ is the principal quantum number of an isolated atom Z_ie, and the branch points for the g- and u-potential curves alternate.

The T series is due to the passage of a pair of (g,u) potential curves through the top of the barrier in the quasiangular equation (5). Here the adiabatic state stops evolving as a function of internuclear distance and higher states of the same symmetry run into it. This is reflected in the appearance of the hidden avoided crossing. The T series contains an inifnite number of branch points but in slow collisions the main contribution is given by the branch point nearest to the real R axis. Its position in the complex R plane can be obtained explicitly using the method of comparison:[7]

$$\begin{aligned} R_c^+&=3n_\infty(2n_\infty-2n_1-m-1)+4in_\infty\ ,\\ R_c^-&=3n_\infty(2n_\infty-2n_1-m-1)+8in_\infty\ , \end{aligned}\tag{6}$$

where $(+,-)$ indicate the parity of the state as $z\to-z$ (the $(+,-)$ parity W is related to the (g,u) parity I by $I=We^{im\pi}$). This simple expression is of major practical importance. Its real part determines the range of impact parameters for which we can expect a nonadiabatic transition due to this avoided crossing, whereas the imaginary part determines the Massey parameter (2) of the same transition. The latter can be calculated by using a convenient parametrization of the energy difference

$$\Delta E(R)=\frac{\Delta E(\mathrm{Re}(R_c))}{\mathrm{Im}(R_c)}[(R-R_c)(R-R_c^*)]^{1/2}\ .$$

The above expression gives the correct energy difference by $R=\mathrm{Re}(R_c)$ and incorporates the square-root behavior in the vicinity of the complex branch-point R_c. In this approach the Massey parameter for the head-on trajectory (zero impact parameter) can be easily evaluated analytically as

$$\Delta=\frac{\pi}{4}\Delta E(\mathrm{Re}(R_c))\mathrm{Im}(R_c)\ .$$

Using the asymptotic expression (6) for R_c and the same approximation for the energy difference we obtain

$$\Delta_+=\frac{\pi}{(n_\infty)^2},\quad \Delta_-=\frac{2\pi}{(n_\infty)^2}\ .\tag{7}$$

In our case the approximation (7) has sufficient accuracy because for saddle-point electrons typical values of the impact parameter are negligible compared with the very large value of $\mathrm{Re}(R_c)$ [see Eq. (6)].

All branch points R_c^+ (or R_c^-) between the states with the same quantum numbers (k,m) form the connected chain of hidden avoided crossings (see Fig. 2). Their positions on the real R axis increase as $(n_\infty)^2$ [see Eq. (6)] and their energies tend to zero as $(n_\infty)^{-2}$. Consecutive

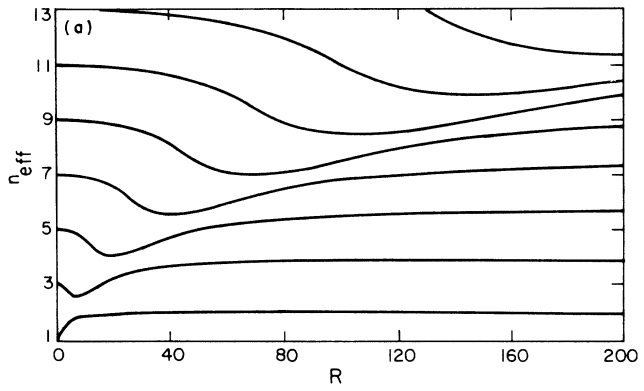

FIG. 2. The sequence of avoided crossings of effective principal quantum number $n_{\text{eff}}=[-2/E(R)]^{1/2}$ as a function of R for H_2^+ (Ref. 6). The adiabatic potential curves are $1s\sigma_g$, $3d\sigma_g$, $5g\sigma_g$, . . . in increasing order of n_{eff}.

passing through all avoided crossings at the separation stage results in ionization. At every point along this path the nonstationary wave function coincides with those adiabatic states with energy levels touching the top of the barrier of the quasiangular equation (5) or the saddle point of the three-dimensional potential. Thus the evolution of the quasimolecule along this path is exactly the same as discussed in Ref. 1.

Now let us consider the wave function of the saddle-point electrons which coincides as $R\to\infty$ with the wave function of the adiabatic states with energy levels touching the top of the quasiangular barrier at $\eta=0$. This situation corresponds to the following values of the parameters in Eqs. (4) and (5): $b=0$, $\lambda=p^2$, $p\to\infty$. In this case the quasiangular equation (5) has the form

$$\frac{d^2G(\eta)}{d\eta^2}+\left[p^2\frac{\eta^2}{(1-\eta^2)}+\frac{1-m^2}{(1-\eta^2)^2}\right]G(\eta)=0\ . \quad (8)$$

To obtain the asymptotic form of $G(\eta)$ it is necessary to employ the method of the comparison equation as developed in Ref. 7. For the region $\eta\approx 0$ the comparison equation is the equation for the parabolic cylinder function

$$\frac{d^2W(z)}{dz^2}+\left[\frac{1}{4}z^2+\nu\right]W(z)=0\ .$$

Its solution is the Whittaker function

$$W_+(z)=z-1/2M_{i\nu/2,+1/4}\left[i\frac{z2}{2}\right]$$

with $W_+(z)$ even and $W_-(z)$ odd as $z\to -z$.

We may construct the solution of the initial equation (8) in the form

$$G_+(\eta)=[z'(\eta)]^{-1/2}W_+(z(\eta))\ . \quad (9)$$

Substituting expression (9) into Eq. (8) we obtain the equation for the scale function $z(\eta)$

$$[z'(\eta)]^2\left[\frac{z^2}{4}+\nu\right]=p^2\frac{\eta^2}{(1-\eta^2)}+\frac{1-m^2}{(1-\eta^2)^2}+\frac{3}{4}\left[\frac{z''(\eta)}{z'(\eta)}\right]^2-\frac{z'''(\eta)}{2z'(\eta)}\ . \quad (10)$$

The scale function must also satisfy conditions of smoothness. Subject to these requirements $z(\eta,\lambda,p,m)$ and $\nu(\eta,\lambda,p,m)$ are found from equation (10) as expansions in p. To first order we obtain

$$\nu=0,\quad z^2(\eta)=4p[1-(1-\eta^2)^{1/2}]\ .$$

The parameter p may be connected to the quantum number n_2 by matching with solutions satisfying the boundary conditions at $\eta=+1$ and $\eta=-1$.

At $\nu=0$ the Whittaker function reduces to a Bessel function

$$G_+(\eta)=\text{const}\times\left[\frac{[1-(1-\eta^2)^{1/2}](1-\eta^2)^{1/2}}{\eta}\right]^{1/2}\times J_{-1/4}(p[1-(1-\eta^2)^{1/2}])\ . \quad (11)$$

Using the asymptotic form of the Bessel function for large argument we can obtain expressions for $G_+(\eta)$ in the region outside of the top of the barrier

$$G_+(\eta)=\text{const}\times\left[\frac{\eta}{(1-\eta^2)^{1/2}}\right]^{1/2}\times\sin\left[p[1-(1-\eta^2)^{1/2}]+\frac{\pi}{4}+\frac{\pi}{8}\right]\ . \quad (12)$$

The solution $G_{-1}(\eta)$ which satisfies the boundary condition at $\eta=-1$ is constructed by using a Bessel equation as the comparison equation. This enables us to take proper account of the existence of a second-order pole caused by a centrifugal term not containing a large parameter. As the standard we search for a solution in the form

$$G_{-1}(\eta)=[y'(\eta)/y(\eta)]^{-1/2}J_m(y(\eta))\ , \quad (13)$$

where $J_m(x)$ is a Bessel function of the first kind. The scale function $y(\eta)$ is determined after the substitution of Eq. (13) into Eq. (5) and in first order is

$$y(\eta)=p(1-\eta^2)^{1/2}\ .$$

Away from the pole $\eta=-1$, $G_{-1}(\eta)$ has the asymptotic form

$$G_{-1}(\eta)=\text{const}\times\left[\frac{-\eta}{(1-\eta^2)^{1/2}}\right]^{1/2}\times\sin\left[p(1-\eta^2)^{1/2}+\frac{\pi}{4}-\frac{m\pi}{8}\right]\ . \quad (14)$$

For $\eta=+1$ a finite solution $G_{+1}(\eta)$ is obtained from $G_{-1}(\eta)$ by the transformation $\eta\to-\eta$ which does not change the quasiangular equation but relocates the end points of the interval. On matching the solution $G_+(\eta)$ to $G_{-1}(\eta)$ and $G_{+1}(\eta)$ we obtain a quantization condi-

tion using the asymptotic formulas (12) and (14):

$$P+=\pi\left[n_2+\frac{m+1}{2}+\frac{1}{8}\right]. \tag{15}$$

The quasiradial equation (4) has no specific features in our case and here the standard asymptotic form for $p\to\infty$ is valid:[11]

$$F(\xi)=\left[\frac{2k!(2p(\xi-1))^{m+1}}{(k+m)!}\right]^{1/2}L_k(2p(\xi-1))e^{-p(\xi-1)} \tag{16}$$

with the quantization condition

$$p^2=-2p(2k+m+1)+2R\ , \tag{17}$$

where $L_k(x)$ is associated Laguerre polynomial.

In the limit $R\to\infty$ the contributions of the regions $|\eta|\approx 1$ vanish and the wave function $\Psi(\eta)$ is concentrated in the vicinity of the top of the quasiangular barrier (see Fig. 3). Therefore the final result as $R\to\infty$ for the three-dimensional wave function corresponding to the saddle-point electrons with normalizing condition

$$\int\Psi^2(\mathbf{r})d\mathbf{r}=P(\rho,v)$$

contains only the quasiangular wave function (11) and has the form

$$\Psi(\mathbf{r})=2p\left[\frac{2P(\rho,v)k!\eta[2p(\xi-1)]m}{(k+m)!R^3\ln(R)}\right]^{1/2}\times L_k(2p(\xi-1))e^{-p(\xi-1)}e^{im\phi}\times J_{-1/4}(p[1-(1-\eta^2)^{1/2}])\ , \tag{18}$$

where $P(\rho,v)$ is the probability of production of the saddle-point electrons, ρ is the impact parameter, and p is expressed through R by the quantization condition (17):

$$p=[(2k+m+1)^2+2R]^{1/2}-(2k+m+1)\ .$$

To obtain the partial amplitude of the angular distribution $A_+(\mathbf{k},\rho)$ it is necessary to calculate the overlap of the wave function (17) with the eigenfunction of the momentum operator

$$A_+(\mathbf{k},\rho)=\frac{1}{(2\pi)^{3/2}}\int\Psi+(\mathbf{r})e^{i\mathbf{kr}}d\mathbf{r}\ .$$

This three-dimensional Fourier integral can be calculated analytically[12] and the final result is

$$A_+(\mathbf{k},\rho)=\frac{(k_\rho R)^m}{4p}\left[\frac{P(\rho,v)k!k_z}{(4p)^m(k+m)!\ln(R)}\right]^{1/2}\times L_k\left[\frac{k_\rho^2R^2}{4p}\right]\times\exp\left[-\frac{k_\rho^2R^2}{8p}\right]J_{-1/4}\left[\frac{k_z^2R^2}{8p}\right]\ .$$

The total angular distribution $\Sigma_+(\mathbf{k})$ is obtained by integrating $[A+(\mathbf{k},\rho)]^2$ over the impact parameter

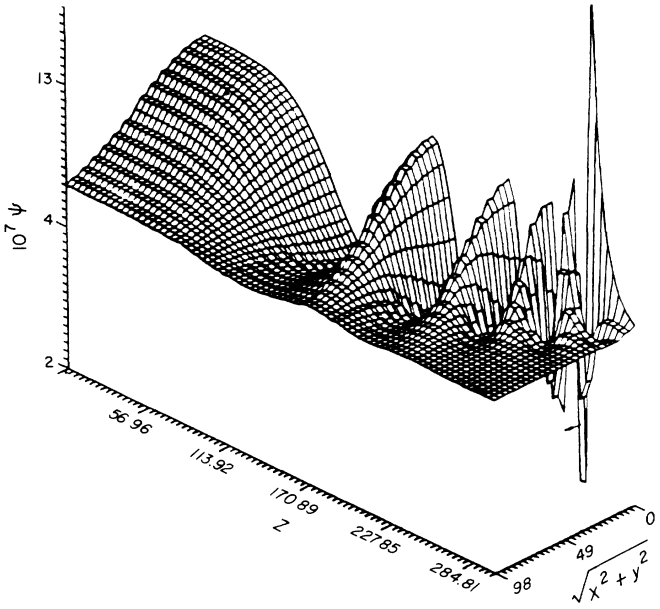

FIG. 3. Three-dimensional adiabatic wave function $\Psi(\mathbf{r})$ of the H_2^+ quasimolecular ion with quantum numbers $k=0$, $q=20$, $m=0$ in $[z,(x^2+y^2)^{1/2}]$ plane. The quasiradial part is Eq. (16) and the quasiangular part is a composite from Eqs. (11) and (14) obtained by matching in the overlap region.

$$\Sigma_+(\mathbf{k})=2\pi\int_0^\infty[A_+(\mathbf{k},\rho)]^2\rho\,d\rho\ .$$

As $A_+(\mathbf{k},\rho)$ depends on ρ only through $P(\rho,v)$ this integral is trivially evaluated

$$\Sigma_+(\mathbf{k})=\frac{\sigma(v)k!k_z(k_\rho R)^{2m}}{(4p)^{m+2}(k+m)!\ln(R)}\times\left[L_k\left[\frac{k_\rho^2R^2}{4p}\right]\exp\left[-\frac{k_\rho^2R^2}{8p}\right]\times J_{-1/4}\left[\frac{k_z^2R^2}{8p}\right]\right]^2, \tag{19}$$

where

$$\sigma(v)=2\pi\int_0^\infty P(\rho,v)\rho\,d\rho$$

is the total cross section for the production of the saddle-point electrons.

It is seen from expression (19), that the width of this distribution tends to zero as $R\to\infty$. To apply this result to the actual situation it is necessary to take into account the following circumstance. We are using the adiabatic approach which is valid as long as the probability of transition (1) remains small. In our case consecutive inelastic passing through the hidden avoided crossings is accompanied by a decrease in the Massey parameter (7) and, therefore by a increase in the probability (1). From the physical point of view it is clear that when the probability reaches the value $P\approx 0.5$ then there is no longer a correlation between the motion of the nuclei and the distribution of saddle-point electrons. The internuclear distance, at which this occurs, can be estimated using the analytical expressions (6), (7), (15), and (17). We obtain

$$R_+ = \frac{\pi^4}{2v}, \quad R_- = \frac{\pi^4}{v}, \tag{20}$$

which can be substituted into Eq. (19) to yield $\Sigma_+(\mathbf{k})$ and $\Sigma_-(\mathbf{k})$, respectively.

The process of formation of the saddle-point electrons is very interesting phenomenon. The final state can be described as a Rydberg state of the quasimolecule with large quasiangular quantum number frozen at internuclear separation (20) which depends on the relative velocity of the nuclei. This quantum number can be estimated using Eqs. (15), (17), and (20) as $n_2^+ = \pi/\sqrt{v}$, $n_2^- = \pi/\sqrt{2v}$ for the symmetric and antisymmetric cases, respectively. This process is interesting also as an example of the application of the adiabatic approach which allows us to obtain the final result in analytic form using only the small magnitude of the velocity of the nuclei without any additional assumptions. For this case the close coupling method is in difficulty because it is necessary to take into account many higher excited states and to carry the calculation out to very large values of the internuclear distance.

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[1]R. E. Olson, Phys. Rev. A **27**, 1871 (1983); **33**, 4397 (1986); R. E. Olson, T. J. Gay, H. G. Berry, E. B. Hale, and V. D. Irby, Phys. Rev. Lett. **59**, 36 (1987).

[2]L. D. Landau and E. M. Lifshitz, *Quantum Mechanics: Non-Relativistic Theory,* 2nd ed. (Pergamon, Oxford, England, 1965).

[3]J. Neumann and E. Wigner, Phys. Z. **30**, 467 (1929).

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

[5]S. Yu. Ovchinnikov and E. A. Solov'ev, Zh. Eksp. Teor. Fiz. **90**, 921 (1986) [Sov. Phys.—JETP **63**, 538 (1986)].

[6]J. M. Rost, J. S. Briggs, and P. T. Greenland, J. Phys. B **22**, L353 (1989).

[7]D. I. Abramov, S. Yu. Ovchinnikov, and E. A. Solov'ev, Ioffe Physico-technical Institute, Leningrad, Report No. 1002, 1988.

[8]S. Yu. Ovchinnikov and M. Piksma, J. Phys. B (to be published).

[9]W. Meckbach, P. J. Focke, A. R. Goni, S. Suarez, J. Macek, and M. G. Menendez, Phys. Rev. Lett. **57**, 1587 (1986); S. Suarez, W. Meckbach, C. G. Bernardi, and P. Focke, Z. Phys. D **7**, 309 (1988).

[10]D. H. Jakubassa-Amundsen and J. Macek, J. Phys. A **22**, 4151 (1989).

[11]C. A. Coulson and P. D. Robinson, Proc. Phys. Soc. London **71**, 815 (1958).

[12]A. Erdelyi, *Tables of Integral Transforms* (McGraw-Hill, New York, 1954).