

New Method for Treating Slow Multielectron, Multicenter Atomic Collisions

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The method of hidden crossings is generalized to treat multielectron systems utilizing molecular Hartree-Fock and configuration interaction methods, extended into the plane of complex internuclear distance. Diabatic promotion of low lying states to the continuum in a two-electron, two-center system via a series of localized transitions is shown for the first time. Excellent agreement with experiments is found regarding single ionization in 50 eV to 1 keV H+H collisions. [S0031-9007(96)01249-5]

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Slow atomic collisions involving several electrons play a substantial role in astrophysical, fusion, and technical plasma processes, in chemical reactions, and in collision spectroscopy. For example, knowledge of the ionization cross section in the collision of hydrogen atoms is critical for modeling the collapse of protostellar material as well as the divertor and edge regions of tokamak plasmas. Still, few reliable results are available. Experiments involving collisions of slow neutral particles are difficult, while theoretical calculations suffer because of the enormous number of molecular states needed for the reliable description of ionization.

We introduce in this Letter an alternative method to the coupled channels approach and, for the fundamental case of ionization in H + H collisions, demonstrate its relative simplicity by readily identifying the main reaction channels, obtaining an accurate estimate of the cross section, and thus creating a new method for treating multielectron heavy particle collisions.

The essential foundations and inspiration for the present work come from the "hidden crossing theory" [1]. In this approach the electronic quasimolecular Hamiltonian and its eigenfunctions are analytically continued into the plane of complex internuclear distance R . The resulting eigenvalue problem is no longer Hermitian and the complex eigenenergies of states of the same symmetry cross at isolated points R_c , which have the structure of square-root branch points. The physical significance of such branch points lies in the fact that the radial matrix element between the states has a sharp local maximum at $\text{Re}\{R_c\}$, causing localization of the electronic transition in a slow atomic collision. The hidden crossing theory may be considered as a generalization of the multichannel Landau-Zener method to include those regions of localized nonadiabatic transitions not conventionally recognized as avoided crossings of the electronic quasimolecular terms. The main triumph of this theory when applied to two-center, one-electron systems has been the identification of a very localized series of branch points at small internuclear distances. This series has been called the S series and it represents a strong channel for ionization by almost diabatic promotion of low

lying quasimolecular states into the continuum [1,2]. A main objective of this work is to confirm the existence of such a series in a two-center, multielectron system.

The principal obstacle in applying hidden crossing theory to more complicated problems lies in the difficulties connected with the solution of the adiabatic multielectron, multicenter eigenvalue problem in the plane of complex R . The conventional real- R problem is most often solved by the molecular orbital Hartree-Fock (HF) and configuration-interaction (CI) approaches, based on the variational principle and Gaussian basis expansions [3]. The validity of the variational principle and the HF procedure even when the Hamiltonian is a complex, non-Hermitian, but symmetric operator follows from its analyticity [4]. Several researchers [5] have successfully extended molecular HF-CI procedures into the plane of complex internuclear distance and/or electronic coordinate for studies of chemical resonances, thus establishing the mathematical foundations for further exploitation of this basic idea.

To facilitate solution of the complex eigenvalue problem utilizing standard procedures and computer codes, two steps are crucial. First, we perform a scaling [1,6] of the electronic coordinates $\{\vec{r}\}$ such that $\{\vec{q}\} = \{\vec{r}\}/R$, which transforms the eigenvalue problem into one in which R is factored out in all interactions. The Gaussian basis primitives are first transformed into the form $\exp[-\alpha R^2(\vec{q} \pm \hat{R}/2)^2]$, with α and q real and R complex. This form is unbounded if the phase of R is $\varphi_R \geq \frac{\pi}{4}$, which implies a need for transforming α into a complex quantity α_R , simultaneously with R . By comparison with known exact complex eigenenergies of one-electron, two-center systems we find that the optimal choice is $\alpha_R = \alpha \text{Re}\{R\}/R$. We have thus generalized the HF and all-single-electron-excitations CI (CIS) procedures [3] to work in a fast and stable fashion everywhere in the plane of complex R except in the very vicinity of branch points. Inside the latter narrow regions, where two eigenenergies become degenerate, diagonalization is carried out to reach the Jordan form [4]. For the H_2 eigenvalue problem we used the $[6s3p2d]$ basis (22 functions), initially optimized [7] for the excited (triplet-ungerade)

states. In our calculation the first configuration is the HF wave function of the ground singlet $(1\sigma_g)^2$, while the excited configurations are the $(1\sigma_g n\sigma_g, n = 2, 11)$ and $(1\sigma_g n\sigma_u, n = 1, 11)$ singlets and triplets.

Promotion of the triplet-ungerade states is the dominant channel for the single ionization at low collision energies. In particular, the system of two colliding unpolarized H atoms in the ground state evolves along binding singlet-gerade and repulsive triplet-ungerade energy curves. Radial coupling connects the interacting states of the same symmetry and divides them into these two mutually uncoupled groups. The result of our calculation is shown in Fig. 1 for the five lowest lying triplet-ungerade states as a function of real R . The zero of energy is chosen to be the ground state of the H_2^+ system, $1s\sigma$, which is the continuum edge for single ionization. Thus we plot $\epsilon(R) = E(R) - E_{1s\sigma}(R)$. The states are denoted by the number N ($N^3\Sigma_u^+$), in order of ascending energy. The correlation of the single-electron orbitals in the separated and united atom limits is also shown [7]. Presented in this way the singly excited triplet-ungerade states show a promotive feature at small internuclear distances, which is not the case with the singlet-gerade set of states. This is typical also of the ungerade states of the H_2^+ system

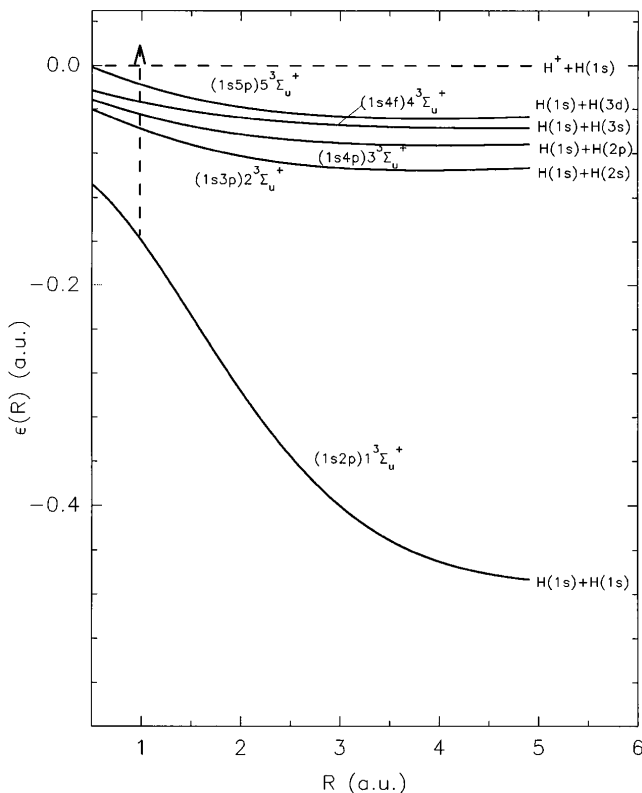


FIG. 1. Adiabatic electronic eigenenergies (solid lines) for the first five singly excited ungerade triplet states for the H_2 system. The energies are presented relative to the $1s\sigma$ state (dashed line) of the H_2^+ system. The arrow shows the location of the promoting series of hidden crossings.

where it indicates the existence of the S superseries of branch points.

Detailed investigation of the complex eigenenergies of the triplet-ungerade states for $0.5 < \text{Re}\{R\} < 5$ (atomic units are used throughout except where noted) and $\text{Im}\{R\} < 1.5 \text{Re}\{R\}$ on a numerical mesh with a step of 0.01, shows the existence of only one series of branch points that starts from the lowest triplet state. This is localized about a real internuclear distance of 1, starting from the first point $R_c = (0.99, 0.83)$ between the $1^3\Sigma_u^+$ and $2^3\Sigma_u^+$ states, and with the branch points between the subsequent states at $(0.97, 0.83)$, $(0.96, 0.80)$, $(0.95, 0.84)$. This result is in accord with calculated [7] radial matrix elements between the few first triplet states, all of which show maxima at about $R = 1$. A three-dimensional plot of the real parts of the three lowest triplet eigenenergy surfaces in the vicinity of this S series is shown in Fig. 2. The $\text{Re}\{\epsilon(R)\}$, relative to the $1s\sigma$ complex eigenenergy surface of the H_2^+ system is presented in terms of $n(R) = 1/\sqrt{-2\text{Re}\{\epsilon(R)\}}$ since in this form the sheets have better visibility of their topology. Although the system is neutral, the surface shows a strong resemblance to those obtained previously in ion-atom systems, indicating the principal cause for the single ionization: electron-charged core interaction. The possible paths in the complex R plane leading to subsequent excitations between the first three triplets are also shown. As a reflection of the time ordering of subsequent transitions along the $\text{Re}\{R\}$ axis, the branch points must be encompassed counterclockwise

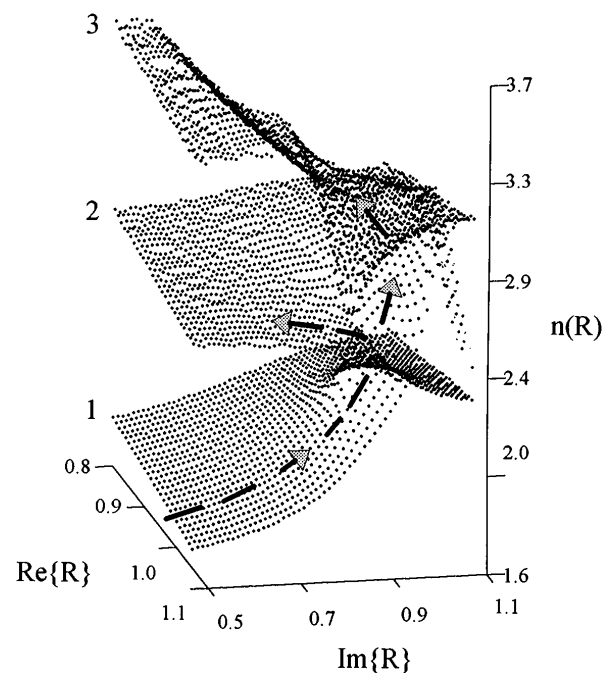


FIG. 2. Locus of the scaled, calculated complex electronic eigenenergies for the first three ungerade triplets, in the vicinity of the series of branch points. The transition path is indicated by arrowed dashed lines.

on the incoming phase, and clockwise on the receding phase of the collision. The distribution of the branch points (the real part of branch points decreases with increasing index of the state N) then enables the consecutive promotion from the lowest triplet to the third one and, further on, to the continuum only in the incoming phase of the collision. Further details of the topology for the H_2 system will be given elsewhere while here we describe the essential details of our computation of the ionization cross section.

For each value of nuclear angular momentum L , the probability of ionization is the product of the individual probabilities $\exp[-2\Delta_{ij}(L)]$, where $\Delta_{ij}(L)$ [8,9] is the Stueckelberg parameter for the excitations of the consecutive coupled triplet-ungerade states (i.e., $1^3\Sigma_u^+ \rightarrow 2^3\Sigma_u^+$, $2^3\Sigma_u^+ \rightarrow 3^3\Sigma_u^+$, etc.). We have judged the convergence of the sum by examining values of the Massey parameter [8] for zero impact parameter $\delta_{ij}^{(0)} = |\text{Im}\{\int_{\text{Re}\{R_c\}}^{R_c} (E_j - E_i)dR\}|$, obtained by numerical integration. The values between the first five triplets are 0.071, 0.024, 0.014, and 0.007, yielding the sum 0.116. We estimate the correction due to the transitions among ungerade triplets with $N \geq 5$ assuming scaling of energy levels as $1/N^2$ and summing up to $N = \infty$. This correction to the sum of Massey parameters is

$$\delta_{N\infty}^{(0)} = \delta_{N-1,N}^{(0)} \frac{\left(\frac{1}{N^2} - \frac{1}{(N+1)^2}\right) + \left(\frac{1}{(N+1)^2} - \frac{1}{(N+2)^2}\right) + \dots}{\left(\frac{1}{(N-1)^2} - \frac{1}{N^2}\right)},$$

which equals 0.012 for $N = 5$. This yields $\delta_{1\infty}^{(0)} = 0.128$.

Alternatively [9], the path of integration in the complex plane can be distorted to encircle all branch points, including the limiting one ($N \rightarrow \infty$), without making "stops" at the bound states. For example, the total Massey parameter for ionization of the $N = 5$ state, obtained by direct numerical integration between the $N = 5$ energy surface and the surface $1s\sigma$ of the single ionization continuum, $\delta_{5\infty}^{(0)} = |\text{Im}\{\int_{\text{Re}\{R_c\}}^{R_c} (E_\infty - E_5)dR\}| = 0.014$, where E_∞ is approximated by $E_{1s\sigma}$. This is very close to the estimated value of 0.012.

Having demonstrated satisfactory convergence the Stueckelberg parameters [9] were calculated by numerical integration taking into account the variation of the radial velocities $v_r(R, L)$ for consecutive transitions between states $N = 1, 2, \dots, 5, \infty$ and the resulting values were summed to obtain the total Stueckelberg parameter $\Delta(L)$ for ionization of the ground triplet state. The cross section [8] is obtained by summation of ionization probability $P(L) = \exp[-2\Delta(L)]$ over nuclear angular momentum until the (real) radial velocity of the initial state becomes zero, i.e., $\sigma = \pi/K_i^2 \sum_{L=0}^{L_{\max}} (2L+1)P(L)$, where K_i is the asymptotic nuclear momentum of initial state.

We display the result in Fig. 3 for impact energies between 0.05 and 4 keV comparing it with experimental data [10,11] and other theoretical [12] results. The agreement of the present cross section with the experiments of

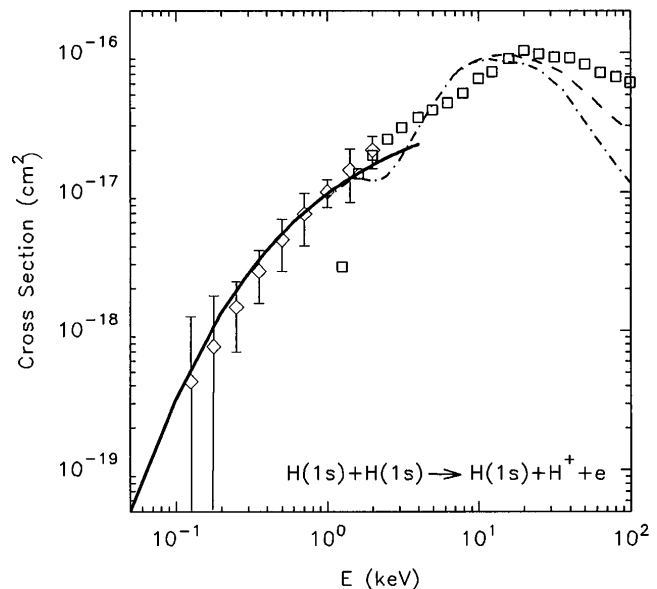


FIG. 3. Present result for single ionization in H+H collisions (solid line). The experimental measurements of Gealy *et al.* [10] (diamonds) and of McClure [11] (squares), as well as the theoretical results of Shingal *et al.* [12] (dash-dot line) are shown for comparison. Correction for simultaneous ionization of one electron and excitation of the other computed by Shingal *et al.* [12] is also shown (dashed line).

Gealy *et al.* [10] at the lowest energies is excellent. At about 1 keV all the data shown in Fig. 3 agree, while at higher energies our result slowly diverges from the experimental ones. This is a consequence of neglecting the promotion of the ground singlet-gerade state through the consecutive excitations of the singlet-gerade states at larger internuclear distances in the receding phase of the collision. In addition, rotational coupling with the Π states at small internuclear distances could trigger the promotion through the triplet Π states. These channels are expected to contribute only at larger collision energies [2]. Therefore we expect that the cross section changes its slope due to the singlet promotion contribution in the range of a few keV, which might be indicated also by the theoretical results of Shingal *et al.* [12]. These authors estimate that the contribution to the ionization from doubly excited states is small for collision energies below 10 keV and therefore does not influence our low energy results.

In conclusion, our calculations show that promotion of the lowest triplet state through a localized series of hidden crossings accounts for single ionization in slow collisions of hydrogen atoms. Since in the triplet state electrons tend to be far from each other due to the Pauli exclusion, the interaction of either of the electrons with the opposite nucleus is the main cause for ionization. Partial screening of the nuclei by the electrons shifts the position of the S series in comparison to the one found for proton-hydrogen impact [2].

The importance of these results extends far beyond the present example and opens the possibility to study in de-

tail the low-energy dynamics of multielectron systems, particularly regarding ionization which is the greatest success of the hidden crossing theory. The present approach is the synthesis of ongoing extensive work in the one-electron, two-center hidden crossing theory, as well as numerous contributions in quantum chemistry. It represents the beginning of the development of more comprehensive procedures utilizing representations in the plane of complex R involving multielectron interactions. The inclusion of doubly excited states and multiconfiguration interactions in this approach is the objective of further work.

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$$\Delta_{i,j}(L) = \left| \text{Im} \left[\int_{\text{Re}\{R_c\}}^{R_c} \frac{E_i(R) - E_j(R)}{\bar{v}_r(R, L)} dR \right] \right|,$$

where $\bar{v}_r(R, L)$ is the average (complex) radial internuclear velocity on the two energy branches. In the limit of classical nuclear motion $\Delta_{i,j}$ reduces to δ_{ij}/v , where δ_{ij} is the Massey parameter and v is the collision velocity.

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