

# Hidden crossings theory beyond single electron systems

Predrag Krstić

**Abstract.** What are hidden crossings, in what atomic systems do they emerge? What do we gain in studying and developing the underlying theory? Where, when and the hidden crossings theory is applied? Meaning of the hidden crossings and techniques for their detection and application are discussed for multielectron systems. Particular attention is paid to the slowly colliding H+H and H<sup>+</sup>+He systems.

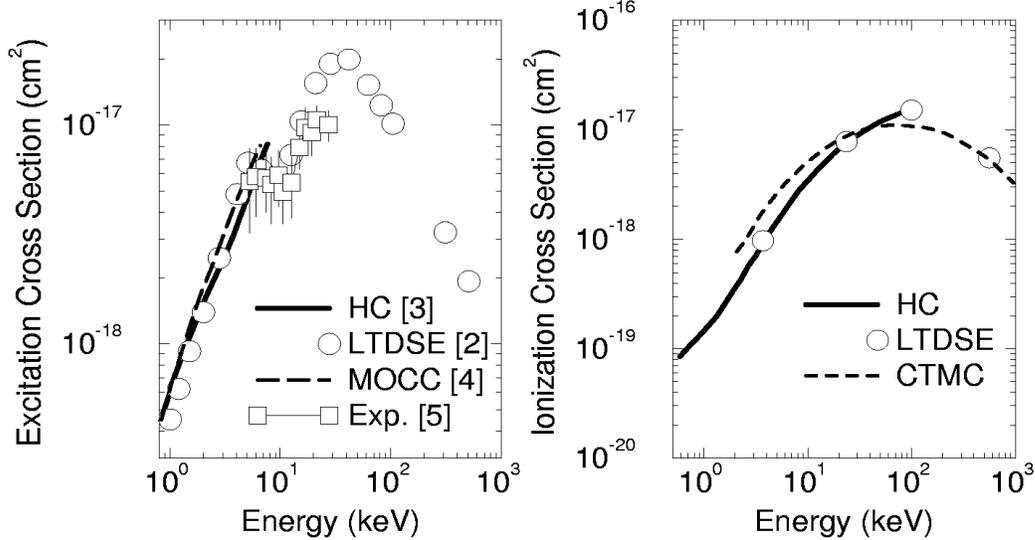
## INTRODUCTION

A unique feature of the Hidden Crossings (HC) theory [1] is that it provides a relatively easy description of the physical processes where other theories have difficulties. Thus, ionization in slow ion-atom collisions, at least at the level of cross sections is simply and accurately described and calculated with the HC theory. On the other hand, Molecular and Atomic Orbital Close Coupling (MOCC and AOCC, respectively) methods, based on the expansion in discrete basis functions, require large bases and quasi-discretization of the continuum to reach the results often with questionable accuracy. Even the methods based on a direct solution [2] of the time-dependent Schrödinger equation on numerical lattice (LTDSE) are ineffective at low energies due to a large number of time steps needed. In these cases the HC-based calculations are hundreds to thousands times more effective concerning the CPU time, even if one counts the time needed to find the topology of the hidden crossings for a considered collision system. Besides, the method provides the treatment of all inelastic processes “on the same footings” and with the same accuracy [3]. To illustrate, Fig. 1 shows comparisons of the HC results with the “benchmarking”, LTDSE calculations for excitation and ionization for the low-energy heavy particle collisions.

The HC approach is limited to the phenomena which are slowly varying on the time scale of the considered quantum system, like are atomic systems in slowly varying external fields or slow heavy-particle collisions. It is an asymptotic approach, exact in the adiabatic limit. For a collision at relative velocity  $v_{coll}$  the range of validity is, thus, defined by the adiabatic condition

$$v_{coll} < v_{at} , \tag{1}$$

where  $v_{at}$  is the characteristic velocity of the active electron. A significant part of the phase of an ionizing electron wave function is built through the Rydberg states where adiabaticity is lost and, thus, the electron angular spectra cannot be accurately calculated with the standard HC approach. This drawback might be corrected to a certain extent and probably removed by expansion of the  $(Z_1, e, Z_2)$  wavefunction in terms of the complex-energy two-center Sturmians [4].



**FIGURE 1.** Comparison of the HC and LTDSE results for a) excitation  $H(1s) \rightarrow H(2s)$  by proton impact and b) ionization of  $He^+(1s)$  by antiproton impact [7,8].

The HC theory strongly relies on existence of well separated electronic part,  $H_{el}$ , of the total Hamiltonian  $H$  of the system. The conditions for separation of fast “internal” (electronic) and slow “external” (nuclear) motion (Born-Oppenheimer approximation) rely on the large difference in masses between an electron and a nucleus, i.e. on the smallness of the characteristic electron momentum in comparison to the nuclear one. This defines the lower bound of  $v_{coll}$  for the applicability of the HC theory.

The hidden crossings are crossings of the complex eigenenergy surfaces of the same symmetry at complex values of  $R$ . These emerge from the electronic adiabatic problem

$$H_{el}(\{\vec{r}\}, \vec{R})\Phi_{el}(\{\vec{r}\}, \vec{R}) = E_{el}(R)\Phi_{el}(\{\vec{r}\}, \vec{R}) \quad (2)$$

when solved for a fixed complex “parameter”  $R$ . Since the adiabatic quasi-molecular terms of the same symmetry do not cross, the HC’s can appear only for complex  $R$ , when the  $H_{el}$  is not Hermitian, and the Neuman-Wigner non-crossing rule is

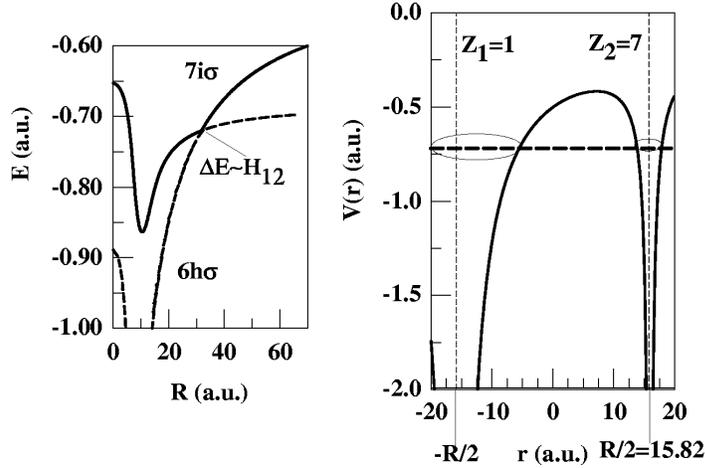
not applicable.  $\{\vec{r}\}$  is here a set of electronic coordinates, while the complex parameter  $R$  characterises the (slowly varying) perturbation of the problem, which causes transitions: Internuclear distance (collisions), external field (electric or magnetic), envelope of a laser pulse (in Floquet space), ... The physical conditions for appearance of a hidden crossing for a particular  $R$  are discussed in Section II, on the example of a three-body ( $Z_1, e, Z_2$ ) collision system. Multielectron Hidden Crossings theory (MEHC), discussed in Section III, is conceptually straightforward multi-body generalization of the three-body HC theory, but technically this is a formidable problem which reduces to a multielectron molecular eigenvalue problem in the plane of complex internuclear distance  $R$ .

## I SINGLE-ELECTRON HC THEORY

Collisionally induced inelastic transition cannot occur in the adiabatic limit,  $v_{coll} \rightarrow 0$  (with exception for the exothermic ones). As  $v_{coll}$  increases from zero, a tunneling may take place at the internuclear distances  $R_{LZ}$  of the so called accidental (dynamic) quasi-resonances, known also as Landau-Zener or avoided crossings of the adiabatic quasi-molecular terms. This is shown in Fig. 2a), for the example of  $N^{7+} + H$ . At  $R \sim R_{LZ} \sim 30$  a.u. the small coupling between the states  $|7i\sigma\rangle$  and  $|6h\sigma\rangle$ ,  $H_{12}$ , is proportional to the small energy gap  $\Delta E_{12}$  between the terms  $E_{7i\sigma}$  and  $E_{6h\sigma}$ , causing a slow tunneling through the radial potential barrier between the two centers, (Fig. 2b)), with an exponentially small, velocity dependent probability  $p \sim \exp(-a/v_{coll})$ . The tunneling lasts only as long as the quasi-resonance, which implies a transition localized for particular values of  $R$ . The terms which experience LZ avoided crossings cross for a complex internuclear distance  $R_c^{LZ}$ . These have very small imaginary part  $\text{Im}\{R_c^{LZ}\} \sim \Delta E_{12}$ , and are not generally considered as hidden crossings. Besides the avoided crossings, which for single-electron-two-center systems occur only if  $Z_1 - Z_2 > 1$ , there is a physically different type of localized transitions, which occur for internuclear distances where the top of potential barrier touches the populated energy term [9]. A prominent example is the case of the radial barrier between a two Coulomb centers (Fig. 4). For  $Z_1 = Z_2 = Z$  and the coordinate origin at  $\vec{r} = 0$ , along the internuclear z-axis the electronic potential energy is

$$V_{el}(r, R) = -\frac{Z}{|z - R/2|} - \frac{Z}{|z + R/2|} \quad (3)$$

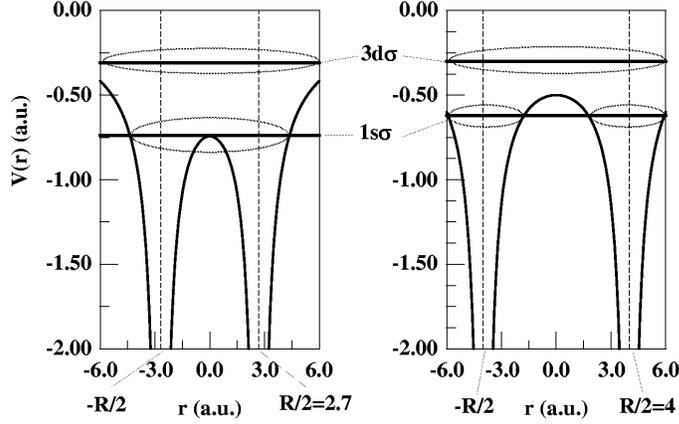
which maximizes to  $V_{el}^{\max} = -4\frac{Z}{R}$  at  $z=0$ . As long as the barrier separates the two centers at larger internuclear distances, the electronic wave function has atomic character, being localized at one of the centers.  $V_{el}^{\max}$  decreases as the colliding partners approach to each other. When the top of barrier touches the populated electronic term of the state  $|0\rangle$ , the wave function is free to “diffuses” to the other center and is now shared between the two centers, becoming the molecular in character. The other eigenfunctions of the problem adapt to the new situation.



**FIGURE 2.** a) Avoided (LZ) crossings of the molecular terms results in b) slow tunneling through the radial potential barrier.

This sudden change of the wave function with  $R$  results in its large derivative  $\partial/\partial R$ , and thus in a peak in the nonadiabatic radial matrix element  $H_{i0} \sim \langle i | \partial/\partial R | 0 \rangle$ ,  $i = 1, 2, \dots$ , where  $i$  and  $0$  belong to the same symmetry group of radially coupled adiabatic eigen-levels. A peak in the matrix element  $H_{i0}$  for  $\text{Re}\{R_{c_i}\}$  is associated to its complex-conjugated poles [10] at  $R_{c_i}$  and  $R_{c_i}^*$  (Fig.5), to a root singularity in the normalization coefficients of the relevant eigenfunctions and to a square root branch point. The relevant eigenenergies coincide (cross) at complex  $R_{c_i}$ , i.e.  $\Delta E_{i0} \sim \sqrt{R - R_{c_i}}$ ,  $\Delta E^* \sim \sqrt{R - R_{c_i}^*}$ . These branch points, shared between the complex terms  $i$  and  $0$  form the so called Q-series of closely localized branch points. The largest peak of all  $H_{i0}$  and thus, the smallest imaginary part of  $R_{c_i} = R_{c_0}$  is for adjacent terms. Collection of all  $R_{c_0}$  obtained when the barrier touches various levels of the system in course of changing  $R$  is called a Q-superseries. This promotes terms to higher excited states and continuum in the receding phase of the collision. In calculations of the system dynamics it is in most cases enough to consider only contributions from superseries, neglecting the higher order transitions.

For the same example-system, dynamics of the electron in the united-atom limit (UA) is described by atomic wavefunctions, generated by the potential  $V_{ell}^{UA}(r, R \rightarrow 0) \sim -2Z/r + \ell(\ell + 1)/r^2$ . The emerging centrifugal barrier while moving toward the  $R \rightarrow 0$  pulls the consecutive terms upward in a localized region around  $R \sim 0$ . During that process the molecular character of the electronic wave functions is changed to the atomic one while passing a narrow range of  $R$ , thus causing highly localized peaks in matrix elements of  $\partial/\partial R$  between the states of a fixed  $\ell$ . This is further associated with the poles in the radial matrix elements for complex  $R_c^{(\ell)}$  as well as to the branch points between the relevant eigenenergies. These branch points, localized for small  $R$  promote in consecution and pairwise all terms of a



**FIGURE 3.** Hidden crossings occur when top of the potential barrier touches the populated energy term, causing sudden change of the wave function. Shown is an example of the radial barrier (Q-type HC).

fixed  $\ell$  in the incoming phase of the collision and constitute a Coulomb-like  $S^{(\ell)}$ -superseries, which is in many cases the most effective channel for ionization at low energies.

While the  $S$ -series do not exist for the terms with zero angular momentum there is an important exception from that rule: Collision of an antiparticle of charge  $Z_1 < 0$  with a single electron ion of charge  $Z_2$  [15]. For small  $R \ll r$  electronic potential contains an electric dipole in addition to the unbalanced Coulomb charge,

$$V_{ell}^a \sim \frac{(Z_1 - Z_2)\vec{R} \cdot \hat{r}}{r^2} - \frac{Z_1 + Z_2}{r} + \frac{\ell(\ell + 1)}{r^2} \quad (4)$$

Since the dipole term has the same structure as the centrifugal term, the  $S$ -series emerges even for the  $\ell = 0$  state. This is the main mechanism for ionization of the low-lying states of ions in collision of antiprotons, in a broad collision-energy range, since there is no radial potential barrier to support the  $Q$ -superseries [8].

Knowledge on topology of the hidden crossings in the plane of complex  $R$  is equivalent to knowing where the strong, localized couplings for a particular system are. In addition, the LZ avoided crossings constitute a physically different category of localized transitions which are treated separately. All these define the low-energy dynamics of a collision system and an important issue is how to extract from them the most detailed and accurate information on the system evolution. Thus one can use the topology of the hidden crossings to estimate the nonadiabatic matrix elements, which in the adiabatic limit takes the form [11,12,10]

$$\langle i | \partial / \partial R | j \rangle \approx \frac{1}{4} \frac{\text{Im}\{R_c\}}{(R - \text{Re}\{R_c\})^2 + (\text{Im}\{R_c\})^2}$$

for each particular hidden crossing  $R_c$ . These matrix elements do not suffer from the defects of the usual radial matrix elements between the adiabatic states (like are incorrect  $R \rightarrow \infty$  limit, dependence on electron origin) and could be used in the MOCC-like system of coupled equations to obtain the transition amplitudes among the low lying states, with either classical ( $R = R(t)$ ) or quantum internuclear motion. This approach leads to the correct transition amplitudes (including their phases) as long as the adiabatic condition (1) is preserved within the coupled states. A more appropriate treatment for obtaining ionization cross sections is the "quasi-elastic" approach [1,10], which relies on features of the adiabatic Schrödinger equation when analytically extended in the plane of complex  $R$ . The relevant Hamiltonian loses Hermiticity and has only one, though multivalued and multiple connected complex eigenenergy surface  $E(R)$ , and the branch points (hidden crossings) are the only singularities. By deforming the evolution path of the system through the complex  $R$  plane one evolves quasi-elastically. Various Riemann (branch) surfaces  $E_i(R)$  coincide with the eigenenergy terms for  $\text{Re}\{R\}$ , which enables proper definition of the initial and boundary conditions of the problem. The elastic evolution operator, in the adiabatic limit and for a classical  $R = R(t)$  is  $\alpha_i(t) = \exp\{i \int_C E_i[R(t)]dt\}$ , where a path  $C$  connects initial and final states through the complex time (i.e. complex  $R$ ). Starting from  $E_i$  at  $R \rightarrow \infty$ , the path is promoted to a different Riemann surface whenever  $C$  encircle a branch point. At any  $R$  the path can make exit to the real axis, ending at a state  $E_j(\text{Re}\{R\})$ . Thus, to encircle a branch point is equivalent to an inelastic transition. The transition amplitude between states  $|i\rangle$  and  $|j\rangle$  is

$$\alpha_{ij}(t) = \exp\{i \int_{C_{ij}} E_i[R(t)]dt\} = \exp\{i \int_{C_{ij}} E(R)dR/v_R\} \quad (5)$$

where  $v_R = dR/dt$  is the radial velocity. This yields the transition probability in form of  $P_{ij} = \exp(-2\Delta_{ij}/v)$ , where  $\Delta_{ij}$  is the Massey parameter,  $\Delta_{ij} = \text{Im}\{\int_{C_{ij}} E(R)dR/[v_R/v]\}$ . In a good approximation  $\Delta_{ij} \approx \Delta E_{ij} \text{Im}\{R_{c_{ij}}\}$ . Shape of the path-curve  $C$  is arbitrary as long as it keeps a track of causality for real times, and can be, for example, deformed to ionize a ground state level through an S-superseries by either a set of pairwise and consecutive excitations or by a path encircling the whole superseries. Similar quasi-elastic evolution of the system through the complex  $R$ -plane can be realized for semiclassical (WKB) motion of the nuclei [8].

## II MULTI-ELECTRON HIDDEN CROSSINGS THEORY

Occurrence of the hidden crossings is likely in any system for which the electronic motion is influenced by a parametrically dependent potential barrier. The system dynamics induced by slowly changing parameter can be described similarly as described in the previous Section. Still, nonseparability of the problem Hamiltonina,

as is a multielectron case, may cause a lot of difficulties in searching for the hidden crossings, even if one restricts to only low lying states.

The adiabatic problem of a two-center-two-electron system like is H+H is described by the electronic Hamiltonian of the form

$$H_{el}(\{\vec{r}\}, \vec{R}) = h(\vec{r}_1, \vec{R}) + h(\vec{r}_2, \vec{R}) + h_{12}(\vec{r}_1, \vec{r}_2), \quad (6)$$

$$h(\vec{r}_i, \vec{R}) = -\frac{1}{2\mu}\nabla_{\vec{r}_i}^2 - \frac{1}{|\vec{r}_i - \frac{\vec{R}}{2}|} - \frac{1}{|\vec{r}_i + \frac{\vec{R}}{2}|}, i = 1, 2, \quad (7)$$

$$h_{12}(\vec{r}_1, \vec{r}_2) = \frac{1}{|\vec{r}_1 - \vec{r}_2|} \quad (8)$$

where  $\vec{r}_i$  are the electronic coordinates,  $\{\vec{r}\} = \{\vec{r}_1, \vec{r}_2\}$ ,  $\vec{R}$  the internuclear vector,  $\mu$  is the electron reduced mass. If the electron correlation is neglected, the two electrons evolve separately producing the identical single-electron hidden crossings topologies. The electron correlation term,  $h_{12}$ , introduces novelty in the hidden crossings, either by modifying the single-electron ones that emerge from  $h_i$ , or by inducing new series. If the electrons are not equivalent in the initial configuration, one can expect separate promotive superseries for each of them. New types of series associated to the double-excited quasi-molecular terms could be expected, too. If the electron correlation is weak any significant couplings, associated to the hidden crossings is more likely to describe single-electron excitation, while keeping the second electron inactive.

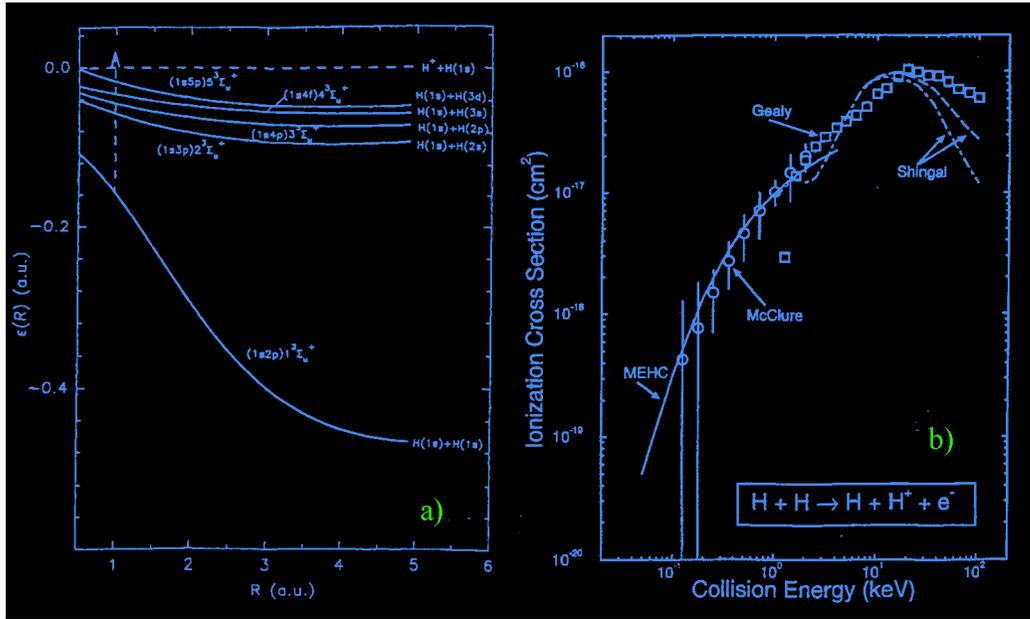
An important feature of all matrix elements  $\Omega_{ij}(R)$  of an operator  $\Theta$  analytically extended into the complex plane of parameter  $R$  is their symmetry  $\Omega_{ij}(R) = \Omega_{ji}(R)$ , a consequence of the analyticity requirement to both Hamiltonian and the wave function [13,14]. This can be fulfilled only with the definition

$$\Omega_{ij}(R) = \int \Phi_i^*(\vec{r}, R^*)\Theta\Phi_j(\vec{r}, R)d\vec{r} \quad (9)$$

It has been shown that the variational principle is valid [13], for real and imaginary parts of the eigenenergies, separately (“bi-variational principle”), for a complex, nonhermitian but symmetric hamiltonian. Thus, the adiabatic eigenvalue problem for a nonseparable systems like H+H or H<sup>+</sup>+He can be solved for complex  $R$  by expanding the wave function in a convenient truncated bases, and with application of the bi-variational principle. This is enough to support generalized Hartree-Fock and Configuration Interaction (CI) procedures [15–17].

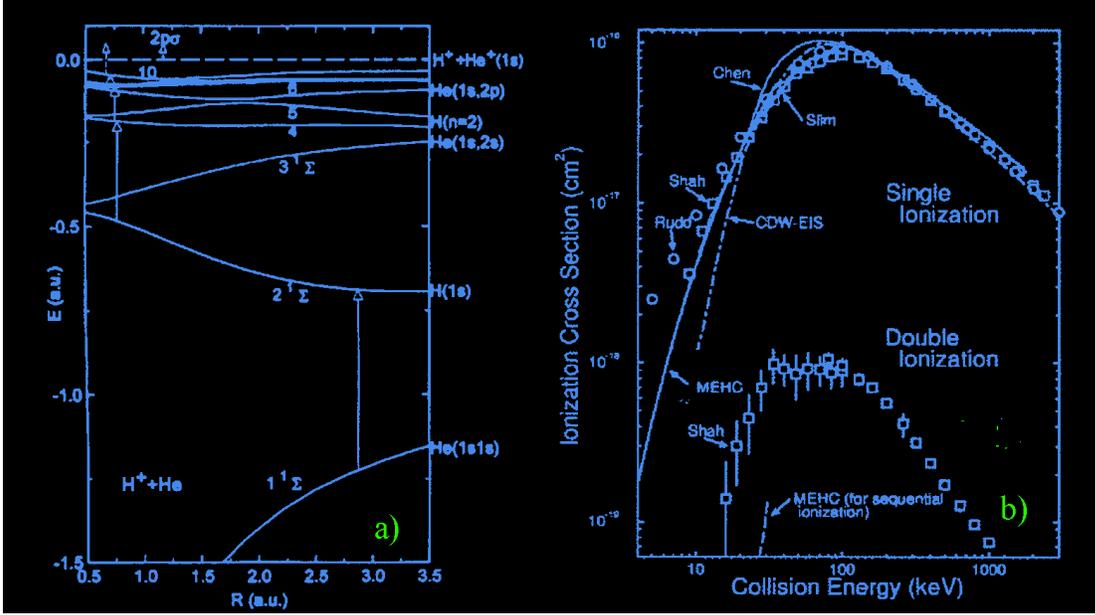
An important step in construction of a complex solver is scaling of the electronic radial coordinates  $r_i$  by complex  $R$ , thus introducing hypergeometric coordinates  $q_i=r_i/R$ , and then rotating  $q_i$ 's back to the real axis. This scaling enables good definitions and convergence of all analytical matrix elements for complex  $R$ . The scaled Gaussian primitives  $\exp(\alpha R^2(\vec{q} - \hat{R}/2)^2)$  become nonintegrable functions in  $q$  if the complex  $R$  is in the upper half of the first quadrant. This was handled [15] to a certain extent by redefining the exponent  $\alpha \rightarrow \alpha_R$  as a complex,  $R$ -dependent

quantity, and  $\alpha_R = \alpha$  when  $R$  is real. Validity of the redefinition must be checked for each system and for various ranges of  $R$ . Unrestricted Hartree-Fock (UHF), combined with the single-excited CI codes were developed for the complex  $R$  and applied to the  $H+H$  and  $H^++He$  systems [15,17], using appropriate uncontracted bases of gaussian primitives, optimized for  $\text{Re}\{R\}$ . The branch points were detected by "triple coincidence" of crossings of the complex eigenenergies, of singularities in the corresponding  $\partial E/\partial R$  and singularities in the relevant radial matrix elements of  $\partial/\partial R$ .



Single-electron ionization of  $H+H$ . a) S-superseries promotion (dashed arrow) to the single-electron continuum edge ( $H^++H(1s)$ ) through the single-excited electronic triplet terms (solid lines). b) MEHC (solid line); experiments: McClure et al [19], Gealy et al [18]; MOCC: Shingal et al [20].

Fig. 4a) shows the term diagram of the single-excited triplet ungerade states of the  $H+H$  system,  $n^3\Sigma^+$ . The ground level of  $H^++H$  system (single-electron ionization edge) is chosen for zero of energy. A single excited superseries of hidden crossings of the S-type was found about  $R = 1$  a.u. (dashed-line arrow in Fig. 4a)) and used to calculate the single-electron ionization cross section (Fig. 4b). Excellent agreement with the experiment in the range of 50 eV - 4 keV is obtained. This implies that the principal mechanism for the single-electron ionization in this case is the interaction of an electron with the nucleus of the incoming atom. The ionization is realized when the two clouds penetrate into each other.



Ionization of He by proton impact. a) Single excitation singlet electronic terms; localizations of the hidden crossings transitions are indicated by arrows. b) The MEHC results in comparison to various experimental and theoretical data.

Somewhat different is the mechanism for single ionization of the He ground state by proton impact. [16,17]. An electron first makes the transition from the ground to the first excited singlet state ( $2^1\Sigma^+$ ) by the Q-transition at the branch point  $Re\{R_{c1}\}=2.87$  a.u.. Because of the large energy splitting of these two states (Fig. 5a)) the transition is weak at low collision energies and this is responsible for suppression of both single and double ionization cross sections (Fig. 5b)). The  $2^1\Sigma^+$  is the charge exchange state, the active electron is localized at proton at large internuclear distances. During a further approach of the nuclei, the electron is promoted to the continuum through the S-type series which starts at  $Re\{R_{c2}\}=0.76$  a.u. and runs through only these excited states which are asymptotically localized at hydrogen. This yields the single ionization cross section in good agreement with the measurements of Shah et al [21], as well as with the coupled channel calculations of Slim et al [22] and Chen et al [23]. Double ionization cannot be explained with the sequential mechanism (Fig. 5b)). It requires a ladder type mechanism through the double excited states.

### III CONCLUSIONS

Hidden crossings are associated with the top(s) of potential barrier(s) and their occurrence and positions in an arbitrary atomic system can be predicted by analysis of the electronic adiabatic potentials. Application of hidden crossings to study the system dynamics in response to a slowly changing perturbation is limited by the near-adiabatic requirements. Multielectron hidden crossings theory has been

successfully applied to two-electron ( $\text{H}+\text{H}$ ,  $\text{H}^+ + \text{He}$ ,  $\bar{\text{p}}+\text{He}$ ) as well as to six-electron ( $\text{C}^+ + \text{H}$ ) collision systems, to the processes which involve excitations of only one electron (for example, single electron ionization). This was accomplished by the performing Hartree-Fock and Single-Excited- Configuration Interaction calculations in the plane of complex internuclear distance. Study of highly correlated processes, with inclusion of the multiple electron excitations is underway.

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