NEARLY-ADIABATIC ATOMIC PHYSICS:
METHODS-DATA-DEVICES

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Abstract. When an atomic or molecular system is perturbed slowly in the time scale defined by its characteristic frequencies, it experiences nearly adiabatic change, both adapting its internal motion and performing weak inelastic transitions. Quantum-mechanical methods for the treatment of the transition dynamics of nearly-adiabatic systems are reviewed. Models for nearly-adiabatic transitions, united under the generalized hidden crossings theory, bring up a physically transparent picture of the processes in a wide energy range. These are applied to a variety of ion-atom and ion-molecule collisions. The role of adiabatic atomic physics in the fully quantum description of electron transport through molecular electronic devices as well as in the theoretical simulation of the self assembled molecular monolayers are also briefly reviewed.

1. METHODS FOR SOLVING SCHRÖDINGER EQUATION

Recent novelties in atomic physics such as Bose-Einstein condensation and cold collisions are prominent examples of nearly-adiabatic atomic systems. Still, the newest developments of divertors in fusion tokamaks, recordings of interstellar spectra that may give clues for evolution of the early universe, and increased demands for the precise plasma etching in the semiconductor based electronics have made modelers of fusion, astrophysical and technical plasmas the most active consumers of slow collision data. Due to difficulties in their production, these have been persistently sparse which makes nearly-adiabatic collision physics one of the most needed activities in traditional atomic physics.

A typical binary collision of heavy particles is characterized by the internuclear distance vector $\vec{R}$ as well as a set of electronic coordinates $\{\vec{r}\}$. If the motion of nuclei is assumed along a classical path, $\vec{R} = \vec{R}(t)$, obtained by solution of classical equations of motion in the interparticle potential, then the Schrödinger equation of the system is reduced to a time

dependent partial differential equation for the electron dynamics (atomic units are used throughout)

$$i\frac{d}{dt}\Psi = H_{el}(\vec{r},\vec{R})\Psi \qquad (1)$$

where $H_{el}(\vec{r},\vec{R})$ is the electronic Hamiltonian, which defines the adiabatic eigenstates of the problem

$$H_{el}(r,R)\Phi_n(r,R) = E_n(R)\Phi_n(r,R) \qquad (2)$$

The adiabatic eigenfunctions, $\Phi_n(r,R)$, describe the motion of the electron(s) for a fixed value of the vector $\vec{R}$. In what follows and, without loss of generality, we will consider only the transition dynamics caused by the radial motion of the nuclei, assuming that R is a scalar variable. Transitions between electronic states are caused by the time-dependence of $\vec{R}$(t). For center-of-mass collision energies of the order of eV or less, the size of the wavelength of nuclear motion, h/Mv_R, becomes of the order of the characteristic collision length and dimensions of the system, where $v_R = dR/dt$ is the internuclear radial velocity and M is the reduced mass of the system. The classical prescription for the nuclear motion is not good anymore and the problem must be described by the full, time-independent Schrödinger equation for both the electronic and nuclear motions, $H\Psi = E\Psi$, coupled through the common electronic-internuclear potential, where H is the total Hamiltonian of the system.

The adiabatic eigenfunctions, $\Phi_n(r,R)$, are good representations of the states of the electron(s) as long as the relative nuclear motion R(t) is much slower than the electronic motion. According to the adiabatic theorem [1], endoergic transitions are not possible in the strict adiabatic limit, $v_R = 0$. Besides, the adiabatic terms, $E_n(R)$, of a Hermitian Hamiltonian never cross [1]. Intuitively, the tunneling mechanism, localized to the vicinity of the closest approach of the terms (so called avoided crossings) will dominate the transitions when v_R is small.. This localization justifies the treatment of electronic transitions in a pair wise fashion (between two adjacent adiabatic states at a time), which is the main motivation for using two-state approximations in localized ranges of R.

Many general features of the collision dynamics can be understood by modeling a collision system by two (diabatic) states only, with matrix elements of the Hamiltonian.

satisfying $H_{22}(R \to \infty) > H_{11}(R \to \infty)$, $H_{12}(R \to \infty) \to 0$. Diagonalization of this Hamiltonian

yields adiabatic energy terms $E_{2,1}(R)$

$$E_{2,1} = \bar{E}(R) \pm \Delta E_{2,1}(R),$$
$$\bar{E}(R) = \frac{H_{11} + H_{22}}{2} \tag{3}$$
$$\Delta E_{2,1}(R) = \frac{1}{2}\sqrt{(H_{11} - H_{22})^2 + 4H_{12}^2}$$

Although $E_{2,1}(R)$ do not cross for real R, these still can cross for complex R, at $R = R_c$, R_c^*, (where electronic Hamiltonian is not Hermitian)

$$H_{11}(R) - H_{22}(R) = \pm i2H_{12}(R) \tag{4}$$

The crossings of adiabatic energy terms for complex R_c's are known as hidden crossings [3]. Linearization of H_{12} in the vicinity of R_c (and R_c^*) yields

$$\Delta E_{2,1}(R \approx R_c) = C\sqrt{R - R_C},$$
$$\Delta E_{2,1}(R \approx R_C^*) = C^*\sqrt{R - R_C^*}, \tag{5}$$

indicating that the energy terms have square-root branch singularities at R_c and R_c^*. Thus, if the Hamiltonian is an analytical function of R, the hidden crossings are the only additional singularities of the eigenenergy and these are branch points of the square-root type [3]. The adiabatic eigenenergy for the complex R is a single, multi-valued function, containing two (in this case) Riemann sheets, which coalesce at the branch point, and coincide with adiabatic terms along the Re{R} axis. Of course, a collision system evolves along this axis. Still, one can choose to deform the path in the complex R. Thus, starting from real R at state |1>, encircling a branch point and returning to the real R axis, the system is "switched" to another Riemann sheet, i.e. promoted to the state |2>. Remarkably, the quasi-elastic evolution of the system in the complex R-plane may lead to an inelastic transition.

Since the complex "evolution path" can be deformed from real R axis, infinitesimally close to Re{R_c}, to encircle R_c in the direction of the Im{R} axis, it follows that the transition region is infinitesimally narrow around Re{R_c}. We show that this counter-intuitive statement is, strictly speaking, valid only in the adiabatic limit, $v_R \to 0$. By linearization of $H_{i,j}(R)$ in the vicinity of R_c and R_c^*, the matrix element of the nonadiabatic coupling, $U_{1,2}(R) = < \Phi_1 \,|\, d/dR \,|\, \Phi_2 >$ takes the form

$$U_{2,1}(R \approx R_c) \approx -\frac{i}{4}\frac{1}{R-R_c}, \quad U_{2,1}(R \approx R_c^*) \approx \frac{i}{4}\frac{1}{R-R_c^*}, \tag{6}$$

which reduces to a Lorentzian form along the real R axis

$$U_{2,1}(R) = \frac{1}{2}\frac{\text{Im}\{R_c\}}{(R-\text{Re}\{R_c\})^2 + (\text{Im}\{R_c\})^2} \tag{7}$$

Thus, $U_{2,1}(R)$ exhibits a peak along real axis at $R=\text{Re}\{R_c\}$ whose width is proportional to $\text{Im}\{R_c\}$. On the other hand, by expanding the total electronic wave function into adiabatic eigenstates one obtains the Molecular Orbital Close Coupling (MOCC) equations, which in the time-dependent representation read as

$$\frac{dA_n}{dt} = -v_R \sum_k A_k U_{n,k} \exp(i\int_0^t dt'\Delta E_{n,k}), \quad \lim_{t\to-\infty} A_n = \delta_{n,i}, \lim_{t\to\infty} A_n(t) = S_{n,i} \tag{8}$$

The $S_{n,i}$ is the S-matrix element for the transition from $|i\rangle$ to $|n\rangle$. Similarly, one could expand the wave function in the diabatic basis, which would yield the exponent of the phase factor in the coupled equations in form $\varphi_{2,1} = i\int (H_{11} - H_{22})dR/v_R$. By linearization, $H_{11} - H_{22} = G(R - R_{AC})$, where $R_{AC} = \text{Re}\{R_C\}$, (which, together with the assumption $H_{12}(R \approx R_{AC}) = const$ constitutes the famous Landau-Zener (LZ) model, [2]), and from the requirement $\varphi_{12} \approx 1$ a range ΔR in R around $\text{Re}\{R_c\}$ follows where the fast oscillating phase (for $v_R \to 0$) is not suppressing the transition

$$|\Delta R| \sim \left[\frac{v_R}{G}\right]^{1/2} = \left[\frac{\text{Im}\{R_c\}v_R(R_{AC})}{\Delta E_{2,1}(R_{AC})}\right]^{1/2} \tag{9}$$

This range becomes infinitesimally narrow in the limit $v_R \to 0$, i.e. the transitions become perfectly localized in the adiabatic limit.

When considering nonadiabatic transitions in the adiabatic limit, it is often assumed that the Landau-Zener like avoided crossing of adiabatic terms (or crossings of the diabatic ones) is the only mechanism that produces the transitions. In fact, LZ avoided crossings can be associated to the hidden crossings of very small imaginary part, and are a consequence of accidental resonances of the states in the two atomic potential wells, separated by a moving barrier, below the top of the barrier, Fig. 1a). The mechanism of LZ transitions is tunneling through the barrier between the quasi-resonant states. On the other hand, hidden crossings are associated with the top of the potential barrier. While the system evolves from the separated

atom limit, the electron is localized at one well, on a given side of the barrier, Fig. 1b). Thus, the electron wave function is atomic in character. The top of barrier decreases as the particles approach and at some R it is low enough for the electron in a particular state to move over the top of the barrier. From that moment on the electron is shared between the two wells, and the electron wave function becomes molecular in character. For those R values where the electron wave function suddenly changes the character, its derivative (with respect to R) maximizes, and the radial nonadiabatic matrix elements have peaks. These peaks are signatures of poles of $U_{2,1}(R)$ for complex R, as well as of branch points of the adiabatic eigenfunctions and eigenenergies. Because the wave function adapts to the change of a particular state of the electron, the hidden crossings appear in series, localized at almost the same values of R [3]. Since, during the course of collision, one state after another changes the character, the hidden crossings associated with a particular potential barrier appear in superseries.

On the real adiabatic term diagram, the hidden crossings are not necessarily seen as avoided crossings, and localization of the transitions around $Re\{R_c\}$ is due to maxima in nonadiabatic coupling matrix elements.

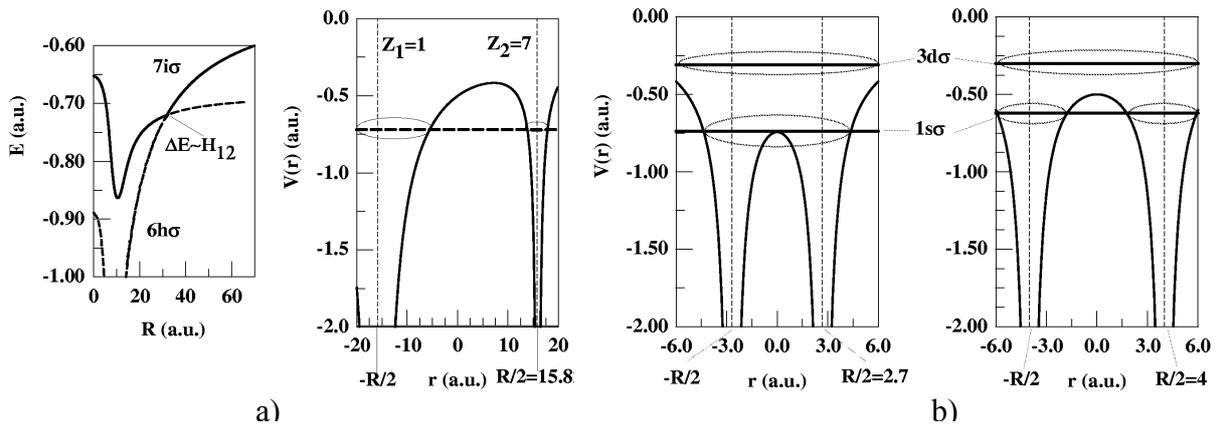

Figure 1 a) LZ transition mechanism on an example of charge transfer in N^{7+} +H collisions, $Z_{1,2}$ are the nuclear charges, E is the adiabatic energy for a two accidentally degenerate states, V(r) is radial potential of the electron, with coordinate r, in the field of nuclei. b) HC transition mechanism on an example of excitation in H^++H transitions; V(r) has the same meaning as in a).

The main motivation for using an adiabatic basis in the MOCC expansion (8) is the assumption that a small number of adjacent basis states is needed to describe the nearly adiabatic problem. Still, especially with a small basis, MOCC method has deficiencies that are difficult to handle. The most important of these deficiencies are appearances of nonzero couplings $U_{n,k}(R)$ when $R \rightarrow \infty$ and the dependence of $U_{n,k}(R)$ on the choice of electronic origin. This can be improved by the so called electron translation factors (ETF), which

artificially add velocity dependent terms to the Hamiltonian. Still, the choice of the ETF factors is not unique for a given problem and solutions of the MOCC equations may vary, depending on this choice. Another possibility is to use the HC nonadiabatic matrix elements, Eq. (7). These do not have any of the deficiencies of a regular MOCC, but are strictly valid only in the adiabatic limit, where localization of the transitions justifies the linearization used for their derivation. This approach is called MOCC HC [4,5].

A new mechanism has been found recently [4] that might dominate the transitions in the adiabatic limit, over the hidden crossings and Landau-Zener transitions. This is associated to the abrupt change of the wave function at the turning point, which is dominant for small impact parameters, b. This can be seen from the MOCC equations, Eq. (8), where the couplings are proportional with the radial velocity, v_R, which has additional branch points, not present in the adiabatic energy. For example, in the simplest case of a straight line trajectory, $R = \sqrt{v^2 t^2 + b^2}$, the radial velocity $v_R = v^2 t / R$ has branch points along the imaginary axis, at $t = \pm i b / v$. If these branch points are also taken into account in the two-state modeling of nearly-adiabatic transitions, the total S matrix for transition in the two-state case is $S_{2,1} = S_{2,1}^{HC} + S_{2,1}^{TP}$, i.e. a coherent sum of the HC contributions and the turning point (TP) contributions, where

$$S_{2,1}^{TP} = -2ibU_{2,1}(R=0)K_1\left(\frac{b\Delta E_{2,1}(R=0)}{v}\right) \tag{10}$$

and K_1 is the modified Bessel function of the second kind [4]. Having in mind the asymptotic form of this function for large and small values of the argument, we get that the TP contribution define the transitions inside a radius b defined by

$$\lambda = \frac{b\Delta E_{2,1}(R=0)}{v} \leq 1 \tag{11}$$

The transition probability is proportional to v^2 for small λ, and to $\exp(-\lambda)$ for large λ, i.e. it is very sensitive to the value of the impact parameter b. The leading term of the TP contribution in an expansion of the cross section in powers of v is
The polynomial rather than exponential decrease of the cross section in the adiabatic limit, proportional to v^4, is a remarkable result because TP contributions dominate over the

$$\sigma_{2,1}^{TP} = 2\pi \int_0^\infty bP(b) = \frac{64}{3}\pi \left|\frac{U_{2,1}(0)}{\Delta E_{2,1}(0)}\right|^2 \left(\frac{\frac{1}{2}v^2}{\Delta E_{2,1}(0)}\right)^2 \tag{12}$$

exponentially decreasing hidden crossings and LZ transitions in the adiabatic limit. This conclusion is valid as long as $U_{2,1}(R = 0) \neq 0$. Since this is not a case for nuclear symmetric collision systems, the next term (proportional to the second derivative of $U_{2,1}(R=0)$) gives a contribution to the cross section proportional to v^8. Although these conclusions are strictly valid only for a straight line trajectory approximation, the polynomial decrease of the cross section stays valid for more sophisticated trajectories [4], changing only the leading power of v. The two-state system and the straight-line trajectory have served here only as simple illustrations. The obtained conclusions are valid for all Hamiltonians that are meromorphic functions of R. A general method that takes into account all TP, HC and LZ transitions, can be devised based on the MOCC equations (in both the time-dependent and the time-independent approach) with the modified noadiabatic coupling matrix elements, written in the form

$$U_{i,j}^{HC+TP}(R) = U_{i,j}^{HC}(R) + [U_{i,j}(0) - U_{i,j}^{HC}(0)]\exp\left[-\frac{\Delta E_{i,j}(0)}{v}R\right] \quad (13)$$

where $U_{i,j}^{HC}(R)$ are in the Lorentzian form, Eq. (7), for a two adiabatic states i,j coupled with a hidden crossing, and $U_{i,j}(0)$ is the exact value of the nonadiabatic coupling at R=0, obtained numerically. This method (MOCC HC+TP) yields excellent results in all test cases, in comparison with "exact" results (i.e. with a direct solution of Schrödinger equation on numerical lattice, LTDSE) and experiments, as is shown in the next section.

2. TESTS AND DATA

As a convenient test of the adiabatic theory in the previous Section we take a 1D case of two colliding harmonic oscillators, defined by the potential [6]

$$H_{el}(R) = \frac{p^2}{2} + \frac{1}{2}\left(|x| - R/2\right)^2 \quad (14)$$

where $R = \sqrt{v^2 t^2 + b^2}$ is modeled with a nonzero impact parameter to make a closer analogy with the 3D case. As can be seen in Fig. 2, this case contains a moving potential barrier, with a change of he character of the wave function across it. Thus, one can expect a hidden crossings series [4] close to the barrier (Fig. 2b), divided in two groups, due to the parity symmetry of the system.

In Fig. 3a) we present a comparison of the transition probability for a small value of the velocity, v=0.2 a.u., as a function of the impact parameter. At small impact parameters the TP
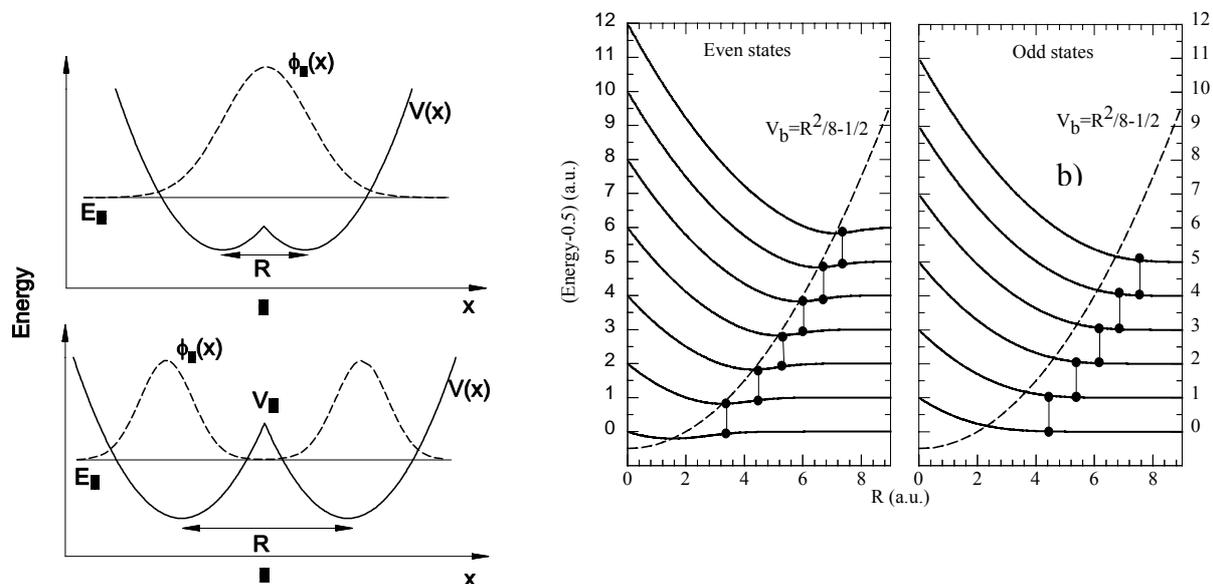

Fig. 2 a) Potential and the ground state electronic wave function of the double harmonic oscillator at small (upper figure) and large (lower figure) internuclear distance and, b) Hidden crossings between even (left) and odd (right) states. The dashed line is the top of the potential barrier [4].
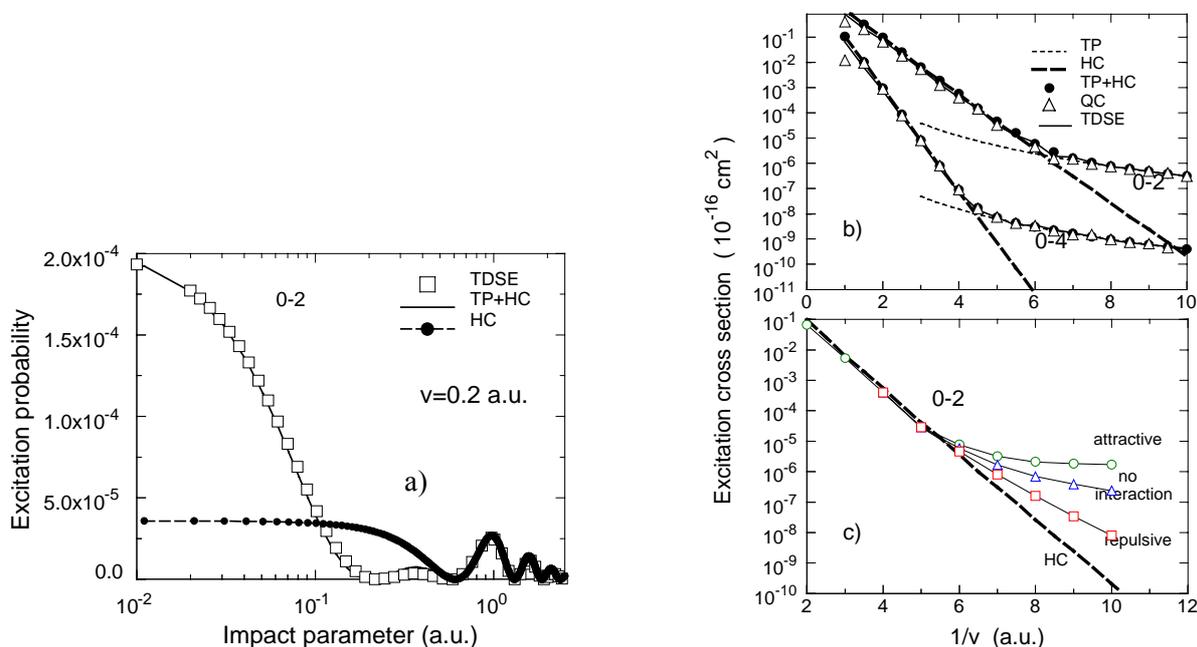

Fig. 3 a) Excitation probability from the n=0 to n=2 state as a function of impact parameter for v=0.2 a.u.; b) Cross sections for 0-2 and 0-4 excitations as functions of 1/v; c) Cross section for 0-2 excitation for various internuclear potentials [4]; dashed line is the HC theory.

contribution is by far larger than the HC one. Still, if TP and HC contributions are both taken into account, the total transition probability agrees with the exact result [4]. Similar conclusions are applicable for the cross sections, as shown in Fig. 3b). We note that the TP contribution is significant only when small impact parameters play an important role. This is the case with straight-line trajectories, as well as with attractive potentials between the nuclei. For a repulsive potential, TP effects are suppressed, Fig. 3c), still having polynomial rather the HC-exponential character.

It is interesting to note that the ORNL merged beam experiment [7] on charge transfer in collisions of C^+ and H shows the v^4 dependence at low energies rather than exponential, in support of the predicted TP effect [Fig. 4].
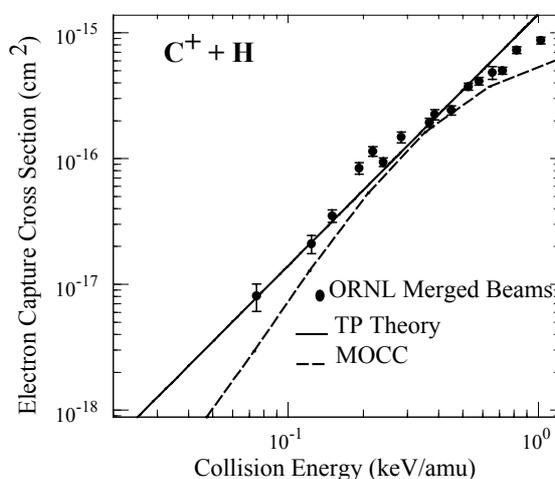

Fig.4 Charge transfer for C^+ +H collision: Solid line is proportional to v^4 .(the TP effect).

Another interesting comparison is charge transfer in collisions of Cl^{7+} with H. Since Cl^{7+} is a closed shell ion, the calculation on the charge transfer from a bare ion, N^{7+} on H, was done here, using the MOCC HC approach (the TP effects are not expected to be significant because of the high nuclear repulsion at small R's). The agreement between experiment and a calculation based on four HC's, in Fig. 5b), is excellent [5]

A significant novel development in the adiabatic theory is for inelastic processes with more-than-one active electrons. The main difficulty with these systems is that they are not separable, which is a big challenge for computational quantum chemistry (CQC) in solving the adiabatic eigenvalue problem for complex R. For example, typical CQC approaches are the Hartree-Fock (HF) and Configuration Interaction (CI) methods, based on the variational principle and a Gaussian basis expansion. When the Hamiltonian of such problems is extended into the complex plane, the problem becomes nonhermitian (symmetric), while the

Gaussian basis expansion is convergent only in the lower quarter of the first quadrant of the complex R-plane. The variational principle is replaced by the so-called bi-variational principle, which is applied separately to the real and imaginary parts of the eigenenergy. The basis convergence is improved by using the R-dependent coefficients in exponents of the Gaussian primitives [8].

Fig. 6a) shows real triplet terms of H+H system, with the approximate position of a localized S-type series (arrow) of hidden crossings [3] that governs the single electron ionization of the system [8]. The first three Riemman sheets of the unique, multi-valued,
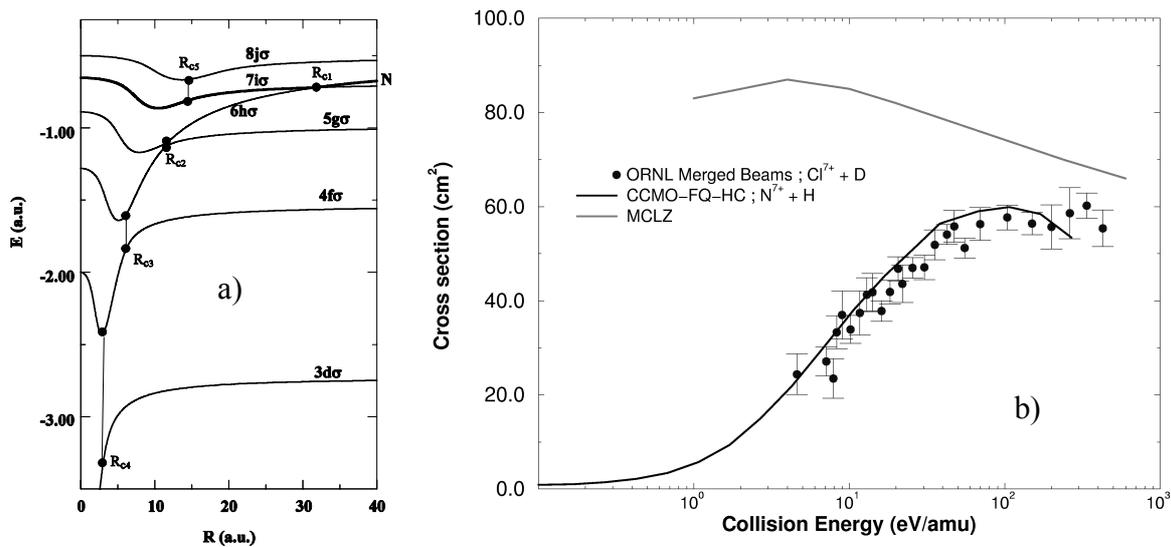

Fig. 5 a) Adiabatic term diagram for N^{7+} +H; The hidden crossings used in calculation are shown by symbols; b) Cross section for charge transfer in N^{7+} +H collision, obtained by CCHC (solid line), compared with the experiment (symbols), and multilevel LZ calculation (dashed line) [5].

multiple-connected eigenenergy surface of the H+H, and the most direct path for single-electron ionization is shown in Fig. 6b). Finally, the cross section for the single-electron ionization of H in slow collisions with H atom, obtained by multielectron hidden crossings theory (MEHC) is shown in Fig. 7 and compared with existing experimental data.

Similar agreement was obtained for ionization of He by proton impact [12], and ionization of ions by antiproton impact [13]. Oscillations in excitation cross sections for low-to-medium collision energies were also explained by the HC nearly-adiabatic methods [14]. The application of the discussed adiabatic theories goes far beyond ion-atom collisions. An important group of systems are ion-molecule collisions, in particular collisions of protons with H_2 molecules [15], where series of hidden crossings were found between vibronic adiabatic states.
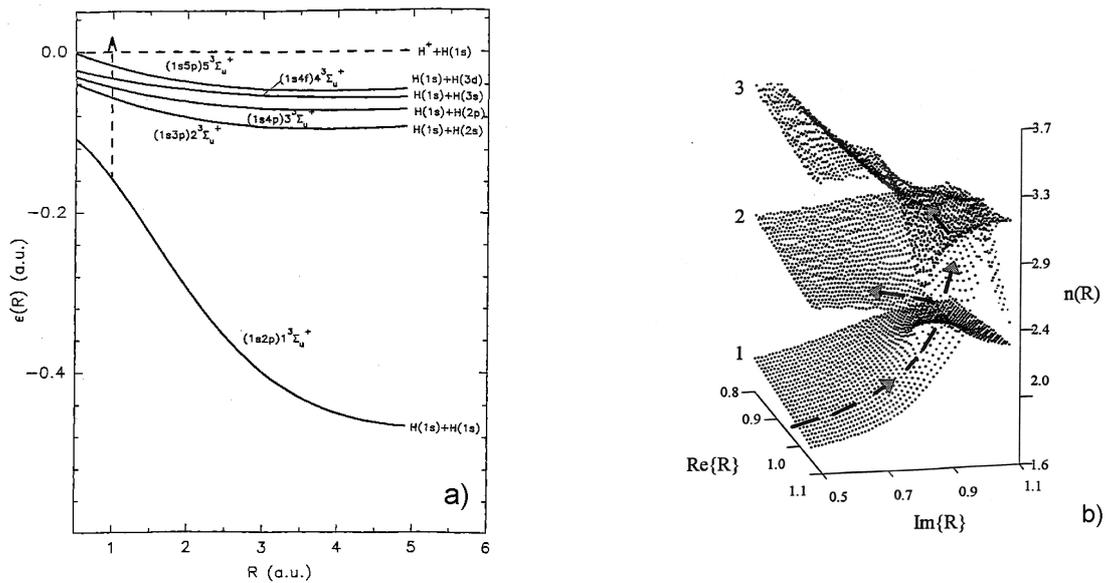
Fig. 6 a) Adiabatic term diagram for the H+H collision system; Dashed arrow shows position of the S-promotion series through the single-excited triplet states; b) Complex adiabatic energy surface of the triplet adiabatic states of the H+H system; arrow shows the direction for ionization in the complex plane, $n(R) = 1/\sqrt{2\,|\,E(R)\,|}$
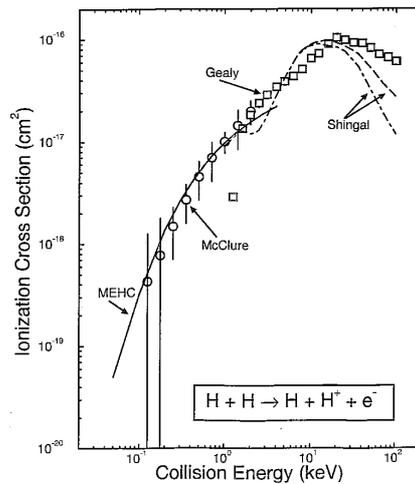

Fig. 7 Cross section for single-electron ionization in H+H collision, obtained by MEHC (solid line) [8], experiments (symbols) of McClure [9], Gealy [10] and Shingal [11]..

3. ATOMIC DEVICES: A LOOK AT THE FUTURE

The fast emerging, multidisciplinary field of nanotechnologies leads to mesoscopic devices like molecular electronic switches, whose functionality can be fully described quantum-mechanically. Nearly adiabatic atomic physics may play a prominent role in these

simulations. Nonlinear transport and tunneling in an electrically biased, open quantum system is a nearly adiabatic, electron correlated, scattering process modified by an external field. Molecular dynamics simulations of a spontaneous molecular monolayer formation on a metal substrate is strongly dependent on adiabatic intermolecular potentials.

Quantum transport (of electrons) in molecules has become one of the "hot" multidisciplinary areas of study due to a possibility of design of controllable, "few electron" molecular scale devices, with a potential for developing new concepts in electronics (replacement of the flip-flop circuitry by a single-molecule switch). A critical step is a possibility of self-assembly of the molecular electronic elements into mono- (SAM) and poly- (SAP) layers. Such a possibility, together with nanometer dimensions of a few-electron molecular switch device promises a fulfillment of a dream of continuation and even acceleration of the Moore's law (of approximately doubling the computer power each two years). One can anticipate a factor of about 1000 in increase of packing density and the switch quality (on-to-off ratio), accompanied with a decrease in power dissipation.

What is the role of atomic physics in the molecular electronics development? Since, in addition to the molecule, there are metal leads which connect the molecule to the rest of an electronic circuit, and at least closest layers of the leads strongly influence the levels of the molecule, a computational chemistry calculation of the adiabatic electronic structure of a large organic molecule + metal combination is a first step. On the other hand, conduction of an electron through the molecule is an electron-molecule scattering process, and in spite of different boundary conditions applied to a scattering state of the metal electron (Bloch states), many methods and experiences of the atomic scattering theory can be applied successfully.

The ultimate goal is to understand and control a molecular device in detail. What is the current status in this field? Critical knowledge is absent. So far, only proof of principle exists for the self-assembly of mono-layers. It is also clear that there is a strong relation of the device functionality to the details of the molecule-lead junction as well as details of the chemistry of the molecule. A response of the device to the temperature, electric bias (steady and time-dependent), and chemical dynamics are far from a complete description. Finally, the control of various electronics functions (transistor, diode, resistor) with molecular devices has not been established yet. On the other hand, experiments are very expensive and exclusive, which increases the importance of the theoretical approach, with simulations that incorporate quantum mechanics, not only to explain but to predict and design future molecular devices.
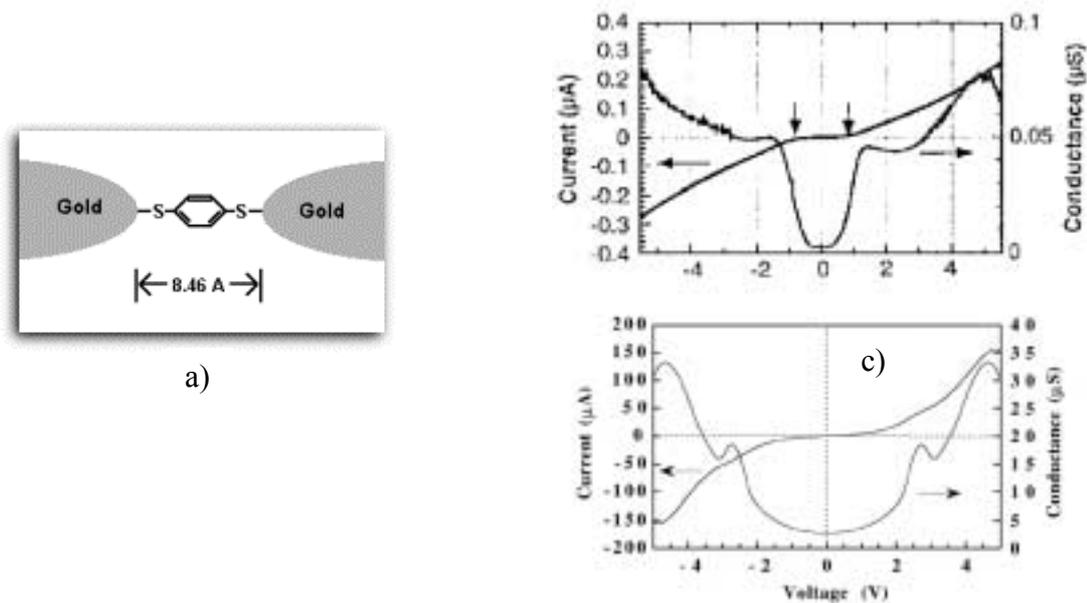
Fig. 8 a) The setup for the pioneering measurement [16] of conductance of the BDT molecule; b) Conductance and IU characteristics of the BDT molecule obtained experimentally [16] and c) theoretically [17].

A benzene 1,4 dithiolate (BDT) molecule with gold leads is used in recent experiments of M Reed [16], Fig. 8a). The thiol (sulphur) groups, attached at two ends of benzene, provide a strong covalent connection of the molecule and the gold leads. The pi-conjugated, nonlocalized electronic orbitals around the benzene ring enables the molecular conduction. The conductance through the whole system is dominated by tunneling of an electron through the potential barrier between the Fermi level in the metal and molecular states of BDT. The theoretical, nonlinear UI-characteristic of the system [16], Fig. 8c), although qualitatively looks similar to the experimental data, Fig. 8b), differs in absolute values up to the three orders of magnitude. It is not clear yet what is the cause of this disagreement. Is it the unknown detailed structure and geometry of the metal surface-molecule interface? Is it the use of inadequate correlation functionals in Density-Functional Theory (DFT)? Is it the role of neighboring molecular strands, or probably the effects of nonlinearity caused by external electric bias and temperature?

A molecular switch was realized in the laboratory with a BDT molecule [16], by attaching NH_2 and NO_2 groups on the BDT ring. Changes in the external field create a twisting effect (rearrangement of the electronic orbitals) that induces a switching function. The memory element is realized by removing the NH_2 group from the switch. A charge stored on the NO_2 group acts as a sink for a conducting electron, which creates a "binary 0" state (no conduction). With no charge on the nitro group, conduction is reinstated ("binary 1"). It is interesting that the spontaneous lifetime of the molecular binary state is of the order of 10 minutes, which is about 10^5 times longer than that of a conventional silicon device.

The first step and important part of the theoretical simulation of a molecular device is the computational chemistry (ab initio) calculation of the system structure. This provides the basic quantum-mechanical information which is further used for electron transport calculations and SAM formations. Density-functional theory, with a Gaussian or plane wave basis, is the only practical "method of choice", that is efficient enough to treat very large molecules with currently existing computer power. Still, DFT is inherently inaccurate. This is caused by an ad hoc choice of exchange and correlation functionals. Implementation of these functionals in the DFT Hamiltonian reduces the problem to calculation of the single-electron orbitals, which is the main reason for effectiveness of the method. But, although the functionals are known with some certainty for various types of organic molecules, and for different types of metals, none of these might be applicable for the organic molecule-metal combinations, as is the case with molecular electronic devices. Therefore, a theory that incorporates many-body effects, and would go beyond DFT is highly needed.

Even with the DFT approach, structure calculations of the mesoscopic system are numerically demanding. As illustration, Fig. 10 shows an example of a geometry optimization calculation for a set of three BDT's, connected to the top and bottom gold leads (in (100) geometry). This system contains 70 atoms and 590 active electrons and requires 47 hours on 320 processors IBM SP3 parallel computer, i.e. 14,930 processor-hours for calculation of its electronic structure.
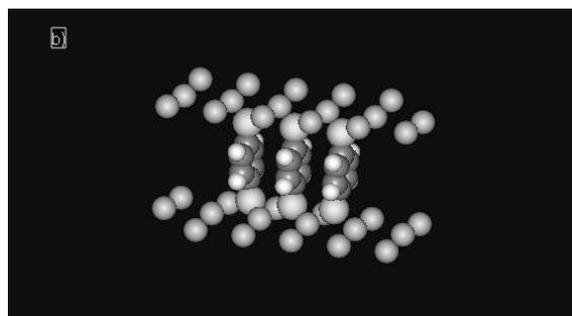

Fig. 10 A computer simulation of self-assembled monolayer of BDT molecules between two gold substrates
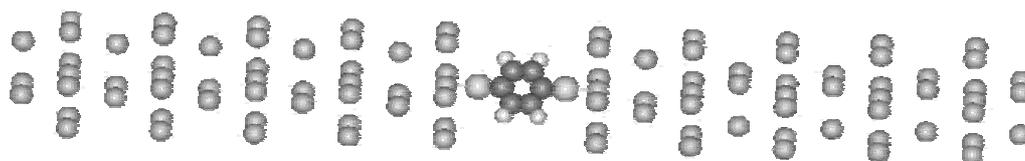

Fig. 11 A typical geometry of the BDT molecule with gold (111) nanowire leads.

Since molecular structure calculations describe closed quantum systems, there is a need for a theoretical approach that would extend them to treat the open quantum system (scattering) boundary conditions. One possibility is to apply the generalized tight binding model, requiring that only adjacent layers are coupled [18]. Once the electronic structure is available, the transmission function (the T-matrix for the scattering on the molecule) is found using the Green's function technique. This enables propagation of the electron from the "infinite" electron reservoir on one end of the periodic lattice (left lead, Fig. 11), through the molecule, to the right periodic lattice (lead) and "infinite" reservoir on its right end. The constant potential difference is set between the reservoirs.

As an illustration, Fig. 12a) shows the transmission function of the BDT molecule, for the device in Fig. 11. The selectivity of the transmission is a consequence of pairing of the molecular states of the BDT (deformed by the leads) with those in the leads. The transmission
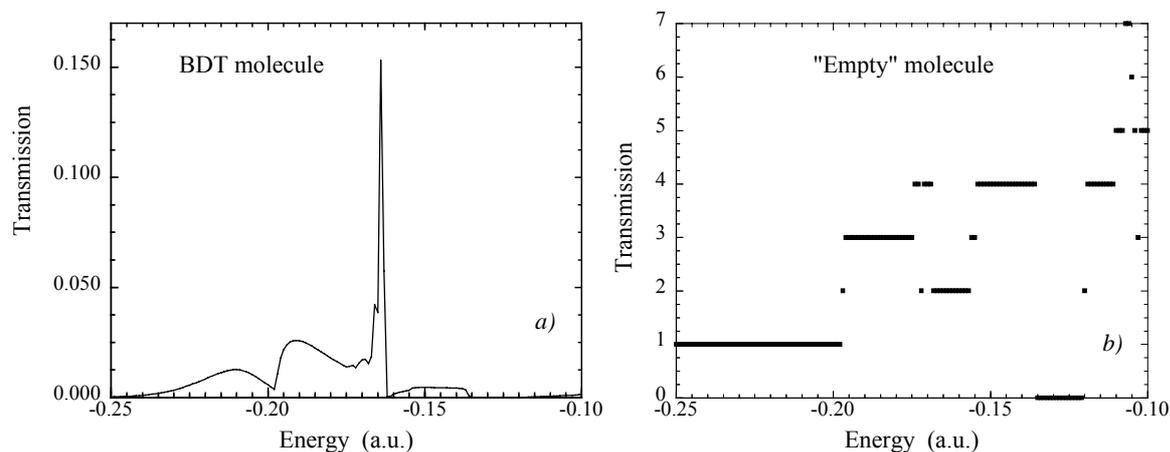

Fig. 12 a) Transmission through the BDT molecule; b) Transmission through the infinite gold nanowire, Krstic et al, [18].

function of the infinite nanowire obtained from the system in Fig. 11 by replacing BDT molecule by a gold layer, is shown in Fig. 12b). This is always an integer, equal to the number of energy bands of the wire.

ACKNOWLEDGEMENTS

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