DYNAMICAL ADIABATIC POTENTIAL ENERGY CURVES OF HeH^{2+} SYSTEM: CROSSINGS IN COMPLEX PLANE OF INTERNUCLEAR SEPARATIONS

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Abstract. Inelastic transitions in slow ion-atom(ion) collisions He^{2+}+H or He^{+}+H^{+} are determined by properties of the quasi-molecule HeH^{2+}. Assuming straight-line trajectories of the heavy particles one can define dynamical adiabatic potential energy curves (DAPEC) which depend on internuclear separation R and an additional parameter $\omega = \rho v$ - product of the impact parameter and relative collision velocity. We study the analytic continuations of DAPEC into the complex R-plane. Probabilities of the non-adiabatic transitions are determined by the positions of the branch points connecting various DAPEC surfaces. We investigate how the positions of various branch points change with the variation of the parameter ω.

1. INTRODUCTION

The crossings of electronic adiabatic eigenvalues (potential energy curves (PEC))in the complex plane of internuclear separations R, play the key role in the standard (separable) one-electron two-Coulomb-center problem (see review paper [1]). They can be verified only by direct numerical calculation in the complex R-plane as branch points R_b connecting two PEC $\varepsilon_i(R)$ and $\varepsilon_f(R)$ of the same symmetry - $\Delta\varepsilon_{if}(R) \sim \sqrt{R - R_b}$. If the distance from the real R-axis to the branch point R_b is proportional to $\hbar$ it is named *hidden crossing*, whereas if it is exponentially small with respect to the inverse of Planck constant $\hbar$ it is named *avoided crossing.* In fact, $\varepsilon_i(R)$ and $\varepsilon_f(R)$ are different branches of a single (multivalued) analytic function $\varepsilon(R)$. If we adopt the impact-parameter method for description of a collision problem, that is assume that nuclei follow classical trajectories defined by the given function $R = R(t, \rho, v)$ of time t, impact parameter ρ, and asymptotic relative collision velocity v, then the "single pass" electron transition probability via crossing is determined by expression

$$p_{if}(\rho, v) = \exp\Big(-\frac{2}{\hbar}\Big|\mathrm{Im}\int_L \varepsilon(R)\frac{dR}{v_R(R, \rho, v)}\Big|\Big), \tag{1}$$

where $v_R(R, \rho, v) = dR/dt$ is the radial collision velocity. The contour L in complex R-plane starts at any real R_1 where $\varepsilon(R_1) = \varepsilon_i(R_1)$ goes around complex branch point R_b and ends up back on any real R_2 where $\varepsilon(R_2) = \varepsilon_f(R_2)$.

The transitions caused by the rotation of the internuclear axis which are known to be localized in the regions of degeneracies (exact crossings) of PEC corresponding to states with different symmetries, in the standard adiabatic approach can be taken into account only by numerical close-coupling calculations.

2. DYNAMICAL ADIABATIC THEORY

We consider a collision system consisting of a single electron and two bare nuclei of charges Z_A and Z_B travelling along the straight-line trajectories in the (x, y)-scattering plane, so that $\mathbf{R}(t) = \mathbf{R}_B(t) - \mathbf{R}_A(t) = vt\hat{\mathbf{x}} + \rho\hat{\mathbf{y}}$. We next modify the electronic time-dependent Schrödinger equation (for details see Ref.[2]): the electronic coordinates (x, y, z) are divided by the internuclear separation $R(t)$ and subsequently transformed to the rotating (molecular) coordinate system (q_1, q_2, q_3) with the q_1 axis directed along the internuclear axis. Finally, one arrives at the eigenvalue problem for DAPEC:

$$H(R, \omega)\Phi_j(\mathbf{q}, R, \omega) = E_j(R, \omega)\Phi_j(\mathbf{q}, R, \omega), \tag{2}$$

with (we use atomic units throughout)

$$H(R, \omega) = -\frac{1}{2}\Delta_q - R\left(\frac{Z_A}{|\mathbf{q} + \alpha\hat{\mathbf{q}}_1|} + \frac{Z_B}{|\mathbf{q} - \beta\hat{\mathbf{q}}_1|}\right) + \omega L_3 + \frac{1}{2}\omega^2 q^2 \tag{3}$$

where $\hat{\mathbf{q}_1}$ is the unit vector along q_1 axis, α and β $(\alpha + \beta = 1)$ define the position of the coordinate origin on the internuclear axes and L_3 is the operator of the projection of the electronic angular momentum onto the direction perpendicular to the scattering plane. The parity $\Pi_3(q_3 \to -q_3)$ is the only conserved symmetry.

The general properties of DAPEC $E_j(R, \omega)$ for the complete range of real internuclear separations $R \in (0, +\infty)$ have been studied in our recent work [2]. An example for $\omega = 1$ in the case of HeH^{2+} system is show in Fig.1. Note, that any DAPEC $E_j(R, \omega)$ is related to the usual PEC $\varepsilon_j(R)$ of the two-Coulomb center problem by relation $E_j(R, 0) = \varepsilon_j(R)R^2$.

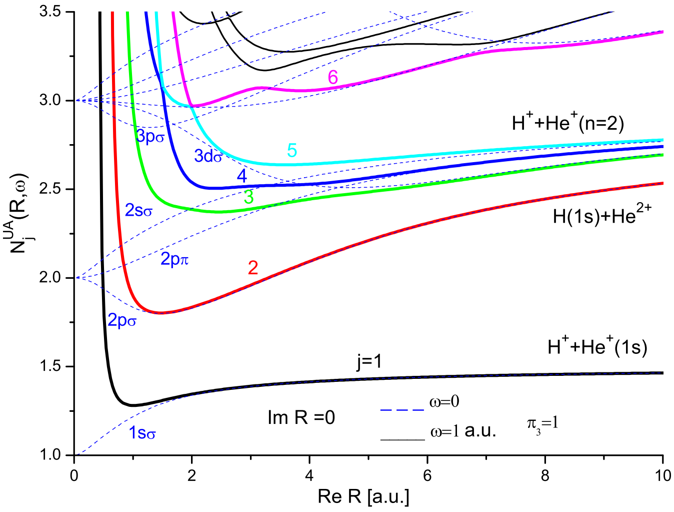

Figure 1. Solid lines are low-lying scaled DAPEC represented in terms of "effective united atom principal quantum number" $N_j^{UA}(R,\omega) = (Z_A + Z_B)[-2E_j(R,\omega)/R^2]^{-1/2}$. Dashed lines correspond to standard PEC of the $(\mathrm{HeH})^{2+}$ molecular ion labeled by united-atom quantum numbers

3. RESULTS

Here, we are interested in analytic continuations of DAPEC into the complex R-plane, i.e. the solutions of the eigenvalue problem Eq.(2) for complex values of R. The numerical method used is the same as described in our previous work [2] for real values of R. The solutions enable us to detect the various branch points $R_b(i, f; \omega)$ connecting the pairs of complex DAPEC $E_i(R, \omega)$ and $E_f(R, \omega)$. The single-pass electron transition probabilities will be given by Eq.(1) with substitution: $\varepsilon(R) \to E(R, \omega)/R^2$.

In dynamical adiabatical representation the rotational transitions are transformed into radial transitions through the operator L_3 in Eq.(3), generating the so cold $L_3 - crossings$. Two examples of the L_3 -crossings are shown in Fig.2. At $\omega \to 0$ they correspond to $2p\sigma - 2p\pi$ or $(i, f) = (2, 3)$ and $2s\sigma - 2p\pi$ or $(i, f) = (3, 4)$ rotational coupling in the united-atom limit. However, as ω increases, one can notice the transformations: $R_b(2, 3; 0.3) \to R_b(2, 4; 0.5)$ and $R_b(2, 4; 0.75) \to R_b(2, 5; 0.8)$. This kind of transformations are caused by the relative motion of other branch points in the complex R-plane. For example, the first of these transformations occurs due to the change of position of the branch points in the other shown L_3-trajectory, namely due to the fact that Re $R_b(3, 4; 0.3) <$ Re $R_b(2, 3; 0.3)$

and Re $R_b(3,4;0.5) >$ Re $R_b(2,4;0.5)$. Also sown in Fig.2 as full squares in the limited region are hidden crossings labeled as $\omega = 0-1(1-2),(1-5)$ which at $\omega \rightarrow 0$ correspond to 1sσ 2pσ (i.e. (j=1 - j'=2)-radial coupling between the ground and the first excited state. As detailed calculations show they undergo the transition $R_b(1,2;0.75) \rightarrow R_b(1,5;0.8)$ which can be explained by the positions of the branch points from the L_3 - trajectory just below them: $R_b(2,4;0.75) <$ Re $R_b(1,2;0.75)$ and Re $R_b(2,5;0.8) >$ Re $R_b(1,5;0.8)$. Additional types of branch pints and their transformations will be discussed at the conference.

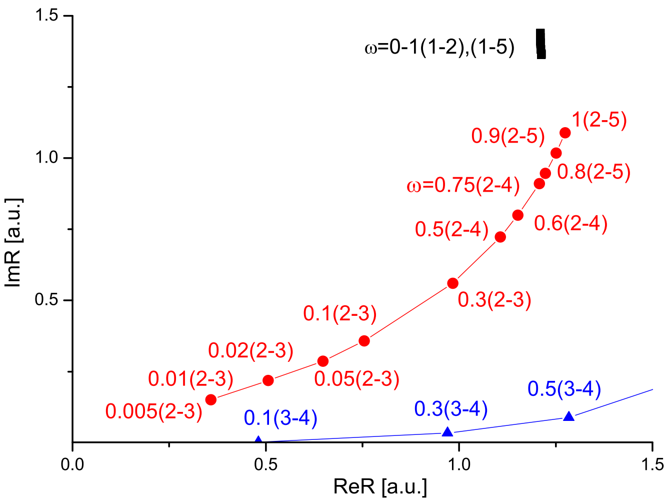

Figure 2. Each branch point $R_b(i,f;\omega)$ is labeled as $\omega(i-f)$. Full circles are L_3-crossings which undergo transformations $R_b(2,3;0.3) \rightarrow R_b(2,4;0.5)$ and $R_b(2,4;0.75) \rightarrow R_b(2,5;0.8)$. Full triangles are part of the L_3-crossings trajectory $R_b(3,4;\omega)$. Full squares labeled $\omega = 0-1(1-2),(1-5)$ are the hidden crossings.

Acknowlendgements

This work was partly supported by Serbia-JINR collaboration program and by the Ministry of Education, Science and Technological Development of the Republic of Serbia through the project No. 171020.

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