Dissociative recombination of $\text{H}_2^+$ with slow electrons for a rigorous examination of theory

H Takagi$^1$, S Hara$^2$ and H Sato$^3$

$^1$ Center for Natural Science, Kitasato University, 1-15-1 Kitasato, Sagamihara, Kanagawa, 228-8555 Japan
$^2$ Tsukuba University of Technology, 4-12-7 Kasuga, Tsukuba-shi, Ibaraki, 305-8521, Japan
$^3$ Faculty of Science, Ochanomizu University, 2-1-1 Ootuka, Bunkyou, Tokyo, 112-8610, Japan

E-mail: $^1$takagi@kitasato-u.ac.jp

Abstract. The Lippmann-Schwinger (LS) equation for the K matrix is numerically solved for the collision of $\text{H}_2^+$ + e interacting by the configuration interaction (CI), of which magnitude is carefully deduced from ab-initio calculation of electron scattering. The LS equation is extended to the negative collision energies in the context of multichannel quantum defect theory (MQDT) for the dissociative recombination (DR). Using the MQDT method for the DR, the DR cross section of $\text{H}_2^+$ is obtained. It has turned out that the DR at low energy is induced by the indirect process with rotational excitation and the off-the-energy-shell contribution is indispensable for the accurate description. The present calculation represents the recent state specific experiment [1], and has assured the effectiveness of the MQDT method for DR.

1. Introduction

The major mechanism of dissociative recombination (DR) of $\text{H}_2^+$ is considered as the incident electrons are captured into the two-electron excited resonance state of which potential curve is dissociative[2]. This mechanism, known as the ‘direct process’, is induced by the configuration interaction (CI) between the one- and two-electron excited states. Another mechanism named the ‘indirect process’ is the DR, where the incident electron is temporarily recombined into the rotationally and/or vibrationally excited Rydberg states[3]. These recombed Rydberg states finally dissociate into the two-electron excited state. The non-adiabatic interaction (NAI) is thought to be the main mechanism of the indirect process. The NAI in the Rydberg and electronic continuum states is known to be well represented by the multichannel quantum defect theory (MQDT)[4]. So called ‘two-step’ method[5] enabled to take account both those interactions uniformly. In the first step of this method, a scattering problem of electrons by the CI needs to be solved accurately. Next, the problem of NAI is solved by the MQDT using the electronic state obtained by the first step.

In this paper, we carefully investigate the CI strength at all over the energy. Using the resultant CI strength, we calculate the DR cross section in the framework of ‘two-step method’ as accurate as possible. On the recent experimental study, the DR cross section specified the vibrational and rotational quantum number of the initial state has been measured[1] for $\text{H}_2^+$. By comparing the calculation with the experiment, we aim at a rigorous examination of the DR theory besides theoretical analysis of the experiment. The reliable theory can make clear the mechanism of the DR at the low collision energies.
2. electron-molecule scattering by configuration interaction

A brief report of this section is seen in the progress report by one of the authors (HT)\[6, 7\]. We here show a minimum required formulation for the calculation.

We adopt the Born-Oppenheimer expansion in order to represent a system interacting by the CI. The CI considered now is the interaction between a two-electron excited state labeled by suffix $d$ and one-electron excited one, which is specified by the energy of excited electron $\epsilon$. Putting the radial coordinate of electron $r$, we present the wave functions of those states by $\phi_{d}(r)$ and $\phi_{\epsilon}(r)$. The radial nuclear wave functions associated with those electronic functions are respectively represented by $F_{\epsilon}^{J}(R)$ and $\chi_{N}^{J}(R)$, where $R$ is internuclear distance. The former is the dissociative wave function of the dissociating energy $\epsilon$ and the total angular momentum $J$. The latter is the wave function of vibrational state $v$ with rotational state $N$. The strength of the CI is represented by the following matrix elements of electronic Hamiltonian of fixed nuclei at $R$: $H_{ele}^{d\epsilon}(r; R)$. 

$$V_{\nu, e, d}^{N, J} = \langle \chi_{\nu}^{N}(R) | V_{e, d}(R) | F_{\epsilon}^{J}(R) \rangle_R, \quad (1)$$

where

$$V_{e, d}(R) = \langle \phi_{\epsilon}(r; R) | H_{ele}^{d\epsilon}(r; R) | \phi_{d}(r; R) \rangle_r. \quad (2)$$

Since the molecular orientation is fixed during the electron collision for the inner region of the MQDT, we assume the rotational transition is frozen for the CI: $N = J$. The rotational transition is taken into account at the second step of the two-step method separated from the first step. Thus, we omit the fixed parameter $N$ and $J$ in this section. The total energy is sum of the energies of electronic and nuclear motion; $E^{T} = E_{\nu} + \epsilon = E_{d}(R = \infty) + \epsilon$. When we write the total energy as $E^{T}_{\nu}$ for the channel $\nu$, and $E^{T}_{e}$ for the channel $d$, the CI strength is represented by

$$V_{\nu, e, d} = V_{e, d}(E^{T}_{\nu}, E^{T}_{e}), \quad (3)$$

which is the off-the-energy-shell element for $E^{T}_{\nu} \neq E^{T}_{e}$.

We use Greek character, for example $\alpha$, for identifying the channel and $E_{\alpha}$ for the total energy of the channel $\alpha$: $\{\alpha\} = \{v\} \oplus \{d\}$. $\{E_{\alpha}\} = \{E^{T}_{\nu}\} \oplus \{E^{T}_{e}\}$. The energy resolved Lipmann-Schwinger (LS) equation for the K matrix becomes

$$K_{\beta\alpha}(E_{\beta}, E_{\alpha}) = -\pi V_{\beta, \alpha}(E_{\beta}, E_{\alpha}) + \sum_{\gamma} \phi_{\nu} \int_{-\infty}^{\infty} dE_{\gamma} \frac{V_{\beta\gamma}(E_{\beta}, E_{\gamma})}{E_{\alpha} - E_{\gamma}} K_{\gamma\alpha}(E_{\gamma}, E_{\alpha}). \quad (4)$$

The above equation is the same form as equation (7.62) given by Newton\[8\] except for the integral region being extended to the negative energy region. In the MQDT formalism, the CI is represented at the inner region, where the boundary condition on the energy is not imposed. As the Coulombic basis functions in the inner region of the MQDT, the scattering channel functions should be free from the control of the asymptotic energy boundary condition. The Rydberg states are treated as open channels for the CI interaction.

We can solve this equation by replacing the principal value integral of $E_{\gamma}$ to appropriate numerical integration. Using the Chebyshev polynomial $T_{n}$ and $n$-th order Chebyshev polynomial of the second kind $U_{n}$, equation (4) is rewritten as

$$\sum_{\gamma} \sum_{i=1}^{M} \left[ m(y_{\beta}, y_{\gamma_{i}}, y_{\alpha}; \beta, \gamma, \alpha) - \delta_{\beta, \gamma} \delta_{E_{\beta}, E_{\gamma}} \right] K_{\gamma\alpha}(E_{\gamma_{i}}, E_{\beta}) = \pi V_{\beta, \alpha}(E_{\beta}, E_{\alpha}). \quad (5)$$

with

$$m(y_{\beta}, y_{\gamma_{i}}, y_{\alpha}; \beta, \gamma, \alpha) = \frac{2\pi}{M} (1 + y_{\alpha}) \sqrt{1 - \frac{y_{\alpha}}{1 + y_{\gamma_{i}}} V_{\beta\gamma}(E_{\beta}, E_{\gamma_{i}})} \sum_{n=1}^{N} T_{n}(y_{\gamma_{i}}) U_{n-1}(y_{\alpha}). \quad (6)$$
In the above equation, we adopted following transformation from the total energy $E$ to $y$.

$$
y = \frac{2C}{E - a + C} - 1,
$$

where $a(\leq 0)$ and $C$ is arbitrary parameter. The parameter $a$ means the lowest energy of the integration and $C$ controls the domain of integration.

3. Electron and H$_2^+$ collisions by the CI

3.1. Adiabatic CI strength

We here take into account only the lowest two-electron excited state $^1\Sigma_g(2p\sigma_u)^2$ as the dissociative states $\phi_d$. The Rayleigh-Ritz variational method is employed to calculate the two-electron excited state $\phi_d$. The ionizing state $\phi_e$ is calculated in the static exchange approximation with the adiabatic polarization potential. Using those wave functions $(\phi_d, \phi_e)$ into equation (2), we obtain the CI strength $V_{e,d}(R)[9, 10]$. The adiabatic resonance width $\Gamma(\epsilon, R)$ is given by

$$
\Gamma(\epsilon, R) = 2\pi |V_{e,d}(R)|^2.
$$

These approximations adopted to the present calculation are appropriate to estimate the dynamical interaction between the resonance and continuum electronic states. The boundary condition of asymptotic region is satisfied by the direct product of two-electron excited states and the dissociative nuclear motion, or the direct product of ionizing continuum states and vibrational nuclear motion. The neglected higher order coupling between the two-electron excited states and ionizing continuum states in fixed nuclei is to be recovered by taking account the CI in the dynamical process.

The crucial important quantity is the strength of interaction $V_{e,d}(R)$ or $\Gamma(\epsilon, R)$ as a function of two variables $\epsilon$ and $R$. The calculation was done for the internuclear distance $R = 1.0 \sim 2.6$ au with the interval of 0.2 au, and the collision energy $\epsilon = \sim 0.001 \sim 5$ au. In the present method, the calculation of adiabatic resonance width $\Gamma$ is confined to positive collision energies but we need it in all energy region including the negative collision energies. This means we must extrapolate the calculated values to the all $R$ and $\epsilon^T$ region. The asymptotic behavior of the $\Gamma$ is important in the extrapolation.

1. $\Gamma = 0$ for $\epsilon < -1/2$.
2. $\Gamma = 0$ for $\epsilon \rightarrow \infty$.
3. $\Gamma = 0$ for $R \rightarrow 0$.
4. $\Gamma = 0$ for $R > R_m$.

where for $R \geq R_m$, the two-electron excited state merges to the Rydberg state: $R_m \sim 4.5$ au[11]. The conditions for the asymptotic behavior (i)~(iv) confine the $\Gamma$ in the full region of $(\epsilon^T, R)$ space, where $\epsilon^T$ is the total electronic energy: $\epsilon$+potential energy of the ion.

We employed the bicubic B-spline interpolation [12] using the calculated $(\epsilon, R)$ points. In the outside of the calculated $R$ region, we need extrapolate the calculated values. The B-spline works well for the extrapolation to $R < 1.0$ au because the strength monotonically decreases as $R$ becomes zero. For the $R$ larger than 2.6 au, the extrapolation using the calculated values diverges. Because the $\Gamma$ forms an isolated island on the sea level as is shown in Fig. 1, we extrapolate the contour lines of some $\Gamma$ values at the boundary of calculated region $(R = 2.6$ au) assuming that the contour shape could be represented by quadratic form of $\epsilon^T$ and $R$. We chose tree contour lines of $\Gamma = 0.005$, 0.03, and 0.07 au.

Adding those values on the contour, we could interpolate and extrapolate the calculated values to the larger $R$ by two dimensional B-spline method. The adiabatic resonance width $\Gamma(\epsilon^T, R)$ on the whole $\epsilon^T$-$R$ space is shown in Fig. 1. The shape of $\Gamma$ is not simple, especially there is bump at the low energies of $1.7 < R < 2.4$ au, of which effect will be investigated on the low energy dissociative recombination.
3.2. Transition probability by the CI
The K matrix elements were calculated by solving equation (5). The values of parameters C and a in equation (5) were adopted to $C = 0.3$ and $a = -0.625\text{au}$ (energy of dissociation limit). The number of energy points $M$ in equation (5) is adopted to $M = 100$ after confirming the obtained $K$ matrix to be converged[7]. twelve vibrational functions ($v = 0 \sim 11$) are employed in the calculation. The energy region of the present interest is the incident electron energy lower than 1 eV for $v = 0 \sim 2$ initial vibrational states, which correspond to the total energies between -0.6 and -0.5 au. The dissociation probability is defined by square absolute value of the $S$ matrix element $|S_{d,v}(E)|^2$, where $S$ matrix element is deduced from the calculated $K$ matrix:

$$S = (1 + iK)(1 - iK)^{-1}.$$

The calculated dissociation probability was compared with the first order calculation in Fig. 2. The higher order effect drastically enhances the dissociation from the initial vibrational state $v = 0$ and reduces that from $v = 2$ around the zero collision energy. As the result, the probabilities from $v^+ = 0$ and $v = 2$ become similar magnitude. The $v = 2$ initial state is energetically more suitable for the dissociation than the $v = 0$ since the energy level of $v = 2$ exceeds to the energy of the potential-curve crossing between the ionic and dissociative states whereas the $v = 0$ energy level does not. The vibrational excitation by the CI compensates for this energetic advantage. The difference between the first order and the higher order calculation is outstanding at the low energies. The off-the-energy-shell contribution has turned out to be crucial for precise description of the dynamics.

4. Dissociative recombination
The calculation of DR cross section by the MQDT was given in the previous studies[13, 14]. We employed the same electronic parameters as the previous calculation[15, 16]: potential curves and the adiabatic quantum defect. The contribution from the two-electron excited state was carefully excluded from the adiabatic quantum defect. The minor component $s\sigma$ contributes about 30% at most to the DR [17]. We consider that the contribution of $s$ wave is negligible at low energies because the $s$ wave does not induce the rotational excitation, which turns out to be the main mechanism of the DR.
Dissociation probability by the CI: effect of off-the-energy-shell contribution. The full curve shows the result with off-the-energy-shell contribution, the dotted curve does the result by the first order perturbation. The initial vibrational states are indicated: circle: \( v^+ = 0 \), square: \( v^+ = 1 \), triangle: \( v^+ = 2 \). The arrow below the top axis indicates the position of zero energy for each \( v^+ \).

In Fig. 3, we show an example of the present DR cross section of \( \text{H}_2^+ \) of which initial vibrational state \( v^+ \) is \( v^+ = 0 \), and the rotational state \( N^+ \) is \( N^+ = 0 \). The vertical axis shows the cross section multiplied by the collision energy, which is sometimes called reduced cross section (cm\(^2\) eV), in order to see the cross section accurately over wide range of collision energy. The energy of rotationally and/or vibrationally excited Rydberg state are shown by the bar and cross mark in the figure. Almost all peak structures appear at the energies of rotationally excited and vibrationally unexcited Rydberg states. This indicates that the indirect process through the rotational excitation is the dominant mechanism of the DR at low energies.

To see the overall feature of the DR and compare to experiments, we convolute the calculated cross section with a thermal distribution [18]. For rotational distribution, we assume the temperature of 300K. For the energy fluctuation of electron beam, we assume the temperature of 1 meV for transversal to the incident beam direction and 0.05 meV for the longitudinal.

The dependence of DR rate coefficient on the initial vibrational state \( v^+ \) is shown in Fig. 4. The rate coefficient of \( v^+ = 1 \) is about four times larger than that of \( v^+ = 0 \) and 2 over all collision energies. The magnitude of the rate agrees with those of previous study[15], where the rate is \( 2.31 \times 10^{-8} \) for \( v^+ = 0 \), \( 1.81 \times 10^{-7} \) for \( v^+ = 1 \), and \( 1.34 \times 10^{-8} \) for \( v^+ = 2 \) at the collision energy of 4.35meV (100K). This agreement is, however, accidental coincidence because the previous study was footing on the first order perturbation on the CI and the important rotational motion was neglected. The off-the-energy-shell contribution remarkably affects the dependence on the initial vibrational state in the DR as is seen in Fig 2.

The DR cross section has been measured for \( \text{H}_2^+ \) of which the initial rotational and vibrational state is specified[1]. In Fig 5, we compare this experiment for para-\( \text{H}_2^+ \) with the result of present calculation for \( v^+ = 0 \) and for each \( N^+ \). We compare the DR rate coefficient multiplied by the square root of the collision energy for precise comparison. The calculated cross section is convoluted on the collision energy assuming the fluctuation temperature of 2.5 meV for the transversal direction and 0.05 meV for the longitudinal one. Except for the lowest peak around 1 meV, we can find corresponding peak structures between the calculation for \( N^+ = 0 \) and
Figure 3. Reduced DR cross section of $\text{H}_2^+ (v^+ = 0, N^+ = 0)$

The bars with cross marks present the energies of rotationally($N$) and/or vibrationally($v$) excited Rydberg states, of which principal quantum numbers are less than 58. The series limit of Rydberg states is indicated by $\text{inf}$. The lowest bar is for $v = 0$, and the higher bar presents the higher $v$ up to $v = 7$.

Figure 4. Dependence of DR rate coefficient for $\text{H}_2^+$ on the initial vibrational quantum number $v^+$. The kind of curves indicates the initial vibrational state, thin solid: $v^+ = 0$, bold solid: $v^+ = 1$, dotted: $v^+ = 2$. See the text on the electron fluctuation and the rotational state distribution.
The lowest peak structure in the calculation comes from the electron capture into the Rydberg state of $n = 13$ with $N = 4$ or $n = 24$ with $N = 2$, where $n$ is the principal quantum number and $N$ is rotational quantum number. Since the energy of this peak is at quite low energy as below 2 meV, if the peak is slightly shifted, it must be disappeared. It is open question for theory and experiment whether this structure is real or not.

We compared the calculation with the experiment of normal H$_2^+$ in Fig 6. The result by calculation is average over the initial rotational states $N^+ = 0$ and $N^+ = 1$ with the weight of one and three respectively. The calculation reproduce the structure seen in the experiment although the magnitude of the peak does not always agree with each other. At the collision energies lower than 30meV, the peak positions are shifted about 3meV.

5. Concluding remarks
The off-the-energy-shell contribution to the DR of HD$_2^+$ was investigated based on the realistic electronic states obtained by ab-initio method. The dissociative processes are largely affected by the off-the-energy-shell contribution of negative energies. The DR at low energy has turned out to be induced by the indirect process with rotational excitation. The DR rate coefficient of the H$_2^+$ including the off-the-energy-shell contribution nicely represents the resonance structure in DR rate coefficient obtained by the state specific experiment. We have assured the effectiveness of the MQDT method for DR.

Acknowledgments
Authors wish to thank Professor W. J. van der Zande for providing us with their experimental data before publication and for having profitable discussion.
Collision energy (eV)

Figure 6. The rate coefficient multiplied by the square root of the collision energy for normal $\text{H}_2^+$ of $v^+ = 0$. The experiment[1] is shown by full circle and the present calculation is shown by solid curve.

References

[1] Zhaunerchyk V et al. 2007 Phys. Rev. Lett. 99 013201
[2] Bates D R 1950 Phys. Rev. 77 718
[3] Bardsley J N 1968 J. Phys. B 1 349
[4] Jungen C and Atabek O 1977 J. Chem. Phys. 66 5584
[5] Giusti A 1980 J. Phys. B 12 3867
[6] Takagi H 1998 Atomic Collision Research in Japan vol 24 p 3
[7] Takagi H 2000 Dissociative Recombination: Theory, Experiment, and Application iv (World Scientific) p 180
[8] Newton R G 1982 Scattering Theory of Wave and Particles 2nd ed (Springer-Verlag: Springer-Verlag)
[9] Hara S and Sato H 1984 J. Phys. B 17 4307
[10] Sato H and Hara S 1986 J. Phys. B 19 2611
[11] Wolniewicz L and Dressler K 2077 J. Mol. Spectrosc. 67 416
[12] Press W H, Teukolsky S A, Vetterling W T and Flannery B P 1992 Numerical Recipes 2nd ed (Cambridge Univ. Press)
[13] Takagi H, Kosugi N and Dourneuf M L 1991 J. Phys. B 24 711
[14] Takagi H 1993 J. Phys. B 26 4815
[15] Nakashima K, Takagi H and Nakamura H 1987 J. Chem. Phys. 86 726
[16] Takagi H and Nakamura H 1988 J. Chem. Phys. 88 4552
[17] Schneider I F et al. 1997 J. Phys. B 30 2687
[18] Takagi H 2005 J. Phys. Conference series 4 155