Multi-channel quantum defect theory to dissociative recombination with and without electronic resonance scattering

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Abstract. The multichannel quantum defect theory (MQDT) of dissociative recombination (DR) is summarized by classifying into two cases whether an electronic resonance state as the dissociative channel exists or not. The DR and dissociative excitation of the isotopes of hydrogen molecular ion are calculated using recent sophisticated MQDT method where the electronic resonance state exists. On the other hand, an adiabatic quantum defect and a mixing matrix of the partial waves in HeH\(^+\) + e collisions are investigated. These parameters are crucial in MQDT calculation without electronic resonance state. A new approach is proposed by unifying the two cases in a above MQDT treatment.

1. Introduction

The mechanism of dissociative recombination (DR) has been considered as a capture process of an incident electron into an electronic resonance state and sequential stabilization by molecular dissociation [1]. This mechanism is possible when there is a potential-curve crossing between the resonance state and the target molecular ionic state at the energy lower than the total energy of collision system. The DR cross section had been considered to be quite small unless the molecular system has such a potential-curve crossing. However, large cross section has been confirmed for the DR of HeH\(^+\) [2], where there is no potential-curve crossing. Hereafter, we abbreviate ‘potential-curve crossing’ as ‘crossing’.

There are two kinds of theoretical approaches depending on whether the crossing exists or not. In the crossing case, the resonance state is the main dissociative channel and the Rydberg states contribute to DR through the indirect process [3], where the incident electron is temporally captured into a rotationally and vibrationally excited Rydberg state. In the non-crossing case, the dissociative channels are the Rydberg states. It is well known that the multichannel quantum defect theory (MQDT) can describe the dynamics by the strong non-adiabatic interactions (NAI) among the Rydberg states [4]. We here summarize and investigate MQDT method for DR with and without the crossing. As an extension of these theories, we shall propose a new approach based on MQDT. Examples will be shown for cases both with and without crossings.
2. MQDT formulation with and without the crossing

2.1. With the crossing

In the crossing case, DR is caused by two different types of interactions. One is the configuration interaction (CI) between the initial continuum electronic state and the resonance state, which is dissociative. The other is the non-adiabatic interaction (NAI) between the initial state and the Rydberg state of which nuclear motion is bound. The so called "two-step method" enables to solve the dynamic process induced by these two interactions stepwise [5]. This two-step method is nothing but MQDT method with crossing.

To make clear the theories, the basis functions have to be compared. In the crossing case, we distinguish the nuclear motion depending on the electronic configuration; The dissociative is nothing but MQDT method with crossing.

The configuration interaction (CI) between \( \phi_e(r; R) \) and \( \varphi_d(r; R) \) induces transitions between \( \{ \phi_e(r; R) \} \otimes \{ \chi_v(R) \} \) and \( \{ \varphi_d(r; R) \} \otimes \{ F_e(R) \} \), which are driving DR in the crossing case. Assuming an adiabatic representation for the CI, the coupling element is given by

\[
V^{N\ell J}_{ve,dc} = \langle \chi_v(R) | V_{\ell d}(R) | F^{J}_e(R) \rangle_R,
\]

where

\[
V_{\ell d}(R) = \langle \phi_e(r; R) | H^{\text{ele}}(r; R) | \varphi_d(r; R) \rangle_r.
\]

In the above equation, \( H^{\text{ele}}(r; R) \) is the Hamiltonian at fixed nuclei coordinate, and \( N \) and \( J \) are the angular momentum of the molecular ion and the total system respectively [6]. It is required to solve the scattering problem by the CI with the accuracy beyond the perturbation theory. This could be achieved by solving the Lippmann-Schwinger equation fully taken account the off-the-energy-shell contribution beside the on-the-energy shell [7, 8]. The off-the-energy-shell contribution induces the transition among \( \{ \phi_e(r; R) \} \otimes \{ \chi_v(R) \} \) other than between \( \{ \phi_e(r; R) \} \otimes \{ \chi_v(R) \} \) and \( \{ \varphi_d(r; R) \} \otimes \{ F_e(R) \} \). The solution of the scattering problem gives new basis functions of which the CI coupling elements constitute diagonal matrix.

The residual interaction is NAI mainly among \( \{ \phi_e(r; R) \} \otimes \{ \chi_v(R) \} \). The scattering problem by the NAI could be effectively solved by MQDT adopting the new basis functions diagonalizing the CI coupling. The NAI affects the DR at the low energies when an incident electron is temporally captured into a Rydberg state by exciting rotational motion of molecular ion [3, 8].

2.2. Without the crossing: discretization

In the non-crossing case, where the doubly excited state \( \{ \varphi_d(r; R) \} \) is missing, the DR is driven only by the NAI, which is described by MQDT with dissociative motion [9, 10]. Large cross section of the DR process is obtained when the adiabatic quantum defect (AQD) and the mixing parameter of the partial waves of incident electrons vary strongly with the internuclear distance [9]. The precise information on those electronic parameter is crucial to the DR. To include the dissociative continuum states besides the vibrational states, a discretizing method of continuum states is required not only to the basis expansion but also to set in MQDT as we shall see in subsection 2.3. The dissociative state \( \chi^S_j(R) \) is an extension of the vibrational state \( \chi_v(R) \) to the positive energy.

\[
\chi^S_j(R) = \frac{1}{\sqrt{\Delta}} \int_{\epsilon_j - \frac{\Delta}{2}}^{\epsilon_j + \frac{\Delta}{2}} \chi^S_{\ell}(R) d\varepsilon
\]
Dirac’s process without crossing can be described. The function which is discretized with the energy interval of $\Delta$. The state normalization means

$$
\langle \chi_j^S | \chi_j^S \rangle = \delta_{i,j}
$$

with the Kronecker’s delta $\delta$, and the energy normalization does

$$
\langle \chi_j^E \big| \chi_j^E \rangle = \delta^{D}(\epsilon’ - \epsilon),
$$

with the Dirac’s $\delta$ function $\delta^D$. Using the basis set $\{ \phi_i(r; R) \} \otimes \{ \{ \chi_j^E(R) \} \}$ in MQDT, the DR process without crossing can be described. The function $\phi_i(r; R)$ represents both the Rydberg states and continuum electronic states. MQDT analytically imposes the normalization condition upon the basis functions according to the energy $\epsilon$. MQDT including the dissociative channel $\chi_j^S(R)$ also impose the proper normalization condition upon $\chi_j^S(R)$ depending on the energy $\epsilon_j$ [9].

2.3. MQDT with dissociative channels

In MQDT, the energy normalized Coulombic wave function is adopted in the inner region, regardless of whether the energy $\epsilon$ is negative or positive. The asymptotic function of the inner region is expressed as

$$
\Psi(r_e, \bar{r}, R) \sim \sum_{i,i', j} \left\{ \delta_{i,i'} \phi_i^{E}(r_e) + K_{i,i'} \phi_i^{E}(r_e) \right\} \psi_i(\bar{r}) \chi_j^S(R),
$$

where the radial coordinate of a outer electron in Rydberg/continuum state is $r_e$, and the other coordinates of all electrons are represented by $\bar{r}$, $i$, $i'$ represent electronic channels, $K_{i,i'}(R)$ is electronic K matrix element at $R$, and $\chi_j^S$ represents nuclear state $j$, which indicates both vibrational and dissociative states. The function $\phi_i^{E}(r_e)$ is the energy normalized Coulombic function with an asymptotic form of a sine function. The function $\phi_i^{E}(r_e)$ is another independent Coulombic function with a advanced phase difference of $\pi/2$ relative $\phi_i^{E}(r_e)$. The nuclear state $\chi_j^S(R)$ is determined by the electronic state $i$ in the Born-Oppenheimer representation. The wave function in the inner region contains all information of the interactions in the scattering and is almost independent of the normalization condition in the outer region [4].

The wave function of the outer region is represented as

$$
\Psi(r_e, \bar{r}, R) \sim \sum_{j,i,j', j'} \left\{ \delta_{i,i'} \phi_i^{E}(r_e) \psi_j(\bar{r}) \chi_j^S(R) + K_{i,i'} \phi_i^{E}(r_e) \psi_{j'}(\bar{r}) \chi_{j'}^S(R) \right\},
$$

if the channel of nuclear motion is closed as vibrational state or ‘closed dissociative state’ [9]. The indices $(i’j’)$, $(ij)$ represent physical channels and $K_{ij,ij'}$ is the K matrix, which is determined by the frame-transformation between the inner and outer regions [4, 11]. When the channels are composed of the partial waves of incident electron $\ell^+$, vibrational and dissociative Rydberg states $j$, and rotational states of molecular ion $N$, we obtain the K matrix $K$ [9].

$$
K = R_{oo} + R_{oc} (R_{cc} - \tan \pi \nu_c)^{-1} R_{co},
$$

where $\tan \pi \nu_c$ is the diagonal matrix composed of effective principal quantum numbers $\nu$, sufix $o(c)$ indicates open (closed) channel, and

$$
R_{j,N|\ell^+}^{J} = \sum_{\Lambda} \langle N'|\Lambda \rangle \langle J^e|\Lambda^+ \rangle \sum_{\ell^+} \chi_j^{S|\Lambda^+} \chi_j^{S|\Lambda^+} \langle \Lambda|N \rangle \langle J|\ell^+ \rangle (R) \langle \Lambda|N \rangle \langle J|\ell^+ \rangle \Lambda^+ (8)
$$

for $J$ total angular momentum. Good quantum numbers in the inner region are the angular momentum around the molecular axis $\Lambda$ ($\Lambda^+$ for molecular ion) and the eigen state of partial
waves \tilde{t}. The factor \langle \Lambda | \mathcal{N} \rangle^{J_{\tilde{t}}+\Lambda^+} is represented by
\begin{equation}
\langle \Lambda | \mathcal{N} \rangle^{J_{\tilde{t}}+\Lambda^+} = \sqrt{\frac{2N+1}{2J+1}} C(\ell^+ N J; \Lambda - \Lambda^+, \Lambda^+),
\end{equation}
using the Clebsch Gordan coefficient C \([12, 4]\). The cross section of dissociative recombination is defined by the ratio of the flux of dissociated fragments to the incident electron’s flux. Thus, we should take energy normalization for the dissociative states. The eigen state of the system does not change from equation (6) except for a constant multiplier C. The asymptotic form using the alternative normalization for electric closed channel and nuclear open channel is
\begin{equation}
\Psi(r; \tilde{t}, R) \xrightarrow{r \to \infty} \sum_{j,i,j',i'} C_{j,i,j',i} \delta_{ij,i'j'} \phi_i^S(r; \varepsilon) \psi_{i'}(\tilde{r}) \chi_{j'}^{\varepsilon}(R) + K_{j,i,j',i}^{(ecno)} \phi_i^S(r; \varepsilon) \psi_{i'}(\tilde{r}) \chi_{j'}^{\varepsilon}(R),
\end{equation}
where the function \chi_{j'}^{\varepsilon}(R) is the energy normalized nuclear wave function of which asymptotic form is a sine function, and the function with superscript (c) has cosine-type asymptotic form.

The relation between the two K matrix elements is given by
\begin{equation}
K_{j,i,j',i'}^{(ecno)} = \Delta^{-1/2} \nu_i^{-3/2} K_{j,i,j',i'}.
\end{equation}

2.4. Energy higher than several eV
At the collision energies higher than several eV, the electronic excitation to Rydberg states having various excited ionic core can occur. The potential energy curves of these Rydberg states are usually dissociative. Thus, the doubly excited states should be expanded by the basis set of \(\{\varphi_d(r; R)\} \otimes \{F_{\varepsilon}(R)\}\) \cup \(\{\varphi_e(r; R)\} \otimes \{\chi_{j'}^{S}(R)\}\), where \(\varphi_i(r; R)\) represents both core excited Rydberg state and electronically inelastic scattering state whereas \(\varphi_d(r; R)\) is Rydberg type electronic state, and \(\chi_{j'}^{S}(R)\) represents discretized nuclear dissociative motion under the ground electronic state of molecular ion. In such high energy region, the Rydberg states having ground state ion core also could dissociate. The basis function in the non-crossing case could be adopted for the single electron excited states: \(\{\phi_i(r; R)\} \otimes \{\chi_i^{S}(R)\}\) \cup \(\chi_{j'}^{S}(R)\), where the superscript \(g\) indicates the nuclear motion under the ground electronic state of molecular ion. Using this basis set in the two-step method \([5]\), we can calculate DR cross section \([13]\). However, we cannot help adopting the first order perturbation theory to solve the scattering problem by the CI except for the lowest doubly excited state.

2.5. New approach
A new method alternative to the ‘two-step method’ can be possible by using a basis set of \(\{\varphi_i(r; R)\} \cup \{\phi_i(r; R)\}\) \otimes \(\chi_{j'}^{S}(R)\) \cup \(\chi_{j'}^{gS}(R)\). First, by solving the electron scattering problem in the space of \(\{\varphi_i(r; R)\} \cup \{\phi_i(r; R)\}\), we obtain the adiabatic K matrix \(K_{i',i}^{(\Lambda_{i',i})}(R, \varepsilon)\), where \(i'\) and \(i\) indicate electronic scattering states including inelastic scattering.

The smooth K matrix in MQDT is given by
\begin{equation}
\mathcal{R}_{i,j,N_{i',i},N_{i',i}}^{\Lambda_{i',i}N_{i',i}} = \sum_{\Lambda} \langle N|\Lambda \rangle^{J_{\tilde{t}}'+\Lambda^+} \sum_{\tilde{t}} \langle \chi_{j'}^{\Lambda_{i',i}+\Lambda^+} | K_{i',i}^{\Lambda_{i',i}+\Lambda^+}(R, \varepsilon) | \chi_{j}^{N_{i',i}+\Lambda^+} \rangle \langle \Lambda | \mathcal{N} \rangle^{J_{\tilde{t}}+\Lambda^+}
\end{equation}
instead of equation (8) in the MQDT without the crossing. Owing to taking into account the energy \(\varepsilon\) dependence, the basis set \(\{\varphi_i(r; R)\} \cup \{\chi_{j'}^{S}(R)\}\) is expected to represent even the valence type electronic state \(\varphi_d(r; R)\). The physical K matrix is obtained by imposing the physical boundary condition as for the non-crossing case (subsection 2.2, 2.3) \([9]\). We show
the smoothed K matrix of the conventional two-step method below by fitting its form with equation (12) for comparison.

\[ R_{k'N'\ell'v',kN\ell v}^{J} = \sum_{\Lambda} \langle N'|\Lambda \rangle^{J+\ell'} \sum_{\alpha \ell} U_{k',\alpha}^{J}\chi_{v'}^{N'\Lambda'} | K_{k'\ell'v',k\ell v}^{n\ell} (R) | \chi_{v}^{N\Lambda} \rangle U_{\alpha,\Lambda}^{J} | \Lambda | N \rangle^{J+\ell}, \]  

(13)

where the matrix \( U \) diagonalizes the K matrix of the electron scattering by the CI, that eigen state is \( \alpha \), and \( k \) and \( k' \) indicate either the vibrational state \( \chi_{v}(R) \) or the dissociative state \( F_{v}(R) \) in section 2.1.

If this new method works well, it has great advantage because this method requires only the adiabatic electronic information on the energy shell. This means that the cross sections of DR and other dynamical processes can be accurately calculated only if the electron scattering problem at fixed nuclei is solved.

3. DR of isotopes of H$_2^+$

3.1. Energy lower than 1 eV

Using the method briefly introduced in section 2.1, the cross sections for DR of H$_2^+$ and HD$^+$ at low energies (< 1eV) are calculated [8, 7]. This method seems to work well although it is difficult to extend to a wider collision energy region or to other complex molecules. Using the method of MQDT, the cross sections of DR of D$_2^+$, T$_2^+$, DT$^+$ are calculated. The complete set of the DR cross sections for various vibrational and rotational initial states will be provided as a data base from the Japan Atomic Energy Agency and International Atomic Energy Agency. In Figure 1, we show the calculated cross sections under the condition of a typical storage ring experiment: the initial rotational state is in the thermal distribution of 300 K, the ground vibrational state is assumed, and the transversal and longitudinal energy widths are assumed to be 1 meV and 0.05 meV respectively. There is a tendency that the heavier molecular ion has the smaller DR cross section. The energy dependent structure are very different for the different isotopes.

3.2. Higher energy

When the energy of an incident electron becomes high or the target molecular ion is highly excited, the electronic excited states of molecular ions contribute to the DR process and the
Cross section (cm$^2$)

Collion energy (eV)

(a) (b)

Figure 2. Cross sections of dissociative recombination (a) and dissociative excitation (b) for the initial vibrational state $v = 0$. Bold grey line: H$_2^+$, bold black line: D$_2^+$, bold dotted line: T$_2^+$, thin black line: HD$^+$, thin grey line: DT$^+$.

dissociative excitation (DE) process also occurs. In section 2.4, the method to calculate these processes is briefly introduced. We here take into account the effect of AQD of $p\sigma, p\pi, d\sigma$ partial waves [4, 14], which are neglected in the previous paper [13]. This means that the NAI is taken into account in the present calculation although it is less than perfect. For the CI of the lowest doubly excited state, we used the newest solution of scattering state mentioned section 2.1. The calculated cross section for the isotopes of H$_2^+$ is shown in Fig. 2. The DR cross section of H$_2^+$ and HD$^+$ ($v^+ = 0$) is distributed in a wider energy region than for the other isotopes (Figure 2(a)). In the DE cross section of $v^+ = 0$ (Figure 2(b)), the cross section of H$_2^+$ become smaller than the cross section calculated when NAI is neglected [13]. Other isotopes have larger cross section than H$_2^+$.

4. DR of HeH$^+$

We need to investigate the DR process of a non-crossing system in detail to develop the new method proposed in section 2.5. The important factor for the DR process is the integral of the adiabatic K matrix in equation (8). The adiabatic K matrix is represented by using the AQD $\mu_{\ell\lambda}(R)$.

$$K_{\ell',\ell}^{\lambda'}(R) = M_{\ell',\ell}(R) \tan \gamma_{\lambda\lambda'}(R) M_{\ell,\ell}(R),$$

(14)

where the $M_{\ell,\ell'}(R)$ is the mixing matrix element for the partial waves. As a typical non-crossing system, we investigate these quantities of the HeH$^+$ + e system.

According to the previous study [9], large internuclear dependence of the AQD and mixing matrix brings large DR cross section. Especially the most important factor is that the AQD of $p\sigma$ partial wave changes one unit when the internuclear distance varies from small to large distance. This change is expected by the correlation diagram between the united atom limit (Li*) and the separated atom limit (He + H*). However, we could not find clearly these characteristic
in the AQD calculated by Haxton and Greens, which are obtained using an accurate R-matrix calculation [10]. We thus calculate the AQD and the mixing matrix to investigate the character of the Rydberg states.

The UK R-matrix code was used for the electron scattering calculation, where the basis set of cc-pVTZ was employed in the full CI calculation [15]. The adopted partial waves are $\ell^+ = 0 \sim 3$ and $\Lambda \leq 2$ of which origins are centered at the gravity center of the molecule, and the R-matrix radius is 15 bohr. The AQD is shown in Figure 3 for $\Lambda = 0$, which contribute to the DR most dominantly. The values at the nearest internuclear distances are smoothly connected by line in the figure. The AQD connected by the same line is labeled by $\tilde{\ell}$. The value of $\tilde{\ell}$ itself does not have physical meaning but only symbol. The mixing matrix elements are shown in Figure 4 for $\tilde{\ell} = 0, \Lambda = 0$.

The $p\sigma$ AQD is about 0.07 at 0.5 $a_o$, and it exceeds 0.5 at 1.4 $a_o$. It decreases at the larger than 2.5 $a_o$ after reaching the maximum value 0.6 at 2.5 $a_o$. At the large internuclear distance, the $d\sigma$ component increases. It should be $p\sigma$ partial wave centered on the H atom physically. We should take care of the asymptotic behavior of the electronic states for the dissociative processes.

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