

Study on the dissociative recombination of HeH^+ by multi-channel quantum defect theory

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Abstract. The dissociative recombination of HeH^+ is studied using multi-channel quantum defect theory. We investigated how the partial waves of incident electrons affect the DR cross section. The DR cross section depends on the position of the center of partial wave expansion for the adiabatic S -matrix of electron scattering. When the Rydberg states correlate with the Rydberg states of the hydrogen atom at large internuclear distances, the center should be on the hydrogen atom for a better convergence of the expansion.

1. Introduction

There is no crossing of potential curves between the ionic and the dissociative states in the $\text{HeH}^+ + e$ system. No two-electron excited state contributes to dissociative recombination (DR) of HeH^+ at low energies. The DR is induced by the non-adiabatic interaction between single-electron excited states, which is efficiently represented by the multi-channel quantum defect theory (MQDT) [1]. Since HeH^+ is the simplest molecule without crossing, the DR of HeH^+ is the most suitable process to investigate the validity of the MQDT including dissociative channels. A method to add dissociative channels into the MQDT is adopting state-normalized dissociative states besides vibrational wave functions as expansion basis functions of the MQDT [2, 3]. Another method is to use Siegert pseudo-states as expansion functions [5], where the vibrational and dissociative states can be uniformly treated.

A former study of DR of HeH^+ by the MQDT [2, 3] adopted the adiabatic quantum defects of s and p partial waves calculated by Surpal using the R-matrix method. They concluded that the large DR cross section comes from large internuclear dependence of the adiabatic quantum defect of $p\sigma$ partial wave. More complete calculation adopting s , p , d , and f partial waves was performed by Haxton and Greene [5]. Their quantum defect of the $p\sigma$ partial waves does not show so outstanding internuclear dependence as in the former study but large dependences are seen for the quantum defects of the other partial waves. It is one of key problems whether the $p\sigma$ partial wave is the dominant partial wave for the DR or not. In this paper, we investigate the relation between the partial waves and the DR cross section, and make sure the partial waves expansion is converged.

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2. MQDT with dissociative channels

The MQDT of molecules is based on the frame transformation between the basis functions by the Born-Oppenheimer approximation and those of the close coupling method [1]. The asymptotic functions in the outer region are labeled by the quantum numbers of $v^+N^+\ell^+$ used in the close coupling method, where v^+ and N^+ represent vibrational and rotational states of the target molecular ion, respectively, and ℓ^+ is the partial wave of the incident electron. The functions in the inner interaction region are labeled by the quantum numbers $A v \tilde{\ell}$ of the Born-Oppenheimer approximation, where A shows the electronic angular momentum projected onto the molecular axis and v indicates the vibrational state of the complex of the molecular ion and incident electron, and $\tilde{\ell}$ is the eigenchannel of the partial wave. The Jost function representing the half collision between the outer region and inner region is given by the following formula omitting the magnetic quantum states, which could be reduced algebraically [7].

$$(\tilde{\mathcal{J}}_{\pm})_{u^+N^+\ell^+,Au\tilde{\ell}}^J = \langle A|N^+\rangle^{J\ell^+A} \langle \chi_{u^+}^{SN^+A^+} | e^{\mp i\pi\mu_{\tilde{\ell}A}(R)} M_{\ell^+\tilde{\ell}}(R) | \chi_u^{SJA^+} \rangle. \quad (1)$$

The quantum number $u^+(u)$ indicates both $v^+(v)$ and discretized dissociative state with dissociation energy $\varepsilon_{u^+}(\varepsilon_u)$, J is for the total angular momentum, and the unitary matrix M is the mixing matrix of partial waves. The superscript S indicates that the function is normalized as a discrete state (not as continuous energy). The factor $\langle A|N^+\rangle$ introduced by Jungen and Atabek [1] is represented using the Clebsch-Gordan coefficient C .

$$\langle A|N^+\rangle^{J\ell^+A^+} = \sqrt{\frac{2N^++1}{2J+1}} C(\ell^+N^+J; A-A^+, A^+). \quad (2)$$

According to MQDT, we obtain the DR cross section, σ^{DR} , through the scattering matrix $\tilde{\mathbf{S}}$.

$$\tilde{\mathbf{S}} = \tilde{\mathcal{X}}_{oo} - \tilde{\mathcal{X}}_{oc} [\tilde{\mathcal{X}}_{cc} - e^{-2\pi i\nu_c}]^{-1} \tilde{\mathcal{X}}_{co} \quad (3)$$

with

$$\tilde{\mathcal{X}} = \tilde{\mathcal{J}}_- \tilde{\mathcal{J}}_+^{-1}, \quad (4)$$

where the suffix o(c) indicates the open(closed) channels. The cross section becomes

$$\sigma_{\varepsilon, v^+N^+}^{DR} = \frac{\pi}{k^2} \rho \sum_J \sum_{N^+} \sum_{\ell^+\ell^+} \frac{2J+1}{2N^++1} |\tilde{\mathbf{S}}_{\varepsilon N^+\ell^+, v^+N^+\ell^+}^J|^2, \quad (5)$$

where ρ is ratio of the final electronic spin multiplicity to the initial one; now $\rho = 1$. In the present calculation, we removed the closed dissociative channel, which is proposed by one of the author (HT) [3]. All adopted basis functions are on-the-energy-shell.

If the basis functions $\chi_{u^+}^{JA}$ form a complete set, then

$$\tilde{\mathcal{X}}_{ji}^J = \sum_{Au\tilde{\ell}} \langle N_j^+|A\rangle^{J\ell_j^+} \langle \chi_{u_j^+}^{N_j^+} | e^{i\pi\mu_{\tilde{\ell}A}(R)} M_{\ell_j^+\tilde{\ell}}(R) | \chi_{u^+}^{JA} \rangle \langle \chi_{u^+}^{JA} | e^{i\pi\mu_{\tilde{\ell}A}(R)} M_{\tilde{\ell}\ell_i^+}(R) | \chi_{u_i^+}^{N_i^+} \rangle \langle A|N_i^+\rangle^{J\ell_i^+} \quad (6)$$

$$= \sum_A \langle N_j^+|A\rangle^{J\ell_j^+} \langle \chi_{u_j^+}^{N_j^+} | S_{\ell_j^+\ell_i^+}^A(R) | \chi_{u_i^+}^{N_i^+} \rangle \langle A|N_i^+\rangle^{J\ell_i^+}, \quad (7)$$

because $\sum_u \chi_u^{JA}(R)^* \chi_u^{JA}(R') = \delta(R-R')$ is the Dirac's δ function. The adiabatic scattering matrix $S_{\ell_j^+\ell_i^+}^A(R) = \sum_{\tilde{\ell}} M_{\ell_j^+\tilde{\ell}}(R) e^{2i\pi\mu_{\tilde{\ell}A}(R)} M_{\tilde{\ell}\ell_i^+}(R)$ can be calculated as an electron scattering problem by the

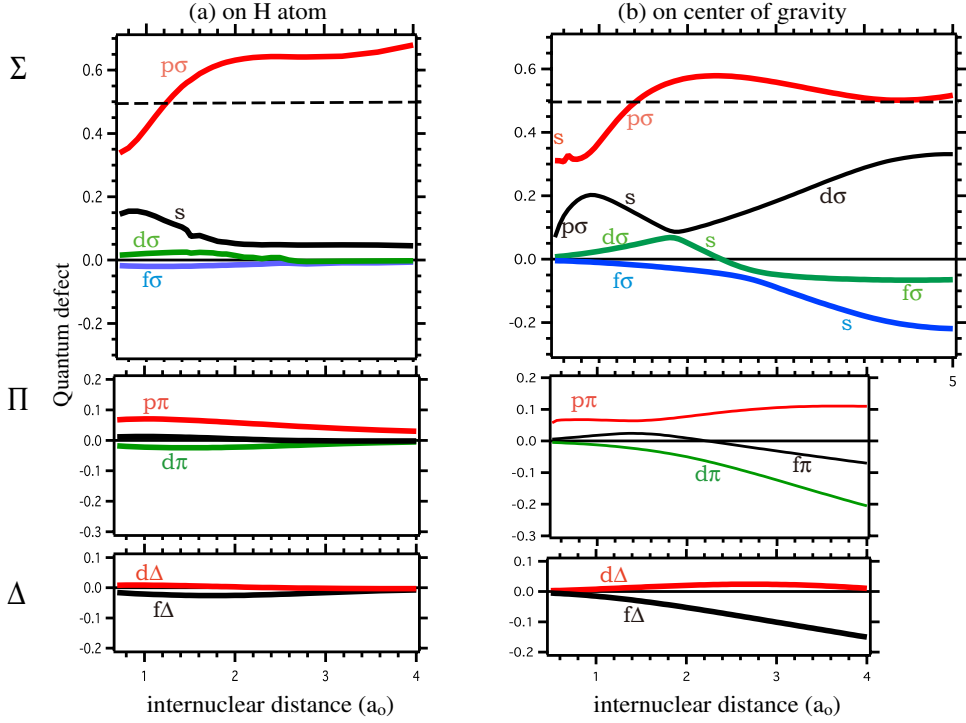


Figure 1. Adiabatic quantum defect for s , p , d , and f partial waves. The center of partial waves is (a) on the hydrogen atom, and (b) on the center of gravity. The dominant partial wave is shown for each adiabatic quantum defect.

molecular ion fixed at R . The unitarity of the matrix requires that the matrix $\tilde{\mathcal{X}}$ should be unitary according to Eq. (3). The unitarity of $\tilde{\mathcal{X}}$ is proved if we neglect the centrifugal distortion of $\chi_{u^+}^{N^+}$.

The Eq. (7) may be extended to electronic inelastic collisions. Specifying the electronic state by the index I , we could write down the matrix $\tilde{\mathcal{X}}_{ji}^J$ if each channel of electronic core states is common to inner and outer regions.

$$\tilde{\mathcal{X}}_{ji}^J = \sum_A \langle N_j^+ | A \rangle^{J\ell_j^+} \langle \chi_{u_j^+}^{I_j^+ N_j^+} | S_{I_j^+ \ell_j^+, I_i^+ \ell_i^+}^A(R) | \chi_{u_i^+}^{I_i^+ N_i^+} \rangle \langle A | N_i^+ \rangle^{J\ell_i^+}, \quad (8)$$

where the suffix represents $j = (I_j u_j^+ N_j^+ \ell_j^+)$ and the same for i .

3. Results

3.1 Quantum defect

The quantum defects is calculated using the UK-R matrix code [4]. The condition of the present calculation is almost the same as the the study by Haxton and Greene [4, 5]: the adopted basis set is cc-pVTZ [6] and the included partial waves are s , p , d , and f waves except the $f\epsilon$ wave. We adopt two cases of the center of partial wave expansion: one is on the center of gravity and the other is on the hydrogen atom. Figure 1 shows adiabatic quantum defect, which is deduced from the eigenphase shift. The dominant partial wave of each adiabatic quantum defect is also shown in the figure. A Rydberg state with an ionic core in the electronic ground state correlates to Rydberg states of the hydrogen and ground

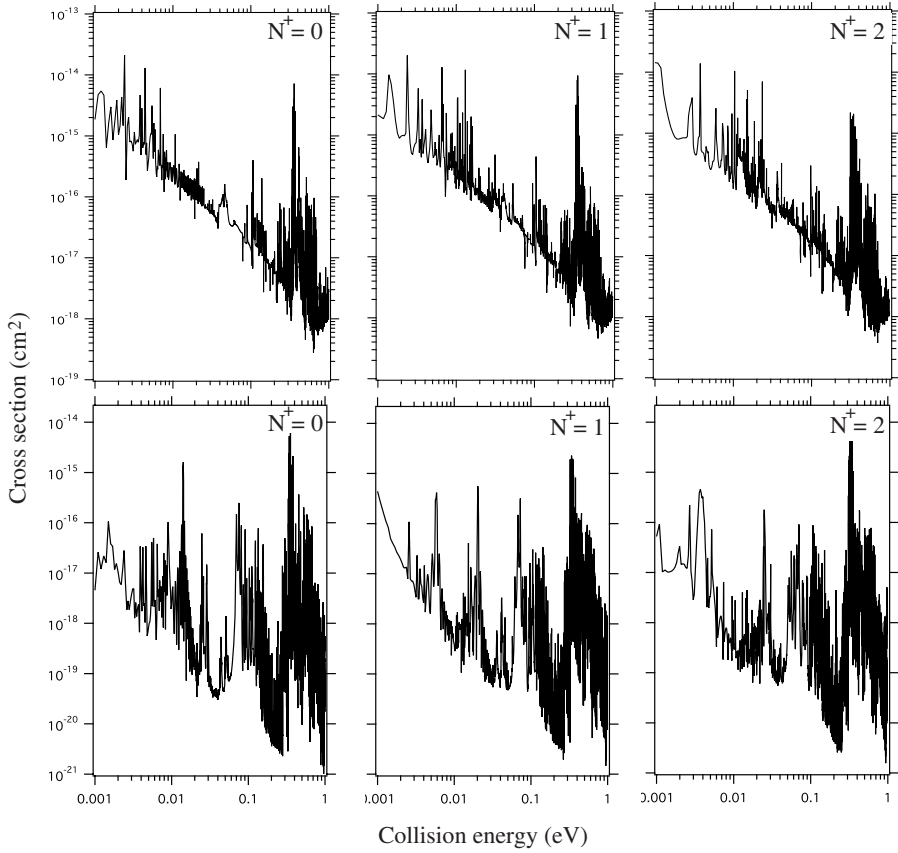


Figure 2. Cross section of DR for $v^+ = 0$. The upper row is computed using the center on hydrogen atom, the lower row is obtained using the center on gravity point. The number N^+ shows initial rotational state.

state of helium atom at large internuclear distances. Then the quantum defects centered on the hydrogen atom become small at large internuclear distances, moreover have weak internuclear dependence except for the $p\sigma$ states, which seems to play dominant role in the DR [3]. In the calculation adopting center of gravity, the quantum defect becomes large except for the $p\sigma$ states, especially at large internuclear distances. This feature is common to the result of Haxton and Greene, though the agreement with them is not complete.

3.2 S-matrix and unitarity

The unitarity of the matrix $\tilde{\mathcal{X}}$ is guaranteed if the basis functions of the vibrational and discretized dissociative states $\chi_{u^+}^{N^+}(R)$ satisfy these two conditions: (1) the set of these basis functions is complete, and (2) the centrifugal distortion of them is negligible. The adopted states in the present calculation are all vibrational states and 80 discretized dissociative states with 0.0014 au intervals of their energies ε_{u^+} , which are smaller than the interval of the highest vibrational energy and the nearest lower one: the separation is 0.0017 au for $N^+ = 0$, and 0.0024 au for $N^+ = 10$. The accuracy of numerical integration on R is kept more than five digits. The product of a unitary matrix and its adjoint (\dagger) matrix is a unit matrix (I): $\tilde{\mathcal{X}}^\dagger \tilde{\mathcal{X}} = I$. The product of the present calculated matrix $\tilde{\mathcal{X}}$ coincides with I more than five digits for the matrix elements of $v^+ \leq 3$ and discretized dissociative states. For the elements of

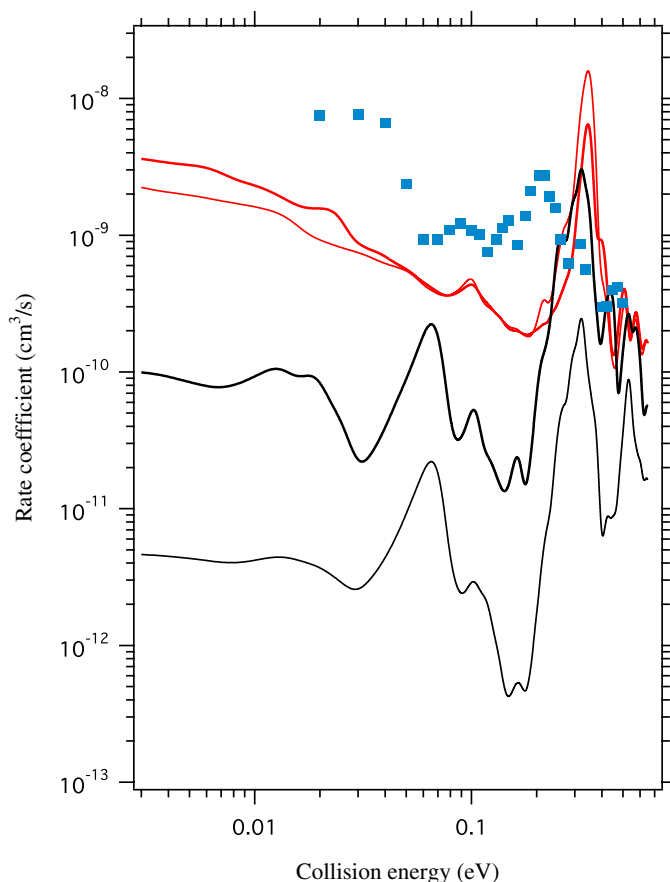


Figure 3. Rate coefficient of DR of $v^+ = 0$. It is averaged over the rotational states with temperature of 300 K. Result is convoluted by an experimental condition of 10 meV for the transversal beam direction and 0.1 meV for the longitudinal direction. Upper two curves (red): result of the center on H atom, lower two curves (black): results from the center on gravity point, thin curves: s , p partial waves, bold curves: s , p , d , f partial waves, square: experiment [8].

$4 \leq v^+ \leq 6$, the agreement becomes more than four digits, and above $v^+ = 7$, it becomes three digits. Thus the unitarity seems to be valid for lower vibrational states.

3.3 Convergence

The center of partial waves affects the calculated quantum defect. Figure 2 shows the DR cross section of the HeH^+ in vibrational ground state $v^+ = 0$ and three rotational states $N^+ = 0, 1, 2$, which is obtained using the calculated quantum defects shown in Fig. 1. The calculated cross section depends on the position of the expansion center to a great extent.

To see the effect of higher partial waves on the DR, we calculated the DR cross section using partial waves limited to s and p waves. The S matrix is deduced from the K matrix of s and p waves, which is a sub-matrix of full K matrix composed of s , p , d , and f waves. Using the sub-matrix K of full K matrix calculated by the R matrix method, we deduce the S matrix of the limited partial waves by the equation of $S = (1 + iK)(1 - iK)^{-1}$.

Figure 3 shows rate coefficient of $v^+ = 0$ for the two cases of center of partial wave expansion. It is averaged over the rotational states assuming temperature of 300 K, and convoluted with an experimental resolution of 10 meV for the transversal beam direction and 0.1 meV for the longitudinal direction. When we use the center on the gravity point, the result of s and p partial wave is not converged and the d and f waves give large contribution over one order of magnitude. Since the contribution of higher partial waves become important, the convergence of the DR cross section becomes slow with increasing the partial waves to higher angular momentum. When we choose the center on the hydrogen atom, the dominant contribution comes from p and s waves. The calculation adopted up to the p partial wave is almost converged.

4. Conclusion

The present MQDT calculation strongly depends on the choice of the center of partial wave expansion for the DR of HeH^+ . It seems better that the center is chosen to represent properly the dissociation limit: the center on hydrogen atom in this case. If not, the partial wave expansion could not converge but might be diverge for higher vibrational states because of spurious increase of quantum defect at large internuclear distances.

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