Rates for dissociative recombination of LiH$^+$ ions

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Abstract. We review recent progress in developing a theoretical treatment of the dissociative recombination (DR) process for the LiH$^+$ molecule, in which a low energy electron is captured and causes the molecule to dissociate into neutral fragments. This e$^+$LiH$^+$ system is prototypical of the indirect class of DR processes, in which the incident electron destroys the molecule through Rydberg capture pathways. The conventional mechanism characteristic of most species with a high DR rate, which normally involves direct capture into a dissociative resonance potential curve, is entirely absent here. We have adopted ab initio multichannel quantum defect theory (MQDT) and a rovibrational frame transformation based on Siegert pseudostates to calculate indirect dissociative recombination for this simple diatomic ion. It is based on a set of ab-initio quantum defects as functions of the internuclear distance, which have been calculated using the R-matrix approach. The calculated DR rate coefficient is found to agree with recent experimental data [1].

1. Introduction

The diatomic molecule lithium hydride has served extensive duty as a test case for quantum chemistry methodologies. An online search for this tantalizingly simple molecule returns thousands of publications to date. One of the simplest chemical processes imaginable for this prototype species is the dissociative recombination (DR) reaction, which converts electronic energy into bond-breaking nuclear kinetic energy:

$$e^+ + LiH^+ \rightarrow Li + H$$  \hspace{1cm} (1)

The DR process for this simple species has seemed enigmatic because of two apparently conflicting facts: first, there is no curve crossing between the ground state of the ionic target LiH$^+$ and a resonance potential curve of the neutral LiH molecule that can provide a direct pathway from the incident electron scattering continuum into a dissociative Born-Oppenheimer state Li(nl$\lambda$)+H(1s). Second, this molecule has a high measured DR rate coefficient [1], in the vicinity of $6(\pm 2) \times 10^{-7}$ cm$^3$/sec at $T = 139K$; when DR occurs this rapidly, it is normally believed to imply that a direct DR curve-crossing exists. On the other hand, this expectation has increasingly been recognized as an overgeneralization, because other ionic molecules exist, notably HeH$^+$ and H$_3^+$, where DR occurs rapidly via mediating Rydberg state captures.

Nevertheless, the first detailed theoretical study [2] of the dissociative recombination reaction for LiH$^+$ obtained a DR rate coefficient that was approximately 23 times lower than the lone storage ring experiment [1, 3, 4]. That discrepancy between a single theoretical result and a single experimental measurement stimulated our interest in studying this reaction using a
different toolkit [5], which has found success in describing another system dominated by indirect Rydberg state captures, the \( \text{H}_3^+ \) molecule. The goal of this theoretical study [6, 7] has thus been two-fold: it would provide a test of the approximation scheme introduced in Ref.[5], and hopefully it would help to resolve the existing discrepancy and thereby shed light on the question of which (if either) of the theoretical and experimental results are quantitatively accurate. The components of that theoretical description relevant to a diatomic target ion include multichannel quantum defect theory (MQDT) [8], the rovibrational frame transformation [9, 10], and the use of Siegert pseudostates as the ionic vibrational channel functions in order to describe the actual dissociation of the complex into neutral Li+H fragments following the electron capture into a Rydberg state. The outcome of those calculations was very good agreement between our new theoretical results and the experiment; the largest remaining discrepancies occur only at sub-meV (parallel) collision energies, where our theoretical curve lies slightly below the experimental error bars.

We add that interest exists in the LiH\(^+\) molecule because it participated in early universe chemistry and contributed to the cooling of primordial gas [11, 12, 13, 14]. As is the case with many molecular ions, the relative LiH\(^+\), Li, H, and LiH abundances are controlled by photoionization, collisions, and by the dissociative recombination (DR) collisions with free electrons. This astrophysical interest makes it worth noting that even in the most recent detailed study of astrophysical processes that include LiH\(^+\) DR, by Lepp et al. [15], a comparatively crude value for the DR rate coefficient was used in the modeling. Changing that rate coefficient from the value initially guessed by [11] to the experimentally measured one [3, 4] reduced the predicted abundance of LiH\(^+\) for redshifts in the range \( z < 25 \) by approximately a factor of 3 in the latest model [15].

The purpose of the present article is to summarize our theoretical description, and to discuss the information that has been gleaned from this study and from the comparison between theory and experiment, as well as to present a few new results that shed light on other aspects of this system. For instance, we present the dependence of the DR rate on the initial rotational state of the ion, and new calculations of the dependence on the initial vibrational state.

2. Quantum Defects

In the present study we make use of the familiar MQDT theorem [8] that smoothly connects \( R \)-dependent quantum defects \( \mu_{l}^{\Lambda}(R) \) (multiplied by \( \pi \)) at energies just below the ionization threshold to \( R \)-dependent short-range scattering phase shifts just above the threshold:

\[
\mu_{l}^{\Lambda}(R) = \frac{1}{\pi} \sum_{\gamma} X_{\ell\gamma}(R) \delta_{\gamma}^{\Lambda}(R) X_{\ell'\gamma}(R),
\]

where the \( \delta_{\gamma}^{\Lambda} \) are the low-energy eigenphases for an \( \text{e}^- + \text{LiH}^+ \) collision, and the eigenvector matrix \( X(R) \) transforms the short-range \( K \)-matrix into diagonal form:

\[
K_{l\ell}^{\Lambda}(R) = \sum_{\gamma} X_{\ell\gamma}(R) \tan \delta_{\gamma}^{\Lambda}(R) X_{\ell'\gamma}(R).
\]

On the other hand Rydberg energy levels \( U_{m\gamma}^{\Lambda}(R) \) of the neutral molecule LiH are described by eigenquantum defects \( \mu_{\gamma}^{\Lambda}(R) \) that are eigenvalues of the \( \mu_{l}^{\Lambda}(R) \) matrix as follows:

\[
U^{+}(R) - U_{m\gamma}^{\Lambda}(R) = \frac{1}{2 \left[n - \mu_{\gamma}^{\Lambda}(R)\right]}. \tag{4}
\]

In this equation \( U^{+}(R) \) is the potential curve of the LiH\(^+\) ion and \( \Lambda \) denotes the projection of the Rydberg electron angular momentum \( l \) onto the axis of the diatomic molecule. We also
introduced eigenindex $\gamma$ distinguishing different Rydberg series of the LiH molecule as $l$ is not a conserved quantum number.

In the previous theoretical study carried out by Florescu et al [2] the eigenquantum defects were obtained by use of Mulliken’s formula (4) and the off-diagonal partial-wave couplings were neglected. However, in the present work we used the diatomic UK R-matrix package [16] to calculate the short-range $K$-matrix (3) by matching to coulomb functions at an R-matrix boundary of $r_0 = 25a_0$ and thus we were able to obtain all the partial-wave couplings as displayed in Fig. 1.

The lower panels of Fig. 1 also show the radial dependence of the calculated eigenquantum defects $\mu^\Lambda(R)$, and demonstrate that they compare well with eigenquantum defects extracted from the $n=4$ CI calculations carried out by Florescu et al [2]. This agreement is a numerical evidence for Seaton’s theorem represented by eq.(2). Quantum defects calculated for $^1\Pi$ and $^3\Pi$ symmetries are displayed in Fig. 1 c) and d). Their values are an order of magnitude smaller than the $\Sigma$ quantum defects, and for this reason they have negligible impact on the final DR results.

Nevertheless, the small $\Pi$ quantum defects can produce small shifts of individual resonances in the DR spectrum, and for this reason we include them in our calculations despite their minimal effect on the average DR rate.

3. Frame transformations

3.1. Vibrational frame transformation

The internuclear distance $R$ is a good body frame “quantum number” when all electrons are confined within the box specified by $r_0$ and the Born-Oppenheimer approximation is accurate. The vibrational frame transformation connects $R$ with the laboratory-frame quantization expressed by vibrational wave functions $\phi_{j\nu}(R)$. In the present study we have chosen a complete set of vibrational functions represented by Siegert pseudostates [17, 18]. They were obtained by solving the vibrational Schrödinger equation with the following boundary conditions:

$$\left[-\frac{d^2}{dR^2} + 2MU^+(R) + \frac{j(j+1)}{R^2} - k_{j\nu}^2\right] \phi_{j\nu}(R) = 0,$$

$$\phi_{j\nu}(0) = 0; \quad \left(\frac{d}{dR} - ik_{j\nu}\right) \phi_{j\nu}(R)|_{R_0} = 0.$$

Figure 1. Dependence of calculated quantum-defect matrix elements on internuclear distance - Upper panels: a) $^1\Sigma^+$, b) $^3\Sigma^+$, c) $^1\Pi$, d) $^3\Pi$. Lower panels: The full curves are eigenvalues of the quantum defect matrices shown in the upper panels. The black dots are the $n=4$ eigenquantum defects extracted from the extensive CI calculations of Ref.[2].
In the above equations $j$ is a rotational quantum number of the ion, $M$ stands for its reduced mass, while $R_0$ denotes a nuclear radius beyond which we approximate the interaction potential in (5) to be constant. The standard vibrational frame transformation integral [20, 10] is modified by a surface term included because of the modified orthogonality relations of Siegert states [18, 23], yielding

$$S_{l,e';j',\nu'}^{\Lambda}(j,j') = \int_0^{R_0} dR \phi_{jv}(R) \left( e^{2\pi i \mu^A(R)} \right)_{l',\nu'} \phi_{j'v'}(R) + i \frac{\phi_{jv}(R_0) \left( e^{2\pi i \mu^A(R_0)} \right)_{l',\nu'} \phi_{j'v'}(R_0)}{k_{jv} + k_{j'v'}} .$$

The underline in this equation denotes that $\mu^A$ is a matrix with indices $\mu_{l,l'}^A(R)$. Siegert pseudostate functions $\phi_{jv}(R)$ describe bound states and they also span over continuum space. We found all of the following results to be converged when the vibrational continuum is described by 20 outgoing-wave Siegert pseudostates for each $j$.

### 3.2. Rotational frame transformation

The rotational frame transformation transforms a set of body-frame angular functions (for further details see [21])

$$X_{jM}^{l\nu}(\hat{r}, \hat{R}) = \left( \frac{2J + 1}{8\pi(1 + \delta_{l0})} \right) \frac{1}{2} \left[ Y_{l\nu}(\theta', \varphi') D_{jM}^{jM}(0, \theta, \varphi) + (-1)^l \eta Y_{l\nu}(\theta', \varphi') D_{jM}^{jM}(0, \theta, \varphi) \right]$$

leading to laboratory-frame angular functions

$$\Phi_{jM}^{l\nu}(\hat{r}, \hat{R}) = \sum_m Y_{jm}(\theta, \varphi) Y_{jM-m}(\theta, \varphi) (lm, jM - m | JM) .$$

In the above equations $\hat{R} \equiv (\theta, \varphi)$ defines molecular axis orientation while $\hat{r} \equiv (\theta, \varphi) \equiv (\theta', \varphi')$ denotes a direction of scattered electron. Unprimed coordinates pertain to the laboratory frame and the primed ones to the body frame. The total angular momentum $J$ is defined as a sum of molecular rotational quantum number $j$ and electron angular momentum $l : J = l + j$. It is important to mention that in eqs. (8), (9) it has already been assumed that the target molecule is in a $\Sigma^+$ state. Both wave functions have definite parity $\eta$ under inversion $I$ of all coordinates:

$$IX_{jM}^{l\nu} = \eta X_{jM}^{l\nu} ,$$

$$I\Phi_{jM}^{l\nu} = (-1)^{l+j}\Phi_{jM}^{l\nu} .$$

The LiH$^+$ ion is treated in Hund’s case (b), with spin-orbit coupling neglected. The eigenstates possess a definite inversion parity, namely $\eta = (-1)^{l+j}$. This procedure transforms the body frame scattering matrix (7) into the laboratory frame, as follows:

$$S_{l,e';j',\nu'}^{\Lambda}(j,j') = \sum_{\nu} U_{j\nu l; j'\nu l} S_{l,e';j',\nu'}^{\Lambda}(j,j') U_{j\nu l; j'\nu l} .$$

The real, orthogonal rotational transformation matrix $U_{j\nu l; j'\nu l}$ is taken from [21].

### 4. Dissociative recombination rates

The scattering matrix $S$ on the left-hand side of Eq.(12) represents an amplitude for electron-ion scattering from an initial channel defined by $(l'j'\nu')$ into a final channel defined by $(lj)$. However at a particular collision energy not all of the final channels are typically open. Complicated Rydberg structure associated with closed-channels resonances is generated by the “elimination
of closed channels” formula [22] that reduces the unphysical $S$ matrix (12) down to the physically-observable open-channel subspace:

$$S_{\text{phys}}^{\text{oo}} = S_{\text{oo}}^{\text{oo}} S_{\text{oc}}^{\text{oc}} S_{\text{cc}}^{\text{cc}} e^{2i \beta(E)}$$  \hspace{1cm} (13)

The superscripts o and c respectively denote open- and closed-channel sub-blocks of the unphysical $S$-matrix (12), while $\beta(E)$ is a diagonal matrix of effective Rydberg quantum numbers with respect to the closed-channel thresholds. Because the high ionization thresholds are described by a Siegert pseudo-continuum state with finite width, $\beta(E)$ becomes complex. This fact results in the $S_{\text{phys}}^{\text{phys}}$ matrix becoming sub-unitary. Physically, the lost flux is associated with an electronically closed channel attached to a vibrational wave function described by a dissociative outgoing-wave Siegert state. The departure from unitarity was identified [23, 5, 6] as the dissociation probability following electron impact in the specified incident channel $i' \equiv \langle \nu' j' |v' \rangle$:

$$\sigma_{i'j'}^{\nu}(\varepsilon_{i'}) = \frac{\pi}{2 \pi'} \left[ 1 - \sum_i S_{i'i'}^{\text{phys}}(E) S_{i'i}^{\text{phys}}(E) \right]$$  \hspace{1cm} (14)

with the incident electron collision energy $\varepsilon_{i'} = E - E_{j'i'}$. The experimentally observable cross-section for dissociation following electron impact is then

$$\sigma_{j'j'}^{\nu}(\varepsilon_{j'j'}) = \frac{1}{2j' + 1} \sum_{nJ'} (2J + 1) \sigma_{i'j'}^{\nu}(\varepsilon_{j'j'})$$  \hspace{1cm} (15)

The corresponding DR rate is then obtained after multiplying the cross-section by the incident electron velocity.

This calculated DR rate exhibits an infinite number of resonances accumulating near each closed-channel ionization threshold. They are also called vibrational (or rotational) Feshbach resonances, and they represent autoionizing and predissociating states of LiH. In all practical applications, the raw DR rate obtained in this manner is averaged over the relevant energy and eigenstate distributions of the ions and of the colliding electrons. In the following we discuss two important cases:

i) In the storage-ring experiments as [1], the electrons and ions are not in thermal equilibrium. The temperature of the electron beam is usually lower than the temperature of the ions. Furthermore, the momentum spread of the electrons is anisotropic. The parallel energy spread $\Delta E_{\parallel}$ is very well controlled, while the distribution is much broader in the perpendicular components of the relative velocity vector. ($\Delta E_{\parallel} = 0.1$ meV and $\Delta E_{\perp} = 12$ meV in [1]). The convolution over parallel and perpendicular energy distributions has been performed as was outlined in [5] and elaborated in detail in [24]. Figure 2 summarizes our results along with previous experimental and theoretical results. This figure also demonstrates the results of a numerical test conducted to interpret the discrepancy between our theoretical results and those of [2]. Specifically, we have performed one set of calculations that neglect the off-diagonal $l$-mixing to mimic the calculations performed by [2], i.e. using only the diagonal eigenvalue form $\mu_{l}^{\nu}(R)$ of quantum-defect matrix (shown in fig. 1 a, b). Introduction of this approximation lowers the DR rate by an order of magnitude, and this artificially restricted calculation agrees with the results of [2].

ii) In the interstellar medium we assume that the electrons are distributed isotropically in momentum space. Thus the thermal rate coefficient is obtained by averaging the DR rate over a Maxwellian distribution of electrons at a temperature $T$:

$$\alpha_{th}(j', j'', T) = \frac{8\pi}{(2\pi kT)^{3/2}} \int_{0}^{\infty} dE \exp \left( -\frac{E}{kT} \right) \sqrt{\frac{E}{2}} \alpha_{j', j''}(E)$$  \hspace{1cm} (16)
In Fig. 3 we show the calculated thermal rate coefficient $\alpha_{th}$ as a function of the temperature $T$ of electrons for a number of ionic initial states $(j', v')$. Our calculations are compared with the estimates used in models of lithium chemistry of the early universe [11, 15] (thick full and dashed curves in the right panel). Drops of the thermal DR rates together with some small oscillations under 10K visible in the Fig. 3 are caused by the fact that the energy distributions of such cold electrons are narrow enough to distinguish vibrational Feshbach resonances occuring close to zero collision energy. In other words, with different initial rotational level the zero collision energy threshold moves through the dense structure of the closed-channel resonances resulting in an oscillatory behavior of the DR rate at very low temperatures.

Figure 2. DR rate: The solid curve is our calculated, anisotropically-averaged rate for $\Delta E_\parallel = 0.1$ meV and $\Delta E_\perp = 12$ meV. The broken curve shows the calculation of [2]. The dotted curve is our truncated result obtained by neglecting the off-diagonal couplings in the quantum-defect matrix (see the fig. 1). The crosses denote the experimental data [3], with a few characteristic error bars shown.

5. Summary and Conclusions

We applied ro-vibrational frame-transformation techniques to calculate indirect dissociative recombination of LiH$^+$ ions. The short-range scattering matrices and quantum defects necessary for the technique were calculated by the fully $ab$-$initio$ R-matrix method. The diagonal form of the quantum defect matrix agrees very well with the eigenquantum defects extracted from standard quantum chemistry calculations of Florescu $et$ $al$ [2].

Encouraged by the very good agreement between our calculated anisotropically-averaged DR rate and the storage rings experiments [1, 3] we also calculated isotropic thermal rate coefficient used in models of lithium chemistry in the early universe [11, 15]. We explored the dependence of the thermal rate coefficients on the initial ro-vibraional state of the LiH$^+$ ion. As the higher vibrational states are more strongly coupled to the continuum it is not surprising that the dissociation is faster for the vibrationally hotter cations.(fig. 3, left panel) However, we have found very weak dependence of the DR rate on the initial rotational state of the molecule with the temepterature of the electrons larger than 20 K. For lower temperatures the energy distribution...
Figure 3. Dependence of the thermal rate $\alpha_{th}$ on the electron temperature and on the initial state of the ion: Left panel: Dependence on the initial vibrational state, with the initial rotational state fixed as $j' = 0$. Right panel: Dependence on the initial rotational state, with the initial vibrational state fixed as $v' = 0$. The thick dashed line is the theoretical estimate utilized by [11] while the thick full line displays the later correction that was published in [15].

window is narrow enough to distinguish different close-channel resonances occurring near zero-energy threshold and oscillatory structures appear (fig. 3, right panel). Our results suggest that rates used in some models of lithium chemistry in the early universe [11] are underestimated by an order of magnitude. The more recent corrected values used in astrophysical modeling [15], on the other hand, appear to be overestimated at temperatures higher than a few Kelvin, by as much as a factor of 4 at 1000K.

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