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TIME DEPENDENT WAVE PACKET CALCULATIONS AT STATE-TO-STATE LEVEL: $Li+H_2^+$ EXAMPLE

ABSTRACT

In this work, the dynamics and kinetics of the $Li+H_2^+$ reaction and its isotopic variance have been studied by means of quantum mechanical (QM) real wave packet method on the ab initio potential energy surface of Martinazzo et al.[1]. Initial state selected reaction probabilities and ro-vibrational distributions integral cross section at fix collision energies are obtained.

Keywords: Reaction Dynamics, Reactive Scattering,
Reaction Probability, Cross-Section, Rate Constants

BİRESEL KUANTUM SEVİYELERİ İÇİN ZAMANA BAĞLI DALGA PAKETİ HESAPLAMALARI: $Li+H_2^+$ ÖRNEĞİ

ÖZET

Bu çalışmada, Martinazzo ve diğerleri tarafından [1] hesaplanan bir ab initio potansiyel enerji yüzeyi üzerinde $Li+H_2^+$ ve izotopları için kuantum mekaniksel dalga paketi metodu kullanılarak reaksiyon ihtimaliyetleri ve titreşim-dönme dağılımları için integral tesir kesitleri sabit çarpışma enerjilerinde elde edildi.

Anahtar Kelimeler: Reaksiyon Dinamiği, Reaktif Saçılma,
Reaksiyon İhtimaliyeti, Tesir Kesiti,
Hız Sabitleri

1. INTRODUCTION (GİRİŞ)

In the last years, the study of molecular processes has gained increasingly more attention in the field of astrophysics because of the often discovered importance of molecules in a variety of cosmic environments. According to current mechanisms of interstellar radiative cooling, primordial lithium chemistry was involved in the onset of the stellar evolution of the universe [2 and 3]. Most of the studies the relevance Chemistry of the early universe is due to the possible importance of the LiH molecules and relative ions in the primordial universe chemistry. Although it is still not clear what could be the role of LiH in the early universe chemistry, since experimentally important data are indeed still missing and its relevance may be limited by the small abundance of Li molecular species that is thought to exist at the recombination era [4].

The interaction among Li atoms and H_2^+,D_2^+,T_2^+ molecules the highly endothermic reactions which involve alkali atoms with hydrogen molecules are usually initiated by electronic excitation of the atom, a feature which implies the presence of some nonadiabatic coupling during the reaction and a collision mechanism that requires knowledge of more that one of the adiabatic reactive potential energy surfaces of the reagents [5 and 6].

2. RESERCH SIGNIFICANCE (ÇALIŞMANIN ÖNEMİ)

Very little is known about LiH_2^+ . A preliminary work of Hobza and Schleyer speculated somewhat on its connection with the neutral LiH_2 system in order to interpret ionization experiments [7]. Subsequent accurate calculations around the C_{2v} (ground-state) equilibrium structure were done by Searles and Nagy-Felsobuki: the system was found to be weakly bound by the polarization forces acting between Li and H_2 [8]. This equilibrium structure was also inferred in previous studies on the inelastic Li^+ + H_2 dynamics which could be compared with beam experimental results [9 and 10].

Recently global three-dimensional adiabatic potential energy surfaces (PES) for the ground and first excited states of LiH_2^+ system have been calculated and fitted by Martinazzo et al. [1]. Dynamical calculations for the LiH_2^+ system on the first excited-state PES are scarce. The first excited surface has a more complicated structure than the ground-state, mainly because of the different electrostatic forces that are now acting between the reagents and between the products for reaction [11].

$$Li+H_2^+ \rightarrow LiH + H^+ \qquad (1)$$
$$Li+D_2^+ \rightarrow LiD + D^+ \qquad (2)$$
$$Li+T_2^+ \rightarrow LiT + T^+ \qquad (3)$$

In the present work, we have calculated state-to-state reaction probabilities and rotational integral cross-section distribution at three fix collision energies for the title reaction. This will give a comprehensive idea to the reader in the reaction dynamics area and the theoretical results would be very important for the experimental works.

Table 1. Numerical run parameters used for calculations (all parameters are given in atomic units)
Tablo 1. Hesaplamalar için kullanılan parametreler (bütün parametreler atomik birimde verilmiştir)

Description	Variable and value
Scattering coordinate range	Rmin=3.019; Rmax=60.388
Diatomic coordinate range	rmin=0.916; rmax=16.809
Number of grid points in R and r	N_R=512; N_r=64
Number of angular grid points	j=50
Gaussian width factor s	σ=2.5
Centre of initial wave packet at t=0	R_0=33.942
Initial kinetic energy of wave packet	E_0=0.35
Time step	Δt=50

3. COMPUTATIONAL DETAILS (HESAPLAMA DETAYLARI)

Time dependent wave packet method that used in this work developen by Gray and the G.G.Balint Kurti,called the Real Wavepacket method, for computing reactive scattering probabilities[11] . Their starting point was an iterative equivalent to the time-dependent Schrödinger equation. Some details of the method have been given below. The time-dependent Schrödinger equation is:

$$i\hbar \frac{\partial \Phi(t)}{\partial t} = \hat{H}\,\Phi(t) \tag{1}$$

If the Hamiltonian, $\hat{H}$, does not depend on time, this equation has the analytic solution:

$$\Phi(t) = \exp\left[\frac{-i\hat{H}t}{\hbar}\right]\Phi(t=0) \tag{2}$$

$\exp\left[\frac{-i\hat{H}t}{\hbar}\right]$ is the time-evolution operator and propagates the wavepacket forward in time from t = 0 to t = τ
Expanding the propagator in terms of cosines and sines,

$$\Phi(t+\tau) = Cos\left[\frac{\hat{H}\tau}{\hbar}\right]\Phi(t) - iSin\left[\frac{\hat{H}\tau}{\hbar}\right]\Phi(t) \tag{3}$$

The corresponding expression for the backward propagation, from t to t-τ is:

$$\Phi(t-\tau) = Cos\left[\frac{\hat{H}\tau}{\hbar}\right]\Phi(t) + iSin\left[\frac{\hat{H}\tau}{\hbar}\right]\Phi(t) \tag{4}$$

By adding Eqs. (3) and (4) we obtain [12] :

$$\Phi(t+\tau)=2Cos\left[\frac{\hat{H}\tau}{\hbar}\right]\Phi(t)-\Phi(t-\tau) \tag{5}$$

This equation is exact and constitutes an iterative equation equivalent to the time-dependent Schrödinger equation [12 and 14]. The iterative process itself does not involve the imaginary number i and therefore, if $\Phi(t)$ and $\Phi(t-\tau)$ were the real parts of the wavepacket, then $\Phi(t+\tau)$ would also be real and would be the real part of the exact wavepacket at time (t + τ). Thus the real part of a complex wavepacket can be propagated forward in time without reference to the imaginary part. This is the basis of the Real Wavepacket method. The iterative procedure of Eq. (5) involves the evaluation of the cosine of $\hat{H}$ acting on a wavepacket. This is a difficult operation to perform. In the Real Wavepacket method a mapping of the Hamiltonian operator is performed to overcome this problem.

$$f(\hat{H}_s)=\frac{\hbar}{\tau}\cos^{-1}(\hat{H}_s) \tag{6}$$

where $\hat{H}_s$ is a shifted and scaled Hamiltonian. This shifting and scaling is required so as to make the mapping single valued and is such as to make the range of the Hamiltonian operator lie in the interval -1≤ $\hat{H}_s$ ≤1;

$$\hat{H}_s=\frac{\hat{H}-\hat{I}(\frac{\Delta E}{2}+V_{\min})}{\frac{\Delta E}{2}} \tag{7}$$

where we have replaced Emin, the minimum energy, by Vmin. As Vmin ≤ Emin this is always permissible and just leads to a slight overestimate of the range of the Hamiltonian operator. Note that this scaling and shifting of the spectrum is identical to that required for the use of the Chebyshev expansion of the time-evolution operator [15 and 17]. The use of this mapping (Eq. 6) means that we are no longer solving the time-dependent Schrödinger equation, but rather a modified equation of the form:

$$i\hbar\frac{\partial\Phi_f(t)}{\partial t}=f(\hat{H_s})\Phi_f(t) \tag{8}$$

where a subscript ``f '' has been placed on the wavefunction to emphasise that it is the solution of a mapped equation rather than of the original timedependent Schrödinger equation. The same arguments which led to the iterative equation equivalent to the time dependent Schrödinger equation Eq. (5), now lead to the simplified form:

$$\Phi_f^R(t+\tau)=2\hat{H}_s\Phi_f^R(t)-\Phi_f^R(t-\tau) \tag{9}$$

where the superscript R in $\Phi_f^R(t)$ indicates that only the real part of the wavepacket is used. I emphasise again that this equation is exact and is completely equivalent to the time-dependent Schrödinger equation. Gray has shown that, when an absorbing technique is included in the propagation of the wavepacket to prevent it from reaching the edge of a finite grid [12], the absorption should be performed in the same way as was later discussed by Mandelstam and Taylor namely [18]:

$$\Phi_f^R(t+\tau) = \hat{A}\left\{2\hat{H}_s\,\Phi_f^R(t) - \hat{A}\Phi_f^R(t-\tau)\right\} \tag{10}$$

where $\hat{A}$ is a damping operator and may have the form $\exp[-V_{abs}(r\tau)\hbar$ such that Vabs(r) is non-zero only in an absorbing region close to the edge of the grid and is in general similar in form to the negative imaginary part of the more widely used negative imaginary absorbing potentials [19 and 20] . As mentioned above the key to the calculation is the definition of an analysis line. This analysis line is drawn in the asymptotic region of the potential energy surface and is defined by a constant value of the scattering coordinate, R=R∞ The function of analysis line is that we take a cut through the wavepacket at each time step and we then project the function obtained in this way onto the asymtotic product fragment wavefunctions, thus obtaining the time-dependent coefficents $C_{\nu j}^{JK}(t)$;

$$C_{\nu j}^{JK}(t) = \left\langle \Theta_{JK}(\theta)\chi_{\nu j}(r) \middle| \Phi_f^R(r, R=R_\infty, \theta, t \;\middle|\right\rangle \tag{11}$$

The half Fourier transform over time of this coefficient then yields an energy-dependent amplitude, $A_{\nu j}^{JK}(E)$

$$A_{\nu j}^{JK}(E) = \frac{1}{2\pi}\int_{t=0}^{\infty} \exp(iEt/\hbar)C_{\nu j}^{JK}(t)dt \tag{12}$$

The transition probabilities for the production of specific final vibrational-rotational states from a specified initial reactant level are given by [21 and 22]

$$P_{j\nu,j'\nu'}(E) = \frac{\hbar^2}{\mu\mu'}k_{\nu'j'}k_{\nu j}\left|\frac{A_{\nu'j'}(E)}{f(k)}\right|^2 \tag{13}$$

where $A_{\nu j}^{JK}(E)$ are the Fourier transform of time-dependent coefficients $C_{\nu j}^{JK}(t)$. $k_{\nu j}$ is related to total energy and rovibrational energy states of the diatomic molecule.

4. RESULTS AND DISCUSSION (SONUÇLAR VE TARTIŞMA)

The grid parameters employed in the present study are given in Table 1. The initial state selected and energy resolved reaction probabilities for the (1),(2) and (3) reactions are presented and discussed in this section. The reaction probabilities are calculated up to a collision energy of 1.0 eV. Figure 1 compares the product vibrational resulved reaction probabilities as a function of collision energy for *J* =0. The wave packet probabilities show a threshold energy value of ≈0.217 eV collision energy which corresponds to the endothermiticy of the reaction on the PES when the zero point energies of reagents and products are considered. The potential energy surface of Martinazzo et al has been employed [1]. After threshold, the wave packet probabilities increase monotonically up to an average value of 1eV at collision energies. Product vibrational reaction probabilities for all the isotopes show oscillatory structures with many sharp peaks as a function of collision energy. Reaction probabilities deacreasing when the mass of the reagent molecule are increased. This can be explained as this reaction has a big isotopic effect in the studied collision energy range.

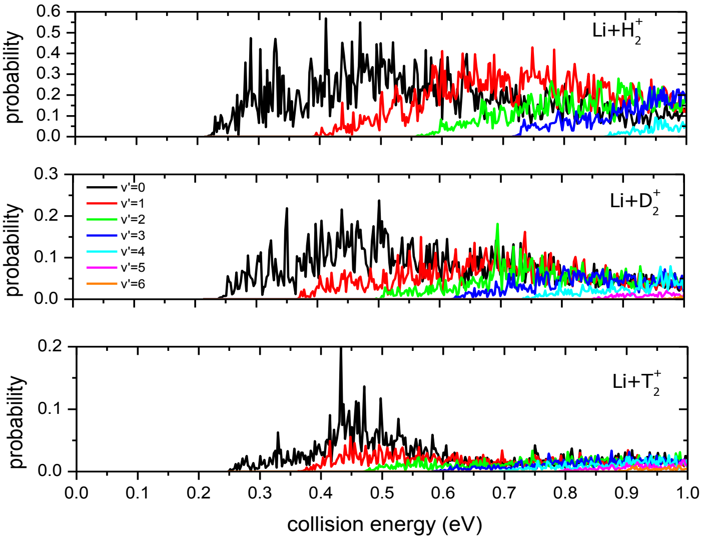

Figure 1. product vibrational reaction probabilities as a function of collision energy at *J* = 0 for the (1),(2),(3) reactions
(Şekil 1. (1),(2),(3)reaksiyonları J=0 için toplam reaksiyon ihtimaliyetinin çarpışma enerjisi ile değişimi)

Figure 2 display calculated rotational distribution integral cross-sections at three fix collison energies for the Li+H$_2^+$ reaction. As can be seen, all the product rotational distribution of integral cross-sections show a gaussian distribution. At 0.25 eV fix collision energy only v'=0 quantum state populated and with increasing collision energy much more product rotational quantum numbers populated.

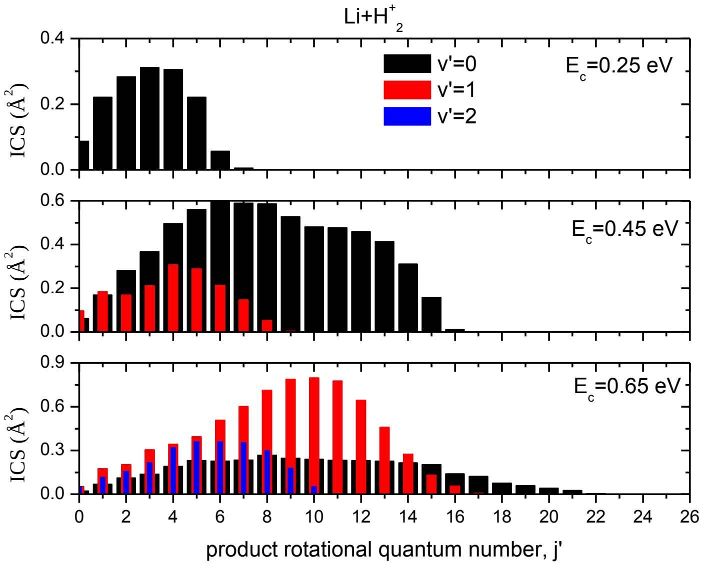

Figure 2. total integral cross-section as a function of product rotational quantum number for the LiH$_2^+$ reaction
(Şekil 2. Li+H$_2^+$ reaksiyonu için toplam tesir kesitlerin ürün dönme kuantum sayılarıyla değişimi)

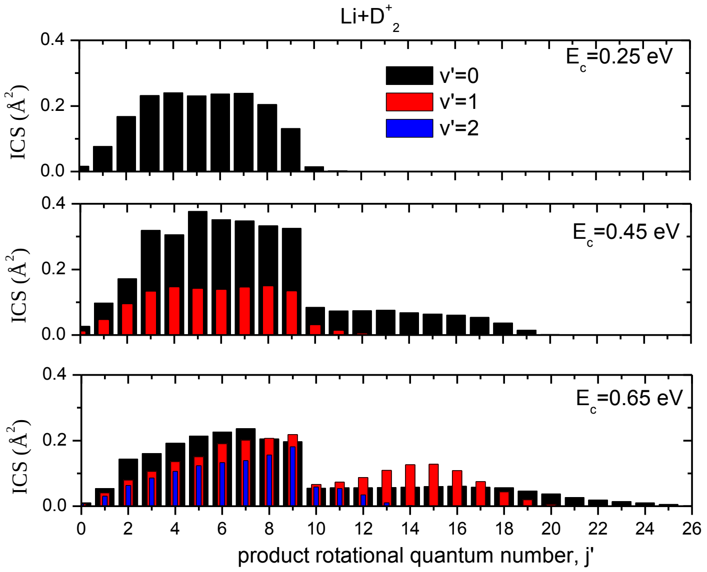

Figure 3. total integral cross-section as a function of product rotational quantum number for the Li+D$_2^+$ reaction
(**Şekil 3.** LiD$_2^+$ reaksiyonu için toplam tesir kesitlerin ürün dönme kuantum sayılarıyla değişimi)

Figure 3 shows the calculated integral cross-sections as a function of product rotational quantum number for the Li+D$_2^+$ reaction. At 0.45eV and 0.65 eV fix collision energy integral cross-sections display a bimodality behaviour. These bimodalities starts at j'=10 rotational quantum number for both collision energies. This can be explained as at j'=10, translational energy transforms to the vibration and rotational nodes of the product molecule and molecule state at quasi bond states of the potential energy surface.

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