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Calculation of non-adiabatic coupling matrix elements in the molecular orbital expansion method

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Abstract

Calculation of adiabatic potentials and corresponding non-adiabatic coupling matrix elements has been carried out rigorously for HLi^+ system by using the ALCHEMY. The adiabatic potentials and some of the coupling matrix elements are compared with those previously obtained, and are found to be in good agreement. For some states, however, the present results are found to be more in the high precision. We have carried out the preliminary study of collision dynamics by solving the coupled equation derived, and some tentative results are included.

1 Introduction

A study of dynamics in ion-atom collision processes is one of the most interesting and important issues in atomic physics, and is applied to many fields. For example, it is applied to fusion sciences, astrophysics, radiology, and material sciences. Further, it is important as a basic study for understanding of fundamental physics. Dominant processes observed in ion-atom collisions are elastic scattering, electron excitation, charge transfer, and ionization. Accurate description of the behavior of electrons during collision is essential for better understanding of dynamics, and accurate determination of cross sections for these processes. Therefore, for a study on dynamical mechanism of collisions, a close investigation of electronic states of a colliding pair would be necessary. Many experimental studies to obtain cross sections for these processes have been carried out. So far, most of theoretical studies are concerned with one- or two- electron system. That is because calculations of adiabatic potential energies and corresponding dynamical coupling matrix elements are very difficult and time-consuming. For many electron systems, we calculate potential energy curves by using a molecular state calculation code the ALCHEMY [1], and develop programs to calculate dynamical coupling matrix elements. Then, calculations are performed on $H^+ + Li$ system, and results of the calculation are compared with previous studies.

2 Ion-atom collision

We consider an ion-atom collision system with collision energy of several eV/amu to several keV/amu. In this energy region, the velocity of an incident ion is slower, or equivalent to that of valence electrons of the target atom. Furthermore in this energy region, electronic excitation and a charge transfer is expected to be dominant processes among all inelastic processes, and, the ionization process is considered to be secondary. The perturbed stationary state (PSS) method with the semi-classical approximation is considered to be the most appropriate to describe the collision at low-to-intermediate energy region accurately. The reduced mass of the nucleus is very large in comparison with the electron mass.

Therefore, in this energy region, the approximation to describe the relative motion of the nucleus classically is reasonable. Hence, we adopt the approximation that the relative motion of nuclei is described classically, and the motion of electrons is treated quantum mechanically. This is called the semi-classical approximation. In this report, we use an atomic unit system, $e = m = \hbar = 1$, where e is the electronic charge, m the electronic mass, and $\hbar$ the Plank constant $/2\pi$.

Relative coordinate $\vec{R}(t)$ is given by the Newton's equation

$$M\frac{d^2\vec{R}}{dt^2} = -\nabla V(\vec{R}), \tag{1}$$

$$M = \frac{M_a M_b}{M_a + M_b}, \tag{2}$$

where M_a, and M_b are the mass of the target atom, and the incident ion, respectively. We assume that a potential $V(\vec{R})$ does not depend on electronic states. Time dependence of the relative coordinate can be determined by solving the equation of motion (1) for given impact parameter $\vec{b}$ and initial velocity $\vec{v}_0$,

$$\vec{R} = \vec{R}(t). \tag{3}$$

A linear trajectory is a good description when the collision energy is lager than several keV/amu. Therefore, straight-line approximation is normally adopted

$$\vec{R}(t) = \vec{b} + \vec{v}_0 t. \tag{4}$$

As stated earlier, we have to deal with the motion of an electron by using the quantum mechanics. The electron motion is described by the Schrödinger equation

$$i\frac{\partial}{\partial t}\Psi(\vec{r},t;\vec{R}(t)) = H_{el}\Psi(\vec{r},t;\vec{R}(t)), \tag{5}$$

where H_{el} is the electronic Hamiltonian, and $\Psi(\vec{r},t;\vec{R}(t))$ is a wave function of the electron.

The Hamiltonian is given by

$$\begin{aligned} H_{el} &= \sum_k h_k + \sum_{k<l}\frac{1}{r_{kl}} + \frac{Z_a Z_b}{R}, \\ h_k &= -\frac{1}{2}\nabla_k^2 - \frac{Z_a}{r_{ak}} - \frac{Z_b}{r_{bk}}, \end{aligned} \tag{6}$$

where Z_a and Z_b are the nuclear charges corresponding to the target atom and incident ion, respectively. Position vectors $\vec{R}, \vec{r}_{kl}, \vec{r}_{ak}$, and $\vec{r}_{bk}$ are shown in Figure 1. In the collision energy region concerned in which many channels couple strongly, the perturbation theory, or the Born approximation is not considered appropriate. The close coupling method is the more suitable approach and is often used.

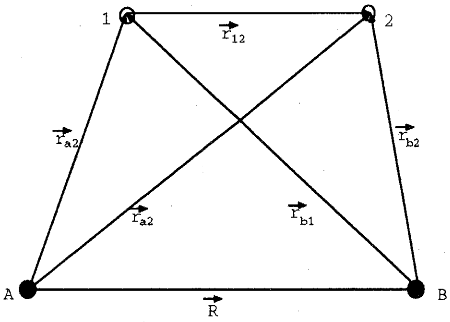

Figure 1: Configuration of particles.

In the close coupling method, by using a set $\{\Psi_j\}$ of known functions, the total wave function Ψ is expanded to

$$\Psi(\vec{r},t;\vec{R}(t)) = \sum_j c_j(t)\Psi_j(\vec{r},t;\vec{R}(t)). \tag{7}$$

Substituting the expansion (7) into the Schrödinger equation (5), a coupled set of equations is derived in terms of the expansion coefficient $c_j(t)$ as follows

$$i\sum_j < \Psi_i|\Psi_j > \frac{dc_j}{dt} = \sum_j c_j < \Psi_i|H_{el} - i\frac{\partial}{\partial t}|\Psi_j > . \tag{8}$$

We solve this equation under the appropriate initial condition $\{c_j(-\infty)\}$, and obtain the transition probability to the state j

$$P_j(b) = |c_j(\infty)|^2. \tag{9}$$

Then, by integrating the transition probability over the impact parameter b, we obtain the partial cross section

$$\sigma_j = 2\pi \int P_j(b) b db. \tag{10}$$

In the PSS method, eigen functions Ψ_j of the electronic Hamiltonian are chosen as

$$H_{el}\Psi_j(\vec{r};\vec{R}) = E_j(R)\Psi_j(\vec{r};\vec{R}), \tag{11}$$

where Ψ_j satisfies an orthonormal condition

$$\int \Psi_i^*(\vec{r};\vec{R})\Psi_j(\vec{r};\vec{R})d\vec{r} = \delta_{ij}. \tag{12}$$

An electronic wave function is expanded in terms of the eigen function of the equation (11)

$$\Psi(\vec{r},t;\vec{R}(t)) = \sum_j c_j(t)\Psi_j(\vec{r};\vec{R}(t))F \exp[-i\int E_j(R(t))dt]. \tag{13}$$

Here, F represents the so-called electron translation factors (ETFs). The ETFs are introduced to take into account an effect that electrons are moving together with moving nuclei. We choose the ETF as follows

$$F = \exp[i\sum_k f(\vec{r}_k;\vec{R}(t))\frac{d\vec{R}(t)}{dt}\cdot\vec{r}_k]. \tag{14}$$

Although generally the function f is not clearly defined at the intermediate separation, the asymptotic form in the limit $R \rightarrow \infty$ is given by

$$f(\vec{r}_k;\vec{R}) \sim \begin{cases} -\dfrac{M_b}{M_a+M_b} & \text{(for an electron k belongs to the target atom)} \\ \dfrac{M_a}{M_a+M_b} & \text{(for an electron k belongs to the incident ion).} \end{cases} \tag{15}$$

By substituting the equation (13) into the Schrödinger equation (5), multiplying it by $\Psi_i^* F^*$ from the left, and integrating it over the electronic coordinate with the help of the orthonormal condition (12), then we can derive the coupled equation which is more suitable for numerical computation

$$\begin{aligned} i\frac{dc_i}{dt} &= \sum_j c_j[< \Psi_i| - i\frac{\partial}{\partial t}|\Psi_j > + < \Psi_i|F^*[H_{el},F] - iF^*\frac{\partial F}{\partial t}|\Psi_j >] \\ &\quad \times \exp[i\int\{E_i(R(t)) - E_j(R(t))\}dt]. \end{aligned} \tag{16}$$

As mentioned above, a partial cross section can be obtained easily by solving this coupled equation.

3 Non-adiabatic coupling terms

When the incident ion is not moving, the right-hand side of the coupling equation (16) becomes zero. That is, the eigen function Ψ_j of the Schrödinger equation (11) becomes the stationary state. In this case, the state changes adiabatically, and hence, no transition between the states occurs. If the relative speed is not zero, the right-hand side becomes non-zero. Then the transition becomes possible between the states. We can rewrite the first term of the matrix element in the right-hand side of the equation as follows

$$< \Psi_i| - i\frac{\partial}{\partial t}|\Psi_j >= \frac{d\vec{R}}{dt}\cdot < \Psi_i|\vec{P}|\Psi_j >, \tag{17}$$

where

$$\vec{P} = -i\nabla_R. \tag{18}$$

Operator $\vec{P}$ is called a non-adiabatic coupling term. When a relative speed is finite, the transition is driven by the term $\vec{P}$. The second term of the matrix element is due to the ETF effect included in the expansion (13). Because the relative speed of the nucleus is assumed to be slow compared to that of orbital electrons, we ignore the term beyond the square of the relative speed. Then by using equation (14),

$$\begin{aligned} F^*[H_{el}, F] &= F^*[T, F] \\ &= F^*\{-\frac{1}{2}\sum_k \nabla_k^2\}F - \{-\frac{1}{2}\sum_k \nabla_k^2\} \\ &= \sum_k\{-\frac{1}{2}F^*(\nabla_k^2 F) - F^*(\nabla_k F)\cdot\nabla_k\}, \end{aligned} \tag{19}$$

where

$$\begin{aligned} F^*(\nabla_k F) &= i\{\nabla_k f(\vec{r}_k;\vec{R})(\frac{d\vec{R}}{dt}\cdot\vec{r}_k)\} \\ &= i\{\nabla_k f(\vec{r}_k;\vec{R})\}(\frac{d\vec{R}}{dt}\cdot\vec{r}_k) + i f(\vec{r}_k;\vec{R})\frac{d\vec{R}}{dt} \\ &\sim i f(\vec{r}_k;\vec{R})\frac{d\vec{R}}{dt}, \end{aligned} \tag{20}$$

$$\begin{aligned} F^*(\nabla_k^2 F) &= i\{\nabla_k^2 f(\vec{r}_k;\vec{R})(\frac{d\vec{R}}{dt}\cdot\vec{r}_k)\} - \{\nabla_k f(\vec{r}_k;\vec{R})(\frac{d\vec{R}}{dt}\cdot\vec{r}_k)\}^2 \\ &\sim i\{\nabla_k^2 f(\vec{r}_k;\vec{R})(\frac{d\vec{R}}{dt}\cdot\vec{r}_k)\} \\ &= i\{\nabla_k^2 f(\vec{r}_k;\vec{R})\}(\frac{d\vec{R}}{dt}\cdot\vec{r}_k) + 2i(\{\nabla_k f(\vec{r}_k;\vec{R})\}\cdot\frac{d\vec{R}}{dt}) \\ &\sim 0, \end{aligned} \tag{21}$$

and

$$\begin{aligned} F^*\frac{\partial F}{\partial t} &= i\sum_k\{\frac{\partial}{\partial t}f(\vec{r}_k;\vec{R})(\frac{d\vec{R}}{dt}\cdot\vec{r}_k)\} \\ &= i\sum_k\{(\frac{d\vec{R}}{dt}\cdot\{\nabla_R f(\vec{r}_k;\vec{R})\})(\frac{d\vec{R}}{dt}\cdot\vec{r}_k) + f(\vec{r}_k;\vec{R})(\frac{d^2\vec{R}}{dt^2}\cdot\vec{r}_k)\} \\ &\sim 0 \end{aligned} \tag{22}$$

are obtained. Then the following formula

$$< \Psi_i|F^*[H_{el}, F] - iF^*\frac{\partial F}{\partial t}|\Psi_j >= \frac{d\vec{R}}{dt}\cdot < \Psi_i|\vec{A}|\Psi_j > \tag{23}$$

is derived, where

$$\vec{A} = -i \sum_k f(\vec{r}_k; \vec{R}) \nabla_k. \tag{24}$$

Operator $\vec{A}$ is called the correction due to the ETF. By using the operators (18) and (24), the coupled equation (16) can be expressed as

$$\frac{dc_i}{dt} = -\sum_j c_j \frac{d\vec{R}}{dt} \cdot < \Psi_i | i(\vec{P} + \vec{A}) | \Psi_j > \exp[i \int \{E_i(R)) - E_j(R)\} dt]. \tag{25}$$

Generally the Schrödinger equation (11) is calculated with the molecular coordinates. Therefore, it is convenient to represent the coupled equation in terms of the molecular coordinates. We use $\vec{i}$,$\vec{j}$,$\vec{k}$: basic unit vectors, and M : a subscript for various quantity in the molecular coordinates. Figure 2 expresses the molecular coordinates$(0 - x'y'z')$ by the center of mass coordinates $(0 - xyz)$.

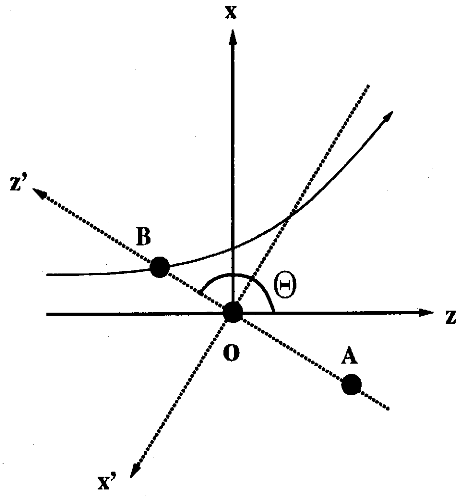

Figure 2: The molecular coordinates.

Using the expression with the molecular coordinates as

$$\frac{d\vec{R}}{dt} \cdot (\vec{P} + \vec{A}) = \frac{dR}{dt} (P + A)^R + \frac{d\Theta}{dt} (P + A)^\Theta, \tag{26}$$

the following expression

$$\begin{aligned} \frac{dc_i}{dt} &= -\sum_j c_j \{ \frac{dR}{dt} < \Psi_i | i(P + A)^R | \Psi_j > + \frac{d\Theta}{dt} < \Psi_i | i(P + A)^\Theta | \Psi_j > \} \\ &\quad \times \exp[i \int \{E_i(R) - E_j(R)\} dt], \end{aligned} \tag{27}$$

$$\begin{aligned} i(P + A)^R &= \vec{k}_M \cdot i(\vec{P} + \vec{A}), \\ i(P + A)^\Theta &= R \vec{i}_M \cdot i(\vec{P} + \vec{A}) \end{aligned} \tag{28}$$

can be derived. Here, $i(P + A)^R$ is called a radial coupling term due to the radial motion of the nucleus. $i(P + A)^\Theta$ is called a rotational coupling term which takes place because the molecular axis rotates in the space.

Using these coordinates,

$$\begin{aligned} iP^R &= \vec{k}_M \cdot \nabla_R = \frac{\partial}{\partial R}, \\ iP^\Theta &= R \vec{i}_M \cdot \nabla_R = \frac{\partial}{\partial \Theta} \end{aligned} \tag{29}$$

are obtained. A derivative with respect to Θ can be rewritten as follows

$$\begin{aligned}\frac{\partial}{\partial\Theta} &= \sum_k\{\frac{\partial z_{kM}}{\partial\Theta}\frac{\partial}{\partial z_{kM}}+\frac{\partial x_{kM}}{\partial\Theta}\frac{\partial}{\partial x_{kM}}\}\\ &= \sum_k\{x_{kM}\frac{\partial}{\partial x_{kM}}-z_{kM}\frac{\partial}{\partial x_{kM}}\}\\ &= -i\sum_k(l_y)_{kM}=-iL_{yM},\end{aligned}\tag{30}$$

where L_y is a vertical element to the collision plane for orbital angular momentum of the electron. Thus, each component of the coupling terms becomes

$$\begin{aligned}iP^R &= \frac{\partial}{\partial R},\\ iP^\Theta &= \frac{\partial}{\partial\Theta}=-iL_{yM},\end{aligned}\tag{31}$$

and

$$\begin{aligned}iA^R &= \sum_k f(\vec{r}_k;\vec{R})\frac{\partial}{\partial z_{kM}},\\ iA^\Theta &= \sum_k f(\vec{r}_k;\vec{R})R\frac{\partial}{\partial x_{kM}}.\end{aligned}\tag{32}$$

In latter section, we omit the subscript M, since all discussion are concerned within the molecular coordinate framework.

4 Molecular wave function

In order to study ion-atom collision by using the molecular representation described above, we first solve the Schrödinger equation (11), and obtain the molecular wave function Ψ_j and energy $E_j(R)$. Next, by using the wave function, non-adiabatic coupling matrix elements should be evaluated. We adopted the ALCHEMY which calculate molecular wave functions readily.

As other programs, the ALCHEMY is based on the LCAOMO approximation. We can use the basis function of either the Slater-type atomic orbitals (STOs), or the Gaussian-type atomic orbitals (GTOs). We have chosen to use the STO here. Namely,

$$\chi(\vec{r}_s)=\sqrt{\frac{(2\zeta)^{2n+1}}{(2n)!}}r_s^{n-1}\exp[-\zeta r_s]Y_{lm}(\theta_s,\phi_s),\qquad (s=a,\ b),\tag{33}$$

where Y_{lm} denotes the spherical harmonic given by

$$Y_{lm}(\theta,\phi)=(-1)^m\sqrt{\frac{2l+1}{4\pi}\frac{(l-m)!}{(l+m)!}}P_l^m(\cos\theta)\exp[im\phi].\tag{34}$$

In the LCAOMO approximation, molecular orbital (MO) is expanded as

$$\psi_j(\vec{r})=\sum_i c_{ij}^a\chi_i(\vec{r}_a)+\sum_i c_{ij}^b\chi_i(\vec{r}_b),\tag{35}$$

where the coefficient c is determined by the self-consistent field (SCF) method.

We calculate the molecular wave function by using the configuration interaction (CI) method. At the beginning, the MO obtained from the SCF method is multiplied by the spin function, and we construct the spin orbital (SO)

$$\varphi(\vec{x})=\psi(\vec{r})\alpha\ \text{ or }\ \psi(\vec{r})\beta.\tag{36}$$

Then, by selecting appropriate electron configurations, we can obtain a Slater determinant X. The Slater determinant is defined as

$$\begin{aligned} X_i &= \|\varphi_{i_1}\,\varphi_{i_2}\,\cdots\,\varphi_{i_N}\| \\ &= \frac{1}{\sqrt{N!}}\begin{vmatrix} \varphi_{i_1}(1) & \varphi_{i_2}(1) & \cdots & \varphi_{i_N}(1) \\ \varphi_{i_1}(2) & \varphi_{i_2}(2) & \cdots & \varphi_{i_N}(2) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_{i_1}(N) & \varphi_{i_2}(N) & \cdots & \varphi_{i_N}(N) \end{vmatrix} \\ &= \frac{1}{\sqrt{N!}}\sum_P \delta_P P(\varphi_{i_1}\,\varphi_{i_2}\,\cdots\,\varphi_{i_N}), \end{aligned} \tag{37}$$

where P expresses a substitution as follows

$$\delta_P = \begin{cases} 1 & (\text{P : even substitution}) \\ -1 & (\text{P : odd substitution}). \end{cases} \tag{38}$$

Generally, the single Slater determinant is not an eigen function of the total angular momentum. A linear combination of the Slater determinant is called a configuration state function (CSF)

$$\Phi_j = \sum_i a_{ij} X_i, \tag{39}$$

which satisfies the molecular symmetry, and moreover, is an eigen function of the total angular momentum. In the CI method, the molecular wave function is expanded in terms of this configuration function as follows

$$\Psi_j = \sum_i C_{ij}\Phi_i, \tag{40}$$

where energy $E_j(R)$ and coefficient C_{ij} are variedly determined.

5 Radial coupling matrix elements

Using the molecular wave function (40), the radial coupling matrix element can be calculated.

$$\begin{aligned} <\Psi_i|\frac{\partial}{\partial R}|\Psi_j> &= \sum_{k,l} C^*_{ki}\{\frac{dC_{lj}}{dR} <\Phi_k|\Phi_l> + C_{lj} <\Phi_k|\frac{\partial}{\partial R}|\Phi_l>\} \\ &= \sum_k C^*_{ki}\frac{dC_{kj}}{dR} + \sum_{k,l} C^*_{ki}C_{lj} <\Phi_k|\frac{\partial}{\partial R}|\Phi_l>, \end{aligned} \tag{41}$$

then

$$<\Psi_i|i(P+A)^R|\Psi_j> = \sum_k C^*_{ki}\frac{dC_{kj}}{dR} + \sum_{k,l} C^*_{ki}C_{lj} <\Phi_k|i(P+A)^R|\Phi_l>, \tag{42}$$

where the derivative term is approximated as

$$\frac{dC_{kj}}{dR} = \frac{C_{kj}(R+\Delta R) - C_{kj}(R-\Delta R)}{2\Delta R}. \tag{43}$$

Furthermore, by using the expansion (39), the expression

$$<\Phi_i|i(P+A)^R|\Phi_j> = \sum_{k,l} a^*_{ki}a_{lj} <X_k|i(P+A)^R|X_l> \tag{44}$$

can be derived.

Next, we consider a matrix element represented by using the Slater determinant.

$$
\begin{aligned}
< X_i|\frac{\partial}{\partial R}|X_j > &= \frac{1}{N!}\sum_P\sum_Q \delta_P\delta_Q \int P(\varphi_{i_1}\varphi_{i_2}\ldots\varphi_{i_N})^* \frac{\partial}{\partial R} Q(\varphi_{i_1}\varphi_{i_2}\ldots\varphi_{i_N})d\vec{r} \\
&= \sum_P \delta_P \int P(\varphi_{i_1}\varphi_{i_2}\ldots\varphi_{i_N})^* \frac{\partial}{\partial R}(\varphi_{i_1}\varphi_{i_2}\ldots\varphi_{i_N})d\vec{r} \\
&= \sum_P \delta_P \int P(\varphi_{i_1}\varphi_{i_2}\ldots\varphi_{i_N})^* \{(\frac{\partial\varphi_{i_1}}{dR}\varphi_{i_2}\ldots\varphi_{i_N}) \\
&\qquad +(\varphi_{i_1}\frac{\partial\varphi_{i_2}}{dR}\ldots\varphi_{i_N}) + \ldots + (\varphi_{i_1}\varphi_{i_2}\ldots\frac{\partial\varphi_{i_N}}{dR})\}d\vec{r}. \qquad (45)
\end{aligned}
$$

Then we arrive

$$
\begin{aligned}
&< X_i|\frac{\partial}{\partial R}|X_j > \\
&= \begin{cases} < \varphi_{i_k}|\frac{\partial}{\partial R}|\varphi_{j_k} > & \text{(for only the } k\text{th electron configuration is different)} \\ 0 & \text{(otherwise).} \end{cases} \qquad (46)
\end{aligned}
$$

Thus the following formula can be obtained

$$
\begin{aligned}
&< X_i|iP^R|X_j > \\
&= \begin{cases} < \varphi_{i_k}|iP^R|\varphi_{j_k} > & \text{(for only the } k\text{th electron configuration is different)} \\ 0 & \text{(otherwise).} \end{cases} \qquad (47)
\end{aligned}
$$

Then, since A^R is the one electron operator, the relationship similar to the equation (47) is valid. Therefore

$$
\begin{aligned}
&< X_i|i(P+A)^R|X_j > \\
&= \begin{cases} < \varphi_{i_k}|i(P+A)^R|\varphi_{j_k} > & \text{(for only the } k\text{th electron configuration is different)} \\ 0 & \text{(otherwise)} \end{cases} \qquad (48)
\end{aligned}
$$

can be obtained, where the operator A^R is given by the equation (32) except for the summation.

Since the operator being considered here does not contain the spin variable, we can perform the integration over the spin variable, and a matrix element for the spin orbital is expressed by the matrix element for molecular orbital $< \psi_i|i(P+A)^R|\psi_j >$ immediately. The molecular orbital is expanded in terms of the equation (35) with the atomic orbital, and the expansion coefficient c depends on the inter-nuclear distance R. Then, as the same procedure to derive the equation (42) is applied, the expression

$$
\begin{aligned}
< \psi_i|i(P+A)^R|\psi_j > &= \sum_{k,l} c_{ki}^{a*}\frac{dc_{lj}^a}{dR} < \chi_k^a|\chi_l^a > + \sum_{k,l} c_{ki}^{a*}c_{lj}^a < \chi_k^a|i(P+A)^R|\chi_l^a > \\
&+ \sum_{k,l} c_{ki}^{b*}\frac{dc_{lj}^b}{dR} < \chi_k^b|\chi_l^b > + \sum_{k,l} c_{ki}^{b*}c_{lj}^b < \chi_k^b|i(P+A)^R|\chi_l^b > \\
&+ \sum_{k,l} c_{ki}^{a*}\frac{dc_{lj}^b}{dR} < \chi_k^a|\chi_l^b > + \sum_{k,l} c_{ki}^{a*}c_{lj}^b < \chi_k^a|i(P+A)^R|\chi_l^b > \\
&+ \sum_{k,l} c_{ki}^{b*}\frac{dc_{lj}^a}{dR} < \chi_k^b|\chi_l^a > + \sum_{k,l} c_{ki}^{b*}c_{lj}^a < \chi_k^b|i(P+A)^R|\chi_l^a > \qquad (49)
\end{aligned}
$$

can be obtained.

Let us define that the function $f(\vec{r};\vec{R})$ in the ETF satisfies the asymptotic form (15) on every inter-nuclear separation R. The asymptotic forms are approximated as follows

$$
\begin{aligned}
f(\vec{r};\vec{R})\chi_l^a &\sim -\frac{M_b}{M_a+M_b}\chi_l^a, \\
f(\vec{r};\vec{R})\chi_l^b &\sim \frac{M_a}{M_a+M_b}\chi_l^b. \qquad (50)
\end{aligned}
$$

Then, we have

$$\begin{aligned} i(P+A)^R\chi_l^a &= \{\frac{\partial}{\partial R} - \frac{M_b}{M_a+M_b}\frac{\partial}{\partial z}\}\chi_l^a \\ &= \{\frac{\partial z_a}{\partial R} - \frac{M_b}{M_a+M_b}\frac{\partial z_a}{\partial z}\}\frac{\partial \chi_l^a}{\partial z_a}, \end{aligned} \tag{51}$$

where

$$z_a = z + \frac{M_b}{M_a+M_b}R. \tag{52}$$

Therefore

$$\frac{\partial z_a}{\partial z} = 1, \qquad \frac{\partial z_a}{\partial R} = \frac{M_b}{M_a+M_b}, \tag{53}$$

and

$$i(P+A)^R\chi_l^a = 0. \tag{54}$$

In the same way

$$i(P+A)^R\chi_l^b = 0 \tag{55}$$

can be obtained. Consequently, the equation (49) is expressed as follows

$$\begin{aligned} <\psi_i|i(P+A)^R|\psi_j> &= \sum_{k,l} c_{ki}^{a*}\frac{dc_{lj}^a}{dR} <\chi_k^a|\chi_l^a> + \sum_{k,l} c_{ki}^{b*}\frac{dc_{lj}^b}{dR} <\chi_k^b|\chi_l^b> \\ &+ \sum_{k,l} c_{ki}^{a*}\frac{dc_{lj}^b}{dR} <\chi_k^a|\chi_l^b> + \sum_{k,l} c_{ki}^{b*}\frac{dc_{lj}^a}{dR} <\chi_k^b|\chi_l^a>, \end{aligned} \tag{56}$$

where the derivative terms are approximately written as before

$$\frac{dc_{lj}^s}{dR} = \frac{c_{lj}^s(R+\Delta R) - c_{lj}^s(R-\Delta R)}{2\Delta R}, \qquad (s = a, b). \tag{57}$$

6 Rotational coupling matrix elements

As in the similar way as the radial coupling matrix has been derived, we can calculate the rotational coupling matrix element

$$<\Psi_i|i(P+A)^\Theta|\Psi_j> = \sum_{k,l} C_{ki}^* C_{lj} <\Phi_k|i(P+A)^\Theta|\Phi_l> . \tag{58}$$

Further, by using the expansion (39), equation (58) can be reduced

$$<\Phi_i|i(P+A)^\Theta|\Phi_j> = \sum_{k,l} a_{ki}^* a_{lj} <X_k|i(P+A)^\Theta|X_l> . \tag{59}$$

Since P^Θ and A^Θ are the one electron operators,

$$\begin{aligned} &<X_i|i(P+A)^\Theta|X_j> \\ &= \begin{cases} <\varphi_{i_k}|i(P+A)^\Theta|\varphi_{j_k}> & \text{(for only the } k\text{th electron configuration is different)} \\ 0 & \text{(otherwise),} \end{cases} \end{aligned} \tag{60}$$

where the operator A^Θ is given by the equation (32) except for the summation.

In order to calculate this matrix element, it needs to be represented in terms of the molecular orbital

$$\begin{aligned} &< \psi_i | i(P+A)^\Theta | \psi_j > \\ &\quad = \sum_{k,l} c_{ki}^{a*} c_{lj}^{a} < \chi_k^a | i(P+A)^\Theta | \chi_l^a > + \sum_{k,l} c_{ki}^{b*} c_{lj}^{b} < \chi_k^b | i(P+A)^\Theta | \chi_l^b > \\ &\quad + \sum_{k,l} c_{ki}^{a*} c_{lj}^{b} < \chi_k^a | i(P+A)^\Theta | \chi_l^b > + \sum_{k,l} c_{ki}^{b*} c_{lj}^{a} < \chi_k^b | i(P+A)^\Theta | \chi_l^a > . \end{aligned} \tag{61}$$

Similarly to the case of the radial coupling term, if the ETF satisfies the equation (50), we have

$$i(P+A)^\Theta \chi_l^a = \{-il_y - \frac{M_b}{M_a+M_b} R \frac{\partial}{\partial x}\} \chi_l^a . \tag{62}$$

And, by using the equation (52), the first term of equation (62) can be rewritten, as

$$\begin{aligned} -il_y &= -z\frac{\partial}{\partial x} + x\frac{\partial}{\partial z} \\ &= -(z_a - \frac{M_b}{M_a+M_a} R)\frac{\partial}{\partial x_a} + x_a \frac{\partial}{\partial z_a} \\ &= -il_y^a + \frac{M_b}{M_a+M_b} R \frac{\partial}{\partial x}, \end{aligned} \tag{63}$$

then we have

$$i(P+A)^\Theta \chi_l^a = -il_y^a \chi_l^a . \tag{64}$$

Similarly,

$$i(P+A)^\Theta \chi_l^b = -il_y^b \chi_l^b . \tag{65}$$

Therefore, equation (61) is given as follows

$$\begin{aligned} &< \psi_i | i(P+A)^\Theta | \psi_j > \\ &\quad = \sum_{k,l} c_{ki}^{a*} c_{lj}^{a} < \chi_k^a | -il_y^a | \chi_l^a > + \sum_{k,l} c_{ki}^{b*} c_{lj}^{b} < \chi_k^b | -il_y^b | \chi_l^b > \\ &\quad + \sum_{k,l} c_{ki}^{a*} c_{lj}^{b} < \chi_k^a | -il_y^b | \chi_l^b > + \sum_{k,l} c_{ki}^{b*} c_{lj}^{a} < \chi_k^b | -il_y^a | \chi_l^a > . \end{aligned} \tag{66}$$

The matrix element of the operator il_y can be expressed in the simpler form numerically more tractable by using the next relationship

$$-il_y = \frac{1}{2}(l_- - l_+), \tag{67}$$

$$l_\pm \chi_{nlm}(\vec{r}) = \sqrt{(l \mp m)(l \pm m + 1)} \chi_{nlm\pm 1}(\vec{r}). \tag{68}$$

7 Results and discussions

We have carried out the calculations of the adiabatic potentials and corresponding coupling matrix elements based on the theory described in details above. We have chosen the system in which the hydrogen ion collides with lithium atom as a sample. The calculations are performed in the following steps: (i) we determine the wave function of the molecule. We use the ALCHEMY for this purpose, and obtain the wave function based on the CI method. (ii) we calculate the radial and rotational coupling matrix elements. (iii) we solve the coupled equations (27) by using the 3rd-order Runge-Kutta method, and obtain the expansion coefficient c_j as a function of time. The results thus obtained are as follows.

7.1 Molecular wave function

The bases functions employed in the ALCHEMY are shown in Table 1. We have adopted the same bases functions for all inter-nuclear distance R. By using these bases functions for the CI method, molecule wave functions Ψ_j, and energies $E_j(R)$ are determined accurately. After the SCF calculation, we depicted the molecule wave function of ten σ states, and four π states for the CI calculation. Figure 3 illustrates the adiabatic potential energies $E_j(R)$.

Table 1: The bases functions.

Li		H^+	
	orbital exponents ζ		orbital exponents ζ
1s	2.47673	1s	1.0
1s	4.69873	2s,2p	0.5
2s,2p	0.3835		
2s,2p	0.66055		
2s,2p	1.07		
2s,2p	1.632		
3s,3p	1.0		

7.2 Radial and rotational coupling matrix elements

We calculated the radial, and the rotational coupling matrix elements by using the wave function Ψ_j which was determined in the previous section. The lowest molecular state of $1^2\Sigma^+$ ($Li^+(1s^2)+H(1s)$) is separated energetically from other states (see Figure 3); therefore, we expect a weak transition to this state and hence, excluded the state from the calculation.

We select the next six channels in the calculation,
$2^2\Sigma^+$ ($Li(1s^22s)+H^+$), $3^2\Sigma^+$ ($Li(1s^22p\sigma)+H^+$), $4^2\Sigma^+$ ($Li^+(1s^2)+H(2p\sigma)$), $5^2\Sigma^+$ ($Li^+(1s^2)+H(2s)$), $1^2\Pi$ ($Li(1s^22p\pi)+H^+$), $2^2\Pi$ ($Li^+(1s^2)+H(2p\pi)$).

Figures 4 and 5 show the results for the radial and rotational coupling matrix elements as a function of inter-nuclear distance R, respectively. The radial and rotational coupling matrix elements should satisfy the following relations (the hermiticity) because of their symmetry,

$$< \Psi_i|i(\vec{P}+\vec{A})|\Psi_i >= 0,$$
$$< \Psi_i|i(\vec{P}+\vec{A})|\Psi_j >= - < \Psi_j|i(\vec{P}+\vec{A})|\Psi_i > .$$

However, the hermiticity breaks down because of the inclusion of the ETF in the calculation.

7.3 Coupled equations

The coupled equations (27) are solved based on the Runge-Kutta method. Energies E_i and coupling matrix elements are evaluated by means of interpolation with the 3rd-order spline function for the numerical results obtained above. Relative inter-nuclear coordinate $\vec{R}(t)$ is derived from the linear approximation (see equation (4)).

Here, as discussed above, the symmetry for the coupling matrix elements is lost, and hence, some care should be taken for the determination of scattering amplitudes numerically. Therefore, we use the following three methods for solving the coupled equations:

method1 Using the numerical results for the couplings without any modification.

method2 Based on the consideration for the symmetry, only the diagonal elements of the couplings for the same states ($< \Psi_i|i(\vec{P}+\vec{A})|\Psi_i >$) is set to zero.

method3 Based on the non-hermiticity, ($< \Psi_i|i(\vec{P}+\vec{A})|\Psi_i >$) is set to zero as in method2, and other elements $< \Psi_i|i(\vec{P}+\vec{A})|\Psi_j >$ are replaced with $(< \Psi_i|i(\vec{P}+\vec{A})|\Psi_j > - < \Psi_j|i(\vec{P}+\vec{A})|\Psi_i >)/2$.

The calculations have been performed under the following initial conditions: Initial velocity is $v_0 = 0.5$ a.u., the impact parameter $b = 1.0$ a.u., and the initial state is chosen as $2^2\Sigma^+$. We investigate the time-variation (or collision history) of the expansion coefficients from - infinity (-80 a.u.) in collision time to + infinity (80 a.u.). The results by using method1, method2, and method3 are presented in Figures 6, 7, and 8, respectively.

Next, we compare with the results based on the three methods. Figure 9 shows the results for the impact parameters b(a.u.) at 1.0 a.u., and 13.0 a.u., respectively. The method1 gives similar transition probabilities to those of obtained by the method2. On the other hand, the differences between results of method1, 2 and of the method3 are considerable.

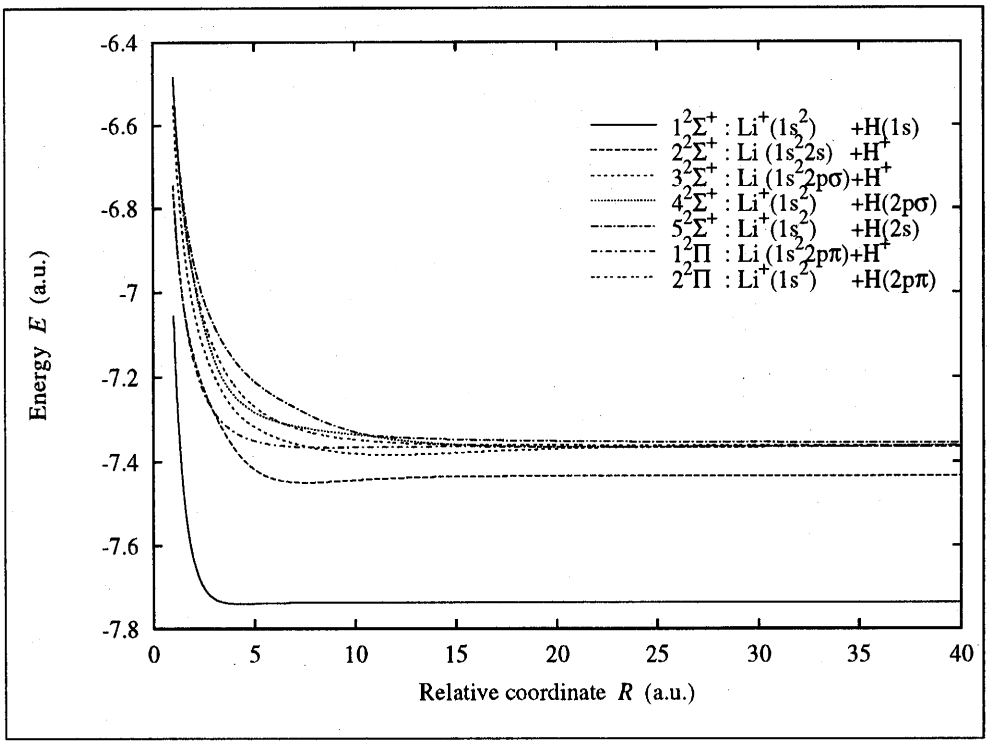

Figure 3: Potential energy curves for LiH^+.

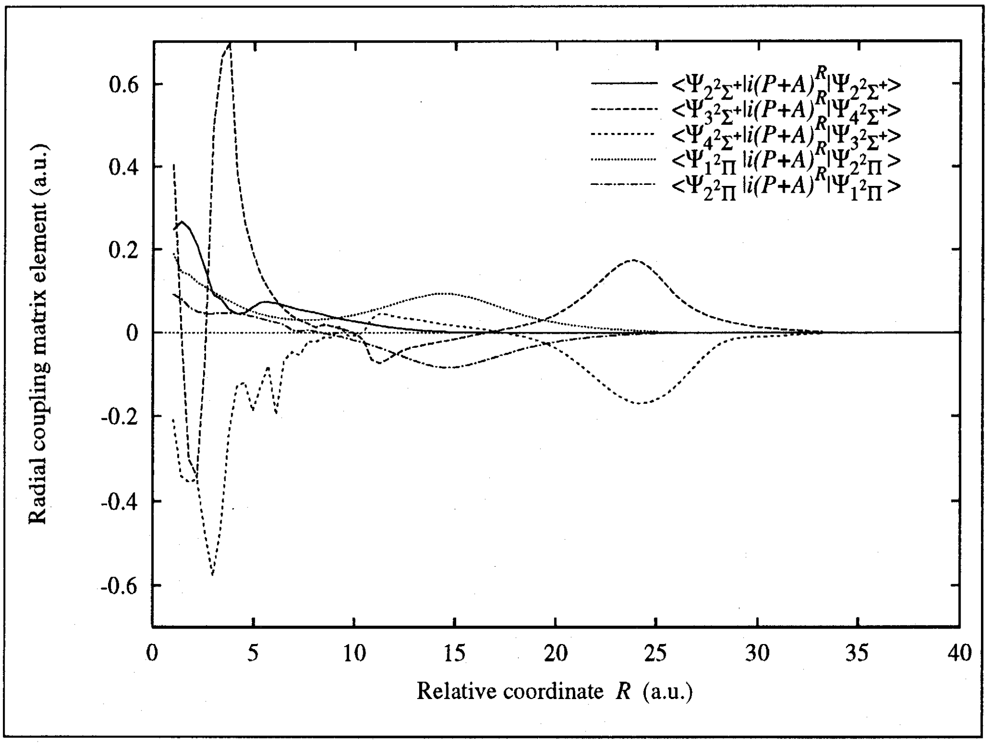

Figure 4: Radial coupling matrix elements.

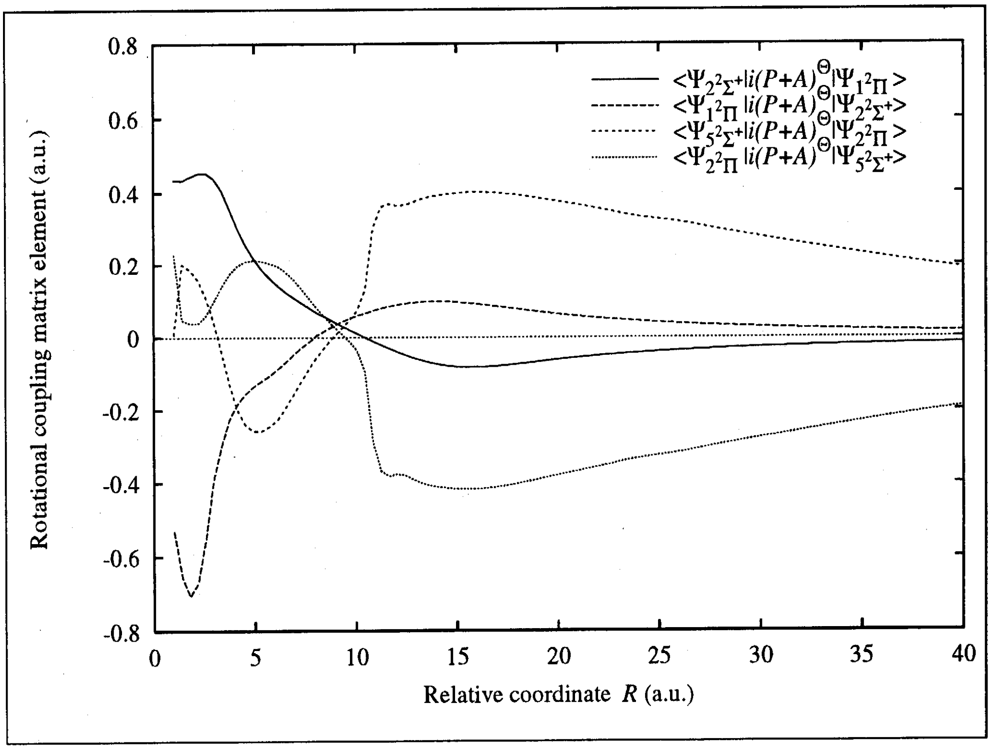

Figure 5: Rotational coupling matrix elements.

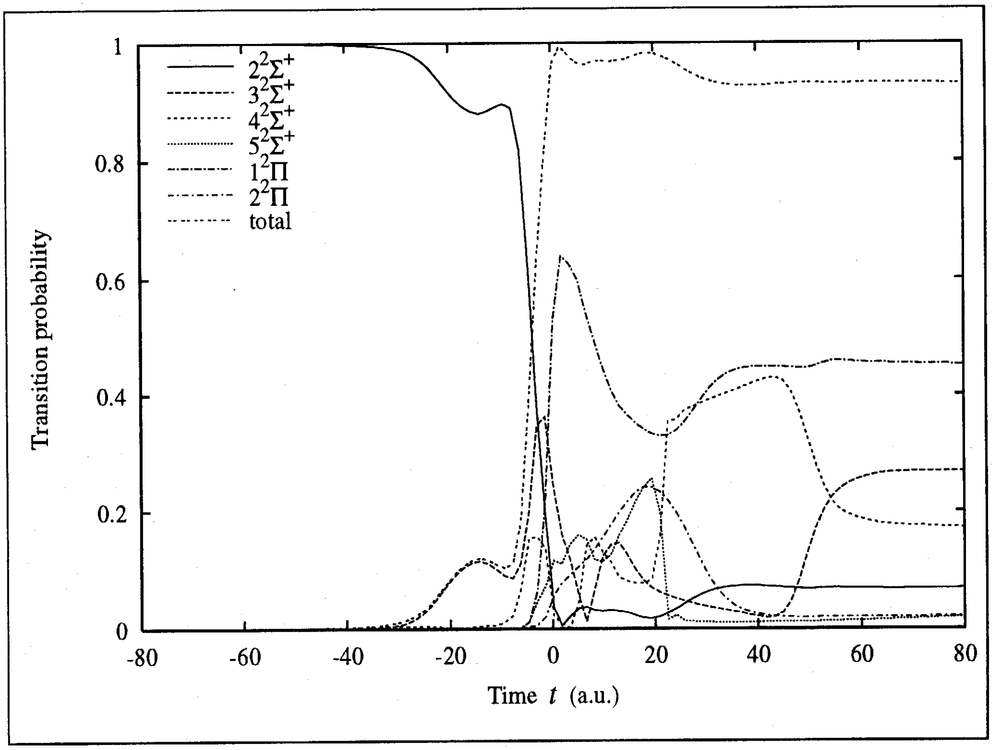

Figure 6: Transition probabilities, using method1 ($b = 1.0$ a.u.).

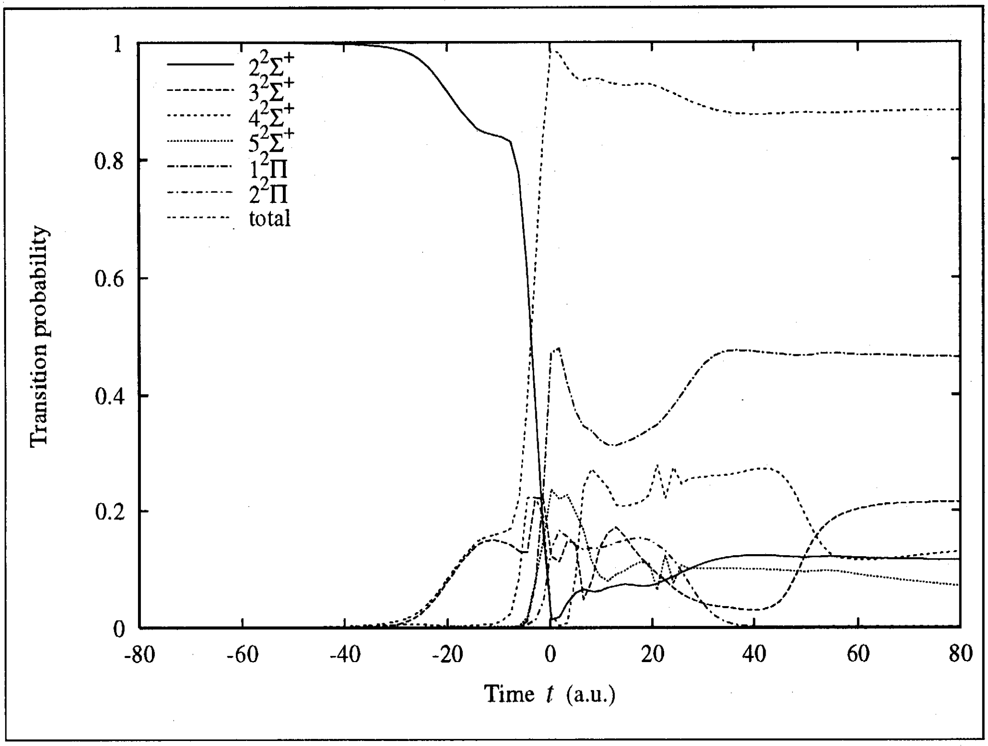

Figure 7: Transition probabilities, using method2 ($b = 1.0$ a.u.).

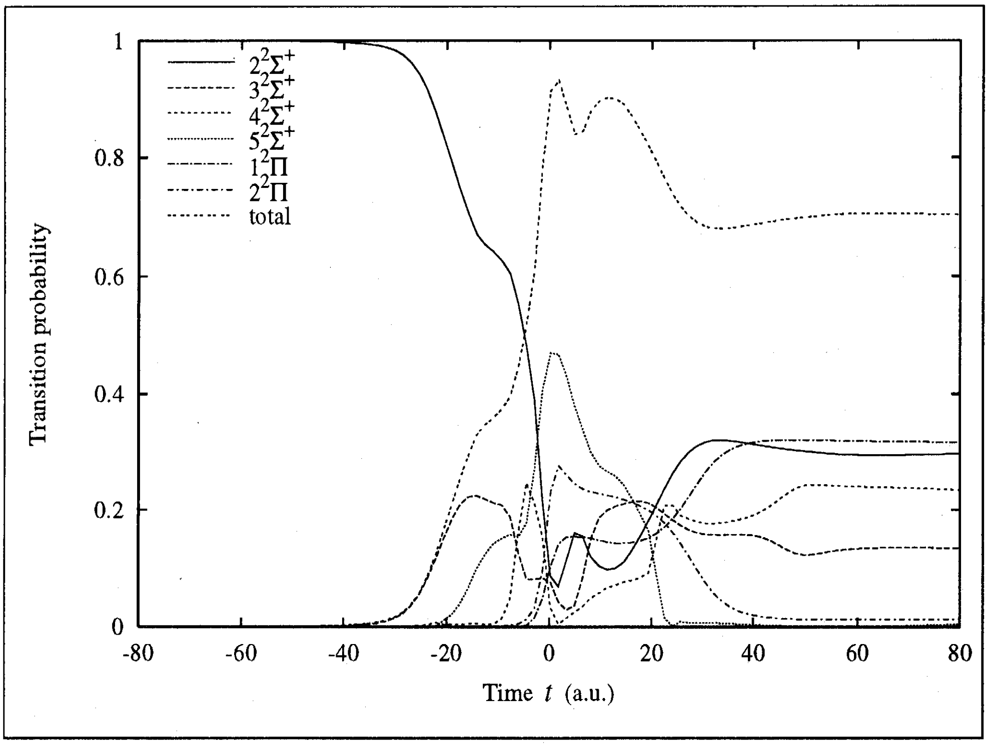

Figure 8: Transition probabilities, using method3 ($b = 1.0$ a.u.).

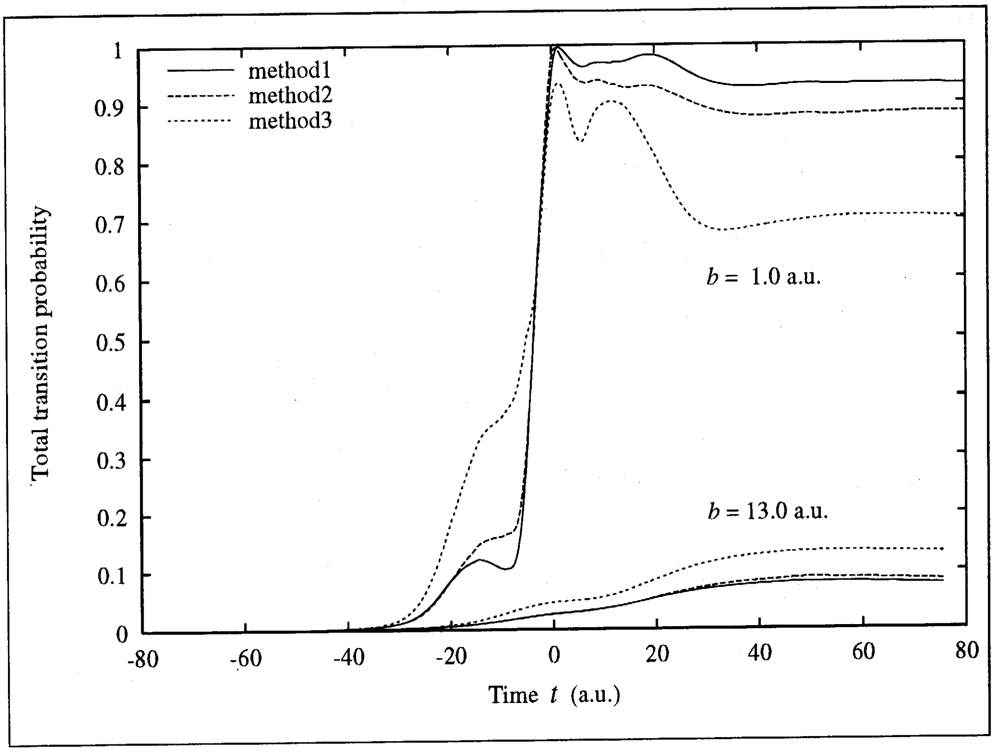

Figure 9: Total transition probabilities, using method1, method2, and method3.

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Appendix Overlap integral

Overlap integral for STO is calculated in this Appendix.

1. One center overlap integrals

$$< \chi_i^a|\chi_j^a >= \delta_{l_il_j}\delta_{m_im_j}N_iN_j\frac{(n_i+n_j)!}{(\alpha_i+\alpha_j)^{n_i+n_j+1}}, \tag{69}$$

where N is the normalization factor given by

$$N=\sqrt{\frac{(2\zeta)^{2n+1}}{(2n)!}}. \tag{70}$$

2. Two center overlap integrals

$$\begin{aligned} < \chi_i^a|\chi_j^b > &= N_iN_j\int r_a^{n_i-1}r_b^{n_j-1}\exp[-(\zeta_ir_a+\zeta_jr_b)] \\ &\quad \times Y^*_{l_im_i}(\theta_a,\phi_a)Y_{l_jm_j}(\theta_b,\phi_b)dv. \end{aligned} \tag{71}$$

Using elliptic coordinates

$$\begin{cases} \xi=\frac{r_a+r_b}{R} \\ \eta=\frac{r_a-r_b}{R} \\ \phi=\phi, \end{cases}$$

$$dv=(\frac{R}{2})^3(\xi^2-\eta^2)d\xi d\eta d\phi, \tag{72}$$

equation (71) can be written as follows

$$\begin{aligned} < \chi_i^a|\chi_j^b > &= N_iN_j\int_1^\infty\int_{-1}^1\int_0^{2\pi}(\frac{(\xi+\eta)R}{2})^{n_i-1}(\frac{(\xi-\eta)R}{2})^{n_j-1} \\ &\quad \times\exp[-(\zeta_i+\zeta_j)(\frac{R}{2})\xi-(\zeta_i-\zeta_j)(\frac{R}{2})\eta] \\ &\quad \times Y^*_{l_im_i}(\theta_a,\phi_a)Y_{l_jm_j}(\theta_b,\phi_b)(\frac{R}{2})^3(\xi^2-\eta^2)d\xi d\eta d\phi, \end{aligned} \tag{73}$$

and is expressed by using familiar functions

$$P_n(\zeta R)=\int_1^\infty\xi^n\exp[-\zeta R\xi]d\xi, \tag{74}$$

$$Q_n(\zeta R)=\int_{-1}^1\eta^n\exp[-\zeta R\eta]d\eta. \tag{75}$$

As for the following, we use P_n and Q_n instead of $P_n((\zeta_i+\zeta_j)R/2)$ and $Q_n((\zeta_i-\zeta_j)R/2)$ for simplicity.

$$< 1s|1s >=\frac{N_iN_j}{2}(\frac{R}{2})^3\{P_2Q_0-P_0Q_2\}$$

$$< 1s|2s >=\frac{N_iN_j}{2}(\frac{R}{2})^4\{P_3Q_0-P_2Q_1-P_1Q_2+P_0Q_3\}$$

$$< 1s|2p_0 >=\sqrt{3}\frac{N_iN_j}{2}(\frac{R}{2})^4\{P_3Q_1-P_2Q_0-P_1Q_3+P_0Q_2\}$$

$$< 1s|3s >=\frac{N_iN_j}{2}(\frac{R}{2})^5\{P_4Q_0-2P_3Q_1+2P_1Q_3-P_0Q_4\}$$

$$< 1s|3p_0 >= \sqrt{3}\frac{N_iN_j}{2}(\frac{R}{2})^5\{P_4Q_1 - P_3Q_0 - P_3Q_2 + P_2Q_1 - P_2Q_3 + P_1Q_2 + P_1Q_4 - P_0Q_3\}$$

$$< 1s|3d_0 >= \sqrt{5}\frac{N_iN_j}{4}(\frac{R}{2})^5\{-P_4Q_0 + 3P_4Q_2 - 4P_3Q_1 + 3P_2Q_0 - 3P_2Q_4 + 4P_1Q_3 - 3P_0Q_2 + P_0Q_4\}$$

$$< 1s|4s >= \frac{N_iN_j}{2}(\frac{R}{2})^6\{P_5Q_0 - 3P_4Q_1 + 2P_3Q_2 + 2P_2Q_3 - 3P_1Q_4 + P_0Q_5\}$$

$$< 2s|2s >= \frac{N_iN_j}{2}(\frac{R}{2})^5\{P_4Q_0 - 2P_2Q_2 + P_0Q_4\}$$

$$< 2s|2p_0 >= \sqrt{3}\frac{N_iN_j}{2}(\frac{R}{2})^5\{P_4Q_1 - P_3Q_0 + P_3Q_2 - P_2Q_1 - P_2Q_3 + P_1Q_2 - P_1Q_4 + P_0Q_3\}$$

$$< 2s|3s >= \frac{N_iN_j}{2}(\frac{R}{2})^6\{P_5Q_0 - P_4Q_1 - 2P_3Q_2 + 2P_2Q_3 + P_1Q_4 - P_0Q_5\}$$

$$< 2s|3p_0 >= \sqrt{3}\frac{N_iN_j}{2}(\frac{R}{2})^6\{P_5Q_1 - P_4Q_0 - 2P_3Q_3 + 2P_2Q_2 + P_1Q_5 - P_0Q_4\}$$

$$< 2s|3d_0 >= \sqrt{5}\frac{N_iN_j}{4}(\frac{R}{2})^6\{-P_5Q_0 + 3P_5Q_2 - 5P_4Q_1 + 3P_4Q_3 + 3P_3Q_0 - 4P_3Q_2 - 3P_3Q_4$$
$$+3P_2Q_1 + 4P_2Q_3 - 3P_2Q_5 - 3P_1Q_2 + 5P_1Q_4 - 3P_0Q_3 + P_0Q_5\}$$

$$< 2s|4s >= \frac{N_iN_j}{2}(\frac{R}{2})^7\{P_6Q_0 - 2P_5Q_1 - P_4Q_2 + 4P_3Q_3 - P_2Q_4 - 2P_1Q_5 + P_0Q_6\}$$

$$< 2p_0|2p_0 >= 3\frac{N_iN_j}{2}(\frac{R}{2})^5\{P_4Q_2 - P_2Q_0 - P_2Q_4 + P_0Q_2\}$$

$$< 2p_0|3s >= \sqrt{3}\frac{N_iN_j}{2}(\frac{R}{2})^6\{P_5Q_1 + P_4Q_0 - 2P_4Q_2 - 2P_3Q_1 + 2P_2Q_4 + 2P_1Q_3 - P_1Q_5 - P_0Q_4\}$$

$$< 2p_0|3p_0 >= 3\frac{N_iN_j}{2}(\frac{R}{2})^6\{P_5Q_2 - P_4Q_3 - P_3Q_0 - P_3Q_4 + P_2Q_1 + P_2Q_5 + P_1Q_2 - P_0Q_3\}$$

$$< 2p_0|3d_0 >= \sqrt{15}\frac{N_iN_j}{4}(\frac{R}{2})^6\{-P_5Q_1 + 3P_5Q_3 - P_4Q_0 - P_4Q_2 - P_3Q_1 - 3P_3Q_5 + 3P_2Q_0 + P_2Q_4$$
$$+P_1Q_3 + P_1Q_5 - 3P_0Q_2 + P_0Q_4\}$$

$$< 2p_0|4s >= \sqrt{3}\frac{N_iN_j}{2}(\frac{R}{2})^7\{P_6Q_1 - 3P_5Q_2 + 2P_4Q_3 + P_1Q_6 - 3P_2Q_5 + 2P_3Q_4$$
$$-3P_4Q_1 + 2P_2Q_3 + P_5Q_0 - 3P_1Q_4 + 2P_3Q_2 + P_0Q_5\}$$

$$< 2p_1|2p_1 >= 3\frac{N_iN_j}{4}(\frac{R}{2})^5\{P_4Q_0 - P_4Q_2 - P_2Q_0 + P_2Q_4 + P_0Q_2 - P_0Q_4\}$$

$$< 2p_1|3p_1 >= 3\frac{N_iN_j}{4}(\frac{R}{2})^6\{P_5Q_0 - P_4Q_1 - P_5Q_2 + P_4Q_3 - P_3Q_0 + P_3Q_4 + P_2Q_1 - P_2Q_5$$
$$+P_1Q_2 - P_1Q_4 - P_0Q_3 + P_0Q_5\}$$

$$< 2p_1|3d_1 >= 3\sqrt{5}\frac{N_iN_j}{4}(\frac{R}{2})^6\{P_5Q_1 - P_5Q_3 - P_4Q_0 + P_4Q_2 - P_3Q_1 + P_3Q_5 + P_2Q_0 - P_2Q_4$$
$$+P_1Q_3 - P_1Q_5 - P_0Q_2 + P_0Q_4\}$$

$$< 3s|3s >= \frac{N_iN_j}{2}(\frac{R}{2})^7\{P_6Q_0 - 3P_4Q_2 - P_0Q_6 + 3P_2Q_4\}$$

$$< 3s|3p_0 >= \sqrt{3}\frac{N_iN_j}{2}(\frac{R}{2})^7\{P_6Q_1 + P_5Q_2 - 2P_4Q_3 + 2P_3Q_2 + P_1Q_6 + P_2Q_5 - 2P_3Q_4 + 2P_2Q_3$$
$$-P_5Q_0 - P_4Q_1 - P_0Q_5 - P_1Q_4\}$$

$$< 3s|3d_0 >= \sqrt{5}\frac{N_iN_j}{4}(\frac{R}{2})^7\{3P_6Q_2 + 6P_5Q_3 - 9P_4Q_2 + 6P_3Q_1 - 3P_2Q_6 - 6P_3Q_5 + 9P_2Q_4 - 6P_1Q_3$$
$$-P_6Q_0 - 6P_5Q_1 + 3P_4Q_0 + P_0Q_6 + 6P_1Q_5 - 3P_0Q_4\}$$

$$< 3s|4s >= \frac{N_iN_j}{2}(\frac{R}{2})^8\{P_7Q_0 - P_6Q_1 - 3P_5Q_2 + 3P_4Q_3 + P_0Q_7 - P_1Q_6 - 3P_2Q_5 + 3P_3Q_4\}$$

$$< 3p_0|3p_0 >= 3\frac{N_iN_j}{2}(\frac{R}{2})^7\{P_6Q_2 + 2P_2Q_2 - P_4Q_0 + P_2Q_6 - 2P_4Q_4 - P_0Q_4\}$$

$$< 3p_0|3d_0 >= \sqrt{15}\frac{N_iN_j}{4}(\frac{R}{2})^7\{3P_6Q_3 + 3P_5Q_4 - 2P_5Q_2 - P_3Q_2 - 3P_3Q_6 - 3P_4Q_5 + 2P_2Q_5 + P_2Q_3$$
$$-P_6Q_1 - P_5Q_0 + 3P_3Q_0 + 3P_2Q_1 + P_1Q_6 + P_0Q_5 - 3P_0Q_3 - 3P_1Q_2$$
$$-P_4Q_3 + P_3Q_4 - 2P_4Q_1 + 2P_1Q_4\}$$

$$< 3p_0|4s >= \sqrt{3}\frac{N_iN_j}{2}(\frac{R}{2})^8\{P_7Q_1 - 2P_6Q_2 - P_5Q_3 + 4P_3Q_3 + P_1Q_7 - 2P_2Q_6 - P_3Q_5 + 4P_4Q_4$$
$$-2P_5Q_1 - P_4Q_2 + P_6Q_0 - 2P_1Q_5 - P_2Q_4 + P_0Q_6\}$$

$$< 3p_1|3p_1 >= 3\frac{N_iN_j}{4}(\frac{R}{2})^7\{-P_6Q_2 + 2P_2Q_2 - P_4Q_0 - P_2Q_6 + 2P_4Q_4$$
$$-P_0Q_4 + P_6Q_0 - P_4Q_2 + P_0Q_6 - P_2Q_4\}$$

$$< 3p_1|3d_1 >= 3\sqrt{5}\frac{N_iN_j}{4}(\frac{R}{2})^7\{P_6Q_3 + P_5Q_4 - 2P_5Q_2 + P_3Q_2 - P_3Q_6 - P_4Q_5 + 2P_2Q_5 - P_2Q_3$$
$$-P_6Q_1 + P_5Q_0 - P_3Q_0 - P_2Q_1 + P_1Q_6 - P_0Q_5 + P_0Q_3 + P_1Q_2$$
$$-P_4Q_3 + P_3Q_4 + 2P_4Q_1 - 2P_1Q_4\}$$

$$< 3d_0|3d_0 >= 5\frac{N_iN_j}{8}(\frac{R}{2})^7\{9P_6Q_4 - 6P_6Q_2 + P_6Q_0 + 3P_4Q_2 - 9P_4Q_6 + 6P_2Q_6 - P_0Q_6 - 3P_2Q_4$$
$$-6P_4Q_0 + 9P_2Q_0 - 9P_0Q_2 + 6P_0Q_4\}$$

$$< 3d_0|4s >= \sqrt{5}\frac{N_iN_j}{4}(\frac{R}{2})^8\{3P_7Q_2 - 9P_6Q_3 + 6P_5Q_4 + 9P_3Q_4 + 3P_2Q_7 - 9P_3Q_6 + 6P_4Q_5 + 9P_4Q_3$$
$$+7P_6Q_1 - 15P_5Q_2 - 9P_4Q_1 + 6P_3Q_2 + 7P_1Q_6 - 15P_2Q_5 - 9P_1Q_4 + 6P_2Q_3$$
$$+3P_5Q_0 + 3P_0Q_5 - P_7Q_0 - P_0Q_7\}$$

$$< 3d_1|3d_1 >= 15\frac{N_iN_j}{4}(\frac{R}{2})^7\{P_6Q_2 + P_2Q_0 - P_4Q_0 - P_6Q_4 - P_2Q_6 - P_0Q_2 + P_0Q_4 + P_4Q_6\}$$

$$< 3d_2|3d_2 >= 15\frac{N_iN_j}{16}(\frac{R}{2})^7\{-2P_6Q_2 + P_2Q_0 - 2P_4Q_0 + P_6Q_4 + 2P_2Q_6 - P_0Q_2 + 2P_0Q_4 - P_4Q_6$$
$$+3P_4Q_2 - P_0Q_6 - 3P_2Q_4 + P_6Q_0\}$$

$$< 4s|4s >= \frac{N_iN_j}{2}(\frac{R}{2})^9\{P_8Q_0 - 4P_6Q_2 + 6P_4Q_4 + P_0Q_8 - 4P_2Q_6\}$$