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**ASYMPTOTICALLY ADAPTED
ADIABATIC REPRESENTATION**

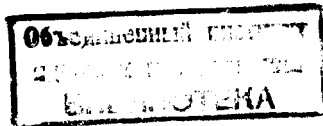
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1. INTRODUCTION

In this paper we consider the asymptotic properties of the atomic collision problem in the adiabatic representation defined by Smith (1970), though introduced much earlier and called the "perturbed stationary states" method (Mott and Massey, 1965). The derivation of the basic equation has been completed in a new and compact way which clarifies the geometric or kinematic nature of the unwanted long-range matrix elements lately discussed by Pack and Hirschfelder (1970), Thorson (1969) and Chen, et al. (1973). Another difficulty which appears in thus formulated stationary-state scattering theory is the fact that the asymptotic incoming and outgoing states are hardly identified in this representation (Mott and Massey, 1965, p. 428). See also the paper of Bates and McCarrol (1958) and Laue (1967). A common origin of both the difficulties was demonstrated by Matveenko and Ponomarev (1972).

The purpose of this paper is to formulate a procedure for passing smoothly from adiabatic representation in which the electronic motion is strongly coupled to the internuclear axis in the interaction region to an uncoupled description in the asymptotic region. This can be made with the help

of matrix transformations which are constructed to be inverse of the operator transformations used in introducing the adiabatic representation. Thus all nuclear-electronic cross derivatives and long-range matrix elements asymptotically disappear. Both the collision and the discrete spectrum problem can then be formulated for any diatomic system. For the sake of simplicity we shall consider the one-electron diatomic system only where the transformation matrices have been found explicitly. We shall not include the electron spin in the discussion.

2. ADIABATIC REPRESENTATION FOR ONE-ELECTRON DIATOMIC SYSTEM

We consider a system of two nuclei with masses m_1 and m_2 , electrical charges Z_1 and Z_2 , and an electron with mass denoted by m_3 and charge $-e$. Let $\vec{R}^{(1)}$, $\vec{R}^{(2)}$ and $\vec{R}^{(3)}$ be the coordinate vectors of the particles, then the usual coordinate transformation

$$\begin{aligned}\vec{R} &= (m_1 \vec{R}^{(1)} + m_2 \vec{R}^{(2)} + m_3 \vec{R}^{(3)}) / M_1, \\ \vec{r} &= \vec{R}^{(3)} - (m_1 \vec{R}^{(1)} + m_2 \vec{R}^{(2)}) / (m_1 + m_2), \\ \vec{R} &= \vec{R}^{(2)} - \vec{R}^{(1)}; \quad M_1 = m_1 + m_2 + m_3\end{aligned}\quad (1)$$

will enable us to separate the motion of the CM of the system and will give the internal Hamiltonian of the form

$$H = -\frac{1}{2M} \Delta_{\vec{R}} + \frac{Z_1 Z_2}{R} + H_0 \quad (2)$$

$$H_0 = -\frac{1}{2m} \Delta_{\vec{r}} - \frac{Z_1}{r_1} - \frac{Z_2}{r_2} \quad (2a)$$

and the Schrodinger CM equation

$$H \Psi(\vec{R}, \vec{r}) = E \Psi(\vec{R}, \vec{r}). \quad (3)$$

Here we put $\hbar = e = 1$ and introduce the notation

$$\begin{aligned}1/M &= 1/m_1 + 1/m_2, \quad 1/m = 1/m_3 + 1/(m_1 + m_2) \\ \vec{r}_1 &= \vec{R}^{(1)} - \vec{R}^{(3)}, \quad \vec{r}_2 = \vec{R}^{(2)} - \vec{R}^{(3)}\end{aligned}\quad (2b)$$

Next we use spherical polar coordinates R, Θ, Φ for the internuclear vector \vec{R} , then as usual

$$\begin{aligned}H &= -\frac{1}{2M} \left(\frac{1}{R} + \frac{\partial}{\partial R} \right)^2 - \frac{1}{2MR^2} \left\{ \frac{1}{\sin \Theta} \frac{\partial}{\partial \Theta} \left(\sin \Theta \frac{\partial}{\partial \Theta} \right) + \frac{\partial^2}{\partial \Phi^2} \right\} \\ &+ \frac{Z_1 Z_2}{R} + H_0\end{aligned}\quad (4)$$

and transform the electronic coordinates to the "body-fixed" coordinate system with the help of the rotation

$$D(\Phi, \Theta, 0) = e^{i\Phi l_z} e^{i\Theta l_y} \quad (5)$$

In this received representation the Schrodinger equation will read

$$\bar{H} \bar{\Psi}(\vec{R}, \vec{r}) = E \bar{\Psi}(\vec{R}, \vec{r}) \quad (6)$$

with the new Hamiltonian \bar{H} and wave function $\bar{\Psi}$ given by

$$\bar{H} = D^{-1} H D, \quad (6a)$$

$$\bar{\Psi} = D^{-1} \Psi. \quad (6b)$$

To clarify and compare it will be useful here to consult the paper of Hirooka and Sunakava (1974). Then it follows from (4) and (5) that the effect of the transformation is reduced to the substitutions in Hamiltonian (4) the transformed partial derivatives

$$D^{-1} \frac{\partial}{\partial \Theta} D = \frac{\partial}{\partial \Theta} - i l_y, \quad (7)$$

$$D^{-1} \frac{\partial}{\partial \Phi} D = \frac{\partial}{\partial \Phi} - i(l_z \cos \Theta - l_x \sin \Theta). \quad (8)$$

At this step the origin of the electronic coordinates is taken to be the CM of the nuclei. In order to use the prolate spheroidal coordinates for the electronic motion the transformation to the "geometric center of the nuclei" electronic coordinates should be accomplished. This will be done by a further change of the representation

$$\tilde{H} \tilde{\Psi}(\vec{R}, \vec{r}) = E \tilde{\Psi}(\vec{R}, \vec{r}), \quad (9)$$

$$\tilde{H} = T^{-1} \bar{H} T, \quad (9a)$$

$$\tilde{\Psi} = T^{-1} \bar{\Psi}, \quad (9b)$$

with the operator of finite translation

$$T = e^{-i\kappa \frac{R}{2} p_z}, \quad \kappa = \frac{m_2 - m_1}{m_2 + m_1}. \quad (10)$$

This transformation will produce the substitutions in \bar{H}

$$T^{-1} l_x T = l_x - \kappa \frac{R}{2} p_y, \quad (11a)$$

$$T^{-1} l_y T = l_y + \kappa \frac{R}{2} p_x, \quad (11b)$$

$$T^{-1} \frac{\partial}{\partial R} T = \frac{\partial}{\partial R} - i \frac{\kappa}{2} p_z. \quad (11c)$$

One more substitution is induced by the transformation from the "geometric center of nuclei" rectangular coordinates to the prolate spheroidal coordinates ξ, η, ϕ

$$x = \frac{R}{2} \sqrt{(\xi^2 - 1)(1 - \eta^2)} \cos \phi$$

$$y = \frac{R}{2} \sqrt{(\xi^2 - 1)(1 - \eta^2)} \sin \phi \quad (12)$$

$$z = \frac{R}{2} \xi \eta$$

and leads to the change

$$\frac{\partial}{\partial R} \rightarrow \frac{\partial}{\partial R} + \hat{c}, \quad (13)$$

where

$$\hat{c} = \frac{1}{R(\xi^2 - \eta^2)} \left\{ \xi(\xi^2 - 1) \frac{\partial}{\partial \xi} + \eta(1 - \eta^2) \frac{\partial}{\partial \eta} \right\}. \quad (14)$$

Thus we receive the transformed CM diatomic Hamiltonian

$$H_T = -\frac{1}{2M} \left(\frac{1}{R} + \frac{\partial}{\partial R} + \hat{c} - i \frac{\kappa}{2} p_z \right)^2$$

$$- \frac{1}{2MR^2} \left[\frac{1}{\sin \Theta} \left\{ \frac{\partial}{\partial \Theta} - i \left(l_y + \frac{\kappa R}{2} p_x \right) \right\} \sin \Theta \left\{ \frac{\partial}{\partial \Theta} - i \left(l_y + \frac{\kappa R}{2} p_x \right) \right\} \right.$$

$$\left. + \left\{ \frac{\partial}{\partial \Phi} - i \left(l_z \cos \Theta - \left(l_x - \frac{\kappa R}{2} p_y \right) \sin \Theta \right) \right\}^2 \right] \quad (15)$$

$$+ H_0 + \frac{Z_1 Z_2}{R}$$

and the Schrödinger equation

$$H_T \Psi_T(\vec{R}, \vec{r}) = E \Psi_T(\vec{R}, \vec{r}). \quad (16)$$

The equation of this type was first derived in the early work of Van Vleck (1929) and Kronig (1930), and since that time was reproduced by many authors. The forms of the unitary transformation operators (5) and (10) were chosen to make the Hamiltonian (15) coincide with that of Vinitzkij and Ponomarev (1974). We consider the derivation of H_T presented here to be the simplest available because of its pure geometric or kinematic nature. Various authors partitioned the Hamiltonian (15) in different ways. For our purpose we shall use its original form.

The adiabatic representation for the Schrodinger problem (16) with Hamiltonian (15) is introduced by an expansion of the wave function in the form

$$\Psi_T(\vec{R}, \vec{r}) = \sum_a \Psi_a^{(1)}(\vec{R}) \phi_a^{(1)}(\vec{r}; \vec{R}) + \sum_\beta \Psi_\beta^{(2)}(\vec{R}) \phi_\beta^{(2)}(\vec{r}; \vec{R}). \quad (17)$$

where $\phi_a^{(1)}(\vec{r}; \vec{R})$ and $\phi_\beta^{(2)}(\vec{r}; \vec{R})$ are the solutions of the fixed nuclei two-center problem in quantum mechanics

$$H_0 \phi_a^{(i)}(\vec{r}; \vec{R}) = E_a^{(i)}(\vec{R}) \phi_a^{(i)}(\vec{r}; \vec{R}). \quad (18)$$

Two summations in (17) represent two types of solutions of equation (18) which account for the electron forming either $Z_1 e + Z_2$ or $Z_2 e + Z_1$ system in the limit of large R . For references on the solution of equation (18) the paper of Power (1973) can be consulted.

The substitution of (17) in the equation (16) with further integration over electronic coordinates converts the equation (16) into the system of equations for $\Psi_a^{(i)}(\vec{R})$.

The matrix elements forming this system can be calculated (Ponomarev and Puzynina, 1970). This makes the problem (15), (16), to be of practical value. Here is worthwhile to mention that three coordinate transformations, namely, those given by (5), (10) and (12) had been accomplished beginning from the center of mass Hamiltonian (2) and arriving at the problem (15), (16).

3. ASYMPTOTICALLY ADAPTED ADIABATIC REPRESENTATION

We shall write the system of equations in the adiabatic representation in the form

$$H_{\ell k}^{(i)} \Psi_k^{(i)}(\vec{R}) = E \Psi_k^{(i)}(\vec{R}), \quad (19)$$

where

$$\begin{aligned} H_{\ell k}^{(i)} = & -\frac{1}{2M} \left\{ \left\langle \frac{\partial}{\partial R} \right\rangle + \frac{1}{R} \right\}^2 \delta_{\ell k} \\ & - \frac{1}{2MR^2} \left\{ \frac{1}{\sin \Theta} \left\langle \frac{\partial}{\partial \Theta} \right\rangle \sin \Theta \left\langle \frac{\partial}{\partial \Theta} \right\rangle - \frac{1}{\sin^2 \Theta} \left\langle \frac{\partial}{\partial \Phi} \right\rangle^2 \right\} \delta_{\ell k} \\ & + \left\{ \frac{Z_1 Z_2}{R} + E_{\ell}^{(i)}(\vec{R}) \right\} \delta_{\ell k} \end{aligned}$$

with matrices

$$\begin{aligned} \left\langle \frac{\partial}{\partial R} \right\rangle &= \frac{\partial}{\partial R} + \left\langle \hat{c} - i \frac{\kappa}{2} p_z \right\rangle \\ \left\langle \frac{\partial}{\partial \Theta} \right\rangle &= \frac{\partial}{\partial \Theta} - i \left\langle l_y + \frac{\kappa}{2} R p_y \right\rangle \end{aligned} \quad (20)$$

$$\left\langle \frac{\partial}{\partial \Phi} \right\rangle = \frac{\partial}{\partial \Phi} - i \langle l_z \cos \Theta - \sin \Theta (l_x - \frac{\kappa}{2} R p_y) \rangle. \quad (20)$$

We have not so far made approximations in our analysis that is why the system (19) in the $R \rightarrow \infty$ limit should account for an experimental situation of the atom $Z_1 e$ colliding with nucleus Z_2 and also for the $Z_2 e + Z_1$ case. It is absolutely clear that the coordinate system in which Hamiltonian $H_{lk}^{(i)}$ has been written down is kinematically inconvenient to represent these asymptotic states. Earlier we had shown in a simple case that in order to receive the correct electronic energy in the limit of $R \rightarrow \infty$ the transformation of the adiabatic representation is required (Matveenko and Ponomarev, 1972). Now we shall try to simplify system (19), the main goal being to diagonalize the operator of kinetic energy in the $R \rightarrow \infty$ limit.

At large nuclear separation the matrix $H_{lk}^{(i)}$ degenerates into the two-component form due to a different asymptotic character of the two subsets $\phi_a^{(1)}(\vec{r}; \infty)$ and $\phi_\beta^{(2)}(\vec{r}; \infty)$ of the two-center basis. We then have

$$H_{R \rightarrow \infty} \rightarrow \begin{pmatrix} H^{(1)} & 0 \\ 0 & H^{(2)} \end{pmatrix} \quad (21)$$

with

$$H_{kl}^{(i)} = -\frac{1}{2M} \left\{ \left(\frac{\partial}{\partial R} - i \frac{\kappa \pm 1}{2} \langle p_z^{(i)} \rangle_\infty \right)^2 \right\}_{kl} - \frac{1}{2MR^2} \left\{ \frac{1}{\sin \Theta} \left\langle \frac{\partial}{\partial \Theta} \right\rangle_\infty^{(i)} \sin \Theta \left\langle \frac{\partial}{\partial \Theta} \right\rangle_\infty^{(i)} + \frac{1}{\sin^2 \Theta} \left(\left\langle -\frac{\partial}{\partial \Phi} \right\rangle_\infty^{(i)} \right)^2 \right\}_{kl} + E_k^{(i)}(\infty) \delta_{kl}$$

and the Schrodinger system becomes in this limit

$$\begin{bmatrix} H^{(1)} & 0 \\ 0 & H^{(2)} \end{bmatrix} \begin{bmatrix} \Psi^{(1)} \\ \Psi^{(2)} \end{bmatrix} = E \begin{bmatrix} \Psi^{(1)} \\ \Psi^{(2)} \end{bmatrix}. \quad (23)$$

In the asymptotic form (22) the use is made of the fact that

$$\begin{aligned} \langle \hat{c} \rangle_{R \rightarrow \infty} &\rightarrow -i \frac{1}{2} \langle p_z^{(1)} \rangle_\infty, \quad i=1 \\ &i \frac{1}{2} \langle p_z^{(2)} \rangle_\infty, \quad i=2. \end{aligned} \quad (24)$$

Thus we can see that in the adiabatic representation the scattering and the rearrangement channels can be treated separately in the asymptotic region (Matveenko and Ponomarev, 1972), (Chen, Ponce and Watson, 1973) in agreement with the fact that, in general, different coordinate systems are required for the direct and rearrangement channels (see §5 for a discussion).

The matrices which form the asymptotic Hamiltonian (22) arise from the operators (20) calculated at infinite nuclear separation. It is a well known fact that they have non-zero matrix elements in the $R \rightarrow \infty$ limit. These matrix elements become dominant in the asymptotic region though they have nothing in common with the real interaction as they are only the artificial products of the nuclear kinetic energy operator transformed to the new coordinate system. To get rid of them we form the matrix

$$\hat{A} = D_\infty T_\infty \quad (25)$$

with D_∞ and T_∞ given by

$$T_\infty = T_1^{(\pm)} T_\kappa = \begin{bmatrix} T_1^{(+)} & 0 \\ 0 & T_1^{(-)} \end{bmatrix} \begin{bmatrix} T_\kappa^{(1)} & 0 \\ 0 & T_\kappa^{(2)} \end{bmatrix}, \quad (26)$$

where

$$T_\kappa^{(i)} = e^{i\kappa \frac{R}{2} \langle p_z^{(i)} \rangle_\infty} \quad (27a)$$

$$T_1^{(\pm)} = e^{\pm i \frac{R}{2} \langle p_z^{(i)} \rangle_\infty} \quad (27b)$$

and

$$D_\infty = \begin{bmatrix} D^{(1)} & 0 \\ 0 & D^{(2)} \end{bmatrix}, \quad (28)$$

where

$$D^{(i)} = e^{i\Theta \langle l_y^{(i)} \rangle_\infty} e^{i\Phi \langle l_z^{(i)} \rangle_\infty} \quad (29)$$

To apply this transformation to the adiabatic set of equations (19) we first note that

$$T_\kappa^{-1} \left\langle \frac{\partial}{\partial \Theta} \right\rangle T_\kappa = \frac{\partial}{\partial \Theta} - i T_\kappa^{-1} \langle l_y + \frac{\kappa R}{2} p_x \rangle T_\kappa \xrightarrow{R \rightarrow \infty} \frac{\partial}{\partial \Theta} - i \langle l_y^{(i)} \rangle_\infty \quad (30)$$

$$T_\kappa^{-1} \left\langle \frac{\partial}{\partial \Phi} \right\rangle T_\kappa = \frac{\partial}{\partial \Phi} - i T_\kappa^{-1} \langle l_z \cos \Theta - \sin \Theta (l_x - \frac{\kappa R}{2} p_y) \rangle T_\kappa$$

$$\xrightarrow{R \rightarrow \infty} \frac{\partial}{\partial \Phi} - i \langle l_z \cos \Theta - l_x \sin \Theta \rangle_\infty^{(i)}; \quad i=1,2 \quad (30a)$$

The transformation $T_1^{(\pm)}$ is introduced to get rid of the asymptotic value of the operator \hat{c} (24). It will not influence the $R \rightarrow \infty$ limits of (30) and (30a) because, as it will be shown, in this limit $T_1^{(\pm)}$ becomes the unity matrix. The effect of the total A-transformation on the operators $\langle \frac{\partial}{\partial \Theta} \rangle$ and $\langle \frac{\partial}{\partial \Phi} \rangle$ then will be

$$D_\infty^{-1} T_\infty^{-1} \left\langle \frac{\partial}{\partial \Theta} \right\rangle T_\infty D_\infty \xrightarrow{R \rightarrow \infty} \frac{\partial}{\partial \Theta}, \quad (31)$$

$$D_\infty^{-1} T_\infty^{-1} \left\langle \frac{\partial}{\partial \Phi} \right\rangle T_\infty D_\infty \xrightarrow{R \rightarrow \infty} \frac{\partial}{\partial \Phi}, \quad (31a)$$

as it should be because we constructed the transformation A to be inverse of the operator transformations used in introducing the adiabatic representation.

Thus when the system of equations (19) is transformed into

$$\hat{H} \hat{\Psi}(\mathbf{R}) = E \hat{\Psi}(\mathbf{R}), \quad (32)$$

with \hat{H} and $\hat{\Psi}(\mathbf{R})$ given by

$$\hat{H} = A^{-1} H A \quad (33a)$$

$$\hat{\Psi} = A^{-1} \Psi \quad (33b)$$

then the new Hamiltonian (33a), as it follows from (30) and (31), is reduced in the $R \rightarrow \infty$ limit to

$$\hat{H}^{(i)}(\infty) = -\frac{1}{2M} \left(\frac{\partial}{\partial R} + \frac{1}{R} \right)^2$$

$$-\frac{1}{2MR^2} \left\{ \frac{1}{\sin \Theta} \frac{\partial}{\partial \Theta} \left(\sin \Theta \frac{\partial}{\partial \Theta} \right) + \frac{1}{\sin^2 \Theta} \frac{\partial^2}{\partial \Phi^2} \right\} + A^{-1}(\infty) E^{(i)}(\infty) A(\infty), \quad i=1,2. \quad (34)$$

The transformed adiabatic representation (32) with Hamiltonian (33a) whose asymptotic form is given by formula (34) we shall call the asymptotically adapted adiabatic representation. The asymptotic Hamiltonian (34) is much simpler of that given by (22) but the "potential energy" matrix becomes to be a function of the orientation angles of the nuclear axis. This accounts for the fact that in the decomposition of the total wave function we used the two-center basis which was naturally quantized with respect to the nuclear axis, and tried to represent in this way the collision problem with the atomic states quantized with respect to an axis fixed in space (Mott and Massey, 1965, p. 435).

4. TRANSFORMATION MATRICES

As $R \rightarrow \infty$ the prolate spheroidal coordinates turn into the parabolic coordinates λ_i, μ_i, ϕ ($i=1,2$)

$$\begin{aligned} \xi &\rightarrow 1 + \lambda_1/R & \text{or} & \quad 1 + \lambda_2/R \\ \eta &\rightarrow -1 + \mu_1/R & \text{or} & \quad 1 - \mu_2/R \end{aligned} \quad (35)$$

and the solutions of the two-center problem (8) become hydrogen atom type parabolic wave functions $\phi_{n_1 n_2 m}^{(1)}(\vec{r}_1; \infty)$ and $\phi_{n_1 n_2 m}^{(2)}(\vec{r}_2; \infty)$ (Power, 1973). Thus we need the matrix ele-

ments of finite rotation

$$D_{\alpha\beta}^{(i)} = \langle \beta | e^{i\Theta \ell_y} e^{i\Phi \ell_z} | \alpha \rangle \quad (36)$$

and those of finite translation

$$T_{\alpha\beta}^a = \langle \beta | e^{i a p_z} | \alpha \rangle \quad (37)$$

between parabolic states. The first of them are found from

$$\begin{aligned} &\langle n'_1 n'_2 m' | e^{i\Theta \ell_y} e^{i\Phi \ell_z} | n_1 n_2 m \rangle \\ &= D_{m_1 m'_1}^{(n-1)/2}(0, -\Theta, -\Phi) D_{m_2 m'_2}^{(n-1)/2}(0, -\Theta, -\Phi) \end{aligned} \quad (38)$$

where (Hughes, 1967)

$$\phi_{n_1 n_2 m}(\vec{r}; \infty) = (-1)^{(2n_2 + |m| - m)/2} |n_1 n_2 m \rangle \quad (39)$$

Here n_1, n_2, m are parabolic quantum numbers and $n = n_1 + n_2 + |m| + 1$ is the principal quantum number; $m_1 = 1/2(m + n_2 - n_1)$, $m_2 = 1/2(m + n_1 - n_2)$. As an interesting example of matrix elements (38) used for a collision problem of the type considered here the paper by Ostrovsky and Soloviev (1974) should be noted.

An explicit form of matrix (37) can also be found. Let us write the Schrodinger equation for the hydrogen atom

$$\left(-\frac{1}{2m} \Delta_{\vec{r}} - \frac{q}{r} \right) \phi(\vec{r}) = E \phi(\vec{r}) \quad (40)$$

then for the transformed function $\phi^{(a)} = e^{-i a p_z} \phi$ we receive

$$\left(-\frac{1}{2m} \Delta_{\vec{r}} - \frac{q}{r_1} \right) \phi^{(a)}(\vec{r}) = E \phi^{(a)}(\vec{r}) \quad (41)$$

with $r_1^2 = x^2 + y^2 + (z-a)^2$. But the solutions of (41) are the well known spheroidal hydrogen atom wave functions. Thus the matrix elements of the finite translation are the coefficients of the expansion

$$\psi_{nkm}^{(a)} = \sum C_{kn}^{n_1 n_2}(-a) \phi_{n_1 n_2 m} \quad (42)$$

As it follows from $R \rightarrow \infty$ equalities (35) the matrix $C_{kn}^{n_1 n_2}(\infty)$ becomes a unity matrix, the result already used by us. The way in which matrix $C_{kn}^{n_1 n_2}(a)$ can be computed is outlined by Coulson and Joseph (1966). To apply their results directly the matrix transformation connecting the parabolic (Stark) and the polar coordinates hydrogen atom wave functions should be used (Kulkarni, 1972).

Thus matrix $A(25)$ which transforms the system of adiabatic equations (19) to that of asymptotically adapted adiabatic equations with asymptotic Hamiltonian given by (33) can be constructed. This matrix consists of two sets of submatrices of finite order. Every submatrix is operating within the manifold of asymptotically degenerate states. For R finite the matrix A is a function of internuclear coordinates $A = A(R, \Theta, \Phi)$ and in the $R \rightarrow \infty$ limit its dependence on R vanishes.

5. TRANSLATIONAL FACTORS

The appropriate CM variables for the scattering channels of the process $Z_1 e + Z_2 \rightarrow Z_2 e + Z_1$ consisting of an incident nucleus Z_2 and an electron bounded on nucleus Z_1 , are (\vec{r}_1, \vec{R}_1) .

Here \vec{r}_1 is the position vector of the electron with respect to nucleus Z_1 and \vec{R}_1 is the position vector of nucleus Z_2 with respect to the CM of the atom $Z_1 e$. For the rearrangement channels the appropriate coordinates are (\vec{r}_2, \vec{R}_2) . Here \vec{r}_2 is the position vector of the electron with respect to nucleus Z_2 and \vec{R}_2 is the position vector of nucleus Z_1 with respect to the CM of the atom $Z_2 e$.

In this paper we have begun with the independent CM variables (\vec{r}, \vec{R}) with \vec{r} being the position vector of the electron with respect to the CM of the nuclei and \vec{R} being the internuclear vector. Translational factors should then be introduced in transforming the equations from the (\vec{r}, \vec{R}) coordinates to the (\vec{r}_1, \vec{R}_1) coordinates for the scattering channels and from the (\vec{r}, \vec{R}) coordinates to the (\vec{r}_2, \vec{R}_2) coordinates for the rearrangement channels. To that end we consider two unitary transformations

$$T_1 = e^{\beta_1 \vec{r}_1 \nabla_{\vec{R}} + \alpha_1 \vec{R} \nabla_{\vec{r}}} \quad (43)$$

with $\alpha_1 = m_2 / (m_1 + m_2)$ and $\beta_1 = -m_3 / (m_1 + m_3)$ and

$$T_2 = e^{\beta_2 \vec{r}_2 \nabla_{\vec{R}} + \alpha_2 \vec{R} \nabla_{\vec{r}}} \quad (44)$$

with $\alpha_2 = -m_1 / (m_1 + m_2)$ and $\beta_2 = m_3 / (m_2 + m_3)$.

It is easy to verify that T_1 and T_2 operators do effect the necessary coordinate transformations

$$\begin{aligned} T_i \vec{r} T_i^{-1} &= \vec{r}_i \\ T_i \vec{R} T_i^{-1} &= \vec{R}_i \end{aligned} \quad (45)$$

The transformed center of mass wave functions will be given by

$$\Psi^{(1)}(\vec{r}_1, \vec{R}_1) = T_1 \Psi(\vec{r}, \vec{R}) \quad (46)$$

and

$$\Psi^{(2)}(\vec{r}_2, \vec{R}_2) = T_2 \Psi(\vec{r}, \vec{R}). \quad (47)$$

Thus operators (43) and (44) are nothing else but the explicit forms of the translational factors. Since no mention of this fact had been made till now (Mott and Massey, 1965, p. 428), (Chen, Ponce and Watson, 1973) it appears to the author that the operator form of the translational factor had not been appreciated adequately.

When the adiabatic state expansion (17) is introduced the translational factor operators become matrices. It is an interesting fact that the effect of matrix transformation (25), which produces the translation between the adiabatic and asymptotically adapted adiabatic representations, is partially that of translational factors operator transformation. Indeed as it follows from (26) and (27) the operator

$$\vec{T}_1^{(+)} \vec{T}_\kappa = e^{i \frac{\kappa+1}{2} R \langle p_z^{(1)} \rangle_\infty} \quad (48)$$

with $(\kappa+1)/2 = m_2/(m_1+m_2)$ effects $\vec{r} \rightarrow \vec{r}_1$ transformation and the operator

$$\vec{T}_1^{(-)} \vec{T}_\kappa = e^{i \frac{\kappa-1}{2} R \langle p_z^{(2)} \rangle_\infty} \quad (49)$$

with $(\kappa-1)/2 = -m_1/(m_1+m_2)$ effects $\vec{r} \rightarrow \vec{r}_2$ transformation in the $R \rightarrow \infty$ limit. Thus a different kinematic nature of two subspaces of

the two-center problem solutions (17) can be exploited, as was already shown by Matveenko and Ponomarev (1972) and by Chen, Ponce and Watson (1973).

6. CONCLUSION

The system of equations of the adiabatic representation (19) has been transformed to that of the asymptotically adapted adiabatic representation. This new representation, is constructed in such a way that the kinetic energy operator $-\frac{1}{2M} \Delta_{\vec{R}}$ becomes diagonal as internuclear distance R tends to infinity. While producing the transformation to the new representation one can see that all asymptotically degenerate states are strongly coupled even in the $R \rightarrow \infty$ limit. This circumstance indicates a minimal dimension of the matrix Schrodinger system to be solved for a given collision process.

The asymptotic form of the new Hamiltonian (34) implies that radial and angular parts of the wave function $\Psi(\vec{R})$ should be separated by substituting

$$\hat{\Psi}(\vec{R}) = \chi(R) Y_{LM}(\Theta, \Phi)/R.$$

The further integration over angular variables will produce the system of radial equations which will be still coupled in the $R \rightarrow \infty$ limit. The direct diagonalization of this radial asymptotic Hamiltonian will lead to the asymptotically uncoupled system of equations (clarify with Matveenko and Ponomarev, 1972). As the asymptotically free description is possible only in the (\vec{r}_1, \vec{R}_1) and (or) (\vec{r}_2, \vec{R}_2) CM coordinate sys-

tems this last transformation will approximately account for the translational factor operators (43) and (44) transformations.

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