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ELEMENTARY CHEMICAL REACTION AS A QUANTUM THREE BODY PROBLEM

(This is the 4th lecture)

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NOTES ON THE ELEMENTARY CHEMICAL REACTION AS A
QUANTUM THREE BODY PROBLEM

To study features which are definitely associated with purely kinematic effects or with general characteristics of the Potential Energy Surface (PES), it has been necessary in recent years to reconsider the elementary reactive act as a rearrangement problem in quantum (or classical, or semi-classical) mechanics. This will enable one to efficiently answer the complicated question of how to deal with rotations and eventually to reduce the full problem to an understanding of the relative importance of vibrational and kinetic energy.

Earlier there have been extensive computations which have been carried out on the dynamics of the reactions of type A+BC. They were founded either on classical or quantum mechanics and are to be considered either "exact" or involving more or less drastic approximations based either in the real 3D world, and in somewhat artificial spaces of lower dimension. Now we shall attempt to understand the 3 body problem as a rearrangement process.

a) Coordinates for Rearrangement Processes:

The main difficulty which arises in understanding the interplay of the various factors which influence a reaction is that both the description of reactants and of products are bound to fail somewhere in the course of a reaction, and it is necessary to perform a trasformation whose nature and characteristics are hardly understood, although some formal progress has been made recently. To be specific, we recall that there are basically three differrent definitions of the Jacobi vectors, which describe the motion of three particles in a frame where the conservation of the centre of mass is exploited (Fig. 1). In terms of them the quantum mechanical problem requires solution of the equation:

$$\left[\frac{h^2}{2\mu_{k,ij}}\left(\frac{1}{R^k_0}\,\frac{\partial}{\partial R_0{}^k}\,R_0{}^k\,\frac{\partial}{\partial R^k_0}-\frac{\underline{l}^2{}_k}{(R_0{}^k)^2}\right)+\right.$$

$$\left.\frac{h^2}{2\mu_{ij}}\left(\frac{1}{r^k_0}\,\frac{\partial}{\partial r^k_0}\,r_0{}^k-\frac{\underline{j}^2{}_k}{\left(r^k_0\right)^2}\right)-V\,(R_0{}^k,\ r_0{}^k,\ \gamma_k)+E\right]\Psi=0$$

(1)

Here (k,i,j) are any permutation of 1,2 and 3, and μs are reduced masses, and V is the potential energy surface.

$$\mu_{k,ij}=\frac{m_k\,(m_i+m_j)}{m_k+m_i+m_j}$$

and $\mu_{ij}=\dfrac{m_i\,m_j}{m_i+m_j}$

The angular momentum operators $\underline{l}^2{}_k$ and $\underline{j}^2{}_k$ are associated with the orbital motion of k around (ij) and with the molecule (ij), respectively.

An alternative to the Jacobi vectors can be obtained by making the transformation

$R^k = a_k\,R^k{}_0$ and $r^k = a_k{}^{-1}\,r_0{}^k$

where $a_k = (\mu_{k,ij}/\mu_{ij})^{1/4}$

This allows the kinetic energy operator $\underline{K}$ to be written as:

$$\underline{K}=\frac{h^2}{2\mu}\left(\Delta_{R_k}+\Delta_{rk}\right)$$

where μ is the 3 body reduced mass

$$\mu=\left(\frac{m_i,\ m_j,\ m_k}{m_i+m_5+m_k}\right)^{1/2}$$

to be a good choice as a nearly separable variable for many problems as will be substantiated later: other choices are of couse possible, but may lead to the appearance of additional coupling terms in certain equations that will given subsequently.

Expressing: $R^k = \rho \operatorname{Sin} \chi^k$

and $\gamma^k = \rho \operatorname{Cos} \chi^k$

leads to $\rho^2 = (R^k)^2 + (\gamma^k)^2$

and $\chi^k = () \, (R^k / r^k)$

ρ is known as hyperadius and χ as hyperangle.

So in terms of ρ and χ

$$\underline{K} = \frac{h^2}{2\mu} \left[\rho^{-5} \frac{\partial}{\delta\rho} \left(\rho^5 \frac{\partial}{\delta\rho}\right) + \rho^{-2} \Delta(\Omega_5) \right] = - \frac{h^2}{2n} \Delta(\rho, \Omega_5) \tag{2}$$

For a particle problem the number of relevant coordinates in 3 D space= (9-3 centre of mass)=6 coordinates. In expressions (2) ρ is a variable which we define below; l_k^2 and j^2_k $[l_k(l_k+1)$ and $j_k(j_k+1)$, respectively) are good quantum numbers, and this is so only as long as atom K is well separated from the () (i,j). In a reaction, this requirement cannot be fulfilled for reactions and products at the same time because only the vector sum $l_k + j_k = J$, the total angular momentum, is conserved: strong scrambling of orbital and rotational angular momentum will occur specially in the trasnsition region where rearrangement between reactants and products takes place.

b) Adiabatic and Diabatic representations.

For definiteness, consider the case of a (n+1) dimensional problem. When the total wavefunction is expanded in an adiabatic basis set:

$$\underline{\Psi}(\rho, \Omega n) = \rho^{-n/2} \, \underline{\Phi}^a(\rho, \Omega_n) \, \underline{F}^a(\rho) \tag{3}$$

the hyperradial adiabatic functions $\underline{F}^a$ are to be found as the solutions with proper boundary conditions of the infinite set of coupled linear differential equation

$$\left(- \frac{h^2}{2m} \left[\underline{1} \frac{d}{d\rho} + \underline{P}(\rho) \right]^2 + \underline{\xi}(\rho) - E \, 1 \right) \underline{F}^2(\rho) = 0 \tag{4}$$

Here, the matrix of adiabatic eigenfunctions $\underline{\Phi}^a(\rho, \Omega_n)$ and the diagonal matrix of adiabatic potential energy curves $\underline{\varepsilon}(\rho)$ are separated from others and is defined by setting up a polar system in properly mass scaled space of Jacobi vector components. It is the radial coordinate of the dimensional sphere. In terms of ρ which is independent of the rearrangement channel it is possible to follow the reaction as evolving from the intermediate state, where the particles are close together, to reactant and product valleys. The remaining 5 coordinates are denoted by Ω_5.

Such a representation for the many body problem is being actively explored because using it the kinetic energy operator $\underline{T}$ becomes essentially a Laplacian of a hyperspace (see equation (2)). Also ρ has proven and to arrive at equation (6) use has been made of the Hellmann-Feynman theorem.
Such a representation will foster a convenient channel expansion whenever the eigenvalues $\underline{\varepsilon}$ solution of the eigenvalue problem:

$$\left(- \frac{h^2}{2m\rho^2} \left[\underline{\Lambda}^2 + \frac{n^2}{4} - \frac{n^2}{2} \right] + V(\rho, \Omega_n) - \underline{\varepsilon}(\rho) \right) \underline{\Phi}^a(\rho, \Omega_n) = 0 \tag{5}$$

where the operator $\underline{\Lambda}^2$ is the angular part of the laplacian of the (n+1)- dimensional space, and $V(\rho, \Omega_n)$ is the interaction potential. The infinite sets are meant to be solved after proper truncation.

The mass parameter m, which appears in equation (4), depends on the definition of the hyperadius ρ. For instance in 3 body problems in 3D, ρ is most often defined so that m is the three body reduced mass.

The adiabatic approximation consists of neglecting all coupling in equation (4) i.e. neglecting elements of the antisymmetric matrix $\underline{\rho}(\rho)$ (a matrix introduced by F.T. Smith for treatment of nonadiabatic (diabatic) couplings in atomic collisions).

$$P_{\nu\nu'} = \left\langle \Phi^a_\nu \,\middle|\, \frac{\partial}{\partial\rho} \, \Phi^a_{\nu'} \right\rangle = (\varepsilon_\nu - \varepsilon_{\nu'})^{-1} \left\langle \Phi^a_\nu \,\middle|\, \frac{\partial V}{\partial\rho} \, \Phi^a_{\nu'} \right\rangle = -P_{\nu'\nu} \tag{6}$$

The brackets denote integration over hyperangles Ωn.

Schemes for further corrections to the adiabatic approximation have been developed. Diabatic representation correspond to an alternative expansion:

$$\underline{\Psi}\,(\rho,\ \Omega_n) = \rho^{-n/2}\ \underline{\Phi}^d\,(\Omega_n)\ \underline{F}^d\,(\rho) \qquad (7)$$

By comparison with equation (3), equation (7) implies the definition of an orthogonal trasformation matrix $\underline{T}\,(\rho)$

$$\underline{\Phi}^a\,(\rho,\ \Omega_n) = \underline{\Phi}^d\,(\Omega_n)\ \underline{T}\,(\rho)$$

and

$$\underline{F}^d\,(\rho) = \underline{T}\,(\rho)\ \underline{F}^a(\rho)$$

which can be obtained once equation (5) has been solved by requiring that the orthogonal matrix $\underline{T}\,(\rho)$ sstisfies the system

$$\underline{P}(\rho) = \tilde{T}(\rho)\ \frac{d}{d\rho}\ \underline{T}\,(\rho)$$

As a result, first derivatives disappear from equation (4), which becomes

$$\left[-\frac{h^2}{2m}\left(\frac{d^2}{d\rho^2} + E\right)\underline{1} + \underline{V}\,(\rho)\right]\underline{F}^d\,(\rho) = 0 \qquad (9)$$

the coupling being transferred from the kinetic term in equation (4) to the potential, which now is a non-diagonal diabatic matrix:

$$\underline{V}\,(\rho) = \underline{T}(\rho)\ \underline{\varepsilon}\,(\rho)\ \underline{\tilde{T}}\,(\rho) \qquad (10)$$

The prescription is not unique, since <u>any</u> ρ-indipendent rotation of T in also a solution: Boundary conditions are imposed on (9) by requiring V(ρ) to coincide with ε(ρ) at some ρ (local diabaticity)

c) Applications and Phenomenology

In the 3 body problem, representations symmetrical for at least some of the particles have been investigated: none of them is however "full range" in the reaction, because they do not correlate smoothly with reactants and products, and some kind of trasformation has in any case to be performed in order to describe the transition.

There are two different ways of achieving this: The first one is based on the idea that sudden switch during the collision from the reactant configuration to the product configuration could serve as a good starting point for following the evolution of the reaction; the second approach exploits the apposite view, that the starting point could be the individuation of the smoothest (adiabatic) path from reactants to products.

Let us now elaborate on the latter approach. The adiabatic idea attempts a simplification of the 3 body problem by individuating a variable which can be nearly separated from the others: this is possible when the overall motion can be considered as taking place slowley with respect to this variable, so that the faster motion associated with the others can be effectively averaged. Non-adiabatic effects have to be introduced in any case for an exact description, but many significant features are likely to be displayed when the adiabatic coordinate is wisely chosen.

In using this approach to chemical reactions it is very important to set up a hyperspherical coordinate system, for which there are several possibilities. Most of the investigations carried out so far have dealt with the somewhat artificial constraint of particles moving on a line: progress in the extensions of these promising techniques to the full 3 dimensional case has been limited to the development of simple test cases. In the following we will discuss in some detail what we have learned from the one-dimensional case and believe to be of interest also for the real three dimensional world.

From purely kinematic considerations a configuration such as 1 + 2-3 will be best described by scaling the two corresponding Jacobi vectors as shown in Fig. 1. When the same is done also for the configuaration of products 1-2 + 3, resulting from an exchange of the atom 2, the properties of kinetic energy operator such as in (1) are such that the newly scaled vectors are orthogonal but the potential energy surface is confine to a sector defined by the reaction skewing angle α, a function of the particle masses

$$\alpha = \arctan\,[m_2(m_1+m_2+m_3)/m_1m_3]^{1/2} \qquad (11)$$

The confinement to such a sector sets boundaries to the dynamics, which physically correspond to the prohibition for masses on a line of passing each other. It also shows that very different kinematic effects are likely to be associated with different mass combinations. Considering (11) we observe that the fully symmetrical exchange of an atom A in the process A +AA → AA +A involves an angle of 60°. For the exchange of the atom B in the nearly symmetrical processes A + BA → AB + A, the relative masses of A and B determine the full range of variation for the skewing aangle: from near zero when B is much ligheter than A, to near 90° when B is much heavier than A. The two limiting cases, illustrated in Fig. 2, provide effects, so that the full dynamics obtained by introducing explicitly the potential energy surface will be dramatically effected.

Consider first the case of a very large skewing angle. The path from reactants to products invloves a bend of nearly 90°: any coordinate system which aims at describing the reaction path from reactants to products will introduce a centrifugal distortion at the bend, but it may maintain a reasonable descriptive power in the qualitative treatment of the reactive process. From a computational point of view, setting up a coordinate system more or less based on the idea of following the evolution of the system along the reaction path entails the introduction of strong coupling between channels in a quantum mechanical framework, or strong centrifugal distorsions requiring fine grid integration of trajectories in a classical mechanical framework. This effect is likely to be especially important in the region where the bend is sharp, and this most often occurs when the system overcomes the saddle which separates the valley of reactants from that of the products. Introducing a nonorthogonal system which follows the evolution from reactants to products becomes increasingly difficult as thesk ewing angle decreases, because the distortion required to straighten the path into a Cartesian coordinate induces terms in the Jacobian trasformation matrix which correspond physically to centrifugal forces.

Therefore evolution along the reaction path provides a good description of the trajectory that is really followed, only in the adiabatic limit, i.e. for any infinitely slow process. It is apparrent that the procedure becomes impractical even for computational purposes since extensive channel coupling has to be introduced explicitly. In fact, the practical computation of quantum mechanical one-dimensional chemical reaction rates for small skewing angles, is a strong motivation for the use of hyperspherical coordinates. The hyperspherical view, allows full characterization of reaction with small to moderate skewing angles. When matched with more conventional methods involving reaction coordinates which follow the reaction, we have a complementary view for full evolution along the reaction path.

Which are observed in elaborate computational studies of atomic exchange processes. The paradigmatic situation illustrated in fig. 3 and 4, is that of 3 particles on a line, involving the partially symmetric system A + BA → AB + A. For other systems, reactant and product valleys are unsymmetrical and additional complications are introduced by channel coupling, however the general picture already outlined for the more symmetrical cases is confirmed.

The following view of reactive processes emerges: instead of an evolution from reactants towards products, a reactive process may be considered as a decay of the intermediate state, located in the region where interaction is the strongest. This corresponds, of courses, for simple situations to the transition state characterized by a symmetric sfreted vibration of a abound character, and an asymetric state vibration leading to dissociation. The system reaches this potential energy saddle configuration climbing from the reaction vlley; sequentially in time it may come back again to give an elastic (vibration - conserving) collision or inelastic transitions between vibrational states.

Alternatively it may discend to product volley, litter leading to the corresponding state of the products connected adiabatically to the original one the of the reactants (adiabatic reaction), or may lead to vibrational states corresponding to nonadiabatic events. Detailed studies of these effects have () that contrary to the previonsly commonly held beliet that decisions are taken by the system in the saddle region, they are actually taken along watershed (rdge), the uniagrinary line that separates reactants from products.

The main conclusions from these studies are that the stepper the ridge the higher the nonadiabatic vibrational energy exchange. This exchange in general will be favoured by large skewing angles: The detailed analysis reported in the literature points ont that aarrasibound states (resonances) appear as vibrational predissociating states and can be accurately individuated and described in energy and litetime by simple semiclassical arguments.

The very promising theoretical advances outlined above, are likely tools for further progress. In this regard one can mention sample calcualations for J=0, for the three dimensional H + H_2 exchange (shown in Fig. 5 and 6) that have been made using hyper spherical coordinates.

d) **Unimolecular Dissociation Rates**

Now let us attempt to characterize the problem of unimolecular dissociation rates.

An analysis for the specificity of unimolecular decompositions and intramoleculars vibrational relaxation may be started by focussing on simple models for coupled oscillators, for which diffeent modes (and transitions between then) have been well characterized. Asymptotic techniques, which are essentially semiclassical in nature will be considered here. They involve the introduction of a reaction radius as an adiabatic curves along which the system evolves in a first approximation, the evaluation of non-adiabatic coupling terms, responsible for transitions between curves.

In the treatment that follows we refer to the case of isolated resonances, corresponding to poles of the scattering matrix for complex values of the energy $E - i\Gamma/2$: the lifetime is then given by $\tau(E_r) = \tau^{-1}$.

The starting point for the following developments is the solutiopn to the problem of three turning points, which forms the basis for the semiclassical theory of shape resonances, supported by a one-dimensional potential well with barrier. In the classical regions on both sides of the barrier, the coefficients of the incoming and outgoing parts of wavefunction denoted by arrows oriented fowards left and right, respectively are connected by the two by two matrix $(H)^{(j)}$ as follows:

$$\begin{pmatrix} \overrightarrow{B}_j \\ \overleftarrow{B}_j \end{pmatrix} = (\underline{H})^{(j)} \begin{pmatrix} \overrightarrow{A}_j \\ \overleftarrow{A}_j \end{pmatrix} \qquad (12)$$

Here the A's and B's refer ton the external and internal side of the barrier, respectively, and the index j is introduced in anticipation of the following generalization to many channels, as in Fig. 7. The matrix $(H)^{(j)}$ is expecitly:

$$(\underline{H})^{(j)} = \begin{pmatrix} (1+k_j^2)^{1/2} \exp(i\phi_j) & ik_j \exp(i\theta_j) \\ -ikj \exp(-i\theta j) & (1+k_j^2)1/2 \exp(-i\phi_j) \end{pmatrix} \qquad (13)$$

where th tunnel probability K_j^{-2} contains the phase integral for the barrier, and ϕj, and θ_j are corrections. The many channel generalization is illustrated in Fig. 7: Many approximately parallel curves, each displaying a barrier separating a well from a dissociation continuum, arise when a multidimensional problem is trasformedd into a coupled system in the adiabatic representation. The simplest origin for such a situation is for a 2 dimensional potential energy surface; such as that drovn in Fig.8. Characteristic orthogonal trajectories on this surface are the valley bottom line, representing the steepest descent from the saddle, and the ridge, i.e., the line of steepest descent from the minimum, In a polar coordinate system centred at the minimum, the profile of these trajectories are shown, together with a few adiabatic curves, such as would be obtained solving for bound states on wides at fixed distances from the minimum. Extensive experience for problems having similar topological features has shown that the adiabatic curves can be considered as satisfactory one-dimensional effective potentials for the 2 - dimensional problem, except for those regions where non-adiabatic coupling in the strongest: Fortunately, these regions can be localized in particular where the curves cross the ridge.

A pattern of adiabatic curves such as shown in Fig. 7 can be considered typical of many situations of interest for unimolecular decomposition but the effective humps need not necessarily arise from saddle in a single potential surface. They can be due to rotational barriers or to avoided crossing with upper surfaces etc. Also the abscissa in the general case need not be necessarily a reaction radius, but may be any convenient variable describing the progress of the reaction. However, a reaction radius (hypperadius in problems of higher dimensionality) may be more convenient than the conventional reaction path, especially when the latter has large curvature or bifurcates its use often simplifies treatment of symmetry of the transition state.

In the spirit of transition state theory our formulation exploits the separation between behaviour in the well (properties of the molecule) and behaviour on the mountain pass (properties of the transition state). Molecular properties enter into the description as a matrix $\underline{\sigma}$ (E) which has the features of a scattering matrix but accounts only for the evolution and mixing of states within the turning points b_j (Fig.7).

It connects ontgoing and incoming coefficients

$$\overrightarrow{\underline{B}} = \underline{\sigma}\ \overleftarrow{\underline{B}} \qquad (14)$$

Properties and limiting cases for the $\underline{\sigma}$ matrix, which is crucial for any applications of the theory, will be considered in the following: Assuming now that non-adiabatic coupling is negligible at the transition state, the connection between the coefficients for evolution on each curve in given by (12). We can then obtain the connection A coefficients at the external turning points a_j:

$$\underline{\vec{A}} = \underline{S}\,\underline{\overleftarrow{A}} \qquad (15)$$

where square matrix $\underline{S}$ is now effectively a scattering matrix, except for propagation from each a_j to infinity. Introducing (12) into (14) and rearranging we get

$$\underline{S} = \left[(\underline{1} + \underline{k}^2)^{1/2}\, e_{i\underline{\phi}} + i\underline{\sigma}\,\underline{k}\, e^{-i\underline{\theta}} \right]^{-1} \left[-i\underline{k}\, e^{i\underline{\theta}} + \underline{\sigma}\,(\underline{1}+k^2)^{1/2}\, e^{-i\underline{\phi}} \right] \qquad (16)$$

where $\underline{k}$, $\underline{\phi}$, $\underline{\theta}$ are all diagonal matrices having elements the k_j, ϕ_j, and θ_j, quantities appearing in (13). Eq. (16) is in a form suitable for the search for resonances: Poles of the $\underline{S}$ matrix can be obtained, for example, by equating to zero the determinant of the matrix whose inverse appears in (16), or slightly rearranging:

$$\det \left[(\underline{1}+\underline{k}^{-2})^{1/2}\, e^{i\underline{\xi}} + i\underline{\sigma} \right] = 0 \qquad (17)$$

where $\underline{\xi} = \underline{\phi} + \underline{\theta}$

This formula yields familiar results is limting cases. When all the barriers are so thick that alla channels are effectively closed, the diagonal matrix $\underline{k}^{-2}$ tends to zero, the extra phases can be neglected and $\det\,[\underline{1} + i\underline{\sigma}] = 0$ will have as solutions the real values of the energy corresponding to bound states.

Consider now the case where $j^{\underline{th}}$ adiabatic state is effectively decoupled from the others. The corresponding $\underline{\sigma}$ matrix is the simply an element of unit modulus which is conveniently written:

$$\sigma_j = -i \exp(2i\delta_j) \qquad (18)$$

where δ_j is the phase integral for the well and the $-i$ factor accounts for the reflection at the uinner turning point.

Eq. (17) then becomes, dropping index j,

$$(1 + k^{-2})^{1/2} + \exp[i(2\delta-\xi)] = 0 \qquad (19)$$

It is well known that this equation for poles of the $\underline{S}$ matrix, that in this case is simply $S = \exp(2i\eta)$, leads to the following expression for the resonance phase shift

$$\eta = \arctan \left(\frac{(1+k^{-2})^{1/2} - 1}{(1+k^{-2})^{1/2} + 1} \tan(\delta - \phi/2) \right) \qquad (20)$$

A convenient way to obtain the widht Γ of the resonance at E_r is to plot a "cross section" $\mathrm{Sin}^2\,\eta$ as a function of energy. Assuming in the neighbourhood of a resonance a lorentzian shape

$$\mathrm{Sin}^2\eta = [\,1 + 4\,(E-E_r)^2/\Gamma^2\,]^{-1} \qquad (21)$$

one has

$$\Gamma = 2\,(E - E_r)\,\tan(\delta - \phi/2)\, \frac{(1+k^{-2})^{1/2} - 1}{(1+k^{-2})^{1/2} + 1} \qquad (22)$$

Useful formulas for the width are obtained by the following identification

$$\tan(\delta-\phi/2) \sim h\omega/[\pi(E-E_r)] \qquad (23)$$

valid around resonance where $h\omega$ is the local level spacing. The formula:

$$\Gamma = \frac{2h\omega}{\pi}\, \frac{(1+k^{-2})^{1/2} - 1}{(1+k^{-2})^{1/2} + 1} \qquad (24)$$

tends to the familiar Gamow result:

$$\Gamma = h\omega/2\pi k^2 \qquad (25)$$

when the energy is well below the barrier maximum ($k^{-2} \to 0$). The accuracy of these formulae to calculate positions and width of resonances has been extensively studied.

A similar formulation can also be given in the multichannel case, provided that only one adiabatic barrier is effectively open to tunneling, i.e., when for only one channel (for definiteness the one labeled by the index 1) the corresponding tunneling probability k_1^{-2} is significantly different from zero. Eq. (17) then becomes

$$\det\left(\underline{1} + [(1+k_1^{-2})^{1/2} - 1]\,\underline{N} + i\underline{\sigma} \right) = 0 \tag{26}$$

where the matrix $\underline{N}$ has different from zero only its first element, which is 1. The analysis becomes most transparant if we exploit the unitarity and symmetry of the $\underline{\sigma}$ matrix to decompose it as

$$\underline{\sigma} = \tilde{\underline{T}} \exp (2i\underline{\delta})\, \underline{T} \tag{27}$$

where $\underline{\delta}$ is the diagonal matrix of eigenphases, and $\underline{T}$ is an orthogonal matrix, its transpose $\underline{T}$ being thus its inverse. Then (26) becomes

$$\det \{[(1+k_1^{-2})^{1/2} - 1]\, \underline{T}\,\underline{N}\,\tilde{\underline{T}} + [\underline{1} + i\exp (2i\delta)]\} = 0 \tag{28}$$

which can be arranged as a secular equation,

$$\det \{[((1+k_1^{-2})^{1/2} - 1)\, \underline{T}\,\underline{N}\,\tilde{\underline{T}}\, (\underline{1} + i\exp (2i\underline{\delta}))] + 1\} = 0 \tag{29}$$

showing that -1 can be interpreted as the eigenvalue of the matrix in square brackets in (29). But the characteristic of this matrix is one, being determined by that of $\underline{N}$. Therefore -1 is the only eigen value different from zero and coincides with the trace:

$$[(1 + k_1^{-2})^{1/2} - 1] \sum_j [1 + \exp(2i\delta_j)]^{-1}\, t_{j1}^{\;2} = -1 \tag{30}$$

where t_{j1} are now the elements of the first column of the orthogonal matrix $\underline{T}$. Defining now an effective phase Δ

$$\Delta = \arctan \left[\sum_j t_{ji}^{\;2} \tan(\delta_j + \pi/4)\right] \tag{31}$$

Eq. (30) can be arranged to look like (19)

$$(1 + k_1^{-2})^{1/2} + \exp (2i\Delta) = 0 \tag{32}$$

where the effective phase Δ given by (31) contains the eigenphase δ_j for the various channels in the well and the coefficients $t_{j1}^{\;2}$ account for their mixing, Formula (32) can be handled in the some way as (19), in particular to give the resonance eigenphase H

$$H = \arctan\left(\frac{(1+k_1^{-2}) - 1}{(1+K_1^{-2}) + 1} \tan \Delta \right) \tag{33}$$

which includes information on the resonance position and width in the same way as its one channel counterpart η, eq. (20).

Specifically it exhibits the desired property that the description of the transition state (contained in k_1^{-2}) and that of the 'molecule' (contained in Δ) are separeted. Applications of the theory require essentially the construction of Δ for any specific limiting cases. Comparisons with standard RRKM results shows that the latter is a reasonable average of the quantum behaviour.

(E) Bibliographical note

Recent reviews on the topics discussed here can be found in the books "The Theory of Chemical Reaction Dynamics" Reidel (1986), pp. 384-413, and "Nonequilibriom Vibrational Kinetics" Springer (1986) pp. 159-180 where references are also given to papers relevant for the development of the viewpoint followed in these notes.

Further information on coordinate systems for chemical dynamics and more details on the hyperspherical approach can be found in J. Chem. Phys. 85 135 (1986) and 85 1362 (1986)

The resonance theory of unimolecular decay is presented in Chem. Phys. Letters 133 531 (1987) and 133 538 (1987) , where limiting cases are derived and comparisons with RRKM and quantum calculations are presented.

Perugia, January 1989

Potential energy surfaces in skewed coordinate. The 2 situations correspond to large & small skewing ∠s. - - - is the ridge line.

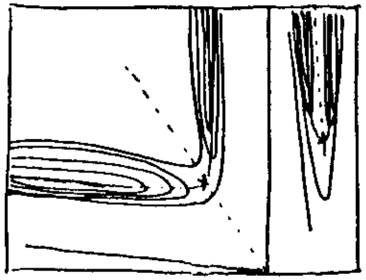


Fig 2.

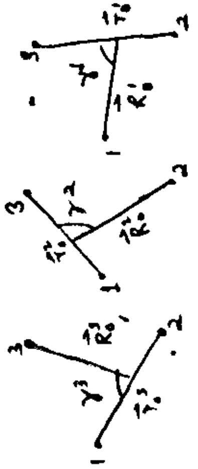


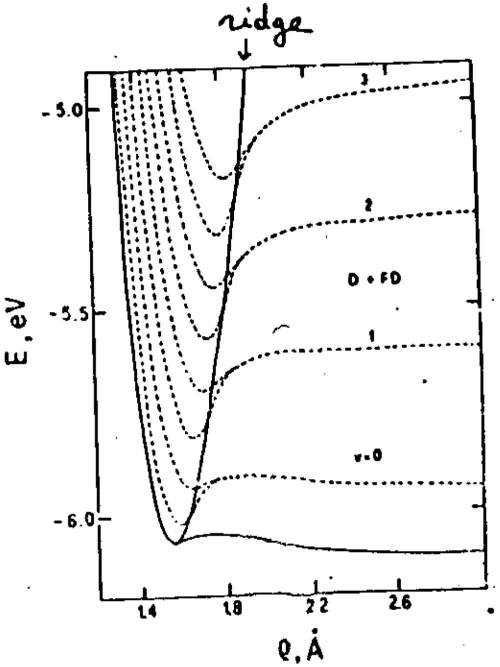
Fig 1

COLLINEAR D + FD

light - heavy light

skewing angle 84.5 deg.

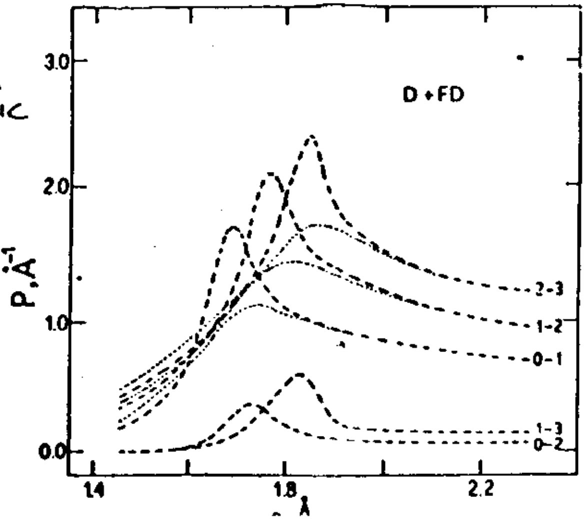
Fig 3



adiabatic curves

Fig 4

non adiabatic coupling



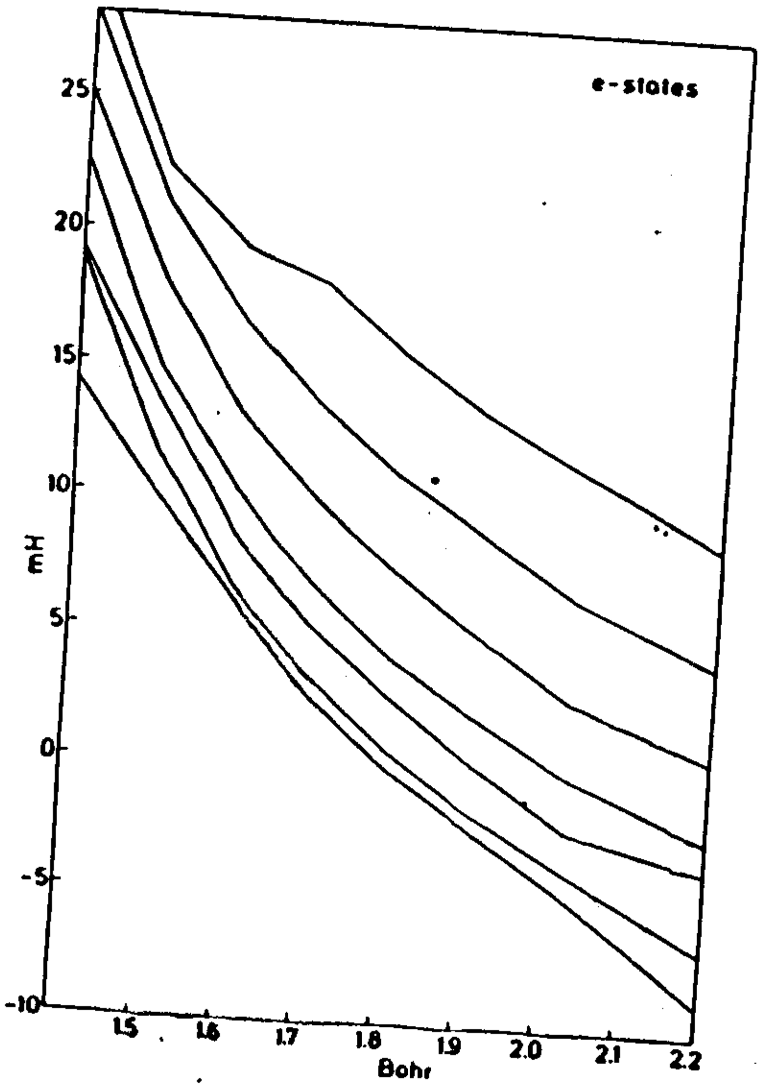


Fig. 1. Adiabatic energy curves for e type states for H + H_2 as functions of the hyperspherical radius.

Mishra, Linderberg & Öhrn
C.P.L. 111 434 (84)

Fig 5

3-D H + H_2, J=0

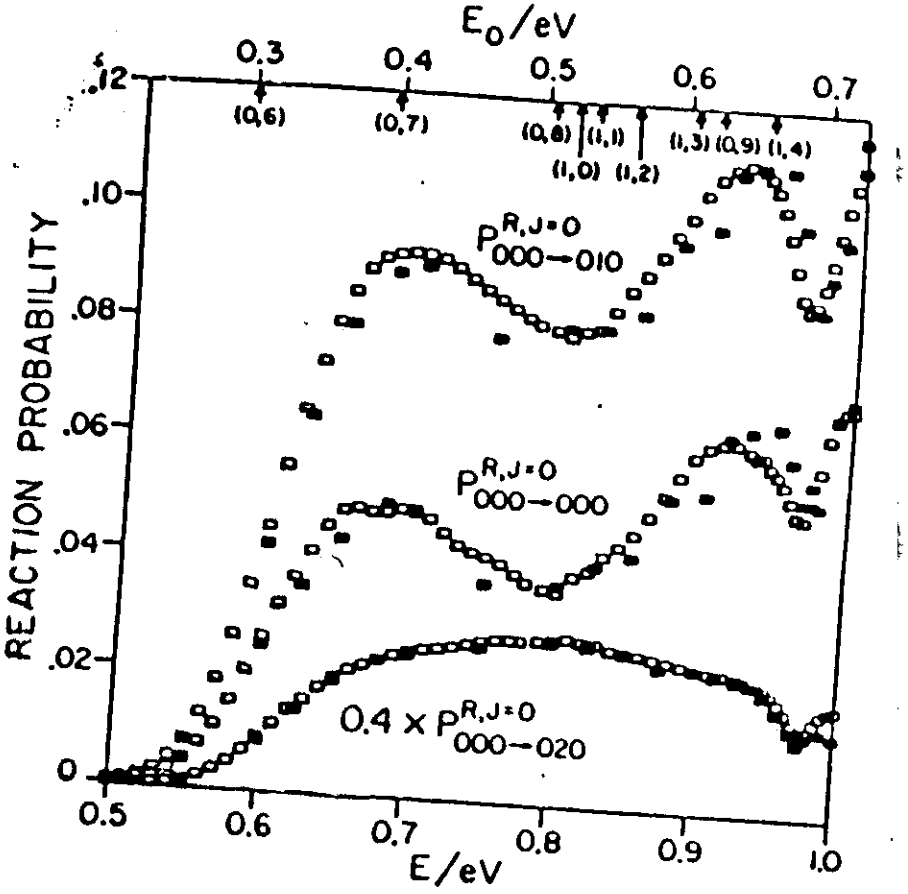
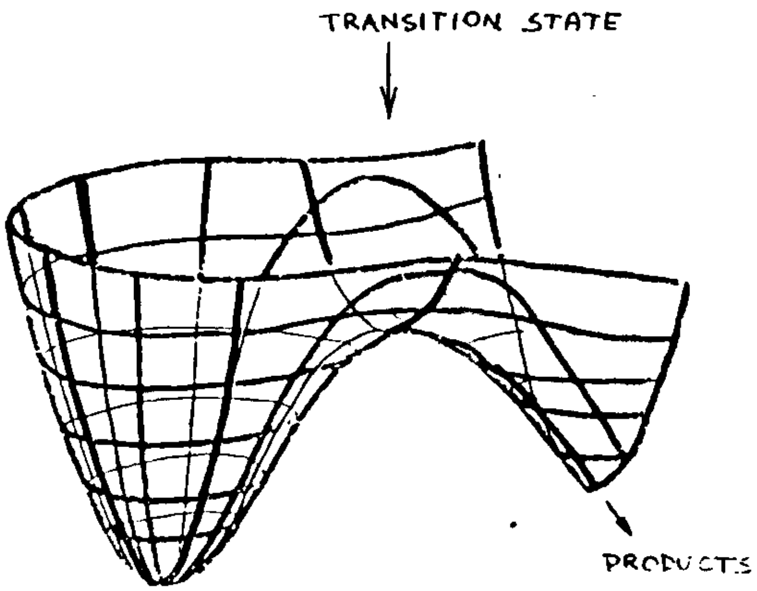


FIG. 1. Distinguishable atom $J = 0$ partial wave reaction probabilities as a function of energy for the $H + H_2(v, j, 0) \to H_2(v', j', 0)$ reaction on the Porter–Karplus potential energy surface (Ref. 29). The probabilities are denoted by the symbol $P^{R,J=0}_{vj0\to v'j'0}$. The lower abcissa is the total energy and the upper abcissa the reagent translational energy. The vertical arrows on the upper abcissa denote the energy at which the corresponding $H_2(v, j)$ channel opens up. The open symbols represent the present results and the full ones those of a previous calculation (Ref. 1). The $P^{R,J=0}_{000\to020}$ results were multiplied by 0.4 prior to plotting.

Kuper

Fig 8



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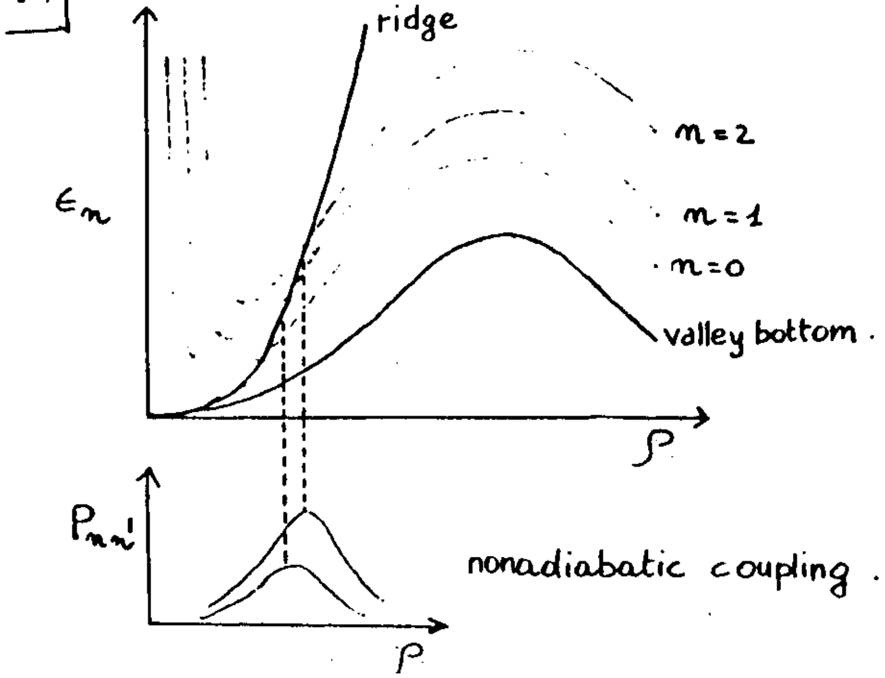

Semiclassical (short wave) mechanics: some mathematical background

1. Preliminaries

The qualitative or even semiquantitative understanding of molecular dynamics can be based on a semiclassical (*i.e.* short wave) approach [1], which generalizes old quantum mechanics (Bohr-Sommerfeld, JWKB techniques, ...) and can be given a rigorous generalization using the asymptotic theory of differential equations. An introduction to this theory follows.

The Schrödinger equation for a monodimensional system

$$\{\epsilon^2 \frac{d}{dx^2} + p(x)\}\Psi(x) = 0 \tag{1}$$

(where $\epsilon^2 = \hbar/2m$ is a small parameter and $p(x) = E - V(x)$ is a real analytic function with turning points) admits asympotic solutions as $\epsilon \to 0$ which are uniformly valid throughout the turning points. The uniform asymptotic solution of (1) is represented in terms of the solution Ψ and its derivative of a given comparison equation. This method was first devised by R.E. Langer [2] who studied the solutions of Eq. (1) in the case of one turning point ($p(x) = 0$), and then it was employed by many others, for an historical survey see [3]. T.M. Cherry [4] developed a different method which is based on transformation of the independent variable. He constructed a comparison equation as well, but in this case the asymptotic expansion of the solution doesn't depend on the derivative of the solution of the comparison equation. Later Lynn and Keller [5] entented the Langer's method [2] to obtain uniform asymptotic solution when $p(x)$ has an arbitrary number of turning points of any order. Zauderer [6] and Rubenfeld and Willner [7] made the same developing Cherry's idea. Important work by Wasow [8] also stresses relationship with perturbation theory.

Basically, we follow Lynn and Keller [5] to obtain the asymptotic solution of Eq. (1): for sake of clearity it is useful to review briefly the key points of this method. The asymptotic solutions of Eq.(1) as $\epsilon \to 0$ when $p(x)$ has $N+1$ turning points of order m_j are represented in terms of the solution of the following comparison equation with polynomial coefficients:

$$\epsilon^2 V''(t) + \sum_{k=0}^{\mu} \gamma_k t^k V(t) = 0 \tag{2}$$

where μ is the sum of the orders of the turning points and γ_k are to be specified. The function $f(t)$ depends at least on $\mu - 1$ parameters.

2. The hamiltonian system

For the further developments, we found that the analysis will be more transparent if Eqs. (1) and (2) are replaced by the equivalent systems:

$$\epsilon \frac{d}{dx}\begin{pmatrix} \Psi(x) \\ \Phi(x) \end{pmatrix} = \begin{pmatrix} 0 & 1 \\ -p(x) & 0 \end{pmatrix}\begin{pmatrix} \Psi(x) \\ \Phi(x) \end{pmatrix} \tag{3}$$

$$\epsilon \frac{d}{dt}\begin{pmatrix} Q(t) \\ P(t) \end{pmatrix} = \begin{pmatrix} 0 & 1 \\ -f(t) & 0 \end{pmatrix}\begin{pmatrix} Q(t) \\ P(t) \end{pmatrix} \tag{4}$$

where $\epsilon\frac{d}{dx}\Psi(x) = \Phi(x)$ and $\epsilon\frac{d}{dx}Q(t) = P(t)$. We indicate with $A(x)$ and $B(t)$ respectively the matrices containing $p(x)$ and $f(t)$ in the above equations. A change of the dependent variable of the following form

$$\begin{pmatrix} \Psi(x) \\ \Phi(x) \end{pmatrix} = N(x,\epsilon)\begin{pmatrix} P(t) \\ Q(t) \end{pmatrix} \tag{5}$$

takes the system (3) into the system (4), where the last is easier to solve asymptotically. We want to stress that (3) and (4) represent real hamiltonian systems, *i.e.* $-JA(x)$ and $-JB(t)$ (J is a two dimensional matrix with the diagonal elements equal to zero and the off diagonal elements $J_{12} = -J_{21} = 1$) are symmetric and the change of the dependent variable (Eq.(5)) is canonical. This is true if and only if the matrix N in (5) is symplectic. A symplectic matrix has the following property [9]

$$NJ\tilde{N} = J \tag{6}$$

From Eq.(6) it follows that the determinat of the matrix N is equal to 1. The original Schrödinger equation (Eq.(1)) can be transformed asymptotically to a well defined related equation by a symplectic tranformation. The related equations we find in the literature are linear second order differential equations with polynomial coefficients. In the case of one turning point of first order the solutions of the related equation are the Airy functions or Bessel functions of order one third; if there are two turning points of first order or one turning point of second order the solutions are Weber functions. Sibuya [10] has studied some properties of the solutions for problems with a number of turning points greater than two.

In general, the function $f(t)$ in the related equation (see Eq.(2)) can be different from a polynomial. The important point that we want to pin down, is that the original differential equation and the related one are linked by a symplectic transformation. The related equations are the canonical reference equations for all the systems with the same structure of the turning points. We can define an equivalence as $\epsilon \to 0$ between those systems that can be transformed by the same related equations. They will exhibit similar qualitative behavior.

3. The symplectic transformation

We follow the formulation of Lynn and Keller [5] but we exploit the property of symplecticity of the matrix N. As we shall see this provide some remarkable semplifications. Inserting Eq.(5) into Eq.(4) and replacing the variable x with the variable t we find the equations for the elements of N:

$$\dot{x}AN - NB = \epsilon\dot{N} \tag{7}$$

where the dot indicates differentiation with respect to the variable x. In the spirit of the Langer's method [2], Eq.(7) can be satisfied formally by a power series for the matrix N:

$$N = \sum_{n=0}^{\infty}\epsilon^n N_n \tag{8}$$

Inserting Eq.(8) in Eq.(7) and making equal terms with the same power in ϵ we find four equations for the elements of the matrix N at the k order in the parameter ϵ:

$$\dot{x}N^k_{21} + f(t)N^k_{12} = \dot{N}^{k-1}_{11} \tag{9}$$

$$\dot{x}N^k_{22} - N^k_{11} = \dot{N}^{k-1}_{12} \tag{10}$$

$$-N^k_{11}p(x)\dot{x} + f(t)N^k_{22} = \dot{N}^{k-1}_{21} \tag{11}$$

$$-N^k_{12}p(x)\dot{x} - N^k_{12} = \dot{N}^{k-1}_{22} \tag{12}$$

Equations (9) and (10) with some algebraic manipulations are transformed into

$$\dot{N}^k_{22} + \dot{N}^k_{11}\dot{x}^{-1} = 0 \tag{13}$$

$$\dot{N}^k_{21} + \dot{N}^k_{12}f(t)\dot{x}^{-1} = 0 \tag{14}$$

Lynn and Keller solve this system of four equations and find that at any order k it is necessary to solve two integrals, one to obtain N^k_{11} and the other one to obtain N^k_{12}. In the following, exploiting the simolecticity of N we show that it is necessary to calculate only the integrals for N^k_{12} and only when k is an odd number.

Considering that the matrix N is symplectic we can prove that N^0 and N^2 have only their diagonal elements along the different from zero and N^1 has different from zero only the off diagonal elements. The elements of a matrix which is required to be symplectic at the order k in ϵ have to satisfy the following conditions:

$$N^0J\tilde{N}^0 = J \tag{15}$$

$$\sum_{n=0}^{l} N^nJ\tilde{N}^{l-n} = 0 \quad l = 1,2,\ldots,k \tag{16}$$

or explicitly form

$$\dot{x}^{1/2}N^l_{22} + \dot{x}^{-1/2}N^l_{11} = \sum_{n=1}^{l-1}(N^n_{11}N^{l-n}_{22} - N^n_{12}N^{l-n}_{21}) \tag{17}$$

Defining $N^{-1} = 0$ and using Eqs.(15), *i.e* $det\, N^0 = 1$ and Eqs. (9) and (10), we find that:

$$N^0 = \begin{pmatrix} \dot{x}^{1/2} & 0 \\ 0 & \dot{x}^{1/2} \end{pmatrix}$$

and from Eq.(11) we obtain the relationship between the variables x and t:

$$(\frac{dx}{dt})^2 = \frac{f(t)}{p(x)} \tag{18}$$

this is a univocal transformation only if $p(x)$ and $f(t)$ are holomorphic functions and if $p(x)$ and $f(t)$ have the same number of turning points of the same order in the domain in which x varies. In order that the above transformation be regular, it has to be verified that

$$\int_{t_i}^{t_j} f(t)^{\frac{1}{2}} = \int_{x_i}^{x_j} p(x)^{\frac{1}{2}}$$

for any couple of turning points z_i and z_j. This can be recognised as an equivalence of phase integrals of importance in the physical applications. These equivalences allow to determine the $\mu - 1$ parameters which define $f(t)$ (see Eq.(2)). From Eq. (16) we have

$$\dot{z} N_{22}^1 = -N_{11}^1$$

and from Eq. (10) we have

$$\dot{z} N_{22}^1 = N_{11}^1$$

these two equations are satisfied only if $N_{22}^1 = N_{11}^1 = 0$. The expression for calculating N_{12}^n, obtained with some algebraic work on Eqs. (9) and (14), is:

$$N_{12}^n = \dot{z}^{1/2} f(t)^{-1/2} [c_2^n - \frac{1}{2} \int^t f(t)^{-1/2} \dot{z}^{1/2} (\frac{d\dot{N}_{11}^{n-1}}{dt}) dt] \qquad (19)$$

$c_2^n = 0$ because N_{12}^n is holomorphic, so when $n = 1$ the integrand in the above equation is symply $\frac{f(t)}{2\sigma}$ and N_{21}^n can be calculated from Eq. (9). When $l = 2$ the Eq.(17) is

$$\dot{z}^{1/2} N_{22}^2 + \dot{z}^{-1/2} N_{11}^2 = -det\ N^1 = -N_{12}^1 N_{21}^1$$

and from Eq.(10) we can calculateN_{22}^1 and N_{11}^1 without performing any new integration. From Eq.(19) if $n = 2$ we have $N_{12}^2 \neq 0$ and from (9) follows that $N_{21}^2 = 0$. We want to prove that the matrices N^{2n-1} where $2n - 1$ is an odd number have only off diagonal elements different from zero and the matrices N^{2n} with n an even number have different from zero only the elements along the diagonal, for any n. We prove this by the method of induction, requiring that the matix N is symplectic to the order $2n + 1$. If

$$N^{2n-1} = \begin{pmatrix} 0 & N_{12}^{2n-1} \\ N_{21}^{2n-1} & 0 \end{pmatrix}$$

we prove that

$$N^{2n} = \begin{pmatrix} N_{11}^{2n} & 0 \\ 0 & N_{22}^{2n} \end{pmatrix}$$

From Eqs. (17) and (10) we see that N_{11}^n and N_{22}^n are different from zero, and from (19) it follows that $N_{12}^{2n} = 0$ because by hypothesis $N_{11}^{2n-1} = 0$ and $c_2^{2n} = 0$ because N_{12}^{2n} has to be holomorphic. We make the hypothesis that N^{2n} is a diagonal matrix and we prove that N^{2n+1} has different from zero only the off diagonal elements. From Eq. (17) we obtain

$$\dot{z} N_{22}^{2n+1} + N_{11}^{2n+1} = 0$$

and from Eq.(10)

$$\dot{z} N_{22}^{2n+1} - N_{11}^{2n+1} = 0$$

so $N_{22}^{2n+1} = N_{11}^{2n+1} = 0$. N_{12}^{2n+1} and N_{21}^{2n+1} can be obtained from Eqs. (19) and (9) respectively. The total symplectic transformationmatrix N^{2n+1} is

$$N^{2n+1} = \begin{pmatrix} \dot{z}^{1/2} & 0 \\ 0 & \dot{z}^{-1/2} \end{pmatrix} \begin{pmatrix} 1 + \sum_{i=0}^{2n} \epsilon^{2i} N_{11}^{2i} & \sum_{i=0}^{2n} \epsilon^{2i+1} N_{12}^{2i+1} \\ \sum_{i=0}^{2n} \epsilon^{2i+1} N_{21}^{2i+1} & 1 + \sum_{i=0}^{2n} \epsilon^{2i} N_{22}^{2i} \end{pmatrix}$$

The only integrals we need to eveluate are N_{12}^{2n+1} for $i = 1, 2, \ldots, n$. As shown in [6] to complete the proof it is necessary to prove the integral (19) is regular at the turning points. The case we have treated (see Eq.(1)) is a particular case of the method treated in [5] because the function $p(z)$ here is independent on the small parameter ϵ. The regularity conditions that the integral (19) has to satisfy are [5]:

$$\int_{t_0}^{t_j} f(t)^{-1/2} \dot{z}^{1/2} (\frac{d}{dt} \frac{\dot{N}_{11}^{n-1}}{\dot{z}}) dt = 0$$

for any t_j, and

$$\frac{d^q}{dt^q} \dot{z}^{1/2} f(t)^{-1/2} \frac{d}{dt} (\frac{d\dot{N}_{11}^{n-1}}{\dot{z}}) = 0 at t = t_j$$

for any $q = 0, \ldots, m_j - 2$.

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