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Analysis of Least Motion Paths for Molecular Deformations¹

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Abstract: The fundamental basis of nuclear least motion correlations of reactivity order is demonstrated through analytical form comparisons with the theory of small vibrations and extensions thereof. The analytic motion equations are developed both for small deformations around arbitrary reactivity structures, including transition states, as well as for the gross changes between conventional (reactant and product) end-point states. A number of ramifications of the analysis are explored with particular emphasis on weighting of individual atom motions, directional effects of such motions, and on the choice of end points for optimal characterization of reactions. An example is made of a molecular system having modes of distortion which are simultaneously pertinent as regards reactivity and fully tractable in terms of the theory of small vibrations, preliminary to application of the principle of least motion to more complicated systems in an accompanying paper.

The current literature on analysis of reaction mechanisms contains an increasing number of references to paths of least motion and speculation as to whether these are favored paths for reactivity. With few exceptions, however, this aspect is usually only qualitatively and superficially considered and thereafter is essentially ignored. Three main reasons, to a degree interconnected, appear to be responsible for this strategy. Whereas least nuclear motion is recognized as complementary to least electronic motion, in that both are invoked in the Rice and Teller generalization which has come to be known as the principle of least motion (PLM),² it has not been formalized to the extent of the latter (*cf.* conservation of orbital symmetry rules³). Consequently, there is uncertainty in what constitutes a least motion path, especially for systems of any complexity, and confusion exists in how to quantitatively gauge motions along given paths. The third reason appears to be based on doubts that gross structural changes between reactants and products contain necessary and sufficient information of the dynamics of the reacting system.

Hine, subsequent to an examination of the history of PLM, has developed a quantitative procedure to test its validity on several reactions of resonance stabilized species⁴ and later on problems of stereochemical control in elimination reactions.⁵ Tee has presented details of a nonlinear least-squares technique for intramolecular invariant transformations,⁶ generalizing Hines' har-

monic distortion procedure, and has examined a number of other interesting reactivities, also principally involving stereochemical differentiation.⁷ These studies while contributing information necessary to resolve the question of limits of applicability of PLM⁸ do so entirely pragmatically and thereby cannot resolve the expressed uncertainties.

A preliminary analysis of these questions was presented at a recent meeting concerned with problems of chemical and biochemical reactivity.⁹ Several generalizations were obtained from this analysis, relating to the potential enhancement of the correlational value of the PLM through consideration of structures of transition states and reactive intermediates, and differential distortions therefrom, rather than just of reactant and products and gross differences among them. In particular, it was shown that Hines coupled harmonic springs ensemble model for evaluating distortions in reaction systems is amenable to closed form analysis. The expressions obtained for systems of rather broad generality are sufficiently simple to allow recognition of individual atom or group contributions within the easily computed overall molecular least motion distortions. Application of the differential distortion relationships allows recognition of least motion, as distinguished from greater and most motion paths for reaction. Moreover, for geometry changes of any size, but particularly for differential changes, it appeared that these analytic terms could be compared with expressions and results obtainable from more firmly grounded theoretical methods.

In the present paper, development of these analytic formalisms will be detailed and continued. The major

(1) Research performed under the auspices of the U. S. Atomic Energy Commission.

(2) F. O. Rice and E. Teller, *J. Chem. Phys.*, **6**, 489 (1938); **7**, 199 (1939). As stated therein, "those elementary reactions will be favored that involve the least change in atomic position and electronic configuration."

(3) *Cf.* R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Weinheim/Bergstr., Germany, 1970.

(4) J. Hine, *J. Org. Chem.*, **31**, 1236 (1966).

(5) J. Hine, *J. Amer. Chem. Soc.*, **88**, 5525 (1966).

(6) O. S. Tee, *J. Amer. Chem. Soc.*, **91**, 7144 (1969).

(7) O. S. Tee and K. Yates, *J. Amer. Chem. Soc.*, **94**, 3074 (1972).

(8) See, *e.g.*, S. I. Miller, *Advan. Phys. Org. Chem.*, **6**, 185 (1968), who concludes from an examination of a number of stereoselection cases that the concept would be better labeled a hypothesis.

(9) S. Ehrenson, "Chemical and Biochemical Reactivity," Proceedings of the International Jerusalem Symposium, 6th, 1973, in press.

emphasis is on exploration of correspondences with other theoretical methods, particularly vibrational force constant analysis and some simple aspects of molecular trajectory dynamics. Parametrization, in the sense of weighting of the individual nuclear motions, also enters, as do other aspects of amendment of the PLM model. In an accompanying paper, the formalisms developed here and their correspondences to force constant theory are employed in examination of the reactivities of a number of chemical systems of interest. All efforts are ultimately directed toward a better understanding of the correlational utility and physical significance of the least motion concept.

Method and Derivations

Limited Closed Forms for Motion Calculation. For initial and final molecular states, conventionally reactant and product, with N common atoms located in Cartesian space having respective coordinates x_i, y_i, z_i and x_i', y_i', z_i' , the weighted sum of squares of the individual atom position distortions, which characterizes the coupled harmonic springs ensemble model, is written

$$D_{\mu}^2 = \sum_{i=1}^N \mu_i d_i^2 = \sum_{i=1}^N \mu_i \{ (x_i' - x_i)^2 + (y_i' - y_i)^2 + (z_i' - z_i)^2 \} \quad (1)$$

In this framework, the spring (force) constants are μ_i and the minimization of D_{μ}^2 , by intramolecularly invariant translations and rotations of one state with respect to the other, is sought.

If the final state structure is rotated (about the x, y , and z axes respectively by α, β , and γ , all rotations clockwise when viewed along the axis toward the origin) and then translated by δ_x, δ_y , and δ_z , its coordinates are transformed to

$$\begin{bmatrix} \bar{x}_i' \\ \bar{y}_i' \\ \bar{z}_i' \end{bmatrix} = (x_i', y_i', z_i') \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos \alpha & \sin \alpha \\ 0 & -\sin \alpha & \cos \alpha \end{bmatrix} \times \begin{bmatrix} \cos \beta & 0 & \sin \beta \\ 0 & 1 & 0 \\ -\sin \beta & 0 & \cos \beta \end{bmatrix} \begin{bmatrix} \cos \gamma & \sin \gamma & 0 \\ -\sin \gamma & \cos \gamma & 0 \\ 0 & 0 & 1 \end{bmatrix} + \begin{bmatrix} \delta_x \\ \delta_y \\ \delta_z \end{bmatrix} = \begin{bmatrix} X_i' + \delta_x \\ Y_i' + \delta_y \\ Z_i' + \delta_z \end{bmatrix} \quad (2)$$

whereupon

$$\begin{aligned} D_{\mu}^2 &= \sum_{i=1}^N \mu_i \{ (\bar{x}_i' - x_i)^2 + (\bar{y}_i' - y_i)^2 + (\bar{z}_i' - z_i)^2 \} \\ &= \sum_{i=1}^N \mu_i \{ (r_i^2 + (r_i')^2 + \rho^2 + 2[(X_i' - x_i)\delta_x - x_i X_i' + (Y_i' - y_i)\delta_y - y_i Y_i' + (Z_i' - z_i)\delta_z - z_i Z_i'] \} \quad (3) \end{aligned}$$

and

$$\begin{aligned} r_i^2 &= x_i^2 + y_i^2 + z_i^2 \\ (r_i')^2 &= (x_i')^2 + (y_i')^2 + (z_i')^2 = \\ &\quad (X_i')^2 + (Y_i')^2 + (Z_i')^2 \\ \rho^2 &= \delta_x^2 + \delta_y^2 + \delta_z^2 \end{aligned}$$

Three equations are obtained upon taking partials with respect to the translations (minimizing D_{μ}^2 with respect to these degrees of freedom)

$$\frac{\partial D_{\mu}^2}{\partial \delta_p} = \sum \mu_i \left\{ \frac{\partial \rho^2}{\partial \delta_p} + 2[P_i' - p_i] \right\} = 0 \quad (4)$$

Here, the p and P symbols are the appropriate Cartesian coordinates and the particle summation indices are suppressed, as they will be henceforward except where necessary to avoid ambiguity.

Hence, since $(\partial \rho^2 / \partial \delta_p) = 2\delta_p$, the translational minimization conditions are

$$\delta_p = \sum \mu_i (p_i - P_i') / \sum \mu_i = \omega_p - \omega_p' \quad (5)$$

This is equivalent to having the centers of gravity of both states coincident. Making the point of coincidence the origin yields.¹⁰

$$\begin{aligned} (D_{\mu}^2)_R &= \sum \mu_i \{ (X_i' - x_i)^2 + (Y_i' - y_i)^2 + (Z_i' - z_i)^2 \} = \sum \mu_i \{ r_i^2 + (r_i')^2 - \\ &\quad 2[x_i X_i' + y_i Y_i' + z_i Z_i'] \} \quad (6) \end{aligned}$$

The general rotational transformations are cumbersome and hence of limited analytic use. If, however, cases are restricted to those where both states share a plane of symmetry (have a least C_s symmetry) with respect to all participating atoms, very simple and tractable analytic motion expressions may be developed. This symmetry condition for simplification is recognizable upon inspection of the three partial derivative equations for angle optimization, *i.e.*, if all cross terms, $\sum \mu_i (p_i q_i' - p_i' q_i) = 0$, rotational optimization is accomplished.¹¹

Choosing the xy plane as the symmetry plane, a single rotation of the product (about the z axis by γ) is sufficient to complete the positional optimization.

$$\frac{\partial (D_{\mu}^2)_R}{\partial \gamma} = -2 \sum \mu_i \left(x_i \frac{\partial X_i'}{\partial \gamma} + y_i \frac{\partial Y_i'}{\partial \gamma} + z_i \frac{\partial Z_i'}{\partial \gamma} \right) = 0 \quad (7)$$

From eq 7 and eq 2, with $\alpha = \beta = 0$, it follows that

$$\tan \gamma = \frac{\sum \mu_i (y_i x_i' \mp x_i y_i')}{\sum \mu_i (y_i y_i' \pm x_i x_i')} \quad (8)$$

and the optimized (minimized) D^2 value is

$$\begin{aligned} (D_{\mu}^2)_{R\gamma} &= \sum \mu_i \{ r_i^2 + (r_i')^2 \} - \\ &\quad 2 \{ [(\sum \mu_i (y_i y_i' \pm x_i x_i'))^2 + \\ &\quad (\sum \mu_i (y_i x_i' \mp x_i y_i'))^2]^{1/2} \pm \sum \mu_i z_i z_i' \} \quad (9) \end{aligned}$$

The \pm sign allows for the possibility of reflection during the state change; normally, without reflection, the upper sign pertains. At any rate, that option is chosen to maximize the last curly bracketed term.

D^2 Values for Small Displacements. From the alternative imaginary coordinate projection form of eq 9

$$\begin{aligned} (D_{\mu}^2)_{R\gamma} &= (D_{\mu}^2)_R + \{ (\sum \mu_i (x_i - iy_i)(x_i' + iy_i'))^{1/2} - \\ &\quad (\sum \mu_i (x_i + iy_i)(x_i' - iy_i'))^{1/2} \}^2 \quad (10) \end{aligned}$$

(10) All distances here and henceforth refer to centers-of-gravity placement of both species. In general, the product sums, $\sum \mu_i p_i q_i$, within and between states, may be obtained from those for arbitrary placement by subtraction of $\omega_p \omega_q \sum \mu_i$.

(11) Note, the plane of symmetry requirement here is not to be confused with that required in application of orbital symmetry rules.³ Here, it may be *any* plane common to the two states, which is a much less stringent requirement than being normal to the "reacting" bond.

and expression of the coordinates of the final state as Taylor expansion increments to those of the initial state, *i.e.*

$$p_i' = p_i + \sum_k (\partial p_i / \partial \varphi_k) \Delta \varphi_k \quad (11)$$

one obtains

$$(\Delta D_{\mu}^2)_{R\gamma} = (\Delta D_{\mu}^2)_R - \frac{(\sum_k \Delta \varphi_k \sum_i \mu_i \{x_i (\partial y_i / \partial \varphi_k) - y_i (\partial x_i / \partial \varphi_k)\})^2}{\sum_i \mu_i (x_i^2 + y_i^2)} \quad (12)$$

$$(\Delta D_{\mu}^2)_R = \sum_i \mu_i \sum_{p=x,y,z} \left[\sum_k \frac{\partial p_i}{\partial \varphi_k} \Delta \varphi_k \right]^2 \quad (13)$$

The variables φ , k in number, are for the individual distortions; they and all distances are referred to the center of gravity of the initial state.

Applications

Small Molecular Vibrations and PLM. The analytic forms developed above present the means for application of the PLM to processes of molecular deformation not conventionally considered in this framework. Two particularly relevant questions may be examined by a comparison of the motion results with those forthcoming from conventional vibrational analysis for small molecular deformations.

The first concerns weighting (by the μ_i factors), and whether appropriate choice of these factors renders the D^2 values equivalent to molecular energies of vibration. It may be straightforwardly shown that the least motion eq 9, 12, and 13 yield proportional forms to those for the potential energy within vibration symmetry species obtained with symmetry coordinate displacements.

If S_1, S_2, \dots are the symmetry coordinates

$$V = \frac{1}{2} \sum_{ik} C_{ik} S_i S_k \quad (14)$$

and C_{ik} is not zero only when S_i and S_k belong to the same symmetry type (species). Now, since the symmetry coordinate displacements which produce the normal coordinate displacements upon linear combination within the symmetry types are constructed to maintain center of mass and lack of molecular rotation, the appropriate corresponding D^2 form is, from eq 9

$$(\Delta D_{\mu}^2)_{R\gamma} = \sum_j \mu_j (x_j^2 + y_j^2 + z_j^2 + (x_j')^2 + (y_j')^2 + (z_j')^2 - 2\{x_j x_j' + y_j y_j' + z_j z_j'\}) - \sum_j \mu_j \{(x_j' - x_j)^2 + (y_j' - y_j)^2 + (z_j' - z_j)^2\} \quad (15)$$

Further, since the symmetry coordinate displacements are linearly related to the rectangular coordinate displacements as long as infinitesimal displacements are considered,¹² the proportionality of the two forms is recognized. The C_{ik} values depend on the force constants for the particular force field chosen. Two simple examples, where valence force constants are easily recognizable, are illustrative of the comparisons and μ value determinations.

For the diatomic AB, undergoing small vibrations, eq 9 yields $(D_{\mu}^2)_R = (\mu_A \mu_B / (\mu_A + \mu_B)) (\Delta R)^2$, which is to be compared to $V = \frac{1}{2} k_{AB} (\Delta R)^2$. Since the μ 's must be

(12) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand, New York, N. Y., 1945, pp 142-147.

proportional to the masses to ensure the translational and rotational minimization in the PLM and, simultaneously, the unambiguous determination of coordinates from knowledge of displacements in "internal" coordinate theory,¹² $\mu_A = \frac{1}{2} k_{AB} m_A / M$ and $\mu_B = \frac{1}{2} k_{AB} m_B / M$, where M is the reduced mass of the system ($m_A m_B / (m_A + m_B)$).

For the linear triatomic $B_1 A B_2$, there are three symmetry types of vibration, Σ_g^+ , Σ_u^+ , and Π_u (degenerate). Locating the molecule along the x axis and defining all deformations positive in the positive coordinate direction, for the Σ_g^+ vibration, $(D_{\mu}^2)_R = \mu_B [(-\Delta r_{AB_1})^2 + (\Delta r_{AB_2})^2]$ and $V = \frac{1}{2} k_{AB} [(\Delta r_{AB_1})^2 + (\Delta r_{AB_2})^2] + k_{AB, AB'} (\Delta r_{AB_1} \Delta r_{AB_2})$. Here, then, since $\Delta r_{B_1} - \Delta r_{B_2} = 0$, $\mu_B = \frac{1}{2} (k_{AB} + k_{AB, AB'})$ and $\mu_A = 0$.

Similarly, for the Σ_u^+ vibration, where $(D_{\mu}^2)_R = \mu_A (\Delta x_A)^2 + \mu_B [(-\Delta x_{B_1})^2 + (-\Delta x_{B_2})^2]$, we find $\mu_A = m_A (k_{AB} - k_{AB, AB'}) / M$ and $\mu_B = m_B (k_{AB} - k_{AB, AB'}) / M$. For the Π_u vibrations, $(D_{\mu}^2)_R = \mu_A (\Delta p_A)^2 + \mu_B [(-\Delta p_{B_1})^2 + (-\Delta p_{B_2})^2]$, with p either y or z , whereupon $\mu_A = 2k_{BAB} m_A / M r_{AB}^2$ and $\mu_B = 2k_{BAB} m_B / M r_{AB}^2$. The reduced mass, M , for this system is $(2m_A m_B / (m_A + 2m_B))$ and $k_{AB, AB'}$ and k_{BAB} are respectively the interaction force constants between the AB bond stretches and the bending force constant.

It seems clear, therefore, that the least motion solutions for simple molecules undergoing small symmetry selected distortions follow the potential energy expressions for these distortions viewed as vibrations and become proportional to them, through appropriate combinations of valence force constants, upon mass weighting of the individual particles whose movements are explicitly contained in the least motion equations. Similar expressions for more complicated molecules are also derivable although the force fields and constants and their combinations turn out to be considerably more complex and less easily visualizable. Later, in consideration of reactivities, we shall return to this comparison, examine another example in full detail, and extend its scope to consider transition states and reactive intermediates, where other than positive force constant analysis in symmetry coordinates will be used in a parallel manner for larger molecular systems undergoing reactions.

The preceding, while providing an extremely significant connection between the PLM and vibrational analysis theory and thereby establishing a rigorous weighting algorithm for the former, is perhaps not unexpected since the harmonic approximation lies at the core of both formulations, and both require similar translation and rotation null conditions. Neither has it thus far revealed the full power of the PLM for correlation of energy effects accompanying small distortions. The comparison may be carried further in response to a second question of interest. That is, can least motion distinguish among and within the various symmetry modes of vibration in the sense of their weakness or strength and, hence, among corresponding gross motions which characterize different reactivity paths?

In Figure 1, an initial planar molecular state is pictured (with three atoms for other purposes but completely generalizable to any number in two or three dimensions). Each nucleus is allowed to undergo movement by a small quantity, ρ , but in a direction defined by the angle θ_i with respect to a projection of the vector

connecting its original position and the center of gravity (\bar{r}_i). The new coordinates of nucleus i are, therefore

$$\begin{aligned} x_i' &= x_i + \frac{\rho}{r_i} \{x_i \cos \theta_i - y_i \sin \theta_i\} - \delta_x, \\ y_i' &= y_i + \frac{\rho}{r_i} \{x_i \sin \theta_i + y_i \cos \theta_i\} - \delta_y, \end{aligned} \quad (16)$$

where δ_x and δ_y are the respective components for movement of the center of gravity accompanying the total nuclear motion. From eq 9 and 16, then

$$(D_\mu^2)_{R\gamma} = \sum \mu_i \{2r_i^2 + 2\rho r_i \cos \theta_i + \rho^2 - \delta_x'^2 - \delta_y'^2\} - 2\Gamma^{1/2} \quad (17)$$

where

$$\Gamma = (\sum \mu_i (r_i^2 + \rho r_i \cos \theta_i))^2 + (\sum \mu_i \rho r_i \sin \theta_i)^2 \quad (18)$$

To obtain the orientational (θ dependent) extrema for the motion, partial derivatives are taken with respect to θ_i and the result set equal to zero. If summation over i is carried out, providing a facile means of removal of various complicated terms such as center-of-gravity derivatives, then

$$\sum \frac{\partial (D_\mu^2)_{R\gamma}}{\partial \theta_i} = -2\rho \sum \mu_i r_i \sin \theta_i \{1 - \Gamma^{-1/2} \sum \mu_i r_i^2\} = 0 \quad (19)$$

It is immediately apparent that one set of extremum conditions is where $\sum \mu_i r_i \sin \theta_i$ is zero; the other set occurs when

$$\rho \{(\sum \mu_i r_i \cos \theta_i)^2 + (\sum \mu_i r_i \sin \theta_i)^2\} + 2\sum \mu_i r_i^2 \sum \mu_i r_i \cos \theta_i = 0 \quad (20)$$

Of the former, the most easily visualizable is where all $\sin \theta_i$ equal zero, corresponding to motion along the vectors r_i (away from or toward the center of gravity). This orientation of distortions produces the *maximum* motion as measured by D^2 . For small ρ , the condition $\sum \mu_i r_i \cos \theta_i = 0$ approximates eq 20. Where all $\cos \theta_i = 0$, the deformation motions are all normal to the r_i vectors. This corresponds to a (although not necessarily the only) *minimum* motion condition.

Since collective motions of nuclei normal to the vectors connecting them to the center of molecular gravity corresponds to a greater proportion of (what is in valence coordinate terms labeled as) bending rather than stretching, and motion along this vector corresponds to a greater proportion of stretching,¹³ it appears that the PLM can distinguish properly between such motions. The minimum motion would appear to correlate with the mode for which the smaller vibrational force constant pertains, the maximum with the larger.

Reaction Path Dynamics and the PLM. Thus far, consideration has been restricted to deformations of stable structures, seeking analogies with conventional vibrational analysis results. It is useful at this time to generalize the model systems to include structures

(13) The extremes of the bending and stretching difference are to be seen in highly symmetric molecules such as the BAB system previously examined. Here, motion along the vectors to the center of mass corresponds to the Σ type, both of which contain admixtures of the simple stretch and bond interaction force (both stretching type) constants. The minimum motion corresponds to the Π -type vibrations, characterized in vibrational analysis by the small bending constant k_{BAB} .

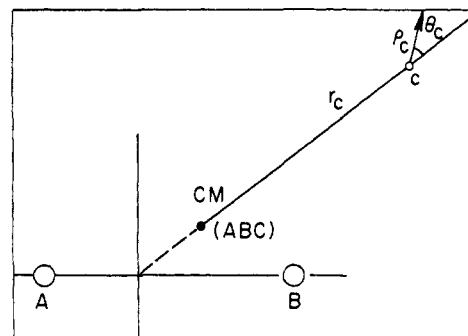


Figure 1. Display of coordinates and variables for differential motion calculations.

which may lie along various pathways approaching, or at, transition states for reactions.

Again referring to Figure 1, a hypothetical diatomic molecule AB, lying along the x axis with its center of gravity at the origin is taken to constitute, with atom C, a model for reactivity, particular details of which depend upon their relative orientations and the potential fields specified for the atomic interactions. If C is in the position corresponding to that for a minimum in the potential energy for the triatomic molecule, and distortions as previously considered (by ρ and θ_i) are allowed, one is presented with the result that least motion corresponds to a high proportion of bending and most motion to a high proportion of stretching deformation. If the stable molecule is triangular, for example, the most motion deformation with distortion *along* the vectors connecting the atoms to the center of mass corresponds to a breathing type vibration. The least motion deformations normal to these vectors, and which more strongly distort the shape of the triangle, look most like a combination of bends.

At the other extreme, one can visualize the atom C approaching the stable diatomic AB and ask what the PLM suggests of the dynamics of their interactions. In a manner exactly analogous to that followed in derivation of eq 16-18, it may be shown that

$$\begin{aligned} (D_\mu^2)_{R\gamma} &= \frac{m_A m_B}{M_{AB}} [R^2 + (R')^2] + \frac{m_C m_{AB}}{M_{ABC}} [2r_C^2 + \\ &\rho^2 + 2\rho r_C \cos \theta] - 2 \left\{ \left(\frac{m_A m_B}{M_{AB}} R R' + \frac{m_C m_{AB}}{M_{ABC}} (r_C^2 + \right. \right. \\ &\left. \left. \rho r_C \cos \theta) \right)^2 + \left(\frac{m_C m_{AB}}{M_{ABC}} \rho r_C \sin \theta \right)^2 \right\}^{1/2} \quad (21) \end{aligned}$$

Here $M_{AB} = m_A + m_B$, $M_{ABC} = m_A + m_B + m_C$, r_C is now the distance of C from the origin (which is the center of mass of AB), R is the original and R' the final distance of separation of AB, ρ is the distance moved by C, and θ ($=\theta_C$) is as previously defined.

The respective maximum and minimum motion paths to be followed from any initial position of C are again, respectively, along and perpendicular (in the limit of infinitesimal ρ) to the vector \bar{r}_C and the corresponding D^2 values are

$$(D_\mu^2)_{R\gamma}^{\parallel} = \frac{m_A m_B}{M_{AB}} (\Delta R)^2 + \frac{m_C m_{AB}}{M_{ABC}} \rho^2 \quad (22)$$

$$(D_\mu^2)_{R\gamma}^{\perp} = (D_\mu^2)_{R\gamma}^{\parallel} - \frac{m_C m_{AB}}{M_{ABC}} \rho^2 \Gamma_{ABC} \quad (23)$$

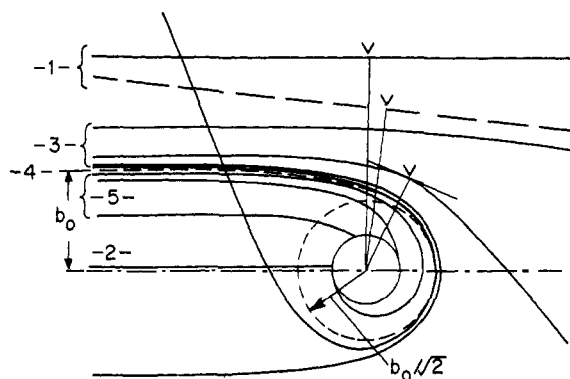


Figure 2. Representative trajectories for the dynamic system AB + C, with AB not vibrating (following Langevin¹⁵ and McDaniel¹⁴). Carets indicate minimum motion positions along scattering paths. Only incoming branches of spiraling trajectories are shown.

where

$$\Gamma_{ABC} = \frac{m_C M_{AB} r_C^2}{\left(\frac{m_A m_B M_{ABC}}{M_{AB}} RR' + m_C M_{AB} r_C^2 \right)} \quad (24)$$

From eq 22, it is quickly ascertained that maximum motion as measured by D^2 occurs along the straight line path from the original position of C toward the center of mass of AB and that D^2 is constant for equal increments of motion of C and varies only because of the oscillation of AB. On the other hand, the minimum motion path is circular (in the limit of very small ρ). D^2 is again constant for static AB, but here because r_C remains constant. In this case there is a term in D^2 where the motions of AB and C are coupled.

Expanding eq 21 for small ρ ($\rho \ll RR'$) and truncating after ρ^2 terms yields, consistent with eq 24

$$(D_{\mu}^2)_{R\gamma} = \frac{m_A m_B}{M_{AB}} (\Delta R)^2 + \frac{m_C M_{AB}}{M_{ABC}} \rho^2 (1 - \Gamma_{ABC} \sin^2 \theta) \quad (25)$$

Here ΔR is $(R' - R)$. With this equation, the least motion measured properties of some simple trajectories for C may be usefully examined. For C traveling in a straight line (described by $y = px + q$, implying no interaction between C and AB), it may be easily shown that the minimum D^2 value occurs where r_C is a minimum ($=q^2/[1 + p^2]$) and $\sin^2 \theta$ is a maximum. That is, minimum D^2 occurs at the distance of closest approach of C to the center of mass of AB (at the impact parameter, in the notation of collision theory for molecules incapable of interaction¹⁴) and normal to the vector connecting this center of mass and C. The maximum D^2 value is obtained at $r_C \rightarrow \pm \infty$. See paths 1 and 2 of Figure 2 where a schematic representation of a variety of simple model trajectories is displayed.

For hyperbolic trajectories such as are encountered in high angular momentum ion-molecule reactions where inverse fourth-power polarization provides the attractive force, the impact parameter distance is again where a minimum D^2 value is obtained and where C moves normal to the vector r_C . Paths 3 are representative. For trajectories characterized by the Langevin

(14) Cf. E. W. McDaniel, "Collision Phenomena in Ionized Gases," Wiley, New York, N. Y., 1964, Chapter 1.

critical impact parameter, b_0 ,¹⁵ path 4, C spirals in and assumes a circular trajectory about the center of mass AB. In this circle of radius $b_0/\sqrt{2}$, the minimum D^2 value (for any motion at this velocity and particle separation distance) pertains and remains constant except for the vibrations of AB. At smaller impact parameter values, paths 5, C falls out of orbit and spirals into AB. D^2 , as in the hyperbolic case, goes through a minimum and then must rise, assuming ρ to be unchanged. Neglect of a repulsive potential of course limits the utility of this, an often used simple model for ion-molecule reaction. This neglect is most serious for the small impact parameter case. Nevertheless, although not carried beyond the rather primitive level of interaction appropriate for the present discussion, we find potentially useful correlations among the least motion measures for nuclear motions and those forthcoming from more detailed theory.

Between these extremes of interaction and structural stability may be placed transition states and reactive intermediates, if the latter are viewed in the limit as inflection points on the applicable potential energy surface. Transition state structures are conventionally described as those for which one mode of vibrational distortion in a normal coordinate sense is characterized by a negative force constant.¹⁶ From the rigorous correspondence established previously between the D^2 and potential energy forms for vibration, it is evident that the least motion path out of the transition state lies along the path corresponding to this mode of vibration. Here, with the weighting by force constants, D^2 will be negative and hence must correspond to the least motion path for distortion. Similarly, proceeding from the limiting reactive intermediate along its vibrational mode characterized by zero force constant must also constitute the path of least motion. Consideration of both types of transitory structures as initial points in the least motion framework, then, must lead to correct ordering among paths for decomposition, but under the following qualifications.

The first is that weighting (by force constants) assumes the predominant role; *i.e.*, differences in kind between positive and negative force constant combinations characterizing the different possible modes for distortion should be recognized. The second, which follows from the first, is that structural details for these transitory states become relatively unimportant. This is seen to be especially so under recognition that there are, in the normal coordinate sense, only two ways out of the transition state (on to product or back to reactant) for which the negative force constant pertains.¹⁷

(15) G. Gioumousis and D. P. Stevenson, *J. Chem. Phys.*, 29, 294 (1958).

(16) Or, correspondingly, an imaginary frequency. See, *e.g.*, L. Melander, "Isotope Effects on Reaction Rates," Ronald Press, New York, N. Y., 1960, Chapter 2.

(17) There is an intriguing possible application of the PLM which is suggested here: that is, in correlation of transmission coefficients, K , in equilibrium reaction rate theory. Since the same force constant weighting should apply to the forward and backward directions (to product or back to reactant, respectively), the PLM would suggest greater transmission in the direction where least geometric change is encountered. While not easily accommodated within usual explanations of the meaning of K ,¹⁸ nor, for that matter, within the proper domain of the PLM-vibrational energy analogy drawn, the suggestion is attractive because of similar invocation of importance of structure as that involved in conventional PLM applications to related equilibria.

(18) Cf. H. Eyring, D. Henderson, B. J. Stover, and E. M. Eyring, "Statistical Mechanics and Dynamics," Wiley, New York, N. Y., 1964, p 31 and Chapter 16.

This change in emphasis from presumption of structural detail to dominance in weighting, suggested when the transition state is taken as the *initial state*, radically alters the entire thrust of the PLM and severely limits its utility. Of course, correct prediction of decomposition mode is assured, but only at the cost of securing reliable force constant information for a transient species, which must be recognized as a considerably more formidable task than obtaining optimal geometry information. Further examination is made of transition states in various motion end-point roles in the following paper. It suffices at this point to recognize that when viewed as *final states* transition state structures appear capable of simultaneously contributing necessary structural detail (*i.e.*, for reactions characterized by nonmonotonic changes in structure, see the following example) and maintaining close correspondence between the PLM and the more firmly grounded theoretical concepts invoked above.

Deformations of AB₃ Molecular Species. Implications for Chemical Reactivity Systems. At this point it is useful to consider a number of the results obtained above as they apply in sample molecular systems undergoing chemically (reactivity) significant distortions. Molecules of the type AB₃ have been chosen as a compromise to allow detailed motion-vibration analysis. For the structure and symmetry coordinates shown in Figure 3,¹⁹ the following (D_{μ}^2)_{R γ} expressions may be derived

$$\begin{aligned}
 (A_1, A_1'): & \quad \frac{3\mu_B(1 + p \cos^2 \beta)\Delta r_{S_1}^2}{\bar{\Delta r} = \Delta r_{S_1}(1 + p \cos \beta)} \\
 (A_1, A_2''): & \quad \frac{3\mu_B(1 + p \sin^2 \beta)\Delta r_{S_2}^2}{\bar{\Delta r} = \Delta r_{S_2}(1 + p \sin \beta)} \\
 (E, E'): & \quad \frac{6\mu_B(1 + \frac{1}{2}p \sin^2 \beta)\Delta r_{S_{3a}}^2}{\bar{\Delta r} = \Delta r_{S_{3a}}\sqrt{2}(1 + \frac{1}{2}p \sin \beta)} \\
 & \quad : \quad \frac{3\mu_B\Delta r_{S_{4a}}}{\bar{\Delta r} = \Delta r_{S_{4a}}}
 \end{aligned} \quad (26)$$

The symmetry species in parentheses are respectively for the pyramidal (C_{3v}) and limiting (D_{3h} , $\beta = \pi/2$) planar species, where β is the angle formed by the AB bonds and the axis of molecular symmetry, and $p = 3\mu_B/\mu_A$. The Δr_s variables are the lengths of the displacement vectors for atom B₁ in each representation as shown, and the $\bar{\Delta r}$ relationships are for conversion to comparable displacements of B with respect to A along these vectors. These D^2 values may be compared with the variety of potential function forms for such species (*cf.* ref 12, Chapter II), revealing the complexity of the weighting factors when expressed in force constant terms.

For planar D_{3h} structures, where the individual A-symmetry species vibrations cannot mix, eq 26 reveals the lesser motion distortion to be the out-of-plane bend (A_2''), compared to the in-plane stretch (A_1'), for equal displacements of B with respect to A. The coefficients are in the proportion of $(1 + p)^{-1}:1$, bend to stretch, in agreement with earlier conclusions concerning directional effects on D^2 (distortions along or normal to vectors connecting the nuclei and center of gravity). Examination of the valence force constants for stable

(19) J. B. Howard and E. B. Wilson, Jr., *J. Chem. Phys.*, 2, 620 (1934).

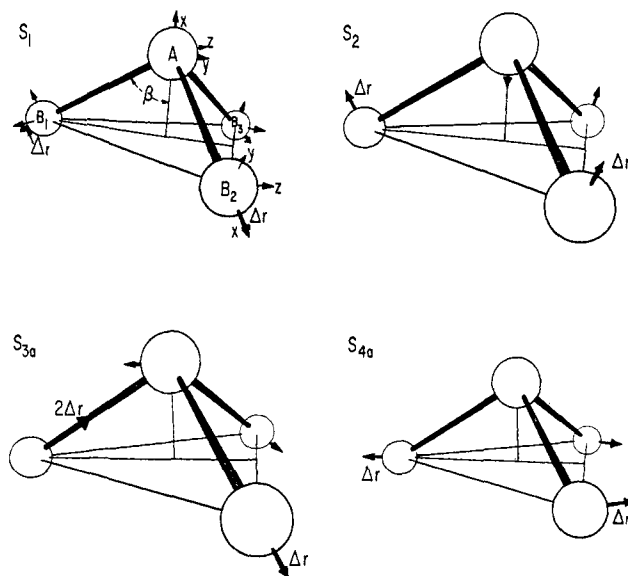


Figure 3. Symmetry coordinates of pyramidal AB₃. The displacement vectors of A, relative to B (unit Δr), are $p \cos \beta$ for S_1 and $p \sin \beta$ for S_2 and S_{3a} where p is $3\mu_B/\mu_A$.

planar AB₃ systems reveals much greater resistance to in-plane symmetric stretching than to either out-of-plane symmetric bending or in-plane angle distortion.²⁰

In the pyramidal structures, where the A-type vibrations can mix, the least motion analysis predicts the bending-like mode to remain softer than that for symmetric stretching for $\beta \geq \pi/4$. This prediction is verified in a large number of molecular systems including group V hydrides and halides where β ranges over 55–70° and a wide variety of p factors pertain. For these molecules, ν_1 , associated mainly with the stretch, is a factor of 2 or more larger than ν_2 , which is associated mainly with the bend.²¹

The frequencies ν_3 and ν_4 are associated within the double degenerate E-symmetry species with vibrations which distort the pyramidal structures. Assuming root-mean-square averaging to normalize the AB displacements along the S_B vectors, the least motion results indicate vibrations of S_3 and S_4 type to be considerably stiffer than the symmetric bends for all group V molecules previously cited. In fact, for these molecules, ν_3 is generally very close in magnitude to ν_1 (an observation of only qualitative significance, however, when contrasted to the motion results, considering the lack of force constant weighting and the method of displacement normalization in the latter).

The E-symmetry (S_{3a}) and A₁-symmetry (S_2) comparison is of interest upon consideration of the possible modes for stereochemical conversion between *d* and *l* forms of resolved AB₁B₂B₃ molecules. The most obvious path for this "reaction" is by direct inversion, a continuation of the motion associated with $S_2(A_1 \rightarrow A_2'')$. Another path would resemble an S_2 -type vibration (actually better pictured as $-S_3$), followed perhaps

(20) See ref 12, p 178. Only in the event $\mu_B/\mu_A (= m_B/m_A)$ is very large, *e.g.*, in BBr₃, can the frequency ratio $\nu_{A_2''}/\nu_{A_1'}$, which is equal to the square root of the force constant ratio weighted by $(1 + p)^{-1}$, be greater than unity.

(21) See ref 12, p 164. It is interesting to note that this ν_1/ν_2 ratio would persist to even smaller β angles upon force constant weighting. Herzberg here quotes a predicted ratio of $2:\sqrt{2}$ assuming a central force field for X₄ molecules, where $\sin \beta = (3)^{-1/2}$, and an observed ratio of 2.00:1.54 for the P₄ molecule.

by what looks like a bend of $B_1-A-(B_2B_3)$ to a planar structure, and thence by repetition of these motions, in reverse order, to the mirror image form.

Least motion analysis predicts that the direct inversion path is to be preferred, if extrapolations of distortions to the planar forms are justified. (*N.b.*, the necessary use of transition state structures to characterize final end-point states for this, and for that matter any other mechanistic distinction.) Spectroscopic results for many AB_3 system indicate the symmetrical bend (direct inversion) mode to be very soft (NH_3 and PH_3 , for example, invert in average times of $\sim 10^{-11}$ and 10^{-7} sec, respectively)²² and extrapolation would appear relatively safe here. For the other mode, which follows a composite of motions, various intermediate structure effects may enter to complicate the extrapolation, although not likely to change the ordering determined.^{23,24} In the following paper, detailed examination is made of such complicating effects as they can

(22) Reference 12, pp 220–225.

(23) Inversion in pyramidal AB_3 molecules, as importantly influenced by changes in ν_2 and the angle β , is discussed by G. F. Koepl, D. S. Sagatys, G. S. Krishnamurthy, and S. I. Miller, *J. Amer. Chem. Soc.*, **89**, 3396 (1967).

(24) R. F. W. Bader, *Mol. Phys.*, **3**, 137 (1960), has employed D_{3h} and C_{3v} symmetry AB_3 molecules undergoing distortion in illustration of the "pseudo-Jahn-Teller" effect which rationalizes the sign of interaction constants for vibration in terms of symmetry and energetics of low lying molecular electronic states. Others have invoked related arguments in rationalization of preferred structures and relative reactivities.^{25,26} Such concepts it appears may be usefully combined with force constant weighted least motion analysis to extend the domain and comprehensibility of the PLM.

(25) L. S. Bartell, *J. Chem. Educ.*, **45**, 754 (1968); L. S. Bartell and B. Anderson, *J. Chem. Soc., Chem. Commun.*, 786 (1973).

(26) L. Salem, *Chem. Phys. Lett.*, **3**, 99 (1969); L. Salem and J. S. Wright, *J. Amer. Chem. Soc.*, **91**, 5947 (1969).

influence reactivity correlation by least motion analysis based on end-point structural information.

Conclusions

To the extent that simple chemical reactions can be viewed as processes where the geometric deformations which characterize them are extensions of the small structural changes which give rise to their vibrational spectra, the principle of least motion for correlation of relative reactivities appears to be satisfactorily rationalizable. With the appropriate weighting of the individual atomic motions by masses and force constants, the harmonic model least motion deformations parallel the vibrational energies within symmetry selected modes. Even in the absence of such weighting, least motion paths for a given amount of collective atom movement usually correlate with those modes which are the softest in energy requirement, although exceptions must certainly be anticipated, notably for deformation of such unstable structures as those which characterize transition states. Along reaction paths, incremental motion perpendicular to the vector directed toward the molecular center of gravity appears to be generally favored over motion along the vector in either direction, a situation analogous to the stable molecule (vibration) results noted.

When applied to the large molecular deformations which are experienced over the entire course of conventional chemical reactions, a number of effects can enter which may mitigate the least motion–vibration theory analogy. A variety of these effects, both of external and internal origin, are examined in detail in the following report, employing the formalisms developed here.

Application of Analytic Least Motion Forms to Organic Reactivities¹

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Abstract: The analytic expressions previously derived to evaluate least motion distortions undergone during reaction are applied to a number of chemically interesting organic molecule systems. Consideration is given to differential changes along reaction pathways as well as to the gross geometry changes which accompany reactant conversions to product or transition states. Adopting the previously demonstrated analogy to the theory of small vibrations, the value of considering these differential changes within the principle of least motion is stressed. As well as reexamining a number of previously correlated reaction systems, some relatively simple examples are considered where dissections of the over-all motions are easily made and where good theoretical structure and energy information are available. These studies reveal least motion and enthalpies of activation usually produce the same ordering of reactivities. In all cases examined, where disagreement with experiment or other more firmly grounded theory is encountered, successful rationalization of the discrepancies appears possible.

Hine's harmonic springs ensemble model used for correlation of organic reactivities within the framework of the principle of least motion (PLM) was examined in detail in the preceding paper.² Closed

forms were presented for computation of least motion distortions for systems of fairly broad generality. Employing these, especially for differential motions around end-point states (reactant, product, and transition states), revealed a number of details of strong correspondence between the PLM and conventional theory of molecular vibrations. Similar and potentially useful

(1) Research performed under the auspices of the U. S. Atomic Energy Commission.

(2) S. Ehrenson, *J. Amer. Chem. Soc.*, **96**, 3778 (1974).