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previous papers,[11] a theory of nuclear substitution has been developed with the aim of providing a quantum mechanically sound framework for interpreting changes in molecular properties in terms of molecular structure. At present, this theory has been carried out to first-order wave function corrections (at the Hartree–Fock level), and a number of established chemical concepts have been shown to follow analytically from the first-order treatment. These include Benson's equivalent group schemes,[8] Pauling's covalent radii and electronegativity relationships,[48,49] free energy relations[49] such as the Hammett[10] and Drago equations,[50] and various rate–equilibrium relationships[12] including the Marcus equation.[2,4c] Preliminary results indicate that behavior derivable from parabolic/linear interpolation models is also closely associated with first-order perturbations, and consequently, this aspect, as well as extension to higher-order perturbations, is undergoing close examination.

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(48) L. Pauling, "The Nature of the Chemical Bond", 3rd ed., Cornell University Press, Ithaca, New York, 1960.

(49) J. R. Murdoch, unpublished. This result can be derived from equations published in ref 11a.

(50) F. L. Slejko, R. S. Drago, and D. G. Brown, *J. Am. Chem. Soc.* **94**, 9210 (1972).

Barrier Heights and the Position of Stationary Points along the Reaction Coordinate

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Abstract: Miller has derived a remarkably simple relationship for predicting the barrier position along a reaction coordinate in terms of the reaction thermodynamics (ΔE) and the barrier height ($\Delta E^{\ddagger}$). This relationship correlates very well with a wide variety of ab initio and empirical potential energy surfaces, and these correlations have prompted an examination of the conditions leading to Miller's result. It is shown that Miller's conditions alone (some properties of double-knot spline functions, arc-length minimization) are *not* sufficient, but that a scaled symmetry relationship (plus Miller's conditions) is sufficient. Miller's result has been obtained by using different spline functions to represent different sections of the reaction coordinate, and it would be of general interest to determine whether the scaled symmetry relationship can be observed for nonspline functions which span the entire reaction coordinate. By use of a general reaction coordinate function, $E(X) = {}^1/_2\Delta E(1 + h_1(X)) + \Delta E_0^{\ddagger}(1 - h_2(X))$, it is found ($\Delta E \neq 0$) that a necessary and sufficient condition for the scaled symmetry relationship is $h_2(X) = h_1(X)^2$. It is also found that the barrier height follows the Marcus equation, and deviations from the Marcus equation can be understood in terms of deviations from the "square" relationship ($h_2 = h_1^2$). The present work emphasizes that the Marcus equation does *not* depend on specialized assumptions such as intersecting parabolas, inverted-parabola-plus-linear-perturbation, intersecting Morse functions, etc., but derives from a more general relationship (i.e., the scaled symmetry relationship or equivalently, the "square" relationship: $h_2 = h_1^2$). It is shown that the scaled symmetry relationship follows from a second-order expansion of the reaction coordinate in terms of suitable functions (e.g., a Fourier series or bond order). It is found that for $h_2 = h_1^2$, the barrier position ($X^{\ddagger}$) is dependent on the degree of nonlinearity in $h_1(X)$. For example, the sigmoid function, $h_1(X) = X^p - (1 - X)^p/[X^p + (1 - X)^p]$, leads to the Marcus relationship for the barrier position ($X^{\ddagger} = {}^1/_2 + \Delta E/8\Delta E_0^{\ddagger} = [1 + (1 - \Delta E/\Delta E^{\ddagger})^{1/2}]^{-1}$) for $p = 1$ and to the Miller relationship ($X^{\ddagger} = [2 - \Delta E/\Delta E^{\ddagger}]^{-1}$) for $p = {}^1/_2$. The scaled symmetry relationship emphasizes the relationship between h_2 and h_1, rather than the specific form of the barrier function, as the key factor in governing the response of the barrier position and height toward changes in the overall thermodynamics of a reaction. The present results provide a sound theoretical foundation for extending the application of Marcus-like expressions from electron, proton, and group transfers to *all* one-step reactions, including pericyclic processes, carbonyl additions, fragmentations, cheletropic reactions, conformational equilibria, isomerizations, and so forth.

I. Introduction

Position of Stationary Points on Potential Energy Surfaces. Recently, Miller[1] proposed a simple relationship for predicting the barrier position along the reaction coordinate, and his proposal was tested against other methods[2-5] of computing the barrier position. Miller concluded that his equations compare favorably with "the best of the methods for computing the barrier position", and this includes the ab initio approaches. Miller's relationship is simple and predicts that the barrier position ($X^{\ddagger}$) depends *only* on the height of the barrier ($\Delta E^{\ddagger}$) and the energy difference between products and reactants (ΔE):

$$X^{\ddagger} = \frac{1}{2 - \Delta E/\Delta E^{\ddagger}} \qquad (1)$$

Miller derived this relationship by representing the reactant and product sides of the reaction coordinate by two separate spline functions (double-knot spline functions, DKSF) which are joined smoothly at the energy maximum. Miller's treatment leaves the choice of function for the splines completely open but imposes several constraints on the parameters so that the barrier function will have derivatives of zero at the initial and final points ($X = 0, X = 1$, respectively) and at the transition state ($X = X^{\ddagger}$). The values of the barrier function, $E(X)$, are constrained to pass

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(1) A. R. Miller, *J. Am. Chem. Soc.*, **100**, 1984 (1978).

(2) (a) F. London, *Z. Elektrochem.*, **35**, 552 (1929); (b) H. Eyring and M. Polanyi, *Z. Physik. Chem., Abt. B*, **B12**, 279 (1931); (c) S. Sato, *J. Chem. Phys.*, **23**, 592 (1955).

(3) H. S. Johnston and C. Parr, *J. Am. Chem. Soc.*, **85**, 2544 (1963).

(4) (a) F. O. Ellison, *J. Am. Chem. Soc.*, **85**, 3540 (1963); (b) J. C. Tully, *J. Chem. Phys.*, **64**, 3182 (1976); (c) J. C. Tully, *ibid.*, **58**, 1396 (1973).

(5) (a) C. F. Bender, S. V. O'Neil, P. K. Pearson, and H. F. Schaefer, III, *Science Washington, D.C.*), **176**, 1412 (1972); (b) B. Liu, *J. Chem. Phys.*, **58**, 1925 (1973); (c) C. F. Bender, B. J. Garrison, and H. F. Schaefer, III, *ibid.*, **62**, 1188 (1975); (d) P. Siegbahn and B. Liu, *ibid.*, **68**, 2457 (1978); (e) R. E. Howard, A. D. McLean, and W. A. Lester, Jr., *ibid.*, **71**, 2412 (1979).

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through zero, $\Delta E^\ddagger$, and ΔE at $X = 0$, $X = X^\ddagger$, and $X = 1$, respectively. These six constraints will be referred to as the barrier-function boundary conditions. The final constraint is that the parameters of the two spline functions are chosen to minimize the arc length of the barrier function, and Miller argues that the position of the barrier maximum ($X^\ddagger$) does not depend on the functional form of the spline functions (as long as the seven constraints are met). The barrier position, $X^\ddagger$, is always given by eq 1 and is completely independent of the two functions chosen to represent the two splines. Consequently, it is not necessary to actually fit splines to the reaction coordinate or even to know the functional form of the reaction coordinate in order to apply eq 1. Miller[1] has empirically shown that one suitable reaction coordinate variable for eq 1 is bond order (vide infra).

Miller's result (eq 1) is quite intriguing for several reasons. Although the same functional form must be used for each spline, Miller's proof places no further restriction on the choice of functions which can be used to fit the barrier surface. Since a very wide variety of admissable functions is available to fit a potential surface and since the path of minimum arc length has an obvious, although intuitive, relationship[6] to the minimum gradient or minimum energy path, eq 1 is a result with extremely general and far-ranging implications. These implications are given further weight by the impressive empirical correlations cited by Miller and the extensive applications[7] which have followed since Miller's original paper.

Theoretically, it is quite mysterious why the barrier position should be independent of the specific functional form of the reaction coordinate and should depend only on the barrier height and the reaction thermodynamics. After examining Miller's results more closely, it became apparent that arc-length minimization and the other criteria listed by Miller are *not* sufficient to give eq 1. There is one additional requirement which amounts to a modified symmetry relationship between the reactant and product halves of the reaction coordinate and is termed a "scaled symmetry relationship" (vide infra). Equation 1 is an apparently reasonable result on empirical grounds,[7] and while the author believes that this new finding does not appreciably reduce the significance of Miller's earlier results, an important question is raised concerning the theoretical significance of the scaled symmetry relationship. The purpose of the present paper is (1) to show that the scaled symmetry relationship plus Miller's other requirements are sufficient conditions leading to eq 1 and (2) to demonstrate that the scaled symmetry relationship provides a simple, but general, foundation for extending the application of Marcus-like equations to all one-step reactions.

II. Scaled Symmetry Relationship and the Barrier Position

Miller's use of double-knot spline functions (DKSF) to represent a potential barrier amounts to describing the reactant "half" of the barrier with one spline function and the product "half" with a second spline function. Thus, a barrier function, $E(X,X^\ddagger)$ is described in terms of $g_1(X,X^\ddagger)$ from $0 \le X \le X^\ddagger$ and in terms of $g_2(X,X^\ddagger)$ from $X^\ddagger \le X \le 1$ or in Miller's notation as

$$\begin{aligned} E(X,X^\ddagger) &= g_1(X,X^\ddagger),\ 0 \le X \le X^\ddagger \\ &= g_2(X,X^\ddagger),\ X^\ddagger \le X \le 1 \end{aligned} \tag{2}$$

The two interpolating functions, g_1 and g_2, are continuous, have continuous first derivatives, and belong to the same k-parameter family of equations. Two functions of X belong to the same k-parameter family if they each contain k functional parameters and if they differ only by the values of the k parameters. For example, all second-degree polynomials belong to the same three-parameter family. As an example, Miller considers a barrier represented by two cubic splines:

$$\begin{aligned} E_1(X,X^\ddagger) &= \Delta E^\ddagger(-2X^3 + 3X^2X^\ddagger)/X^{\ddagger 3},\ 0 \le X \le X^\ddagger \\ &= (\Delta E^\ddagger - \Delta E)[-2X^3 + 3(X^\ddagger + 1)X^2 - 3X^\ddagger(2X - 1) - 1]/(X^\ddagger - 1)^3 + \Delta E,\ X^\ddagger \le X \le 1 \end{aligned} \tag{3}$$

The splines meet the constraint that the first derivatives of $E_1(X,X^\ddagger)$ are zero at $X = 0$, $X = X^\ddagger$, and $X = 1$, and the splines also satisfy the contraints that $E_1(0,X^\ddagger) = 0$, $E_1(X^\ddagger,X^\ddagger) = \Delta E^\ddagger$, and $E_1(1,X^\ddagger) = \Delta E$. For cubic splines the only parameter left undetermined is $X^\ddagger$, and this is chosen by the arc-length minimization criterion.

The two cubic equations can be rewritten as

$$\Delta E^\ddagger\left[-2\left(\frac{X}{X^\ddagger}\right)^3 + 3\left(\frac{X}{X^\ddagger}\right)^2\right] = g_1(X),\ 0 \le X \le X^\ddagger \tag{4}$$

and

$$(\Delta E^\ddagger - \Delta E)\left[-2\left(\frac{1-X}{1-X^\ddagger}\right)^3 + 3\left(\frac{1-X}{1-X^\ddagger}\right)^2\right] + \Delta E = g_2(1-X),\ X^\ddagger \le X \le 1 \tag{5}$$

The rearranged form of the cubic splines illustrates the idea of the scaled symmetry relationship. Note that when $1 - X'$ represents the same fraction of $1 - X^\ddagger$ that X'' represents of $X^\ddagger$, and then $g_2 - \Delta E$ is the same fraction of the reverse barrier ($\Delta E^\ddagger - \Delta E$) that g_1 is of the forward barrier ($\Delta E^\ddagger$). Expressed as equations, if

$$\frac{1 - X'}{1 - X^\ddagger} = \frac{X''}{X^\ddagger} \tag{6}$$

then

$$\frac{g_2(1 - X') - \Delta E}{\Delta E^\ddagger - \Delta E} = \frac{g_1(X'')}{\Delta E^\ddagger} \tag{7}$$

For the cubic splines, the scaled symmetry relationship arises from the boundary conditions imposed at $X = 0$, $X = X^\ddagger$, and $X = 1$, since the four coefficients of each cubic are completely defined by the four boundary conditions. It is also easy to verify that when $X^\ddagger$ is given by eq 1, then the arc length of $E_1(X,X^\ddagger)$ (eq 3) is minimized (Table I*).

Two fourth-order polynomials satisfying the boundary conditions are given by

$$g_1(X,X^\ddagger) = (3 + C_1)\left(\frac{X}{X^\ddagger}\right)^2 - 2(1 + C_1)\left(\frac{X}{X^\ddagger}\right)^3 + C_1\left(\frac{X}{X^\ddagger}\right)^4 \tag{8}$$

$$g_2(X,X^\ddagger) = (3 + C_2)\left(\frac{1-X}{1-X^\ddagger}\right)^2 - 2(1 + C_2)\left(\frac{1-X}{1-X^\ddagger}\right)^3 + C_2\left(\frac{1-X}{1-X^\ddagger}\right)^4 \tag{9}$$

where C_1 and C_2 are arbitrary constants. When $C_1 = C_2$, g_1 and

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[6] The path of minimum arc length will not necessarily be the path of minimum energy. Arc-length minimization includes the effects of displacements along the energy axis and the coordinate axes, whereas energy minimization includes only the former. For certain simple surfaces (e.g., hyperbolic paraboloid) where the shortest path in terms of coordinate length is also the minimum energy pathway, the path of minimum arc length and minimum energy can coincide. In such cases, the fact that arc length involves mixing units of coordinates (Cartesian distance, bond order, etc.) with units of energy will not be troublesome. This situation may be reasonably common since many PES for proton and atom transfers bear a striking resemblance to hyperbolic paraboloids after transformation to bond-order coordinates (ref 22). In any event, the reader should be aware of the fact that the path of minimum arc length or minimum energy is dependent on the choice of coordinates and may have no direct relevance to the dynamic problem of molecules moving over a PES. However, such pathways do serve as a means of characterizing a PES.

[7] (a) B. Schaldach and H. F. Grutzmacher, *Int. J. Mass.*, **31**, 271 (1979); (b) M. M. L. Chen and H. F. Schaefer, III, *J. Chem. Phys.*, **72**, 4376 (1980); (c) R. Shubert and H. F. Grutzmacher, *J. Am. Chem. Soc.*, **102**, 5323 (1980); (d) R. F. Nalewajski, *Chem. Phys.* **50**, 127 (1980); (e) Y. Kondo, T. Yamada, and S. Kusabayashi, *J. Chem. Soc., Perkin Trans. 2*, 414 (1981); (f) D. Cremer, *J. Am. Chem. Soc.*, **103**, 3619, 3627 (1981); (g) D. Cremer, *Angew. Chem., Int. Ed. Engl.*, **20**, 888 (1981); (h) D. V. Ramana and H. F. Grutzmacher, *Org. Mass. Spectrom.*, **16**, 227 (1981); (i) G. Bouchoux, Y. Hoppilliard, M. Golfier, and M. G. Guillerez, *ibid.*, **16**, 29 (1981); (j) E. S. Lewis, C. C. Chen, and R. A. More O'Ferrall, *J. Chem. Soc., Perkin Trans. 2*, 1084 (1981); (k) J. J. Gajewski, *J. Am. Chem. Soc.*, **101**, 4393 (1979).

g_2 satisfy the scaled symmetry relationship, and the arc-length minimization criterion for $E_1(X,X^*)$ leads to a value for X^* which satisfies eq 1 (i.e., $C_1 = C_2 = -1.412$, see Table I*). However, if $C_2 = 10C_1$, then arc-length minimization does *not* lead to a value of X^* consistent with eq 1 (Table I*), and consequently *arc-length minimization and the fact that g_1 and g_2 are members of the same k-parameter family of interpolating functions are not sufficient conditions for leading to a barrier position predicted by eq 1.* When $C_2 = C_1 = -14.12$, the arc-length minimization criterion again leads to X^* given by eq 1 (Table I*). These results prove that additional criteria are necessary for eq 1 to hold, and in Appendix I* it is shown that the scaled symmetry relationship plus Miller's two criteria are sufficient.

III. Simple Functions Leading to the Scaled Symmetry Relationship

For DKS functions, the scaled symmetry relationship is equivalent to using the same scaled spline functions for the left and right halves of the reaction coordinate and to using eq 6 and 7 to establish the scaling relationship. One simple spline function[9] leading to the scaled symmetry relationship is the intersecting parabola model which has been used as a means of obtaining Marcus' equation.[8] Another spline function satisfying the scaled symmetry relationship is Agmon's suggestion,[10] which he obtains by combining Snell's law, describing the reflection of a light ray from a flat surface, with Pauling's definition of bond order[11] and Johnston's[3] approximation of bond-order conservation. A nonspline function[12] is the inverted parabola model,[13] which has also been used to rationalize the Marcus relationship.[14] Since Miller found remarkably consistent agreement between the ab initio or empirical barrier positions and eq 1, one is obviously led to consider the question of whether the scaled symmetry relationship or arc-length minimization have any fundamental significance. Neither the intersecting nor inverted parabola models lead to a minimum arc-length path, and consequently, we will first examine the general class of functions exhibiting the scaled symmetry relationship and then examine the subset of these functions satisfying the minimum arc-length criterion.

IV. General Functions Satisfying the Scaled Symmetry Relationship

Spline functions are a very convenient tool for obtaining approximations to complicated functions, but the fact that different interpolating functions are used for different ranges of the independent variable, X, impairs the interpretation of the parameters in terms of theoretical or physically interpretable quantities. It would be more convenient, and illuminating, to express the scaled symmetry relationship in terms of a single function spanning the domain of $0 \le X \le 1$.

From eq 2, let use consider two spline functions, g_1 and g_2, which are each composed of two parts:

$$g_1(X) = g_{1a}(X)b_{a1} + g_{1b}(X)b_{b1} \tag{10}$$

$$g_2(X) = g_{1a}(X)b_{a2} + g_{1b}(X)b_{b2} \tag{11}$$

where b_{ai}, b_{bi} are appropriate constants and $g_{1a}(X)$ and $g_{1b}(X)$ are any linearly independent functions which span the space of $g_1(X)$ and $g_2(X)$. Miller has used separate splines to represent the left and right halves of the barrier function, $E(X)$, and in Appendix II*, it is shown that necessary conditions for $E(X)$ to match $g_1(X)$ over $0 \le X < X^*$ and to match $g_2(X)$ over $X^* \le X \le 1$ (where the constraint $g_1(X) = g_2(X)$ is imposed)[15] are as follows:

$$g_{1b}(X) = [g_{1a}(X)]^2 \tag{12}$$

$$g_{1a}(X^*) = [1 + (1 - \Delta E/\Delta E^*)^{1/2}]^{-1} \tag{13}$$

From the results in Appendix II*, the energy along the reaction coordinate at position, X, is given by

$$E(X) = \Delta E^* \left[\frac{2g_{1a}(X)}{g_{1a}(X^*)} - \frac{g_{1a}(X)^2}{g_{1a}(X^*)^2} \right] \tag{14}$$

and from Appendix II*,

$$g_{1a}(X^*) + g_{1a}(1 - X^*) = 1 \tag{15}$$

which is equivalent to conservation of the transformed reaction coordinate at the stationary point, X^*. *Equations 12 and 13 follow by imposing the constraint that the two spline functions,* $g_1(X)$

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(8) Marcus has derived two different equations. The first for weak-overlap electron transfer appears in ref 8a and is referred to as the Marcus equation in the present paper. The second is for atom transfer reactions and is discussed in ref 8b: (a) R. A. Marcus, *J. Chem. Phys.*, **24**, 966 (1956); (b) R. A. Marcus, *J. Phys. Chem.*, **72**, 891 (1968).

(9) The intersecting parabola model consists of two parabolas, spaced at a fixed horizontal distance of 1 unit and separated vertically by ΔE. The quadratic coefficient of each parabola is identical. The parabolas are given by $y_1 = aX^2$ and $y_2 = a(1 - X)^2 + \Delta E$ and to establish the scaled symmetry relationship we need to prove the following:

$$\frac{af^2(X^\ddagger)^2}{\Delta E^\ddagger} = \frac{af^2(1 - X^\ddagger)^2}{\Delta E^\ddagger - \Delta E}$$

Eliminating af^2 from each side, substituting $X^\ddagger = {}^1/_2 + \Delta E/2a$ and $\Delta E^\ddagger = (1 + 2\Delta E/a + \Delta E^2/a^2)a/4$, we get

$$\tfrac{1}{2} - \frac{\Delta E^2}{2a^2} = \tfrac{1}{2} - \frac{\Delta E^2}{2a^2}$$

which establishes the scaled symmetry relationship for the intersecting parabola model.

(10) (a) N. Agmon, *J. Chem. Soc., Faraday Trans. 2*, **74**, 388 (1978); (b) for $0 \le X \le X^\ddagger$, Agmon's spline function is

$$\frac{(2\Delta E^* - \Delta E)^q}{\Delta E^{\ddagger q-1}} X^q = E(X)$$

which can be rearranged to give

$$\left(\frac{X}{X^\ddagger} \right)^q = \frac{E(X)}{\Delta E^*}$$

by using $X^\ddagger = \Delta E^\ddagger/(2\Delta E^\ddagger - \Delta E)$. For $X^\ddagger \le X \le 1$, Agmon's spline function is

$$\frac{(2\Delta E^\ddagger - \Delta E)^q}{(\Delta E^\ddagger - \Delta E)^{q-1}}(1 - X)^q + \Delta E = E(X)$$

which is equivalent to

$$\frac{(1 - X)^q}{(1 - X^\ddagger)^q} = \frac{E(X) - \Delta E}{\Delta E^\ddagger - \Delta E}$$

which establishes the scaled symmetry relationship. Note that Agmon's splines have a "cusp" at the transition state rather than a stationary point. Agmon's result also satisfies eq 1.

(11) L. Pauling, *J. Am. Chem. Soc.*, **69**, 542 (1947).

(12) The inverted parabola model requires that a parabola meet the constraints: [(1) $E(0) = 0$; (2) $E(X^\ddagger) = \Delta E^\ddagger$; (3) $\mathrm{d}E(X)/\mathrm{d}X = 0$ at $X = X^\ddagger$; (4) $E(1) = \Delta E$]. A parabola satisfying the first three conditions is given by

$$E(X) = \Delta E^\ddagger \left[\frac{2X}{X^\ddagger} - \left(\frac{X}{X^\ddagger} \right)^2 \right]$$

and another parabola satisfying the second three conditions is given by

$$E(X) = \Delta E_R{}^\ddagger \left[\frac{2(1 - X)}{(1 - X^\ddagger)} - \left(\frac{1 - X}{1 - X^\ddagger} \right)^2 \right] + \Delta E$$

Both parabolas satisfy the scaled symmetry relationship for all values of $X^\ddagger$. When $X^* = 0.5 + \Delta E/8\Delta E_0{}^*$, both parabolas meet all four constraints and are equivalent to the inverted parabola leading to the Marcus equation. Consequently, the inverted parabola leading to the Marcus equation also satisfies the scaled symmetry relationship.

(13) E. R. Thorton, *J. Am. Chem. Soc.*, **89**, 2915 (1967).

(14) J. L. Kurz, *Chem. Phys. Lett.*, **57**, 243 (1978).

(15) The function $g_2(X)$ is the spline covering the domain $X^\ddagger \le X \le 1$. Since we require $g_2(X) = g_1(X)$, $g_2(X)$ can be expanded in terms of $g_{1a}(X)$ and $g_{1b}(X)$.

and $g_2(X)$, are the same function, so that either of them will describe the entire reaction coordinate ($0 \leq X < 1$). A number of interesting consquences result: (1) The barrier position is a function of $1 - \Delta E/\Delta E^{\ddagger}$ and depends *only* on the ratio $\Delta E/\Delta E^{\ddagger}$ (eq 13). (2) If the transformed coordinate, $g_{1a}(X^{\ddagger})$, is interpreted as bond order, then eq 15 is equivalent to *bond-order conservation* which has been assumed in the past for a number of highly successful empirical treatments of group transfer reactions.[16] (3) The analogue of eq 14 for the reverse direction of the reaction is given by

$$E(1 - X) = (\Delta E^{\ddagger} - \Delta E)\left[\frac{2g_{1a}(1 - X)}{g_{1a}(1 - X^{\ddagger})} - \frac{g_{1a}(1 - X)^2}{g_{1a}(1 - X^{\ddagger})^2}\right] + \Delta E \quad (16)$$

By a comparison of eq 16 and 14, it can be seen that the scaled symmetry relationship holds not for the variables $1 - X$ and X, but for the transformed variables [i.e., $g_{1a}(1 - X)$ and $g_{1a}(X)$] so that the analogies to eq 6 and 7 are as follows. If

$$\frac{g_{1a}(1 - X')}{g_{1a}(1 - X^{\ddagger})} = \frac{g_{1a}(X'')}{g_{1a}(X^{\ddagger})} \quad (17)$$

then

$$\frac{E(1 - X') - \Delta E}{\Delta E^{\ddagger} - \Delta E} = \frac{E(X'')}{\Delta E^{\ddagger}} \quad (18)$$

V. Special Cases of the Scaled Symmetry Relationship

A. Arc-Length Minimization. It is noteworthy that there is no function, spanning the domain $0 \leq X \leq 1$, which can be constructed from two identical splines and which satisfies both the scaled symmetry relationship and the arc-length minimization criterion. This can be seen by noting from eq 1 and 14 that the arc-length minimization criterion requires that

$$g_{1a}(X^{\ddagger}) = [2 - \Delta E/\Delta E^{\ddagger}]^{-1} \quad (19)$$

which is in conflict with eq 13, except at $\Delta E = 0$ and $\Delta E = \Delta E^{\ddagger}$. Satisfaction of the arc-length minimization criterion requires two different spline functions. Since the double-knot spline representation (using different splines) is always an approximation to any "true" barrier function, it appears that barrier functions in general do not have to *exactly* satisfy both the scaled symmetry relationship and the arc-length minimization criterion. However, as Miller's empirical relationships clearly demonstrate, real barrier functions come fairly close to meeting both constraints. It may be significant to note that while the two constraints cannot be precisely met for all values of $X^{\ddagger}$ ($0 \leq X^{\ddagger} \leq 1$), arc-length minimization and the scaled symmetry relationship can be satisfied at the midpoint of this range ($X^{\ddagger} = {}^1/_2$, $\Delta E = 0$) and at the end points ($X^{\ddagger} = 1$, $\Delta E = \Delta E^{\ddagger}$; $(1 - X^{\ddagger}) = 1$, $\Delta E = \Delta E_R^{\ddagger}$).

Since the scaled symmetry relationship implies a definite connection between the two halves of the reaction coordinate function, one might anticipate breakdowns for reactions where the forming bond is different from the beaking bond. An example might be the reaction $F\cdot + H_2 \rightarrow F\text{–}H + H\cdot$, for which Bender and Schaefer have calculated the potential energy surface.[17] In order to see how well the corresponding reaction coordinate follows the scaled symmetry relationship, we fit a polynomial, satisfying Miller's boundary conditions, to half of the reaction coordinate ($X^{\ddagger} \leq X \leq 1$). The scaled symmetry relationship was used to generate the other half ($0 \leq X \leq X^{\ddagger}$), and the results are shown in Figure 1.

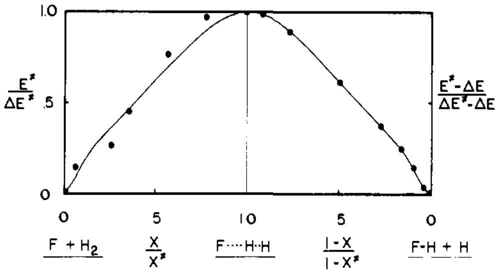

Figure 1. Scaled symmetry relationship for $F\cdot + H_2 \rightarrow F\text{–}H + \cdot H$. The potential surface for this reaction (ref 17) has been transformed from Cartesian coordinates to bond-order coordinates (ref 25) and scaled according to eq 6. The curve on the right half of the figure has been fitted to the transformed potential surface calculated by Bender and Shaefer (ref 17) and gives a reasonably good description of the left half of the surface. The scatter on the left side is largely due to the fact that $\Delta E^{\ddagger} = 1.66$ kcal, and consequently the left-side deviations are only 0.1–0.3 kcal which is close to the degree of optimization achieved by Bender and Schaefer. For comparison, $\Delta E^{\ddagger} - \Delta E = 36.1$ kcal. The scaled symmetry relationship is illustrated for the case where $g_1(X)$ and $g_2(X)$, eq 2, are double-knot spline functions. Miller's relationship is satisfied quite well: predicted $1 - X^{\ddagger}$ (eq 1) = 0.956 ($X^{\ddagger}$ = 0.044); $1 - X^{\ddagger}$ (Bender and Schaefer, ref 17 and 25) = 0.941 ($X^{\ddagger}$ = 0.083). Since $g_1(X)$ and $g_2(X)$ are nonquadratic, Marcus' equation (eq 23) shows significant deviations for the the barrier position: predicted $1 - X^{\ddagger}$ = 0.77 ($X^{\ddagger}$ = 0.23). Note that $E(X^{\ddagger}) = E^{\ddagger} = \Delta E^{\ddagger}$.

B. Scaled Symmetry Relationship and the Marcus Equation. The scaled symmetry relationship leads to eq 14 which gives the energy along the reaction coordinate as a quadratic expression in the arbitrary function $g_{1a}(X)$. Another quadratic expression in $g_{1a}(X)$ is given by

$$E(X) = g_{1a}(X)\Delta E + g_{1a}(X)[1 - g_{1a}(X)]4\Delta E_0^{\ddagger} \quad (20)$$

where $\Delta E_0^{\ddagger}$ equals $E(X_0^{\ddagger})$ at the stationary point ($X_0^{\ddagger}$) for the special case of $\Delta E = 0$. Equation 20 can be rearranged to

$$E(X) = g_{1a}(X)[4\Delta E_0^{\ddagger} + \Delta E] - 4\Delta E_0^{\ddagger}g_{1a}(X)^2 \quad (21)$$

Equating coefficients of the quadratic term in $g_{1a}(X)$ in eq 14 and 21, we have

$$\Delta E^{\ddagger} = g_{1a}(X^{\ddagger})^2 4\Delta E_0^{\ddagger} \quad (22)$$

Equating coefficients of the linear term in $g_{1a}(X)$ in eq 14 and 21, we have

$$g_{1a}(X^{\ddagger}) = {}^1\!/_2 + \Delta E/8\Delta E_0^{\ddagger} \quad (23)$$

Equations 22 and 23 show that the scaled symmetry relationship can be expressed in the equivalent form of eq 21. The barrier height ($\Delta E^{\ddagger}$) given by eq 21 can be obtained by substituting $g_{1a}(X) = g_{1a}(X^{\ddagger})$ and using eq 23:

$$\Delta E^{\ddagger} = \Delta E_0^{\ddagger} + {}^1\!/_2\Delta E + \frac{\Delta E^2}{16\Delta E_0^{\ddagger}} \quad (24)$$

which is the Marcus equation[8,18] and is the same expression obtained by direct differentiation of eq 21. The result is a significant one[19] and demonstrates that Marcus' equation follows from a condition (i.e., a barrier function satisfying the scaled symmetry relationship) which is much more general than often believed (e.g., as a consequence of intersecting parabolas or adding a linear perturbation to a parabola, etc.).

From eq 20, it can be seen that the Marcus relationship depends not on the specific choice of $g_{1a}(X)$, but on the relationship (see eq 20) between the function modifying ΔE (i.e., $g_{1a}(X)$) and the function modifying $\Delta E_0^{\ddagger}$ (i.e., $4g_{1a}(X)[1 - g_{1a}(X)]$). We can obtain a clearer view of this relationship by examining a reaction coordinate function of the form:[20]

$$E(X) = {}^1\!/_2\Delta E[1 + h_1(X)] + \Delta E_0^{\ddagger}[1 - h_2(X)] \quad (25)$$

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(16) E.g., ref 3. Pauling's definition of bond order (ref 11) is given by $n = e^{(r_0 - r)/0.26}$, where n is bond order, r_0 is the equilibrium bond distance, and r is the distance between two nuclear centers. Pauling's definition represents one specific transformation of coordinates based on Cartesian distances (i.e., bond lengths).

(17) C. F. Bender, S. V. O'Neil, P. K. Pearson, H. F. Schaefer, III, *Science (Washington, D.C.)* **176**, 1412 (1972).

(18) Note that the barrier position relationship, eq 23, applies to the transformed variable $g_{1a}(X^{\ddagger})$, not to $X^{\ddagger}$. However, the barrier height relationship is independent of the choice of function for g_{1a} (eq 20 and 24).

(19) Kurz (ref 14) has also shown that eq 21 leads to the Marcus equation. The fact that eq 21 follows from the scaled symmetry relationship is a new result.

where $h_1(X)$ and $h_2(X)$ are linearly independent functions. By comparison of eq 20 and 25, it can be seen that[21]

$$h_1(X) = 2g_{1a}(X) - 1 \tag{26}$$

$$h_2(X) = 1 - 4g_{1a}(X)[1 - g_{1a}(X)] = h_1(X)^2 \tag{27}$$

Consequently, the Marcus equation will hold whenever $h_2(X)$ is the square of $h_1(X)$,[2] which in turn will hold for any function satisfying the transformed scaled symmetry relationship (i.e., eq 17 and 18).

The scaled symmetry relationship has a simple physical origin which can be best illustrated by example. If one considers a two-term Fourier expansion of a reaction coordinate,[23]

$$E(\phi) = 0.5v_1(1 - \cos\phi) + 0.5v_2(1 - \cos 2\phi) \tag{28}$$

it can be shown, after making the substitutions ($v_1 = \Delta E$; $v_2 = \Delta E_0^{\ddagger}$; $\cos 2\phi = 2\cos^2\phi - 1$), that $h_1 = -\cos\phi$ and $h_2 = \cos^2\phi$. Since $h_2 = h_1^2$, eq 28 conforms to the scaled symmetry relationship and follows the Marcus equation exactly as v_1 and v_2 are varied. Equation 28 has been commonly applied to 2-fold rotational barrier problems,[23] but with a suitable definition of ϕ, it could be employed as an approximate expression for any reaction coordinate with a single stationary point between reactants and products.

Another function which leads to a low-order expansion of a reaction coordinate is bond order (n), where

$$n = e^{-a(r-r_0)} \tag{29}$$

a is a constant, r is the bond distance between two fragments (A–B), and r_0 is the equilibrium distance. Morse[24] used this relation in order to transform a vibrational well, which is anharmonic when expressed in Cartesian coordinates, to one which is quadratic when expressed in bond order. The Morse equation, in terms of bond order, is given by

$$E(n) = D_{AB}[n^2 - 2n] \tag{30}$$

where D_{AB} is the A–B bond dissociation energy. If this idea is applied to an A–B–C potential surface where the energy of A–B–C is empirically broken down into pairwise, Morse-like interactions between A–B, B–C, and A–C, it can be shown[25] that the A–B and B–C interactions will contribute terms in n as high as second order and that the A–C interaction will contribute terms up to fourth order. For reactions whose stationary points occur near $n_{BC} \sim 0$, $n_{BC} \sim {}^1/_2$ or $n_{BC} \sim 1$ (n_{BC} is B–C bond order), the quartic terms are relatively unimportant, and application[25] of eq 25 to the potential surface shows that $h_2 \simeq h_1^2$ and that the Marcus equation gives a close description of ΔE^*.

The relationship between h_1 and h_2 has recently been examined for minimum energy pathways of several ab initio potential energy surfaces involving proton, atom, and methyl transfers,[25] pericyclic reactions,[22b,c] additions/fragmentations,[22b,c] and conformational equilibria.[22d] In all cases, the function h_1 is nearly linear in bond order, and the square relationship ($h_2 = h_1^2$) leading to the Marcus equation holds to a high degree in the vicinity of the stationary point for many of the reactions, but in some of the group transfer reactions, substantial deviations from the square relationship (and Marcus' equation) are observed. The deviations are well described in terms of $h_2 = c_2h_1^2 + c_4h_1^4$, and preliminary results[22b] indicate that the origin of the h_1^4 terms derives, at least in part, from the A–C interactions (as described by a pairwise Morse interaction model) in the structure [A–B–C] at the stationary point. These results, which will be reported elsewhere, illustrate that many potential surfaces can be represented as low-order expansions in terms of suitable functions and that, for some reactions, even the quadratic bond-order expansion is not bad.[22a,b] In such cases, the scaled symmetry relationship and the resulting square relationship ($h_2 = h_1^2$) will be good approximations, and the Marcus equation will give a good account of the barrier height.

C. Scaled Symmetry Relationship and the Barrier Position. The Marcus equation can be used to obtain barrier heights without explicitly knowing h_1, h_2, or $g_{1a}(X)$. When the square relationship is applicable, $g_{1a}(X^{\ddagger})$ is given by eq 23, but unless the function g_{1a} is known, $X^{\ddagger}$ cannot be obtained. Fortunately, it appears that for many reactions g_{1a} is close to linear[22a,b,25] in bond order so that $g_{1a}(X^{\ddagger})$ can be approximated as the barrier position when the reaction coordinate is expressed as a fractional displacement in terms of bond order. This approach is equivalent to rewriting eq 23 as

$$g_{1a}(X^{\ddagger}) = {}^1\!/_2 + \frac{\Delta E}{8\Delta E_0^{\ddagger}} \simeq X^{\ddagger} \tag{31}$$

and the rhs has been used by Marcus to obtain the barrier position.[8b]

As a first approximation for a nonlinear relationship between $g_{1a}(X)$ and X (bond order), we could consider a symmetrical sigmoid function ($0 \leq X \leq 1$) with a single inflection point at $X = {}^1/_2$:

$$g_{1a}(X) = \frac{X^{1/2}}{X^{1/2} + (1 - X)^{1/2}} \tag{32}$$

For $X = X^{\ddagger}$, eq 32 can be substituted into eq 13, $g_{1a}(X^{\ddagger})$ can be eliminated, and an expression for $X^{\ddagger}$ can be obtained which is identical with the Miller equation (eq 1). Consequently, if

$$h_1 = \frac{X^{1/2} - (1 - X)^{1/2}}{X^{1/2} + (1 - X)^{1/2}} \tag{33}$$

$$h_2 = h_1^2 \tag{34}$$

then eq 25 gives a *barrier height* which follows the *Marcus* equation and a *barrier position* which follows the *Miller* equation.[26] It is interesting to note that several examples of ab initio reaction coordinates (single stationary points) have recently been found where $\Delta E^{\ddagger}$ is well approximated by the Marcus equation, and $X^{\ddagger}$ is well approximated by the Miller equation.[22a,25]

We could also consider a nonlinear function of the form

$$g_{1a}(X) = \frac{X^p}{X^p + (1 - X)^p} \tag{35}$$

which on substitution into eq 13 gives

$$X^* = \frac{1}{1 + \left(1 - \dfrac{\Delta E}{\Delta E^{\ddagger}}\right)^{1/2p}} \tag{36}$$

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(20) Consider $\Delta E \neq 0$ and arbitrary barrier function, $E(X) = F(X) = F(\epsilon) = F(0.5) + F^1({}^1/_2)(\epsilon - {}^1/_2) + {}^1/_2F^2({}^1/_2)(\epsilon - {}^1/_2)^2 + \ldots$. $E(X)$ can be divided into an even function in $(\epsilon - {}^1/_2)$ and an odd function in $(\epsilon - {}^1/_2)$ where $R_2(\epsilon)$ and $R_1(\epsilon)$ are the even and odd functions, respectively:

$$R_1(\epsilon) = F^1(1/2)(\epsilon - 1/2) + \frac{1}{3!}F^3(1/2)(\epsilon - 1/2)^3 + \ldots$$

$$R_2(\epsilon) = F(1/2) + 1/2F^2(1/2)(\epsilon - 1/2)^2 + \ldots$$

$E(X)$ can be expressed as

$$E(X) = 1/2\Delta E(S_1) + 1/2\Delta E + \Delta E_0^{*}S_2$$

where $S_1 = 2R_1/\Delta E$ and $S_2 = (R_2 - {}^1/_2\Delta E)/\Delta E_0^{\ddagger}$. Setting $h_1 = S_1$ and $h_2 = 1 - S_2$, we obtain eq 25 which is a general expression for any barrier function where $\Delta E \neq 0$.

(21) Equations 26 and 27 are obtained by equating corresponding coefficients of ΔE and ΔE_0^{*} in eq 20 and 25.

(22) (a) Jane Donnella, Thesis, University of California at Los Angeles (1982); (b) J. R. Murdoch, D. E. Magnoli, and J. Donnella, paper presented at James Flack Norris Symposium, Meeting of The American Chemical Society, March, 1982, Las Vegas, NV; (c) J. R. Murdoch and M. S. Berry, unpublished; (d) J. R. Murdoch and M. Chen, *J. Am. Chem. Soc.*, in press.

(23) L. Random, W. J. Hehre, and J. A. Pople, *J. Am. Chem. Soc.*, 94, 2371 (1972).

(24) P. M. Morse, *Phys. Rev.*, **34**, 57 (1929).

(25) J. R. Murdoch and J. Donnella, *J. Am. Chem. Soc.*, in press.

(26) This result illustrates that the arc-length minimization criterion is not a necessary condition for obtaining eq 1. Sufficient conditions leading to eq 1 are the scaled symmetry relationship (and associated restrictions leading to eq 14) and the specific nonlinear relationship between $h_1(X)$ and X given by eq 33.

Note that for $p = {}^1/_2$ we get the Miller relationship for the barrier position, while $p = 1$ gets us the Marcus relationship for the barrier position (eq 31, rhs). It is interesting that two examples of double-minima reaction coordinates have been examined, and it appears that $p > 1$ gives a better account of the nonlinearity seen for $g_{1a}(X)$ vs. X than $p \leq 1$.[22a,25] It is too early to tell whether specific values of p, or ranges of p, will correspond to the number of maxima and minima along the reaction coordinate, but it is clear that a single value of p will not be universal. Since values larger than one and less than one have been found, it would appear that the Marcus relationship for the barrier position (eq 31, rhs), corresponding to $p = 1$, may be a comfortable, although somewhat imprecise, compromise.

VI. Conclusions

Miller has previously developed a simple and remarkably successful relationship for predicting the barrier position in terms of $\Delta E^\ddagger$ and ΔE, and it has been found that at least one new condition is necessary for obtaining Miller's equation. A sufficient condition has been identified and is termed a scaled symmetry relationship. The general class of barrier functions (nonspline) which exhibit the scaled symmetry relationship has been defined. All of them lead to the Marcus relationship for the *barrier height*, and special cases lead to the Marcus or Miller relationships for the *barrier position* along the reaction coordinate. The scaled symmetry relationship follows from limiting the expansion of the reaction coordinate to second-order terms in suitable functions and forms a general basis for extending Marcus-like equations to *all* one-step reactions, including electron, proton, and group transfers, pericyclic processes, additions, fragmentations, cheletropic reactions, conformational equilibria, isomerizations, and so forth. The fundamental basis of the scaled symmetry relationship is undergoing examination.[22,25,27]

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Supplementary Material Available: Arc-length minimization for cubic and quartic polynomials (Table I*), arc length minimization criteria (Appendix I*), and derivation of functions satisfying the scaled symmetry relationship (Appendix II*) (13 pages). Ordering information is given on any current masthead page.

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Intrinsic Barriers in Nucleophilic Displacements. A General Model for Intrinsic Nucleophilicity toward Methyl Centers

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Abstract: The applicability of the Marcus rate–equilibrium formalism to the double-minimum potential energy surface for gas-phase S_N2 reactions is proposed and used to develop a model for intrinsic nucleophilicity toward methyl centers. The key quantities in this model are the energy barriers to degenerate reactions of the form $X^- \cdot CH_3X \rightarrow XCH_3 \cdot X^-$, in which the reacting species are ion–molecule cluster intermediates. Available experimental and theoretical data corroborate several of the model's predictions. A new structure–nucleophilicity correlation is proposed, involving methyl cation affinities. The model suggests that delocalization effects do not greatly influence nucleophile reactivity.

How readily do the species X and Y participate in a nucleophilic displacement reaction such as eq 1? The concept of nucleo-

$$X^- + CH_3Y \rightarrow Y^- + CH_3X \qquad (1)$$

philicity in S_N2 reactions of aliphatic systems has been a cornerstone of organic chemistry ever since the early kinetic and stereochemical investigations of Ingold and co-workers.[1] Some indication of this can be found in the considerable body of work devoted to the quantitative description of nucleophilicity. Results of this effort include linear free energy relationships such as the Swain–Scott[2a] and Edwards[2b] equations and the general treatment of Hudson.[2c] However, a completely satisfactory and unambiguous scheme for this quantification has yet to be presented, and the success and scope of the above treatments are limited. Part of the difficulty arises from solvent effects, as even relative reactivities in S_N2 reactions can be solvent dependent.[3] This factor renders separation of intrinsic and solvent effects on the basis of solution-phase data difficult if not impossible. Also, nucleophilicity is inherently a kinetic property; according to such rate–equilibrium treatments as the Bell–Evans–Polanyi principle,[4] reaction rates can be affected by thermodynamics. Thus, a complete description of nucleophilicity requires some means of compensating for any thermodynamic driving force. In general, this feature has not been included in past efforts.[5]

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[1] Ingold, C. K. "Structure and Mechanism in Organic Chemistry"; Cornell University Press: Ithaca, New York, 1969; p 422 ff.

[2] (a) Swain, C. G.; Scott, C. C. *J. Am. Chem. Soc.* **1953**, *75*, 141. (b) Edwards, J. D. *Ibid.* **1956**, *78*, 1819. (c) Hudson, R. F. *Chimia* **1962**, *16*, 173.

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[5] However, a treatment of S_N2 reactions in solution has appeared recently (Albery, W. J.; Kreevoy, M. M. *Adv. Phys. Org. Chem.* **1978**, *16*, 87) in which the kinetic–thermodynamic separation has been accomplished by using the Marcus equation, as we do here for the analogous gas-phase process. However, this work does not allow separation of solvent and intrinsic effects.

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