31. Bauschlicher Jr., C. W., Schaefer, H. F., Bender, C. F.: J. Am. Chem. Soc. **98**, 1653 (1976)
32. Slanina, Z.: Adv. Quantum Chem. **13**, 89 (1981)
33. Natanson, G. A.: Molec. Phys. **46**, 481 (1982)
34. Laugwitz, D.: Differentialgeometrie, Stuttgart: B. G. Teubner, 1977
35. Arnold, V. I.: Gewöhnliche Differentialgleichungen. Berlin: Akademie-Verlag 1979
36. Eckart, C.: Phys. Review **47**, 552 (1935)
37. Sørenson, G. O.: Topics Curr. Chem. **82**, 97 (1979)
38. Wilson, E. B., Decius, J. C., Cross, P. C.: Molecular vibrations. New York: McGraw Hill 1955
39. Pulay, P.: in: Modern Theoretical Chemistry, Vol. 4, p. 153, H. F. Schaefer, Ed., New York: Plenum 1977
40. Pulay, P.: Molec. Phys. **17**, 197 (1969)
41. Pulay, P.: Theoret. Chim. Acta (Berl.) **50**, 299 (1979)
42. Penrose, R.: Proc. Cambridge Phil. Soc. **51**, 406 (1955)
43. Ben-Israel, A., Greville, T. N. E. in: Generalized inverses and applications, p. 125. M. Z. Nashed, Ed., New York: Academic Press 1976
44. Gardener, M., Rogers, D. E.: J. Chem. Soc. Faraday Trans. II **68**, 1410 (1972)
45. Kornilov, M. Yu., Tolstukha, T. A., Kadziauskas, P., Butkus, E.: Computers & Chem. **6**, 193 (1982)
46. Williams, I. H.: J. Molec. Struct. **94**, 275 (1983); Essén, H.: J. Comput. Chem. **4**, 136 (1983)
47. Korn, G. A., Korn, T. M.: Mathematical handbook for scientists and engineers (Russ.), Chap. 16.7. Moscow: Nauka 1970
48. Stanton, R. E., McIver, J. W.: J. Am. Chem. Soc. **97**, 3632 (1975)
49. Fukui, K. in: The world of quantum chemistry, p. 113. R. Daudel, B. Pullman, Eds., Dordrecht: D. Reidel Publ. Comp. 1974
50. Fukui, K., Kato, S., Fujimoto, H.: J. Am. Chem. Soc. **97**, 1 (1975)
51. Morokuma, K. Kato, S., Kitaura, K., Obera, S., Ohata, K., Hanamura, M. in: New horizons of quantum chemistry, p. 221. P.-O. Löwdin, B. Pullman, Eds., Dordrecht: Reidel 1983
52. Chapuisat, X., Jean, Y.: Topics Curr. Chem. **68**, 1 (1976)
53. Chapuisat, X., Nauts, A., Durand, G.: Chem. Phys. **56**, 91 (1981)
54. Herzberg, G.: Molecular spectra and molecular structure (II), p. 74, p. 160. Toronto: D. van Nostrand Comp. 1945
55. Nauts, A., Chapuisat, X.: Chem. Phys. Letters **85**, 212 (1982)
56. Balin, I., Ban, M. I.: Theoret. Chim. Acta (Berl.) **63**, 255 (1983)
57. Among mathematicians you can hear the joke: An existence proof is the key for a jewel-box lying on the ground of the ocean
58. Hirsch, M. W., Smale, S.: Differential equations, dynamical systems and linear algebra. New York: Academic Press 1974
59. Basilevski, M. V.: Chem. Phys. **24**, 81 (1977)
60. Mezey, P. G.: Theoret. Chim. Acta (Berl.) **54**, 95 (1980)
61. Mezey, P. G. in: Applications of MO theory in organic chemistry, p. 127. Csizmadia, I. G., Ed., Amsterdam: Elsevier 1977
62. Quapp, W., Heidrich, D.: Wiss. Z. Karl-Marx-Univ. Leipzig, Math.-Naturwiss. R. **33**, 410 (1984)
63. Watson, J. K. G.: J. Molec. Spectr. **45**, 99 (1973)

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Analysis of the concept of minimum energy path on the potential energy surface of chemically reacting systems

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Some confusion regarding the properties of minimum energy paths is evident in the literature. We show that a way of steepest descent on a potential surface can be defined independently upon the choice of the coordinate systems. The result is applied to mass-weighted coordinates and their use is critically reviewed. Fukui's IRC appears to be a special case of the steepest descent path starting from a saddle point. The impossibility to define a general ascent path is illustrated and the relations of IRC to real trajectories are discussed.

Key words: Potential energy surface—role of coordinate system—path of steepest descent—curvilinear coordinates—mass weighted coordinates

1. Introduction and formulation of the problem

The concept of potential energy surfaces (PES) as a basis for the understanding of chemical reactions was successfully used in Transition State Theory [1]. Starting point for this concept is the adiabatic separation of the movement of the electrons from that of the nuclei in a given chemical system. The changes in the frame of the nuclei are controlled by a potential function $U(x)$ depending parametrically on the positions of nuclei x^i. Stable arrangements (reactants, products, intermediates) are minima in $U(x)$ characterized by $x_{\min}$; transition states correspond to saddle points (sp) of first order [2] in $U(x)$ characterized by x_{sp}.