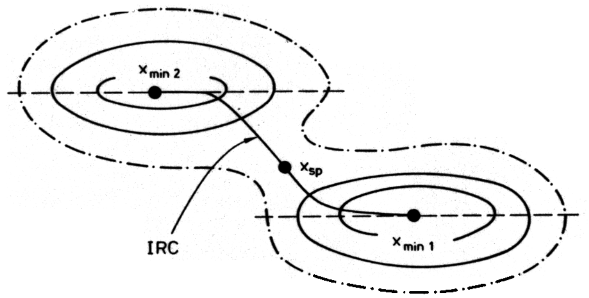

Fig. 1. The IRC on a two-dimensional model potential surface (--- valley paths and displacement lines, see text)

and change the potential surface by mutual displacements of the two rigid minima-hollows along the direction of the eigenvector of the smallest eigenvalue (that means we only change level lines upwards from the (-·-·-)-line) we will observe a change in the relative position of the saddle to those of the both minima. Hence, it results a change of the IRC also for the fixed part of the surface. The knowledge of the local curvatures of the potential in a minimum position does not generally allow a conclusion in which direction the lowest next saddle can be found.

It should be denoted that in Fig. 1 no branching of the (- - -)-valley exists. So we cannot follow one of the branches from the minimum to the saddle obtaining the IRC. Consequently, the idea of the optimal ascent path [6] fails here.

(iii) The solutions of the gradient equations (2, 8, or 23) cross the equipotential surfaces rectangular in every regular point [25, 26]. In a potential hollow the equipotential surfaces are convex, hence the potential has a minimal value on the tangential plane in any point x where this plane touches the potential function (see Fig. 2). The touching point be x_1. - This right insight nevertheless led to considerable trouble, because it suggested a valley-path character ("minimum energy path") of every solution curve $x(t)$. Of course, rectangular to the direction of the descent $-\nabla U$ we have an ascent to both sides. But besides the generally

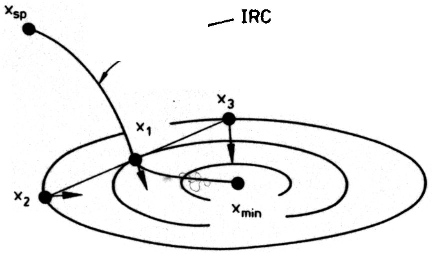

Fig. 2. IRC and its neighborhood (the arrows illustrate length and directions of $-\nabla U$)

strong anharmonic behavior of that section, the conclusions concerning back driving forces connected with this picture are in general wrong. If in a dynamical model by the action of the moment of inertia or, in the computation of the IRC itself by numerical effects we leave the IRC path, say to x_2 or x_3, then these points will be new starting points for other solutions of the gradient system and no "forces" bring back the system to the IRC. The come-back effect (such a curve is called "stable" by Mezey [60]) does only exist, if the IRC corresponds additionally to a valley path. Furthermore, only in this case it makes a sense to deal with vibrational states orthogonal to the path.

Acknowledgment. This study was realized within the "Naturwissenschaftlich-Theoretisches Zentrum" of the Karl-Marx-University Leipzig. We are very grateful to Drs. B. Fiedler, B. Illek, and W. Kliesch for their helpful discussions.

We gratefully acknowledge valuable comments by Prof. Dr. Zahradnik (Prag, ČSSR).

References

1. Eyring, H., Polanyi, M.: Z. Phys. Chem. **B12**, 279 (1931)
2. Murrell, J. N., Laidler, K. J.: Trans. Faraday Soc. **64**, 371 (1968)
3. Dunitz, J. D.: Phil. Trans. R. Soc. Lond. **B272**, 99 (1975)
4. Pancíř, J.: Collect. Czech. Chem. Commun. **40**, 1112 (1975) and **42**, 16 (1977)
5. Cerjan, C. J., Miller, W. H.: J. Chem. Phys. **75**, 2800 (1981)
6. Basilevski, M. V.: Chem. Phys. **67**, 337 (1982)
7. Simons, J., Jørgensen, P., Taylor, H., Ozment, J.: J. Phys. Chem. **87**, 2745 (1983)
8. Dewar, M. J. S., Kirschner, S.: J. Am. Chem. Soc. **93**, 4290, 4292 (1971), **96**, 5244 (1974)
9. Salem, L. in: The new world of quantum chemistry, p. 241, B. Pullman, R. Parr, Eds., Dordrecht: Reidel, 1976

9a. Ermer, O.: Aspekte von Kraftfeldrechnungen, München: Wolfgang Baur Verlag 1981

10. Murrell, J. N.: Structure & Bonding **32**, 93 (1977)
11. Nalewajski, R. F., Carlton, T. S.: Acta Phys. Pol. **A53**, 321 (1978)
12. Fukui, K.: J. Phys. Chem.: **74**, 4161 (1970)
13. Pechukas, P.: J. Chem. Phys. **64**, 1516 (1976)
14. Fukui, K.: Angew. Chem. **94**, 852 (1982)
15. Ishida, K., Morokuma, K., Komornicki, A., J. Chem. Phys. **66**, 2153 (1977)
16. Joshi, B. D., Morokuma, K.: J. Chem. Phys. **67**, 4880 (1977)
17. Kato, S., Morokuma, K.: J. Chem. Phys. **72**, 206 (1980)
18. Kato, S., Morokuma, K.: J. Chem. Phys. **73**, 3900 (1980)
19. Yamashita, K., Yamabe, T., Fukui, K.: Chem. Phys. Lett. **84**, 123 (1981)
20. Yamashita, K., Yamabe, T., Fukui, K.: Theoret. Chim. Acta (Berl.) **60**, 523 (1982)
21. Fukui, K.: Recl. Trav. Chim. Pays-Bas **98**, 75 (1979)
22. Schaefer, H. F.: Chem. Britain **11**, 227 (1975)
23. Müller, K.: Angew. Chem. **92**, 1 (1980)
24. Sana, M., Reckinger, G., Leroy, G.: Theoret. Chim. Acta (Berl.) **58**, 145 (1981)
25. Tachibana, A., Fukui, K.: Theoret. Chim. Acta (Berl.) **49**, 321 (1978)
26. Tachibana, A., Fukui, K.: Theoret. Chim. Acta (Berl.) **51**, 189, 275 (1979)
27. Tachibana, A., Fukui, K.: Theoret. Chim. Acta (Berl.) **57**, 81 (1980)
28. Tachibana, A.: Theoret. Chim. Acta (Berl.) **58**, 301 (1981)
29. Kato, S., Kato, H., Fukui, K.: J. Am. Chem. Soc. **99**, 684 (1977)
30. Baskin, C. P., Bender, C. F., Bauschlicher Jr., C. W., Schaefer, H. F.: J. Am. Chem. Soc. **96**, 2709 (1974)