SURVEY OF INDETERMINACIES OF FITTING PARAMETERS IN MOLECULAR SPECTROSCOPY. II. TRUNCATION PROBLEMS AND CENTRIFUGAL DISTORTION.

JAMES K. G. WATSON, *Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Ontario, Canada K1M 1P2*.

The unitary transformations $e^{iS}He^{-iS}$ discussed in Part I are usually expanded in the form

$$e^{iS}He^{-iS} = H + i[S,H] - \frac{1}{2}[S,[S,H]] - \frac{i}{6}[S,[S,[S,H]]] + \frac{1}{24}[S,[S,[S,[S,H]]]] + \ldots \tag{1}$$

If this expansion is truncated, then the transformation is not in general unitary. Thus the eigenvalues usually change for such a truncated expansion, and the parameters seem to become 'determinate by truncation'. For example, for a sextic centrifugal Hamiltonian the eigenvalues will not be exactly invariant to changes of the parameters, because of truncation effects. Nevertheless, least-squares fits using all of the allowed parameters tend to be ill-conditioned, and systematic errors, such as those involved in truncating the Hamiltonian, will tend to distort the values obtained for the parameters. These truncation problems will be discussed with reference to centrifual distortion in asymmetric tops.