SURVEY OF INDETERMINACIES OF FITTING PARAMETERS IN MOLECULAR SPECTROSCOPY. I. THEORY AND SIMPLE EXAMPLES.

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Effective Hamiltonians $H(\mathbf{q}, \mathbf{p}, \mathbf{s}, \mathbf{i}; \mathbf{c})$ of molecules depend on the dynamical variables **q**,**p**,**s**,**i**, and on a set of parameters (or 'constants') **c**. The latter can be given a theoretical significance by perturbation theory, but they are usually treated as adjustable parameters to be fitted to an observed spectrum, or in effect fitted to the eigenvalues of H. Such fits are used as tests of spectroscopic assignments. If H has the property that a transformation UHU^{-1} by a unitary operator U produces a Hamiltonian $H(\mathbf{q}, \mathbf{p}, \mathbf{s}, \mathbf{i}; \tilde{\mathbf{c}})$ which is identical in form to the original Hamiltonian with a different set of parameters $\tilde{\mathbf{c}}$, then **c** is indeterminate because both **c** and $\tilde{\mathbf{c}}$ correspond to the same set of eigenvalues. In such cases the Hamiltonian has a generalized type of symmetry, because it commutes with operators that act on both the variables and the parameters. Typically U is taken in the form e^{iS}, where S is Hermitian and of odd degree in the momenta and angular momenta. Examples of such indeterminacies of **c** are given for the vibration-rotation spectra of diatomic molecules.