THE OPERATOR METHOD FOR PERTURBATIONS IN THE THEORY OF INFRARED MOLECULAR SPECTRA.

EFFECTIVE HAMILTONIANS. I

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The principles for constructing effective Hamiltonians applicable to molecular spectroscopy are considered. The degree of indeterminacy of a fully effective Hamiltonian is investigated and of a Hamiltonian effective in a subspace. A modification of contact transformations is formulated using the Primas technique of superoperators. Explicit expressions are also given for corrections to effective Hamiltonians of the contact-transformations method up to the sixth order of a small parameter.

1. INTRODUCTION. EFFECTIVE HAMILTONIANS

A full-energy operator $M$ contains considerably more information than one requires to solve problems on the absorption of electromagnetic radiation by a quantum system in some bounded spectral interval. In such a situation the concept of effective Hamiltonians (EH) can be useful; instead of the correct Hamiltonian $H$ one introduces a more simple operator $H_{\text{eff}}$, all eigenvalues of which or a part of them (namely the part that is of interest for the problem under consideration) are identical with the corresponding eigenvalues of $H$, the eigenfunctions being related in a well-known manner to the true wave functions of the system.

It is very expedient to apply $H_{\text{eff}}$ to the problems in which it is possible to "separate" the motions approximately; also in the cases in which an internal motion (interaction) can be separated, the latter being essentially "responsible" for the spectrum in the considered sector. In the latter case $H_{\text{eff}}$ is constructed as an operator that acts on the variables describing this separated type of motion. For example, let the Hamiltonian $H(X, Y)$ operating on the variables $x$ and $y$ be represented in the form

$$H(X, Y) = H_0(X) + \lambda (V_1(Y) + V_2(X, Y)).$$

(1)

The "fine" structure of the nondegenerate [on the function space $f(x)$] state $E_k^{(o)}$ of the operator $H_0$ is due to the existence of "y-motions" ($V(X, 0) = 0$) and, as will be shown in Sec. 6, it can be described by the effective Hamiltonian $H_{\text{eff}}^Y(Y) = E_k^{(o)} + \lambda W_{j_k}(Y)$ that possesses the same eigenvalues $E_k = E_k^{(o)} + \Delta E_{k,i}$ as $H(X, Y)$ but operates only on the $y$ variables. $H_{\text{eff}}$ is a "working instrument" in the theory of molecular spectra. To analyze the spectra of free molecules in the infrared (IR) and microwave (MW) range, by employing qualitative distinctions between intermolecular interactions one is able to simplify the solving of the Schrödinger equation by analyzing instead of the complete electron–nuclear energy operator $H_0$ the effective vibration–rotation (VR) $H_{\text{vib-rot}}$; for spectra in the MW range one uses the effective rotational (centrifugal) $H_{\text{rot}(v)}$ Hamiltonians [1].

There are various methods for constructing $H_{\text{eff}}$. We shall focus our attention on the following: 1) the method of contact transformations (CT) [2–6]; 2) the method of Primas [7, 8]; 3) the method of effective nonrigid spinning top (ENRST) [11] (see also [12–15]); 4) the method of Van Vleck–Jorgensen–Pedersen (VVJP) [16], which employ diverse mathematical tech-
niques and have advantages over other methods when applied to various problems, and result in different $H_{\text{eff}}$.

In this article the relation between various methods is investigated for obtaining either effective on a subspace (Sec. 4) or fully effective Hamiltonians (Sec. 3). It appears that it is possible to find unitary transformations that link together the results of 1)-4) (given in Secs. 7-10 with accuracy up to $O(\lambda^3)$).

The links are analyzed between the construction of $H_{\text{eff}}$ based on the degenerate theory of perturbations and the approximate separation of variables (Sec. 6). It is shown that the intermediate denominators in "global" methods vanish in the nondegenerate case; also the relation between CT and the theory of perturbations (Sec. 12) is studied.

A generalization of the CT method is proposed (Sec. 11) as well as the construction of an "even" $H_{\text{eff}}$ (Sec. 13), from which the results of the methods 1)-4) follow in particular cases for specified values of the "arbitrary parameters" $<A_1>, <A_2>, ... \hat{z}_1, \hat{z}_2, ...$.

The application of the theory to specific spectroscopy problems (analysis of nonuniqueness of centrifugal constants, of random resonances, evaluation of splits in the spectra, etc.) will be dealt separately.

2. DEGENERATE ZEROTH APPROXIMATION. SUPEROPERATORS

2a. Let us consider the Hamiltonian ($\lambda < 1$)

\[ H = H_0 + \lambda V = H_0 + V, \]

with a degenerate zeroth approximation. The space of the functions on which $H, H_0, V$ are defined is denoted by $\Gamma$; the eigensubspaces of the zeroth approximation which correspond to various energies $E_k$ are denoted by $\Gamma_k$, and let $P_k$ and $Q_k = 1 - P_k$ be projectors on $\Gamma_k$ and $\Gamma_k^\perp$. The eigenvalue problem for the operators $H_0$ and $H$ is

\[ H|\kappa, i > = E_k |\kappa, i >, \]

\[ H_0 = \sum_k E_k P_k, \]

\[ H = \sum_{\kappa, i} E_k P_k |\kappa, i > = \sum_{\kappa, i} (E_k - E_k^0) P_k |\kappa, i >. \]

The resolvent $R_k$ of the operator $H_0$ on the subspace $\Gamma_k$ is defined everywhere on $\Gamma$:

\[ R_k = \sum_{m} P_m (E_k^0 - E_m^0)^{-1} Q_k = \frac{Q_k}{E_k^0 - H_0}. \]

To carry out the exponential transformations of the Hamiltonian it is convenient to regard the operators $H, H_0, V, ...$, operating in $\Gamma$, as elements of a linear operator space $U$. Then the relation between the effective and the original Hamiltonians can be expressed by means of the transformation $B$, operating in $U$: $H_{\text{eff}} = B(H)$, that is, the operator operating on the operators. In mathematical terminology such transformations are referred to as transformers in $U$ or superoperators [7-9] (second-rank operators) with respect to $\Gamma$. A special part is played here by the Lie algebra $L(U)$ introduced by Primas [7, 8] and generated by the transformation of $H$ to a representation of a level shift (Sec. 3). It will be shown below that the transformations $B$ to the effective Hamiltonians for the methods 1)-4) can be expressed in terms of the following elementary linear superoperators of two kinds.

2b. Superoperators $D(...), \frac{1}{D}(...), <...>$, Which Are Lie Functions on $L$

(for further details see [7, 8, 5, 6, 17])

(1) The superoperator $D_{H_0}(...)$ of commutation with $H_0$:

\[ D_{H_0}(X) = [H_0, X], \]

\[ D_{H_0}(X) = \sum_{m,n} (E_n^0 - E_m^0) P_n XP_m. \]