Generalized Perturbation Theory: Quality of the First-Order Wave Function*

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A recently proposed version of generalized perturbation theory, in which the whole energy correction is taken care of in second order, is investigated with respect to the quality of its first-order wave function. It is demonstrated that the overlap of the wave function generated in this procedure with the exact solution is in most cases much closer to unity than those of the Rayleigh-Schroedinger or Brillouin-Wigner perturbation theories. Certain approximations, by means of which realistic systems become amenable to investigation within the presently discussed framework, are studied.

Key words: Generalized perturbation theory – First-order wave function

1. Introduction

The idea that a generalized perturbation theory can be formulated so as to include the Rayleigh-Schroedinger (RS) and Brillouin-Wigner (BW) theories as special cases, has been explicitly discussed by Young and March [1], Yaris [2] and Löwdin [3], and is implicit in the work of many others.

Although the formal aspects of this generalization have been studied in considerable detail, relatively little has been done towards applying it to actual computations. An interesting recent exception, in which some earlier references are discussed, is due to Cederbaum et al. [4–6], who have evaluated the extra parameters of their version of the generalized theory by means of a variational computation.

The presently reported investigation is concerned with the situation in which the energy is already known from some external theoretical or experimental source, but the wave function is not. This is a rather commonplace situation in atomic and molecular physics.

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Out of the general theory presented in Ref. [7] we shall only need the expression for the energy up to second order

$$E^{(2)}(\nu) = \varepsilon_0 + V_{00} - \sum_i' \frac{|V_{0i}|^2}{(\varepsilon_i - E) - \nu(\varepsilon_0 - E)}$$

(1)

and that for the wave function up to first order

$$\Psi^{(1)}(\nu) = \Psi^{(0)} - \sum_i' \frac{V_{0i}}{(\varepsilon_i - E) - \nu(\varepsilon_0 - E)} \Psi_i.$$  

(2)

Here $\lambda$ is the strength parameter of the perturbation, $\{\varepsilon_i, \Psi_i\}$ are the eigenvalues and eigenfunctions of the unperturbed system, $E = E(\lambda)$ is the exact energy and $\nu$ is an additional parameter. BW corresponds to $\nu = 0$ and RS to $\nu = 1$.

Our program is as follows:
We shall solve the equation $E^{(2)}(\nu_E) = E$ for $\nu_E = \nu_E(\lambda)$. The number of solutions of this equation is equal to the number of isolated singularities in $E^{(2)}(\nu_E)$, i.e., the number of discrete states of the unperturbed Hamiltonian for which $V_{0i} \neq 0, i \neq 0$.

We shall investigate whether the quality of the wave function up to first order, which is obtained by using particular values of $\nu_E$ in Eq. (2) is actually superior to those corresponding to the standard (RS and BW) formulations. To this effect, the value of $\nu$ corresponding to the maximum of $|\langle \Psi^{(1)}(\nu) | \Psi_\lambda \rangle|^2$, to be denoted by $\nu_\lambda$, will be evaluated for several cases as a reference to the quality of the wave functions obtained with $\nu_E$.

Furthermore, we shall consider certain approximations to $\nu_E$, which may provide the possibility of studying realistic systems with a reasonable amount of effort, without knowledge of the exact energy.