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Perturbation theory for odd perturbations

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Abstract. The eigenvalues of a perturbed Schrödinger equation with an odd perturbation are even functions of the perturbation parameter λ. It is shown how to transform the perturbed equation so that the new perturbation is also explicitly an even function of λ.

Consider the perturbed Schrödinger equation

$$(H_0+\lambda V-E)\psi = 0 \tag{1}$$

where the unperturbed Hamiltonian H_0 commutes with the inversion operator P, $[H_0, P] = 0$. If V also commutes with P, then the states ψ have definite parity, and the perturbation series

$$E(\lambda) = \sum_{n=0}^{\infty} \lambda^n E^{(n)} \tag{2}$$

contains both even and odd powers of λ in general. However, if V anticommutes with P, that is

$$PV+VP = 0 \tag{3}$$

then the states ψ do not have definite parity, but the eigenvalues $E(\lambda)$ are even functions of λ. This situation often occurs when a system is perturbed by an electric field; for example, a rotating or oscillating dipole or an atom in a nondegenerate S state. In such cases the usual Rayleigh–Schrödinger perturbation formulae for the wavefunction and energy are unnecessarily complicated, as many of the terms vanish by symmetry. It would be interesting and convenient if the original equation (1) could be recast into a form only involving λ^2, such as

$$(H_0+\lambda^2\mathscr{V}-E)\phi = 0 \tag{4}$$

when the new perturbation operator $\mathscr{V}$ is at most an even function of λ. The situation is similar to that occurring in the theory of short-range interatomic forces (Byers Brown and Power 1970), or interpolation theory (Morris 1972), where the desired perturbation parameter is $\lambda(1-\lambda)$. The object of this note is to derive a compact form (4) from (1).

Let x stand for the cartesian configuration coordinates, so that $Pf(x) = f(-x)$, and let I be an operator which inverts the perturbation parameter λ: $If(\lambda) = f(-\lambda)$. Define an operator $Q = PI = IP$. Then since Q commutes with the Hamiltonian H, $[H, Q] = 0$, the eigenfunctions $\psi(x;\lambda)$ satisfy the symmetry condition

$$Q\psi(x;\lambda) = \psi(-x;-\lambda) = q\psi(x;\lambda) \tag{5}$$

where $q = +1$ or -1. Note that since $\psi(x;0) = \psi^{(0)}(x)$, the corresponding unperturbed eigenfunction, q is the parity of $\psi^{(0)}(x)$. However, ψ does not have definite P parity, and we can write

$$\psi(x;\lambda) = g(x;\lambda) + u(x;\lambda) \tag{6}$$

where $Pg = g$ and $Pu = -u$. Partition the original Schrödinger equation (1) into even and odd parts

$$(H_0 - E)g + \lambda V u = 0 \tag{7}$$

$$(H_0 - E)u + \lambda V g = 0. \tag{8}$$

Then (8) can be solved to get

$$u = \lambda G_0 V g \tag{9}$$

where $G_0 = (E - H_0)^{-1}$ is the unperturbed Green operator. Substitute (9) into (7) to obtain

$$(H_0 + \lambda^2 V G_0 V - E)g = 0. \tag{10}$$

This equation is satisfied by g or u, and can be written in the form (4), where the self-adjoint operator

$$\mathscr{V} = V G_0 V \tag{11}$$

is an even function of λ through its dependence on the eigenvalue E. Note that for the ground state, for which $E(\lambda) < E^{(0)}$, $\mathscr{V}$ is a negative operator. The function $\phi(x;\lambda)$ is taken to be g or u depending on whether $q = +1$ or -1, so that $\phi(x;0) = \psi^{(0)}(x)$.

It is interesting to see how the perturbation treatment of (10) leads to results in agreement with the Rayleigh–Schrödinger treatment of (1). The operator G_0 can be written in terms of the unperturbed reduced resolvent operator R_0 for the state $|0\rangle = \psi^{(0)}$ of interest as

$$G_0 \mathscr{O} = (1 + R_0 \Delta E)^{-1} R_0 \tag{12}$$

where $\Delta E = E - E^{(0)}$ and $\mathscr{O} = 1 - |0\rangle\langle 0|$. The perturbed energy shift ΔE can be expanded in powers of λ^2

$$\Delta E = \lambda^2 E^{(2)} + \lambda^4 E^{(4)} + \lambda^6 E^{(6)} + \ldots. \tag{13}$$

Hence, by substituting (12) and (13) into (11), the new perturbation operator can be expanded in the space of the state $|0\rangle$:

$$\mathscr{V} = \mathscr{V}^{(2)} + \lambda^2 \mathscr{V}^{(4)} + \lambda^4 \mathscr{V}^{(6)} + \ldots \tag{14}$$

where

$$\mathscr{V}^{(2)} = V R_0 V \qquad \mathscr{V}^{(4)} = -E^{(2)} V R_0^2 V$$

$$\mathscr{V}^{(6)} = (E^{(2)})^2 V R_0^3 V - E^{(4)} V R_0^2 V \tag{15}$$

The formal solution of equation (14) for the perturbed energy shift is (Löwdin 1962)

$$\Delta E = E - E^{(0)} = \lambda^2 \langle 0|\mathscr{V} + \lambda^2 \mathscr{V} T \mathscr{V}|0\rangle \tag{16}$$

where T is the resolvent operator $\mathscr{O}(E - H)^{-1}\mathscr{O}$, which can be written in terms of R_0 as

$$T = \{1 - R_0(\lambda^2 \mathscr{V} - \Delta E)\}^{-1} R_0. \tag{17}$$

By substituting (17) and (14) into (16), expressions for the even perturbation energies in (13) may be found. The first two are as follows:

$$E^{(2)} = \langle 0|VR_0V|0\rangle \tag{18}$$

$$E^{(4)} = \langle 0|VR_0(VR_0V-E^{(2)})R_0V|0\rangle. \tag{19}$$

They agree, of course, as they must, with the result of omitting all the factors which have odd terms in V from the usual formulae.

The transformation from (1) to (10) is a considerable advantage in discussing the branch points of the eigenvalues and eigenfunctions of H which determine the radius of convergence of the perturbation expansions.

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