Perturbation Theory in Wave Mechanics

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(Received October 24, 1957)

This note is intended to supplement a recent article by Speisman by focusing attention on some points of a rather practical nature. In particular, it is shown that the method of Dalgarno and Lewis arises naturally as a special case of the present scheme, and that an upper bound to the energy can be obtained almost immediately once the results of the Rayleigh-Schrödinger theory are known to third order.

WE have been engaged in the study of various applications of Brillouin-Wigner (B-W) and Rayleigh-Schrödinger (R-S) perturbation theories, using an approach which is similar in all essentials to that proposed very recently by Speisman.[1] While there is now no longer need to consider the general theory in detail, we think that the present note may serve as a useful supplement to Speisman's article by drawing attention to one or two points of a rather practical nature.

Using Speisman's notation, we assume that H_0 is a Hermitian operator possessing a complete orthonormal set of eigenvectors given by

$$(E_i-H_0)\xi_i=0. \tag{1}$$

We assume that ξ_0 is nondegenerate and focus attention on the calculation of the corresponding eigenvalue E and eigenvector ψ given by

$$(E-H_0-V)\psi=0, \tag{2}$$

where V is a Hermitian perturbation.

Let us introduce the projection operator P defined by $P\xi_n=\xi_n\delta_{n0}$ and write

$$\frac{(1-P)}{\mathcal{E}-H_0}\equiv(1-P)\frac{1}{\mathcal{E}-H_0}(1-P), \tag{3}$$

which can be taken as a definition of the left-hand side. Then [taking $(\xi_0,\psi)=1$],

$$\psi=\xi_0+(1-P)\psi,$$
$$=\xi_0+\frac{(1-P)}{\mathcal{E}-H_0}(\mathcal{E}-H_0)\psi,$$

and by Eq. (2),

$$\psi=\xi_0+\frac{(1-P)}{\mathcal{E}-H_0}(\mathcal{E}-E+V)\psi,$$
$$=\sum_0^\infty\left\{\frac{(1-P)}{\mathcal{E}-H_0}(\mathcal{E}-E+V)\right\}^n\xi_0. \tag{4}$$

But, from (1) and (2) the energy shift $E-E_0$ is given by $(\xi_0,V\psi)$ and so, from (4)

$$E-E_0=\sum_0^\infty\left(\xi_0,V\left\{\frac{(1-P)}{\mathcal{E}-H_0}(\mathcal{E}-E+V)\right\}^n\xi_0\right). \tag{5}$$

The B-W formulas are given immediately by putting $\mathcal{E}=E$ in (4) and (5). In the R-S case we take $\mathcal{E}=E_0$ and use (5) iteratively [starting in the zeroth approximation by putting $(\xi_0,V\xi_0)$ for $E-E_0$] to obtain $E-E_0$ explicitly in terms of known quantities. Substituting this series into (4) then gives us a series for ψ. Thus in both cases it is possible to derive equations of the type

$$\psi=\sum_0^\infty K_n\xi_0, \tag{6}$$

$$E-E_0=\sum_0^\infty(\xi_0,VK_n\xi_0), \tag{7}$$

where, in the B-W scheme

$$K_n=\left(\frac{1-P}{E-H_0}V\right)^n$$

and in the R-S scheme

$$K_0=1,\quad K_1=\frac{1-P}{E_0-H_0}V,$$
$$K_2=\left(\frac{1-P}{E_0-H_0}V\right)^2-(\xi_0,V\xi_0)\left(\frac{1-P}{E_0-H_0}\right)^2V,\cdots.$$

Concentrating only on the formulation in terms of differential equations (this being more powerful than the matrix method), we proceed to evaluate terms of the series (6) and immediately encounter an expression of the type

$$\frac{1-P}{\mathcal{E}-H_0}V\xi_0=(1-P)\frac{1}{\mathcal{E}-H_0}v\xi_0,\quad[v=V-(\xi_0,V\xi_0)].$$

The essential step in the evaluation of the latter is then to find a suitable function f such that

$$\frac{1}{\mathcal{E}-H_0}v\xi_0=f\xi_0. \tag{8}$$

[1] G. Speisman, Phys. Rev. **107**, 1180 (1957).

Taking the case $H_0=-\frac{1}{2}\sum\nabla_i^2+U$, Eq. (8) gives

$$(\mathcal{E}-E_0)f+\sum\nabla_i f\cdot\frac{\nabla_i\xi_0}{\xi_0}+\tfrac{1}{2}\sum\nabla_i^2 f=v. \tag{9}$$

In general, the boundary conditions are imposed by using (8) to give

$$(\xi_i,f\xi_0)=\frac{(\xi_i,v\xi_0)}{\mathcal{E}-E_i},\quad (i>0), \tag{10}$$

although it seems that, at any rate in one-particle cases, f can often be obtained uniquely by requiring only that $f\xi_0$ be quantum-mechanically acceptable.

In the R-S form ($\mathcal{E}=E_0$), the first term of (9) vanishes. Then, considering the one-particle case, it may be noted that the method is equivalent to that introduced by Dalgarno and Lewis,[2] derived by them however from the usual matrix formulation. It will be seen that their method arises very naturally as a special case of the present treatment. In the B-W case ($\mathcal{E}=E$), there is no such simplification and, effectively, a solution of (9) must be found as a function of $\mathcal{E}$. However, while the B-W solution then contains the R-S case ($\mathcal{E}=E_0$), a merit of this latter method is that the vanishing of the first term in (9) leads to a formal reduction in the degree of the equation. By way of illustration, it may be noted that in one-dimensional problems, (9) and all generalizations of (9) encountered to any order take the form

$$\epsilon F+\frac{dF}{dx}\frac{1}{\xi_0}\frac{d\xi_0}{dx}+\frac{1}{2}\frac{d^2F}{dx^2}=g. \tag{11}$$

Then, in the R-S case, $\epsilon=0$ and the general solution is

$$F=A+B\int\frac{dx}{\xi_0^2}+2\int\frac{(\int g\xi_0^2dx)}{\xi_0^2}dx, \tag{12}$$

enabling the wave function and energy to be calculated by quadrature to any order. No such general solution is available in the B-W case ($\epsilon\neq0$).

[2] A. Dalgarno and J. T. Lewis, Proc. Roy. Soc. (London) **A233**, 70 (1955). See also A. Dalgarno, Proc. Phys. Soc. (London) **A69**, 784 (1956) and A. Dalgarno and A. L. Stewart, Proc. Roy. Soc. (London) **A238**, 276 (1956).

However, in more general problems, while higher terms in the series (6) can be dealt with by using a procedure similar in principle to the above, it turns out usually, at a very early stage, that the solution of the appropriate generalization of (9) cannot be found. As illustrated by the simple one-dimensional case, it usually happens that the R-S method can be carried at least as far as, and often further than, the B-W scheme. It may be noted, however, that a knowledge of only the first m terms of (6) allows the first $(2m-1)$ terms of (7) to be computed, since all our operators are Hermitian. This means that the B-W method will yield an upper bound to the ground-state energy, as may be verified directly by inserting the first m terms of (6) in the variational integral.

It frequently happens that it is only possible to evaluate $K_0\xi_0$ and $K_1\xi_0$ of the series (6) and that the effect of the higher terms is very difficult to assess. The merit of the B-W scheme seems then to be that, at least, we obtain an upper bound to the energy. As there is no such bound property in the usual R-S theory, it would seem desirable to be able to obtain one with the few terms at our disposal. This can be done with very little further calculation by taking $K_0\xi_0+K_1\xi_0$ as a variational function as follows.

We suppose that

$$(E_0-H_0)f\xi_0=v\xi_0, \tag{13}$$

and since, by (1), f is indeterminate to the extent of an additive constant, we may assume that $(\xi_0,f\xi_0)=0$. The R-S energy to third order is then given by

$$E=E_0+(\xi_0,V\xi_0)+(\xi_0,vf\xi_0)+(\xi_0,fvf\xi_0)+\cdots. \tag{14}$$

To obtain a bound we write $\Psi=(1+f)\xi_0$ and deduce, after a certain amount of manipulation employing Eqs. (1) and (13), that

$$\frac{(\Psi,[H+V]\Psi)}{(\Psi,\Psi)}=E_0+(\xi_0,V\xi_0)+\frac{(\xi_0,vf\xi_0)+(\xi_0,fvf\xi_0)}{1+(\xi_0,f^2\xi_0)},$$

and all terms in the latter expression are used explicitly in the evaluation of (14).

One of us (W. H. Y.) wishes to acknowledge the award of a Town Trustees Fellowship by the University of Sheffield.