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Proc. R. Soc. Lond. A 1956 **238**, 269-275

doi: 10.1098/rspa.1956.0219

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On the perturbation theory of small disturbances

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(Communicated by D. R. Bates, F.R.S.—Received 11 July 1956)

As a preliminary to a wide range of applications, conventional perturbation theory is re-examined and a number of useful properties emphasized. It is shown in particular that the total, kinetic and potential energies can be obtained to the $(2s+1)$ th order from a knowledge of only the s th-order wave function and that similar though less powerful theorems hold for other diagonal matrix elements. A combination of variational and perturbation techniques is suggested as the best method of calculating small disturbances of a stationary system.

1. INTRODUCTION

For theoretical investigations of physical problems there is available the powerful perturbation theory, which does not appear to have been exploited as fully as is possible and whose range of validity has perhaps been underestimated.

2. DEVELOPMENT OF PERTURBATION THEORY

In order to introduce a notation convenient for our purposes it is necessary to reproduce here the usual derivation of the formulae of conventional perturbation theory. Let H be the Hamiltonian of the unperturbed system, the stationary states of which are described by wave functions ψ_s with associated eigenvalues E_s . Then

$$(H - E_s) \psi_s = 0. \quad (1)$$

If a *small* perturbation λh is applied to the system, which we assume to be in the non-degenerate state described by ψ_0 , the wave function Ψ of the perturbed system satisfies the equation

$$(\mathcal{H} - \mathcal{E}) \Psi \equiv (H + \lambda h - \mathcal{E}) \Psi = 0, \quad (2)$$

and Ψ and \mathcal{E} can be expanded as power series in λ according to

$$\Psi = \sum_{n=0}^{\infty} \lambda^n F_n, \quad \mathcal{E} = \sum_{n=0}^{\infty} \lambda^n \mathcal{E}_n. \quad (3)$$

Substituting (3) into (2) and equating the coefficient of λ^m to zero, we readily obtain the system of equations

$$(H - \mathcal{E}_0) F_0 = 0, \quad (4)$$

$$(H - \mathcal{E}_0) F_1 + (h - \mathcal{E}_1) F_0 = 0 \quad (5)$$

and
$$(H - \mathcal{E}_0) F_n + (h - \mathcal{E}_1) F_{n-1} = \sum_{r=2}^n \mathcal{E}_r F_{n-r} \quad (n > 1). \quad (6)$$

The first equation is simply the wave equation for the unperturbed system so that F_0 is the unperturbed wave function ψ_0 and \mathcal{E}_0 is the corresponding eigenvalue E_0 . Then multiplying (5) and (6) throughout by ψ_0^* and integrating over all space, it follows that

$$\mathcal{E}_1 = \int \psi_0^* h \psi_0 d\mathbf{r} \quad (7)$$

$$\text{and} \quad \mathcal{E}_n = \int \psi_0^* (h - \mathcal{E}_1) F_{n-1} d\mathbf{r} - \sum_{r=1}^{n-2} \mathcal{E}_{r+1} \int \psi_0^* F_{n-r-1} d\mathbf{r} \quad (n > 1). \quad (8)$$

Thus, as is well known, the wave function of the perturbed system can (in principle) be calculated to any order from a knowledge of only the unperturbed wave function and, further, the perturbation energy can be obtained to the n th order from a knowledge of the wave function to the $(n-1)$ th order. In the following section we shall show that this latter conclusion may be replaced by a more powerful one.

The usual perturbation formulae are obtained by expanding F_n in terms of the complete set of eigenfunctions ψ_s of (1)

$$F_n = \sum_s a_s^n \psi_s. \quad (9)$$

Substitution into (5) and (6) gives for $s \neq 0$

$$a_s^n = \frac{1}{E_0 - E_s} \left\{ - \sum_{r=1}^{n-2} \mathcal{E}_{r+1} a_s^{n-r-1} + \sum_t a_t^{n-1} \int \psi_s^* (h - \mathcal{E}_1) \psi_t d\mathbf{r} \right\}, \quad (10)$$

the coefficients a_0^n being determined by the condition that to any order Ψ be normalized to unity.

3. ENERGY OF PERTURBATION

The n th-order contribution to the perturbation energy given by equation (8) can be written

$$\mathcal{E}_n = \int \psi_0^* (h - \mathcal{E}_1) F_{n-1} d\mathbf{r} - \mathcal{E}_2 \int \psi_0^* F_{n-2} d\mathbf{r} - \sum_{r=3}^{n-1} \mathcal{E}_r \int \psi_0^* F_{n-r} d\mathbf{r}. \quad (11)$$

But it follows from equations (5) and (6) that

$$\begin{aligned} \int \psi_0^* (h - \mathcal{E}_1) F_{n-1} d\mathbf{r} &= \int F_1^* (h - \mathcal{E}_1) F_{n-2} d\mathbf{r} - \sum_{r=2}^{n-1} \mathcal{E}_r \int F_1^* F_{n-r-1} d\mathbf{r} \\ &= \int F_2^* (h - \mathcal{E}_1) F_{n-3} d\mathbf{r} + \mathcal{E}_2 \int \psi_0^* F_{n-2} d\mathbf{r} - \sum_{r=2}^{n-1} \mathcal{E}_r \int F_1^* F_{n-r-1} d\mathbf{r} \\ &\quad - \sum_{r=2}^{n-2} \mathcal{E}_r \int F_2^* F_{n-r-2} d\mathbf{r}, \end{aligned}$$

so that (11) becomes

$$\begin{aligned} \mathcal{E}_n &= \int F_2^* (h - \mathcal{E}_1) F_{n-3} d\mathbf{r} - \sum_{r=3}^{n-1} \mathcal{E}_r \int \{ \psi_0^* F_{n-r} + F_1^* F_{n-r-1} + F_2^* F_{n-r-2} \} d\mathbf{r} \\ &\quad - \mathcal{E}_2 \int \{ F_1^* F_{n-3} + F_2^* F_{n-4} \} d\mathbf{r}, \quad (12) \end{aligned}$$

and the evaluation of (12) requires a knowledge of only the $(n-3)$ th-order wave function. The process can be continued until the highest order wave function entering the expression for \mathcal{E}_n is of the $(\frac{1}{2}n)$ th order if n is even or of the $\frac{1}{2}(n-1)$ th order if n is odd. Thus *the energy can be evaluated to the $(2s+1)$ th order provided the wave function is known to the s -th order.*

This is a result of some importance, for there exists in the literature a large number of calculations of second-order energies which may easily be extended to the third order in consequence of equation (12).

It is convenient to tabulate here the first few expressions for \mathcal{E}_n . We may require without loss of generality that $\int \psi_0^* F_1 d\mathbf{r} = 0$ so that defining new functions f_n by

$$F_n = f_n \psi_0 \quad (13)$$

$$\text{and writing} \quad (p | L | q) = \int \psi_p^* L \psi_q d\mathbf{r}, \quad (14)$$

we have

$$\left. \begin{aligned} \mathcal{E}_0 &= E_0, & \mathcal{E}_1 &= (0 | h | 0), & \mathcal{E}_2 &= (0 | h f_1 | 0), \\ \mathcal{E}_3 &= (0 | f_1 (h - \mathcal{E}_1) f_1 | 0), \\ \mathcal{E}_4 &= (0 | f_1 (h - \mathcal{E}_1) f_2 | 0) - \mathcal{E}_2 \{ (0 | f_1^2 | 0) + (0 | f_2 | 0) \}, \\ \mathcal{E}_5 &= (0 | f_2 (h - \mathcal{E}_1) f_2 | 0) - 2\mathcal{E}_2 (0 | f_1 f_2 | 0) - \mathcal{E}_3 \{ (0 | f_1^2 | 0) + 2(0 | f_2 | 0) \}, \\ &\dots\dots\dots \end{aligned} \right\} \quad (15)$$

These expressions can also be derived from the conventional formulae of perturbation theory, as was demonstrated recently by Dalgarno & Lewis (1955). They showed that when $(0 | L | 0) = 0$

$$\frac{(0 | L | q)}{E_0 - E_q} = (0 | M | q), \quad (16)$$

where M satisfies

$$2\nabla M \cdot \nabla \psi_0 + \psi_0 \nabla^2 M = L \psi_0, \quad (17)$$

and make use of the matrix summation rule

$$\sum_{n'} (n | P | n') (n' | Q | n'') = (n | PQ | n'') \quad (18)$$

to evaluate the infinite summations which arise in the conventional formulae. When $(0 | L | 0) \neq 0$, the modification is trivial; equation (17) is replaced by

$$2\nabla M \cdot \nabla \psi_0 + \psi_0 \nabla^2 M = L \psi_0 - (0 | L | 0) \psi_0. \quad (19)$$

An alternative form of (19) is

$$(H - E_0) (M \psi_0) = \{L - (0 | L | 0)\} \psi_0, \quad (20)$$

and comparison with (5) reveals the essential similarity of the two methods of obtaining \mathcal{E}_n (cf. Dalgarno & Lewis 1956). For the discussion of matrix elements of dynamical variables other than the Hamiltonian, the technique suggested by Dalgarno & Lewis appears more flexible and will be used in the following sections.

4. OTHER MATRIX ELEMENTS

Using (10) and applying the normalization requirement, it is easily shown that to the first order the wave function Ψ_1 of the perturbed system is given by the well-known expression

$$\Psi_1 = \psi_0 + \Sigma' \frac{(0|h|s)}{E_0 - E_s} \psi_s. \quad (21)$$

Thus the first-order approximation to the diagonal matrix element of a dynamical variable L is given by

$$\int \Psi_1^* L \Psi_1 d\mathbf{r} = (0|L|0) + 2\Sigma' \frac{(0|h|s)(s|L|0)}{E_0 - E_s}. \quad (22)$$

Using (16), this can be written in two ways as

$$\int \Psi_1^* L \Psi_1 d\mathbf{r} = (0|L|0) + 2(0|\mathcal{F}L|0), \quad (23)$$

where \mathcal{F} satisfies

$$2\nabla\mathcal{F} \cdot \nabla\psi_0 + \psi_0 \nabla^2 \mathcal{F} = h\psi_0 - (0|h|0)\psi_0, \quad (24)$$

or as

$$\int \Psi_1^* L \Psi_1 d\mathbf{r} = (0|L|0) + 2(0|h\mathcal{G}|0), \quad (25)$$

where \mathcal{G} satisfies

$$2\nabla\mathcal{G} \cdot \nabla\psi_0 + \psi_0 \nabla^2 \mathcal{G} = L\psi_0 - (0|L|0)\psi_0 \quad (26)$$

such that

$$(0|\mathcal{G}|0) = 0. \quad (27)$$

The expressions (23) and (25) will be equal, in general, only when ψ_0 , \mathcal{F} and \mathcal{G} are exact solutions of (1), (24) and (26), respectively. In problems where these equations can only be solved approximately, a comparison between (23) and (25) will provide a useful check.

The more important aspects of the sum-rule technique only become apparent when higher order approximations are required. The second-order approximation to $\int \Psi^* L \Psi d\mathbf{r}$ may be shown to be

$$\begin{aligned} \int \Psi_2^* L \Psi_2 d\mathbf{r} = & \int \Psi_1^* L \Psi_1 d\mathbf{r} - \Sigma' \frac{(0|h|s)(s|h|0)}{(E_0 - E_s)^2} (0|L|0) \\ & + 2\Sigma'\Sigma' \frac{(0|h|s)(s|h|r)(r|L|0)}{(E_0 - E_s)(E_0 - E_r)} \\ & + \Sigma'\Sigma' \frac{(0|h|s)(s|L|r)(r|h|0)}{(E_0 - E_s)(E_0 - E_r)}. \end{aligned} \quad (28)$$

By using (16), the second-order terms can be obtained in a number of ways: for example, the last term can be written as $(0|h\mathcal{K}|0) - (0|h|0)(0|\mathcal{K}|0)$, where \mathcal{K} satisfies

$$2\nabla\mathcal{K} \cdot \nabla\psi_0 + \psi_0 \nabla^2 \mathcal{K} = L\mathcal{F}\psi_0 - (0|L\mathcal{F}|0)\psi_0, \quad (29)$$

or as $(0|\mathcal{F}L\mathcal{F}|0)$. The other summations can also be expressed in terms of the functions ψ_0 , \mathcal{F} and \mathcal{G} required for the calculation of the first-order terms. Thus any diagonal matrix element can be calculated to the *second* order from a knowledge of

two first-order wave functions \mathcal{F} and \mathcal{G} ; for if L is regarded as a perturbation, $\psi_0 + \mathcal{G}\psi_0$ can be interpreted as the corresponding first-order wave function. Indeed, expanding $\mathcal{G}\psi_0$ according to $\Sigma b_s \psi_s$ and substituting in (26), it follows that

$$\mathcal{G}\psi_0 = \Sigma' \frac{(0|L|s)}{E_0 - E_s} \psi_s, \quad (30)$$

the conventional formula for the first-order correction to the unperturbed wave function when a perturbation L is applied. Similar considerations may be developed for higher order approximations by use of (16).

5. SOME SPECIAL RELATIONS

Many special relations, of which we shall demonstrate only three, hold between elements of certain dynamical variables. Applying the operator $F_0^* \mathbf{r}_s \cdot \nabla_s$, where \mathbf{r}_s is the position vector of the s th particle, to (4) and supposing that the Hamiltonian H can be written as

$$H = -\sum_t \nabla_t^2 + V(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_t), \quad (31)$$

where V is the potential energy of the unperturbed system, it follows that

$$-F_0^* \mathbf{r}_s \cdot \nabla_s \Sigma \nabla_t^2 F_0 + F_0^*(V - \mathcal{E}_0) \mathbf{r}_s \cdot \nabla_s F_0 + F_0^*(\mathbf{r}_s \cdot \nabla_s V) F_0 = 0. \quad (32)$$

Now multiplying the complex conjugate of (4) by $\mathbf{r}_s \cdot \nabla_s F_0$ and subtracting from (32), there results

$$\mathbf{r}_s \cdot \nabla_s F_0 \Sigma \nabla_t^2 F_0^* - F_0^* \Sigma \nabla_t^2 (\mathbf{r}_s \cdot \nabla_s F_0) + 2F_0^* \nabla_s^2 F_0 + F_0^*(\mathbf{r}_s \cdot \nabla_s V) F_0 = 0, \quad (33)$$

from which it follows, after integration over all configuration space, that

$$(0|f_0(\mathbf{r}_s \cdot \nabla_s V)f_0|0) = -2(0|f_0 \nabla_s^2 f_0|0). \quad (34)$$

By following essentially the same procedure with $F_1^* \mathbf{r}_s \cdot \nabla_s$ and using (5), (32) and (33), it can be shown that

$$2(0|f_0(\mathbf{r}_s \cdot \nabla_s V)f_1|0) + (0|f_0(\mathbf{r}_s \cdot \nabla_s h)f_0|0) = -2(0|f_0 \nabla_s^2 f_1|0) - 2(0|f_1 \nabla_s^2 f_0|0), \quad (35)$$

$$\text{and} \quad 2(0|f_0(h - \mathcal{E}_1)\mathbf{r}_s \cdot \nabla_s f_0|0) = -(0|f_0(\mathbf{r}_s \cdot \nabla_s h)f_0|0). \quad (36)$$

Many similar relations can be established which connect the matrix elements of other dynamical variables. Those involving the kinetic energy and potential energy are particularly important, since by extending (34) and (35) to higher orders it can be shown that the kinetic energy calculated to any particular order n is equal to its virial calculated to the same order n . When V and h correspond to electrostatic interactions

$$\Sigma \mathbf{r}_s \cdot \nabla_s V = -V, \quad \Sigma \mathbf{r}_s \cdot \nabla_s h = -h, \quad (37)$$

and (34) and (35) become respectively after summation over s

$$(0|f_0 V f_0|0) = 2(0|f_0 \nabla^2 f_0|0), \quad (38)$$

$$2(0|f_0 V f_1|0) + (0|f_0 h f_0|0) = 2(0|f_0 \nabla^2 f_1|0) + 2(0|f_1 \nabla^2 f_0|0), \quad (39)$$

where $\nabla^2 = \sum_i \nabla_i^2$. In the case of a diatomic molecule whose nuclei are joined by a vector \mathbf{R} , (38) and (39) may be written

$$\int \Psi_0^* T' \Psi_0 d\mathbf{r} + \frac{1}{2} \int \Psi_0^* V' \Psi_0 d\mathbf{r} = -\frac{1}{2} R \frac{\partial}{\partial R} \int \Psi_0^* (T' + V') \Psi_0 d\mathbf{r}, \quad (40)$$

$$\int \Psi_1^* T' \Psi_1 d\mathbf{r} + \frac{1}{2} \int \Psi_1^* V' \Psi_1 d\mathbf{r} = -\frac{1}{2} R \frac{\partial}{\partial R} \int \Psi_1^* (T' + V') \Psi_1 d\mathbf{r}, \quad (41)$$

where T' and V' are the kinetic and potential energies of the electrons only. These equations express the fact that the quantal virial theorem in the fixed nucleus approximation† (cf. Eyring, Walter & Kimball 1949) is satisfied to the zero and first orders. This can be extended to any order (though requiring heavy algebra) so that in conjunction with § 3, it follows that the *total, potential and kinetic energies can be evaluated to the $(2s+1)$ th order provided that the wave function is known only to the s -th order.*

6. APPROXIMATE METHODS

Except in some one-electron problems, it is not possible to solve the equations for the perturbed wave function exactly and resort must be made to approximate methods. In the calculation of the energy, the usual approximations are due to Unsöld (1927) and to Lennard-Jones (1930). Unsöld supposes that in the perturbation formula

$$\mathcal{E}_2 = \Sigma' \frac{(0|h|s)(s|h|0)}{(E_0 - E_s)} \quad (42)$$

$E_0 - E_s$ can be replaced by a constant μ_1 . Then using (18) it follows that

$$\mathcal{E}_2 = \frac{1}{\mu_1} \{(0|h^2|0) - (0|h|0)^2\}. \quad (43)$$

The choice of μ_1 can frequently be made quite accurately by various methods (cf. Vinti 1932; Dalgarno & Lewis 1956). Lennard-Jones writes (42) in the form

$$\mathcal{E}_2 = \frac{1}{E_0} \{(0|h^2|0) - (0|h|0)^2\} + \frac{1}{E_0} \Sigma' \frac{E_s}{E_0 - E_s} (0|h|s)(s|h|0), \quad (43a)$$

and ignores the last term. Provided the continuum states are unimportant, this should be a very accurate approximation.

These methods may be generalized to other matrix elements without difficulty. For example, noting that (43) is equivalent to writing $f_1 = \{h - (0|h|0)\}/\mu_1$ in (15), we can approximate the last term of (28) by

$$\frac{1}{\mu_1^2} \{(0|hLh|0) - 2(0|h|0)(0|Lh|0) + (0|h|0)^2(0|L|0)\} \quad (44)$$

following Unsöld, or by (44) with $\mu_1^2 = E_0^2$ following Lennard-Jones.

† We have been unable to find any rigorous proof of this theorem in the literature. It may be established by following a procedure similar to that adopted to prove (34) and using (37).

The most powerful approximate method would, however, seem to be a combination of the perturbation and variational approximations. Dalgarno & Lewis (1956) have pointed out that equation (19) can be written as $\delta W = 0$, where W is given by

$$W = \int \Psi^* \{H + L - (0 | L | 0)\} \Psi \, d\mathbf{r}, \quad (45)$$

and terms of order in L higher than the second are ignored. Thus by assuming trial functions for Ψ and minimizing W with L taken equal to h and equal to the dynamical variable of interest successively (cf. Dalgarno & Stewart 1956) approximations to the first-order functions \mathcal{F} and \mathcal{G} can be obtained. The accuracy of the approximate forms of \mathcal{F} and \mathcal{G} may be checked by comparing (23) and (25). They may then be used in (28) to calculate the matrix element to the second order, a procedure which avoids the considerable additional labour involved in a variational calculation of the second-order wave functions.

Extensions to higher orders may be made in an exactly similar way.

The methods described in this paper have been applied to the calculation of properties of the $1s\sigma$ and $2p\sigma$ states of HeH^{2+} and the results are given in the following paper.

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