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ITERATIVE SOLUTION OF PERTURBATION EQUATIONS

by

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ITERATIVE SOLUTION OF PERTURBATION EQUATIONS[†]

by

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ABSTRACT

Iterative procedures for the solution of perturbation equations are considered. Limitations of a procedure recently proposed by Harriss and Hirschfelder^[3] are discussed, and modifications are suggested. The relationships between the various procedures are shown. Illustrative applications are given.

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Introduction

Few of the differential equations in perturbation theory have yielded to attempts to determine exact analytic solutions. Exact solutions can be obtained by direct quadrature for those equations which are strictly separable or which allow finite expansions of the perturbation and perturbed wave function in complete orthonormal sets.^[1] For nonseparable problems, attempts to determine exact solutions are usually based on an assumption of the functional form of the solution. If the complete form is assumed known, it then becomes necessary to determine the coefficients recursively. If the form is only partially assumed, a subsidiary set of differential equations must be solved to complete the solution. For most nonseparable problems either the functional form is still unknown or the subsidiary differential equations are intractable, and one usually resorts to variational approximations to the solution.

In some cases investigators have determined approximate solutions, applicable to a particular region of space, by considering only that portion of the differential equation important in that region.^[2] A procedure recently proposed by Harriss and Hirschfelder determines an initial approximation in this manner and then iteratively refines the approximations.^[3] In the following sections this procedure will be developed, its limitations pointed out, modifications suggested, and its relationship to other iterative schemes shown.

Iterative Procedures^[4]

If the Rayleigh-Schrödinger perturbation equations,

$$(H_0 - E_0) \psi^{(1)} + (V - E_0^{(1)}) \psi_0 = 0 ; \quad \psi^{(0)} = \psi_0 \quad (1)$$

$$(H_0 - E_0) \psi^{(n)} + (V - E_0^{(1)}) \psi^{(n-1)} = \sum_{k=2}^n E_0^{(k)} \psi^{(n-k)} \quad (2)$$

$$n = 2, 3, \dots$$

are assumed to have solutions of the Dalgarno-Lewis form,^[5]

$$\psi^{(k)} = F^{(k)} \psi_0, \text{ they can be written in the form}$$

$$\nabla \psi_0^2 \cdot \nabla F^{(1)} + \psi_0^2 \nabla^2 F^{(1)} = 2 \psi_0 (V - E_0^{(1)}) \psi_0 \quad (3)$$

$$\begin{aligned} \nabla \psi_0^2 \cdot \nabla F^{(n)} + \psi_0^2 \nabla^2 F^{(n)} &= 2 \psi_0 (V - E_0^{(1)}) \psi^{(n-1)} \\ &- 2 \psi_0 \sum_{k=2}^n E_0^{(k)} \psi^{(n-k)}. \end{aligned} \quad (4)$$

Boundary and normalization conditions^[6] for the solutions are given by

$$F^{(k)} \psi_0 = \psi_0^2 \nabla F^{(k)} = 0 \text{ on the boundaries,} \quad (5)$$

$$\sum_{k=0}^n \langle F^{(k)} \psi_0 | F^{(n-k)} \psi_0 \rangle = 0, \quad n = 1, 2, \dots \quad (6)$$

The initial proposal of the iterative procedure was based on a consideration of Eqs. (3) and (4). If ψ_0 is a simple exponential or a power series times an exponential

and $F^{(k)}$ is expressible as a power series then, for large values of the variables the first term on the left-hand side of Eqs. (3) and (4) is dominant in magnitude over the second. Or, it could be stated that the behavior of $F^{(k)}$ in that region of space is primarily determined by $\nabla \Psi_0^2 \cdot \nabla F^{(k)}$ with $\Psi_0^2 \nabla^2 F^{(k)}$ having only a minor effect. This suggested an iterative procedure in which the first approximation to $F^{(k)}$, $F_0^{(k)}$, neglects the contributions from $\Psi_0^2 \nabla^2 F^{(k)}$, and the effect of this term is only included in higher approximations. Since all of the equations have the same form, we shall drop the superscript (k) and represent the inhomogeneous portion of the equation by f . The iterative procedure, which we shall call Proc. A, is then

Proc. A

$$\nabla \Psi_0^2 \cdot \nabla F_0 = f \quad (7a)$$

$$\nabla \Psi_0^2 \cdot \nabla F_{i+1} = f - \Psi_0^2 \nabla^2 F_i \quad (7b)$$

Some simple examples were presented in the initial work^[3] in which F_n did converge in a finite number of iterations, $F_{n+1} = F_n$, and these functions proved to be formal solutions obeying boundary conditions; therefore actual solutions.

Several problems can be encountered in the practical application of Proc. A. First, the solution of Eqs. (7) reduces, through use of the method of characteristics, to the problem of solving a set of simultaneous, ordinary first-order differential equations. These equations may prove to be intractable due either to Ψ_0 being very

complicated or to the fact that many one-dimensional integrals cannot be evaluated in closed form or in a convergent series. In these cases the procedure is simply not applicable.

A more serious problem may arise if individual iterates cannot be made to meet boundary conditions. Proc. A attempts to generate the solution of a second-order differential equation by solving a sequence of first-order differential equations; and one can expect the solution of each first-order equation to meet only half the boundary conditions imposed on the original equation. For some systems the procedure converges to an actual solution even though early iterates do not meet boundary conditions. This type of behavior was found in the determination of the spherical component of the second-order wave function for a ground-state hydrogen atom in a uniform, unit electric field.^[3] The equation^[7] being solved was

$$(H_0 - E_0) \Psi_0 = (-2.25 + r^2/3 + r^3/6) \Psi_0 ,$$

where

$$\Psi_0 = \pi^{-1/2} \exp(-r)$$

and

$$H_0 = -\frac{1}{2} \nabla^2 - 1/r .$$

The sequence of iterates^[8] found by Proc. A is

i	F_i
0	$- 2.25r + r^3/9 + r^4/24$
1	$- 2.25\ln r - 2.25r + r^2/3 + r^3/4 + r^4/24$
2	$1.125/r - 2.25\ln r - 1.25r + 3r^2/4 + r^3/4 + r^4/24$
3	$1.125/r - 1.25\ln r + 3r^2/4 + r^3/4 + r^4/24$
4	$0.625/r + 3r^2/4 + r^3/4 + r^4/24$
5	$3r^2/4 + r^3/4 + r^4/24$
6	$3r^2/4 + r^3/4 + r^4/24$

Although F_1 - F_4 are ill-behaved at $r=0$, the iterates converge to an actual solution with $F_6 = F_5 = F$.

The appearance of objectionable terms, those not obeying boundary conditions, in the F_k caused no real problem in the above example since convergence was obtained in so few steps. In the general case one cannot expect convergence in a few iterations and it is desirable to modify the procedure so that these terms either are eliminated or do not occur. Many modifications are possible. A particularly simple one, applicable in situations such as the above, will now be described. This modification, called Proc. B, prevents the propagation of those terms which violate the boundary conditions. If we define A_n to be the collection of objectionable terms in F_n , (e.g. in the example above, $A_0 = 0$ while $A_1 = -2.25\ln r$), we can eliminate A_n from the equation determining F_{n+1} . This procedure is given by

Proc. B

$$\nabla \Psi_0^2 \cdot \nabla F_0 = f \quad (8a)$$

$$\nabla \Psi_0^2 \cdot \nabla F_{i+1} = f - \Psi_0^2 \nabla^2 (F_i - A_i) \quad (8b)$$

Proc. B corresponds to initiation of the iterative process in Proc. A with a particular type of function. This function may be considered to represent, in some sense, a zeroth-order approximation to the solution, (see Appendix). For Proc. B, convergence is attained when

$F_{i+1} = F_i - A_i$. Note that Proc. B retains the attractive feature of requiring only the solution of first order partial differential equations.

Application of Proc. B to the previous example leads to

<u>i</u>	<u>A_i</u>	<u>(F_i - A_i,</u>
0	0	- 2.25r + r ³ /9 + r ⁴ /24
1	- 2.25lnr	- 2.25r + r ² /3 + r ³ /4 + r ⁴ /24
2	- 2.25lnr	- 1.25r + 3r ² /4 + r ³ /4 + r ⁴ /24
3	- 1.25lnr	3r ² /4 + r ³ /4 + r ⁴ /24
4	0	3r ² /4 + r ³ /4 + r ⁴ /24

where we see convergence with $F_4 = F_3 - A_3 = F$.

The primary limitation imposed by the use of Proc. B seems to be that it is difficult for this procedure to yield certain types of solutions, those that meet boundary conditions by mutual cancellation among several terms. In view of this limitation it seems best to use Proc. A when possible, using Proc. B only if the integrals due to the undesirable terms become intractable or if the procedure requires so many iterations that the number of terms becomes unmanageable.

In some instances it is found that all of the terms generated by Proc. A are ill-behaved at the boundaries, i.e. $F_n = A_n$ for all n . A system exhibiting this type of behavior is the Hooke's law model of the helium atom. In this model the electron-nucleus coulombic forces are replaced with Hooke's law forces, but the coulombic inter-electron

repulsion is retained. This system, as a model for correlation, has been studied extensively by Kestner and Sinanoglu,^[9] White and Byers Brown,^[10] and Benson and Byers Brown.^[11] The perturbation problem, in atomic units, is

$$H_0 = -\frac{1}{2} (\nabla_1^2 + \nabla_2^2) + \frac{1}{2} (r_1^2 + r_2^2)$$

where $V = 1/r_{12}$. Also

$$\psi_0^2 = \pi^{-3} \exp[-(r_1^2 + r_2^2)]$$

where $E_0 = 3$ and $E_0^{(1)} = (2/\pi)^{\frac{1}{2}}$.

The analytic solution to the first-order perturbation equation has been determined by White and Byers Brown^[10] to be

$$\begin{aligned} \psi^{(1)} = F \psi_0 = \psi_0 \left\{ (1 - \exp(r_{12}^2/2) \operatorname{erfc}(r_{12}/2^{\frac{1}{2}})) / r_{12} \right. \\ \left. + 2^{\frac{1}{2}} \int_0^{r_{12}/\sqrt{2}} e^{s^2} \operatorname{erfc}(s) ds - (2/\pi)^{\frac{1}{2}} (1 + \ln 2) \right\} \end{aligned}$$

where

$$\operatorname{erfc}(x) = 2 \pi^{-\frac{1}{2}} \int_x^\infty e^{-t^2} dt.$$

We obtain, by Proc. A. the following iterative sequence, ill-behaved at the origin:

$$\begin{array}{l}
 \frac{1}{F_1} \\
 0 \quad (2/\pi)^{\frac{1}{2}} \ln r_{12} + 1/r_{12} \\
 1 \quad (2/\pi)^{\frac{1}{2}} \ln r_{12} + 1/r_{12} - (2/\pi)^{\frac{1}{2}} / r_{12}^2 \\
 2 \quad (2/\pi)^{\frac{1}{2}} \ln r_{12} + 1/r_{12} - (2/\pi)^{\frac{1}{2}} / r_{12}^2 + (2/\pi)^{\frac{1}{2}} / 2r_{12}^4 \\
 \vdots \\
 \vdots \\
 \vdots
 \end{array}$$

and

$$\begin{aligned}
 F_{\infty} &= (2/\pi)^{\frac{1}{2}} \ln r_{12} + 1/r_{12} - (2/\pi)^{\frac{1}{2}} / r_{12}^2 \\
 &+ (2/\pi)^{\frac{1}{2}} \sum_{j=2}^{\infty} (-1)^j (2j-3)! / (j! 2^{j-2} (j-2)! r_{12}^{2j}) .
 \end{aligned}$$

White and Byers Brown developed the "large r_{12} " form^[10] of F which, except for an additive constant, is identical with F_{∞} .

In cases such as the above, Eq. (7a) is a very poor initial approximation. Instead, one should consider what might be called the procedure complement to Proc. A. That is, with reference to Eq. (3), consider the region of space where the first approximation is determined by $\Psi_0^2 \nabla^2 F$ and $\nabla \Psi_0^2 \cdot \nabla F$ is assumed to have only a minor effect. This is called Proc. C,

Proc. C

$$\nabla^2 F_0 = f/\Psi_0^2 \tag{9a}$$

$$\nabla^2 F_{i+1} = f/\Psi_0^2 - \nabla \ln(\Psi_0^2) \cdot \nabla F_i . \tag{9b}$$

In the systems we have examined, if Proc. A failed for the reasons given above, Proc. C would have yielded a solution satisfying the criteria

of successive iterates meeting boundary conditions and leading to a formal solution. For the Hooke's law model, Proc. C generates the following set of iterates:

$$\begin{array}{l}
 \underline{1} \quad \frac{F_1}{r_{12}/2 - r_{12}^2/3(2\pi)^{\frac{1}{2}}} \\
 0 \quad F_0 + r_{12}^3/24 - r_{12}^4/30(2\pi)^{\frac{1}{2}} \\
 1 \quad F_1 + r_{12}^5/240 - r_{12}^6/315(2\pi)^{\frac{1}{2}}
 \end{array}$$

and

$$F_{\infty} = \sum_{n=1}^{\infty} (-1)^{n+1} r_{12}^n / \left(n \left(\frac{n+1}{2} \right)! 2^{\frac{n+1}{2}} \right)$$

F_{∞} , except for a normalization constant, is the power series expansion of F given by White and Byers Brown.^[10]

In no cases considered have both Proc. A and Proc. C yielded satisfactory solutions. As an example, the application of Proc. C. to the earlier considered hydrogen atom in an electric field leads to

$$\begin{array}{l}
 \underline{1} \quad \frac{F_1}{3r^2/4 - r^4/30 - r^5/90} \\
 0 \quad 3r^2/4 - r^4/30 - r^5/90 \\
 1 \quad 3r^2/4 + r^3/4 - r^4/30 - r^5/50 - r^6/378 \\
 2 \quad F - r^5/50 - r^6/210 - r^7/1764 \\
 3 \quad F - r^6/210 - r^7/880 - r^8/9072
 \end{array}$$

The major difficulties encountered in the use of Proc. C are:

- (1) Eqs. (9) often do not have unique solutions.
- (2) Solutions to Eqs. (9) are normally difficult to obtain, and in the n-dimensional case, $n > 3$, essentially impossible. Solutions^[12] to

$$\nabla^2 U(\underline{x}) = -4\pi \mu(\underline{x})$$

$$\underline{x} = (x_1, x_2, \dots, x_n)$$

are, in principle, given by

$$U(\underline{x}) = \int \dots \int \mu(\underline{x}') \gamma(r) d\underline{x}'$$

where

$$r = |\underline{x} - \underline{x}'|$$

$$\gamma(r) = r^{2-n}/(n-2) \omega_n, \quad n > 2$$

$$\omega_n = 2\pi^{n/2} / \Gamma(n/2) ;$$

but these integrals become intractable for $n > 3$.

Appendix - Relationship between Proc. A and Proc. B

An iterative process always can be modified to include a zeroth-order approximation. For Proc. A, the inclusion of an initial approximation, $\mathcal{F}$, would give

Proc. D

$$\nabla \Psi_0^2 \cdot \nabla F_0' = f - \Psi_0^2 \nabla^2 \mathcal{F} \quad (A1)$$

$$\nabla \Psi_0^2 \cdot \nabla F_{i+1}' = f - \Psi_0^2 \nabla^2 \mathcal{F}_1' \quad (A2)$$

Proc. A can be considered to be the special case of Proc. D when

$$\mathcal{F} = 0.$$

The equivalence of Procs. B and D can be demonstrated by showing that a function $\mathcal{F}$ exists such that the results of the k-th iterations are the same, $F_k = F_k'$. The utilization of Proc. B does not require any knowledge of $\mathcal{F}$, but it is possible to determine a function which satisfies this requirement.

The relationship between $\mathcal{F}$ and the (A_i, F_i) can easily be obtained for the first few iterations. In the following we shall assume that the F_i and A_i of Proc. B are known and $\mathcal{F}$ will be labelled with a subscript $\mathcal{F}_k$ to show that this is the function for which $F_k' = F_k$.

$\mathcal{F}_0$ Trivial case, $F_0' = F_0$ implies $\nabla^2 \mathcal{F}_0 = 0$.

$\mathcal{F}_1$

Proc. B

$$\nabla \Psi_0^2 \cdot \nabla F_0 = f$$

$$\nabla \Psi_0^2 \cdot \nabla F_1 = f - \Psi_0^2 \nabla^2 (F_0 - A_0)$$

Proc. D

$$\nabla \Psi_0^2 \cdot \nabla F_0' = f - \Psi_0^2 \nabla^2 \mathcal{F}_1$$

$$\nabla \Psi_0^2 \cdot \nabla F_1' = f - \Psi_0^2 \nabla^2 F_0'$$

$$F_1' = F_1 \text{ implies } F_0' = F_0 - A_0$$

$$\begin{aligned} \nabla \Psi_0^2 \cdot \nabla F_0' &= \nabla \Psi_0^2 \cdot \nabla F_0 - \nabla \Psi_0^2 \cdot \nabla A_0 \\ &= f - \nabla \Psi_0^2 \cdot \nabla A_0 \\ &= f - \Psi_0^2 \nabla^2 \mathcal{F}_1, \end{aligned}$$

and $\mathcal{F}_1$ can be determined from

$$\nabla^2 \mathcal{F}_1 = \nabla \ln(\Psi_0^2) \cdot \nabla A_0.$$

 $\mathcal{F}_2$ Proc. B

$$\nabla \Psi_0^2 \cdot \nabla F_0 = f$$

$$\nabla \Psi_0^2 \cdot \nabla F_1 = f - \Psi_0^2 \nabla^2 (F_0 - A_0)$$

$$\nabla \Psi_0^2 \cdot \nabla F_2 = f - \Psi_0^2 \nabla^2 (F_1 - A_1)$$

Proc. D

$$\nabla \Psi_0^2 \cdot \nabla F_0' = f - \Psi_0^2 \nabla^2 \mathcal{F}_2$$

$$\nabla \Psi_0^2 \cdot \nabla F_1' = f - \Psi_0^2 \nabla^2 F_0'$$

$$\nabla \Psi_0^2 \cdot \nabla F_2' = f - \Psi_0^2 \nabla^2 F_1'$$

$$F_2' = F_2 \text{ implies } F_1' = F_1 - A_1 ,$$

$$\begin{aligned} \nabla \Psi_0^2 \cdot \nabla F_1' &= \nabla \Psi_0^2 \cdot \nabla F_1 - \nabla \Psi_0^2 \cdot \nabla A_1 \\ &= f - \Psi_0^2 \nabla^2 F_0 + \Psi_0^2 \nabla^2 A_0 - \nabla \Psi_0^2 \cdot \nabla A_1 \\ &= f - \Psi_0^2 \nabla^2 F_0' . \end{aligned}$$

Therefore

$$\nabla^2 (F_0' - F_0) = \nabla^2 A_0 - \nabla \ln(\Psi_0^2) \cdot \nabla A_1 ,$$

and $\mathcal{F}_2$ can be determined from

$$\begin{aligned} \nabla^2 \mathcal{F}_2 &= f / \Psi_0^2 - \nabla \ln(\Psi_0^2) \cdot \nabla F_0' \\ &= \nabla \ln(\Psi_0^2) \cdot \nabla F_0 - \nabla \ln(\Psi_0^2) \cdot \nabla F_0' \\ &= - \nabla \ln(\Psi_0^2) \cdot \nabla (F_0' - F_0) . \end{aligned}$$

Note that the determination of $\mathcal{F}_k$ requires the solution of k Poisson equations.

For the hydrogen atom in an electric field, the $\mathcal{F}_k$ which force all iterates to be well-behaved (i.e. F_k' of Proc. D equals F_k of Proc. B) have been determined to be:

$$\begin{array}{l} \frac{1}{\mathcal{F}_1} \\ 1 \quad 3r^2/4 \\ 2 \quad 3r^2/4 + r^3/4 \\ 3 \quad 3r^2/4 + r^3/4 + r^4/24 = F . \end{array}$$

When Proc. B is applied to the Hooke's law model we find $F_i = A_i$ for all i , and by Eq. (8b) $F_i = F_0$. The $\mathcal{F}_k$ of Proc. D which correspond to this are:

$$\begin{array}{l} \frac{1}{1} \quad \frac{\mathcal{F}_i}{r_{12}/2 - r_{12}^2/3(2\pi)^{\frac{1}{2}}} \\ 2 \quad \mathcal{F}_1 + r_{12}^3/24 - r_{12}^4/30(2\pi)^{\frac{1}{2}} \end{array}$$

$$\mathcal{F}_\infty = \sum_{n=1}^{\infty} (-1)^{n+1} r_{12}^n / (n \left(\frac{n+1}{2}\right)! 2^{\frac{n+1}{2}}),$$

the well-behaved result obtained by applying Proc. C to this system.

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