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AN APPRAISAL OF THE FOPIM FAST-CONVERGING PERTURBATION METHOD*

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ABSTRACT

The practicality of the First-Order-Perturbation-Iteration-Method (FOPIM) is appraised. After the first iteration, the expectation value of the energy is given by a non-analytic function of the perturbation parameter λ. The asymptotic expansion of this function gives the energy accurately up to $O(\lambda^8)$. The convergence of the asymptotic expansions is discussed. Two examples are considered: a perturbed ground state hydrogen atom, and a perturbed ground state linear harmonic oscillator.

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The First-Order-Perturbation-Iteration-Method (FOPIM) for solving time-independent quantum mechanical problems[1,2] requires careful scrutiny. After the n-th iteration the expectation value of the energy is given by a complicated non-analytic function of the perturbation parameter λ which may be expanded in an asymptotic series in λ accurate up to terms of the order of λ raised to the 2^{n+1} power. Thus, FOPIM requires the solution of fewer differential equations to obtain high precision than would be required by other procedures. However, the method is not easy to apply. The integrations and the differential equations involved soon become intractable, and numerical techniques are required for further progress. The difficulties are illustrated by two rather trivial examples: (1). A ground state hydrogen atom perturbed by a small additional charge at the nucleus, and (2). A ground state linear harmonic oscillator perturbed by an additional quadratic potential. Before proceeding with the examples, we briefly recall the relevant theory and also consider the question of the convergence of the iterated perturbation series.

II. THEORY

We start with the usual Rayleigh-Schrödinger perturbation theory for non-degenerate states. Let h_o be the unperturbed Hamiltonian which has ϵ_o and ψ_o as its eigenvalue and normalized eigenfunction for the state under consideration. The perturbed Hamiltonian is

$$H = h_o + \lambda v_o \tag{1}$$

We seek the perturbed energy $E(\lambda)$ and the perturbed eigenfunction $\Psi(\lambda)$. If E and Ψ are analytical functions of λ,

$$E(\lambda) = \epsilon_0 + \lambda \epsilon_0^{(1)} + \lambda^2 \epsilon_0^{(2)} + \lambda^3 \epsilon_0^{(3)} + \cdots \tag{2}$$

$$\Psi(\lambda) = \Psi_0 + \lambda \Psi_0^{(1)} + \lambda^2 \Psi_0^{(2)} + \lambda^3 \Psi_0^{(3)} + \cdots \tag{3}$$

The first three corrections to the energy can be expressed[2] in terms of v_0, Ψ_0, and $\Psi_0^{(1)}$,

$$\epsilon_0^{(1)} = \langle \Psi_0 , v_0 \Psi_0 \rangle \tag{4}$$

$$\epsilon_0^{(2)} = \langle \Psi_0 , (v_0 - \epsilon_0^{(1)}) \Psi_0^{(1)} \rangle \tag{5}$$

$$\begin{aligned} \epsilon_0^{(3)} = {} & \langle \Psi_0^{(1)} , (v_0 - \epsilon_0^{(1)}) \rangle \\ & - \epsilon_0^{(2)} \left[\langle \Psi_0^{(1)} , \Psi_0 \rangle + \langle \Psi_0 , \Psi_0^{(1)} \rangle \right] \end{aligned} \tag{6}$$

Here $\Psi_0^{(1)}$ satisfies the equation

$$(h_0 - \epsilon_0) \Psi_0^{(1)} + (v_0 - \epsilon_0^{(1)}) \Psi_0 = 0 \tag{7}$$

In the usual situation where h_0 consists of a kinetic energy operator T plus a potential energy function u_0, it is convenient

to let $\Psi_o^{(1)} = F_o \Psi_o$ where F_o is a function of the coordinates. Then Eq. (7) reduces to

$$[T, F_o] \Psi_o + (v_o - \epsilon_o^{(1)}) \Psi_o = 0 \tag{8}$$

This is a differential equation for F_o which can, in principle, be solved by quadrature in one-dimensional or separable multi-dimensional problems. Thus, there is a fairly clear-cut way of deriving $\Psi_o^{(1)}$ and the energy up to terms of the order of λ^4.

The basic idea of FOPIM is to iterate the perturbation procedure starting with the improved unperturbed eigenfunction

$$\Psi_1 = N(\Psi_o + \lambda \Psi_o^{(1)}) = N(1 + \lambda F_o) \Psi_o \tag{9}$$

where N is the normalization factor

$$N = \left[1 + \lambda [\langle \Psi_o, \Psi_o^{(1)} \rangle + \langle \Psi_o^{(1)}, \Psi_o \rangle] + \lambda^2 \langle \Psi_o^{(1)}, \Psi_o^{(1)} \rangle \right]^{-1/2} \tag{10}$$

Actually, Eq. (8) only determines F_o up to an additive constant C_o. If $\Psi_o^{(1)}$ is the (asymptotically) correct first-order function for which $\langle \Psi_o, \Psi_o^{(1)} \rangle = 0$ and $\Psi_o^{(1)\prime}$ differs from $\Psi_o^{(1)}$ by $\Psi_o \delta C_o$, that is, in a different choice of C_o, then one may write for the first iterated wave function

$$\Psi_1' = N_1' \left[\Psi_0 + \lambda \Psi_0^{(1)\prime} \right]$$

$$= N_1' \left[(1 + \lambda \delta C_0) \Psi_0 + \lambda \Psi_0^{(1)} \right]$$

$$= N_1'' \left[\Psi_0 + \frac{\lambda}{1 + \lambda \delta C_0} \Psi_0^{(1)} \right]$$

$$= N_1'' \left[\Psi_0 + (\lambda - \lambda^2 \delta C_0) \Psi_0^{(1)} + \cdots \right]$$

Thus Ψ_1' differs from Ψ_1 by terms of order λ^2. This is not equivalent to altering a multiplicative normalization constant. The energy expectation value $\mathcal{E}_1 = \langle \Psi_1, H \Psi_1 \rangle$ is not affected by the choice of C_0 up to terms of $O(\lambda^4)$. Furthermore, if Ψ_2 is the normalized function obtained after the first iteration, the energy $\mathcal{E}_2 = \langle \Psi_2, H \Psi_2 \rangle$ is not affected by the choice of C_0 up to terms of $O(\lambda^8)$. Thus, for our purposes, the choice of C_0 is immaterial and may be made (as in our first example) to simplify the calculations. It is easy to verify that $h_1 \Psi_1 = \epsilon_1 \Psi_1$ where

$$h_1 = h_0 + \frac{\lambda V_0 + \lambda^2 \epsilon_0^{(1)} F_0}{1 + \lambda F_0} \tag{11}$$

and

$$\epsilon_1(\lambda) = \epsilon_0 + \lambda \epsilon_0^{(1)} \tag{12}$$

Thus the perturbed Hamiltonian can be written in the form

$$H = h_1 + \lambda^2 v_1 \tag{13}$$

where

$$v_1(\lambda) = \frac{(v_0 - \epsilon_0^{(1)})F_0}{1+\lambda F_0} = \frac{(H-\epsilon_1)\Psi_1}{\Psi_1} \tag{14}$$

The $\lambda^2 v_1(\lambda)$ now plays the role of a perturbation. Corresponding to Eqs. (2) and (3), we have the expansions

$$E(\lambda) = \epsilon_1(\lambda) + \lambda^2 \epsilon_1^{(1)}(\lambda) + \lambda^4 \epsilon_1^{(2)}(\lambda) + \lambda^6 \epsilon_1^{(3)}(\lambda) + \cdots \tag{2a}$$

$$\Psi(\lambda) = \Psi_1(\lambda) + \lambda^2 \Psi_1^{(1)}(\lambda) + \cdots \tag{3a}$$

The new first-order wave function $\Psi_1^{(1)}(\lambda)$ may be expressed in the form $\Psi_1^{(1)}(\lambda) = F_1(\lambda)\Psi_1(\lambda)$ where $F_1(\lambda)$ is a function satisfying the equation

$$[T, F_1(\lambda)]\Psi_1(\lambda) + (v_1(\lambda) - \epsilon_1^{(1)}(\lambda))\Psi_1(\lambda) = 0 \tag{8a}$$

The $\epsilon_1^{(1)}(\lambda)$, $\epsilon_1^{(2)}(\lambda)$, and $\epsilon_1^{(3)}(\lambda)$ are given by

$$\epsilon_1^{(1)}(\lambda) = \langle \psi_1, V_1 \psi_1 \rangle \tag{4a}$$

$$\epsilon_1^{(2)}(\lambda) = \langle \psi_1, (V_1 - \epsilon_1^{(1)}) \psi_1^{(1)} \rangle \tag{5a}$$

$$\begin{aligned} \epsilon_1^{(3)}(\lambda) = {} & \langle \psi_1^{(1)}, (V_1 - \epsilon_1^{(1)}) \psi_1^{(1)} \rangle \\ & - \epsilon_1^{(2)} \left[\langle \psi_1^{(1)}, \psi_1 \rangle + \langle \psi_1, \psi_1^{(1)} \rangle \right] \end{aligned} \tag{6a}$$

Eq.(8a) only determines the function $F_1(\lambda)$ to within an additive constant C_1. However, Eqs. (5a) and (6a) are written in such a form that the values of $\epsilon_1^{(2)}$ and $\epsilon_1^{(3)}$ are independent of the value of C_1.

If the expansion of the energy, Eq.(2a), is terminated after the third-order term $\lambda^6 \epsilon_1^{(3)}(\lambda)$, then $E(\lambda)$ should be accurate up to terms of the order of λ^8. This is the same accuracy as could be obtained from the usual Rayleigh-Schrödinger perturbation theory with the expansion of the wave function, Eq.(3), truncated after the third order term $\lambda^3 \psi_o^{(3)}$. The advantage of FOPIM is that to obtain this degree of accuracy it is only necessary to solve two differential equations for $\psi_o^{(1)}$ and for $\psi_1^{(1)}(\lambda)$ instead of the three differential equations for $\psi_o^{(1)}$, $\psi_o^{(2)}$, and $\psi_o^{(3)}$.

In order to obtain higher accuracy, the FOPIM procedure can be repeated as often as required.

III. CONVERGENCE.

The theorems[3] of Rellich, Kato, Titchmarsh, and others enables one to discuss the convergence of the Rayleigh-Schrödinger energy series Eq.(2) in terms of the mathematical properties of h_o and v_o. The convergence of the FOPIM energy series Eq.(2a) is more difficult to assess since h_1 and v_1, as well as the ϵ_1, $\epsilon_1^{(1)}$, etc., are functions of λ. An additional difficulty arises from $\lambda^2 v_1(\lambda)$ not being a <u>regular</u> perturbation in the region of configuration space for which $|\lambda F_o| > 1$. In this region, the Taylor series expansion in powers of λ does not converge for the factor $(1 + \lambda F_o)^{-1}$ which occurs in $v_1(\lambda)$. No matter how small the value of λ, there will always be such a region unless F_o is a bounded function (which it seldom is). Very little is known about the convergence of a perturbation series having such complications. However, intuitively, one expects that a given number of FOPIM energy terms should give a far better energy than the same number of Rayleigh-Schrödinger energy terms.

If the $\epsilon_1^{(j)}$'s are analytic functions of λ in some neighborhood of $\lambda = 0$ (i.e. if they have convergent Taylor series for $|\lambda|$ less than some fixed λ_o), it is possible to compare the FOPIM series (2a) with the Rayleigh-Schrödinger series (2) as expansions in powers of λ. From Eq.(12), it is clear that ϵ_1 is analytic in λ. From Eqs. (4a), (9), and (14) we see that $\epsilon_1^{(1)}$

is also analytic since it has the form $(a_o + a_1\lambda)/(b_o + b_1\lambda + b_2\lambda^2)$. The behavior of $\epsilon_1^{(2)}$ and $\epsilon_1^{(3)}$ is different. Generally, as the following argument shows, we cannot expect them to be analytic in any neighborhood of $\lambda = 0$, no matter how small the value of λ.

Eqs.(5a) and (6a) express $\epsilon_1^{(2)}$ and $\epsilon_1^{(3)}$ as integrals involving $\Psi_1^{(1)} = F_1 \Psi_1$. The function F_1 is found by solving Eq.(8a). In a simple one-dimensional case with Ψ_1 assumed real, $T = -\frac{1}{2} d^2/dx^2$ and F_1 is the integral of

$$\frac{dF_1}{dx} = 2\Psi_1^{-2} \int_{-\infty}^{x} (V_1 - \epsilon_1^{(1)}) \Psi_1^2 \, dx \tag{15}$$

Consideration of the factors of $(1 + \lambda F_o)$ occurring in Ψ_1 and v_1 indicate that dF_1/dx has terms involving $(1 + \lambda F_o)^{-2}$ and $(1 + \lambda F_o)^{-1}$, and thus F_1 involves $(1 + \lambda F_o)^{-1}$ and $\log |1 + \lambda F_o|$. The logarithm is unpleasant as it cannot cancel with any of the factors of $(1 + \lambda F_o)$ in the numerators in the integrals of Eqs. (5a) and (6a). These integrations for $\epsilon_1^{(2)}$ and $\epsilon_1^{(3)}$ are taken over all configuration space including the region $|\lambda F_o| > 1$ in which the Taylor series for $\log |1 + \lambda F_o|$ in powers of λ does not converge. It follows that $\epsilon_1^{(2)}$ and $\epsilon_1^{(3)}$ themselves do not have convergent Taylor series in powers of λ in any neighborhood of $\lambda = 0$ if F_1, and hence Ψ_1, contains $\log |1 + \lambda F_o|$. One would still expect $\epsilon_1^{(2)}$ and $\epsilon_1^{(3)}$ to have <u>asymptotic</u> expansions in ascending powers of λ, since the smaller the value of λ, the less significant is the troublesome region where $|\lambda F_o| > 1$. But these asymptotic

expansions are not convergent for any value of λ.

Thus, it is only in an asymptotic sense that one should expect to compare three or more terms in the FOPIM series Eq.(2a) with the Rayleigh-Schrödinger series Eq.(2). In that sense, n terms of Eq.(2a) should agree with 2n terms of Eq.(2). This is evident because of the powers of λ^2 (rather than λ) which multiply the terms in (2a). Experience with asymptotic perturbation series has shown that frequently only three or four terms are relevant before the series must be corrected and terminated. On this account, the assertions about agreement of the two series (2) and (2a) through high powers of λ must be tentative and questionable.

Comparison of the two series, Eqs.(3) and (3a), for the perturbed eigenfunction $\Psi(\lambda)$ is sometimes possible provided that the norms of the two series are adjusted to be equal through the power of λ under consideration. With this proviso, it is evident that, for example, $\Psi_1(\lambda) + \lambda^2 \Psi_1^{(1)}(\lambda)$ agrees with $\Psi_o + \lambda\Psi_o^{(1)} + \lambda^2\Psi_o^{(2)} + \lambda^3 \Psi_o^{(3)}$ whenever $\Psi_1^{(1)}(\lambda)$ is expandable in ascending powers of λ, that is when $|\lambda F_o| < 1$.

IV. EXAMPLE: THE PERTURBED HYDROGEN ATOM.

A ground-state hydrogen atom perturbed by the addition of a charge $-\lambda e$ at the nucleus is a simple example which can be used to test our FOPIM. This example has previously been used by Wigner[4], Trees,[5] and Dalgarno[6] to test perturbation theories. In atomic units, the exact solutions are

$$E(\lambda) = -\tfrac{1}{2}(1-\lambda)^2 \quad \text{and} \quad \Psi(\lambda) = \pi^{-\frac{1}{2}}(1-\lambda)^{3/2}\, e^{-r} e^{\lambda r} \tag{16}$$

We start with the unperturbed wave function

$$\Psi_o = \pi^{-\frac{1}{2}} \exp(-r) \tag{17}$$

corresponding to

$$h_o = -\tfrac{1}{2}\nabla^2 - r^{-1} \quad \text{and} \quad \epsilon_o = -\tfrac{1}{2} \tag{18}$$

The perturbation potential and first order energy are

$$v_o = r^{-1} \quad \text{and} \quad \epsilon_o^{(1)} = 1 \tag{19}$$

It is easy to solve Eq.(8) for F_o giving

$$F_o = r \quad \text{and} \quad \Psi_o^{(1)} = \pi^{-\frac{1}{2}}\, r \exp(-r) \tag{20}$$

Here the constant of integration has been adjusted so as to simplify the FOPIM calculations rather than to make $\Psi_o^{(1)}$ orthogonal to Ψ_o. From Eqs.(5) and (6) we find that

$$\epsilon_o^{(2)} = -\tfrac{1}{2} \quad \text{and} \quad \epsilon_o^{(3)} = 0 \tag{21}$$

Indeed, as Dalgarno[6] points out, all of the subsequent $\epsilon_o^{(j)}$'s are zero so that the first three terms of the Rayleigh-Schrödinger

energy series Eq. (2) suffice to give the exact energy of the perturbed system, Eq.(16). This feature of the example is fortunate.

In accordance with Eq. (9), the first-iterated FOPIM normalized "unperturbed" wave function is

$$\Psi_1(\lambda) = \pi^{-1/2}(1+3\lambda+3\lambda^2)^{-1/2}(1+\lambda r)e^{-r} \tag{22}$$

We note that $\Psi_1(\lambda)$ agrees with the exact wave function $\Psi(\lambda)$ through the first-order in λ. From Eqs. (12) and (14),

$$\epsilon_1(\lambda) = -\frac{1}{2} + \lambda \quad \text{and} \quad v_1(\lambda) = \frac{1-r}{1+\lambda r} \tag{23}$$

Using Eq. (4a), it follows that

$$\epsilon_1^{(1)}(\lambda) = -\frac{1}{2}(1+3\lambda)(1+3\lambda+3\lambda^2)^{-1} \tag{24}$$

When $|\lambda| < (7/12)^{\frac{1}{2}} \doteq 0.764$, the expansion of Eq. (24) in powers of λ is convergent giving

$$\epsilon_1^{(1)}(\lambda) = -\frac{1}{2} + \frac{3}{2}\lambda^2 - \frac{9}{2}\lambda^3 + 9\lambda^4 + \cdots \tag{25}$$

Solution of Eq. (8a) yields

$$\lambda^2(1+3\lambda+3\lambda^2)F_1 = a\lambda r + (b-2a)\log|1+\lambda r| + (b-a)(1+\lambda r)^{-1} + C_1 \tag{26}$$

Here C_1 is an arbitrary constant and

$$a = 1 + \frac{5}{2}\lambda + \frac{3}{2}\lambda^2 , \qquad b = 1 + 3\lambda + 2\lambda^2 \tag{27}$$

Setting $\Psi_1^{(1)} = F_1 \Psi_1$ in Eq. (5a) , we find after some tedious but straightforward integration,

$$\epsilon_1^{(2)}(\lambda) = -\frac{(1+\lambda)^2}{\lambda^2(1+3\lambda+3\lambda^2)^2}\left[\frac{10\lambda+67\lambda^2+129\lambda^3+27\lambda^4}{-\frac{1}{2\lambda}+\frac{5}{4}-\frac{7\lambda}{2}} + \left\{\frac{(1+3\lambda)(1-3\lambda+3\lambda^2)}{1+3\lambda+3\lambda^2} + \frac{2}{\lambda^2}-\frac{4}{\lambda}+5-3\lambda\right\} I(\lambda)\right] \tag{28}$$

Here

$$I(\lambda) = \int_0^\infty (\log|1+\lambda r|)\, e^{-2r}\, dr$$
$$= \frac{1}{2} e^{2/\lambda}\, Ei^*(2/\lambda) \tag{29}$$

in terms of the exponential integral $Ei^*(t) = \int_t^\infty (e^{-x}/x)\, dx$. If λ is negative so that the integrand of $I(\lambda)$ has a singularity at the point $r = -1/\lambda$, then we must use the Cauchy <u>principle value</u> of $Ei^*(2/\lambda)$. The <u>asymptotic</u> expansion of $I(\lambda)$ in ascending powers of λ is

$$I(\lambda) \approx \frac{\lambda}{4}\left[1 - 1!\left(\frac{\lambda}{2}\right) + 2!\left(\frac{\lambda}{2}\right)^2 - 3!\left(\frac{\lambda}{2}\right)^3 + \cdots\right] \tag{30}$$

Expanding Eq. (28) with the use of Eq. (30), we obtain the asymptotic expansion

$$\epsilon_1^{(2)}(\lambda) \approx -\frac{3}{2} + \frac{9}{2}\lambda - \lambda^2 + \cdots \tag{31}$$

Thus, from Eqs. (23), (25), and (31), it follows that

$$\epsilon_1 + \lambda^2 \epsilon_1^{(1)} + \lambda^4 \epsilon_1^{(2)} \approx -\frac{1}{2}(1-\lambda)^2 + 8\lambda^6 \tag{32}$$

This illustrates the <u>asymptotic</u> agreement of the first <u>three</u> terms of the FOPIM series (2a) with the first <u>six</u> terms of the Rayleigh-Schrödinger series (2). Using Eq. (6a), we could evaluate $\epsilon_1^{(3)}(\lambda)$ but the integrations would be very lengthy. We should get a result similar to (but more complicated than) that for $\epsilon_1^{(2)}(\lambda)$ and no new features would emerge. We would expect to find

$$\epsilon_1 + \lambda^2 \epsilon_1^{(1)} + \lambda^4 \epsilon_1^{(2)} + \lambda^6 \epsilon_1^{(3)} \approx -\frac{1}{2}(1-\lambda)^2 + O(\lambda^8) \tag{33}$$

The unnormalized first-order corrected first-iterated eigenfunction is $\Psi_1 + \lambda^2 \Psi_1^{(1)} = (1 + \lambda^2 F_1)\Psi_1$. Here Ψ_1 is given by Eq. (22) and F_1 is given by Eq. (26). When $|\lambda r| < 1$, the logarithm terms may be expanded so that

$$\psi_1 + \lambda^2 \psi_1^{(1)} = K e^{-r} \left[\left\{ C_1 + \frac{\lambda}{2}(1+\lambda) + (1+3\lambda+3\lambda^2) \right\} (1+\lambda r) + \frac{\lambda^2 r^2}{2}(1+3\lambda+2\lambda^2) + (1+\lambda)^2 \left\{ \frac{\lambda^3 r^3}{6} - \frac{\lambda^4 r^4}{12} + \frac{\lambda^5 r^5}{20} - \cdots \right\} \right] \tag{34}$$

Here $K = (1 + 3\lambda + 3\lambda^2)^{-1}$. If C_1 is chosen so as to make the <u>asymptotic</u> expansion of $\psi_1^{(1)}$ orthogonal to ψ_1, then the <u>asymptotic</u> expansion of $\psi_1 + \psi_1^{(1)}$ is proportional to

$$e^{-r}\left[1 + \lambda r + \frac{\lambda^2 r^2}{2} + \frac{\lambda^3 r^3}{6}\right] + O(\lambda^4) \tag{35}$$

Thus the agreement between the two series (3) and (3a) is also <u>asymptotic</u>.

In this example it is evident from the complicated nature of F_1 that a further iteration based on the perturbation $\lambda^4 (v_1 - \epsilon_1^{(1)}) F_1 (1 + \lambda^2 F_1)^{-1}$ would be impractical.

V. EXAMPLE: THE PERTURBED, LINEAR HARMONIC OSCILLATOR.

Another simple example is the linear harmonic oscillator in its ground state, perturbed by addition of λ to the force constant. Using atomic units, and taking the unperturbed force constant to be unity,

$$h_0 = -\frac{1}{2}\frac{d^2}{dx^2} + \frac{1}{2}x^2 \tag{36}$$

$$V_0 = \frac{1}{2}x^2 \tag{37}$$

$$\left.\begin{aligned} \Psi_0 &= \pi^{-1/4}\exp\left(-\frac{1}{2}x^2\right) \\ \epsilon_0 &= \frac{1}{2} \end{aligned}\right\} \tag{38}$$

The exact energy and wave function of the perturbed system are

$$\begin{aligned} E &= \frac{1}{2}(1+\lambda)^{1/2} \\ &= \frac{1}{2} + \frac{1}{4}\lambda - \frac{1}{16}\lambda^2 + \frac{1}{32}\lambda^3 - \frac{5}{256}\lambda^4 + \frac{7}{512}\lambda^5 \\ &\quad - \frac{21}{2048}\lambda^6 + \frac{33}{4096}\lambda^7 - \frac{429}{65536}\lambda^8 + \cdots \end{aligned} \tag{39}$$

$$\begin{aligned} \Psi &= \pi^{-1/4}(1+\lambda)^{1/8}\exp\left[-\frac{1}{2}(1+\lambda)^{1/2}x^2\right] \\ &= \Psi_0\left[1 + \lambda\left(\frac{1}{8} - \frac{x^2}{4}\right) + \lambda^2\left(-\frac{7}{128} + \frac{x^2}{32} + \frac{x^4}{32}\right)\right. \\ &\quad \left. + \lambda^3\left(\frac{35}{1024} - \frac{5x^2}{512} - \frac{3x^4}{256} - \frac{x^6}{384}\right) + \cdots\right] \end{aligned} \tag{40}$$

In contrast to the perturbed hydrogen example, let us normalize $\Psi_0^{(1)}$ so as to be orthogonal to Ψ_0 ; that is $\langle \Psi_0^{(1)}, \Psi_0 \rangle = 0.$ Subject to this condition, solution of Eq. (8) yields

$$F_0 = \frac{1}{8} - \frac{1}{4} x^2 \tag{41}$$

or

$$\Psi_0^{(1)} = \left(\frac{1}{8} - \frac{1}{4} x^2\right) \Psi_0 \tag{42}$$

whence

$$\left.\begin{aligned} \epsilon_0^{(1)} &= \frac{1}{4} \\ \epsilon_0^{(2)} &= -\frac{1}{16} \\ \epsilon_0^{(3)} &= \frac{1}{32} \end{aligned}\right\} \tag{43}$$

Now, the FOPIM equation is $h_1 \Psi_1 = \epsilon_1 \Psi_1$, with

$$h_1 = -\frac{1}{2}\frac{d^2}{dx^2} + \frac{1}{2}x^2 + \frac{\frac{\lambda}{2}x^2 + \frac{\lambda^2}{16}\left(\frac{1}{2} - x^2\right)}{1 + \lambda\left(\frac{1}{8} - \frac{x^2}{4}\right)} \tag{44}$$

$$\Psi_1 = \left(1 + \frac{\lambda^2}{32}\right)^{-1/2} \left[1 + \lambda\left(\frac{1}{8} - \frac{x^2}{4}\right)\right] \Psi_0 \tag{45}$$

$$\epsilon_1 = \frac{1}{2} + \frac{\lambda}{4} + \frac{-\frac{\lambda^2}{16} + \frac{\lambda^3}{32}}{1 + \frac{\lambda^2}{32}} \tag{46}$$

The new perturbation is

$$\lambda^2 V_1 = \frac{\lambda^2\left(-\frac{1}{32}+\frac{1}{8}x^2-\frac{1}{8}x^4\right)}{1+\frac{\lambda}{4}\left(\frac{1}{2}-x^2\right)} \tag{47}$$

The first integration of Eq. (8a) gives

$$\Psi_1^2 \frac{d}{dx} F_1 = \sum_{n=0}^{3} a_n(\lambda) J_n \tag{48}$$

with

$$J_n = \int_0^x y^{2n} e^{-y^2} dy$$

$$= \frac{(2n-1)!}{2^{2n-1}(n-1)!}\left[J_0 - e^{-x^2}\sum_{j=1}^{n}\frac{(n-j)!\ 2^{2(n-j)}}{[2(n-j)+1]!}x^{2(n-j)+1}\right] \tag{49}$$

Fortunately the $a_n(\lambda)$ are such that $J_0 = \frac{1}{2}\pi^{1/2}\,\mathrm{erf}(x)$ does not appear in Eq. (48). Otherwise $\int_0^x e^{z^2}\int_0^z e^{-y^2}dy\,dz$ and related transcendentals would occur in F_1.

Solution of Eq. (8a) yields

$$\lambda^2\left(1+\frac{\lambda^2}{32}\right)F_1 = A\left(1+\lambda F_0\right)^{-1} + Bx^2 + D\log|1+\lambda F_0| + C_1 \tag{50}$$

with

$$\left.\begin{aligned} A &= -\frac{\lambda}{4} - \frac{5\lambda^2}{32} - \frac{\lambda^3}{32} - \frac{\lambda^4}{512} \\ B &= -\frac{\lambda}{4} - \frac{\lambda^3}{128} \\ D &= -1 - \frac{\lambda}{2} - \frac{\lambda^2}{16} \end{aligned}\right\} \tag{51}$$

The constant C_1 is chosen so as to make the FOPIM wave function in asymptotic agreement with Eq. (40) through third order; that is, by the condition $\langle \Psi_1, \Psi_1^{(1)} \rangle = 0$. Here and in evaluation of the energies $\epsilon_1^{(2)}$ and $\epsilon_1^{(3)}$, one encounters integrals which lead to transcendental functions of the perturbation parameter λ. The integrals are of three types:

$$\left.\begin{aligned} I_1(n) &= \int_{-\infty}^{\infty} e^{-x^2} x^{2n} (1+\lambda F_0)^{-1} dx \\ I_2(n) &= \int_{-\infty}^{\infty} e^{-x^2} x^{2n} \log|1+\lambda F_0| \, dx \\ I_3(n) &= \int_{-\infty}^{\infty} e^{-x^2} x^{2n} \{\log|1+\lambda F_0|\}^2 dx \end{aligned}\right\} \quad (52)$$

In order to express the definite integrals as power series in λ, one must expand the integrands by use of the expansions

$$\left.\begin{aligned} (1+\lambda F_0)^{-1} &= 1 - \lambda F_0 + \lambda^2 F_0^2 - \lambda^3 F_0^3 + \cdots \\ &\text{and} \\ \log|1+\lambda F_0| &= \lambda F_0 - \tfrac{1}{2}\lambda^2 F_0^2 + \tfrac{1}{3}\lambda^3 F_0^3 - \cdots \end{aligned}\right\} \quad (53)$$

which converge for $\lambda^2 F_0^2 < 1$, or $x^4 - x^2 + \frac{1}{4} < \frac{16}{\lambda^2}$. The Gaussian weight factor assures correct values for the definite integrals in the limit of small perturbation.

Thus

$$C_1 = \frac{3}{8}\lambda + \frac{9}{64}\lambda^2 + \frac{47}{768}\lambda^3 - \frac{65}{12288}\lambda^4 - \frac{343}{122,880}\lambda^5 - \frac{281}{491,520}\lambda^6 + \cdots \tag{54}$$

$$\left.\begin{aligned} \epsilon_1^{(1)} &= \left(1+\frac{\lambda^2}{32}\right)^{-1}\left(-\frac{1}{16}+\frac{\lambda}{32}\right) \\ \epsilon_1^{(2)} &= -\frac{11}{512} + \frac{15}{1024}\lambda + \frac{167}{16384}\lambda^2 + \frac{21}{4096}\lambda^3 + \cdots \\ \epsilon_1^{(3)} &= -\frac{167}{8192} + \frac{95}{32768}\lambda + \cdots \end{aligned}\right\} \tag{55}$$

The wave function obtained by the FOPIM procedure is

$$\Psi_2 = \left[1+\lambda^2\langle\Psi_0^{(1)},\Psi_0^{(1)}\rangle\right]^{-1/2}\left[1+\lambda^4\langle\Psi_1^{(1)},\Psi_1^{(1)}\rangle\right]^{-1/2}(1+\lambda F_0)(1+\lambda^2 F_1)\Psi_0 \tag{56}$$

Expansion of the logarithm gives

$$\Psi_2 = \Psi_0 + \lambda\Psi_0^{(1)} + \lambda^2\Psi_0^{(2)} + \lambda^3\Psi_0^{(3)} + \tilde{\Psi}_0^{(4)} + O(\lambda^5) \tag{57}$$

where

$$\left.\begin{aligned} \Psi_0^{(2)} &= \left(-\frac{7}{128} + \frac{x^2}{32} + \frac{x^4}{32}\right)\Psi_0 \\ \Psi_0^{(3)} &= \left(\frac{35}{1024} - \frac{5x^2}{512} - \frac{3x^4}{256} - \frac{x^6}{384}\right)\Psi_0 \\ \tilde{\Psi}_0^{(4)} &= \left(-\frac{39}{16384} - \frac{17}{1024}x^2 - \frac{1}{1536}x^6 - \frac{1}{3072}x^8\right)\Psi_0 \end{aligned}\right\} \tag{58}$$

Thus Ψ_2 is in asymptotic agreement with Ψ through third order.

Now, the approximate energy for the original perturbed system is

$$\begin{aligned}
\mathcal{E}_2 &= \langle \Psi_2, H\Psi_2 \rangle \\
&= \epsilon_1 + \frac{\lambda^4 \epsilon_1^{(2)} + \lambda^6 \epsilon_1^{(3)}}{1 + \lambda^4 \langle \Psi_1^{(1)}, \Psi_1^{(1)} \rangle} \\
&= \frac{1}{2} + \frac{\lambda}{4} - \frac{\lambda^2}{16} + \frac{\lambda^3}{32} - \frac{5\lambda^4}{256} + \frac{7\lambda^5}{512} - \frac{21\lambda^6}{2048} \\
&\quad + \frac{33\lambda^7}{4096} + \frac{22{,}795\lambda^8}{1{,}048{,}576} + \cdots
\end{aligned} \tag{59}$$

This agrees with Eq. (39) through seventh order but the eighth order term is an upper bound to the correct value.[7]

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