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An iterative solution of Schrödinger's equation

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Abstract. The energy function $E(\lambda)$ of a quantum system with Hamiltonian $H(\lambda) = H_0 + \lambda H_1$ is determined by an analytical iterative procedure which yields a rich variety of functional forms. The wavefunction iterates include the solutions of Rayleigh–Schrödinger perturbation theory as well as some additional functions, all of which may be obtained sequentially by standard analytical techniques. At each step, an arbitrary (λ -dependent) constant may be chosen freely so as to improve the results of low-order iterates, thereby enhancing the convergence of the procedure.

1. Introduction

Traditionally, bound-state eigenfunctions and energy eigenvalues of most quantum mechanical systems have been calculated by variational or perturbation procedures. For a very small number of problems, exact (analytic or numerical) solutions are available, and these solutions serve as natural initial (or zero-order) approximations for other, more complicated, systems. There are also well defined iterative procedures for improving the accuracy of an initial (possibly crude) approximation, but they have not been exploited greatly in the present context, although the partitioning technique (see, for example, Löwdin 1982) leads naturally to an iterative solution of Schrödinger's equation. The need for numerical work in the iterative solution of the equations of Brillouin–Wigner (BW) perturbation theory (PT) probably explains the general preference for Rayleigh–Schrödinger (RS) PT, which avoids iteration.

In the present work, we present a very simple iterative procedure for obtaining bound-state solutions for a system with Hamiltonian $H(\lambda) = H_0 + \lambda H_1$, and compare with the results of RSPT. The new procedure does *not* involve numerical iteration, even though our equations are similar, in some respects, to those of BWPT in differential form (Byers Brown and Meath 1964). It should, therefore, be viewed as a *generalised* RSPT, with the advantage that it can yield a variety of functional forms of the energy in a natural manner.

2. Iterative solution of Schrödinger's equation

We treat a completely general system, with Hamiltonian H and seek a bound state eigenfunction ψ and eigenvalue E . Assuming that we have an *approximation* ψ_0 to ψ , obtained by any means whatsoever, (including physical intuition!), we construct an *effective* Hamiltonian H_0 with normalised eigenfunction ψ_0 and eigenvalue E_0 , so that

$$(H_0 - E_0)\psi_0 = 0, \quad \langle \psi_0 | \psi_0 \rangle = 1. \quad (1)$$

We now define an *effective* perturbation H_1 by means of

$$H_1 = H - H_0 \quad (2)$$

and, in order to facilitate comparisons with RSPT, we consider henceforth the generalised Hamiltonian $H(\lambda)$, where

$$H(\lambda) = H_0 + \lambda H_1. \quad (3)$$

Thus, λ may be regarded as a *dummy* variable to be set equal to unity at the end of the calculations, but the procedure clearly applies if the *physical* Hamiltonian $H(\lambda)$ contains a *natural* parameter λ , provided that H_0 has a known solution.

We now *assume* that the required solution of $H(\lambda)$ can be written

$$\psi(\lambda) = \psi_0 + \lambda \phi(\lambda), \quad E(\lambda) = E_0 + \lambda \varepsilon(\lambda) \quad (4)$$

and so obtain from Schrödinger's equation the equivalent forms

$$(H - E)\phi + (H_1 - \varepsilon)\psi_0 = 0 \quad (5)$$

and

$$(H_0 - E_0)\phi + (H_1 - \varepsilon)(\psi_0 + \lambda \phi) = 0. \quad (6)$$

In equations (5) and (6), the λ -dependence of H , E , ϕ and ε has not been written explicitly. Here, and in the following, only operators, energies and functions with *subscripts* are independent of λ ; all other quantities are, in principle, λ -dependent.

Equation (5) implies that ϕ is arbitrary to within a multiple of ψ , and yields (since H is necessarily Hermitian)

$$\varepsilon = \langle \psi | H_1 | \psi_0 \rangle / \langle \psi | \psi_0 \rangle. \quad (7)$$

Alternative forms of ε are now obtained from (6) or (7) (assuming that H_0 and H_1 are also Hermitian operators)

$$\varepsilon = [E_1 + \lambda \langle \psi_0 | H_1 | \phi \rangle] / [1 + \lambda \langle \psi_0 | \phi \rangle] \quad (8a)$$

$$= E_1 + \lambda \langle \psi_0 | H_1 - \varepsilon | \phi \rangle \quad (8b)$$

where E_1 is the RSPT first-order energy coefficient

$$E_1 = \langle \psi_0 | H_1 | \psi_0 \rangle. \quad (9)$$

Equations (5) to (8) are all *exact*, and it is easy to show (see appendix) that (8b) can be rewritten in the form $\varepsilon = f(\varepsilon)$, suggesting solution by iteration.

We now solve equation (6) by iteration, replacing it by the sequence

$$(H_0 - E_0)\phi^{(i+1)} + (H_1 - \varepsilon^{(i+1)})(\psi_0 + \lambda \phi^{(i)}) = 0 \quad (i = 0, 1, \dots) \quad (10)$$

so that, analogous to equations (8), we have

$$\varepsilon^{(i+1)} = [E_1 + \lambda \langle \psi_0 | H_1 | \phi^{(i)} \rangle] / [1 + \lambda \langle \psi_0 | \phi^{(i)} \rangle] \quad (11a)$$

$$= E_1 + \lambda \langle \psi_0 | H_1 - \varepsilon^{(i+1)} | \phi^{(i)} \rangle. \quad (11b)$$

Clearly, when $\phi^{(i+1)} = \phi^{(i)}$ the converged solution of (10) coincides with the exact solution ϕ of (5). Note that $\varepsilon^{(i+1)}$ is known, so that equation (10) must be solved only to determine $\phi^{(i+1)}$; this is just as in RSPT.

3. Comparison with other procedures

To facilitate comparison with other forms of PT, we now rewrite

$$\phi^{(i)} = \sum_{k=1}^i \lambda^{k-1} \chi^{(k)}, \quad \varepsilon^{(i+1)} = \sum_{k=1}^{i+1} \lambda^{k-1} \eta^{(k)} \quad (12)$$

where, for convenience, we have chosen $\phi^{(0)} = 0$. In place of (10), we obtain

$$(H_0 - E_0)\chi^{(1)} + (H_1 - \eta^{(1)})\psi_0 = 0 \quad (13a)$$

and

$$(H_0 - E_0)\chi^{(i+1)} + (H_1 - \varepsilon^{(i)})\chi^{(i)} = \eta^{(i+1)}\left(\psi_0 + \sum_{k=1}^i \lambda^k \chi^{(k)}\right) \quad (i \geq 1). \quad (13b)$$

The λ -dependence of all $\chi^{(k)}$ and $\eta^{(k)}$ for $k \geq 2$ follows at once from (13b). The corresponding RSPT equations, based on Taylor series for $\psi(\lambda)$ and $E(\lambda)$ (with λ -independent coefficients), are

$$(H_0 - E_0)\psi_1 + (H_1 - E_1)\psi_0 = 0 \quad (14a)$$

and

$$(H_0 - E_0)\psi_{i+1} + (H_1 - E_1)\psi_i = \sum_{s=2}^{i+1} E_s \psi_{i+1-s} \quad (i \geq 1). \quad (14b)$$

Finally, the differential BWPT equations, which are easily obtained from the formal expansions

$$\psi(\lambda) = \psi_0 + \sum_{k=1}^{\infty} \lambda^k \psi^{(k)}, \quad \varepsilon(\lambda) = \sum_{k=1}^{\infty} \lambda^{k-1} \varepsilon^{(k)} \quad (15)$$

(note that $\psi^{(k)}$ and $\varepsilon^{(k)}$ are λ -dependent) are

$$(H_0 - E_0 - \lambda\varepsilon)\psi^{(1)} + H_1\psi_0 = \varepsilon^{(1)}\psi_0 \quad (16a)$$

and

$$(H_0 - E_0 - \lambda\varepsilon)\psi^{(i+1)} + H_1\psi^{(i)} = \varepsilon^{(i+1)}\psi_0 \quad (i \geq 1) \quad (16b)$$

(Byers Brown and Meath 1964). At first sight, these are much simpler equations than either (13) or (14) and the convergence of BWPT is often superior to that of RSPT. However, these BW equations can only be solved in terms of an *unknown* parameter ε which must be obtained finally by a numerical iterative procedure, whereas our equations (13) are solved *directly* by any procedure suitable for the conventional RSPT equations (14). In the following, we assume that the RSPT solutions are known, and have been normalised according to ('intermediate normalisation')

$$\langle \psi_0 | \psi_i \rangle = \delta_{0i}, \quad \text{so that } E_{i+1} = \langle \psi_0 | H_1 | \psi_i \rangle \quad (i \geq 0). \quad (17a)$$

As we show below, it is possible to choose the normalisation of the solutions $\chi^{(i)}$ in many different ways, including

$$\langle \psi_0 | \chi^{(i)} \rangle = 0, \quad \text{so that } \eta^{(i+1)} = \langle \psi_0 | H_1 | \chi^{(i)} \rangle \quad (i \geq 1) \quad (17b)$$

and finally, we make the corresponding choice for the BWPT solutions:

$$\langle \psi_0 | \psi^{(i)} \rangle = 0, \quad \text{so that } \varepsilon^{(i+1)} = \langle \psi_0 | H_1 | \psi^{(i)} \rangle \quad (i \geq 1). \quad (17c)$$

Thus, we see that there are some formal similarities between the energy functions of the different procedures.

4. Solutions to the low-order equations

We note first that equations (13a) and (14a) are *identical* since well behaved solutions exist if and only if

$$\eta^{(1)} = \langle \psi_0 | H_1 | \psi_0 \rangle = E_1. \quad (18)$$

It now follows that the first-order iterate $\chi^{(1)}$ has the form

$$\chi^{(1)} = \psi_1 + k^{(1)}\psi_0, \quad (19)$$

where the RSPT solution ψ_1 is normalised as in (17a), and $k^{(1)}$ is an arbitrary constant, which *may* be λ -dependent. Thus, we have (using equations (12), (11a) and (13b) for appropriate i)

$$\langle \psi_0 | \phi^{(1)} \rangle = k^{(1)}, \quad \varepsilon^{(2)} = E_1 + E_2\lambda / (1 + k^{(1)}\lambda). \quad (20)$$

In general, equation (11a) shows that $\varepsilon^{(i+1)}$ has the form of a $[N+1/N+1]$ Padé approximant if $\phi^{(i)}$ has the form of a polynomial of degree N in λ with λ -independent coefficients, a result which has been exploited by Amos (1978). However, our result is richer, since $k^{(1)}$ (and its higher-order counterparts) are *not* λ -independent.

Before considering some possible choices of $k^{(1)}$, let us calculate the second-order iterate $\chi^{(2)}$. Explicitly, we find

$$(H_0 - E_0)\chi^{(2)} + (H_1 - E_1)\chi^{(1)} = E_2(\psi_0 + \lambda\chi^{(1)}) / (1 + k^{(1)}\lambda) \quad (21)$$

with solution

$$\chi^{(2)} = (\psi_2 + k^{(1)}\psi_1 + k^{(2)}\psi_0) + \mu\theta_3, \quad \mu = \lambda / (1 + k^{(1)}\lambda). \quad (22)$$

Here, ψ_2 is the usual second-order RSPT solution, θ_3 satisfies

$$(H_0 - E_0)\theta_3 = E_2\psi_1, \quad \langle \theta_3 | \psi_0 \rangle = 0 \quad (23)$$

and $k^{(2)}$ is a (possibly λ -dependent) constant. Note that $\chi^{(2)}$ is λ -dependent (through θ_3) *even if* we set both the $k^{(i)}$ equal to zero. In general, we now have

$$\langle \psi_0 | \phi^{(2)} \rangle = k^{(1)} + k^{(2)}\lambda \quad (24a)$$

and

$$\varepsilon^{(3)} = E_1 + \frac{E_2\lambda(1 + k^{(1)}\lambda) + E_3\lambda^2 - E_2\lambda^2\mu\langle \psi_1 | \psi_1 \rangle}{1 + k^{(1)}\lambda + k^{(2)}\lambda^2} \quad (24b)$$

where use has been made of an *interchange theorem* (cf Hirschfelder *et al* 1964) based on equations (14a) and (23) to eliminate θ_3 from the expression (11a) for $\varepsilon^{(3)}$. Furthermore, since E_3 may be calculated from the RSPT formula

$$E_3 = \langle \psi_1 | H_1 - E_1 | \psi_1 \rangle \quad (25)$$

we see that $\varepsilon^{(3)}$ requires only ψ_0 and ψ_1 , so that the iterated energy through *third* order requires the iterated function through *first order only*. Even so, note that $E_0 + \lambda\varepsilon^{(3)}$ contains a term of order λ^4 , whereas the RSPT third-order partial sum for the energy terminates with $E_3\lambda^3$.

5. Higher-order solutions

The calculation of higher-order $\chi^{(i)}$ and $\epsilon^{(i+1)}$ proceeds analogously, but the details need not be given here. However, each $\chi^{(i)}$ will contain a new arbitrary constant, $k^{(i)}$, so that in general, $\phi^{(i)}$ will contain i arbitrary constants. Furthermore, if we assume for simplicity that all the $k^{(i)}$ are zero (this is clearly a *possible* choice, though certainly not the optimal one), $\lambda\phi^{(2)}$ and $\epsilon^{(3)}$ contain terms up to $O(\lambda^3)$ so that (10) and (11a) imply that $\lambda\phi^{(3)}$ and $\epsilon^{(4)}$ contain terms up to $O(\lambda^7)$; thus, in general, $\lambda\phi^{(i)}$ and $\epsilon^{(i+1)}$ will contain terms up to $O(\lambda^s)$, where $s = 2^i - 1$, with a strong implication that our iteration procedure is of *second* order. Further evidence of this is presented in the following sections.

6. Choice of the arbitrary constants

Provided that the iterative solution converges, our results must ultimately become independent of the constants $k^{(i)}$. Nevertheless, it is of interest to examine the low-order iterates, in the hope that they may yield accurate results if the $k^{(i)}$ are chosen appropriately. For simplicity, we consider $E_0 + \lambda\epsilon^{(2)}$, and note the following possibilities.

(1) $\langle \psi_0 | \phi^{(1)} \rangle = 0$, so that $k^{(1)} = 0$. We obtain precisely the RSPT partial sum, $E_0 + E_1\lambda + E_2\lambda^2$.

(2) $\langle \psi_0 | H_1 | \phi^{(1)} \rangle = 0$, so that $k^{(1)} = -E_2/E_1$. This yields the [1/1] Padé approximant $E_0 + E_1\lambda / (1 - E_2\lambda/E_1)$.

(3) $k^{(1)} = -E_3/E_2$. This yields the [2/1] Padé approximant $E_0 + E_1\lambda + E_2\lambda^2 / (1 - E_3\lambda/E_2)$. We recall that E_3 is available from equation (25), so that $k^{(1)}$ can be calculated once ψ_1 is known.

(4) If $\psi_0 + \lambda\phi^{(1)}$ is normalised to N , so that $k^{(1)}$ satisfies

$$(1 + k^{(1)}\lambda)^2 = N - S_{11}\lambda^2, \quad S_{11} = \langle \psi_1 | \psi_1 \rangle \tag{26}$$

we find that $\epsilon^{(2)}$ is *not a rational function* of λ . Here, N must be chosen appropriately for $\epsilon^{(2)}$ to remain *real*. Conversely, if we make the natural choice $N = 1$, λ must be restricted. Silverman (1981) has suggested on other grounds that $S_{11}^{-1/2}$ may provide a good estimate of the radius of convergence of the RSPT Z^{-1} -expansion of the energy for atoms. Here, as with the following choices, $k^{(1)}$ is λ -dependent.

(5) For the *ground state* of $H(\lambda)$, the elementary variational upper bound based on the trial function $\psi_0 + \lambda\psi_1$,

$$E_{\text{var}}(\psi_0 + \lambda\psi_1) = \langle \psi_0 + \lambda\psi_1 | H_0 + \lambda H_1 | \psi_0 + \lambda\psi_1 \rangle / \langle \psi_0 + \lambda\psi_1 | \psi_0 + \lambda\psi_1 \rangle \tag{27a}$$

$$= E_0 + E_1\lambda + (E_2\lambda^2 + E_3\lambda^3) / (1 + S_{11}\lambda^2) \tag{27b}$$

is reproduced by $E_0 + \lambda\epsilon^{(2)}$ if we make the choice

$$k^{(1)} = -(E_3 - E_2S_{11}\lambda) / (E_2 + E_3\lambda). \tag{28}$$

(6) An improved variational upper bound based on the trial function $\psi_0 + \eta\lambda\psi_1$ is (Dalgarno and Stewart 1961)

$$E_{\text{var}}(\psi_0 + \eta\lambda\psi_1) = E_0 + E_1\lambda + \eta E_2\lambda^2 \tag{29}$$

where η is a variational parameter which satisfies

$$\lambda^2 S_{11} \eta^2 + (1 - E_3 \lambda / E_2) \eta - 1 = 0. \tag{30}$$

The upper bound (29) is reproduced by $E_0 + \lambda \epsilon^{(2)}$ by choosing

$$k^{(1)} = (1 - \eta) / \eta \lambda. \tag{31}$$

(7) If λ is a natural (rather than a dummy) parameter, a *semi-empirical* procedure may be followed. Thus, if $E(\lambda)$ is known accurately for some isolated values of λ , $k^{(1)}$ may be chosen so as to reproduce these values exactly. Since $k^{(1)}$ is λ -dependent, a *number* of known values of $E(\lambda)$ (not merely one) may be reproduced. Furthermore, if the asymptotic behaviour of $E(\lambda)$ is known to involve inverse *fractional* powers of λ , these may be introduced naturally into $k^{(1)}$.

All these procedures may be extended to higher-order iterates, but there are successively more constants $k^{(i)}$ at our disposal. It is possible to choose some of these so that successive energy iterates are equal ($\epsilon^{(i+1)} = \epsilon^{(i)}$) but we emphasise that this choice does *not* ensure equality of the corresponding function iterates ($\phi^{(i)} \neq \phi^{(i-1)}$). A more satisfactory possibility is the following.

7. Variational energy bounds

If we regard $\psi_0 + \eta \lambda \phi^{(i)}$ as a trial function, we may calculate the variational energy (which is a *rigorous* upper bound for ground states)

$$E_{\text{var}}(\psi_0 + \eta \lambda \phi^{(i)}) = (E_0 + \lambda \epsilon^{(i+1)}) + \lambda [(E_1 - \epsilon^{(i+1)})(1 - \eta)^2 + \lambda \Delta^{(i+1)} \eta^2] / N^{(i)} \tag{32}$$

where

$$N^{(i)} = 1 + 2\eta \lambda \langle \psi_0 | \phi^{(i)} \rangle + \eta^2 \lambda^2 \langle \phi^{(i)} | \phi^{(i)} \rangle \tag{33a}$$

and

$$\Delta^{(i+1)} = \langle \phi^{(i)} | H_1 - \epsilon^{(i+1)} | \psi_0 + \lambda \phi^{(i)} \rangle - \langle \phi^{(i)} | H_1 - \epsilon^{(i)} | \psi_0 + \lambda \phi^{(i-1)} \rangle. \tag{33b}$$

Using equation (10) for two successive values of i , we obtain via an interchange theorem:

$$\Delta^{(i+1)} = \langle \phi^{(i+1)} - \phi^{(i)} | H_1 - \epsilon^{(i)} | \psi_0 + \lambda \phi^{(i-1)} \rangle \tag{34a}$$

or, on using equation (12),

$$\Delta^{(i+1)} = \lambda^i \langle \chi^{(i+1)} | H_1 - \epsilon^{(i)} | \psi_0 + \lambda \phi^{(i-1)} \rangle. \tag{34b}$$

From equation (34a), when $\phi^{(i+1)} = \phi^{(i)} = \phi$ (i.e., when the process has converged), $\Delta^{(i+1)} = 0$ and E_{var} attains its minimum when $\eta = 1$, giving the equality

$$E_{\text{var}}(\psi_0 + \lambda \phi) = E_0 + \lambda \epsilon. \tag{35}$$

This is as expected, since $\psi_0 + \lambda \phi$ is the *exact* solution. But if $\phi^{(i+1)} \neq \phi^{(i)}$, equation (34b) shows that $\Delta^{(i+1)}$ is $O(\lambda^i)$ and may be *small*, particularly if $\lambda \ll 1$ and i is large. If $\Delta^{(i+1)}$ is sufficiently small and η is varied in equation (32), we obtain $\eta \approx 1$ and

$$E_{\text{var}}(\psi_0 + \lambda \phi^{(i)}) \approx E_0 + \lambda \epsilon^{(i+1)}. \tag{36}$$

(The error involved in this approximation is $\lambda^2 \Delta^{(i+1)} / N^{(i)}$, which may be calculated using (33a, b) if desired.)

But it may be possible to choose the constants $k^{(j)}$ ($j = 1, \dots, i$) so that $\Delta^{(i+1)} = 0$, in which case (36) becomes an exact equation, and the resulting $\phi^{(i)}$ (for any i) then satisfies a necessary (but not a sufficient) condition on ϕ . For example, when $i = 1$, $\Delta^{(2)}$ may be calculated from (34b) using (22), and the condition $\Delta^{(2)} = 0$ yields explicitly

$$E_3 + k^{(1)}E_2 - \mu E_2 S_{11} = 0. \tag{37}$$

This is a quadratic equation for $k^{(1)}$ (we recall from equation (22) that $\mu = \lambda/(1 + k^{(1)}\lambda)$) with solutions identical with those of equations (30) and (31). This result is a consequence of the fact that $\psi_0 + \lambda\phi^{(1)}$ is an optimised linear combination of ψ_0 and ψ_1 in this case. If the same procedure is followed with the next iterate, $\psi_0 + \lambda\phi^{(2)}$, and $k^{(2)}$ may be chosen so that $\Delta^{(3)} = 0$, we are in some sense constructing an optimal linear combination of ψ_0 and $\phi^{(2)}$ but with $k^{(1)}$ still arbitrary. (If desired, each of the $k^{(i)}$ may be chosen so that $\psi_0 + \lambda\phi^{(i)}$ makes (36) an equality, but this is not necessary.)

An important consequence of this result is the following. The energy iterate $E_0 + \lambda\varepsilon^{(i+1)}$ involves $\lambda\phi^{(i)}$ which in turn contains $\lambda^i\psi_i$ (as well as terms of higher order in λ); and so, by a well known theorem, $E_{\text{var}}(\psi_0 + \lambda\phi^{(i)})$ contains $\lambda^{2i+1}E_{2i+1}$, where E_{2i+1} is the appropriate RSPT coefficient. Thus, each energy iterate automatically contains contributions from two additional terms of RSPT.

8. An alternative $\phi^{(0)}$

In equation (12), we made the natural choice of $\phi^{(0)} = 0$, mainly so as to simplify our comparisons with other forms of PT. As a very simple alternative, we might consider

$$\phi^{(0)} = \tilde{k}^{(0)}\psi_0, \tag{38}$$

which leaves $\varepsilon^{(1)}$ invariant, and leads to

$$\phi^{(1)} = (1 + \tilde{k}^{(0)}\lambda)\psi_1 + \tilde{k}^{(1)}\psi_0 \tag{39a}$$

and

$$\varepsilon^{(2)} = E_1 + E_2\lambda(1 + \tilde{k}^{(0)}\lambda)/(1 + \tilde{k}^{(1)}\lambda). \tag{39b}$$

Our earlier choice of $\phi^{(0)}$ is thus seen to be a special case (with $\tilde{k}^{(0)} = 0$), and it is clear that if the constants $\tilde{k}^{(0)}$ and $\tilde{k}^{(1)}$ are chosen so that expressions (20) and (39b) for $\varepsilon^{(2)}$ coincide, then

$$k^{(1)} = (\tilde{k}^{(1)} - \tilde{k}^{(0)})/(1 + \tilde{k}^{(0)}\lambda). \tag{40}$$

Thus, a suitable choice of the constant $k^{(1)}$ (which is here explicitly λ -dependent even if $\tilde{k}^{(0)}$ and $\tilde{k}^{(1)}$ are λ -independent) may serve to improve the result even if the initial choice of $\phi^{(0)}$ is less than optimal.

9. A simple application: the energies of four-electron atoms

We now illustrate the efficacy of the procedures described here, and confine our attention to the simplest non-trivial energy iterate, $E + \lambda\varepsilon^{(2)}$. A Z -expansion RSPT calculation of the $1s^2 2s^2 {}^1S$, $1s^2 2s2p {}^1P$ and $1s^2 2p^2 {}^1S$ states of four-electron atoms (Watson and O'Neil 1975) provides approximate E_n values up to $n = 10$, but we will

employ only the first two variationally determined coefficients, E_2 and E_3 , which are presumably more accurate than the higher E_n coefficients. For the $1s^2 2s^2 {}^1S$ state, a more accurate E_2 is available (Watson and O'Neil 1975) but not of E_3 and for consistency, we use the less precise value of E_2 also. In this problem, $\lambda = Z^{-1}$ is a natural expansion parameter and H_0 is a sum of hydrogenic Hamiltonians which is explicitly soluble, so that E_0 and E_1 are known *exactly*.

In table 1, we present total non-relativistic energies calculated from the formula $E = Z^2 E(\lambda)$, where

$$E(\lambda) = E_0 + E_1 \lambda + E_2 \lambda^2 (1 - 2E_3 \lambda / E_2)^{-1/2} \quad (41)$$

which corresponds to choosing $k^{(1)}$ according to

$$(1 + k^{(1)} \lambda) = (1 - 2E_3 \lambda / E_2)^{1/2}. \quad (42)$$

Table 1. Non-relativistic energies ($-E$) of four-electron atoms (in au).

	Z	(1)	(2)	(3)	(4)
$1s^2 2s^2 {}^1S$	4	—	14.6387	14.6358	14.6665†
	5	24.3099	24.3241	24.3223	24.3413‡
	6	36.5036	36.5115	36.5102	36.5334†
	7	51.1951	51.1999	51.1990	51.2128‡
	8	68.3858	68.3889	68.3883	68.4096†
	9	88.0761	88.0784	88.0778	—
	10	110.2664	110.2681	110.2677	—
$1s^2 2s 2p {}^1P^o$	4	—	14.4226	14.4269	14.4725†
	5	23.9324	23.9705	23.9731	23.9603
	6	35.9998	36.0252	36.0269	36.0628†
	7	50.5648	50.5836	50.5849	50.5697
	8	67.6295	67.6444	67.6453	67.6843†
	9	87.1946	87.2066	87.2074	87.1932
	10	109.2599	109.2699	109.2705	109.2572
$1s^2 2p^2 {}^1S$	4	—	14.2658	14.2770	14.2678
	5	—	23.6757	23.6821	23.7150
	6	35.5692	35.6044	35.6085	35.6417
	7	50.0218	50.0429	50.0457	50.0871
	8	66.9735	66.9871	66.9892	67.0366
	9	86.4257	86.4350	86.4366	86.4873
	10	108.3787	108.3854	108.3866	108.4425

(1) RSPT 10th-order sums (Watson and O'Neil 1975).

(2) Screening approximation, equation (43).

(3) Approximant (41).

(4) Variational calculations from †Sims and Whitten (1973), ‡Weiss (1961) and Hibbert (1974).

Thus, (41) correctly reproduces the Taylor expansion of $E(\lambda)$ up to the third-order energy term, and contains no empirical parameters. The square root is suggestive of *quadratic* Padé approximants introduced by Shafer (1974) and reviewed recently by Common (1982), but we make no theoretical claim for the particular form (41).

For comparison, we also list values obtained from the frequently used *screening approximation* (Dalgarno and Stewart 1960):

$$E(Z) = E_0 Z^2 + E_1 Z + E_2 + E_3/(Z - \sigma) \quad (43)$$

in which the screening constant σ is traditionally chosen equal to $-E_1/2E_0$. This procedure corresponds to making the choice

$$k^{(1)} = -E_3/[E_2 + (E_3 - E_2\sigma)\lambda] \quad (44)$$

which seems very different from (42). Although neither (41) nor (43) (with $\sigma = -E_1/2E_0$) provides accurate estimates of the higher-order energy coefficients E_n ($n \geq 4$), nevertheless both (41) and (43) reproduce the RSPT partial sums of Watson and O'Neil (1975) for sufficiently high Z . For low Z , both (41) and (43) (which contain only *four* coefficients) yield more accurate energies than the RSPT sums correct to *tenth* order! Table 1 contains these sums, as well as results of some refined variational calculations (Sims and Whitten 1973, Weiss 1961, Hibbert 1974).

There is, in general, little to choose between (41) and (43) for the ions and states considered here, and it may be fortuitous that the calculated energies are upper bounds to the most accurate variational values. In this connection, it should be noted that Hibbert's (1974) wavefunctions contain no K-shell correlation, and his values of $-E$ should probably be increased by approximately 0.045 au (the average difference between the $1s^2 2s^2 \ ^1S$ energies of Weiss and Hibbert) to obtain more reliable estimates of the non-relativistic energy.

The accuracy obtained in this example may be expected to be quite typical of atomic isoelectronic sequences (since the choice $k^{(1)} = 0$ usually provides a satisfactory approximation for high Z). It remains to be seen how reliable formulae such as (41), and (43) can be in other cases.

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Appendix

The solution of equation (5) of the text may be written formally in terms of the *resolvent operator* $R(\varepsilon)$ defined by

$$R(\varepsilon) = (E_0 + \lambda\varepsilon - H)^{-1} \quad (A1)$$

and is seen to be

$$\phi = R(\varepsilon)\psi(\varepsilon) \quad (A2)$$

where

$$\psi(\varepsilon) = (H_1 - \varepsilon)\psi_0. \quad (A3)$$

Thus, equation (8*b*) of the text can be written

$$\varepsilon = E_1 + \lambda \langle \psi(\varepsilon) | R(\varepsilon) | \psi(\varepsilon) \rangle. \quad (\text{A4})$$

which is clearly of the form

$$\varepsilon = f(\varepsilon). \quad (\text{A5})$$

However, this equation is not immediately useful for *calculating* ε and indeed, it is generally necessary to *approximate* the resolvent $R(\varepsilon)$ in order to make progress.

If $R(\varepsilon)$ is rewritten in terms of

$$R_0(\varepsilon) = (E_0 + \lambda\varepsilon - H_0)^{-1}, \quad (\text{A6})$$

it is easily shown that

$$R(\varepsilon) = R_0(\varepsilon) + \lambda R_0(\varepsilon) H_1 R(\varepsilon). \quad (\text{A7})$$

This may be *iterated*, or solved formally with the result that

$$R(\varepsilon) = [1 - \lambda R_0(\varepsilon) H_1]^{-1} R_0(\varepsilon) \quad (\text{A8})$$

and using this form of $R(\varepsilon)$, equation (A4) yields BWPT. On the other hand, if $R(\varepsilon)$ is rewritten in terms of

$$R_0(0) = (E_0 - H_0)^{-1} \quad (\text{A9})$$

so that

$$R(\varepsilon) = R_0(0) + \lambda R_0(0) (H_1 - \varepsilon) R(\varepsilon) \quad (\text{A10})$$

with solution

$$R(\varepsilon) = [1 - \lambda R_0(0) (H_1 - \varepsilon)]^{-1} R_0(0) \quad (\text{A11})$$

equation (A4) yields RSPT.

The handling of all these inverse operators requires care (see, for example, Löwdin 1982), whereas our differential equation approach is completely straightforward.

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