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An examination of the accuracy of truncated perturbation theory using bounds for the exact energy

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Abstract. A procedure is developed for assessing the accuracy of a truncated perturbation expansion, which leads to upper and lower bounds to some eigenvalue. Improved bounds, which require a lower bound to the overlap of the approximate and exact wavefunctions, are also considered and a lower bound to the overlap is derived. Two examples are presented, using model problems.

1. Introduction

It is well known that many perturbation expansions diverge, but that they are actually *asymptotic* expansions so that the first few terms can yield good approximations. A full discussion of the convergence difficulties, and of ways of overcoming them by using summation techniques such as Padé approximants, is given in the review of Killingbeck (1977). Here we examine the problem of deciding if a truncated perturbation series is accurate. As a consequence of our approach, bounds are obtained for some energy eigenvalue $E(\lambda)$ of the system Hamiltonian $H(\lambda)=H_0+\lambda V$. These bounds are derived in § 2 where the general theory is also given. However, the essentials of the theory can be described by truncating the expansion of the wavefunction at first order.

We assume that we have obtained the solutions of the zero- and first-order equations of Rayleigh-Schrödinger perturbation theory (RSPT):

$$(H_0-E_0)\psi_0=0 \qquad \langle\psi_0|\psi_0\rangle=1 \tag{1.1}$$

$$(H_0-E_0)\psi_1=(E_1-V)\psi_0 \qquad \langle\psi_1|\psi_0\rangle=0. \tag{1.2}$$

These allow us to consider the approximations

$$\phi_1=N_1(\psi_0+\lambda\psi_1) \qquad \varepsilon_p=E_0+\sum_{i=1}^{p}\lambda^i E_i \tag{1.3}$$

for all $p\leqslant 3$, since ψ_0, ψ_1 are sufficient to calculate E_2 and E_3,

$$E_2=\langle\psi_1|V\psi_0\rangle \qquad E_3=\langle\psi_1|(V-E_1)\psi_1\rangle. \tag{1.4}$$

N_1 is a normalisation constant for the truncated first-order expansion of ψ,

$$N_1=(1+\lambda^2\langle\psi_1|\psi_1\rangle)^{-1/2}. \tag{1.5}$$

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In order to assess the accuracy of our approximations (ϕ_1, ε_p) we consider the *residual*

$$\eta(\phi_1, \varepsilon_p) = (H_0 + \lambda V - \varepsilon_p)\phi_1 \tag{1.6}$$

and note that if ϕ_1 and ε_p were exact, $\eta = 0$. Thus, we expect η to be small if ϕ_1 and ε_p are good approximations to the exact solutions ψ and E. Consequently, a good test of the approximations (1.3) may be made by examining the value of the *norm* of η, $\|\eta\| = \langle \eta | \eta \rangle^{1/2}$. Simple calculation now gives

$$\|\eta(\phi_1, \varepsilon_1)\| = N_1 \lambda^2 \langle \psi_1 | (V - E_1)^2 \psi_1 \rangle^{1/2} \tag{1.7}$$

$$\|\eta(\phi_1, \varepsilon_2)\| = N_1 \lambda^2 \{[\langle \psi_1 | (V - E_1)^2 \psi_1 \rangle - E_2^2] - 2\lambda E_2 E_3 + \lambda^2 E_2^2 \langle \psi_1 | \psi_1 \rangle\}^{1/2} \tag{1.8}$$

and

$$\begin{aligned}\|\eta(\phi_1, \varepsilon_3)\| = N_1 \lambda^2 \{&[\langle \psi_1 | (V - E_1)^2 \psi_1 \rangle - E_2^2] - 2\lambda E_2 E_3 + \lambda^2 [E_2^2 \langle \psi_1 | \psi_1 \rangle - E_3^2] \\ &+ 2\lambda^3 E_2 E_3 \langle \psi_1 | \psi_1 \rangle + \lambda^4 E_3^2 \langle \psi_1 | \psi_1 \rangle\}^{1/2}.\end{aligned} \tag{1.9}$$

We note that $\|\eta\|$ is of order λ^2 in each case, a direct consequence of the fact that *both* ϕ_1 and ε_p are correct up to order λ. The only new integral (beyond the usual integrals of RSPT) is seen to be $\langle \psi_1 | (V - E_1)^2 \psi_1 \rangle$. If λ is sufficiently small, it may suffice to consider only the lowest-order terms of (1.7)-(1.9). However, in general, there can be no certainty that $\|\eta(\phi_1, \varepsilon_3)\| \leq \|\eta(\phi_1, \varepsilon_2)\| \leq \|\eta(\phi_1, \varepsilon_1)\|$ even for moderate values of λ (we recall that in applications of RSPT λ is frequently of the order of unity). Thus, it will be necessary to calculate $\|\eta\|$ for each λ of interest.

2. Bounds and the general theory

The inner product $\langle \eta | \eta \rangle$ may also be used to provide upper and lower *bounds* to some eigenvalue of the Hamiltonian $H = H_0 + \lambda V$, since, for any normalised approximation ϕ and real parameter μ,

$$\langle \eta | \eta \rangle = \langle \phi | (H - \mu)^2 \phi \rangle \geq \nu^2 \tag{2.1}$$

where ν^2 is the lowest eigenvalue of $(H - \mu)^2$. The result (2.1) has been used very widely with variational wavefunctions since the pioneering work of Weinstein (1934) and Stevenson and Crawford (1938), but does not seem to have found an application when RSPT is used to obtain ϕ and μ. If μ is closer to one desired eigenvalue E than to any other eigenvalue of H, then

$$\nu^2 = (E - \mu)^2 \tag{2.2}$$

and writing

$$\langle \eta | \eta \rangle = \Delta^2(\mu) \tag{2.3}$$

we have bounds to E:

$$E \leq f_{\pm}(\mu) = \mu \pm \Delta(\mu). \tag{2.4}$$

This technique always provides bounds to *some* eigenvalue of H, and if RSPT yields good approximations (ϕ, μ) to a particular solution (ψ, E), then $\Delta^2(\mu)$ is small and (2.4) gives precise bounds to that E. If, on the other hand, $\Delta^2(\mu)$ is large, the bounds will be wide and probably encompass several true eigenvalues. Thus, wide bounds provide the information that the truncated RSPT energy series is suspect, even if successive partial sums ε_p differ very little.

Now for any fixed ϕ, the bounding functions $f_{\pm}(\mu)$ are easily shown to be monotonic increasing functions of μ so that if $\mu_i \leqslant \mu_j$

$$f_-(\mu_i) \leqslant f_-(\mu_j) \leqslant E \leqslant f_+(\mu_i) \leqslant f_+(\mu_j). \tag{2.5}$$

Thus, it is always desirable to use two *distinct* values of μ to obtain bounds to E.

More generally, if the RSPT wavefunction is truncated at order n, the energy coefficients are determined up to order $(2n+1)$, and we may choose any of the approximations

$$\phi_n = N_n\left(\psi_0 + \sum_{i=1}^{n} \lambda^i \psi_i\right) \qquad \varepsilon_m = E_0 + \sum_{i=1}^{m} \lambda^i E_i \tag{2.6}$$

for $n \leqslant m \leqslant (2n+1)$. All such approximations yield $\|\eta\|$ of order λ^{n+1}; the largest and smallest values ε_l, ε_s selected from this set of truncated energy expansions yield the *optimal* bounds to E:

$$f_-(\varepsilon_l) \leqslant E \leqslant f_+(\varepsilon_s). \tag{2.7}$$

Note that there is no guarantee that $f_+(\varepsilon_s)$ and $f_-(\varepsilon_l)$ provide bounds to *only one* eigenvalue of H; as is usual, rough bounds to the nearest adjacent eigenvalues will be required in order to settle this question uniquely.

However, other choices of μ may give better results than (2.7) if suitable bounds are available for one of the adjacent energy levels; we explore this possibility in § 4 below.

3. The effect of approximate RSPT solutions

Our analysis so far is based on *exact* solutions of the RSPT equations. However, in many applications, the higher-order corrections will be estimated, often variationally. Such approximate RSPT solutions lead to large values of $\|\eta\|$ and to additional terms in the bounds. As before, the effect can be seen already in first order.

Suppose we have an approximation $\bar{\psi}_1$ to the exact ψ_1. This might be the solution of a related equation

$$(H_0 - E_0)\bar{\psi}_1 = (\bar{E}_1 - \bar{V})\psi_0 \qquad \langle \bar{\psi}_1 | \psi_0 \rangle = 0 \tag{3.1}$$

an approach which has found application in Hartree-Fock PT (Burrows 1973). More generally, $\bar{\psi}_1$ will be obtained variationally, at the stationary point of the Hylleraas (1930) functional

$$G(\bar{\psi}_1) = \langle \bar{\psi}_1 | V\psi_0 \rangle + \langle \bar{\psi}_1 | f \rangle \qquad \langle \bar{\psi}_1 | \psi_0 \rangle = 0 \tag{3.2}$$

or of a more general functional (see, for example, Burrows 1974)

$$J_{\pm}(\bar{\psi}_1) = G(\bar{\psi}_1) \pm k_{\pm}\langle f | f \rangle \qquad \langle \bar{\psi}_1 | \psi_0 \rangle = 0. \tag{3.3}$$

Here,

$$f = (H_0 - E_0)\bar{\psi}_1 - (E_1 - V)\psi_0 \tag{3.4}$$

and the constants $k_{\pm}$ depend on the nearest eigenvalues of H_0 above and below E_0.

However $\bar{\psi}_1$ has been derived, we have (analogous to (1.3) above)

$$\bar{\phi}_1 = \bar{N}_1(\psi_0 + \lambda\bar{\psi}_1) \qquad \bar{\varepsilon}_p = E_0 + \sum_{i=1}^{p} \lambda^i \bar{E}_i \tag{3.5}$$

where

$$\bar{E}_1 = E_1 \qquad \bar{E}_2 = \langle \bar{\psi}_1 | V\psi_0 \rangle \qquad \bar{E}_3 = \langle \bar{\psi}_1 | (V - E_1)\bar{\psi}_1 \rangle \tag{3.6}$$

and

$$\bar{N}_1 = (1 + \lambda^2 \langle \bar{\psi}_1 | \bar{\psi}_1 \rangle)^{-1/2} \tag{3.7}$$

so that (for example)

$$\begin{aligned} \|\eta(\bar{\phi}_1, \bar{\varepsilon}_1)\| &= \bar{N}_1 \lambda \{\langle f | f \rangle + 2\lambda \langle f | (V - E_1)\bar{\psi}_1 \rangle + \lambda^2 \langle \bar{\psi}_1 | (V - E_1)^2 \bar{\psi}_1 \rangle\}^{1/2} \\ &\leqslant \bar{N}_1 \lambda \{\langle f | f \rangle^{1/2} + \lambda \langle \bar{\psi}_1 | (V - E_1)^2 \bar{\psi}_1 \rangle^{1/2}\} \end{aligned} \tag{3.8}$$

using the Cauchy-Schwarz inequality.

Since f may be written alternatively

$$f = (H_0 - E_0)(\bar{\psi}_1 - \psi) \tag{3.9}$$

we see that $\|\eta(\bar{\phi}_1, \bar{\varepsilon}_1)\|$ contains an *approximation error* term of order λ, $\langle f | f \rangle^{1/2}$ in addition to the remaining, *truncation error* terms of order λ^2 as before. These results are easily generalised.

But if λ is not very small, the contribution of $\lambda \langle f | f \rangle^{1/2}$ to $\|\eta\|$ may be much smaller numerically than the (formally) higher-order terms. In practice, only the numerical value of $\|\eta\|$ is of any real significance.

4. Overlap bounds and improved energy bounds

The truncated RSPT energy series ε_p or ε_m will not in general yield optimal energy bounds for a given approximate function ϕ_1 or ϕ_n. However, if we regard μ as a variable parameter and follow the procedure of Cohen and Feldmann (1969), we obtain bounds to the kth eigenvalue $E^{(k)}$ of H in the form

$$E^{(k)} \lesseqgtr I \pm \delta \qquad \delta^2 = (1 - a_k^2)\Delta^2 / a_k^2 \tag{4.1}$$

where

$$I = \langle \phi | H\phi \rangle \qquad \Delta^2 = \langle \phi | H^2 \phi \rangle - I^2 \tag{4.2}$$

and a_k is the overlap between ϕ and the (unknown) exact eigenfunctions $\psi^{(k)}$. (For the ground state, we have a better *upper* bound, I.) In order to apply these bounds, we require a lower bound to a_k; this may also be obtained from $\|\eta\|$ by an extension of Weinstein's (1934) procedure.

We have, for any normalised ϕ and real μ,

$$\|\eta\|^2 = \sum_i a_i^2 \langle \psi^{(i)} | (H - \mu)^2 \psi^{(i)} \rangle = \sum_i a_i^2 (E^{(i)} - \mu)^2 \tag{4.3}$$

where $\psi^{(i)}$ and $E^{(i)}$ denote the ith eigenfunction and eigenvalue of H. Focusing attention on the kth state, we have

$$\|\eta\|^2 \geqslant (E^{(m)} - \mu)^2 \sum_{i \neq k} a_i^2 = (1 - a_k^2)(E^{(m)} - \mu)^2 \tag{4.4}$$

provided that μ is closer to $E^{(m)}$ than to any other eigenvalue $E^{(i)}$ except $E^{(k)}$. (In practice, $E^{(m)}$ will generally be either $E^{(k-1)}$ or $E^{(k+1)}$.) Then we have the lower bound

$$a_k^2 \geqslant 1 - \|\eta\|^2 / (E^{(m)} - \mu)^2 \tag{4.5}$$

which requires a lower bound to $E^{(m)}$ if $\mu < E^{(m)}$ or an upper bound if $\mu > E^{(m)}$. These may be obtained by the methods of § 2 or by any other means. Furthermore, $E^{(m)}$ may often be approximated adequately by $E_0^{(m)}$, the mth eigenvalue of H_0. The bound (4.5), though slightly less accurate than the classic lower bound of Eckart (1930) for the ground state, applies to *any* state. Furthermore, it requires knowledge of only a single eigenvalue $E^{(m)}$ whereas Eckart's bound requires two, $E^{(k)}$ as well as $E^{(m)}$. Thus, in calculations aimed at *estimating* $E^{(k)}$, the bound (4.5) is clearly preferable.

If, as will often be the case for reasonable ϕ, it turns out that $a_k^2 \geqslant 0.9$, we have from (4.1)

$$E^{(k)} \lesseqgtr I \pm \Delta/3 \tag{4.6}$$

where for the first-order approximation ϕ_1 of (1.3)

$$I = E_0 + \lambda E_1 + \lambda^2 N_1^2 (E_2 + \lambda E_3) \tag{4.7}$$

and

$$\Delta = N_1 \lambda^2 \{ \langle \psi_1 | (V - E_1)^2 \psi_1 \rangle - N_1^2 (E_2 + \lambda E_3)^2 \}^{1/2}. \tag{4.8}$$

Comparison of these expressions with ε_p and $\| \eta(\phi_1, \varepsilon_p) \|$ shows that the main improvement to the energy bounds arises from the factor $(1 - a_k^2)^{1/2}/a_k$.

5. Some examples

We first consider a soluble matrix eigenvalue problem, $H(\lambda)x(\lambda) = E(\lambda)x(\lambda)$ where

$$H(\lambda) = (a + \alpha\lambda) I + \begin{bmatrix} -(b+\beta\lambda) & \gamma\lambda & 0 \\ \gamma\lambda & 0 & \gamma\lambda \\ 0 & \gamma\lambda & (b+\beta\lambda) \end{bmatrix}. \tag{5.1}$$

I is the unit matrix, and the constants a, b, α, β and γ are all real, while $\lambda \geqslant 0$. The ordered exact eigenvalues are easily found to be

$$(a + \alpha\lambda) - A \qquad (a + \alpha\lambda) \qquad (a + \alpha\lambda) + A \tag{5.2}$$

where

$$A^2 = (b + \beta\lambda)^2 (1 + 2t^2) \qquad t = \gamma\lambda/(b + \beta\lambda) \tag{5.3}$$

and the normalised ground state eigenvector is

$$x^T(\lambda) = (A + (b + \beta\lambda),\ -2\gamma\lambda,\ A - (b + \beta\lambda))/2A. \tag{5.4}$$

If $H(\lambda)$ is decomposed in the usual way with

$$H = H_0 + \lambda V \qquad H_0 = \begin{bmatrix} a-b & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & a+b \end{bmatrix}. \tag{5.5}$$

RSPT yields the leading terms of the appropriate Taylor expansions and, in particular for the ground state,

$$E(\lambda) = (a - b) + (\alpha - \beta)\lambda - (\gamma^2/b)\lambda^2 + (\gamma^2\beta/b^2)\lambda^3 + \ldots \tag{5.6}$$

which is a convergent series expansion of $(a + \alpha\lambda) - A$ provided

$$\left| \frac{2\beta}{b} \lambda + \frac{\beta^2 + 2\gamma^2}{b^2} \lambda^2 \right| < 1. \tag{5.7}$$

However, an alternative decomposition of $H(\lambda)$ is found to be more appropriate. Thus, writing

$$H(\lambda) = H_0(\lambda) + H_1(\lambda) \qquad H_1(\lambda) = \gamma\lambda \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix} \tag{5.8}$$

leads to the series

$$E(\lambda) = [(a+\alpha\lambda) - (b+\beta\lambda)] - (b+\beta\lambda)t^2 + \cdots \tag{5.9}$$

which is a convergent expansion of $(a+\alpha\lambda) - A$ provided that $2t^2 < 1$ (i.e. for *all* λ if $\beta^2 > 2\gamma^2$). Clearly, RSPT based on (5.8) is preferable to the more conventional Taylor expansion based on (5.5). The unnormalised eigenvector corresponding to (5.9) is

$$x^T(\lambda) = (1, 0, 0) - t(0, 1, 0) + \ldots \tag{5.10}$$

and because of the symmetry of $H_1(\lambda)$, all energy coefficients of odd order vanish. Thus we need calculate only

$$\| \eta(\phi_1, \mu) \| = (b+\beta\lambda)t^2 \tag{5.11}$$

where μ is the truncated second-order sum (5.9), yielding the bounds

$$(a+\alpha\lambda) - (b+\beta\lambda)(1+2t^2) \leqslant E(\lambda) \leqslant (a+\alpha\lambda) - (b+\beta\lambda). \tag{5.12}$$

Here, if the half-width $(b+\beta\lambda)t^2$ is small by comparison with the truncated sum μ, we have an acceptable approximation. Note, however, that the bounds (5.12) are valid for *all* λ, and for *all* values of the constants in $H(\lambda)$.

In this model problem, we may calculate the overlap exactly using (5.4) and (5.10):

$$a_0^2 = [1 + (1+2t^2)^{1/2}]/2(1+t^2)^{1/2} \tag{5.13}$$

while the lower bound of (4.5), using the zero-order value of $E^{(1)} = (a+\alpha\lambda)$ (which here coincides with its *exact* value) is

$$a_0^2 \geqslant 1 - t^4/(1+t^2)^2 > \tfrac{8}{9} \qquad \text{if } 2t^2 < 1. \tag{5.14}$$

Since this is the ground state, we have the Rayleigh-Ritz upper bound

$$E^{(0)} \leqslant I = (a+\alpha\lambda) - (b+\beta\lambda)(1+2t^2)/(1+t^2) \tag{5.15}$$

while (4.1) yields the lower bound

$$E^{(0)} \geqslant I - (1-a_0^2)^{1/2}\Delta/a_0 = (a+\alpha\lambda) - A \tag{5.16}$$

i.e. the *exact* value of $E^{(0)}$, if a_0^2 is exact as in (5.13)†. Alternatively,

$$E^{(0)} \geqslant (a+\alpha\lambda) - (b+\beta\lambda)(1+t^2) \tag{5.17}$$

(which coincides with the truncated second-order sum, cf (5.9) above) using the lower bound (5.14) to a_0^2.

Now consider the perturbed harmonic oscillator with Hamiltonian $H = H_0 + V$, where

$$H_0 = -\tfrac{1}{2}(\mathrm{d}^2/\mathrm{d}x^2) + \tfrac{1}{2}x^2 \tag{5.18}$$
$$V = \tfrac{1}{2}(\alpha^2 - 3\beta - 1)x^2 + \alpha\beta x^4 + \tfrac{1}{2}\beta^2 x^6.$$

† This is in accord with a result of Cohen and Feldmann (1974); the approximate x of (5.10) is (accidentally) a linear combination of two eigenvectors.

The exact ground state energy of H is $\frac{1}{2}\alpha$ (independent on β) and the corresponding eigenfunction is

$$\psi^{(0)} = N \exp[-(\tfrac{1}{2}\alpha x^2 + \tfrac{1}{4}\beta x^4)]. \tag{5.19}$$

The excited state solutions cannot be obtained analytically in closed form.

In table 1, we present truncated RSPT energy series, as well as lower and upper bounds from (2.7) based on ε_2 and ε_3. The width of the bounds provides a measure of the quality of these approximations. (For the ground state, we also have the exact energy for comparison.)

For the ground state ($n = 0$) when $\alpha = 0.1$ and $\beta = 0.01$, it appears that the perturbation is large and the RSPT series is clearly not converging rapidly, if at all. In this case the bounds are of *opposite sign*, but this is a consequence of the fact that the exact value is very close to zero. When $\alpha = 1$ and $\beta = 0.1$, the RSPT series provide estimates which are qualitatively correct, but the bounds are still wide, reflecting the fact that here $E_2 = -0.017\,771$ and $E_3 = 0.020\,590$ suggesting poor convergence. In all other cases, including the two excited state calculations ($n = 1, 2$), the bounds are reasonably close, and we may conclude that the RSPT sums give reliable estimates.

In the absence of exact values of E, we would have to adopt the means of the better lower and upper bounds, and it is noteworthy that these means generally provide very accurate results for the ground state (where direct comparison is possible). For convenience, we have indicated the better bounds in each case.

Although the RSPT equations have been solved exactly for this model problem, it is instructive to examine the consequences of using an approximate (variational) solution to the first-order equation. For the ground state, the exact first-order solution has the form

$$\psi_1 = (c_0 + c_2 x^2 + c_4 x^4 + c_6 x^6)\psi_0 \tag{5.20}$$

and the dominant contribution arises from the term $c_4 x^4$. We therefore adopted the variational trial form

$$\bar{\psi}_1 = (\bar{c}_0 + \bar{c}_4 x^4)\psi_0 \tag{5.21}$$

Table 1. Energies of the perturbed oscillator.

				Truncated RSPT sums			Bounds using	
State	α	β	E	ε_1	ε_2	ε_3	ε_2	ε_3
$n = 0$	1.0	0.01	0.5	0.500 094	0.499 993	0.500 001	0.501 940	0.501 948
							0.498 046	0.498 054
	0.9	0.01	0.45	0.451 844	0.450 112	0.450 007	0.454 471	0.454 364
							0.445 752	0.445 650
	0.8	0.01	0.4	0.408 594	0.401 305	0.400 228	0.423 633	0.422 506
							0.378 977	0.377 951
	1.0	0.1	0.5	0.509 375	0.491 604	0.512 193	0.897 718	0.917 267
							0.085 489	0.107 119
	0.1	0.01	0.05	0.245 844	0.181 723	0.149 513	0.406 887	0.370 531
							−0.043 441	−0.071 504
$n = 1$	1.0	0.01		1.515 656	1.514 460	1.514 607	1.523 673	1.523 818
							1.505 246	1.505 395
$n = 2$	1.0	0.01		2.562 344	2.556 815	2.557 873	2.584 168	2.585 185
							2.529 461	2.530 560

Table 2. The effect of approximate first-order RSPT solutions.

	$\alpha = 1, \beta = 0.01$		$\alpha = 1, \beta = 0.1$	
	Variational	Exact	Variational	Exact
ε_1	0.500 094	0.500 094	0.509 375	0.509 375
ε_2	0.499 993	0.499 993	0.491 650	0.491 604
ε_3	0.500 001	0.500 001	0.510 859	0.512 193
Bounds from	0.498 168	0.498 054	0.146 683	0.107 119
(2.7)	0.501 826	0.501 940	0.856 332	0.897 718

in the Hylleraas functional (3.2) and in table 2 we present results using both $\bar{\psi}_1$ and ψ_1 for two cases ($\alpha = 1, \beta = 0.01$) and ($\alpha = 1, \beta = 0.1$) illustrating the effect in both 'small' and 'large' perturbation situations.

It appears that $\bar{\psi}_1$ is an excellent approximation to ψ_1 and also that the approximation $\bar{N}_1(\psi_0 + \bar{\psi}_1)$ is actually better than the formally superior $N_1(\psi_0 + \psi_1)$ (the bounds are tighter!).

Overlap bounds for the approximation $\bar{N}_1(\psi_0 + \bar{\psi}_1)$ may be calculated from (4.5) using the zero-order lower bound $E_0^{(2)} = 2.5$ to the *second* excited state. (This is justified since the eigenfunctions of H are of definite *parity*; the first excited state is necessarily odd, whereas the ground state is even.) We thus obtain (using ε_2)

$$\alpha = 1, \beta = 0.01 \qquad a_0^2 \geqslant 0.999\,999$$

$$\alpha = 1, \beta = 0.1 \qquad a_0^2 \geqslant 0.967\,028$$

so that the lower bound (4.1) and upper bound I are now much tighter:

$$\alpha = 1, \beta = 0.01 \qquad 0.499\,999 \leqslant E^{(0)} \leqslant 0.500\,001$$

$$\alpha = 1, \beta = 0.1 \qquad 0.433\,603 \leqslant E^{(0)} \leqslant 0.510\,849.$$

Both model problems treated in the present work possess well separated eigenvalues, so that our bounds define intervals which contain only a single point of the spectrum. Further work will be required to ensure that this remains true in other, more general, cases.

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References

Burrows B L 1973 *Int. J. Quantum Chem.* 7 345-55
—— 1974 *J. Phys. B: At. Mol. Phys.* 7 881-91
Cohen M and Feldmann T 1969 *Can. J. Phys.* **47** 1877-9

—— 1974 *J. Phys. A: Math. Gen.* **7** 563-71
Eckart C 1930 *Phys. Rev.* **36** 878-92
Hylleraas E A 1930 *Z. Phys.* **65** 209-25
Killingbeck J 1977 *Rep. Prog. Phys.* **40** 963-1031
Stevenson A F and Crawford M F 1938 *Phys. Rev.* **54** 375-9
Weinstein D H 1934 *Proc. Natl Acad. Sci. USA* **20** 529-32