

**Perturbation approach to the complex-rotation method†**

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Non-degenerate and almost degenerate perturbation theory is applied to the problem of calculating autoionizing resonances of the helium atom using the complex-rotation method. The radii of convergence of the series are often found to be too small to allow the perturbation method to have general utility.

## 1. INTRODUCTION

Variation perturbation procedures [1] have recently been used for calculating the autoionizing resonances of atoms such as  $H^-$  and He using the complex-rotation method [2]. In the variational formulation of the complex-rotation method [3, 4], the energy  $E$  and width  $\Gamma$  of autoionizing resonances are associated with the complex eigenvalues of the rotated secular equation

$$|\mathbf{H} - W_\eta \mathbf{S}| = 0, \quad (1)$$

where  $W_\eta$  is a complex eigenvalue and

$$\mathbf{H}_\eta = \eta^2 \mathbf{T} + \eta \mathbf{V}. \quad (2)$$

Here  $\mathbf{S}$ ,  $\mathbf{T}$  and  $\mathbf{V}$ , are the overlap matrix and the matrices of the usual, unrotated kinetic and potential energy operators evaluated within a finite basis of real square-integrable functions. The  $\eta$  is a rotation-scaling parameter,

$$\eta = \alpha \exp(-i\theta), \quad (3)$$

where  $\theta$  is the angle of rotation and  $\alpha$  is the variational scaling parameter for the basis.

Of all the eigenvalues of  $\mathbf{H}_\eta$  only those which are complex and stationary with respect to changes in  $\eta$  are associated with resonances. Thus, if  $\eta_{\text{opt}}$  denotes the value of the rotation-scaling parameter which gives the resonance,

$$W_{\eta_{\text{opt}}} = E - i\Gamma/2, \quad (4)$$

then  $\eta_{\text{opt}}$  is defined by

$$\left( \frac{\partial W}{\partial \eta} \right)_{\eta_{\text{opt}}} = 0. \quad (5)$$

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The details of the complex-rotation method have been discussed adequately in other places [1-5]. The principal computational advantage of the method is that it allows well defined resonance widths to be obtained with square-integrable wavefunctions, thus avoiding the necessity of describing the asymptotic behaviour of continuum wavefunctions. The numerical difficulties which have been encountered are that the calculated resonance widths, and to a lesser extent the positions, are very sensitive to the choice of the basis set and that the iterative solution of equation (5) is often slowly convergent and requires repeated diagonalizations of the complex matrix  $\mathbf{H}_\eta$ . Perturbation theory has been suggested [1] and applied to alleviate some aspects of the latter problem and thus facilitate a more thorough exploration of the former. Here we wish to point out several limitations of perturbative methods in this context.

In the present paper we apply perturbation theory to solve equation (1) by choosing the non-rotated partially scaled hamiltonian as the unperturbed hamiltonian,

$$\mathbf{H}_0 = \alpha_0^2 \mathbf{T} + \alpha_0 \mathbf{V}, \quad (6)$$

where  $\alpha_0$  is a (possibly) non-optimum choice for the real scaling parameter. This choice of unperturbed hamiltonian differs from other work [1] which chooses a partially rotated, partially scaled unperturbed hamiltonian  $\eta_0^2 \mathbf{T} + \eta_0 \mathbf{V}$ . With our choice, equation (6), complex arithmetic can be avoided entirely in solving equations (1) and (5).

Application of perturbation theory to equation (1) is suspect because the eigenvalues of interest are closely spaced, so that the radius of convergence of a perturbation expansion is expected to be small. Typically, perturbation series are limited by branch point singularities which occur when two or more eigenvalues of the unperturbed hamiltonian coalesce for some critical value of the perturbation parameter [6]. Previous work [1] has considered only low-order perturbation theory and ignored questions of convergence. In our work we have investigated the radius of convergence of our perturbation expansion and have used the series solution for  $W_\eta$  only when the optimum scaling parameter  $\eta_{\text{opt}}$  falls within the circle of convergence. We have also investigated the use of almost degenerate perturbation theory [7] as a method of extending the range of validity of the perturbation approach.

We find that for most choices of the pre-scaling parameter  $\alpha_0$  the stationary point  $\eta_{\text{opt}}$  does not fall within the radius of convergence of the non-degenerate expansion. In such cases the almost degenerate theory extends the ranges of validity of the expansions, but not far enough to enclose the stationary point. Thus, while special cases can be found in which perturbation theory can be used to calculate resonance positions, the general result is that the radii of convergence are too small to allow the method to have general utility.

## 2. A MODEL HAMILTONIAN FOR THE $^1S$ RESONANCES OF HELIUM [4,5]; NON-DEGENERATE PERTURBATION THEORY

The true test of a perturbation expansion is comparison with exact solutions of the equation which is being expanded. Thus, we choose a specific example and apply the perturbation theory to it. For the lowest resonance of helium

we choose a basis of twenty Hylleraas-type functions,

$$(1 + P_{12})r_1^l r_2^m r_{12}^n \exp[-\beta_1 r_1 - \beta_2 r_2],$$

where  $P_{12}$  permutes the particle labels,  $r_1$  and  $r_2$  are the scalar distances of each electron from the nucleus and  $r_{12}$  is the interelectron distance. The  $l, m, n$  are pre-selected integers ( $0 \leq [l, m] \leq 3$ ,  $0 \leq n \leq 1$ ) while  $\beta_1 = 1.5$  and  $\beta_2 = 2.5$  are scaling parameters. The position and width of the lowest three resonances previously obtained with this basis are given in table 1 (1 hartree (a.u. of energy)  $\approx 4.35981$  aJ).

Table 1. Variational estimates of helium  $^1S$  resonances. (See equations (3)–(5) and references [4, 8]).

Designation	$\alpha_{opt}$	$\theta_{opt}/\text{rad}$	$-E/\text{a.u.}$	$10^2 \times \Gamma/\text{a.u.}$
$(2s)^2$	0.589	0.141	0.7713	0.4328
$(2p)^2$	0.332	0.198	0.5711	0.3208

Anticipating the application of perturbation theory, we show in figure 1 the dependence of the eigenvalues of  $\mathbf{H}_0$ , equation (6), on the pre-scaling parameter  $\alpha_0$ . As has been suggested [8] by Holøien and Midtdal, the resonance positions can be approximated by the regions of avoided crossings of the eigenvalues of  $\mathbf{H}_0$ . Figure 1 suggests that the basis set is capable of describing at least two resonances, one at approximately  $-0.77$  hartrees and a second at approximately  $-0.57$  hartrees. These estimates agree with the 'exact' results shown in table 1.

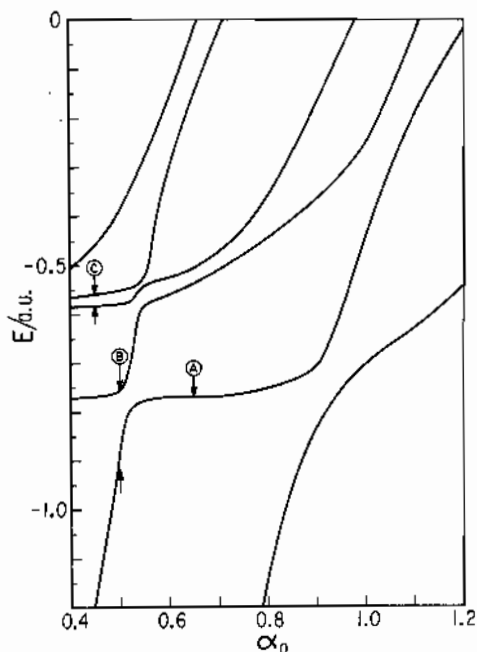


Figure 1. Eigenvalues of  $\mathbf{H}_0$  as a function of the pre-scaling parameter  $\alpha_0$  (see equation (6)). Perturbation theory was applied at points A, B and C.

With the unperturbed hamiltonian defined in equation (6), the natural perturbation parameter is

$$\lambda \equiv (\eta/\alpha_0) - 1. \quad (7)$$

Then,

$$\mathbf{H}_\eta = \mathbf{H}^{(0)} + \lambda \mathbf{H}^{(1)} + \lambda^2 \mathbf{H}^{(2)}, \quad (8)$$

where

$$\mathbf{H}^{(1)} = 2\alpha_0^2 \mathbf{T} + \alpha_0 \mathbf{V} \quad (9)$$

and

$$\mathbf{H}^{(2)} = \alpha_0^2 \mathbf{T}. \quad (10)$$

We have investigated branch points in the spectrum of  $\mathbf{H}_\eta$ . Figure 2 shows how two eigenvalues of  $\mathbf{H}_0$  coalesce in the complex plane when  $\lambda$  is increased from zero to a critical value. We note that if  $\lambda_b$  is a branch point, then  $\lambda_b^*$  is also a branch point. We now discuss how the position may be obtained from an analysis of the perturbation series, rather than by a direct search.

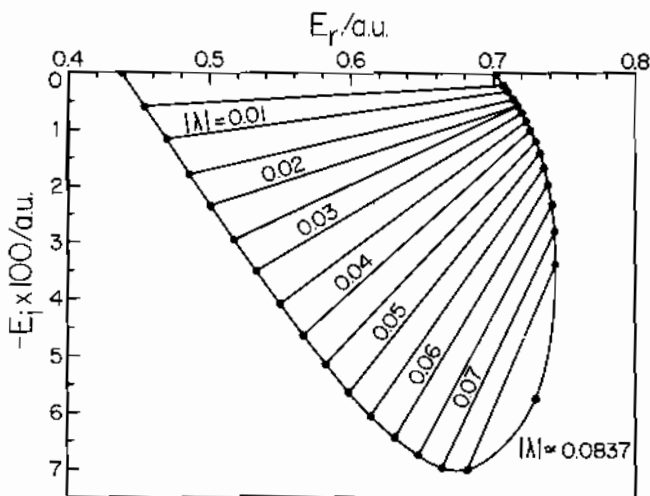


Figure 2. Eigenvalues of  $\mathbf{H}_\eta$  as a function of the rotation-scaling parameter  $\eta$  (see equations (7) and (8)) showing a branch point in the complex plane at  $|\lambda| \cong 0.0837$ .

Standard Rayleigh-Schrödinger perturbation theory [9] gives a power series expansion of  $W_\eta$ ,

$$W_\eta = \sum_{n=0} \lambda^n W^{(n)}. \quad (11)$$

The resonance position is determined by the stationary condition

$$(\partial W_\eta / \partial \lambda)_{\lambda_{\text{opt}}} = \sum_n n \lambda_{\text{opt}}^{n-1} W^{(n)} = 0. \quad (12)$$

Since in practice the expansion of  $W_\eta$  is truncated after  $N$  terms, there are in fact  $N-1$  solutions of equation (12). As we discuss below, most of these solutions are artifacts of the perturbation expansion and do not correspond to resonances.

Table 2 contains the first 30 perturbation energies for the pre-scaling parameter  $\alpha_0=0.65$ . It is seen that the perturbation energies grow very rapidly with increasing order, which suggests a small radius of convergence.

Table 2. Perturbation energy coefficients. (See equations (7) and (11);  $\alpha_0=0.65$ ).

$n$	$W^{(n)}/\text{a.u.}$	$n$	$W^{(n)}/\text{a.u.}$
0	-0.769491	16	-0.109064 $\times 10^9$
1	0.284151 $\times 10^{-1}$	17	0.509508 $\times 10^9$
2	0.606564 $\times 10^{-1}$	18	-0.237481 $\times 10^{10}$
3	0.412454	19	0.110427 $\times 10^{11}$
4	-0.408374	20	-0.512178 $\times 10^{11}$
5	0.434377 $\times 10^1$	21	0.236933 $\times 10^{12}$
6	-0.215674 $\times 10^2$	22	-0.109305 $\times 10^{13}$
7	0.972637 $\times 10^2$	23	0.502807 $\times 10^{13}$
8	-0.434084 $\times 10^3$	24	-0.230590 $\times 10^{14}$
9	0.209559 $\times 10^4$	25	0.105409 $\times 10^{15}$
10	-0.100225 $\times 10^5$	26	-0.480199 $\times 10^{15}$
11	0.475759 $\times 10^5$	27	0.217954 $\times 10^{16}$
12	-0.223920 $\times 10^6$	28	-0.985342 $\times 10^{16}$
13	0.105497 $\times 10^7$	29	0.443549 $\times 10^{17}$
14	-0.496233 $\times 10^7$	30	-0.198728 $\times 10^{18}$
15	0.232951 $\times 10^8$		

The behaviour of the high-order perturbation energies is dominated by the singularity which determines the radius of convergence. In figure 2 we have shown that this singularity is a branch point of order  $\frac{1}{2}$  which occurs when two energy eigenvalues coalesce. Thus to obtain the position of the branch point [10], we write the energy as

$$W_\eta = W_b \sqrt{[(\lambda - \lambda_b)(\lambda - \lambda_b^*)]} + \omega(\lambda), \quad (13)$$

where  $\lambda_b = \alpha_b \exp(-\theta_b)$  is the critical value of the perturbation parameter. We expand  $W_\eta$  in a power series in  $\lambda$  to obtain the perturbation energies ( $n \geq 2$ )

$$W^{(n)} = [P_{n-2}(\cos \theta_b) - P_n(\cos \theta_b)] / (2n-1) \alpha_b^{n-1} + R^{(n)}, \quad (14)$$

where  $P_n(x)$  is a Legendre polynomial and  $R^{(n)}$  is a remainder term which we assume can be neglected. By making use of well known recurrence relations for the Legendre polynomials, it can be shown that if  $R^{(n)}$  is neglected, then the  $W^{(n)}$  satisfy

$$\alpha_b^2 W^{(n)} - 2\alpha_b \cos \theta_b (1 - 3/2n) W^{(n-1)} + (1 - 3/n) W^{(n-2)} = 0. \quad (15)$$

Introducing the ratio  $r_n \equiv W^{(n)}/W^{(n-1)}$ , we solve this relation for  $\cos \theta_b$ ,

$$\cos \theta_b = [n/(2n-3)](\alpha_b r_n) + [(n-3)/(2n-3)](\alpha_b r_{n-1})^{-1}. \quad (16)$$

Eliminating  $\cos \theta_b$  by applying this equation for two successive values of  $n$  gives

$$\alpha_b^2 = [(n-4)(2n-3)/r_{n-2} - (n-3)(2n-5)/r_{n-1}] / [n(2n-5)r_n - (n-1)(2n-3)r_{n-1}]. \quad (17)$$

If the ratios  $r_n$  are consistent with the assumed functional form, equation (13),  $\alpha_b^2$  will be positive,  $\cos \theta_b$  will lie between  $-1$  and  $+1$ , and the estimate of  $\lambda_b$  provided by equations (16) and (17) will converge as  $n$  increases. When this analysis is applied to the perturbation energies given in table 2, the estimates given in table 3 are obtained.

Table 3. Branch point analysis of the energy expansion. (See equations (16) and (17)).

$n$	$\alpha_b$	$\cos \theta_b$
3	$0.327130 \times 10^1$	$0.222443 \times 10^2$
4	$0.622428 \times 10^{-1}$	0.423242
7	0.308502	$-0.112275 \times 10^1$
8	0.312446	$-0.113107 \times 10^1$
11	0.205285	-0.993022
12	0.195571	-0.987627
13	0.280904	$-0.107689 \times 10^1$
14	0.187537	-0.991984
15	0.204764	-0.995465
16	0.200901	-0.994263
17	0.213573	-0.998794
18	0.207398	-0.996422
19	0.207472	-0.996443
20	0.206546	-0.996225
21	0.207825	-0.996487
22	0.207612	-0.996448
23	0.207566	-0.996441
24	0.207428	-0.996424
25	0.207510	-0.996432
26	0.207522	-0.996433
27	0.207523	-0.996433
28	0.207510	-0.996432
29	0.207512	-0.996432
30	0.207515	-0.996432

We have applied the analysis to determine the radius of convergence of the energy series for a range of values of the pre-scaling parameter  $\alpha_0$ . The behaviour of  $\alpha_b$  (denoted by  $|\lambda_b|$ ) is shown in figure 3. As expected, the radius of convergence is very small in the vicinity of the almost-crossing points of figure 1. The simple analysis fails in the intermediate region because two different branch points influence the behaviour of the high-order perturbation coefficients.

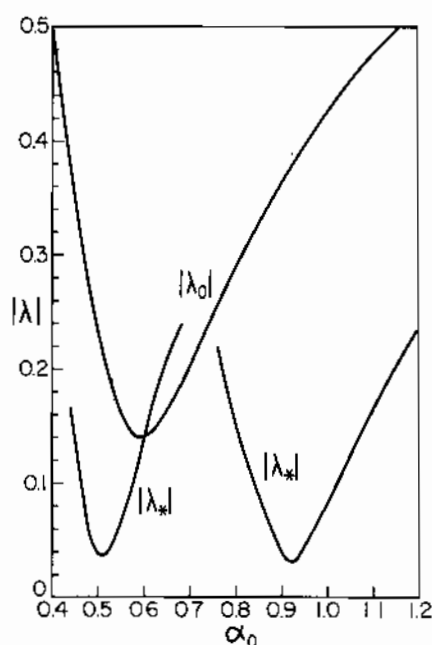


Figure 3. Radius of convergence  $|\lambda^*|$  and resonance parameter  $|\lambda_0|$  as function of the pre-scaling parameter  $\alpha_0$ . The  $|\lambda^*|$  is referred to as  $\alpha_b$  in the text (§ 2).

The absolute value of  $\lambda_{opt}$ , corresponding to the known position of the resonance, is also shown in figure 3. It is seen that only for a small range of  $\alpha_0$  is it possible to use non-degenerate perturbation theory to calculate the resonance position, since the radius of convergence  $\alpha_b$  is usually less than  $|\lambda_{opt}|$ .

The position of the resonance is determined by a solution of equation (12). There are  $N-1$  roots to this equation, so the question arises as to which root corresponds to the resonance. A clue is provided by the theorem which states that every point on the circle of convergence of a perturbation series is a limit point for the zeroes of partial sums of the series [11]. Thus as the order to the perturbation theory increases, we expect that most solutions of equation (12) approach the circle of convergence, except for those solutions which correspond to the resonances. Figure 4 is a plot of the zeroes of the partial sums and we see that this expectation is borne out by the present example. Thus, most solutions of equation (12) are unrelated to the desired resonance solution of equation (5).

We see from figure 4 that for any fixed order of perturbation theory there is a number of zeroes of  $dW/d\eta$  which might correspond to a resonance. Only by observing the behaviour of the zeroes as the perturbation order is increased are we able to identify the correct resonance root.

To summarize, it is indeed possible to calculate the lowest resonance position and width by a perturbation approach, if careful attention is paid to questions of convergence and  $\alpha_0$  is chosen properly. Moreover, while it was necessary to go to quite high order in the theory, the total computational effort is significantly less than that required for a direct search for the resonance using the exact eigenvalues of  $\mathbf{H}_q$ . The successful treatment of the lowest resonance cannot

be taken as a general characteristic of the perturbation approach, however. For example, there is no value of the pre-scaling parameter  $\alpha_0$  which allows non-degenerate perturbation theory to be applied to the second lowest resonance of the present example (point C of figure 1).

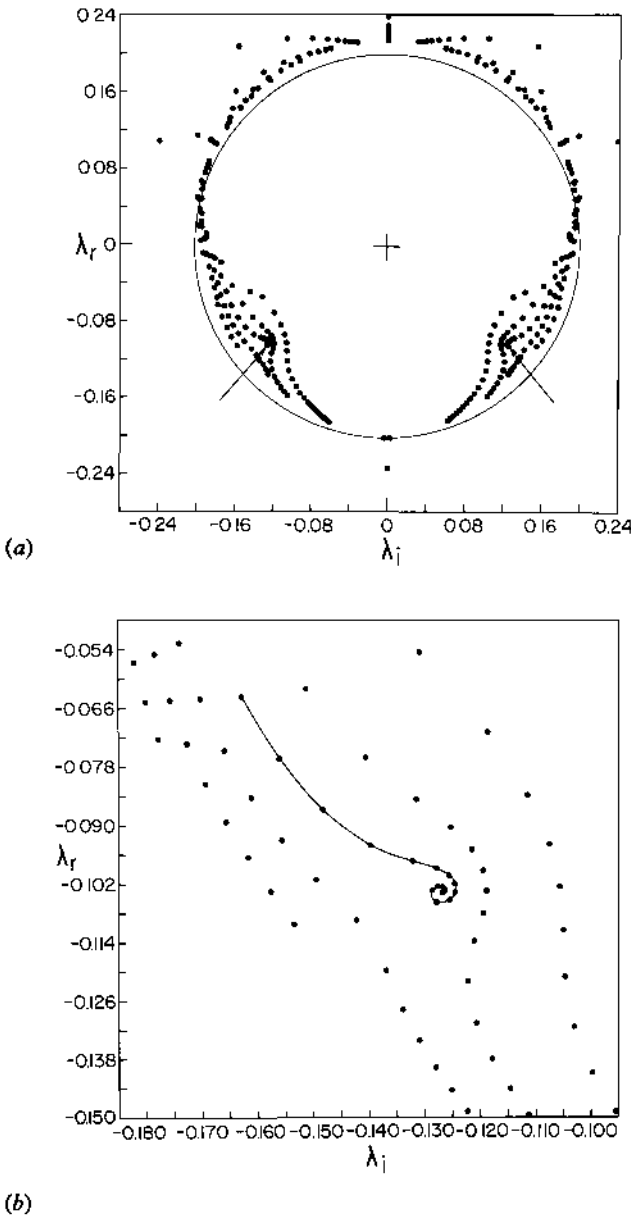


Figure 4. (a) Zeroes of partial energy sums for non-degenerate perturbation theory applied to point A of figure 1. The branch points are indicated by a pair of dots at  $\lambda_r \cong 0.20$ . The arrow designates the sequence of roots which converges to the resonance position. (b) Detail of figure 4 (a) showing convergences of a sequence of zeroes to the resonance position. The convergent sequence is joined by lines for clarity.

## 3. ALMOST-DEGENERATE PERTURBATION THEORY

We have seen that for certain ranges of the pre-scaling parameter  $\alpha_0$ , non-degenerate perturbation theory cannot be applied to calculate the position of the lowest resonance and, moreover, it cannot be applied at all to the higher resonance. Since the singularity which limits the radius of convergence is a branch point where the eigenvalue of interest coalesces with a nearby eigenvalue, almost degenerate perturbation theory suggests itself as a way of extending the range of validity of the perturbation expansion. In almost degenerate perturbation theory the interaction between the two coalescing energy branches are treated exactly, while the coupling with other states is treated as a perturbation.

The general development of almost degenerate perturbation theory has been described previously [7]. In the present problem we wish to solve the matrix eigenvalue problem

$$[\mathbf{H}_\eta - W_{j\eta} \mathbf{1}] \mathbf{C}_j = 0, \quad (18)$$

where the  $(M \times M)$ -dimensional matrix  $\mathbf{H}_\eta$  is defined in equation (2). We are particularly interested in two eigenvalues,  $W_{1\eta}$  and  $W_{2\eta}$ , which evolve from an almost degenerate pair of unperturbed energies  $W_1^{(0)}$  and  $W_2^{(0)}$ . Instead of solving equation (18) directly we introduce two new vectors  $\mathbf{u}_1$  and  $\mathbf{u}_2$  which span the same space as  $\mathbf{C}_1$  and  $\mathbf{C}_2$

$$\mathbf{C}_j = \sum_i \mathbf{u}_i a_{ij} \quad j=1, 2, \quad (19)$$

where the  $a_{ij}$  are expansion coefficients to be determined. If we let  $\mathbf{U}$  denote the  $M \times 2$  matrix whose columns are  $\mathbf{u}_1$  and  $\mathbf{u}_2$  and  $\mathbf{a}$  denote the  $2 \times 2$  matrix of expansion coefficients  $\{a_{ij}\}$  it is easily seen that

$$\mathbf{H}\mathbf{U} = \mathbf{U}\mathbf{W}, \quad (20)$$

where

$$\mathbf{W} = \mathbf{a}^{-1} \begin{bmatrix} W_{1\eta} & 0 \\ 0 & W_{2\eta} \end{bmatrix} \mathbf{a}. \quad (21)$$

Since eigenvalues of  $\mathbf{W}$  are also eigenvalues of  $\mathbf{H}_\eta$ , the procedure is to first calculate  $\mathbf{W}$  and then extract its eigenvalues.

The matrices  $\mathbf{U}$  and  $\mathbf{W}$  are defined by perturbation expansions. We put

$$\mathbf{U} = \sum_n \lambda^n \mathbf{U}^{(n)} \quad (22)$$

$$\mathbf{W} = \sum_n \lambda^n \mathbf{W}^{(n)}, \quad (23)$$

where  $\mathbf{W}^{(0)}$  is diagonal with elements  $W_1^{(0)}$  and  $W_2^{(0)}$ . The  $\mathbf{U}^{(0)}$  is partitioned into a  $2 \times 2$  unit matrix and a  $(M-2) \times 2$  null matrix; hence

$$\mathbf{U}^{(0)\dagger} \mathbf{U}^{(0)} = \mathbf{1}. \quad (24)$$

Expanding equation (20) into its perturbation orders yields the equation

$$\mathbf{H}^{(0)} \mathbf{U}^{(n)} + \mathbf{H}^{(1)} \mathbf{U}^{(n-1)} + \mathbf{H}^{(2)} \mathbf{U}^{(n-2)} = \sum_{l=0}^n \mathbf{U}^{(n-l)} \mathbf{W}^{(l)}, \quad (25)$$

which may be solved iteratively.

The transformation  $\mathbf{U}$  is not completely fixed by these equations, so we complete its specification by the requirement

$$\mathbf{U}^{(0)\dagger} \mathbf{U}^{(n)} = 0 \quad n \geq 1. \quad (26)$$

This is analogous to intermediate normalization in non-degenerate perturbation theory; however, it has the effect of making  $\mathbf{W}$  non-hermitian.

The perturbation equations may be solved straightforwardly. The specific formulae for the matrix elements of  $\mathbf{W}^{(n)}$  and  $\mathbf{U}^{(n)}$  are

$$W_{ij}^{(n)} = \sum_{l=1}^n [H_{il}^{(2)} U_{lj}^{(n-2)} + H_{il}^{(1)} U_{lj}^{(n-1)}], \quad i, j = 1, 2 \quad (27)$$

and

$$U_{lj}^{(n)} = \left[ \sum_{l'=3}^M (H_{ll'}^{(2)} U_{l'j}^{(n-2)} + H_{ll'}^{(1)} U_{l'j}^{(n-1)}) - \sum_{n'=1}^{n-1} \sum_{i=1}^2 U_{li}^{(n-n')} W_{ij}^{(n')} \right] / (W_j^{(0)} - W_l^{(0)}), \quad j = 1, 2, \quad l \geq 3. \quad (28)$$

In these formulae, any quantity corresponding to a negative perturbation order (for example,  $U_{lj}^{(-1)}$ ) is defined to be zero.

Having obtained the matrix  $\mathbf{W}$ , accurate to  $N$ -th order in  $\lambda$ , its eigenvalues  $W_{j\eta}$  may be obtained trivially,

$$W_{j\eta} = \frac{1}{2}(W_{11} + W_{22}) + (-)^j [(W_{11} - W_{22})^2/4 + W_{12}W_{21}]^{1/2}, \quad j = 1, 2. \quad (29)$$

Here the elements  $W_{ij}$  are  $N$ -th degree polynomials so that  $(dW_{j\eta}/d\eta)$  can be evaluated analytically and the stationary points found as the zeroes of a derived polynomial. Letting  $f$  denote  $(W_{11} + W_{22})/2$  and  $g$  denote  $(W_{11} - W_{22})^2/4 + W_{12}W_{21}$  the derived polynomial is

$$p(\lambda) = 4(df/d\lambda)^2 g(\lambda) - (dg/d\lambda)^2 \quad (30)$$

and the resonance parameter  $\lambda_{\text{opt}}$  is a solution of

$$p(\lambda_{\text{opt}}) = 0. \quad (31)$$

We have applied the almost degenerate perturbation theory to calculate the lowest resonance when the pre-scaling parameter  $\alpha_0$  has the value 0.5 (point B of figure 1). For this value of  $\alpha_0$ , non-degenerate perturbation theory fails to converge in the vicinity of the resonance ( $\alpha_b < |\lambda_{\text{opt}}|$ ). Thus figure 5, which shows the zeroes of the partial (non-degenerate) energy sums for  $\alpha_0 = 0.5$ , gives no indication of where the resonance might be. Figure 6 shows the zeroes of the partial sums of the derived polynomial  $p(\lambda)$ . From this figure, the radius of convergence of the almost-degenerate perturbation expansion is estimated to be  $\alpha_b = 0.08$ , which is approximately twice as large as the radius of convergence of the non-degenerate theory. In this sense, the almost degenerate theory is an improvement; however, it fails to give the position of the resonance since it is still the case that  $\alpha_b < |\lambda_{\text{opt}}|$ . The zeroes of  $p(\lambda)$  along the real axis in figure 6 are not converged values, but are extraneous zeroes which occur in only a few perturbation orders.

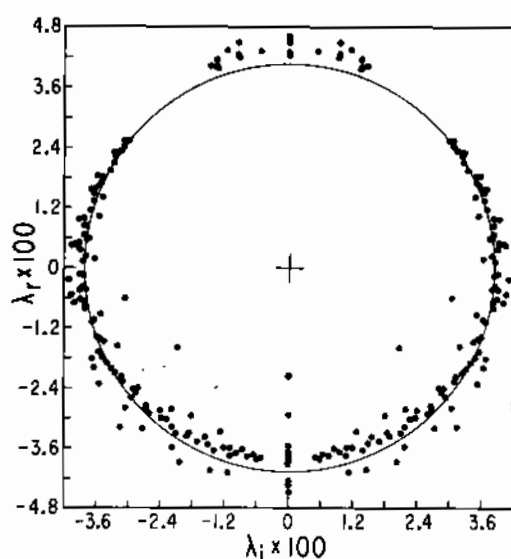


Figure 5. Zeroes of partial energy sums for non-degenerate perturbation theory applied to point B of figure 1. No resonance falls within the circle of convergence.

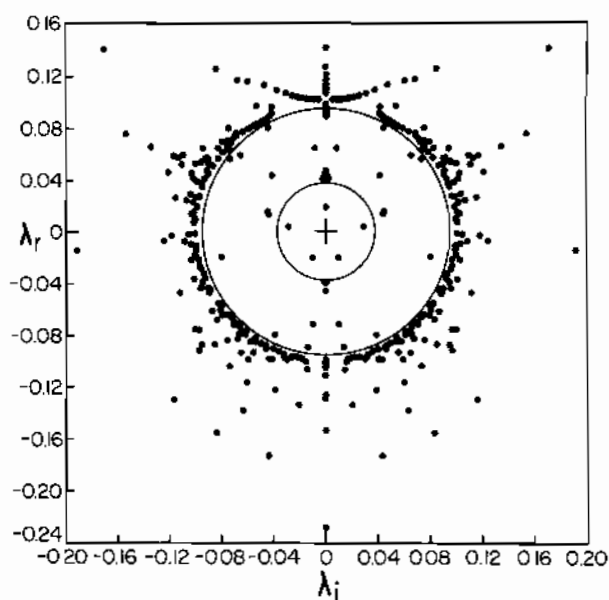


Figure 6. Zeroes of partial sums for almost-degenerate perturbation theory applied to point B of figure 1. The inner circle is the radius of convergence for the non-degenerate expansion.

#### 4. SUMMARY

Our study has shown that perturbation expansions may facilitate the application of the complex-rotation method in special cases, but the method cannot be assumed to have general utility. Extension to the almost degenerate case does

not appear to improve the situation. In any case, the theory must be taken to high enough order so that information about the radius of convergence of the perturbation series can be obtained. Any results obtained with second- and third-order perturbation theory are likely to be spurious. Although these remarks apply specifically to our choice of unperturbed hamiltonian, they are likely to be also applicable to other choices.

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