

# Binding Energies for Discrete Nonlinear Schrödinger Equations

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Received June 6, 1991; accepted July 3, 1991

## Abstract

The standard quantum discrete nonlinear Schrödinger equation with periodic boundary conditions and an arbitrary number of freedoms ( $f$ ) is solved exactly at the second and third quantum levels. If  $f \rightarrow \infty$  at a sufficiently small level of anharmonicity ( $\gamma$ ), the value for soliton binding energy from quantum field theory (QFT) in the continuum limit is recovered. For fixed  $f$ , however, the QFT result always fails for  $\gamma$  sufficiently large and also for  $\gamma$  sufficiently small. Corresponding calculations are discussed for the quantized Ablowitz-Ladik equation at the second quantum level with periodic boundary conditions.

## 1. Introduction

In this paper we consider two quantum discrete nonlinear Schrödinger equations. The first of these is

$$i \frac{d\hat{\phi}_j}{dt} + \varepsilon(\hat{\phi}_{j+1} + \hat{\phi}_{j-1}) + \gamma\hat{\phi}_j^\dagger\hat{\phi}_j\hat{\phi}_j = 0 \quad (1)$$

where  $j = 1, 2, 3, \dots, f$  and  $\hat{\phi}_j(\hat{\phi}_j^\dagger)$  are boson lowering (raising) operators acting on products of number states, which (for typographical convenience) will be written in the form

$$|n_1\rangle|n_2\rangle|n_3\rangle \dots |n_f\rangle = [n_1 n_2 n_3 \dots n_f]. \quad (2)$$

We note that this is a special case of the quantum discrete self-trapping equation [3, 10, 22, 23] that includes only nearest neighbor coupling along a linear chain; thus it can be applied to studies of small molecules [5, 23, 24], polymer chains [5, 20], quasi-one-dimensional molecular crystals [6, 9], and (possibly) biological polymers [11, 17, 18]. We call eq. (1) the quantum discrete nonlinear Schrödinger (QNLDS) equation.

For  $\gamma/\varepsilon \ll 1$  and  $f \gg 1$ , a perturbation analysis of eq. (1) has suggested an expression for soliton binding energy that differs from the result of quantum field theory (QFT) [19]. Our aim here is to resolve this discrepancy and to show how large the number of degrees of freedom ( $f$ ) must be for the results of QFT to be valid.

The quantum theory that we use to study eq. (1) is not standard, thus the salient features are reviewed in the following section. Our main results for the QDNLS equation are presented in Section 3 for the second and third quantum levels with some general comments on the case of an arbitrary quantum level.

The second equation that we consider, in Section 4, is the quantum Ablowitz-Ladik (QAL) equation [1, 2]

$$i \frac{d\hat{\phi}_j}{dt} + \varepsilon(\hat{\phi}_{j+1} + \hat{\phi}_{j-1}) + \frac{\gamma}{2} \hat{\phi}_j^\dagger \hat{\phi}_j (\hat{\phi}_{j+1} + \hat{\phi}_{j-1}) = 0, \quad (3)$$

which can be solved using methods that are based upon its integrability [14, 16]. In this case we have results only for the second quantum level.

Finally, in Section 5, we discuss implications of this work for the interpretation of spectra in molecular crystals.

## 2. Quantum analysis

Since the classical system corresponding to eq. (1) is Hamiltonian and conserves the standard norm, an eigenfunction of the quantum problem  $|\psi\rangle$  must be an eigenfunction of both the energy operator

$$\hat{H} = - \sum_{j=1}^f [\varepsilon(\hat{\phi}_j^\dagger \hat{\phi}_{j+1} + \hat{\phi}_j^\dagger \hat{\phi}_{j-1}) + \frac{1}{2} \gamma \hat{\phi}_j^\dagger \hat{\phi}_j \hat{\phi}_j] \quad (4)$$

and the number operator

$$\hat{N} = \sum_{j=1}^f \hat{\phi}_j^\dagger \hat{\phi}_j. \quad (5)$$

If we impose periodic boundary conditions,  $|\psi\rangle$  must also be an eigenfunction of the translation operator  $\hat{T}$  for which

$$\hat{T}[n_1 n_2 n_3 \dots n_f] = [n_f n_1 n_2 \dots n_{f-1}]. \quad (6)$$

Thus  $\hat{H}|\psi\rangle = E|\psi\rangle$ ,  $\hat{N}|\psi\rangle = n|\psi\rangle$ , and  $\hat{T}|\psi\rangle = t|\psi\rangle$  where  $E$ ,  $n$ , and  $t$  are (respectively) the energy, number, and translation eigenvalues of  $|\psi\rangle$ .

For a particular value of  $n$  the most general eigenfunction of  $N$  is

$$|\psi\rangle = \sum_{k=1}^p c_k |\psi(k, n)\rangle \quad (7)$$

where  $|\psi(k, n)\rangle$  is a product state having the form indicated in eq. (2) with  $n_1 + n_2 + \dots + n_f = n$  and the index  $k$  ranges over the  $p$  ways that  $n$  quanta can be placed on  $f$  degrees of freedom. Thus

$$p = \frac{(f+n-1)!}{(f-1)!n!}. \quad (8)$$

In eq. (7) the  $c_k$  are arbitrary constants that are determined by requiring  $|\psi\rangle$  to be an eigenfunction of  $\hat{H}$  with eigenvalue  $E$ . Then

$$Hc = Ec \quad (9)$$

where  $H$  is a real, symmetric,  $p \times p$  matrix with elements ( $h_{ik}$ ) that are easily determined as

$$h_{ik} = \langle \psi(i, n) | \hat{H} | \psi(k, n) \rangle \quad (10)$$



value of  $f$ , in this case  $f_c \approx 40$ , below which

$$E_0 \approx -4\epsilon - \frac{\gamma}{f} - \frac{1}{24} \left(1 - \frac{1}{f^2}\right) \frac{\gamma^2}{\epsilon}. \quad (20)$$

For  $f \gg f_c$ , on the other hand,

$$E_0 \rightarrow -4\epsilon - 0.005 \quad (21)$$

as  $f \rightarrow \infty$ .

From eq. (16) we see that the minimum energy eigenvalue for  $\gamma = 0$  is  $-4\epsilon$ . Thus with  $\gamma = 0.2$  and  $\epsilon = 1$  the binding energy ( $E_b$ ) of a soliton is equal to 0.005, in agreement with the quantum field theory result that [15, 25]

$$E_b = \frac{1}{48} \left(\frac{\gamma^2}{\epsilon}\right) n(n^2 - 1). \quad (22)$$

This resolves the discrepancy noted in [19] and mentioned in the Introduction. Only one third of the total soliton binding energy comes from the  $\gamma^2/\epsilon^2$  term in the perturbation expansion of eq. (16). The other two thirds comes from the residual term, which (although of order  $\gamma^3/\epsilon^3$ ) does not converge to zero uniformly in  $f$  as  $\gamma \rightarrow 0$ .

Next we consider how to determine the critical number of freedoms ( $f_c$ ) above which eq. (21) can be used with confidence and below which the binding energy is given by

$$E_b \approx \frac{\gamma}{f} + \frac{1}{24} \left(1 - \frac{1}{f^2}\right) \frac{\gamma^2}{\epsilon}. \quad (23)$$

Consider first the classical version of eq. (1) in which the  $\phi_j$  are complex numbers rather than operators. Assuming that the continuum approximation is valid, we find that the binding energy of a single, classical soliton is

$$E_b = \frac{n^3 \gamma^2}{48\epsilon} \left[ \frac{(2 - k^2)}{E^2} + (1 - k^2) \frac{K}{E^3} \right] \quad (24)$$

where  $n \equiv \sum |\phi_j|^2$ , and  $K = K(k)$  and  $E = E(k)$  are complete elliptic functions of the first and second kind of modulus  $k$  [4]. The corresponding number of freedoms can be computed from

$$f = \frac{8\epsilon EK}{n\gamma}. \quad (25)$$

As  $k \rightarrow 1$ , the classical waveform becomes "solitonic" and the binding energy reduces to

$$E_b = \frac{n^3 \gamma^2}{48\epsilon} \quad (26)$$

in agreement with the first (classical) term of eq. (22). As  $k \rightarrow 0$ , the classical waveform becomes uniformly distributed over the system ( $|\phi_j|^2 = n/f$ ) and the binding energy reduces to

$$E_b = \frac{n^2 \gamma}{2f}. \quad (27)$$

Thus it is convenient to define a classical critical or "corner" number of freedoms, for which the asymptotic expressions in eqs. (26) and (27) are equal, as

$$f_c = \frac{24\epsilon}{n\gamma}. \quad (28)$$

The value of  $f_c$  can be understood as follows: The width of a

classical soliton (defined between half values of  $|\phi|^2$ ) is

$$W = 7.051 \frac{\epsilon}{n\psi}; \quad (29)$$

thus when  $f$  is much larger than about three times  $W$ , the soliton is fully formed and eq. (26) holds. If  $f$  is much less than about three times  $W$ , then the classical waveform is uniformly distributed over the system.

A similar situation holds for the quantum case. Equating the first term of eq. (23) to eq. (22) with  $n = 2$ , we obtain a quantum critical number of freedoms (for  $n = 2$ ) of

$$f_c = \frac{8\epsilon}{\gamma}. \quad (30)$$

For the quantum field theory result – eq. (22) – to be used with confidence at the second quantum level ( $n = 2$ ), the number of degrees of freedom must therefore be

$$f \gg 2W. \quad (31)$$

where  $W$  is the width of a classical soliton.

Another perspective on the situation may be obtained with reference to Fig. 2. In this figure the number of freedoms  $f = 50$  and we plot the binding energy for  $n = 2$  and  $\epsilon = 1$  as a function of anharmonicity ( $\gamma$ ). We see that the binding energy agrees with the QFT result – eq. (22) – over about a decade below  $\gamma = 1$ . At lower values of  $\gamma$  the binding energy is given by the perturbation theory – eq. (23) – which diverges from the QFT calculation. This is because the classical soliton eventually becomes larger than  $f$  as  $\gamma$  is decreased as is indicated in eq. (29). Thus for a larger number of freedoms (than 50) the divergence of the QDNLS curve from the QFT curve would be displaced to lower values of  $\gamma$ . For finite  $f$ , however there will always be some value of  $\gamma$  below which the perturbation theory gives the correct binding energy.

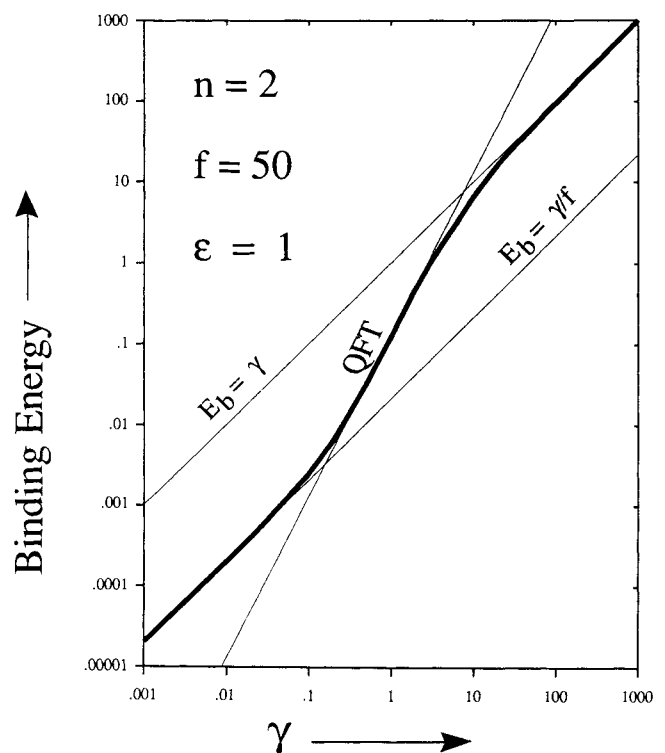


Fig. 2. Total binding energy as a function of  $\gamma$  for the QDNLS equation with  $n = 2$ ,  $f = 50$ , and  $\epsilon = 1$ .





tote ( $E_b \sim 3\gamma$ ) occurs when all the energy is localized at a single site [3, 20, 21]. The small  $\gamma$  asymptote ( $E_b \sim 3\gamma/f$ ) is obtained from eq. (44). Just as in Fig. 2 the effect of increasing the number of freedoms is to displace the lower asymptote ( $E_b \sim 3\gamma/f$ ) downward. In principle we can construct a diagram corresponding to Fig. 1, but the matrices involved become inconveniently large.

### 3.3. Arbitrary $n$

In this subsection we suggest how the log-log plots for  $n = 2$  and  $n = 3$  in Figs. 2 and 3 might be generalized to an arbitrary value of  $n$ . Apart from the ‘‘fillets’’ these figures are constructed from three straight line asymptotes. The middle one, where QFT holds, is given for general  $n$  by eq. (22). The upper asymptote corresponds to a ‘‘local mode’’ in which all the energy is concentrated at a single site and  $|\psi\rangle = [n, 0, 0, \dots, 0] + O(\varepsilon/\gamma)$  [3]. From eq. (4) the binding energy is  $n(n-1)/\gamma$ . The lower asymptote corresponds to a state in which the energy is evenly distributed over the  $f$  freedoms. In the classical limit the binding energy is given by eq. (27). A quantum correction to this equation that gives zero binding energy for  $n = 0$  and  $n = 1$  is

$$E_b = \frac{n(n-1)\gamma}{2f}. \quad (46)$$

Since eq. (46) agrees with our detailed calculations for  $n = 2$  and  $n = 3$ , we are led to the conjecture that it gives the correct lower asymptote for all values of  $n$ . If this conjecture is correct, then the QFT expression for binding energy holds only for values of anharmonicity that lie within the range

$$\frac{24\varepsilon}{(n+1)f} < \gamma < \frac{24\varepsilon}{(n+1)}. \quad (47)$$

### 4. The quantized Ablowitz–Ladik equation

In this section we present corresponding results eq. (3), which is a quantum version of the Ablowitz–Ladik equation [1, 2]. Since the classical version of eq. (3) is integrable [14], it can be quantized but not by the method sketched in Section 2 [16]. For an even number of freedoms,  $f$ , and periodic boundary conditions, the binding energy for the second excited level ( $n = 2$ ) is given by

$$\frac{E_b}{\varepsilon} = \frac{2(y_m - 1)^2}{y_m} \quad (48)$$

where  $y_m$  is the largest real root of

$$y^{f+2} - y^f - y^2 + 1 = \frac{\gamma}{2\varepsilon} (y^f + y^2). \quad (49)$$

Perturbation analysis of eq. (49) for  $\gamma \ll \varepsilon$  leads to

$$y_m = 1 + \left(\frac{\gamma}{2f\varepsilon}\right)^{1/2} + \frac{\gamma}{4f\varepsilon} + \frac{\sqrt{f/2}}{48} \left(1 - \frac{6}{f} + \frac{8}{f^2}\right) \times \left(\frac{\gamma}{\varepsilon}\right)^{3/2} + O\left(\frac{\gamma^2}{\varepsilon^2}\right). \quad (50)$$

The  $(\gamma/\varepsilon)^{3/2}$  term clearly shows a lack of uniformity as  $f \rightarrow \infty$ . Proceeding as in the previous section we write

$$\frac{E_b}{\varepsilon} = \lambda_1 \frac{\gamma}{\varepsilon} + \lambda_2 \frac{\gamma^2}{\varepsilon^2} + R(\gamma, \varepsilon, f) \quad (51)$$

where

$$\lambda_1 = \frac{1}{f}, \quad (52)$$

and

$$\lambda_2 = \frac{1}{24} \left(1 - \frac{5}{f}\right) \left(1 - \frac{1}{f}\right). \quad (53)$$

In this case the residual has the form

$$R(\gamma, \varepsilon, f) = \frac{(f-1)(2f^3 - 28f^2 + 97f - 53)}{1440f^3} \left(\frac{\gamma^3}{\varepsilon^3}\right) + O\left(\frac{\gamma^4}{\varepsilon^4}\right), \quad (54)$$

which does not converge uniformly in  $f$ . It is possible to show this explicitly by expanding  $y_m$  up to terms in  $(\gamma/\varepsilon)^{5/2}$  and hence calculating the  $O(\gamma^3/\varepsilon^3)$  term for  $E_b/\varepsilon$ , which is  $O(f)$  as  $f \rightarrow \infty$ .

For large  $f$  we find the asymptotic formula

$$y_m^2 = 1 + \frac{\gamma}{2\varepsilon} + \frac{\gamma/\varepsilon + \gamma^2/4\varepsilon}{(1 + \gamma/2\varepsilon)^{f/2}} \times \left[1 - \frac{f(\gamma/\varepsilon + \gamma^2/4\varepsilon)}{2(1 + \gamma/2\varepsilon)^{f/2+1}} + \dots\right], \quad (55)$$

which converges rapidly for large  $f$  at a fixed value of  $\gamma$ . The derivation of this result is given in Appendix B. From eq. (48) and (55) we see that as  $f \rightarrow \infty$

$$\frac{E_b}{\varepsilon} \rightarrow \frac{2(\sqrt{1 + \gamma/2\varepsilon} - 1)^2}{\sqrt{1 + \gamma/2\varepsilon}}. \quad (56)$$

Thus if the number of freedoms is arbitrarily large,  $E_b \rightarrow \gamma^2/8\varepsilon$  as  $\gamma \rightarrow 0$ . Again this is in agreement with the quantum field theory result of eq. (22).

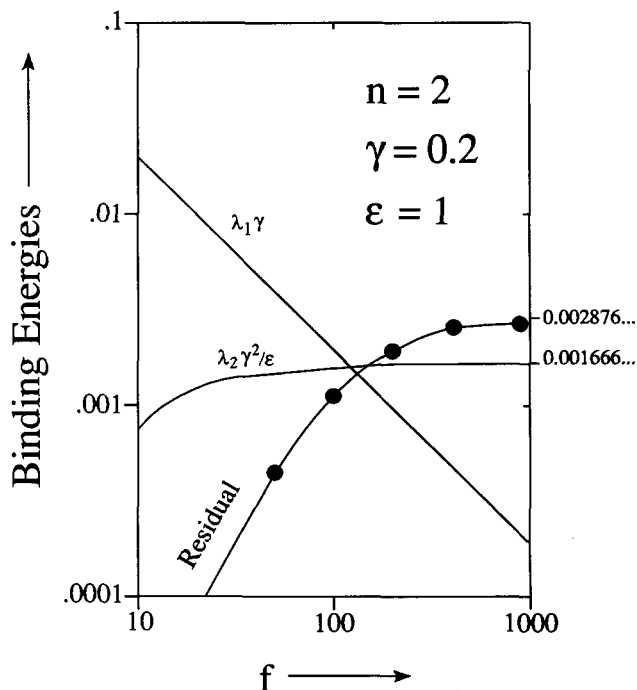


Fig. 4. Binding energies for the QAL equation in eq. (47) as a function of the number of freedoms.

Figure 4 has been prepared in a manner similar to Fig. 1 to show the nonuniform convergence of the residual graphically. In this case the sum of the residual and  $1/24$  approaches the value given by eq. (56). For  $\gamma = 0.2$  and  $\varepsilon = 1$ , eq. (56) gives a limit of 0.004542875, so the residual approaches 0.002876208 as  $f \rightarrow \infty$ . Thus  $\gamma = 0.2$  is too large for the QFT expression for the soliton binding energy to hold. For large  $\gamma$  eq. (56) reduces to

$$\frac{E_b}{\varepsilon} \sim 2 \sqrt{\frac{2\varepsilon}{\gamma}} \left( \sqrt{\frac{\gamma}{2\varepsilon}} - 1 \right)^2, \quad (57)$$

which differs from eq. (32).

## 5. Discussion

That the above considerations are of more than theoretical interest has been pointed out by Bruinsma, Maki and Wheatley who suggest that eq. (1) can be used to study the binding energies of local modes in small molecules, such as benzene, and in low dimensional solids, such as polyacetylene [5]. In these examples the fundamental boson (number) states of eq. (1) correspond to C-H stretching oscillations. Since Bruinsma *et al.* do not use the exact quantum theory outlined above, their results are approximate, but they state: "For general  $n$  and weak anharmonicity the Hamiltonian [our eq. (4)] can be diagonalized by the Bethe Ansatz, and the binding energy of the  $n$ -boson bound state . . . below the  $n$ -particle [normal mode] band edge is [their eq. (5)]." The intent is clear and the differences between the quantum field theory (AFT) result [our eq. (22)] and their eq. (5) are probably typographical errors.

From the perspective of our exact quantum theory we see that the situation is somewhat more complex. For a fixed number of freedoms (however large) the QFT result will always fail for sufficiently small  $\gamma$  (when the perturbation expansion becomes valid) and for sufficiently large  $\gamma$  (when the soliton becomes "pinned" to a single lattice site as a local mode) [3]. This effect is shown in Fig. 2 for  $n =$  and in Fig. 3 for  $n = 3$ .

Recently Fillaux and Carlile have used quantum field theory results for the sine-Gordon breather [7] to interpret the inelastic neutron scattering spectra of isotopic mixtures of 4-methyl-pyridine crystals (4MP) [12, 13]. These crystals suspend methyl ( $\text{CH}_3$ ) groups in one dimensional chains that can be approximately described by the Hamiltonian for a discrete sine-Gordon equation. Since sine-Gordon breathers are similar to solitons of the nonlinear Schrödinger equation, we expect that eq. (1) should also be useful in interpreting these spectra. This, in turn, suggests that there may be corresponding limits to the range of validity of quantum field theory results. We expect to address this question in the near future.

Finally we note that several energy eigenvalues lie between the lowest level for  $\gamma > 0$  and the lowest level for  $\gamma = 0$ . We suppose that these intermediate states correspond to quantum levels for " $N$ -soliton interactions," and again we expect to consider this in a future publication.

### A. Appendix: Construction of $Q(3, 1)$

In this appendix we list a pseudocode to build the Hamil-

tonian matrix  $Q(3, 1)$  with anharmonicity measured by  $\gamma$  and dispersion measured by  $\varepsilon$ .

```

subroutine makematrix(Q,Gamma,Epsilon,f,D)
real Q(D,D),Gamma,sr2,sr3
integer D,f,base,limit,j

case (f mod 3) of
    0: limit = D-4
    1: limit = D-5
    2: limit = D-2
endcase
sr2 = -Epsilon*sqrt(2)
sr3 = -Epsilon*sqrt(3)
for j = 2 to f-2
    Q(j,j) = -Gamma
    Q(j,j+1) = -Epsilon
    Q(j+1,j) = -Epsilon
    Q(j+f-1,j) = sr2
    Q(j+f-1,j+1) = sr2
    Q(j,j+f-1) = sr2
    Q(j+1,j+f-1) = sr2
endfor
Q(1,1) = -3*Gamma
Q(1,2) = sr3
Q(2,1) = sr3
Q(f,1) = sr3
Q(1,f) = sr3
Q(f,2) = -2*Epsilon
Q(2,f) = -2*Epsilon
Q(f-1,f-1) = -Gamma
Q(f-1,f) = -Epsilon
Q(f,f-1) = -Epsilon
Q(f+1,f-1) = sr2
Q(f-1,f+1) = sr2
Q(f,f) = -Gamma
Q(f,f+1) = sr2
Q(f+1,f) = sr2
base = f
f = f-3
while base < limit do
    for j = 1 to f-2
        Q(base+j,base+j+1) = -Epsilon
        Q(base+j+1,base+j) = -Epsilon
        Q(base+j+f-1,base+j) = -Epsilon
        Q(base+j+f-1,base+j+1) = -Epsilon
        Q(base+j,base+j+f-1) = -Epsilon
        Q(base+j+1,base+j+f-1) = -Epsilon
    endfor
    Q(base+f-1,base+f) = -Epsilon
    Q(base+f,base+f-1) = -Epsilon
    Q(base+f-1,base+f+1) = -Epsilon
    Q(base+f+1,base+f-1) = -Epsilon
    Q(base+f,base+f+1) = -Epsilon
    Q(base+f+1,base+f) = -Epsilon
    base = base + f
    f = f - 3
endwhile
case (f mod 3) of
    0:
    begin
        Q(base+1,base+2) = -Epsilon

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Q(base+1,base+3) = -Epsilon
Q(base+2,base+1) = -Epsilon
Q(base+3,base+1) = -Epsilon
Q(base+2,base+3) = -2*Epsilon
Q(base+2,base+4) = -3*Epsilon
Q(base+3,base+2) = -2*Epsilon
Q(base+4,base+2) = -Epsilon
Q(base+3,base+4) = -3*Epsilon
Q(base+4,base+3) = -Epsilon
end
1:
begin
Q(base+5,base+5) = -2*Epsilon
Q(base+1,base+2) = -Epsilon
Q(base+1,base+4) = -Epsilon
Q(base+2,base+1) = -Epsilon
Q(base+4,base+1) = -Epsilon
Q(base+2,base+3) = -Epsilon
Q(base+2,base+4) = -Epsilon
Q(base+2,base+5) = -Epsilon
Q(base+3,base+2) = -Epsilon
Q(base+4,base+2) = -Epsilon
Q(base+5,base+2) = -Epsilon
Q(base+3,base+4) = -Epsilon
Q(base+3,base+5) = -2*Epsilon
Q(base+4,base+3) = -Epsilon
Q(base+5,base+3) = -2*Epsilon
Q(base+4,base+5) = -Epsilon
Q(base+5,base+4) = -Epsilon
end
2:
begin
Q(base+2,base+2) = -2*Epsilon
Q(base+1,base+2) = -2*Epsilon
Q(base+2,base+1) = -2*Epsilon
end
endcase
return(Q)
end

```

## B. Appendix: Derivation of eq. (55)

In this Appendix we derive the asymptotic formula (55) for the largest real root  $y_m$  of eq. (49). Fix  $\alpha = (\gamma/2\varepsilon) > 0$  so that (49) takes the form

$$h(y) = y^f [y^2 - (1 + \alpha)] - (1 + \alpha)y^2 + 1 = 0. \quad (58)$$

A straight forward calculus argument shows that (58) has a unique real root larger than 1 so that  $y_m = y_m(f) > 1$ .

Since  $h(1) = 2\alpha$ , the sequence of roots  $\{y_m(f)\}$  is bounded away from 1. Hence  $y_m^2 \rightarrow \infty$  as  $f \rightarrow \infty$  so that  $y_m^2 = 1 + \alpha + O(1)$ . Using this in (58) gives

$$y_m^2 = 1 + \alpha + (2\alpha + \alpha^2)(1 + \alpha)^{-f/2}u \quad (59)$$

with  $u = u(f) \rightarrow 1$  as  $f \rightarrow \infty$ . To obtain more terms in the asymptotic series we consider the equation for  $u$  obtained by substituting (59) into (58):

$$[1 + u(2\alpha + \alpha^2)(1 + \alpha)^{-f/2-1}]^{f/2} - (1 + \alpha)^{-f/2+1}u = 0. \quad (60)$$

For large  $f$ , (60) takes the form

$$\left[1 + \frac{f}{2}u(2\alpha + \alpha^2)(1 + \alpha)^{-f/2+1}\right]u + O[(1 + \alpha)^{-f/2}] = 0 \quad (61)$$

from which eq. (55) follows.

## Acknowledgements

We are grateful to NATO for support of a collaborative program, to the SERC for funding under the Nonlinear Systems Initiative, to the EC for funding under SCI-0220-C89-100079/JU1, the (US) Air Force Office of Scientific Research and the NSF for funding under DMS-8902579.

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