LETTER TO THE EDITOR

One-dimensional band calculations

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Abstract. Recent calculations on one-dimensional energy bands are improved remarkably by using a simple perturbation approach with D^4 as the perturbation. The theoretical approach used is also relevant to the problem of including relativistic mass corrections in the Schrödinger equation.

In a recent work, Vigneron and Lambin (1979) have used a continued fraction approach to calculate one-dimensional band structures. They started from the Schrödinger equation

$$-D^2\psi + V\psi = E\psi \tag{1}$$

which must be solved with the periodic boundary condition

$$\psi(x+L) = e^{ikL}\psi(x) \tag{2}$$

where L is the length of the unit cell and k the wavenumber of the Bloch function being considered. They converted equation (1) to the finite difference form

$$\frac{1}{h^2}[\psi(x+h) + \psi(x-h) - 2\psi(x)] = (V-E)\psi(x). \tag{3}$$

Killingbeck (1977) treated (3) by a numerical integration process, whereas Vigneron and Lambin (1979) used a continued fraction approach. We wish to point out here that the accuracy of both techniques can be remarkably improved by the almost trivial expedient of adding the extra term $\frac{1}{12}h^2(V-E)^2\psi(x)$ to the right-hand side of (3). This is much simpler than modifying the equations of the theory so that the Numerov method of treating differential equations can be applied; this latter course was suggested by Vigneron and Lambin (1979) in their concluding discussion. The simple procedure of this Letter has not previously been applied to band theory calculations, but has been used for perturbed oscillator problems (Killingbeck 1980).

The theory of the correction term can be described briefly as follows. If we denote the finite difference operator on the left of (3) by δ^2, then a simple Taylor expansion gives

$$\delta^2\psi = D^2\psi + \tfrac{1}{12}h^2D^4\psi + \ldots \tag{4}$$

$$= (V-E)\psi + \tfrac{1}{12}h^2D^4\psi + \ldots \tag{5}$$

if we use (1). To first order of perturbation theory the energy shift caused by the perturbing term $\frac{1}{12}h^2D^4$ (which represents the difference between the true Schrödinger equation and our simulation of it) will be given by the expectation value $\frac{1}{12}h^2\langle D^4\rangle$ taken

with respect to the function ψ which obeys (1). This ψ is unknown, but for a variety of boundary conditions, including the periodic ones of equation (2), we can use the Dirac operator algebra to obtain

$$\langle \mathrm{D}^4 \rangle = \langle (-\mathrm{D}^2)(-\mathrm{D}^2) \rangle = \langle (V-E)^2 \rangle \tag{6}$$

on using (1). Thus, to lowest order, we can simulate the effect of the term $\frac{1}{12}h^2\mathrm{D}^4\psi$ by the effective operator term $\frac{1}{12}h^2(V-E)^2\psi$ in order to calculate the *energy*. The calculations of Vigneron and Lambin (1979) can therefore be repeated with no change in their equations except that their quantity $b = 2 + h^2(V-E)$ must be modified throughout by adding a term $\frac{1}{12}h^4(V-E)^2$. We have repeated their calculations for the potential $V = 2 \cos 2x$, and the results for the band edges are displayed in table 1. Since $E(k)$ is a monotonic function of $|k|$ in one-dimensional band theory, it is only necessary to deal with the cases $k = 0$ and $k = \pi/L$ to obtain the band edges. For these k-values ψ is real and obeys simple boundary conditions of the homogeneous Neumann type (at $k = 0$) or of the homogeneous Dirichlet type (at $k = \pi/L$), if the potential is inversion-symmetric. We emphasise, however, that the correction term which we use is applicable for any k-value in the Brillouin zone. The $E(N)$ values in the table refer to the calculations of Vigneron and Lambin (1979) for N strips, which we repeated and sharpened to six decimal places. The $E^1(N)$ values are energies calculated by including the extra correction term discussed in this Letter. The $E^1(\infty)$ value is found by an h^4 extrapolation from $E^1(25)$ and $E^1(50)$, and agrees to the accuracy quoted with the exact result from the theory of the Mathieu equation. The improvement produced by the correction term is remarkable: a calculation dividing the unit cell into 25 strips gives much better results than the original 300 strip calculation. An h^4 extrapolation gives very good *energy* values, although the *wavefunction* will still have an error of order h^2. Since only relatively few strips are needed, it would be possible to treat potential functions which are specified numerically; modern programmable calculators have sufficient memory capacity to store the number of data values involved.

Table 1. Band edges for $V = 2 \cos 2x$ (notation as explained in the text).

	Lower band		Upper band	
$E(50)$	$-0.455\,642$	$-0.110\,873$	$1.858\,291$	$3.911\,444$
$E(300)$	$-0.455\,152$	$-0.110\,267$	$1.859\,090$	$3.916\,878$
$E^1(25)$	$-0.455\,145$	$-0.110\,253$	$1.859\,104$	$3.917\,062$
$E^1(50)$	$-0.455\,139$	$-0.110\,249$	$1.859\,108$	$3.917\,027$
$E^1(\infty)$	$-0.455\,139$	$-0.110\,249$	$1.859\,108$	$3.917\,025$

In the preceding discussion we have regarded the D^4 term as arising from a finite-difference procedure, and have taken ψ to be unknown. However, the operator D^4 also appears if we use the relativistic mass correction in the Schrödinger equation; in appropriate units the equation takes the form

$$c^2[(1-2\mathrm{D}^2/c^2)^{1/2}-1]\psi + V\psi = E\psi \tag{7}$$

$$= [-\mathrm{D}^2\psi - (1/2c^2)\mathrm{D}^4\psi + \ldots] + V\psi. \tag{8}$$

To obtain (8) we have used units in which $-\mathrm{D}^2$ is the non-relativistic kinetic energy operator, to be consistent with the rest of this work. Condon and Shortley (1970)

employed units in which $-\frac{1}{2}D^2$ is the non-relativistic kinetic energy operator, but this does not affect the gist of our comments below about their procedure.

Our previous argument shows that the expectation value of the D^4 operator is the same as that of the operator $(V-E)^2$ for the non-relativistic wavefunction (which will be *known* for simple problems). Alternatively, we could get the *energy* correct to lowest order by solving a modified Schrödinger equation in which the term $-(1/2c^2)(V-E)^2$ is added to the potential V. Condon and Shortley (1970) do this, but they derive the modified equation by wrongly asserting that D^2 commutes with $(V-E)$. This leads to the (incorrect) result $D^4\psi = (V-E)^2\psi$ which they treat as exact. In fact D^2 does *not* commute with $(V-E)$: the correct result is as follows, after using (1):

$$D^4\psi = (V-E)^2\psi + (D^2V)\psi + 2(DV)D\psi. \tag{9}$$

What our previous discussion has shown is that the last two terms in (9), although non-zero, can be omitted from the modified Schrödinger equation, since they have no first-order effect on the *energy*; however they *will* affect the wavefunction. Accordingly, the *energy* formula given by Condon and Shortley (1970) is correct to first order in c^{-2} (for their problem of the hydrogen atom) but could be obtained simply and directly by evaluating the first-order energy using the equivalence $D^4 \equiv (E-V)^2$. Strictly speaking, the truncation used in (8) does not give true bound states. This can be seen most easily for the case $V = x^2$; changing to momentum representation converts (8) to the equivalent form

$$-D^2\psi + x^2\psi - (1/2c^2)x^4\psi = E\psi. \tag{10}$$

This perturbed oscillator Hamiltonian has no bound states, whereas the full potential function

$$V = c^2[(1+2x^2/c^2)^{1/2} - 1] \tag{11}$$

does give bound states, the eigenvalues of which can be found by using a numerical procedure such as that of Killingbeck (1977), suitably improved in the manner described in this Letter.

References

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