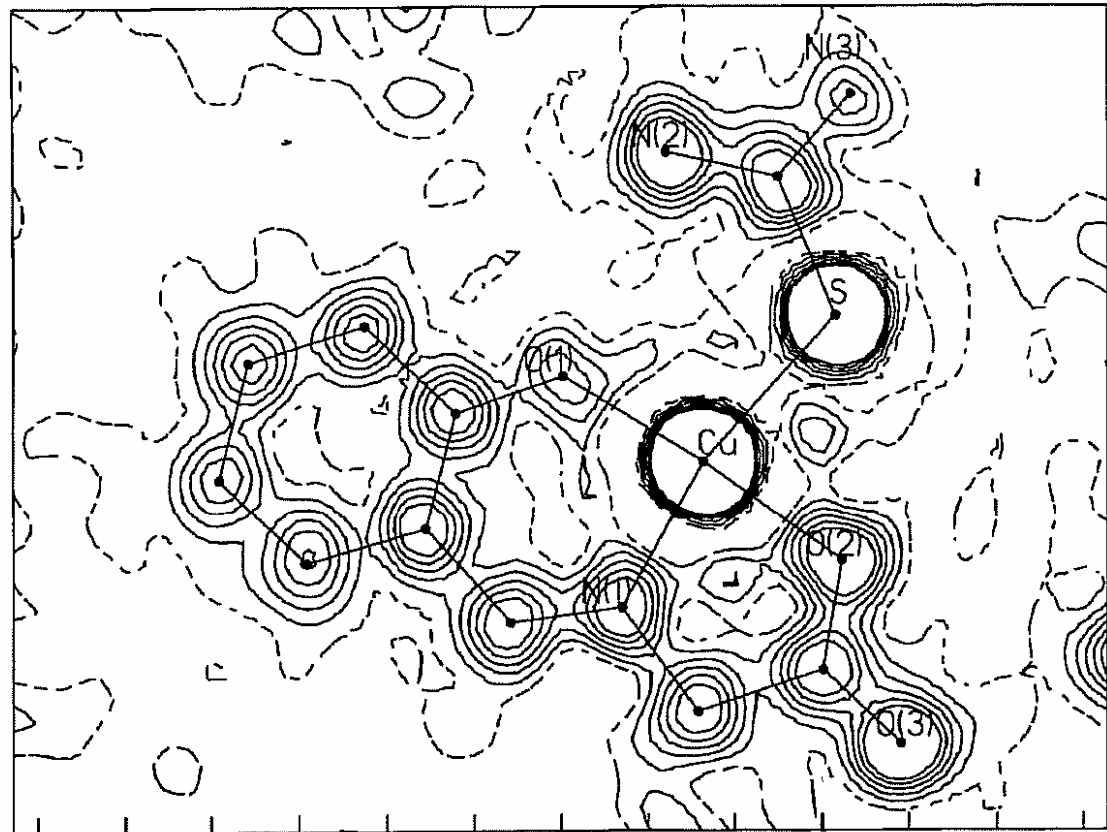


## Fourier series

The periodic arrangement of the unit cells means that the atom positions are periodic, and in turn the atomic electron density  $\rho(x, y, z)$  is periodic. Any periodic function can be represented as a Fourier series

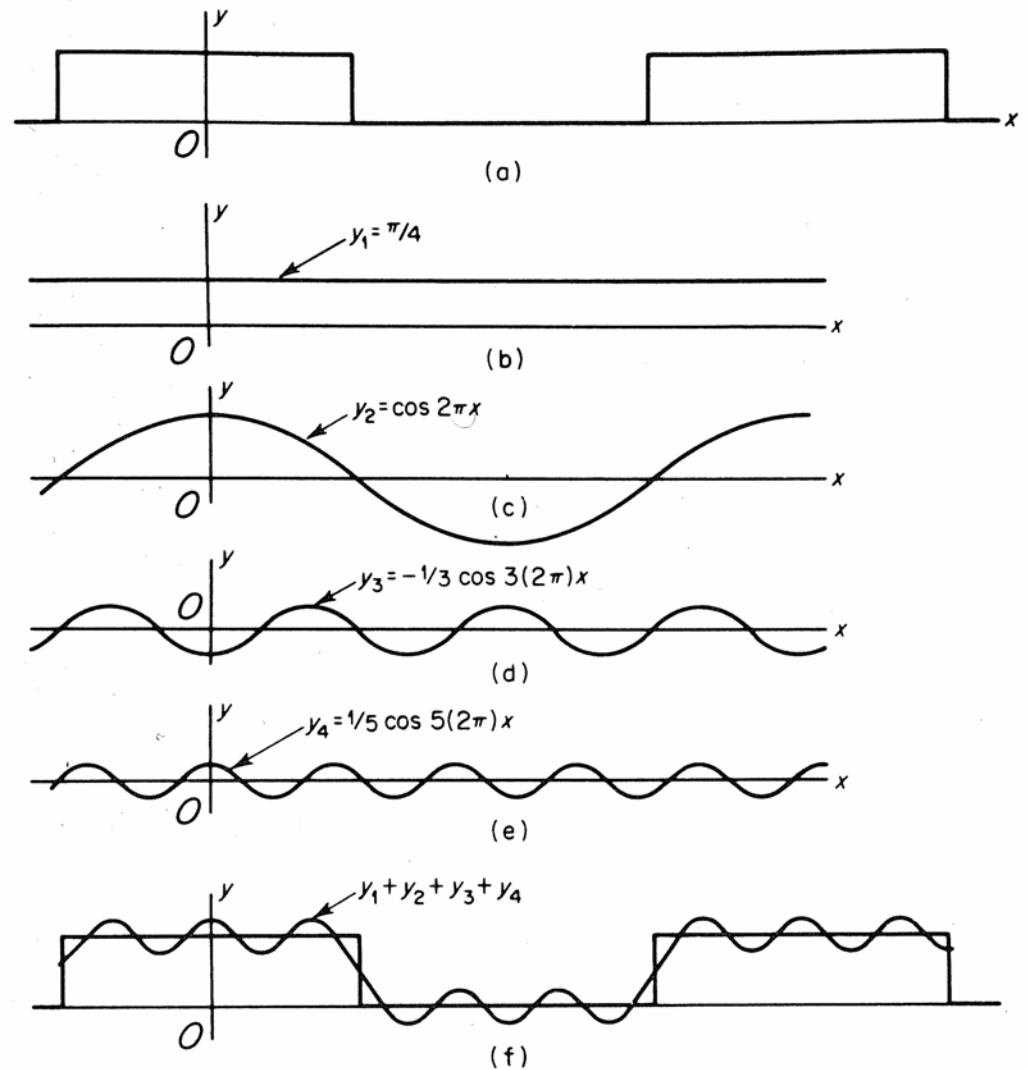


the thiourea derivative of N-salicylideneglycinatocopper(II)

Example of electron density contours. Here we are viewing one plane of the unit cell chosen to correspond to the plane of atoms of the copper chelate complex. The contours are like the contours of a topographic map. Here each contour represents an interval of  $1 \text{ e}\text{\AA}^{-3}$ . The dotted lines represent (physically not meaningful) negative electron density. [So where does it come from?]

A one-dimensional Fourier series represents a periodic function in one dimension. That function can be broken up into even [ $f(-x) = f(x)$ ] and odd [ $f(-x) = -f(x)$ ] components. For the even part only cosine terms are applicable and for the odd part only sine (why?)

A periodic box shape is approximated successively by additional Fourier terms. What will the difference function (real minus approximated) look like? Where biggest? Why? What do you think the next term will be?



$$\begin{aligned}
 f(x) &= a_0 + a_1 \cos 2\pi x + a_2 \cos 2\pi(2x) + \dots + a_n \cos 2\pi(nx) \\
 &\quad + b_1 \sin 2\pi x + b_2 \sin 2\pi(2x) + \dots + b_n \sin 2\pi(nx) \\
 &= a_0 + \sum_{h=1}^n (a_h \cos 2\pi hx + b_h \sin 2\pi hx)
 \end{aligned}$$

It is often convenient to write the Fourier series in exponential form:  
remember

$$\cos x = \frac{e^{ix} + e^{-ix}}{2}$$

$$\sin x = \frac{-i(e^{ix} - e^{-ix})}{2}$$

Substituting into the  
previous formula for a one  
dimensional Fourier series  
(previous slide) gives:

$$f(x) = a_0 + \frac{1}{2}[a_1 e^{2\pi i x} + a_1 e^{-2\pi i x} + a_2 e^{2\pi i(2x)} + a_2 e^{-2\pi i(2x)} + \dots] \\ - (i/2)[b_1 e^{2\pi i x} - b_1 e^{-2\pi i x} + b_2 e^{2\pi i(2x)} - b_2 e^{-2\pi i(2x)} + \dots]$$

$$f(x) = a_0 + \frac{1}{2}[(a_1 - ib_1)e^{2\pi i x} + (a_2 - ib_2)e^{2\pi i(2x)} + \dots \\ + (a_1 + ib_1)e^{-2\pi i x} + (a_2 + ib_2)e^{-2\pi i(2x)} + \dots]$$

$$f(x) = \sum_{-n}^n C_h e^{2\pi i h x}$$

Where now

$$C_0 = a_0, \quad C_h = (a_h - ib_h)/2, \quad \text{and} \quad C_{\bar{h}} = (a_h + ib_h)/2$$

And the equation can be  
rewritten in real and  
imaginary components:

$$f(x) = \sum_{-n}^n C_h (\cos 2\pi h x + i \sin 2\pi h x)$$

For a one dimensional structure of electron density  $\rho(x)$  and unit cell length  $L$ , the normalized ( $\text{e}\text{\AA}^{-1}$ ) form of the Fourier series becomes:

$$\rho(x) = \frac{1}{L} \sum_h C_h e^{-2\pi i h x}$$

What are these coefficients  $C_h$ ?

They are simply the structure factors  $F_h$ !  
(times the normalization quantity  $1/L$ )

For 3 dimensions, remember that the general form of the structure factor is:

$$F_{hkl} = \int_v \rho(x, y, z) e^{2\pi i(hx+ky+lz)} dv = \int_v \rho(\mathbf{r}) e^{2\pi i(\mathbf{h} \cdot \mathbf{r})} dv$$

And the corresponding form of the electron density Fourier series will be:

$$\rho(x, y, z) = \sum_{h'} \sum_{k'} \sum_{l'} C_{h'k'l'} e^{2\pi i(h'x+k'y+l'z)}$$

What are these coefficients?

Substitute the second equation [for  $\rho(x,y,z)$ ] into the first equation [for the structure factor] (next slide)

$$F_{hkl} = \int_v \sum_{h'} \sum_{k'} \sum_{l'} C_{h'k'l'} e^{2\pi i(h'x+k'y+l'z)} e^{-2\pi i(hx+ky+lz)} dv$$

$$F_{hkl} = \int_v \sum_{h'} \sum_{k'} \sum_{l'} C_{h'k'l'} e^{2\pi i[(h+h')x+(k+k')y+(l+l')z]} dv$$

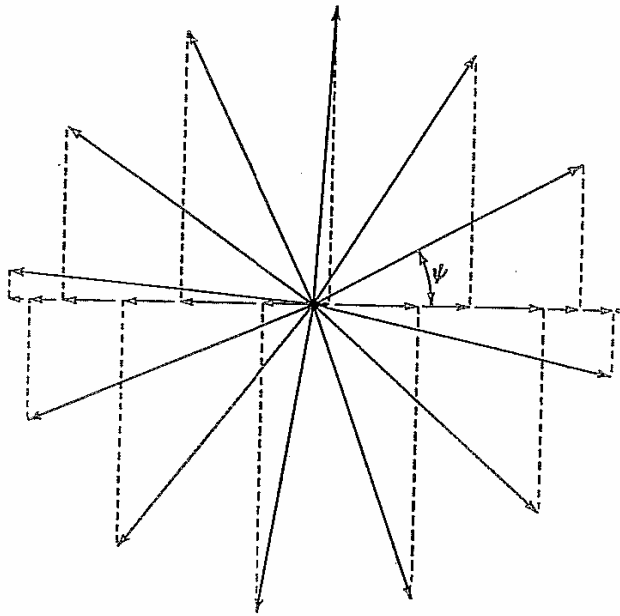
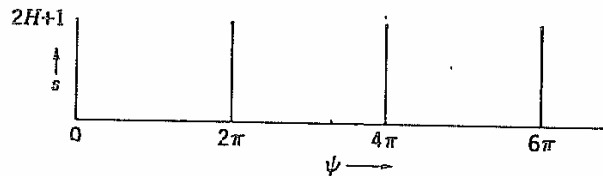


Fig. 2.



The integral is zero for all terms in which  $(h',k',l')$  is not  $-(h,k,l)$

[remember the average value of sine and cosine functions or the exponential form shown at left]

which gives finally:

$$\rho(x, y, z) = \frac{1}{V} \sum_h \sum_k \sum_l F_{hkl} e^{-2\pi i(hx+ky+lz)}$$

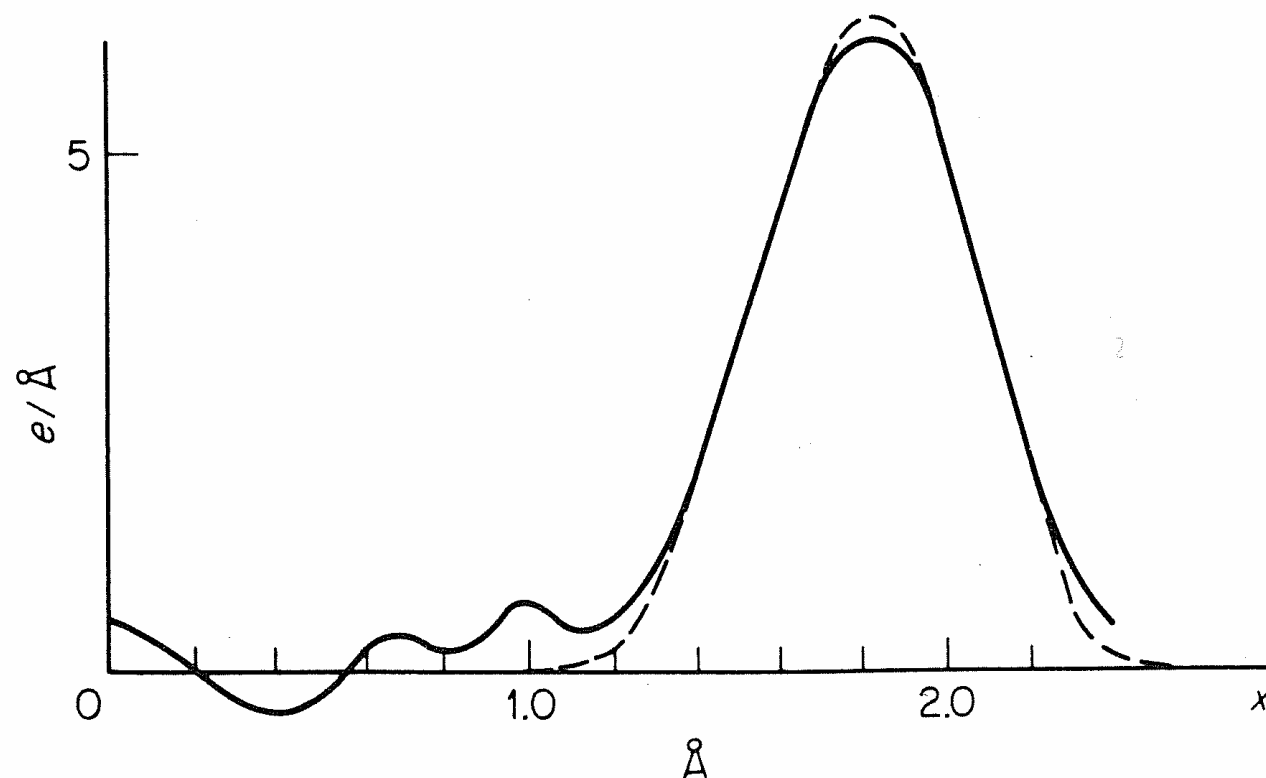
So what is so hard about solving structures?

We know  $\|F\|$  but not its phase.....

What happens if we guess phase wrong?

Example: the one dimensional carbon atom structure (from S&J)

C atom in centrosymmetric structure at 1.833 and -1.833 Å in cell of 10 Å



**Figure 8.9.** Dashed line, electron density in a carbon atom projected onto a line through its center; solid line, its representation by a 13-term Fourier series.

**TABLE 8.1 Data for a One-Dimensional Hypothetical Structure with  $a = 10 \text{ \AA}$**

$$F_h = \sum_{j=1}^2 f_j e^{2\pi i h x_j}$$

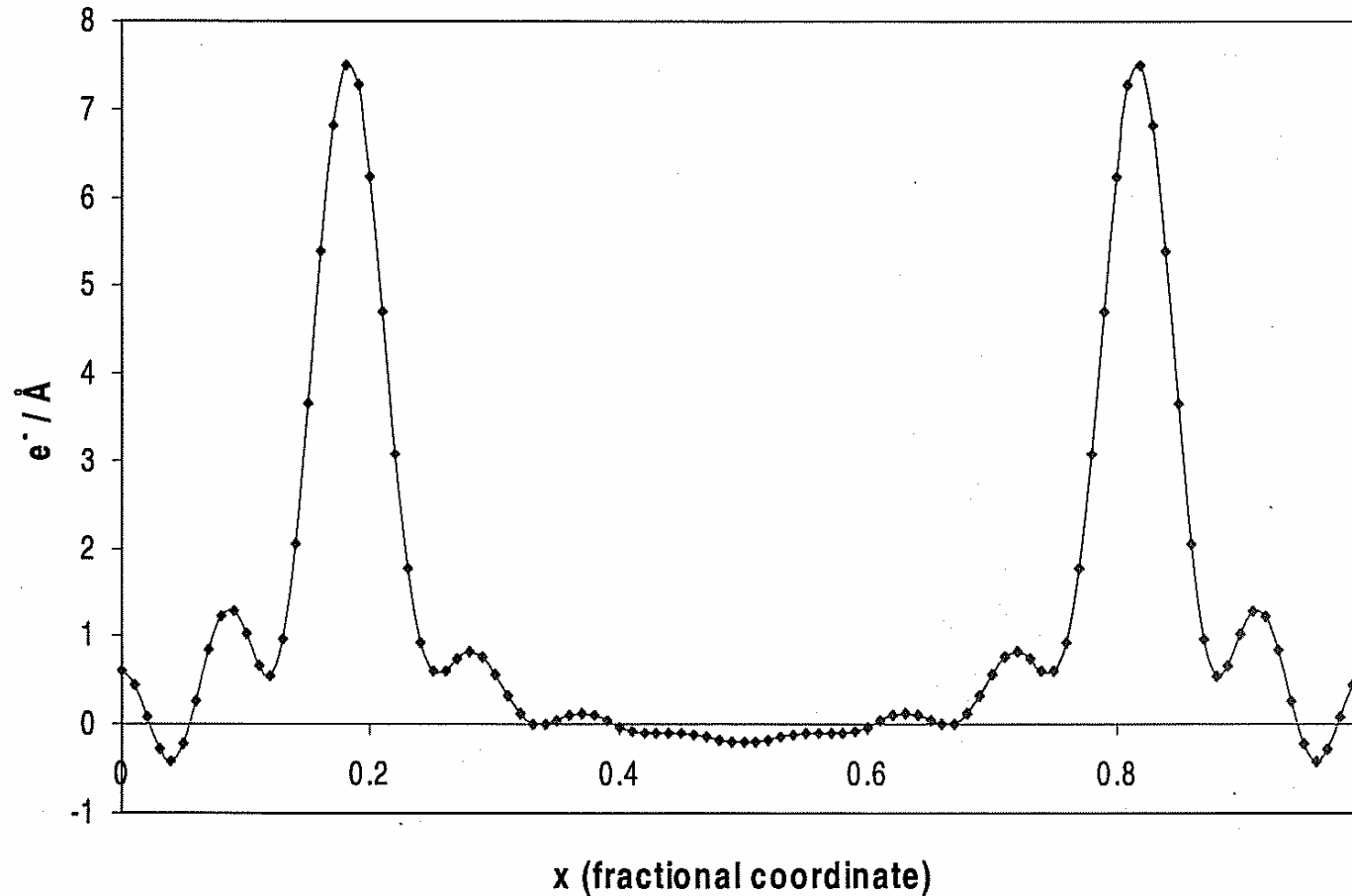
$$F_h = \sum_{j=1}^2 f_j (\cos 2\pi h x_j + i \sin 2\pi h x_j)$$

$$F_h = 2f_C \cos 2\pi h x_{C1}$$

$h$	$\sin \theta$	$F_h$
0	0.000	12
$\pm 1$	0.077	5
$\pm 2$	0.154	-7
$\pm 3$	0.231	-8
$\pm 4$	0.308	-1
$\pm 5$	0.385	5
$\pm 6$	0.462	4
$\pm 7$	0.539	-1
$\pm 8$	0.616	-4
$\pm 9$	0.693	-2
$\pm 10$	0.770	2
$\pm 11$	0.847	3
$\pm 12$	0.924	1

The structure is centrosymmetric, so the sine terms cancel and we can halve the sum (one carbon atom is at the same but negative position of the other). This gives the table of structure factors shown.

## One Dimensional Two Carbon Structure



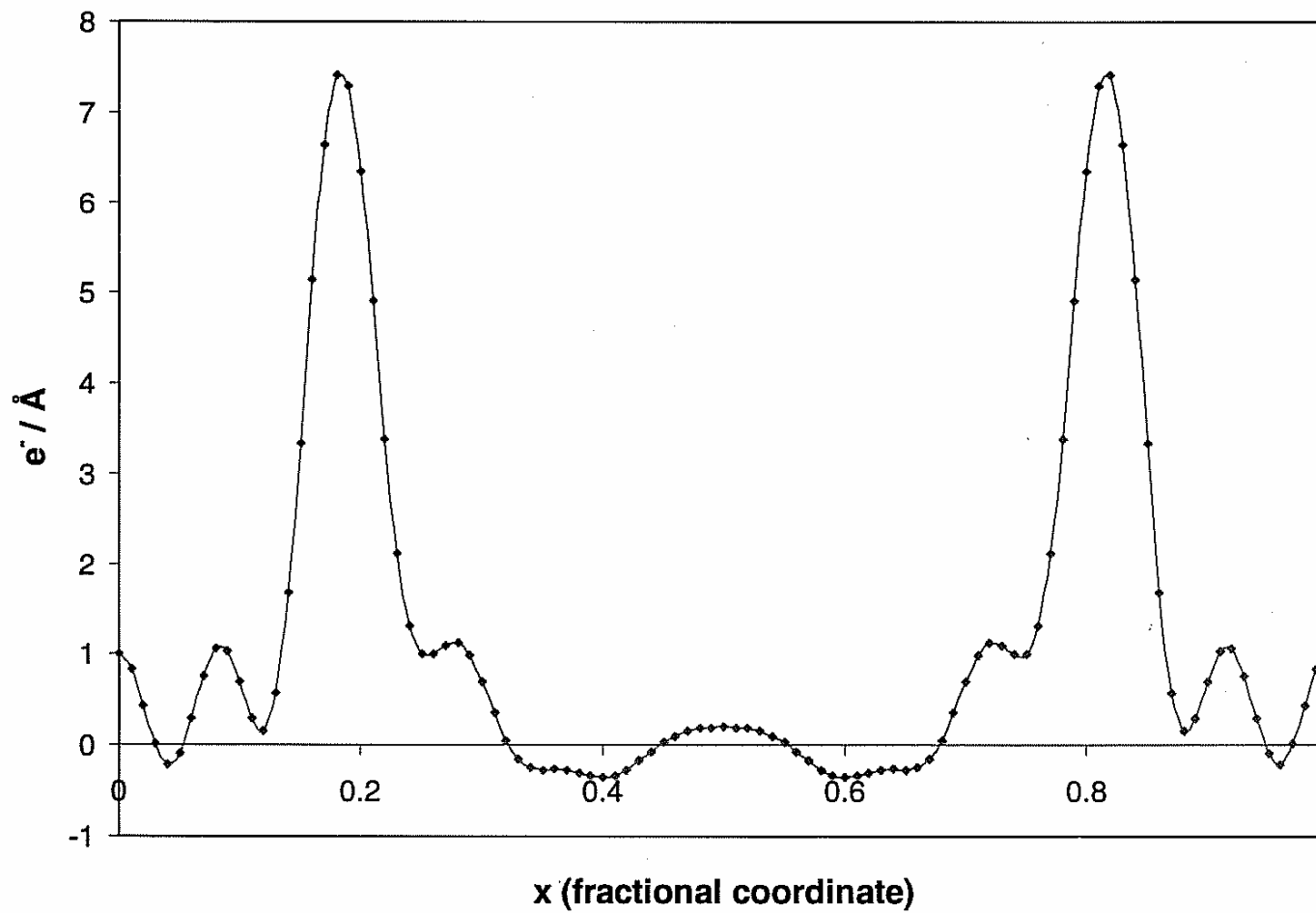
h	F
0	12
1	5
2	-7
3	-8
4	-1
5	5
6	4
7	-1
8	-4
9	-2
10	2
11	3
12	1

Now what happens if there are errors (noted by arrows)?

Here there are no errors

Why the ripples?

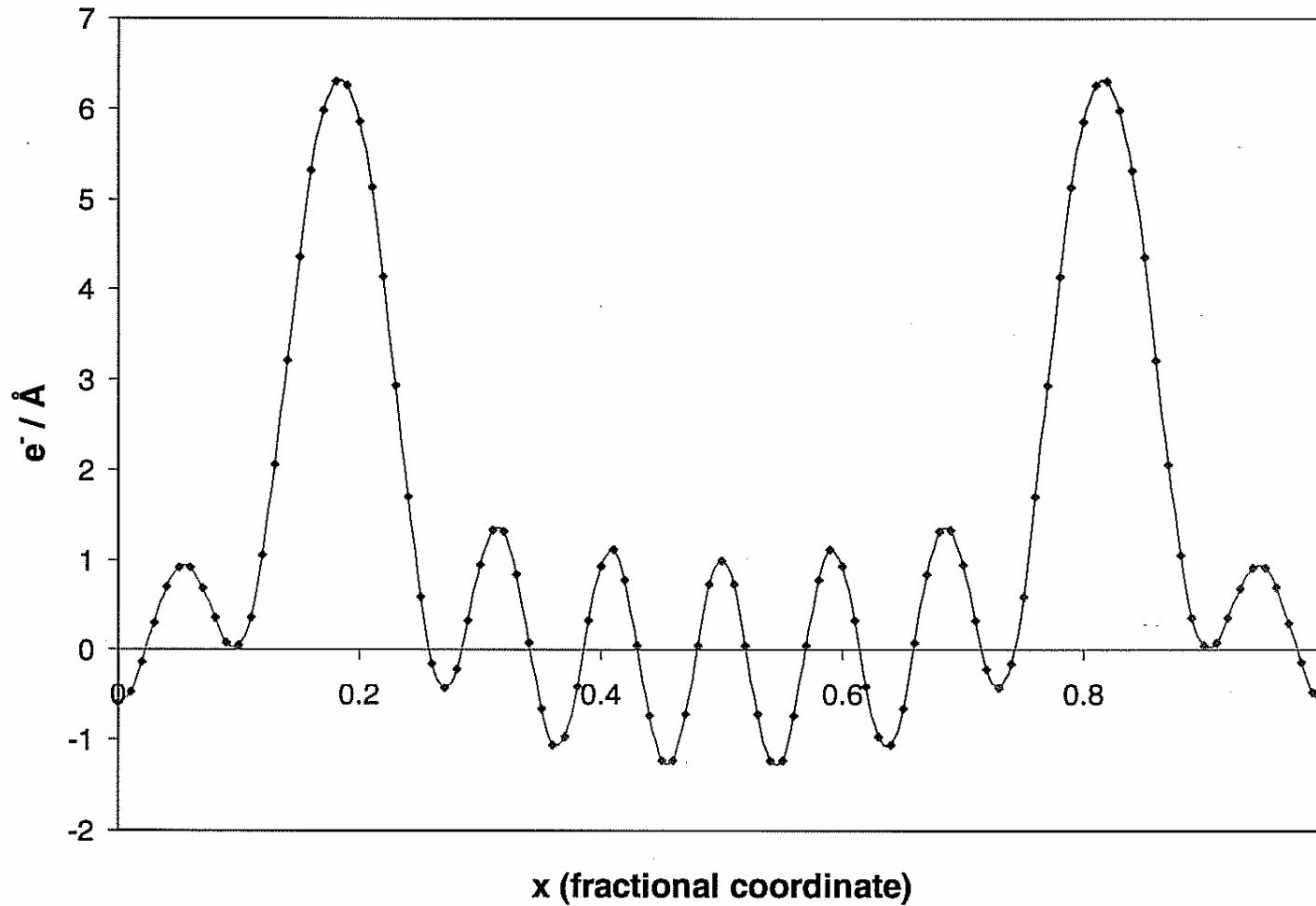
# One Dimensional Two Carbon Structure



h	F
0	12
1	5
2	-7
3	-8
4	1
5	5
6	4
7	-1
8	-4
9	-2
10	2
11	3
12	1

Weak negative peak  
 Otherwise nearly correct

## One Dimensional Two Carbon Structure

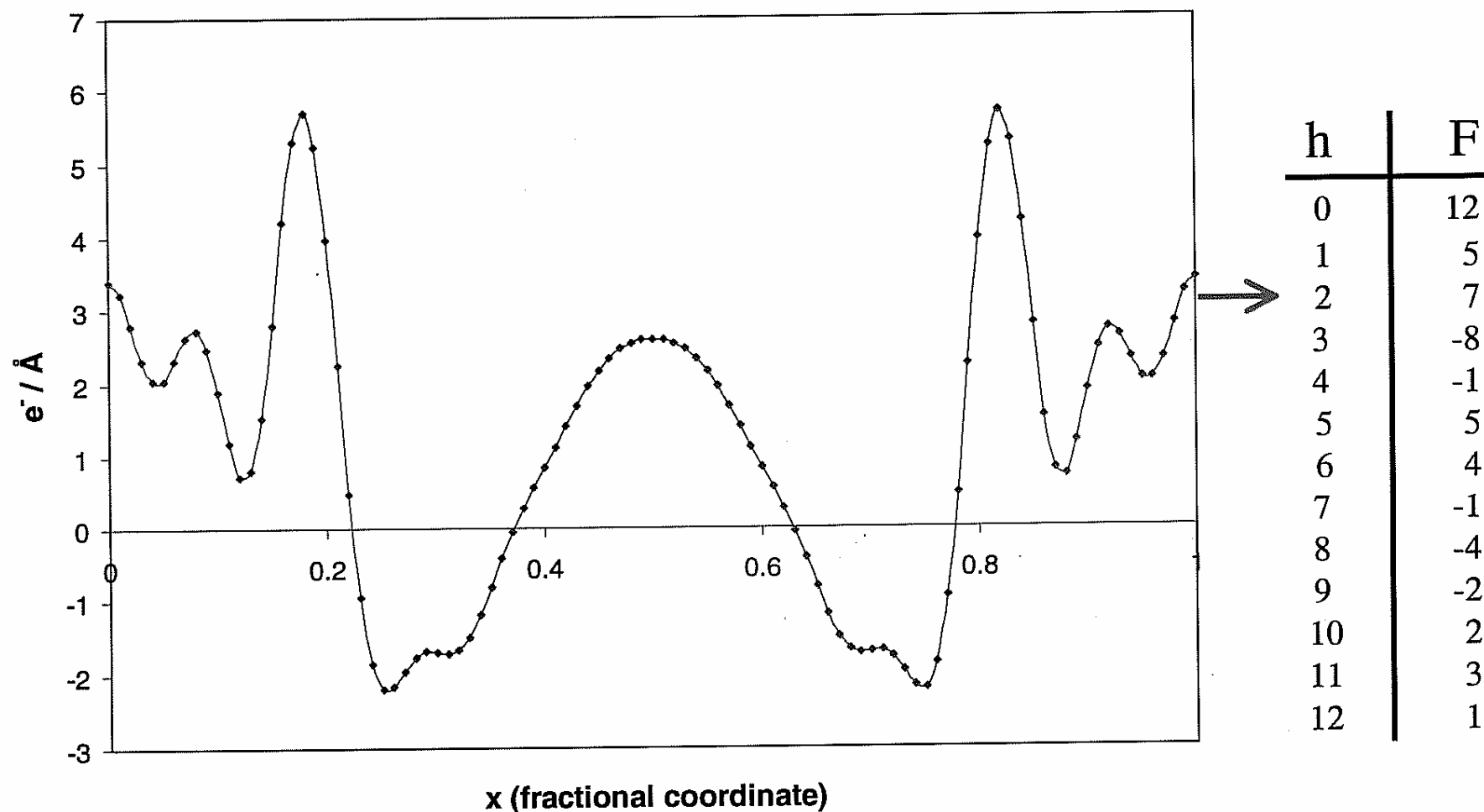


h	F
0	12
1	5
2	-7
3	-8
4	-1
5	5
6	-4
7	-1
8	-4
9	-2
10	2
11	3
12	1

Many small negative peaks

Note the periodicity in the ripple....

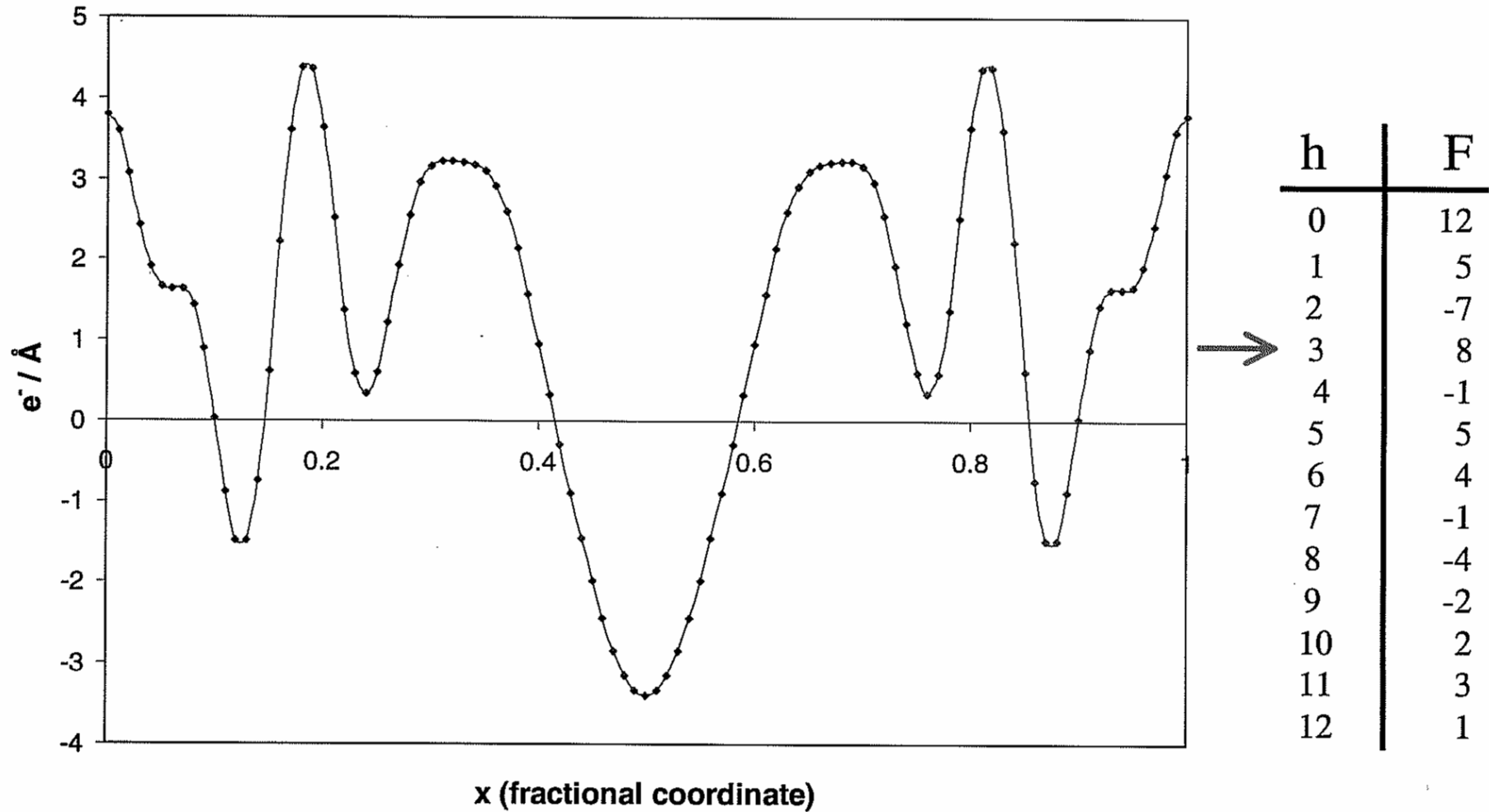
## One Dimensional Two Carbon Structure



Negative  $e^-$  density  
 False positive peaks at 0,  $\frac{1}{2}$

**Things are getting ugly...**  
**What do negative peaks mean?**

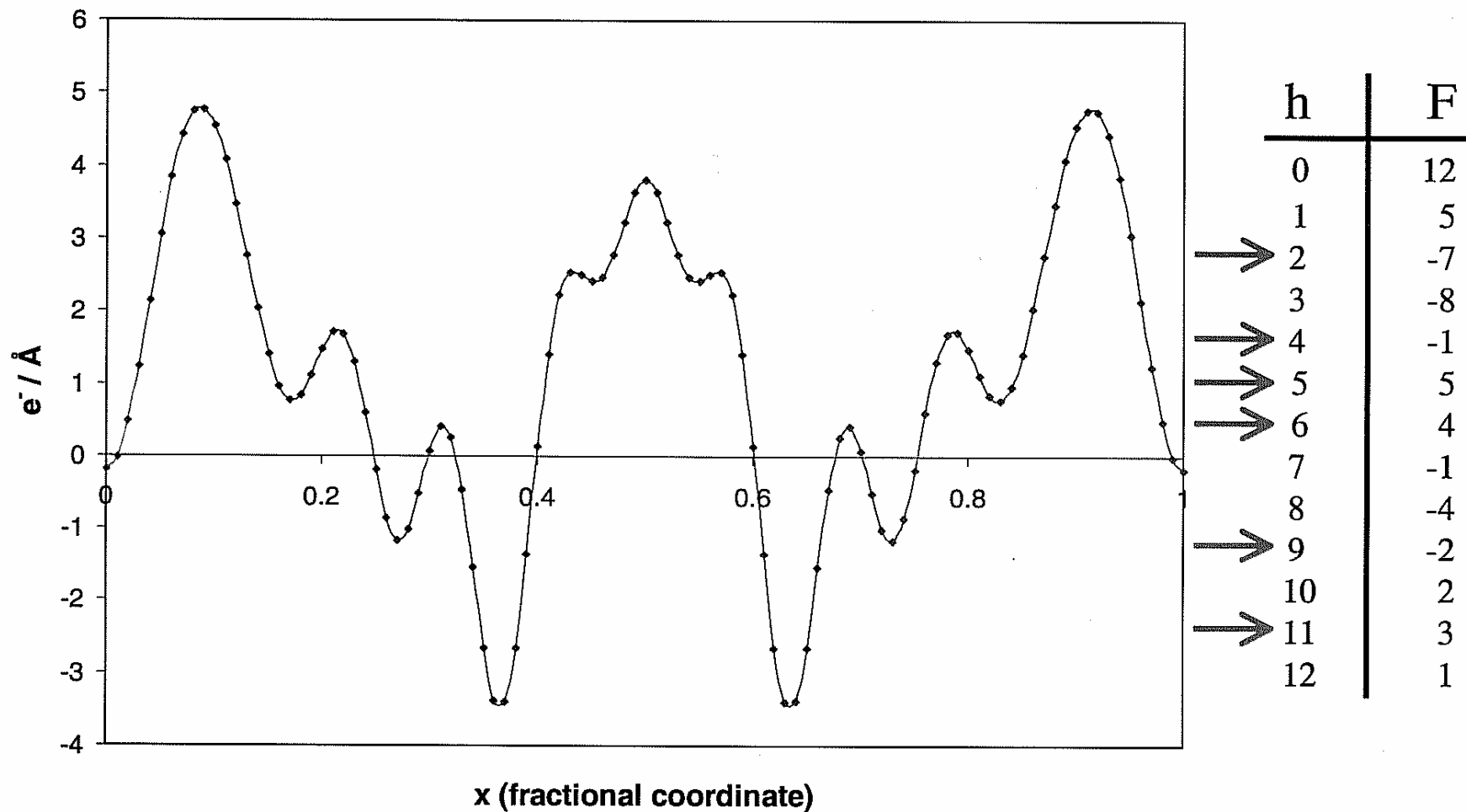
## One Dimensional Two Carbon Structure



Almost random structure  
 Peak at C atom locations  
 Many false peaks

Now very ugly...  
 we can still see structure,  
 but which one?

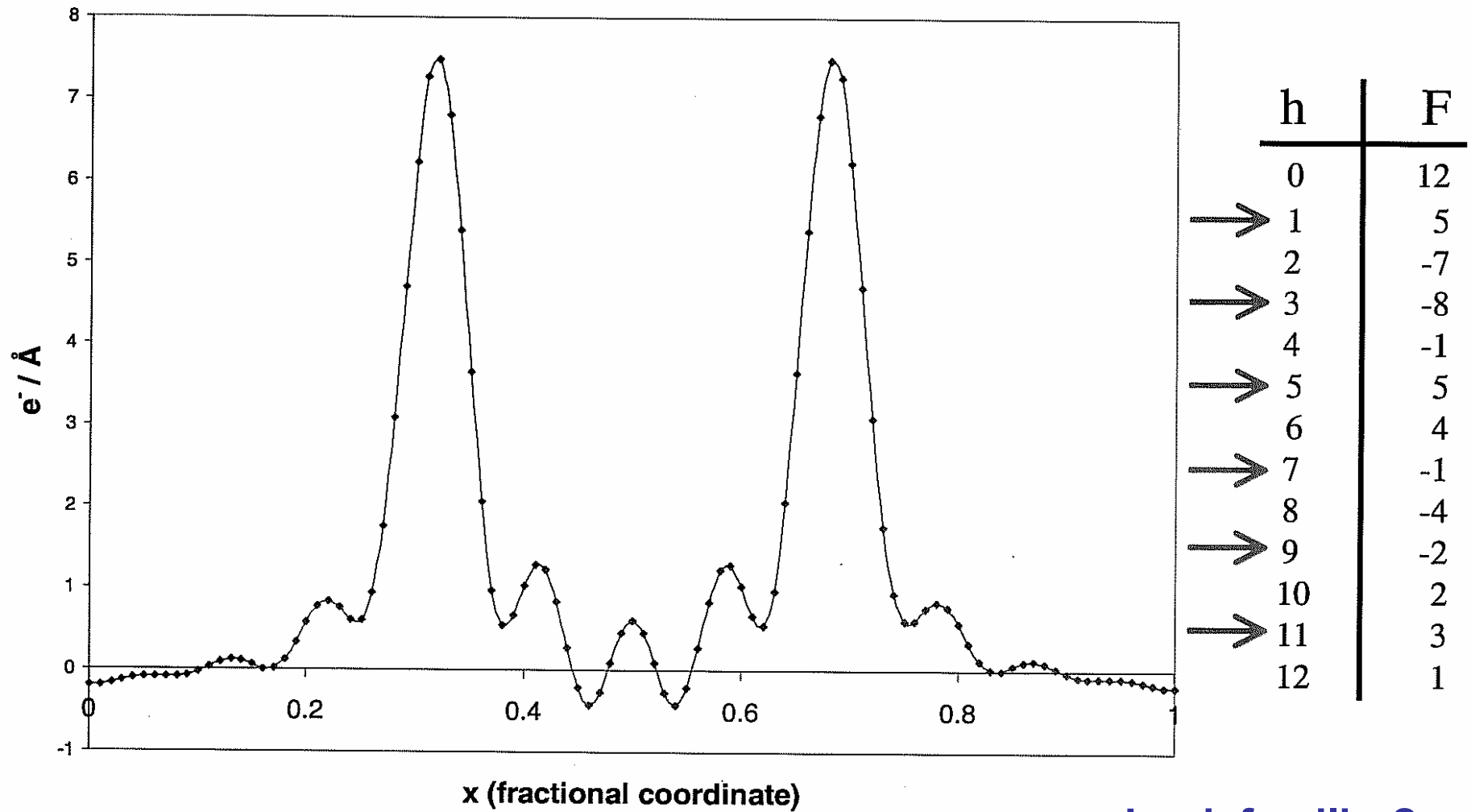
## One Dimensional Two Carbon Structure



Many incorrect peaks  
 Nearly random  
 Carbon atoms gone

**Now essentially random structure.  
 No hint of real structure left.**

## One Dimensional Two Carbon Structure



Carbon atom at 0.3167 ( $\frac{1}{2} - .1833$ )

Note carbon atom positions, lack of negative peaks

Look familiar?

Why?