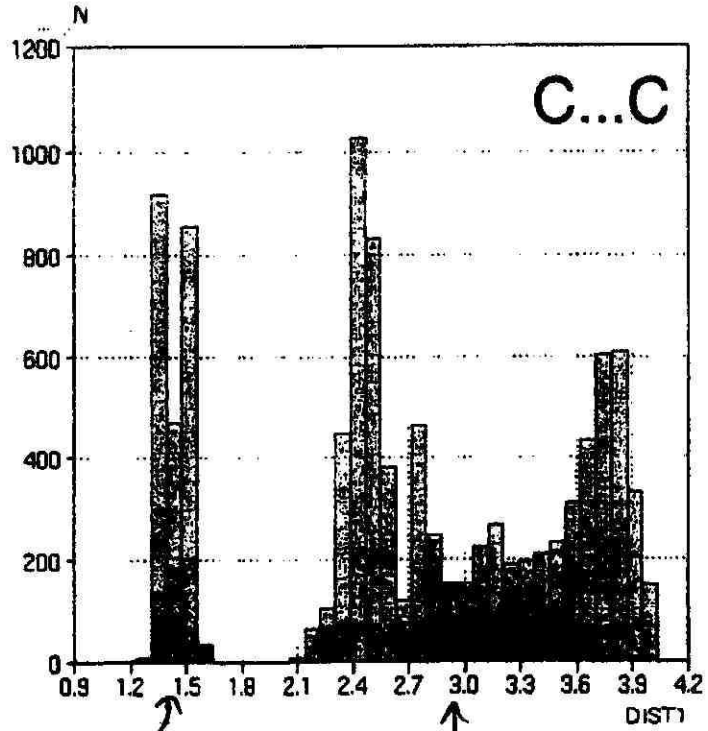
Lecture 34. Hypervalent systems, Lewis acids and bases

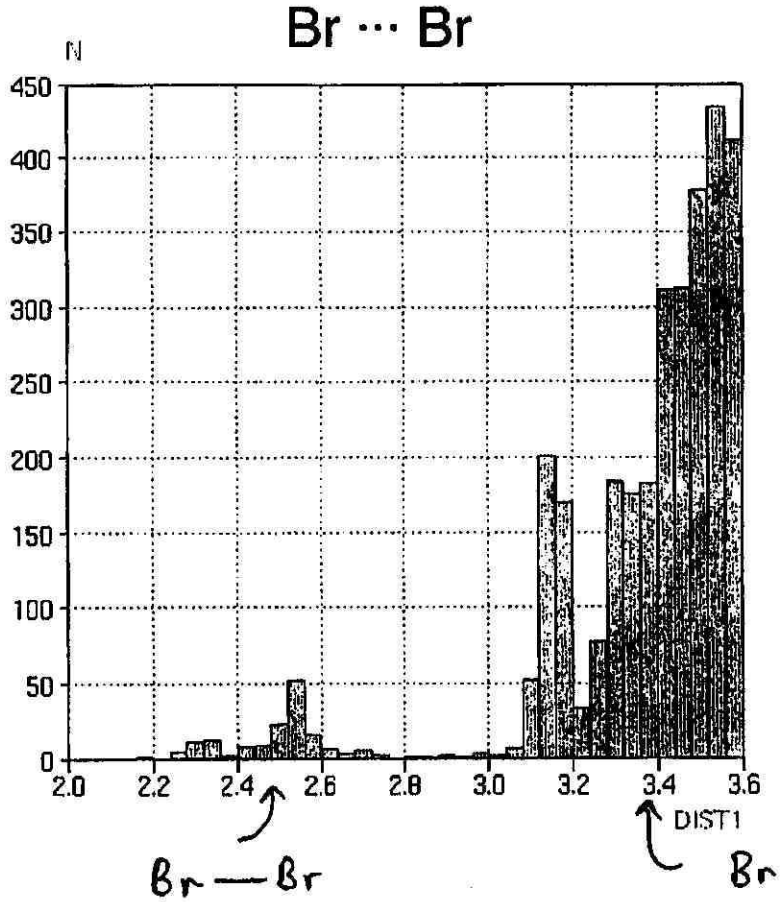
① With organic chemistry & the elements C, N, H, O, F the definition of what is a bond & what is not a bond is experimentally sharp. Pairs of C atoms less than 1.7 Å apart are bonded to eachother. In the 10^8 or more C···C distances which have been determined in molecules no C···C distance has ever been found from 1.7 to 2.0 Å. So we say C···C distances shorter than this are C–C and C···C distances longer than this are not bonds.

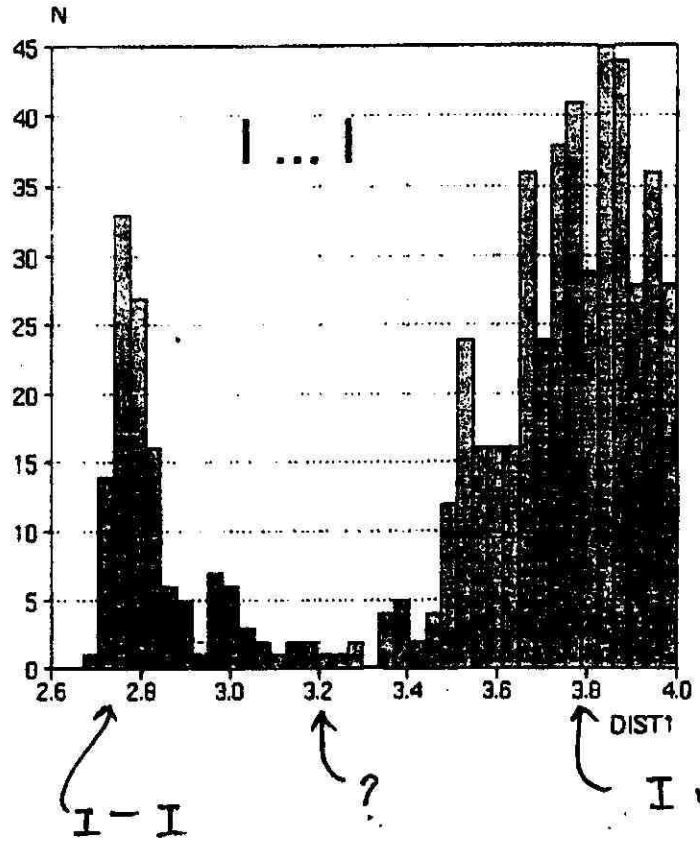
② Data (from solved crystal structure):

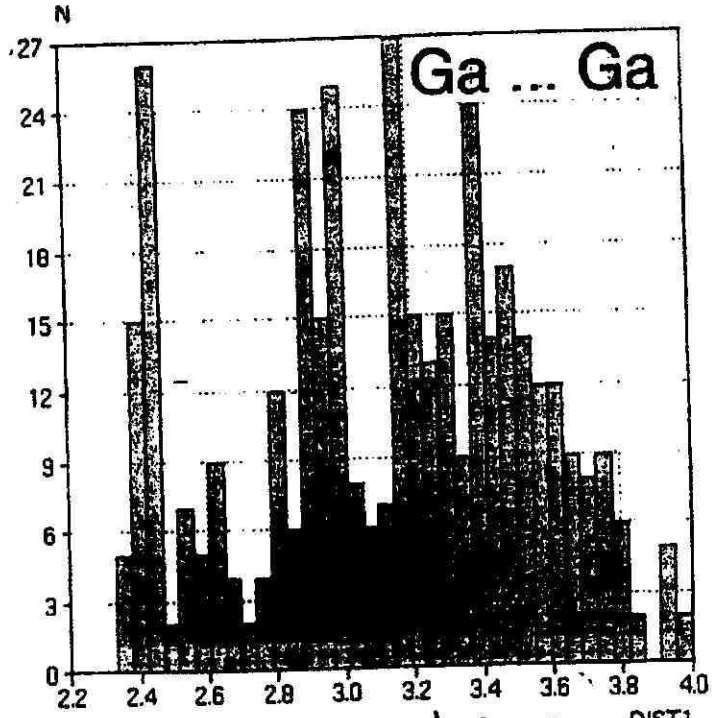


<1% of all C...C crystal data

Compare to Br, I and Ga:



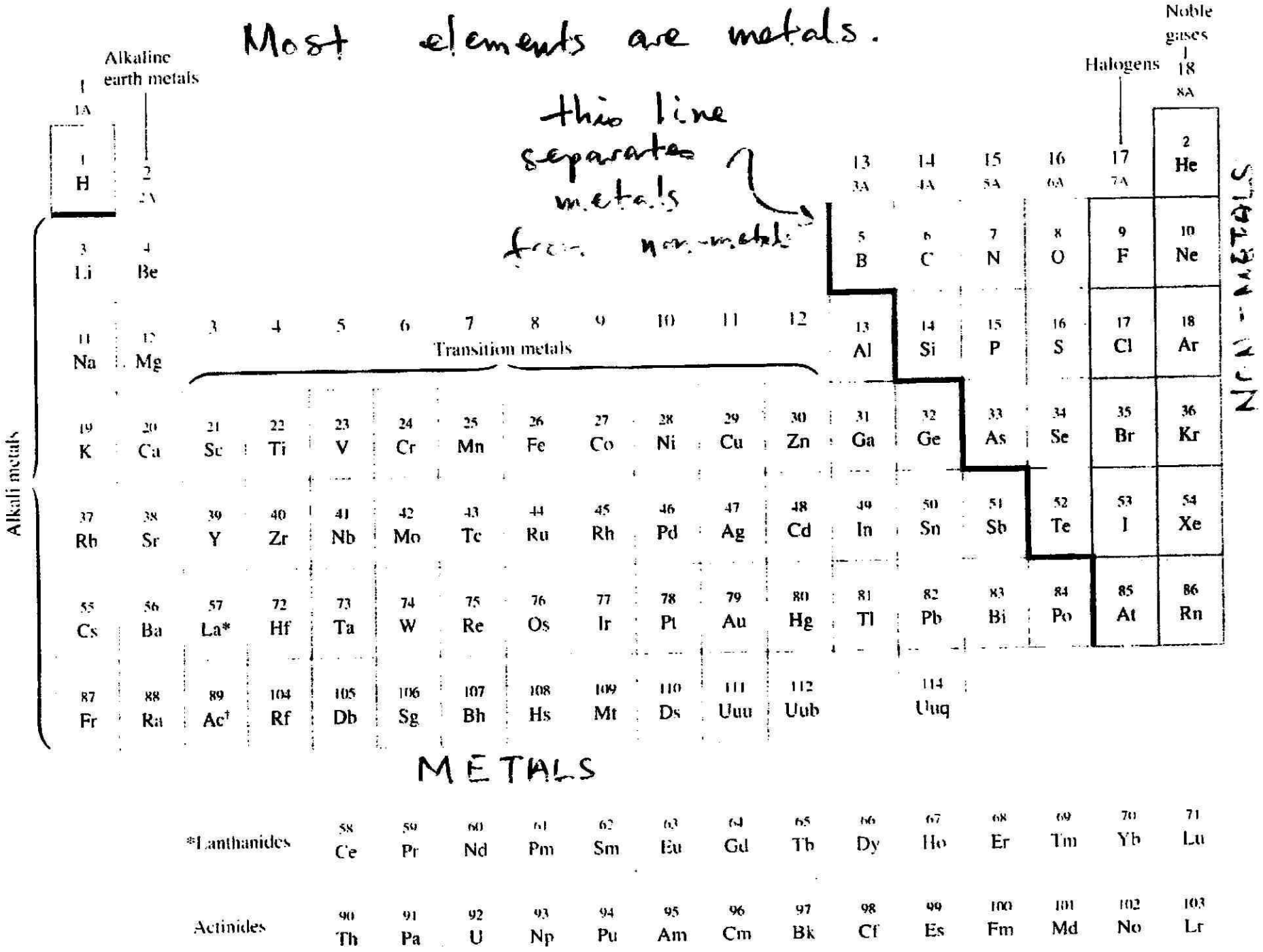




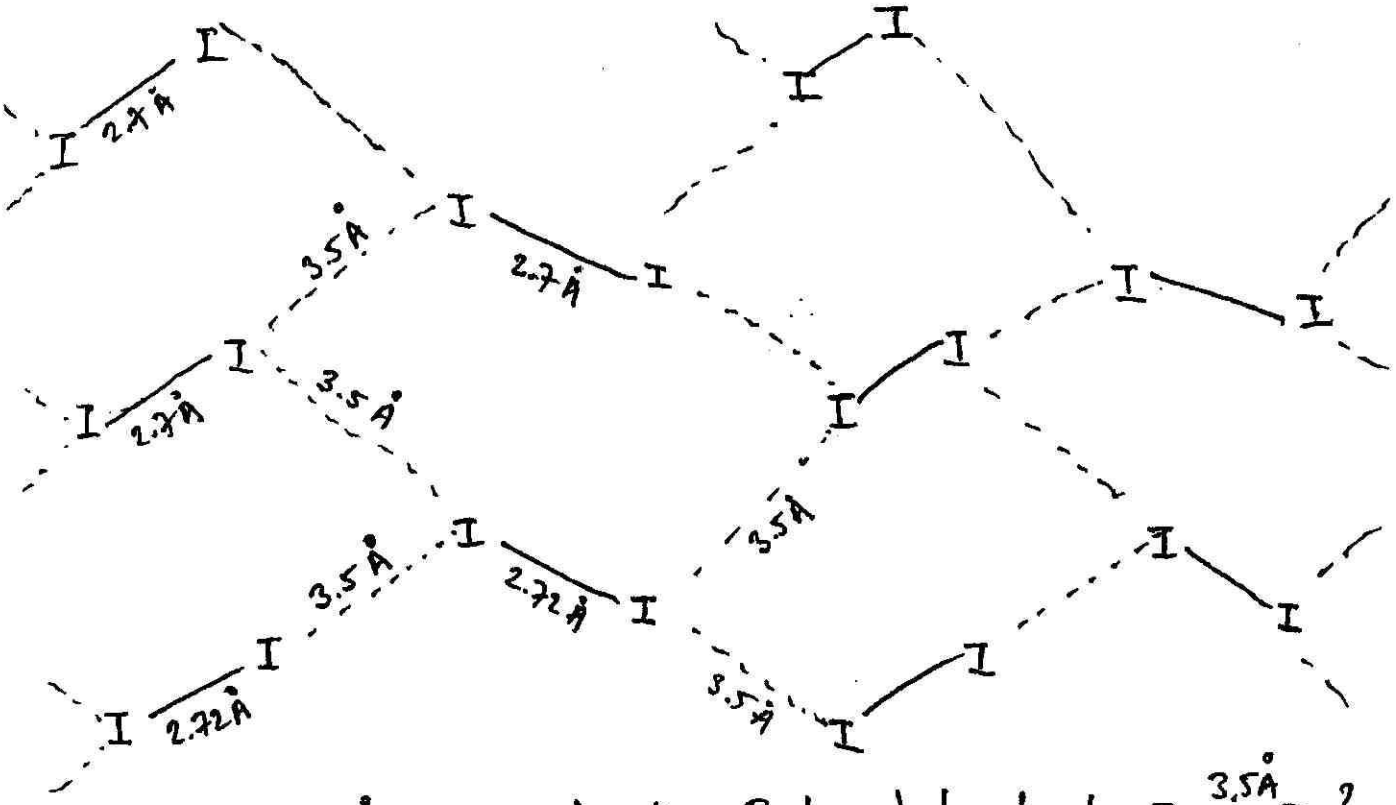
No clear def'n of what Ga is bonded to Ga...

By the time one reaches Ga (which is a metal) the "gap" between bonds and non-bonds is lost.

In general, in metals there are too many contacts for 2 e^- / bond. And in metals, the very comfortable idea of a "bond" becomes somewhat lost.

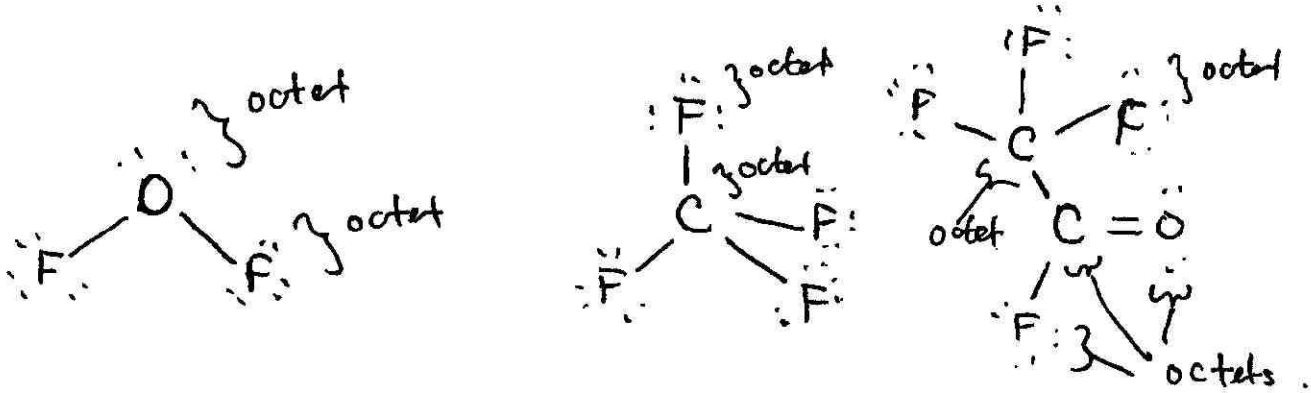

Most elements are metals.
this line separates metals from non-metals
Alkaline earth metals
Halogens
Noble gases
Alkali metals
Transition metals
NON-METALS
METALS
1 1A
2 2A
3 3A
4 4A
5 5A
6 6A
7 7A
8 8A
1 H
2 He
3 Li
4 Be
5 B
6 C
7 N
8 O
9 F
10 Ne
11 Na
12 Mg
3 4 5 6 7 8 9 10 11 12
13 Al
14 Si
15 P
16 S
17 Cl
18 Ar
19 K
20 Ca
21 Sc
22 Ti
23 V
24 Cr
25 Mn
26 Fe
27 Co
28 Ni
29 Cu
30 Zn
31 Ga
32 Ge
33 As
34 Se
35 Br
36 Kr
37 Rb
38 Sr
39 Y
40 Zr
41 Nb
42 Mo
43 Tc
44 Ru
45 Rh
46 Pd
47 Ag
48 Cd
49 In
50 Sn
51 Sb
52 Te
53 I
54 Xe
55 Cs
56 Ba
57 La*
72 Hf
73 Ta
74 W
75 Re
76 Os
77 Ir
78 Pt
79 Au
80 Hg
81 Tl
82 Pb
83 Bi
84 Po
85 At
86 Rn
87 Fr
88 Ra
89 Ac†
104 Rf
105 Db
106 Sg
107 Bh
108 Hs
109 Mt
110 Ds
111 Uuu
112 Uub
114 Uuq
*Lanthanides
58 Ce
59 Pr
60 Nd
61 Pm
62 Sm
63 Eu
64 Gd
65 Tb
66 Dy
67 Ho
68 Er
69 Tm
70 Yb
71 Lu
Actinides
90 Th
91 Pa
92 U
93 Np
94 Pu
95 Am
96 Cm
97 Bk
98 Cf
99 Es
100 Fm
101 Md
102 No
103 Lr

⑨ As we saw in the previous examples, the definition of what is and what is not a bond is not completely well defined for I. Consider the structure of the element iodine itself (the structure is determined by X-ray diffraction)



I – I 2.7 Å is a bond. But what about I ····· I (3.5 Å)?

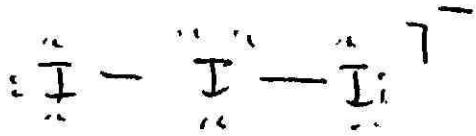
⑯ These extra I connections are unexpected from the chemistry of C, N, O & F. For these elements each atom always keeps an octet of e^- around it (see next page)



⑤ Consider now I_2 & I^-. Each already has an octet of e^- around it:

& yet the reaction

$$I_2 + I^- \longrightarrow I_3^-$$



readily occurs. In this reaction the central I has as a product 10 e^- around it.

⑥ Systems like I_3^- with "extra" bonds are called "hypervalent".

We now consider the MO source for hypervalent interactions.

(7)

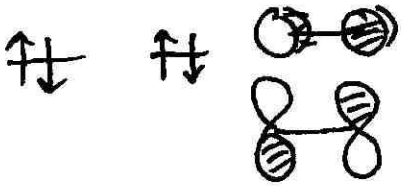
Iodine

$$I_2 + I^- \rightarrow I_3^-$$

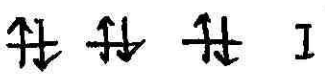
Let's draw MO's of two fragments and then make a Walsh diagram of the two fragments interacting together.

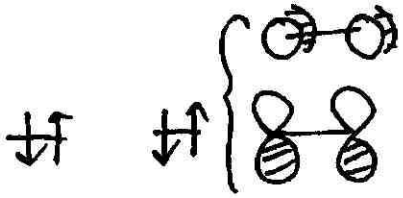
I^- has no valence LOMO.

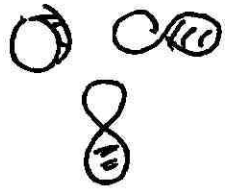
I_2



HOMO





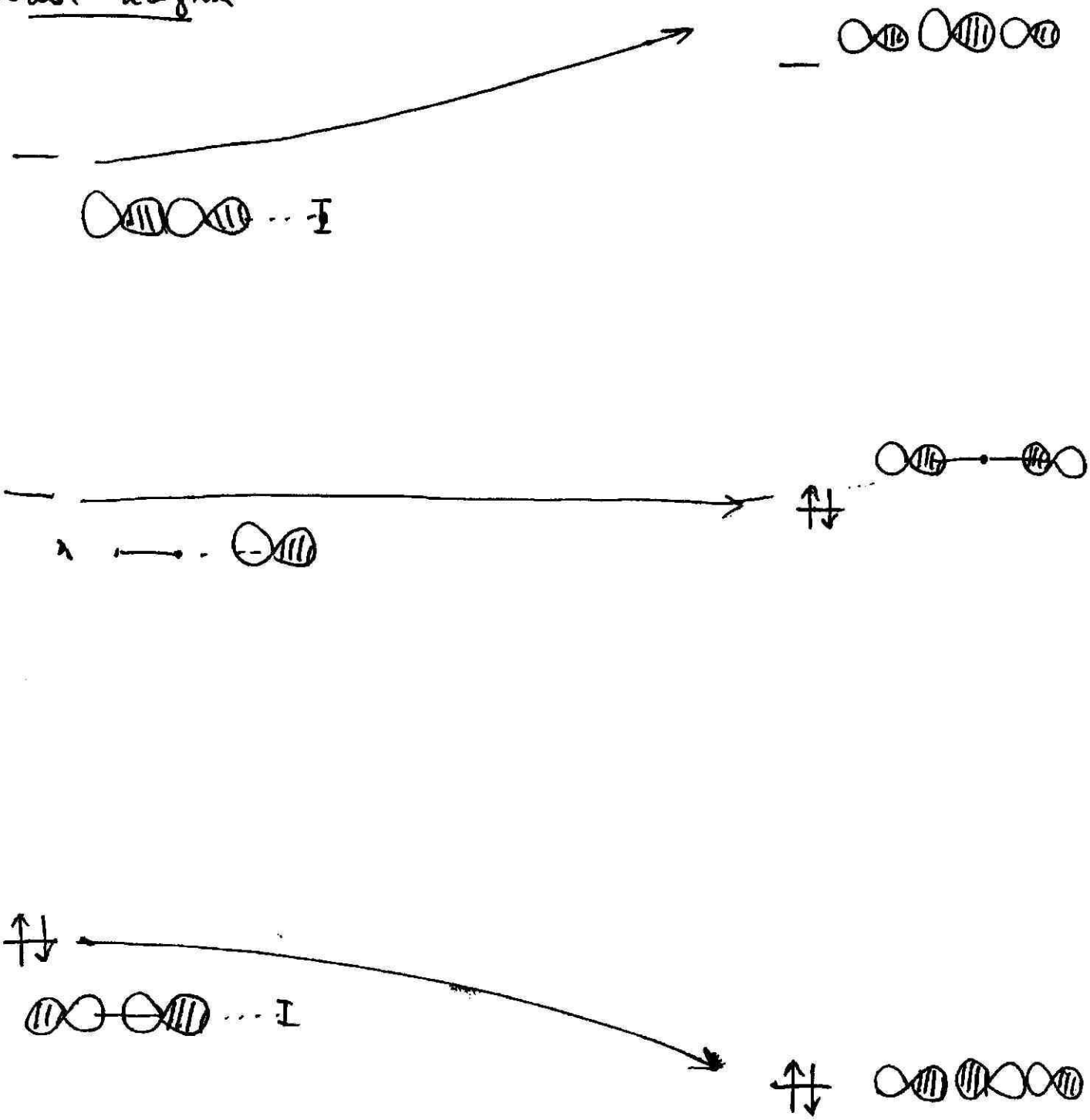


The key interaction : I_2 LUMO + I^- HOMO.

I_2 is a Lewis acid here, I^- a Lewis base

The optimal reaction geometry will be linear;

Walsh diagram



We see the reaction as

$$I - I \quad \longleftarrow \quad I^-$$

$$\Downarrow$$

$$I - I \cdots I^-$$

$$\Downarrow$$

$$I - I^- - I$$

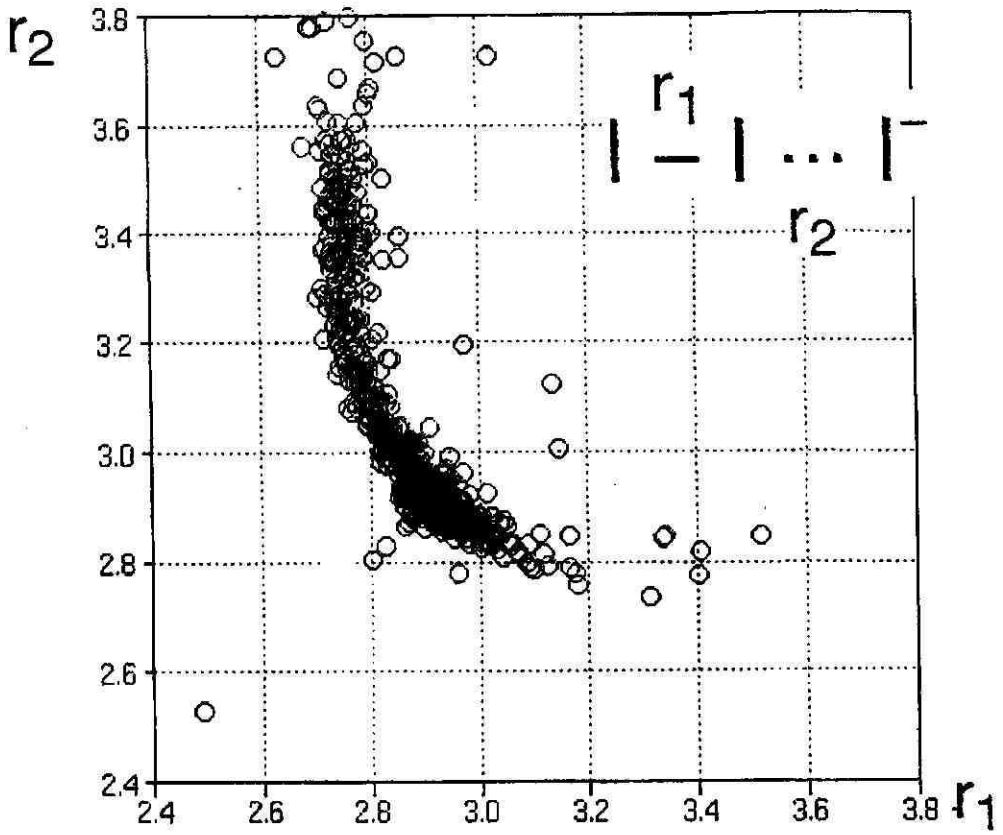
Three atoms stay linear.

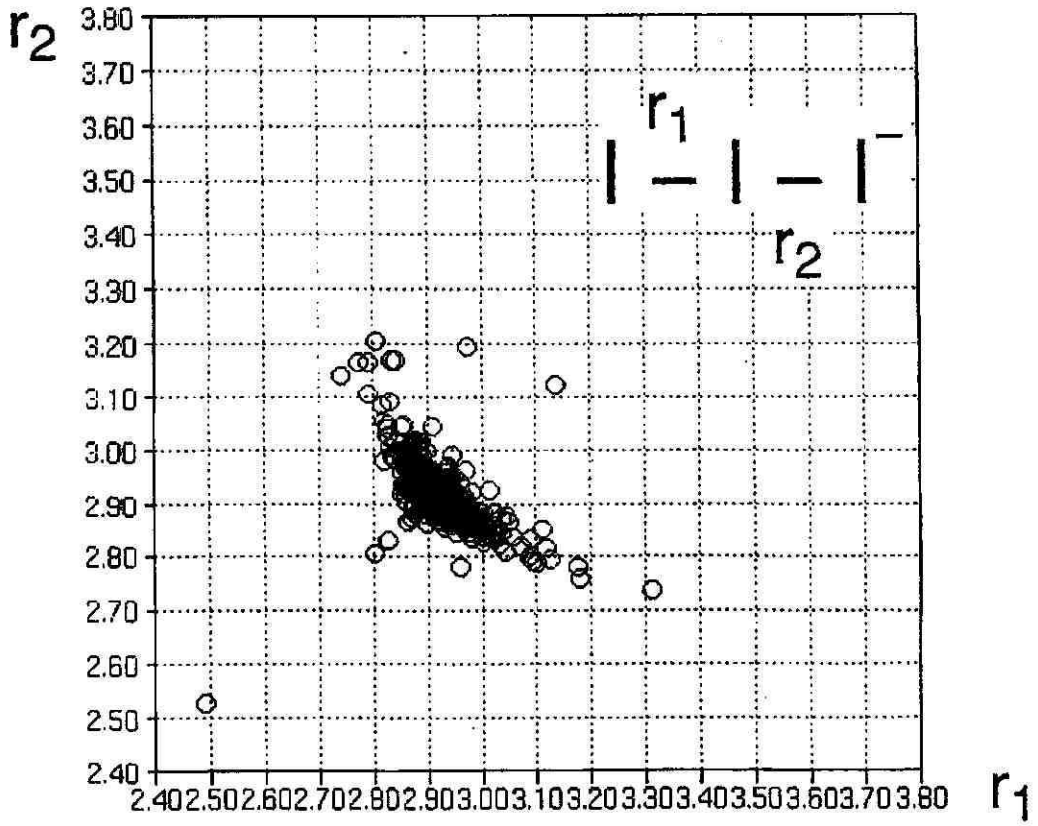
This reaction is "captured" in crystal structures

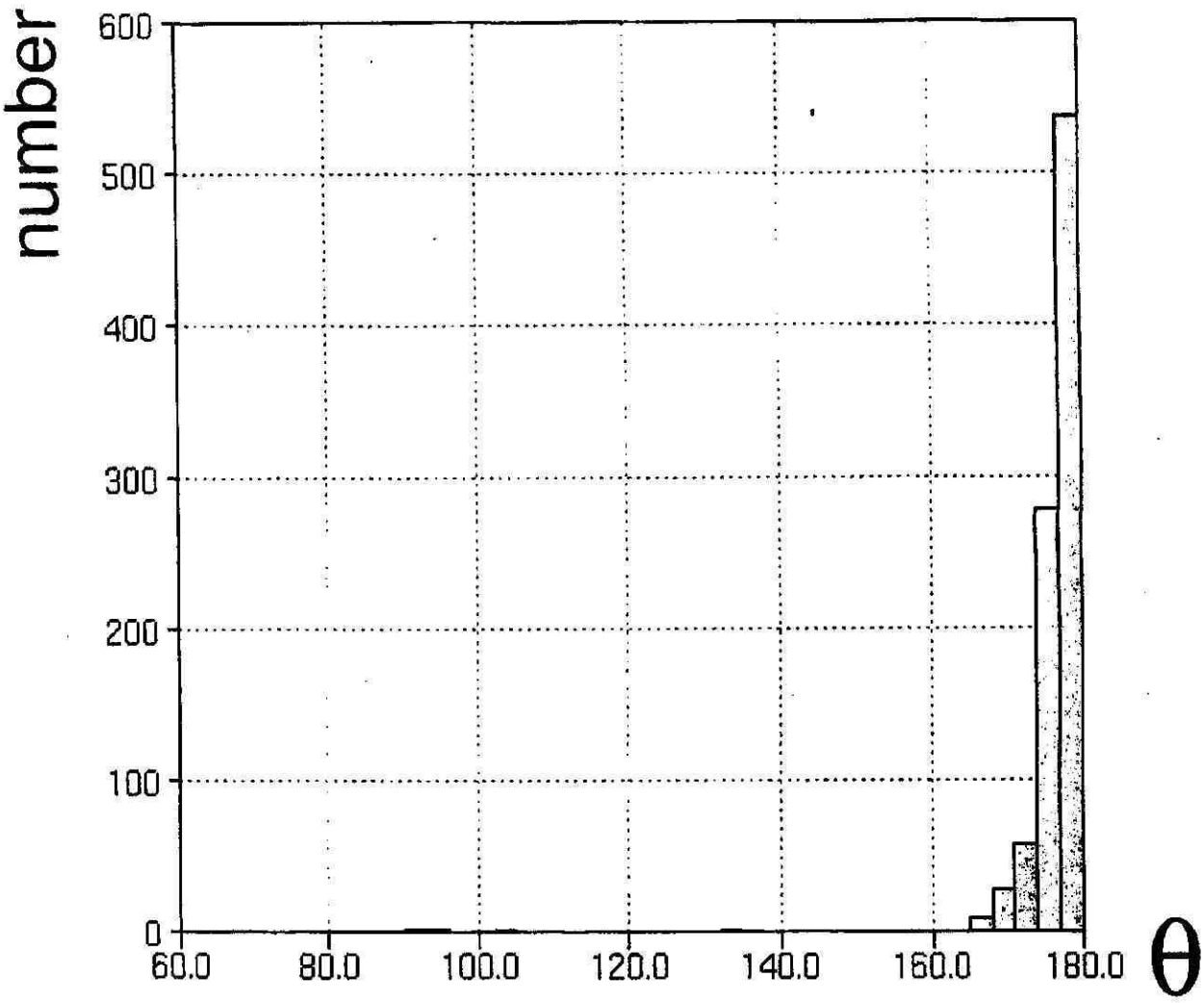
$$I \xrightarrow{r_1} I \cdots \overset{r_2}{\cdots} I^-$$

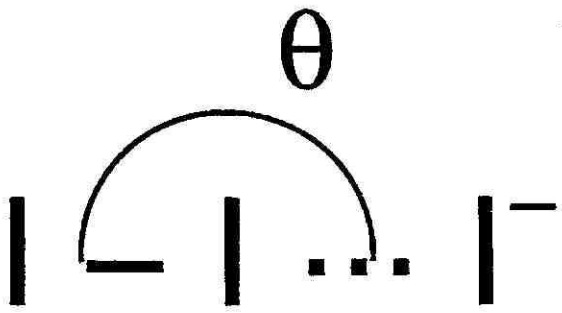
$$\theta$$

See next 2 page


r2
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
r1
I — I ... I
r1
r2
2.4
2.6
2.8
3.0
3.2
3.4
3.6
3.8
r1

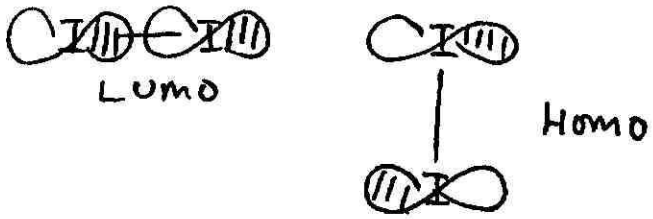

r2
3.80
3.70
3.60
3.50
3.40
3.30
3.20
3.10
3.00
2.90
2.80
2.70
2.60
2.50
2.40
r1
I — I — I
r1
r2
2.40 2.50 2.60 2.70 2.80 2.90 3.00 3.10 3.20 3.30 3.40 3.50 3.60 3.70 3.80
r1


number
600
500
400
300
200
100
0
60.0
80.0
100.0
120.0
140.0
160.0
180.0
θ


θ
I
I
I⁻

This same reasoning can be used to find the optimal arrangements of I_2 molecules

two I_2's



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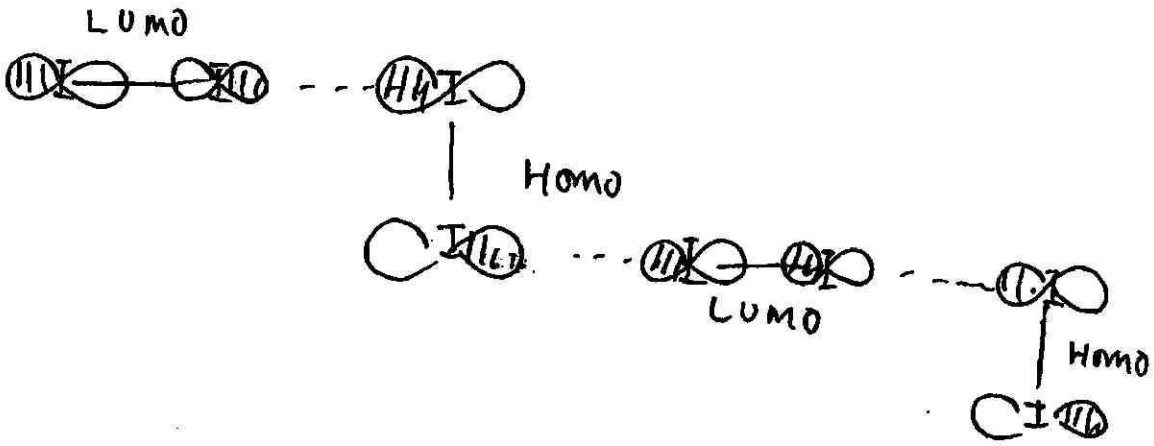
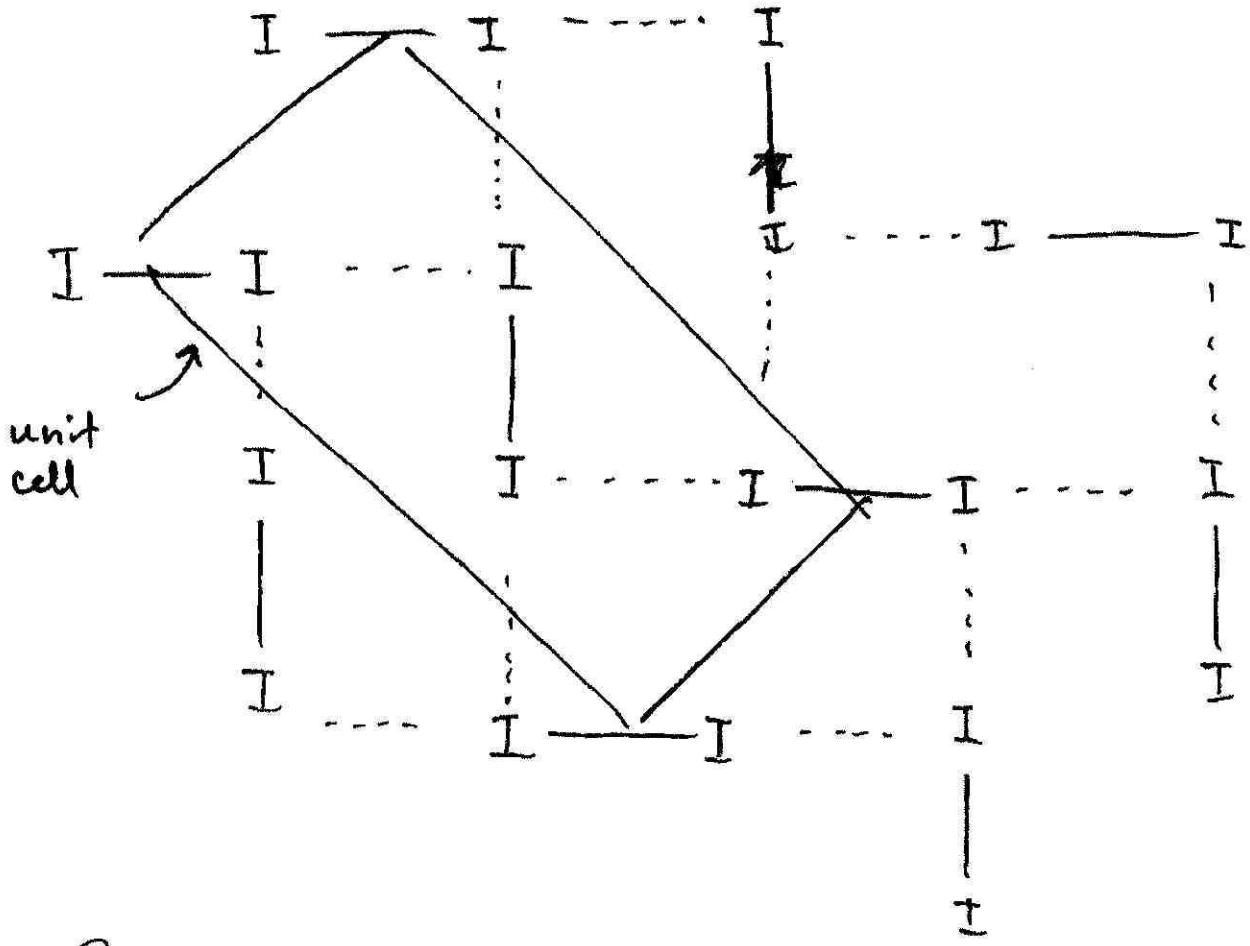
chain of I_2's:



& finally on the next page

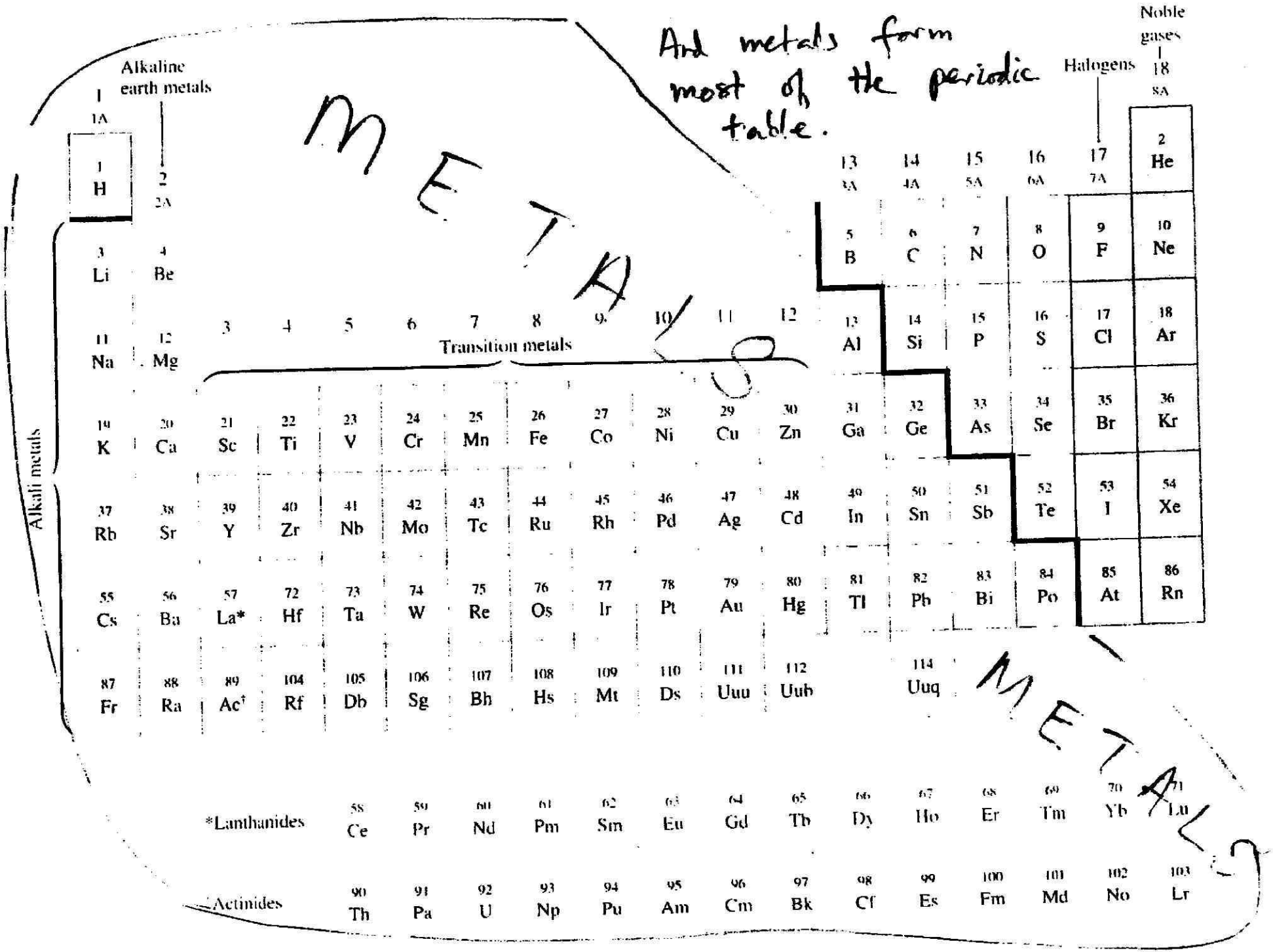
sheets of I_2's.



This is the crystal structure of Iodine, the element.

Conclusion: One of the onsets of metallic bonding is Lewis acid - Lewis base interactions.

In other words: ① In elements which are near metals we begin to see extra bonds ② In metals there are lots of extra bonds ③ We find for I that these extra bonds are Lewis acid / Lewis base related ④ We conclude that for metals, the extra bonds are Lewis acid / Lewis base related.


And metals form most of the periodic table.
METALS
Alkaline earth metals
Halogens
Noble gases
Alkali metals
Transition metals
*Lanthanides
†Actinides
METALS