# 杨振宁 <br> 的三篇学位论文 

Chen Ning Yang＇s Theses With Commentary

朱邦芬 阮东 编

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\begin{array}{ll} 
& \text { 谨 } \\
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\]



西南联大硕士研究生毕业时的杨振宁（1944）


芝加哥大学博士研究生毕业时的杨振宁（1948）

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# Comments on My Three Theses 

Chen Ning Yang

Professors B．F．Zhu and R．Dong proposed to publish the 3 theses which I wrote in the 1940s．Each of the three was very important for my later research work，important in very different ways．So I thought detailing their respective influence on me may be useful for graduate students at the beginning of their careers．

## 1942 thesis for my BSc degree

At the Southwestern Associated Uni－ versity where I matriculated， 1938 to 1942， students were required to submit a thesis for their BSc degree．I had taken a course in quantum theory from Professor T．Y． Wu（吴大猷）．So I went to him asking him to be my supervisor．What then happened I had described，as follows ${ }^{1}$ ：
he gave me a copy of an article


With Professor Wu， 1982 in StonyBrook． by J．E．Rosenthal and G．M．Murphy in the 1936 volume of Reviews of Modern Physics．It was a review paper on group theory and molecular spectra．I was thus introduced to group theory in physics．In retrospect I am deeply grateful to Wu for this introduction，since it had a profound effect on my subsequent development as a physicist．

The importance to me of this early introduction to group theory＇s role in physics cannot be overemphasized．And I was deeply aware of this already in the early 1950s． In October 1957，one day after I learned I was to receive the Nobel Prize jointly with T．D．Lee，I wrote to Professor Wu²：

[^1]At this moment of great excitement，that also calls for deep personal reflection，it is my privilege to express to you my deep gratitude for your having initiated me into the field of symmetry laws and group theory in the spring of 1942．A major part of my subsequent work，including the parity problem，is traceable directly or indirectly to the ideas that I learned with you that spring fifteen years ago．This is something that I have always had an urge to tell you，but today is a particularly appropriate moment．

## 1944 thesis for my MSc degree

This thesis was written under the direction of Professor J．S．Wang（王竹溪）．It consisted of two papers on the spe－ cific heat of alloys，using approximations which were very popular at the time．The main ideas of such approximations are now called mean field theory．Neither paper made any impact in the field，but they did introduce me to statistical mechanics，in two important ways：


Professor Wang，early 1980s in StonyBrook．
（1）I was deeply impressed by Gibbs．I still remember vividly today reading his papers on the phase rule in an obscure journal published in Connecticut．［It is amazing that such an obscure journal was in the library of LianDa．］More important，his little book Elementary Principles of Statistical Mechanics converted me to an ardent admirer of his．I was to write in $1963^{3}$ ：

The beauty of his Elementary Principles of Statistical Mechanics is sheer poetry．
（2）Statistical mechanics became one of my two major areas of research work．I still remember today Professor Wang excitedly telling me，one day in 1945，the breakthrough Onsager had made in the Ising model．I tried to understand this breakthrough，first in Kunming，later in Chicago in 1947，both without success．But finally in 1949，in a station wagon ride，I learned from Luttinger of a new paper by Kaufman and Onsager． And that led to my lifelong interest in statistical mechanics．

[^2]
## 1948 thesis for my PhD degree

During the first 9 month of 1946 I worked closely with Professor Teller. He had around 6 or 7 graduate students, and met us every week or two for lunch, to discuss our research. He also asked me to grade exercise papers of his students. So I had ample opportunity to observe his style of doing physics. He had very good physical intuition, especially about symmetries in atomic, molecular and nuclear physics. But he lacked patience to fill in the logical steps behind his intuition. For example as early as 1941 he had made, in a paper with Critchfield, statements about complexities in nuclear reactions involving particles with spin, but did not give any proofs. I began to think about how to supply complete proofs.


With Professor Teller, 1982 in Brookhaven National Laboratory.

In the late 1940s low energy nuclear physics was one of the most active fields. In particular there began experiments about correlations, such as $\beta-\gamma$ and $\gamma-\gamma$ correlations. Theoretical calculations were published about such correlations, showing very surprisingly that the final results often were very simple after unexpected cancellations. I did some of these calculations and soon realized that


With Professor Teller, 1990s. the cancellations must be mathematical consequences of the spherical symmetry of nuclear physics. But to substantiate such a statement required detailed mathematical analysis. This I succeeded in doing after a few weeks of analysis, and that was how my PhD thesis came about.

This thesis greatly increased my appreciation of the power of symmetry considerations in understanding natural laws. It happened that to study the newly discovered "strange particles" it was necessary to first determine their spin, parity and other quantum umbers, i.e. their symmetry properties. Thus I was able,
one year after my thesis，to publish a paper on the spin and parity of the $\pi^{0}$ meson． This paper made me famous because it was in direct competition with L．Landau．

I should mention here that this $\pi^{0}$ paper used heavily field theory，which I had learned，very thoroughly in 1943－1945，from Professor S．T．Ma（马仕俊）．

In Chicago I was interested in using symmetry considera－ tions not only on experiment re－ lated problems，such as those in my PhD thesis，but also on a more fundamental problem：the basic equations governing inter－ actions between particles．Thus in 1947 I tried to generalize Weyl＇s gauge symmetry to non－ Abelian groups．This effort met with smooth sailing at the be－ ginning，but soon got into messy


With Professors Wu and Ma， 1949. technical problems，and I had to give up．Fortunately I did return to it in 1954，at Brookhaven with Robert Mills．We succeeded in overcoming the technical difficulty and published a short paper on it ${ }^{4}$ ． That paper has now become one of the most important papers in physics after WWII．

[^3]
# Group Theory and the Vibration of Polyatomic Molecules 

# GROUP THEORY AND THE VIBRATION OF POLYATOMIC MOLECULES 

Cheng－Ning Yang（楊振寧）

## INTRODUCTION

Informations about the structure of molecules can always be drawn from the anal－ ysis of their vibrational spectra，but owing to the mathematical difficulties involved in the theoretical calculation，only very simple types of molecules can be studied．The method developed by Bethe ${ }^{1}$ in 1929，and then more completely by Wigner ${ }^{2}$ ，however， removed considerably this difficulty．It is our purpose here to present the method together with some of the developments after them．A new method of finding the sym－ metrical coordinates is given（§4），in which the symmetry is preserved from step to step in spite of the existence of redundant coordinates．The theorem in $\S 5$ which renders the calculation of the degree of degeneracy very simple is also believed to be new．

## The Symmetry of a Molecule

## §1 MATHEMATICAL EXPRESSION OF SYMMETRY

There are reasons to suppose that the nuclei in a molecule arrange themselves in symmetrical positions when in equilibrium；i．e．some operations（Consisting of reflec－ tions and rotations）bring the molecule into itself．（For molecules containing isotopes this statement must be slightly modified．cf．§18）If we choose a set of rectangular coordinate axes with the origin at the centre of mass of the molecule in equilibrium， each covering operation $C$ can be represented by an orthogonal matrix $\Gamma_{c}$（order： $3 \times 3$ ） so that the point $\left(\begin{array}{l}X \\ Y \\ Z\end{array}\right)$ is brought to $\Gamma_{c}\left(\begin{array}{l}X \\ Y \\ Z\end{array}\right)$ by the operation．Let $\boldsymbol{r}_{1}, \boldsymbol{r}_{2}, \cdots, \boldsymbol{r}_{n}$ be a set of coordinates specifying the relative positions of the nuclei（e．g．the distances between the nuclei and the angles between the bonds）in the molecule．When the nuclei
vibrate about their positions of equilibrium，these $\boldsymbol{r}$＇s vary（cf．§6）．Let $R_{1}, R_{2}, \cdots$ ， $R_{n}$ be their increments．Further，let $x_{1}, y_{1}, z_{1}, x_{2}, \cdots, x_{N}, y_{N}, z_{N}$ be the increments of the rectangular coordinates of the $N$ nuclei．For small vibrations the $R$＇s are linear in the $x$＇s，$y$＇s and $z$＇s：

$$
R=\left(\begin{array}{c}
R_{1}  \tag{1}\\
R_{2} \\
\vdots \\
R_{n}
\end{array}\right)=B \mathscr{C}, \quad \text { where } \mathscr{C}=\left(\begin{array}{c}
x_{1} \\
y_{1} \\
\vdots \\
z_{N}
\end{array}\right)
$$

$B$ being a constant matrix of $n$ rows and $3 N$ colomns．Now after the operation $C$ ，the molecule is indistinguishable from its original self，and we have a new equation obtained by writing（1）down for the new molecule：

$$
\begin{equation*}
\stackrel{c}{R}=B \stackrel{c}{\mathscr{C}} \tag{2}
\end{equation*}
$$

Here $\stackrel{c}{R}$＇s are the coordinates of the molecule which will be brought into coincidence with $R$＇s by the operation $C$ ，and

$$
\mathscr{C}=\left(\begin{array}{c}
\Gamma_{c}\left(\begin{array}{c}
x_{C^{-1} 1} \\
y_{C^{-1}} \\
z_{C^{-1}}
\end{array}\right)  \tag{3}\\
\vdots \\
\Gamma_{c}\left(\begin{array}{c}
x_{C-1} \\
y_{C-1 N} \\
z_{C-1 N}
\end{array}\right)
\end{array}\right)
$$

where $C^{-1} i$ is the nucleus which will become after the operation $C$ the nucleus $i$ ．Let $Z_{c}$ be a square matrix of order $3 N$ with the elements

$$
{ }_{i x}\left(Z_{c}\right)_{j x}=\delta_{j, C^{-1} i}, \quad{ }_{i x}\left(Z_{c}\right)_{j y}=0 \quad \text { etc. } \quad i, j=1,2, \cdots, N,
$$

and let $P_{c}$ stand for $\left(\begin{array}{cccc}\Gamma_{c} & & & \\ & \Gamma_{c} & & \\ & & \ddots & \\ & & & \Gamma_{c}\end{array}\right)$ ，then（2）and（3）give

$$
\begin{equation*}
\stackrel{c}{R}=B P_{c} Z_{c} \mathscr{C} . \tag{4}
\end{equation*}
$$

This equation holds for every operation $C$ and is the mathematical expression of the symmetry of the molecule．

EXAMPLE Consider three equivalent nuclei forming an equilateral triangle. Let $C$ be the operation: Rotation counterclockwise through $120^{\circ}$ about $O$. Then


$$
C^{-1} 1=3, \quad C^{-1} 2=1, \quad C^{-1} 3=2
$$

and

Let $R_{1}$ be the increment of the distance $\overline{12}$.

$$
R_{1}=\frac{1}{2} x_{1}+\frac{\sqrt{3}}{2} y_{1}-\frac{1}{2} x_{2}-\frac{\sqrt{3}}{2} y_{2} .
$$

Then $\stackrel{c}{R_{1}}$ is that of $\overline{31}$, and

$$
\stackrel{c}{R_{1}}=-\frac{1}{2} x_{1}+\frac{\sqrt{3}}{2} y_{1}+\frac{1}{2} x_{3}-\frac{\sqrt{3}}{2} y_{3} .
$$

Thus

$$
B=\left(\begin{array}{ccccccccc}
\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0
\end{array}\right) .
$$

(4) becomes the identity

$$
\left.\begin{array}{rl}
-\frac{1}{2} x_{1}+\frac{\sqrt{3}}{2} y_{1}+\frac{1}{2} x_{3}-\frac{\sqrt{3}}{2} y_{3}= & \left(\begin{array}{cccccc}
\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0
\end{array} 0\right. \\
0 & 0
\end{array}\right) 0.0 .
$$

## §2 FUNDAMENTAL RELATIONSHIP

In some instances the coordinates $R_{1}, R_{2}, \cdots, R_{n}$ are sufficient to determine ${ }^{c}{ }_{1}$ ， $\stackrel{c}{R}_{2}, \cdots, \stackrel{c}{R}_{n}$ for all covering operations $C$ ．This is the case if（i）the $R$＇s contain only $R_{1}$
complete sets of equivalent coordinates（e．g．in the last example when $R_{2}=$ increment $R_{3}$
$3 \widehat{12}$
of $1 \widehat{2} 3$ ）；or if（ii）the $R$＇s are all that are necessary to describe the internal structure of $2 \widehat{3} 1$
the molecule．In both cases we have for small vibrations $\stackrel{c}{R}=A_{c} R$ ，where $A_{c}$ is in case （i）an orthogonal matrix having as elements 0 or 1 ，and in case（ii）a matrix of order $n \times n$ ． By （4），

$$
B P_{c} Z_{c} \mathscr{C}=\stackrel{c}{R}=A_{c} R=A_{c} B \mathscr{C} .
$$

But $\mathscr{C}$ is arbitrary（cf．$\S 6$ ），hence

$$
\begin{equation*}
B P_{c} Z_{c}=A_{c} B . \tag{5}
\end{equation*}
$$

This is the fundamental relationship on which all the following deductions are based．

## §3 GROUP PROPERTIES

To make further developments we notice that the covering operations $C$ form a group and that the $P_{c}$＇s，$Z_{c}$＇s and $A_{c}$＇s each form a group isomorphic ${ }^{*}$ with it．The group is known as the＂point group＂．They are of such importance that their properties have been investigated in detail．${ }^{3}$

## Choice of Internal Coordinates

## §4 INDEPENDENT REDUCED COORDINATES

We first choose the coordinates $R_{1}, R_{2}, \cdots, R_{n}$ so that they contain only complete sets of equivalent internal coordinates，and such that they are more than necessary for the determination of the structure of the molecule．The simplest way is to choose the increments of the internuclear distances and the bond angles as the $R$＇s．In the example

[^4]of $\S 1$ we may take the increments of the bonds $\overline{12}, \overline{23}$ and $\overline{31}$ as $R_{1}, R_{2}$ and $R_{3}$; or those of the lengths $\overline{O 1}, \overline{O 2}, \overline{O 3}$ and the angles $1 \widehat{O} 2,2 \widehat{O} 3$ and $3 \widehat{O} 1$ as the $R$ 's. The matrix $B$ can now be determined ( $\S \S 11,12$ ). Evidently our choice belongs to the case (i) of $\S 2$, so that the $A_{c}$ 's are orthogonal and have as elements 0 or 1 . It is plain that ${ }_{i}\left(A_{c}\right)_{j}=0$ if $R_{i}$ and $R_{j}$ are not equivalent. We shall make use of the following theorem in group theory ${ }^{5}$ :

If $A_{c}$ form a group of orthogonal matrices, and $W_{c}^{\alpha}(\alpha=1,2, \cdots, k)$ are the irreducible orthogonal representations of the group, there exists an orthogonal matrix $M$ such that $W_{c}=M A_{c} M^{-1}$ is of the form

$$
\left(\begin{array}{ccccccc}
W_{c}^{1} & & & & & 0 &  \tag{6}\\
& W_{c}^{1} & & & & & \\
& & \ddots & & & & \\
& & & W_{c}^{1} & & & \\
& & & & W_{c}^{2} & & \\
& & & & & \ddots & \\
& 0 & & & & & W_{c}^{k}
\end{array}\right)
$$

We define ${ }^{*} Q=\left(\begin{array}{c}Q_{1} \\ Q_{2} \\ \vdots \\ Q_{n}\end{array}\right)=M R$ as the "reduced coordinates" ${ }^{4}$. Evidently

$$
\stackrel{c}{Q}=M \stackrel{c}{R}=M A_{c} R=M A_{c} M^{-1} Q=W_{c} Q .
$$

Now not all the $Q$ 's are independent. To select out the independent ones we need the following theorem:

THEOREM It is always possible to drop out some of the $Q$ 's so that
(i) the remaining ones are all independent,
(ii) the dropped ones depend on the remaining ones,
and (iii) the remaining ones belong to complete blocks of the group of matrices $W_{c}$.
Because of the properties (i) and (ii), the remaining coordinates $\mathscr{R}=\left(\begin{array}{c}\mathscr{R}_{1} \\ \mathscr{R}_{2} \\ \vdots \\ \mathscr{R}_{3 N-6}\end{array}\right)$ are called the "independent reduced coordinates", and from (iii), $\stackrel{c}{\mathscr{R}}=\mathfrak{A}_{c} \mathscr{R}$ where $\mathscr{A}_{c}$ is

[^5]obtained from $W_{c}$ by dropping some blocks．These coordinates may also be obtained in other ways，and have been given various names by different authors．They are the＂in－ ternal symmetry coordinates＂of Wilson ${ }^{7}$ and the＂geometrical symmetry coordinates＂ of Rosenthal and Murphy ${ }^{8}$ ．The relation between $\mathscr{R}$ and the＂symmetry coordinates＂ of Howard and Wilson ${ }^{11,9}$ will be given in $\S 14$ ．

PROOF OF THE THEOREM Since $Q$ is not entirely arbitrary，there exists a matrix $H$ of order $\nu \times n$ so that

$$
\begin{equation*}
H H^{\prime}=I, \quad H Q=0, \tag{7}
\end{equation*}
$$

where $I$ is the unit matrix and the＇stands for＂transposed＂．We may prove that the rank of $H$ is $\nu$ and that there exists a matrix $H_{1}$ of order $(n-\nu) \times n$ such that $\binom{H}{H_{1}}$ is orthogonal．Put $\binom{H}{H_{1}} Q=\binom{0}{Q_{1}}$ ，then

$$
Q=\left(\begin{array}{ll}
H^{\prime} & H_{1}^{\prime} \tag{8}
\end{array}\right)\binom{0}{Q_{1}}=H_{1}^{\prime} Q_{1} .
$$

We may suppose that $\nu=n-(3 N-6)$ so that $Q_{1}$ is arbitrary．The equ．$H Q=0$ must be invariant under an operation $C$ ：

$$
0=H \stackrel{c}{Q}=H W_{c} Q=H W_{c} H_{1}^{\prime} Q_{1} .
$$

Hence

$$
H W_{c} H_{1}^{\prime}=0 .
$$

Thus

$$
\binom{H}{H_{1}} W_{c}\left(H^{\prime} H_{1}^{\prime}\right)=\left(\begin{array}{cc}
H W_{c} H^{\prime} & 0 \\
H_{1} W_{c} H^{\prime} & H_{1} W_{c} H_{1}^{\prime}
\end{array}\right) .
$$

This matrix is orthogonal（for $\binom{H}{H_{1}}$ and $W_{c}$ are both orthogonal）．Hence

$$
\binom{H}{H_{1}} W_{c}\left(H^{\prime} H_{1}^{\prime}\right)=\left(\begin{array}{cc}
H W_{c} H^{\prime} & 0  \tag{9}\\
0 & H_{1} W_{c} H_{1}^{\prime}
\end{array}\right) .
$$

Thus $H W_{c} H^{\prime}$ is orthogonal and forms a group isomorphic with the one formed by $C$ ； i．e．

$$
\left(H W_{c^{\prime}} H^{\prime}\right)\left(H W_{c} H^{\prime}\right)=H W_{c c^{\prime}} H^{\prime}
$$

By the theorem quoted above there exists an orthogonal matrix $J$ such that $J H W_{c} H^{\prime} J^{\prime}=$ $\omega_{c}$ is of the form (6); i.e. if the "untermatrices" of $W_{c}$ are

$$
{ }_{\alpha \beta}\left(W_{c}\right)_{\alpha^{\prime} \beta^{\prime}}=\delta_{\alpha \alpha^{\prime}} \delta_{\beta \beta^{\prime}} W_{c}^{\alpha}, \quad \alpha=1,2, \cdots, k, \quad \beta=1,2, \cdots, n_{\alpha},
$$

those of $\omega_{c}$ must be

$$
{ }_{a b}\left(\omega_{c}\right)_{a^{\prime} b^{\prime}}=\delta_{a a^{\prime}} \delta_{b b^{\prime}} W_{c}^{a}, \quad a=1,2, \cdots, k, \quad b=1,2, \cdots, \mu_{a} .
$$

By (9), the irreducible blocks of $\omega_{c}$ must all be that of $W_{c}$, hence $\mu_{a} \leq n_{\alpha}$. Now

$$
(J H) W_{c}=J H W_{c}\left(H^{\prime} H_{1}^{\prime}\right)\binom{H}{H_{1}}=\left(\begin{array}{lll}
J H W_{c} H^{\prime} & 0 \tag{10}
\end{array}\right)\binom{H}{H_{1}}=\omega_{c} J H
$$

i.e.

$$
{ }_{a b}(J H)_{\alpha \beta} W_{c}^{\alpha}=W_{c}^{a}{ }_{a b}(J H)_{\alpha \beta} .
$$

But $W_{c}^{\alpha}$ is irreducible, hence ${ }^{6}$

$$
\begin{equation*}
{ }_{a b}(J H)_{\alpha \beta}=\delta_{a \alpha}{ }_{b} \lambda_{\beta}^{\alpha} I, \tag{11}
\end{equation*}
$$

where ${ }_{b} \lambda_{\beta}^{\alpha}$ is an ordinary number. Since $J H$ is of rank $\nu$, the submatrix $\left({ }_{b} \lambda_{\beta}^{\alpha}\right)(b=$ $\left.1,2,3, \cdots, \mu_{\alpha} ; \beta=1,2,3, \cdots, n_{\alpha}\right)$ is of rank $\mu_{\alpha}$. Thus for every $\alpha$ there exists a set $K_{\alpha}$ of $\mu_{\alpha}$ integers all $\leq n_{\alpha}$, such that the square matrix $\left({ }_{b} \lambda_{\beta}^{\alpha}\right)\left(b=1,2, \cdots, \mu_{\alpha} ; \beta\right.$ in $\left.K_{\alpha}\right)$ is nonsingular. Hence $J H$ may be divided into two untermatrices, one (of order $\nu \times \nu$ ) composed of those untermatrices (11) for which $\beta$ is in the set $k_{\alpha}$, and the other those for which $\beta$ is not in $K_{\alpha}$. The former is evidently nonsingular. Let $H_{2}$ and $H_{3}$ be the corresponding untermatrices of $H=J^{-1}(J H)$. Evidently a transposition of columns may bring $H$ into the form $\left(\begin{array}{ll}H_{2} & H_{3}\end{array}\right)$. Now the constraint on $Q$ is $H Q=0$. Hence a corresponding transposition of the rows of $Q$ bring it to $\binom{Q_{2}}{Q_{3}}$ so that

$$
H_{2} Q_{2}+H_{3} Q_{3}=0 .
$$

Since $H_{2}$ is nonsingular, $Q_{3}$ may be chosen as the independent variable, $Q_{2}$ being dependent on it. Thus the latter can be dropped and the conditions (i), (ii) and (iii) are satisfied.

## §5 CALCULATION OF SPUR ( $\mathfrak{A}_{c}$ )

Suppose that the constraints on the $R$ 's are given by

$$
\begin{equation*}
\mathscr{D} R=0 \quad \text { where } \mathscr{D} \mathscr{D}^{\prime}=I . \tag{12}
\end{equation*}
$$

## THEOREM

$$
\begin{equation*}
\operatorname{Spur}\left(\mathfrak{A}_{c}\right)=\operatorname{Spur}\left(A_{c}\right)^{\prime}-\operatorname{Spur}\left(\mathscr{D} A_{c} \mathscr{D}^{\prime}\right) \tag{13}
\end{equation*}
$$

This theorem makes the calculation of $\operatorname{Spur}\left(\mathfrak{A}_{c}\right)$ very simple（because the elements of $A_{c}$ are 0 or 1 ），and before the transformation from $R$ the $Q$ is carried out．Also it enables us to calculate the contributions of the different constraints separately．

PROOF The constraints on $R_{1}, R_{2}, \cdots, R_{n}$ are $\mathscr{D} R=0$ ．Hence we may take the matrix $H$ of（7）to be $\mathscr{D} M^{\prime}$ ．With the notation used there we have

$$
\begin{equation*}
\stackrel{c}{Q_{1}}=H_{1} \stackrel{c}{Q}=H_{1} W_{c} Q=H_{1} W_{c} H_{1}^{\prime} Q_{1} . \tag{14}
\end{equation*}
$$

Since the $\mathscr{R}$＇s are all independent，there exists $M_{1}$ such that $Q_{1}=M_{1} \mathscr{R}$ ．Hence

$$
\stackrel{c}{Q_{1}}=M_{1} \stackrel{c}{\mathscr{R}}=M_{1} \mathfrak{A}_{c} \mathscr{R}=M_{1} \mathfrak{A}_{c} M_{1}^{-1} Q_{1} .
$$

On comparison with（14）it follows that $H_{1} W_{c} H_{1}^{\prime}=M_{1} \mathfrak{A}_{c} M_{1}{ }^{-1}$ ．Thus

$$
\begin{aligned}
\operatorname{Spur}\left(\mathscr{A}_{c}\right) & =\operatorname{Spur}\left(H_{1} W_{c} H_{1}^{\prime}\right) \\
& =\operatorname{Spur}\left[\binom{H}{H_{1}} W_{c}\left(H^{\prime} H_{1}^{\prime}\right)\right]-\operatorname{Spur}\left(H W_{c} H^{\prime}\right) \\
& =\operatorname{Spur}\left(A_{c}\right)-\operatorname{Spur}\left(\mathscr{D} A_{c} \mathscr{D}^{\prime}\right) .
\end{aligned}
$$

EXAMPLE Consider the molecule $\mathrm{CH}_{3} \mathrm{Cl}$ ．Take

$$
\begin{aligned}
R_{1}, R_{2}, R_{3}, R_{4} & =\text { increments of the distances } \overline{\mathrm{CCl}}, \overline{\mathrm{CH}_{\alpha}}, \overline{\mathrm{CH}_{\beta}}, \overline{\mathrm{CH}_{\gamma}}, \\
R_{5}, R_{6}, R_{7} & =\text { increments of the angles } \mathrm{Cl} \widehat{\mathrm{C}} \mathrm{H}_{\alpha}, \mathrm{ClC}_{\beta}, \mathrm{Cl}_{\mathrm{C}}{ }_{\gamma}, \\
R_{8}, R_{9}, R_{10} & =\text { increments of the angles } \mathrm{H}_{\beta} \widehat{\mathrm{C}} \mathrm{H}_{\gamma}, \mathrm{H}_{\gamma} \widehat{\mathrm{C}} \mathrm{H}_{\alpha}, \mathrm{H}_{\alpha} \widehat{\mathrm{CH}}
\end{aligned}, .
$$



The constraint is

$$
\left[R_{5}+R_{6}+R_{7}\right] f+\left[R_{8}+R_{9}+R_{10}\right]=0
$$

where $f$ is a constant．Thus

$$
\mathscr{D}=\sqrt{\frac{1}{3 f^{2}+3}}(0000 f f f 111) .
$$

The theorem leads to

| Operation $C$ |  | $\operatorname{Spur}\left(A_{c}\right)$ | $\operatorname{Spur}\left(\mathscr{D} A_{c} \mathscr{D}\right)^{*}$ | $\operatorname{Spur}\left(\mathfrak{A}_{c}\right)$ |
| :---: | ---: | :---: | :---: | :---: |
| No Motion |  | $: C_{1}$ | 10 | 1 |
| 9 |  |  |  |  |
| Rotation about $\overline{\mathrm{CCl}}$ through | $120^{\circ}: C_{2}$ | 1 | 1 | 0 |
|  | $240^{\circ}: C_{3}$ |  |  |  |
| Reflection about the plane | $\mathrm{Cl} \mathrm{CH}_{\alpha}: C_{4}$ |  |  | 3 |
|  | $\mathrm{Cl} \mathrm{CH}_{\beta}: C_{5}$ | 4 | 1 |  |
|  | $\mathrm{ClCH}_{\gamma}: C_{6}$ |  |  |  |

## The Kinetic and the Potential Energies

## §6 CHOICE OF AXES

Suppose that $\left(\begin{array}{c}R_{1} \\ R_{2} \\ \vdots \\ R_{3 N-6}\end{array}\right)=R$ are the increments of $3 N-6$ independent internal coordinates. For small vibrations, $R=B \mathscr{C}$, where $\mathscr{C}=\left(\begin{array}{c}x_{1} \\ \vdots \\ z_{N}\end{array}\right)$ is defined in $\S 1$. Suppose that the equilibrium positions of the nuclei are, in rectangular coordinates, $\left(X_{1}, Y_{1}, Z_{1}\right),\left(X_{2}, Y_{2}, Z_{2}\right), \cdots,\left(X_{N}, Y_{N}, Z_{N}\right)$. Let $m_{1}, m_{2}, \cdots, m_{N}$ be their masses. Write

$$
F=\left(\begin{array}{llllllll}
m_{1} & 0 & 0 & m_{2} & 0 & 0 & \cdots & 0 \\
0 & m_{1} & 0 & 0 & m_{2} & 0 & \cdots & 0 \\
0 & 0 & m_{1} & 0 & 0 & m_{2} & \cdots & m_{N} \\
0 & m_{1} Z_{1} & -m_{1} Y_{1} & 0 & m_{2} Z_{2} & -m_{2} Y_{2} & \cdots & -m_{N} Y_{N} \\
-m_{1} Z_{1} & 0 & m_{1} X_{1} & -m_{2} Z_{2} & 0 & m_{2} X_{2} & \cdots & m_{N} X_{N} \\
m_{1} Y_{1} & -m_{1} X_{1} & 0 & m_{2} Y_{2} & -m_{2} X_{2} & 0 & \cdots & 0
\end{array}\right)
$$

[^6]Then the first column of $B\left(\begin{array}{ccc}\frac{1}{m_{1}} & & \\ & \ddots & \\ & & \frac{1}{m_{N}}\end{array}\right) F^{\prime}$ is the matrix $B\left(\begin{array}{c}1 \\ 0 \\ 0 \\ 1 \\ 0 \\ 0 \\ \vdots \\ \vdots \\ 0\end{array}\right)$ which is the
value of $R$ when all the nuclei are displaced by 1 unit of length along the $X$－axis．But the $R$＇s are the increments of internal variables，hence $B\left(\begin{array}{c}1 \\ 0 \\ 0 \\ 1 \\ 0 \\ 0 \\ \vdots \\ 0\end{array}\right)=0$ ．In the same way we can show that

$$
B\left(\begin{array}{ccc}
\frac{1}{m_{1}} & & \\
& \ddots & \\
& & \frac{1}{m_{N}}
\end{array}\right) F^{\prime}=0 .
$$

We have thus far described the the molecule in a certain system of rectangular coordinates．But when the molecule moves and rotates in space as well as vibrates，there remains an arbitrariness in fixing the coordinate axes to the molecule．The following method of choosing these axes is，however，the most preferable．The $3 N-6$ internal variables $R_{1}, R_{2}, \cdots, R_{3 N-6}$ is determined uniquely from the structure of the molecule． We define $x_{1}, y_{1}, \cdots, z_{N}$ by

$$
\mathscr{C}=\left(\begin{array}{c}
x_{1}  \tag{15}\\
\vdots \\
z_{N}
\end{array}\right)=\binom{B}{F}^{-1}\binom{R}{0},
$$

so that

$$
\begin{equation*}
F \mathscr{C}=0 . \tag{16}
\end{equation*}
$$

From the definition of $B$, we conclude that a system of axes of reference can be found so that the positions of the nuclei are $\left(X_{1}+x_{1}, Y_{1}+y_{1}, Z_{1}+z_{1}\right),\left(X_{2}+x_{2}, Y_{2}+y_{2}, Z_{2}+z_{2}\right)$, $\cdots,\left(X_{N}+x_{N}, Y_{N}+y_{N}, Z_{N}+z_{N}\right)$ when the molecule is not very much distorted from its equilibrium structure. We have thus 6 external variables specifying the position and orientation of the axes in space and $3 N-6$ variables $R_{1}, R_{2}, \cdots, R_{3 N-6}$ specifying by means of (15) the positions of the nuclei with respect to these axes.

## $\S 7$ THE KINETIC ENERGY IN TERMS OF $\boldsymbol{R}$

Equ. (16) expresses the facts that the origin of our moving axes is at any time the centre of mass of the molecule, and that the moment of momentum of the molecule in this system of reference is of the order of $m x \dot{x}$. Thus if the molecule rotates in space with an angular velocity $\omega$ about its centre of mass, its kinetic energy is

$$
T_{\text {centre of mass }}+T_{\text {rotation }}+\frac{1}{2} \sum_{i} m_{i}\left(\dot{x}_{i}^{2}+\dot{y}_{i}^{2}+\dot{z}_{i}^{2}\right)+\text { term } \sim m x \dot{x} \omega
$$

But

$$
T_{\text {rotation }}=(\text { K.E. of rotation if } \mathscr{C}=0)+\text { term } \sim m \omega^{2} x X .
$$

Now $T_{\text {centre of mass }}+($ K.E. of rotation if $\mathscr{C}=0)$ depends on the external variables only (together, of course, with their time derivatives). And in a gas, due to thermal agitation, $\omega X \sim \dot{x}$.

Thus in the first approximation the equ. of motion is to be derived from (cf. $\S \S 15,16$ )

$$
T=\frac{1}{2} \sum_{i} m_{i}\left(\dot{x}_{i}^{2}+\dot{y}_{i}^{2}+\dot{z}_{i}^{2}\right)=\frac{1}{2}\left(\dot{R}^{\prime} 0\right)\binom{B}{F}^{-1 \prime}\left(\begin{array}{ccc}
m_{1} & & \\
& \ddots & \\
& & m_{N}
\end{array}\right)\binom{B}{F}^{-1}\binom{\dot{R}}{0} .
$$

But

$$
\binom{B}{F}\left(\begin{array}{lll}
\frac{1}{m_{1}} & & \\
& \ddots & \\
& & \frac{1}{m_{N}}
\end{array}\right)\left(B^{\prime} \quad F^{\prime}\right)=\left(\begin{array}{llll}
B\left(\begin{array}{ccc}
\frac{1}{m_{1}} & & \\
& \ddots & \\
& & \frac{1}{m_{N}}
\end{array}\right) B^{\prime} & & & \\
& & & \\
& & & \\
& & F\left(\begin{array}{lll}
\frac{1}{m_{1}} & & \\
& \ddots & \\
& & \\
& & \\
m_{N}
\end{array}\right) F^{\prime}
\end{array}\right) .
$$

Hence writing

$$
G=B\left(\begin{array}{ccc}
\frac{1}{m_{1}} & &  \tag{17}\\
& \ddots & \\
& & \frac{1}{m_{N}}
\end{array}\right) B^{\prime},
$$

we have

$$
\begin{equation*}
2 T=\dot{R}^{\prime} G^{-1} \dot{R} \tag{18}
\end{equation*}
$$

## §8 THE KINETIC ENERGY IN TERMS OF $\mathscr{R}$

If we take the independent reduced coordinates $\mathscr{R}(\S 4)$ to be the $R$＇s of the last section，the results may be summarized：

$$
\mathscr{R}=\mathscr{L} \mathscr{C}, \quad \mathscr{G}=\mathscr{L}\left(\begin{array}{ccc}
\frac{1}{m_{1}} & &  \tag{19}\\
& \ddots & \\
& & \frac{1}{m_{N}}
\end{array}\right) \mathscr{L}^{\prime}, \quad 2 T=\dot{\mathscr{R}}^{\prime} \mathscr{G}^{-1} \dot{\mathscr{R}}
$$

Now by（5），

$$
\mathscr{L} P_{c} Z_{c}=\mathfrak{H}_{c} \mathscr{L} \quad\left(\mathfrak{H}_{c} \text { stands here for } A_{c}, \text { cf. } \S 4\right)
$$

so that

$$
\mathscr{G}=\mathscr{L}\left(\begin{array}{ccc}
\frac{1}{m_{1}} & & \\
& \ddots & \\
& & \frac{1}{m_{N}}
\end{array}\right) \mathscr{L}^{\prime}=\mathscr{A}_{c}^{\prime} \mathscr{L} P_{c} Z_{c}\left(\begin{array}{ccc}
\frac{1}{m_{1}} & & \\
& \ddots & \\
& & \frac{1}{m_{N}}
\end{array}\right) Z_{c}^{\prime} P_{c}^{\prime} \mathscr{L}^{\prime} \mathfrak{A}_{c}
$$

$\operatorname{But}\left(\begin{array}{ccc}\frac{1}{m_{1}} & & \\ & \ddots & \\ & & \frac{1}{m_{N}}\end{array}\right), P_{c}$ and $Z_{c}$ commute $^{*}$ with each other，hence

$$
\mathscr{G}=\mathfrak{A}_{c} \mathscr{L}\left(\begin{array}{ccc}
\frac{1}{m_{1}} & & \\
& \ddots & \\
& & \frac{1}{m_{N}}
\end{array}\right) \mathscr{L}^{\prime} \mathfrak{A}_{c}=\mathfrak{A}_{c}^{\prime} \mathscr{G} \mathfrak{A}_{c}
$$

Suppose

$$
\begin{equation*}
{ }_{\alpha \beta}\left(\mathscr{A}_{c}\right)_{\alpha^{\prime} \beta^{\prime}}=\delta_{\alpha \alpha^{\prime}} \delta_{\beta \beta^{\prime}} W_{c}^{\alpha}, \quad \alpha=1,2, \cdots, k, \beta=1,2, \cdots, n_{\alpha}, \tag{20}
\end{equation*}
$$

where $W_{c}^{\alpha}$ is irreducible．（cf．§4）Since $\mathfrak{A}_{c} \mathscr{G}=\mathscr{G} \mathfrak{A}_{c}$ ，we have

$$
W_{c}^{\alpha}{ }_{\alpha \beta}(\mathscr{G})_{\alpha^{\prime} \beta^{\prime}}={ }_{\alpha \beta}(\mathscr{G})_{\alpha^{\prime} \beta^{\prime}} W_{c}^{\alpha^{\prime}} .
$$

Hence ${ }^{6}$

$$
\begin{equation*}
{ }_{\alpha \beta}(\mathscr{G})_{\alpha^{\prime} \beta^{\prime}}=\delta_{\alpha \alpha^{\prime}{ }_{\beta} g_{\beta^{\prime}}^{\alpha} I . . . . ~}^{\text {. }} \tag{21}
\end{equation*}
$$

If $W_{c}^{\alpha}$ is of order $d_{\alpha}$ ，this shows that the nonvanishing elements of $\mathscr{G}$ are in $\sum_{\alpha=1}^{k} d_{\alpha}$ diagonal blocks of which $d_{\alpha}$ are identical of dimension $n_{\alpha} \times n_{\alpha}$ ．

[^7]
## §9 THE POTENTIAL ENERGY IN TERMS OF $\mathscr{R}$

The potential energy depends on the internal coordinates only. For small vibrations, it is approximately equal to $\frac{1}{2} \mathscr{R}^{\prime} \mathfrak{V} \mathscr{R}$, where $\mathfrak{V}$ is a positive symmetrical matrix, because when in equilibrium the molecule has a minimum potential energy. The covering operations leave the potential energy unchanged:

$$
\frac{1}{2} \mathscr{R}^{\prime} \mathfrak{V} \mathscr{R}=\frac{1}{2} \mathscr{R}^{\prime} \mathfrak{V}{ }^{c} \mathscr{R}=\frac{1}{2} \mathscr{R}^{\prime} \mathfrak{A}_{c}^{\prime} \mathscr{R} .
$$

But $\mathscr{R}$ is arbitrary, hence

$$
\mathfrak{V}=\mathfrak{A}_{c} \mathfrak{V} \mathfrak{A}_{c} .
$$

Thus we have, just as we had (21),

$$
\begin{equation*}
{ }_{\alpha \beta}(\mathfrak{V})_{\alpha^{\prime} \beta^{\prime}}=\delta_{\alpha \alpha^{\prime} \beta} v_{\beta^{\prime}}{ }^{\alpha} I, \quad \alpha=1,2, \cdots, k, \quad \beta=1,2, \cdots, n_{\alpha} . \tag{22}
\end{equation*}
$$

There are therefore totally $\sum_{\alpha=1}^{k} n_{a}^{2}$ independent constants in the potential energy, which are usually unknowns. ${ }^{11}$

## Calculation of the Kinetic Energy

## §10 THE TRANSFORMATION MATRIX $M^{7}$

In $\S 4$ the orthogonal matrix $M$ was introduced to reduce $A_{c}$. Since

$$
A_{c}=\left(\begin{array}{ccc}
A_{c 1} & & 0 \\
& A_{c 2} & \\
0 & & \ddots
\end{array}\right)
$$

where each $A_{c p}$ belongs to a set of equivalent coordinates, (§4)

$$
M=\left(\begin{array}{ccc}
M_{1} & & 0 \\
& M_{2} & \\
0 & & \ddots
\end{array}\right)
$$

where $M_{p}$ is orthogonal. Hence $W_{c p}=M_{p} A_{c p} M_{p}^{-1}$ is of the form (6), i.e.

$$
W_{c p}=\left(\begin{array}{cccc}
W_{c p}^{1} & & & \\
& W_{c p}^{1} & & \\
& & \ddots & \\
& & & W_{c p}^{k}
\end{array}\right) .
$$

Suppose that $W_{c p}^{1}$ is of dimension $d \times d$ ．Denote the first $d$ rows of $M_{p}$ by

$$
L=\left(\begin{array}{cccc}
1\left(M_{p}\right)_{1} & 1\left(M_{p}\right)_{2} & \cdots & \ldots \\
\cdots & \cdots & \cdots & \ldots \\
{ }_{d}\left(M_{p}\right)_{1} & \cdots & \cdots & { }_{d}\left(M_{p}\right)_{g_{p}}
\end{array}\right)
$$

where $g_{p}=$ no．of equivalent coordinates $R$ of the $p$－th set．
Now

$$
W_{c p} M_{p}=M_{p} A_{c p} .
$$

Hence

$$
W_{c p}^{1} L=L A_{c p}
$$

Thus

$$
L^{\prime} L=A_{c p}^{\prime} L^{\prime} L A_{c p}, \quad \text { i.e. } \quad\left(L^{\prime} L\right) A_{c p}=A_{c p}\left(L^{\prime} L\right)
$$

Hence

$$
\sum_{t=1}^{g_{p}}{ }_{1}\left(L^{\prime} L\right)_{t t}\left(A_{c p}\right)_{2}=\sum_{t=1}^{g_{p}}{ }_{1}\left(A_{c p}\right)_{t t}\left(L^{\prime} L\right)_{2} .
$$

There exists an operation $C$ which brings the second coordinate of the $p$－th set to the first，for which $\stackrel{c}{R}=R_{1}$ ，so that ${ }_{1}\left(A_{c p}\right)_{t}=\delta_{t 2},{ }_{t}\left(A_{c p}\right)_{2}=\delta_{t 1}$ ．Hence ${ }_{1}\left(L^{\prime} L\right)_{1}={ }_{2}\left(L^{\prime} L\right)_{2}$ ． Thus all diagonal elements of $L^{\prime} L$ are equal，and

$$
\sum_{\gamma=1}^{d}{ }_{\gamma}\left(M_{p}\right)_{t}^{2}={ }_{t}\left(L^{\prime} L\right)_{t}=\frac{1}{g_{p}} \operatorname{Spur}\left(L^{\prime} L\right)=\frac{1}{g_{p}} \operatorname{Spur}\left(L L^{\prime}\right)=\frac{d}{g_{p}} .
$$

Now $d$ can be determined from the values of $\operatorname{Spur}\left(\mathfrak{A}_{c}\right)$ ，（cf．equ．（39））so that this relation facilitates the calculation of $M$ ．

## §11 VECTORIAL NOTATION ${ }^{7}$

The matrix $\mathscr{G}=\mathscr{L}\left(\begin{array}{ccc}\frac{1}{m_{1}} & & \\ & \ddots & \\ & & \frac{1}{m_{N}}\end{array}\right) \mathscr{L}^{\prime}$ is calculated by first computing $\mathscr{L}$ ．Now $\mathscr{R}$ is a submatrix of $Q$ ．Hence

$$
\begin{equation*}
\mathscr{L}=M_{1} B, \quad \text { where } M_{1}={ }_{\text {some rows }}(M)_{\text {all columns }} \tag{23}
\end{equation*}
$$

Thus we have to find $B$ first．
Now

$$
R=B \mathscr{C}
$$

Write

$$
\left(\begin{array}{lll}
x_{t} & y_{t} & z_{t}
\end{array}\right)=\overrightarrow{\mathscr{C}}_{t}, \quad\left(\begin{array}{ccc}
{ }_{k} B_{t x} & { }_{k} B_{t y} & { }_{k} B_{t z}
\end{array}\right)=\vec{k}_{t} .
$$

Then $R_{k}=\sum_{t} \vec{k}_{t} \cdot \overrightarrow{\mathscr{C}}_{t}$. In a similar way we shall write
${ }_{\alpha \beta \gamma}(\mathscr{L})_{t}=\sum_{k=1}^{n}{ }_{\alpha \beta \gamma}\left(M_{1}\right)_{k}{ }_{k} \vec{S}_{t}={ }_{\alpha \beta \gamma} \vec{S}_{t}, \quad \gamma=1,2, \cdots, d_{\alpha}, \quad t=1,2, \cdots, N$.

## §12 EXPLICIT EXPRESSION OF $\vec{k}_{\boldsymbol{k}}{ }^{7}$

The use of the vectors $\vec{S}$ is advantageous because they are independent of the coordinate axes. Two kinds of $R$ 's are commonly used:
(i) $R=$ the increment of the bond between the nuclei $t^{\prime}$ and $t^{\prime \prime}$ in length. Evidently when $\overrightarrow{\mathscr{C}_{t^{\prime}}}=\overrightarrow{\mathscr{C}_{t^{\prime \prime}}}=0, R=0$. Hence


$$
\overrightarrow{S_{t}}=0 \quad \text { for all } t \text { except } t^{\prime} \text { or } t^{\prime \prime}
$$

If $0=y_{t^{\prime}}=z_{t^{\prime}}=x_{t^{\prime \prime}}=y_{t^{\prime \prime}}=z_{t^{\prime \prime}}$, we have $R=$ $x_{t^{\prime}} \cos \theta$, so that $B_{t^{\prime} x}=\cos \theta$. Hence

$$
\left\{\begin{array}{l}
\overrightarrow{S_{t^{\prime}}}=\text { unit vector from } t^{\prime \prime} \text { to } t^{\prime} .  \tag{25}\\
\overrightarrow{S_{t^{\prime \prime}}}=-\overrightarrow{S_{t^{\prime}}} \\
\text { all other } \vec{S}_{t} \text { are } 0
\end{array}\right.
$$

(ii) $R=$ the increment of the angle $t^{\prime}-t-t^{\prime \prime}$. Evidently all $\vec{S}$ are 0 except $\overrightarrow{S_{t}}, \overrightarrow{S_{t^{\prime}}}$ and $\overrightarrow{S_{t^{\prime \prime}}}$. Suppose that

$$
\overrightarrow{S_{t^{\prime}}}=x^{\prime} \overrightarrow{\xi^{\prime}}+y^{\prime} \overrightarrow{\eta^{\prime}}+z^{\prime} \overrightarrow{\zeta^{\prime}}
$$



When $\overrightarrow{\mathscr{C}}_{t}=\overrightarrow{\mathscr{C}_{t^{\prime \prime}}}=0, \overrightarrow{\mathscr{C}_{t^{\prime}}}=\overrightarrow{\xi^{\prime}}$, we have, since $t^{\prime}$ alone is displaced, $R=\frac{1}{\epsilon}$. Hence $x^{\prime}=\frac{1}{\epsilon}$. Similarly by considering the case when $\overrightarrow{\mathscr{C}}_{t}=\overrightarrow{\mathscr{C}_{t^{\prime \prime}}}=0, \overrightarrow{\mathscr{C}_{t^{\prime}}}=\overrightarrow{\eta^{\prime}}$, we get $y^{\prime}=0$. Proceeding in this way we arrive finally at the first line of (26). Now $R$ vanishes when $\overrightarrow{\mathscr{C}_{t^{\prime}}}=$ $\overrightarrow{\mathscr{C}_{t}}=\overrightarrow{\mathscr{C}_{t^{\prime \prime}}}$. Thus $\left(\overrightarrow{S_{t^{\prime}}}+\overrightarrow{S_{t^{\prime \prime}}}+\overrightarrow{S_{t}}\right)=0$. So that

$$
\left\{\begin{array}{l}
\overrightarrow{S_{t^{\prime}}}=\frac{1}{\epsilon} \overrightarrow{\xi^{\prime}}, \quad \overrightarrow{S_{t^{\prime \prime}}}=\frac{1}{\gamma} \overrightarrow{\xi^{\prime \prime}}  \tag{26}\\
\overrightarrow{S_{t}}=-\left(\overrightarrow{S_{t^{\prime}}}+\overrightarrow{S_{t^{\prime \prime}}}\right) \\
\text { all other } \vec{S}=0
\end{array}\right.
$$

From (25) and (26) we can write down, for all $k$ and $t$, the vector ${ }_{k} \vec{S}_{t}$ from which $\overrightarrow{\mathbb{S}}$ may be calculated through (24).

## §13 KINETIC ENERGY IN TERMS OF THE $\overrightarrow{\mathbb{S}^{\prime}} \mathrm{S}^{7}$

We shall show however，that not all the $\vec{S}$＇s are needed for the calculation of $\mathscr{G}$ ．
Take（5）

$$
\begin{equation*}
\mathscr{L} P_{c} Z_{c}=\mathfrak{A}_{c} \mathscr{L} . \tag{27}
\end{equation*}
$$

By（20）

$$
\sum_{t^{\prime}=1}^{N}{ }_{\alpha \beta} \mathscr{L}_{t^{\prime}} \Gamma_{c} \delta_{t, c^{-1} t^{\prime}}=W_{c \alpha \beta}^{\alpha} \mathscr{L}_{t}, \quad\left(\Gamma_{c} \text { is defined in } \S 2\right)
$$

i．e．

$$
{ }_{\alpha \beta} \mathscr{L}_{c t} \Gamma_{c}=W_{c \alpha \beta}^{\alpha} \mathscr{L}_{t} .
$$

Hence for any $\beta$ and $\beta^{\prime}$ ，

$$
\Gamma_{c \alpha \beta}^{\prime} \mathscr{L}_{c t}^{\prime}{ }_{\alpha \beta^{\prime}} \mathscr{L}_{c t} \Gamma_{c}={ }_{\alpha \beta} \mathscr{L}_{t \alpha \beta^{\prime}}^{\prime} \mathscr{L}_{t},
$$

so that

$$
\begin{equation*}
\operatorname{Spur}\left({ }_{\alpha \beta} \mathscr{L}_{c t}^{\prime}{ }_{\alpha \beta^{\prime}} \mathscr{L}_{c t}\right)=\operatorname{Spur}\left({ }_{\alpha \beta} \mathscr{L}_{t}^{\prime}{ }_{\alpha \beta^{\prime}} \mathscr{L}_{t}\right) \tag{28}
\end{equation*}
$$

Now by（21），

$$
\begin{equation*}
{ }_{\beta} g_{\beta^{\prime}}^{\alpha} I={ }_{\alpha \beta} \mathscr{G}_{\alpha \beta^{\prime}}=\sum_{p}{ }_{\alpha \beta} \mathscr{L}_{p}\left(\frac{1}{m_{p}} I\right)_{\alpha \beta^{\prime}} \mathscr{L}_{p}^{\prime}, \tag{29}
\end{equation*}
$$

where each $p$ refer to a set of equivalent nuclei．
From（27）

$$
{ }_{\alpha \beta}(\mathscr{L})_{p p}\left(P_{c}\right)_{p p}\left(Z_{c}\right)_{p}=W_{c \alpha \beta}^{\alpha}(\mathscr{L})_{p} .
$$

Hence

$$
{ }_{\alpha \beta}(\mathscr{L})_{p \alpha \beta^{\prime}}(\mathscr{L})_{p}^{\prime}=W_{c}^{\alpha}{ }_{\alpha \beta} \mathscr{L}_{p \alpha \beta^{\prime}} \mathscr{L}_{p}^{\prime},
$$

i．e．

$$
\left({ }_{\alpha \beta} \mathscr{L}_{p \alpha \beta^{\prime}} \mathscr{L}_{p}^{\prime}\right) W_{c}^{\alpha}=W_{c}^{\alpha}\left({ }_{\alpha \beta} \mathscr{L}_{p \alpha \beta^{\prime}} \mathscr{L}_{p}^{\prime}\right) .
$$

Thus ${ }^{6}$

$$
\begin{equation*}
{ }_{\alpha \beta} \mathscr{L}_{p \alpha \beta^{\prime}} \mathscr{L}_{p}^{\prime}={ }_{\beta} \mathfrak{l}_{\beta^{\prime}}^{\alpha p} I, \tag{30}
\end{equation*}
$$

where ${ }_{\beta} \boldsymbol{l}_{\beta^{\prime}}^{\alpha p}$ is an ordinary number．From（29）we have，

$$
\begin{equation*}
{ }_{\beta} g_{\beta^{\prime}}^{\alpha} I=\sum_{p} \frac{1}{m_{p}}{ }_{\beta} \boldsymbol{l}_{\beta^{\prime}}^{\alpha p} I . \tag{31}
\end{equation*}
$$

Hence

$$
\begin{equation*}
{ }_{\beta} b_{\beta^{\prime}}^{\alpha p} d_{\alpha}=\operatorname{Spur}\left({ }_{\alpha \beta} \mathscr{L}_{p \alpha \beta^{\prime}} \mathscr{L}_{p}^{\prime}\right)=\operatorname{Spur}\left({ }_{\alpha \beta^{\prime}} \mathscr{L}_{p \alpha \beta}^{\prime} \mathscr{L}_{p}\right)=\sum_{t \text { in } p} \operatorname{Spur}\left({ }_{\alpha \beta^{\prime}} \mathscr{L}_{t}^{\prime}{ }_{\alpha \beta} \mathscr{L}_{t}\right) . \tag{32}
\end{equation*}
$$

Now consider the sum of (28). Since $c t$ goes over all values of $t$ in $p$ when $c$ goes over all the operations of the group,

$$
\operatorname{Spur}\left({ }_{\alpha \beta} \mathscr{L}_{c t}^{\prime}{ }_{\alpha \beta^{\prime}} \mathscr{L}_{c t}\right)=\operatorname{Spur}\left({ }_{\alpha \beta} \mathscr{L}_{c t^{\prime} \alpha \beta^{\prime}}^{\prime} \mathscr{L}_{c t^{\prime}}\right),
$$

if $t$ and $t^{\prime}$ are in the same $p$-th set. Thus (32) becomes

$$
{ }_{\beta} \boldsymbol{l}_{\beta^{\prime}}^{\alpha p} d_{\alpha}=g_{p} \operatorname{Spur}\left({ }_{\alpha \beta} \mathscr{L}_{t \alpha \beta^{\prime}} \mathscr{L}_{t}^{\prime}\right),
$$

where $t$ represents any nucleus of the $p$-th set. Substitute into (31) and make use of (24). We obtain:

$$
\begin{equation*}
{ }_{\beta} g_{\beta^{\prime}}^{\alpha}=\frac{1}{d_{\alpha}} \sum_{p} \frac{g_{p}}{m_{p}} \sum_{\gamma=1}^{d_{\alpha}}{ }_{\alpha \beta \gamma} \overrightarrow{S_{t}} \cdot{ }_{\alpha \beta^{\prime} \gamma} \overrightarrow{S_{t^{\prime}}} . \tag{33}
\end{equation*}
$$

Thus in calculation $\mathscr{G}\left({ }_{\alpha \beta} \mathscr{G}_{\alpha^{\prime} \beta^{\prime}}=\delta_{\alpha \alpha^{\prime}}{ }_{\beta} g_{\beta^{\prime}}^{\alpha} I\right)$ we have only to know ${ }_{\alpha \beta \gamma} \overrightarrow{S_{t}}$ for all $\alpha$ $(=1,2, \cdots, k), \beta\left(=1,2, \cdots, n_{d}\right)$ and $\gamma\left(=1,2, \cdots, d_{\alpha}\right)$; but only for one $t$ in each $p$. From (24) we see that not all $\vec{S}$ are needed.

## Secular Equation and Degeneracy

## §14 NORMAL COORDINATES

In terms of the independent reduced coordinates $\mathscr{R}$ defined in $\S 4$, the kinetic energy and the potential energy are $\frac{1}{2} \dot{\mathscr{R}}^{\prime} \mathscr{G}^{-1} \dot{\mathscr{R}}$ and $\frac{1}{2} \mathscr{R} \mathfrak{V} \mathscr{R},(\S \S 8,9)$ where $\mathscr{G}$ is positive definite. Let $\lambda_{1}, \lambda_{2}, \cdots, \lambda_{3 N-6}$ be the roots of the equ.

$$
\begin{equation*}
\left|\lambda \mathscr{G}^{-1}-\mathfrak{V}\right|=0, \quad \text { i.e. } \quad|\lambda I-\mathfrak{V} \mathscr{G}|=0 . \tag{34}
\end{equation*}
$$

Then there exists a matrix $L$ such that

$$
L \mathscr{G} L^{\prime}=I, \quad L^{-1 \prime} \mathfrak{V} L^{-1}=\left(\begin{array}{cccc}
\lambda_{1} & & & 0 \\
& \lambda_{2} & & \\
& & \ddots & \\
0 & & & \lambda_{3 N-6}
\end{array}\right)=\Lambda .
$$

Put

$$
\mathfrak{N}=\left(\begin{array}{l}
\mathfrak{N}_{1} \\
\vdots \\
\mathfrak{N}_{3 N-6}
\end{array}\right)=L \mathscr{R}
$$

we get immediately

$$
\begin{gather*}
2 \times \text { kinetic energy }=\dot{\mathscr{R}}^{\prime} \mathscr{G}^{-1} \dot{\mathscr{R}}=\dot{\mathfrak{N}}^{\prime} \mathfrak{N}=\sum_{i=1}^{3 N-6} \dot{\mathfrak{N}}_{i}^{2}  \tag{35}\\
2 \times \text { potential energy }=\mathscr{R}^{\prime} \mathfrak{V} \mathscr{R}=\mathfrak{N}^{\prime} \Lambda \mathfrak{N}=\sum_{i} \lambda_{i} \mathfrak{N}_{i}^{2} . \tag{36}
\end{gather*}
$$

These coordinates $\mathfrak{N}_{i}$ are known as the＂normal coordinate＂＇s．They are obtained by first solving（34），thus getting $\lambda_{i}$ ；and then determining $L$ from

$$
\begin{equation*}
L \mathscr{G} \mathfrak{V}=\Lambda L . \tag{37}
\end{equation*}
$$

This $L$ must be normalized by

$$
\begin{equation*}
L \mathscr{G} L^{\prime}=I . \tag{38}
\end{equation*}
$$

The normal coordinates are then calculated from $\mathfrak{N}=L \mathscr{R}$ ．
Now we shall be able to see the role that symmetry plays in simplifying the calcula－ tions．Equs．（21）and（22）show the secular equ．（34）is factored into $\sum_{\alpha=1}^{k} d_{\alpha}$ equations of which $d_{\alpha}$ are identical and are of the $n_{\alpha}$－th degree．The labor of solving for the $\lambda$＇s is considerably saved．Moreover，the no．of unknown constants in $\mathfrak{V}$ is reduced．

The normal coordinates are also a special form of the＂symmetry coordinates＂in－ troduced by Howard and Wilson．${ }^{21}$ The most general form of the symmetry coordinates $\mathfrak{M}$ is given by $\mathfrak{N}=\mathscr{L} \mathfrak{M}$ where

$$
{ }_{\alpha \beta} \mathscr{L}_{\alpha^{\prime} \beta^{\prime}}=\delta_{\alpha \alpha^{\prime} \beta} \ell_{\beta^{\prime}}^{\alpha} U^{\alpha}, \quad \alpha=1,2, \cdots, k, \beta=1,2, \cdots, n_{a},
$$

in which $U^{\alpha}$ is orthogonal and ${ }_{\beta} \ell_{\beta^{\prime}}^{\alpha}$ form an orthogonal matrix when $\beta$ and $\beta^{\prime}$ range over $1,2, \cdots, n_{\alpha}$ ．

## §15 SOLUTION OF THE PHYSICAL PROBLEM—CLASSICAL THEORY

The Lagrangian is，from（35）and（36），

$$
\frac{1}{2} \sum_{i=1}^{3 N-6}\left(\dot{\mathfrak{N}}_{i}^{2}-\lambda_{i} \mathfrak{N}_{i}^{2}\right)
$$

The equs．of motion are therefore

$$
\ddot{\mathfrak{N}}_{i}+\lambda_{i} \mathfrak{N}_{i}=0, \quad i=1,2, \cdots, 3 N-6 .
$$

Hence

$$
\mathfrak{N}_{i}=\left(\mathfrak{N}_{i}\right)_{0} \cos \left(\sqrt{\lambda_{i}} t+\phi_{i}\right) .
$$

The frequencies of vibration are thus

$$
\frac{\sqrt{\lambda_{1}}}{2 \pi}, \frac{\sqrt{\lambda_{2}}}{2 \pi}, \cdots, \frac{\sqrt{\lambda_{3 N-6}}}{2 \pi}
$$

This is correct only in the first approximation; but it serves to give almost all our present knowledge about the forces within the molecules.

## §16 SOLUTION OF THE PHYSICAL PROBLEM—QUANTUM THEORY

Now

$$
T=\frac{1}{2} \sum_{i} \dot{\mathfrak{N}}_{i}^{2}, \quad V=\frac{1}{2} \sum_{i} \lambda_{i} \mathfrak{N}_{i}^{2}
$$

The wave equation is most easily obtained from the variational formulation of the problem:

$$
\delta \int\left\{\sum \hbar^{2} g^{i j} \frac{\partial \psi^{*}}{\partial \mathfrak{N}_{i}} \frac{\partial \psi}{\partial \mathfrak{N}_{j}}+(V-E) \psi^{*} \psi\right\} \sqrt{g} \mathrm{~d} \mathfrak{N}_{1} \cdots \mathrm{~d} \mathfrak{N}_{3 N-6}=0
$$

where $g^{i j}$ is given by $T=g_{i j} \dot{x}^{i} \dot{x}^{j}$. Hence

$$
\sum_{i} \frac{1}{2}\left(-\hbar^{2} \frac{\partial^{2}}{\partial \mathfrak{N}_{i}^{2}}+\lambda_{i} \mathfrak{N}_{i}^{2}\right) \psi=E \psi
$$

The electric moment in any direction is, in the first approximation

$$
D_{0}+\sum_{i=1}^{3 N-6} D_{i} \mathfrak{N}_{i}
$$

where $D_{i}$ is immediately calculable from (15). Thus the wave function and selection rules, hence the frequencies in the vibrational spectra of the molecule, are the same as those of $3 N-6$ independent harmonic oscillators with coordinates $\mathfrak{N}_{1}, \mathfrak{N}_{2}, \cdots, \mathfrak{N}_{3 N-6}$. The frequencies are therefore exactly those obtained classically.

## §17 THE DEGREE OF DEGENERACY

We have seen that the secular equ. (34) is factorized into $d_{1}$ identical equs. of the $n_{1}$-th degree, $d_{2}$ identical equs. of the $n_{2}$-th degree, $\cdots$. There must therefore be $n_{1}$ frequencies each corresponding to $d_{1}$ different normal moods of vibration $\left(d_{1}\right.$-fold degenerate). The nos. $d_{1}, d_{2}, \cdots$, are accordingly called "the degrees of degeneracy".

It is interesting that they can be determined together with $n_{1}, n_{2}, \cdots$, without carrying out the calculation of the normal coordinates. For, by (20)

$$
\sum_{\alpha} n_{\alpha} \operatorname{Spur}\left(W_{c}^{\alpha}\right)=\operatorname{Spur}\left(\mathscr{A}_{c}\right)
$$

But

$$
\sum_{c} \operatorname{Spur}\left(W_{c}^{\alpha}\right) \operatorname{Spur}\left(W_{c}^{\beta}\right)=\delta_{\alpha \beta} h,
$$

where $h=$ order of the group．Hence

$$
\begin{equation*}
n_{\alpha}=\frac{1}{h} \sum_{c} \operatorname{Spur}\left(\mathfrak{A}_{c}\right) \operatorname{Spur}\left(W_{c}^{\alpha}\right) . \tag{39}
\end{equation*}
$$

Now both $\operatorname{Spur}\left(W_{c}^{\alpha}\right)$ and $d_{\alpha}$ can be found ${ }^{3}$ from a table of characters of the point group， and $\operatorname{Spur}\left(\mathfrak{A}_{c}\right)$ can be calculated through the theorem in $\S 5$ ，so that $d_{\alpha}$ and $n_{\alpha}$ are easily calculable from（39）．

EXAMPLE We consider again the molecule $\mathrm{CH}_{3} \mathrm{Cl}$ ．（§5）From the left table of

| Representation | $d_{\alpha}$ | $\operatorname{Spur}\left(W_{c}\right)$ |  |  |
| :---: | :---: | :---: | :---: | :---: |
|  |  | $c=c_{1}$ | $c=c_{2}, c_{3}$ | $c=c_{4}, c_{5}, c_{6}$ |
| $W^{1}$ | 1 | 1 | 1 | 1 |
| $W^{2}$ | 1 | 1 | 1 | -1 |
| $W^{3}$ | 2 | 2 | -1 | 0 | characters we get $n_{1}=$ $3, n_{2}=0, n_{3}=3$ ．It follows that the secu－ lar equ．is factored into 3 cubic equs． 2 of which are identical．

We conclude that there are totally 6 vibrational frequencies， 3 of which are doubly degenerate．

The no．of independent constants in the potential energy is $(\S 9) \sum_{\alpha} n_{a}^{2}=18$.

## Other Developments

## §18 ISOTOPE RULE ${ }^{7}$

In the above example the no．of unknown constants in the potential energy is much greater than the no．of observable frequencies，as is usually the case．The situation is，however，not so hopeless，because the frequencies of the molecule with some of the atoms replaced by their isotopes serve as additional data．The new molecule has evidently the same equilibrium configuration and potential energy as the original one． But in calculating its kinetic energy it must be remembered that all the results of $\S \S 1$ to 7 are correct，（because they do not concern the masses of the nuclei）but that since now $\left(\begin{array}{ccc}\frac{1}{m_{1}} & & \\ & \ddots & \\ & & \frac{1}{m_{N}}\end{array}\right)$ does not necessarily commute with $P_{c},(21)$ does not hold．The secular equ．is therefore not factored as before．The vectorial method is still convenient．

If the new kinetic energy matrix is denoted by $\mathscr{G}^{\prime}$, from (34)

$$
\begin{aligned}
& \Pi \lambda_{i}=|\mathfrak{V} \mathscr{G}|=|\mathfrak{V}||\mathscr{G}|, \\
& \Pi \lambda_{i}^{\prime}=\left|\mathfrak{V} \mathscr{G}^{\prime}\right|=|\mathfrak{V}|\left|\mathscr{G}^{\prime}\right| .
\end{aligned}
$$

Hence

$$
\left.\frac{\Pi \lambda_{i}}{\Pi \lambda_{i}^{\prime}}=\frac{|\mathscr{G}|}{\left|\mathscr{G}^{\prime}\right|}=\frac{\left|\mathscr{L}\left(\begin{array}{ccc}
\frac{1}{m_{1}} & & \\
& \ddots & \\
& & \frac{1}{m_{N}}
\end{array}\right) \mathscr{L}^{\prime}\right|}{\left\lvert\, \mathscr{L}\left({\frac{1}{\frac{1}{1}^{\prime}}}^{\prime}\right.\right.} \begin{array}{ll} 
& \ddots \\
& \\
& \\
{\frac{1}{m_{N}}}^{\prime}
\end{array}\right) \mathscr{L}^{\prime} \mid
$$

## §19 SPLITTING OF HIGH FREQUENCIES ${ }^{7}$

Sometimes it is known that certain force constants are considerably larger than the others, so that the corresponding frequencies of vibration are much greater than the rest. To solve for the low frequencies we may make the approximation of putting the large force constants equal to infinity.

Let

$$
\mathscr{G}=\left(\begin{array}{cc}
\mathscr{G}_{11} & \mathscr{G}_{12} \\
\mathscr{G}_{21} & \mathscr{G}_{22}
\end{array}\right), \quad \mathfrak{V}=\left(\begin{array}{ll}
\mathfrak{V}_{11} & \mathfrak{V}_{12} \\
\mathfrak{V}_{21} & \mathfrak{V}_{22}
\end{array}\right)
$$

We want to find the $\lambda$ 's when $\mathfrak{V}_{11} \rightarrow \infty$. Now

$$
\left|\lambda \mathscr{G}^{-1} \mathfrak{V}^{-1}-I\right|=0,
$$

and when $\mathfrak{V}_{11} \rightarrow \infty, \mathfrak{V}^{-1} \rightarrow\left(\begin{array}{cc}0 & 0 \\ 0 & \mathfrak{V}_{22}^{-1}\end{array}\right)$. Since

$$
\mathscr{G}^{-1}=\left(\begin{array}{ll}
\left(\mathscr{G}^{-1}\right)_{11} & \left(\mathscr{G}^{-1}\right)_{12} \\
\left(\mathscr{G}^{-1}\right)_{21} & \left(\mathscr{G}_{22}-\mathscr{G}_{21} \mathscr{G}_{11}^{-1} \mathscr{G}_{12}\right)^{-1}
\end{array}\right),
$$

we get

$$
\left|\lambda\left(\begin{array}{ll}
0 & \left(\mathscr{G}^{-1}\right)_{12} \mathfrak{V}_{22}^{-1} \\
0 & \left(\mathscr{G}_{22}-\mathscr{G}_{21} \mathscr{G}_{11}^{-1} \mathscr{G}_{12}\right)^{-1} \mathfrak{V}_{22}^{-1}
\end{array}\right)-I\right|=0,
$$

or

$$
\left|\lambda\left(\mathscr{G}_{22}-\mathscr{G}_{21} \mathscr{G}_{11}^{-1} \mathscr{G}_{12}\right)^{-1} \mathfrak{V}_{22}^{-1}-I\right|=0
$$

i.e.

$$
\left|\lambda\left(\mathscr{G}_{22}-\mathscr{G}_{21} \mathscr{G}_{11}^{-1} \mathscr{G}_{12}\right)^{-1}-\mathfrak{V}_{22}\right|=0 .
$$

## Acknowledgement

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2．E．Wigner，Göttingen Nachrichton，（1930），p．133．
3．See 1．and 2．，also Speiser：Theorie der Gruppen von Endlicher Ordnung（Berlin， 1927）．
and J．E．Rosenthal and G．M．Murphy，Rev．Mod．Phys．， 8 （1936）， 317.
The degeneracy and other properties are tabulated by E．B．Wilson Jr．in，J． Chem．Phys．， 2 （1934），432．（complete to molecules containing 7 atoms） The irreducible representations are given in F．Seitz，Zeits．f．Krist．，A88（1934）， 433.

4．E．Wigner，Gruppentheorie．（Braunschweig 1931）This book is always meant when Wigner is referred to．

5．Wigner，p． 86 ．
6．ibid．p． 83.
7．E．B．Wilson Jr．，J．Chem．Phys．， 9 （1941）， 76.
8．J．E．Rosenthal and G．M．Murphy，Rev．Mod．Phys．， 8 （1936）， 317.
9．E．B．Wilson Jr．and B．L．Crawford Jr．，J．Chem．Phys．， 8 （1936）， 223.
10．D．M．Dennison，Rev．Mod．Phys．， 3 （1931）， 280.
11．J．B．Howard and E．B．Wilson，Jr．，J．Chem．Phys．， 2 （1934）， 630.

 binal self，and we have a new equation obtained by writing（1） down for the new molecule：

$$
\begin{equation*}
\stackrel{C}{R}=B \dot{E}_{0} \tag{2}
\end{equation*}
$$

Hut＊R＇s Arc the coordinates of the molecule which will be brought into coincidence with $\mathbb{R}^{\prime}$ by the operation $C$ ，and
where $c^{-1} i$ is the nucla $\quad$ fica will become a ter the operation $c$ the nuclou $i$ ．Let $\boldsymbol{z}_{\mathbf{c}}$ be $\boldsymbol{y}$ source sistrix of order 3 N with the elements＂$\left.\quad i x^{(\vec{z})_{j x}}=\delta_{j, c^{4} j_{i}}, \quad i i^{(z)}\right)_{j y}=0$ atc．$\quad i j=1,2, \cdots N$ ，
and let $\boldsymbol{P}_{\mathbf{c}}$ stand for（ $\boldsymbol{R}_{\boldsymbol{R}_{\boldsymbol{n}}}$ ）
then（2）and（3）give $\hat{k}=B P_{c} z_{c}$ ．
This equation holds for every operation $C$ and is the mathematical expression of the symmetry of the molecule．
EXAMpLE Consider three equivalent nuclei forming an equilateral


Let $\boldsymbol{R}_{1}$ be the increment of the distance $\sqrt{\mathbf{1}} \cdot \boldsymbol{R}_{1}=\frac{1}{2} x_{1}+\frac{\sqrt{3}}{2} y_{1}-\frac{1}{2} x_{4}-\frac{\sqrt{3}}{2} y_{2}$ ． Then $\overrightarrow{k_{1}}$ is that of $\overline{\mathbf{3 1}}$ ，and $\frac{k_{2}}{R_{2}}=-\frac{1}{2} x_{1}+\frac{\sqrt{3}}{2} y_{1}+\frac{1}{2} x_{3}-\frac{\sqrt{3}}{2} y_{3}$.
Thus $B=\left(\frac{1}{2}, \frac{\sqrt{2}}{2}, 0,-\frac{1}{2},-\frac{\sqrt{3}}{2}, 0,0,0,0\right)$ ．
（4）becomes the identity

S？FUNDAWENTAL RELATIONSHIP In some instances the coordinates $\mathbf{R}_{\boldsymbol{t}}, \boldsymbol{R}_{\mathbf{z}}, \cdots \cdot \boldsymbol{R}_{\boldsymbol{n}}$ are sufficient to determine $\boldsymbol{R}_{\mathbf{R}}, \boldsymbol{R}_{\mathbf{2}}, \cdots \mathbf{R}_{\boldsymbol{R}}$ for all co－ vering operations C．This is the case if（i）the $R^{\prime}$ s contain only complete sets of equivalent coordinates（es．in the last
 all that are necessary to describe the internal structure of the molecule．In both cases we have for small vibrations $\dot{R}=A \neq R$ ． where $A_{4}$ is in case（i）an orthogonal matrix having as elements

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                        -5-
O or 1, and in case (ii) a matrix of order nxn. By (4),
```

$B \mathcal{R}_{c} Z_{c} \cdot \mathscr{C}=\hat{R}=A_{c} R=A_{e} B \cdot G$.

But $\mathcal{E}$ is arbitrary (cf. 5 ), hence

## $B P_{c} Z_{c}=A_{c} B$

This is the fundamental relstionship on which all the following deductions are based. Q2 GHOUP PROPERTI ES To take further developments we notice that the covering operations C form a group and that the $\mathbb{R}^{\prime} \mathrm{s}, \boldsymbol{z}_{\mathbf{c}}^{*}$ s and $\boldsymbol{A}_{\boldsymbol{c}}$ s euch form a g ooup isomorphic* ${ }^{*}$ ith it. The group is known as the "point group". They are of such importance that their properties have been investigated in detail. ${ }^{3}$.

Choice of Internal Coordinates
24 INDEPENDENT REDUCED COORDINATES We firet choose the coordinates $\boldsymbol{R}_{\mathbf{1}}, \boldsymbol{R}_{\mathbf{2}}, \cdots \boldsymbol{R}_{\boldsymbol{n}}$ so that they contain only complete sets of equivalent internal coordinates, and such that they are more than necessary for the determination of the structure of the molecule. The simplest way is to choose the increments of the internuclear distances and the bond angles as the $\mathbf{R}^{\prime}$ s. Intie exanple of 81 we may take the incremente of the bonds $\sqrt{2}, 23$ and $\mathbf{3 1}$ as $\boldsymbol{R}_{\mathbf{1}}, \boldsymbol{R}_{2}$ and $\boldsymbol{R}_{\mathbf{3}}$; or those of the lengths dik $\overline{01}, \overline{\sigma_{2}, \overline{03}}$ and the angles $\hat{0}_{\mathbf{2}}$, $2 \hat{0} \mathbf{s}$ and $\mathbf{3 A}_{\boldsymbol{t}}$ as the $\boldsymbol{R}^{\prime} \mathrm{s}$. The patrix $\mathbf{B}$ can now be determined $(\$ \$ 11,22)$. Evidently our choiee belongs to the case (i) of $\$ 2$, so thet the $\boldsymbol{A}_{\boldsymbol{c}}{ }^{\circ}$ are orthogonal and have as elements 0 or l . It is plain that ${ }_{i}\left(A_{c}\right)_{j}=0$ if $\boldsymbol{R}_{i}$ and $\boldsymbol{R}_{j}$ ure not equivalent. We shall make use of the following theorem in group theorys?

If $A_{c}$ fort a group of orthogonal autrices, and $W_{E}^{*}(\alpha=1,2, \cdots k$ are the irreducible orthogonal ropresentations of the group, thure exiats an orthogonal matrlx $M$ such that $W_{c}=M A_{c} \mathcal{M}^{-1} i s$ of the 1010


* Les c' ${ }^{\text {a }}$ be the resultant operation of first operating $C$ and then $\mathrm{C}^{\prime}, \rightarrow$ we have

$$
P_{c c}=P_{c}, P_{c}, \quad Z_{c c}=Z_{c}, Z_{c} \quad \text { but } \quad A_{c c_{c}^{\prime}}=A_{c} A_{c}^{\prime}
$$

We define $Q=\left(\begin{array}{c}Q_{2} \\ Q_{2} \\ Q_{n}\end{array}\right)=M R$ as the＂reduced coordinates＊．Evidently
$Q^{2}=M K^{\prime}=M A_{2} R=M L A_{1} M^{-1} Q=W_{C} Q$.
Now not all the $Q$＇s are independent．Topelect out the independent ones wo nejd the following theorem：
TH：OREA It is always possible to bro out sone of the $Q^{\prime}$ so
that（i）the remaining ones are all irfobendent，
（ii）the dropped ones depend on the remaining ones， and（iii）the remaining ones belong to complete blocks of the group of matrices We ．
Because of the properties（i）and（li），the remaining coordinates

 These coordinates may also be obtained in other ways，and have been given various names by diliferont authors．They are the＂in－ ternal symmetry coordinates＂of Wilson＂and the＂geometrical sym－ Retry coordinates＂of Rosenthal ind Murphy ${ }^{\delta}$ ．The reistion between $\mathcal{R}$ and the＂symmetry coordinates＂of Howard and wilson＂，ill be given in \＄lu．

SROOF OF TIE THEOREM Since $\boldsymbol{Q}$ if not entirely arbitrary，there exists a mutrichoi order $\nu \times n$ so that $H H^{\prime}=1, H Q=0$ ，（7） whore $\mathcal{I}$ a the unit matrix and the＂stands for＂transposed＂． Be may prove that the rank of $H$ is $\gamma$ and that there exists a


$$
\left(\begin{array}{lll}
H_{1}
\end{array}\right) Q=\left(\begin{array}{l}
Q_{Q} \tag{e}
\end{array}\right), \quad Q=\left(H^{\prime} H_{1}^{\prime}\right)\left(Q_{Q_{1}}^{O}\right)=H_{1}^{\prime} Q_{1} .
$$

We may suppose that $\nu=n-(3 N-6)$ s？that $Q$ ，iv arbitrary．The ecu．

$$
\boldsymbol{H Q}=0 \text { must be invariant infer in siecation } C \text { : }
$$

$$
\begin{aligned}
O=H Q^{C}= & H W_{c} Q \\
H W_{c} H_{3}^{\prime}= & =O .
\end{aligned}
$$

Thus
$\left(\begin{array}{l}H_{1}\end{array}\right) W_{c}\left(H^{\prime} H_{1}^{\prime}\right)=\binom{H W_{\mathrm{E}} H^{\prime} \circ}{H_{i} W_{\mathrm{c}} H^{\prime} H_{1} W_{C} H_{1}^{\prime}}$.
 Hone
＇Thus $\boldsymbol{H} \boldsymbol{w}_{\mathrm{c}} \boldsymbol{H}^{\prime}$ is orthogonal
$\left(H_{1}\right) W_{c}\left(H^{\prime} H_{l}\right)=\left(\begin{array}{cc}H W_{c} H^{\prime} & \circ \\ 0 & H_{i} W_{c} H_{0}\end{array}\right)$
one formed by $C$ ；i．e．

## （ Whee $\left.H^{\prime}\right)\left(H W_{e} H^{\prime}\right)=H W_{\mathrm{ce}^{\prime}} H^{\prime}$ ．

＊We duzume pore that $Q$ is real．There is probably no dir－ Iiculty in nardilís duplex coordinates，but they are not neeseary unites moleaulefor tymmetry $\boldsymbol{C}_{n}, \boldsymbol{C}_{n k} \times S_{n}(n>2)$ are studied．
$\because \rightarrow$

By the theoses quoted above there axists an orthogopal matrix $\boldsymbol{J}$ such that JHWc $H^{\prime} J^{\prime}=\omega_{c}$ ie of the fora(6); i.e. if the "urteriaitrices" of $W_{c}$ are $\alpha_{q}\left(W_{c}^{\prime}\right)_{\alpha \beta^{\prime}}=\delta_{\alpha_{\alpha^{\prime}}} \delta_{\not \mathcal{P}^{\prime}} W_{c}^{-q}, \quad \alpha=1,2, \cdots k, \quad \beta=1,2, \cdots n_{\alpha}$, those of $\omega_{c}$ 'auat bo ${ }_{a b}{ }^{(44)^{\prime}{ }^{\prime} b^{\prime}}=\delta_{a a^{\prime}}, \delta_{b b^{\prime}} W_{c}^{a}, a=1,2 \cdots k, \quad b=1,2, \ldots \mu_{a}$. Ey ( 9 ), the irreducib' e blook oi $\omega_{c}$ must all be that of $\dot{w}_{c}$,
 i. . $W_{c}{ }^{*}$ is irreducible, ${ }^{\left.{ }^{a b}(J)_{\alpha \beta}\right)} W_{c}^{*}=w_{c}^{a}{ }_{\alpha}(J H)_{d \beta}$

But $W_{*}^{*}$ is irreducible, herof ${ }^{6} \quad a_{b}(J H)_{\Delta \beta}=\delta_{a d} \phi_{\Delta} \lambda_{A}^{\alpha} I$,
Where $\left.\lambda^{\prime}\right)_{p}^{\alpha}$ i. an ordinary number. Since JH is of rank $v$, tidelsub-thati-i) $\left(\lambda_{\beta}^{\alpha}\right), \underset{\beta=1,2,3, \ldots, n_{d}}{b=1,2,3}$ is of ranic $\mu_{d}$. Thus for evory $\alpha$ these exicta a sot $\kappa_{\alpha} \partial 1 \mu_{\alpha}$ integers all $\leqslant n_{\alpha}$, woll thut tre equare tatrix ( $\rangle_{b} \lambda_{\alpha}^{\alpha}$ )
$b=1,2, \cdots \mu$ i.3 nonsingular. Hence JH may be divided into tivo $\beta$ in $n_{\alpha}$
unternutrices, one (of order $\boldsymbol{\nu} \boldsymbol{x} \boldsymbol{\nu}$ ) conposed of those internatrices (11) Ior whial $\boldsymbol{\beta}$ is in the aet $\boldsymbol{k}_{\alpha}$, and the other those for which $\boldsymbol{\beta}$ is not in $\boldsymbol{K}_{\alpha}$. The former is evidentiy nonsin/sular. Let $\boldsymbol{H}_{2}$ and $\boldsymbol{H}_{3}$ be the corresponding untermatrices of $H=J^{-1}(J H)$. Evidentiy a tranegouition of coluichi ErThet $\boldsymbol{H}$ into the form $\left(H_{2} H_{3}\right)$. Now the constraint on $Q$ is $H Q=0$. Hence a corresponding traneposition of the rows of $\boldsymbol{Q}$ bring it to $\left(Q_{\mathbf{a}}\right)$ an that

## $H_{2} Q_{2}+H_{3} Q_{3}=0$.

Eince $H_{2}$ is nonsingulur, $Q_{3}$ tay be chosen an the indepondentvisiable,
$Q_{2}$ being dependent on it. Thus the latter can be dropned and the conditione (i), (2) and (iii) are satisfied. S5 CAICULATION OF SPUK( $(\mathbb{C})$ Suppose that the constrainta on the $R^{\prime} B^{3}$ are given by $\quad D R=0 \quad$ wher $\mathscr{D} \boldsymbol{A}^{\prime}=\mathbf{I} \quad$ (12)

This theorem makes the calculation of Spur(a) very simple (because the ulements of $\boldsymbol{A}_{\boldsymbol{c}}$ are 0 or 1), and before the trancformation from $\boldsymbol{R}$ t) $\boldsymbol{Q}$ is carried out. Also it enakles us to calculate the contributions of the different conetrainte separately.
PkOOF The constraints on $\boldsymbol{R}_{1} \cdot \boldsymbol{R}_{\mathbf{x}} \cdots \boldsymbol{R}_{\boldsymbol{n}}$ are $\otimes \boldsymbol{R}=0$. Hence we may take the autrix $H$ of (7) to be $2 M^{\prime}$. with the notation used there we have $\quad \mathscr{Q}_{\mathbf{C}}=H_{1} \mathscr{Q}=H_{\mathbf{N}} W_{E} Q=H_{1} W_{c} H^{\prime} Q_{1}$. (1द)
Since the $\mathbb{R}^{\prime}$ s are all independent, tiere exists $M_{1}$ such that $Q_{1}=M, Q_{\text {. }}$. Hence $\quad Q_{1}^{\prime}=M_{0} \mathcal{O}_{\boldsymbol{K}}=M_{1} Q_{c} R=M_{1} Q_{2} M_{1}^{-1} Q_{4}$.
On comparison with (14) it follow that $H_{1} N_{E} H_{1}^{\prime}=M_{1} O_{e} M_{1}^{-1}$. Thue



EDh $\mathcal{C L E E}$ Consider the molecule $\mathrm{CH}_{3} \mathrm{Cl}$ ．Take

$\boldsymbol{R}_{1}, \boldsymbol{R}_{\mathbf{2}}, \boldsymbol{R}_{\mathbf{3}}, \mathbb{R}_{\mathbf{4}}=$ increments of the distances $\overline{\mathrm{CC}}, \overline{\mathrm{CH}_{\alpha}}, \overline{\mathrm{CH}_{\beta}}, \overline{\mathrm{CH}_{r}}$ ， $\boldsymbol{R}_{5}, \boldsymbol{R}_{\mathbf{6}}, \boldsymbol{R}_{\mathbf{7}}=$ increments of the angles $\alpha \hat{C} H_{\mu}, \alpha \hat{C} H_{p}, C \hat{C} H_{r}$ ， $R_{g}, R_{q}, R_{\% 0}=$ increments of the ant？es $H_{p} \hat{c} H_{\gamma}, H_{7} \hat{C} H_{\alpha}, H_{\alpha} \hat{C} H_{p}$ ．
Tho ejpatruintt is
$\left[R_{5}+R_{6}+R_{7}\right] f+\left[R_{8}+R_{9}+R_{0_{0}}\right]=0$.
wherefis a constant．Thus $\mathscr{D}=\sqrt{\frac{1}{5 f+3}}(000 \circ f f f 1,1)$ ．
The theorem leads to


The Kinetic and the Potential Enerities
SG GHOICE OF AXES Suppose that $\binom{R_{1}}{R_{2 N-6}}-R$ are the increments of
3N－6 independent internal coordinates．For smell vibrations，
$R=B \mathscr{G}$ where $\mathscr{G}=\left(\begin{array}{c}x_{1} \\ j \\ j\end{array}\right)$ is defined in $\S l$ ．Suppose that the equili－ brim positions of the nuclei use，in rectangular coordinates， $\left(Z_{1} \mathbf{Y}_{1} \boldsymbol{Z}_{1}\right),\left(\mathbb{X}_{2} \mathbf{Y}_{2} \boldsymbol{Z}_{1}\right), \cdots\left(\boldsymbol{Z}_{\omega} \bar{Y}_{N} z_{N}\right)$ ．Let $m_{1}, m_{2}, \cdots m_{N}$ be their masses．write
 is the value of $\boldsymbol{R}$ when all the nuclei are displaced by 1 unit of lent along the $X-a x i d$ ．But the $\mathbb{R}^{\prime} s$ are the＇increments of internal variables，hence $\boldsymbol{B}\binom{\frac{1}{i}}{!}=0$ ．Inithe same way we can show that

We have thus far descaled the molecule in fa certain system or rectangular coordinates．But when the molecule moves and rota－ tues in apace as Nell as vibrates，there remains an arbitrariness
＊proa this it is immediately seen that any constraint having the same coefficient for equivalent coordinate l contributes 1 to Spur（ © $\left.\otimes A_{\mathrm{c}} \Phi^{\prime \prime}\right)$ ．

## - $1-$

in fixing the coordinate axes to the molecule. The following met; hod of choosing these ayes is, however, the most oreferfable. The $\mathbf{3 N - 6}$ internal variables $\mathbf{R}_{\mathbf{1}}, \boldsymbol{k}_{\mathbf{N}}, \ldots \boldsymbol{R}_{3 \times \mathbf{}}$ is determined uniquely from the structure of the mologula. a confine $x_{1}, y_{1} \cdots g_{n}$ by

$$
r=\binom{x_{j}}{j_{N}}=\left(\begin{array}{l}
B_{F}^{B} \tag{15}
\end{array}\right)^{-1}\binom{k}{0} .
$$

so that $\quad \mathrm{FE}=0$.
From the definition of $\mathbf{B}$, we conclude that a syatdm of axes of reterence can be found so that the positions of the nuclei are
 very aah distorted iron its equilibrima strmoture. We have thus 6 external variables pooidyine tho position and orientation of
 means of (15) the positions of the nuclei with respect to these axes. §7 THE KINETIC AHERGY IN TLAMS OF $R$ EMu. (16) expresses the facts that the origin of our moving axes is at any time the centre of mass of tho nolecirle, and that the moment of momentum of the molecule in that is system of reference is of the order of $m x \dot{x}$. thu e if therpotecule rotates in space with an angular velocity $\omega$ rout its goitre of mass, its kinetic energy is

$T_{\text {rotation }}=(\mathrm{K}, \mathrm{E}$. of rotation if $\mathscr{C}=0)+$ teri $\sim m \omega^{2} \boldsymbol{x} \boldsymbol{X}$.
No: Tcentretof mass $+(K . E . ~ o l ~ r o t a t i o n ~ i f ~ \mathscr{C}=0)$ depends on the extonal variable only (together, of course, with their time devivatives) And $\ln _{7}$ is sows, due to thermal agitation, $\omega \boldsymbol{Z} \sim \dot{x}$.
Thu e infare filet approximation the eau. of motion is to be devi-


But

Hejte writing int

$$
\begin{align*}
& 2 T=\dot{k}^{\prime} \epsilon^{-1} k \text {. } \tag{17}
\end{align*}
$$

SB THE KINETIC ENERGY IN TERMS OE $R$ If we take the independent readied coofdinates $\boldsymbol{Q}(\$ 4)$ to be the $\boldsymbol{R}^{\prime} E$ of the last section, the reality may (be summerized:


 $g=\alpha_{c}^{\prime} \dot{z}\left({ }^{\omega_{5}}, \frac{1}{m_{N}}\right) \dot{x}^{\prime} \alpha_{c}-\alpha_{c}^{\prime} g a_{c}$.
typ 0：



If $w_{c}^{d}$ is of order $d_{d}$ ，trifid chows that the nonvanishing elements of $g$ are in $\sum_{\alpha=1}^{\hbar} d_{\alpha}$ diagonal blocks of which $d_{\boldsymbol{k}}$ are identical 01 dimension $x_{d} \times x_{d}$ ．
Qt THE POTENTIAL ENERGY IN TEFIES OF $\mathcal{R}$ The potential energy de－ verde on the internal coordinates only．For small vibrations，it is approximately equal to $\frac{1}{2} \boldsymbol{Q} \mathscr{P} \boldsymbol{R}$ ，where $\boldsymbol{\mathscr { P }}$ is a positive sym－ metrical matrix，because when in equilibrium the molecule has a minimum potential energy．The covering operations leave the po－ tential energy unchanged：$\quad \frac{1}{2} Q^{\prime} P R=\frac{1}{2} \mathscr{R}^{\prime} 2 P \mathcal{K}^{\delta}=\frac{1}{2} Q^{\prime} \alpha_{c}^{\prime} 2$
But $\mathbb{R}$ is arbitrary，hence $\quad 20=\alpha_{c}^{\prime} 2 \alpha_{c}$
Thus we have，just as we had（21），

$$
\alpha_{\alpha}\left(N_{d \beta}=\delta_{d \alpha_{0}^{\prime}} \beta^{2} \beta^{N} I, \quad \alpha=L, 2, \cdots k, \beta=\iota 2, \cdots n_{\alpha} . \quad\right. \text { (22) }
$$

There are therefore totally $\int_{d=1}^{*} n_{e}^{2}$ independent constants in the potential energy，which are actually unknowns．＂
dalculation of the Kinetic Energy

810 THE THANGOORMATION MATRIX ${ }^{7}$ In §4 the orthogonal matrix $M$ was introduced to reduce $A_{c}$ ．Since

$$
A_{c}=\left(\begin{array}{cc}
A_{c 1} & 0 \\
0 & A_{a} \\
& \\
0 &
\end{array}\right)
$$

where each $A_{c p}$ belongs to a set of equivalent coordinates，$(\$ 4, P, 3)$

$$
M=\left(\begin{array}{lll}
M_{1} & 0 \\
0 & M_{2} & \\
0
\end{array}\right)
$$

where $M_{p}$ is orthogonal．Hence $W_{c p}=M_{p} A_{c} M_{p}^{-1} i s$ of the form（6）， i．e．



No：

$$
\begin{aligned}
& W_{\varphi} M_{p}=M_{p} A_{P P} \text {. } \\
& W_{C q}^{\prime} L=L A_{\text {ep }} \text {. } \\
& \left.L^{\prime} L=A_{\varphi}^{\prime} L^{\prime} L A_{q}^{i} i \cdot C \quad U^{\prime} L\right) A_{c p}=A_{c p}\left(L^{\prime} L\right) .
\end{aligned}
$$

## ＊Cf．$£ 18$

Hence

There exists an operation $C$ which brings the second coordinate OI the moth set to the IIf:i, for which $\frac{R_{1}}{R_{1}}=R_{\mathbf{2}}$ so that, $\left(A_{c p}\right)_{\neq}=\delta_{k 2}$,


Now $d$ can be determined from the values of Spur ( $\boldsymbol{R}_{\mathrm{c}}$ ), (of. eu.
(39)) so that this relation facilitates the ouloulution of $\boldsymbol{M}$.
 by first ciforuting \& . Now $\boldsymbol{A}$ is a subratrix of mia. Hence

$$
\neq=M, B \quad \text { Where } \quad M_{1}==_{\text {same rows }}(M)_{\text {all celoms }} \cdot(23)
$$

Thus we have to find $\boldsymbol{B}$ first.
Now

$$
R=B \mathscr{C} .
$$

Write $\quad\left(x_{x} y_{x} z_{x}\right)=\overrightarrow{x_{x}}, \quad\left(x_{i} B_{x} \quad x^{B}+y \quad x^{B}+z\right)=\overrightarrow{x_{x}}$.
Then $R_{k}=\sum_{k} \sum_{x} \vec{x}_{x} \vec{E}_{k}$.In a wiollaz way we shall write

El EXPLICI'T ESPEESSION OF $\vec{n}^{7}{ }^{7}$ the $u$ on OI the vectors $\overrightarrow{\mathcal{F}}$ is advantageous berates they are indonendent of the coordinate axes. Two kinds of $\boldsymbol{R}^{\prime}$ a are commonly used:
(i) $R \neq$ the increment of the bond between the nuclei $\boldsymbol{t}^{\prime}$ and $\boldsymbol{t}^{\prime \prime}$ in tenth., Evidently when $\overrightarrow{\vec{r}_{t}^{\prime}}=\overrightarrow{\vec{g}_{t}^{\prime \prime}}=0, R=0$. Hence


 $\overrightarrow{\boldsymbol{s}}$ are 0 excess t $\overrightarrow{\boldsymbol{s}_{\boldsymbol{r}}}, \overrightarrow{\boldsymbol{s}_{\boldsymbol{x}^{\prime}}}$ and $\overrightarrow{\boldsymbol{s}_{\boldsymbol{t}}}$. Suppose that

$$
\overrightarrow{s^{\prime}} \overrightarrow{z^{\prime}}=x^{\prime} \overrightarrow{\xi^{\prime}}+y^{\prime} \vec{\eta}+z^{\prime} \overrightarrow{y^{\prime}} .
$$

When $\vec{b}_{k}=\vec{b}_{l^{\prime}}=\overrightarrow{b_{k^{\prime}}}=\vec{\xi} \quad$, we have, since s $t^{\prime}$ alone is $m$ displaced, $\quad R=\frac{1}{\epsilon}$. Hence $x^{\prime}=\frac{1}{\epsilon}$. imilur-
 we get $y^{\prime}=0^{\circ}$. Proceeding in this way we arrive finally at the first line of (20). Now $\boldsymbol{R} \quad \mathbf{v}$ banishes when ${\overrightarrow{b_{k}}}_{k}=\vec{G}_{k}=\vec{G}_{k^{\prime}} \quad$. Thus $\left(\vec{S}_{z^{\prime}}+\vec{S}_{k^{\prime}}+\vec{S}_{k}\right)=0$.

$$
-10-
$$

From（25）and（26）we can write down，for all $\kappa$ and $t$ ，the vec－ tor $\vec{k}_{\boldsymbol{s}}$ from which $\overrightarrow{\mathbb{S}}$ may be calculated through（24）．
 that not＂all the $S^{\prime \prime}$ s are needed for the calculation of $g$ ．
Take（5） $\mathscr{A} P_{c} Z_{c}=d_{c} t$ ．
（27）
By（20）$\sum_{t=1}^{N} \alpha p \mathcal{D}_{t^{\prime}} I_{c} \delta_{t, c^{-} t^{\prime}}=W_{c}^{\alpha}{ }_{\alpha p \beta}^{d_{t}}$ ，
（ $T_{s}$ is defined in 82 ）
i．e．
Hence for any $\beta$ and $\beta^{\prime}$ ，
so that


Now by（ट1），
$\beta g_{p}{ }^{\prime} I={ }_{\alpha \beta} g_{\alpha \beta^{\prime}}=\sum_{p} \alpha_{p} t_{p}\left(\frac{1}{r_{p}} I\right)_{\alpha \beta} J_{p}^{\prime}$,
where each $p$ refer to a set of equivalent nuclei．
From（27）
Hence
i．e．
Thus ${ }^{6}$
so that

$$
\left\{\begin{array}{l}
\overrightarrow{s_{k}}=\frac{1}{\epsilon} \overrightarrow{\xi^{\prime}}  \tag{26}\\
\overrightarrow{s_{t}}=-\left(\overrightarrow{s_{k}}+\overrightarrow{s_{x^{\prime}}}\right)=\frac{1}{\tau} \overrightarrow{\xi^{\prime \prime}} \\
\text { all other } \vec{s}=0
\end{array}\right.
$$

where $s^{f_{p}^{p}} 15$ an ordinary number．Substitute thine into（29）Hence
From（29）Tee have，

$$
A g_{\beta^{\prime}}^{\alpha} I=\frac{\bar{p}}{p} \frac{1}{m_{p}} \beta_{\beta}^{\alpha \beta} I
$$

Now consider the sum of（28）．Since ct goes over all values of tin $p$ when $C$ goes over all the operations of the group，
if $t$ and $t^{\prime}$ are in the same $p$－th set．Thus（ 32 ）becomes

$$
\beta^{b_{p}^{\alpha}} d_{\alpha t}=g S_{p u r}\left(J_{t} \quad \alpha_{t}^{\prime}\right)
$$

where $t$ represents any nucleus of the $f$－th set．Substitute into （31）and make use of（24）．We obtain：

${ }_{\alpha p} \vec{F}_{k}$ for all $\alpha(=1,2, \cdots k), \beta\left(=1,2, \cdots \pi_{d}\right)$ and $\boldsymbol{\gamma}\left(=1,2, \cdots d_{d}\right)$ ；but only
for one $t$ in each $p$ ．From（24）we see that not all $\overrightarrow{\mathbf{s}}$ are needed． Secular Equation and Degeneracy
§14 NORMAL COORDINATES Interns of the independent reduced cor－

$$
\begin{aligned}
& \alpha_{\beta} \mathcal{L}_{p \text { qu }} \text { dup }_{p}^{\prime}=\beta b_{p}^{\alpha p} I,
\end{aligned}
$$

-11-
dinates $\boldsymbol{Q}$ defined in $\$ 4$, the kinetic energy and the potential energy are $\frac{1}{2} \dot{R}^{\prime} \mathscr{G}^{-1} \dot{R}$ and $\frac{1}{2} R^{\prime} P Q R,(\$ \$ 8,9)$ where of is positive definite. Let $\lambda_{1}, \lambda_{2}, \cdots \lambda_{J N-6}$ be the roots of the equ.

$$
\begin{equation*}
\left|\lambda g^{-1}-2\right|=0, \quad \text { i.e. }|\lambda I-2 g|=0 \text {. } \tag{34}
\end{equation*}
$$

Then there existe a matrix $L$ such that


$2 \times$ potential energy $=R N R=x^{\prime} \Lambda \eta=\sum_{i} \lambda_{i} x_{i}^{2}$.
These coordinates $\boldsymbol{\gamma l}_{2}$ are known as the "normal coordinate"'s. They are obtained by first solving (34), thus getting $\lambda_{i}$; and then de-

This $L$ must be normalized by $\quad L g L^{\prime}=I$.
The normal çoordinates are then calculated from $\quad \forall \sim L R$.
Non we shall be able to wee the role that symmetry plays in aimplifying the calculations. Equiw. (21) and (22) shows the secular equ. (34) is factored into $\sum_{3}^{A} d_{d}$ equations of which $d_{\alpha}$ are identical and are of the $n_{\alpha}$-th foffod degree. The labor of salving for the $\lambda^{\prime}$ s ${ }_{n}^{\text {considerably saved. Noreover, the no. of unknown constants }}$ in $\boldsymbol{\mu}$ is reduced.

The normal coordinates are also a special form of the "symmetry coordinates" introduced by Howard and "ilson. The most general form of the symmetry coordinates $\mathscr{M}$ is given by $\boldsymbol{n}$-むanwhere

$$
\alpha_{\alpha} \mathscr{L}_{\alpha \beta^{\prime} \beta^{\prime}}=\delta_{\alpha \alpha^{\prime}} \beta_{\beta}^{\ell^{\alpha}} V^{\alpha}, \quad \alpha=1,2, \cdots k . \beta=1,2, \cdots n_{\alpha},
$$

in which " $U^{\alpha}$ is orthogonal and $\beta \ell_{\rho}^{\alpha}$ form an orthogonal matrix when $\beta$ and $\beta^{\prime}$ range over $1.2, \cdots n_{\alpha}$.
§15 SOLUTION OF THE PHYSICAL PROBLEM - CLASSICAL THEORY The Lagrangian is, from (35) and (36),
$\frac{1}{2} \sum_{i=1}^{5 N-6}\left(\dot{x}_{i}^{2}-\lambda_{i} H_{i}^{2}\right)$.
The equs. of motion are therefore

$$
\begin{aligned}
& \dot{r}_{i}+\lambda_{i} M_{i}=0, \quad i=1,2, \cdots 3 N-6 . \\
& \mu_{i}=\left({M_{i}}_{i} \operatorname{cov}\left(\sqrt{\lambda_{i}} t+\phi_{i}\right) .\right.
\end{aligned}
$$

Hence
The frequencies of vibration are thus

$$
\frac{\sqrt{\pi_{1}}}{2 \pi}, \frac{\sqrt{\lambda_{3}}}{2 \pi}, \cdots \frac{\sqrt{2 N-6}}{2 \pi}
$$

This is corract only in the first approximation; but it serves to give almost all $t$ our present knowledese about the forces within
the molecules．
§16 SOLUTION OF THE PHYSICAL FROBLEM－QUANTUM THEORY NOW

$$
T=\frac{1}{2} \sum_{2} \dot{\mu}_{i}^{2}, \quad \nabla-\frac{1}{2} \sum_{2} \lambda_{i} x_{i}^{2} .
$$

The wave equation is most easily obtained from the variational formulation of the problem：

where $g \dot{j}$ ta given by $T=g_{i g} \dot{x}^{\dot{x}} \dot{j}$ ．Hence
$\sum_{i}^{\frac{1}{2}}\left(-\ell^{2} \frac{\partial^{2}}{\partial \pi^{2}}+\lambda_{i} \pi_{i}^{2}\right) \psi=E \psi$ ．
The electric moment in any direction is，in the first approximation $D_{0}+\sum_{i=1}^{356} D_{i} \pi_{i}$
where $D_{\lambda}$＇15＂immediately calculable from（15）．Thus the wave fun－ action and selection rules，hence the frequencies in the vibrational spectra of the molecule，are the same as those of $3 \boldsymbol{N}-6$ indepen－ dent harmonic oscillators with coordinates $\boldsymbol{\chi}_{1}, \boldsymbol{\gamma}_{2}, \cdots \mathcal{X}_{3 \times-6}$ ．The ere－ quencies are therefore exactly those obtained classically． § 17 THE DEGREE OF DEGENERACY We have seen that the secular equ． （34）is factorized into $d_{1}$ identical equs．of the $n_{1}$－th degree，$d_{z}$ identical equs．of the $n_{2}$－th degree，．．．．．．．．There must there－ fore be frequencies each corresponding to $d_{1}$ different normal moods of＇vibration（ $d_{1}$－fold degenerate）．The nos．$d_{1}, d_{2} \ldots$ ．．．are accor－ dingly called＂the degrees of degeneracy＂．

It is interesting that they can be determined together with $n_{1}, n_{2}, \ldots$ without carrying out the calculation of the normal coordinates．For，by（20）

$$
\sum_{k} n_{d} s_{p u r}\left(w_{c}^{d}\right)=s_{\text {sur }}\left(O_{c}\right) .
$$

But
where $\boldsymbol{K}=$ order of the group．Hence

$$
\begin{equation*}
\left.x_{\alpha}=\frac{1}{k} \sum_{c} \operatorname{spur}^{(0 k}\right) \operatorname{spur}\left(W_{c}^{d}\right) . \tag{39}
\end{equation*}
$$

Now both Spur $\left(W_{c}\right)$ and $d_{\alpha}$ can be found ${ }^{s}$ from a table of characters of the point group，and $\operatorname{Spur}\left(\boldsymbol{a}_{c}\right)$ can be calculated through the theorem in 85 ，so that．$d_{\alpha}$ and $n_{\alpha}$ are easily calculable from（39）． EXAMPLE We consider again the molecule $\mathrm{CH}_{3} \mathrm{Cl}$ ．（\＄5）From the


| $w^{1}$ | 1 | 1 | 1 |
| :---: | :---: | :---: | :---: |
| $w^{2}$ | 1 | 1 | 1 |
| $w^{3}$ | $z$ | 2 | -1 |

$$
n_{1}=3, \quad n_{2}=0, \quad n_{3}=3 .
$$

It follows that the secular equ．is factored into 3 cubic equs． 2 of which

1．von H．Bethe，Ann．d．Physik，3（1929）， 133.
2．E．Wighery Gottingen Nachrichtent，（1930），p．I3j：
3．See 1．and：2．，alao Speiser：Theorie der Gruppen von Endlicher Ordnung（Berlin，1927）．
and d．E．Rosenthal and G．M．Murphy，Rev．Mod．Phys．，

$$
8(2936), 317
$$

The degeneracy and other properties are tabulated by E．B．Wilson HA Jr．in，J．Chem．Bhys．，2（1934）， 432. （complete to molecules containing 7 atoms）
The irreducible representations are given in
F．Seitz，Zeits．f．Krist．，A88（1934）， 433.
4．E．Wigner，Gruppentheorie．（Braunschweig 1931）This book is
always meant when Wigner is referred to．
5．Wigner，p．86．
6．ibid．p．83．
7．E．B．Wilson Jr．，J．Chem．Phys．，9（1941）， 76.
8．J．E．Rosenthal and G．M．Murphy，Rev．Mod．Phys．，8（1936）， 317.
9．B．B．Wiléon Jr．and B．L．Crawford Jr．，J．Chem．Phys．，8（1936），
10．D．M．Dennison，Kev．Mod．Phys．，3（1931）， 280.23.
11．J．B．Howard and E．B．Wilson，Jr．，J．Chem．Phys．，2（1934）， 630.

# Investigations in the Statistical Theory of Superlattices 

National Tsing Hua University

INVESTIGATIONS IN THE STATISTICAL THEORY OF SUPERLATTICES

A Dissertation<br>Submitted to<br>The Faculty of the Graduate School of Science<br>in Candidacy for<br>The Degree of Master of Science

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## CONTENTS

I．The Variation of the Interaction Energy with Change of Lattice Constants and Change of the Degree of Order

II．A Generalization of the Quasi－chemical Method in the Statistical Theory of Superlattices

# THE VARIATION OF THE INTERACTION ENERGY WITH CHANGE OF LATTICE CONSTANTS AND CHANGE OF THE DEGREE OF ORDER 

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#### Abstract

The change of the lattice constants due to the order-disordering process in a superlattice is investigated by using the condition of minimum free energy in Bethe's theory. It is found that the interaction energy depends on the degree of order when the external pressure is kept constant. The specific heat at constant pressure given by the theory is compared with experiment. Another source of the variation of interaction energy is the change of atomic arrangements. This is also investigated from the view point of Wang's formulation of the free energy in Bethe's approximations.


## 1．INTRODUCTION

The binary alloy CuAu is face－centred cubic when disordered and tetragonal when ordered．This change of lattice form can be studied thermodynamically if we know the energy and the entropy of the crystal．Some calculations along this line has already been made by Wilson ${ }^{1}$ who used Bethe＇s method to find the energy but Bragg－Williams＇ method to find the entropy of the crystal．It will be shown in the present paper that Bethe＇s method can be carried through in the calculations，making it self－consistent． The results are comparable with Gorsky＇s measurements ${ }^{2}$ ．

The change of lattice constants evidently affects the interaction energy between the atoms，and must consequently produce a change in the configurational energy and the specific heat of the crystal．We shall see that the effect is in the right direction to bring the theory into closer agreement with experiment，because it tends to make the energy increase more rapidly near the critical temperature．An actual calculation of the specific heat at variable lattice constant but constant external pressure for $\beta$－brass is given in section 3.

Now the interaction energy can also be influenced by a change of the atomic ar－ rangements．Mott ${ }^{3}$ has shown from a study of the electronic distribution in superlattices that the interaction energy decreases as the degree of order decreases．The actual rela－ tion between the two is naturally very complicated．A linear dependence（of the average interaction energy upon the degree of order）has been assumed by Lin ${ }^{4}$ in attempting to explain the occurrence of the maximum critical temperature of a face－centred alloy at the concentration ratio $1: 3$ ．In order to justify the assumption we shall view the problem from a new angle by the introduction of the free energy in Bethe＇s approxima－ tion ${ }^{5}$ ．In this way it is found that the interaction energy as a function of the degree of order must satisfy certain equations obtained from a set of conditions of consistency． This same set of conditions of consistency makes also possible the calculation of the energy of the crystal without appealing to Bragg－Williams＇theory as Lin did．

## 2．THE VARIATION OF LATTICE CONSTANTS

We shall form the partition function at constant lattice constants $l_{1}$ and $l_{2}$ ，and then obtain their equilibrium values from the equations determining the generalized reactions．Let $\frac{1}{2} z N m$ be the number of $A-B$ neighbors in the crystal．If $g(m)$ is the

[^8]number of arrangements of the atoms for the given value of $m$, and $W\left(l_{1}, l_{2}, m\right)$ the configurational energy of the crystal, the configurational partition function is
$$
f\left(m, T, l_{1}, l_{2}\right)=g(m) \exp (-W / k T) .
$$

The equilibrium value $\bar{m}$ of $m$ is determined from the condition of a maximum of $f$ :

$$
\frac{\partial}{\partial \bar{m}} \log f\left(\bar{m}, T, l_{1}, l_{2}\right)=0 .
$$

The generalized reactions are given by

$$
\begin{align*}
L_{i} & =k T \frac{\mathrm{~d}}{\mathrm{~d} l_{i}} \log f\left(\bar{m}, T, l_{1}, l_{2}\right)=k T \frac{\mathrm{~d} \bar{m}}{\mathrm{~d} l_{i}} \frac{\partial}{\partial \bar{m}} \log f+k T \frac{\partial}{\partial l_{i}} \log f=k T \frac{\partial}{\partial l_{i}} \log f \\
& =-\frac{\partial}{\partial l_{i}} W\left(l_{1}, l_{2}, \bar{m}\right) \tag{1}
\end{align*}
$$

To study the change of lattice form in CuAu we divide the face-centred lattice into four simple cubic sublattices $1,2,3,4^{*}$. Let the shortest distance between the sites of 1 and 2 , or 3 and 4 be $l_{1}$, that between the sites of 1 and 3,1 and 4,2 and 3 or 2 and 4 be $l_{2}$, so that the former is the distance between neighbouring $\mathrm{Au}-\mathrm{Au}$ or $\mathrm{Cu}-\mathrm{Cu}$ atoms and the latter that between neighbouring $\mathrm{Au}-\mathrm{Cu}$ atoms when the crystal is perfectly ordered. The interaction energies $V_{A A}, V_{A B}$ and $V_{B B}$ are functions of $l_{1}$, and $l_{2}$.

If the number of sites of each sublattice is $\frac{1}{2} N$, the number of pairs of sites between sublattices 1 and 2 must be $4\left(\frac{1}{2}\right) N=2 N$. Denote by $m_{12}$ the fraction of $A-B$ pairs among these. Then the number of

$$
\begin{array}{ll}
A-A \text { pairs is } & \frac{1}{2}\left[4\left(\frac{N}{2} \theta_{1}+\frac{N}{2} \theta_{2}\right)-2 N m_{12}\right]=N\left[\theta_{1}+\theta_{2}-m_{12}\right], \\
B-B \text { pairs is } & \frac{1}{2}\left[4\left(\frac{N}{2}\left\{1-\theta_{1}\right\}+\frac{N}{2}\left\{1-\theta_{2}\right\}\right)-2 N m_{12}\right]=N\left[2-\theta_{1}-\theta_{2}-m_{12}\right],
\end{array}
$$

where $\theta_{i}$ is the fraction of sites of sublattice $i$ occupied by $A$ atoms. Thus the energy of interaction between the atoms on sublattices 1 and 2 is

$$
N\left[\left(\theta_{1}+\theta_{2}-m_{12}\right) V_{A A}\left(l_{1}\right)+2 m_{12} V_{A B}\left(l_{1}\right)+\left(2-\theta_{1}-\theta_{2}-m_{12}\right) V_{B B}\left(l_{1}\right)\right]
$$

## Writing

$$
c=\frac{1}{4}\left(\theta_{1}+\theta_{2}+\theta_{3}+\theta_{4}\right) \quad \text { and } \quad V=\frac{1}{2}\left(V_{A A}+V_{B B}\right)-V_{A B},
$$

we get the energy of the whole crystal

$$
\begin{align*}
W= & N\left[4 c V_{A A}\left(l_{1}\right)+4(1-c) V_{B B}\left(l_{1}\right)-2\left(m_{12}+m_{34}\right) V\left(l_{1}\right)\right]+ \\
& N\left[8 c V_{A A}\left(l_{2}\right)+8(1-c) V_{B B}\left(l_{2}\right)-2\left(m_{13}+m_{14}+m_{23}+m_{24}\right) V\left(l_{2}\right)\right] . \tag{2}
\end{align*}
$$

[^9]With this value for $W$ ，（1）becomes

$$
\begin{equation*}
L_{1}=-N\left[4 c V_{A A}^{\prime}\left(l_{1}\right)+4(1-c) V_{B B}^{\prime}\left(l_{1}\right)-2\left(\bar{m}_{12}+\bar{m}_{34}\right) V^{\prime}\left(l_{1}\right)\right], \tag{3}
\end{equation*}
$$

and

$$
\begin{equation*}
L_{2}=-N\left[8 c V_{A A}^{\prime}\left(l_{2}\right)+8(1-c) V_{B B}^{\prime}\left(l_{2}\right)-2\left(\bar{m}_{13}+\bar{m}_{14}+\bar{m}_{23}+\bar{m}_{24}\right) V^{\prime}\left(l_{2}\right)\right] . \tag{4}
\end{equation*}
$$

To solve for $l_{1}$ and $l_{2}$ as functions of $T$ we must first know the $\bar{m}$＇s，which are usually very complicated．Wilson ${ }^{1}$ discussed the values of $l_{1}$ and $l_{2}$ only in the cases when the alloy is disordered and when the order is nearly perfect．We shall also confine our attention to these cases．
（i）Disordered．In this case there is no difference between the four sublattices so that all the $\bar{m}_{i j}$＇s are equal to $\bar{m}$ ．（3）and（4）reduce to

$$
\begin{align*}
& L_{1}=-N\left[4 c V_{A A}^{\prime}\left(l_{1}\right)+4(1-c) V_{B B}^{\prime}\left(l_{1}\right)-4 \bar{m} V^{\prime}\left(l_{1}\right)\right],  \tag{5}\\
& L_{2}=-N\left[8 c V_{A A}^{\prime}\left(l_{2}\right)+8(1-c) V_{B B}^{\prime}\left(l_{2}\right)-8 \bar{m} V^{\prime}\left(l_{2}\right)\right] .
\end{align*}
$$

If $L_{1}=L_{2}=0$ ，this shows that $l_{1}=l_{2}$ ，so that the crystal is cubic．
（ii）Order nearly perfect．When $c=\frac{1}{2}$ ，and the order is nearly perfect，

$$
\theta_{1}=\theta_{2} \cong 1, \quad \theta_{3}=\theta_{4} \cong 0, \quad \theta_{1}+\theta_{3}=1, \quad \theta_{1}-\theta_{3}=s
$$

There are only a few $B$ atoms on sublattices 1 and 2．Hence approximately

$$
\bar{m}_{12}=\left(1-\theta_{1}\right)+\left(1-\theta_{2}\right)=2 \theta_{3}=1-s .
$$

By the same reason we can obtain the number of $A-A$ pairs of neighbours between the sublattices 1 and 3：

$$
N\left(\theta_{1}+\theta_{3}-\bar{m}_{13}\right)=4\left(\frac{1}{2} N \theta_{3}\right) .
$$

Thus

$$
\bar{m}_{13}=\theta_{1}-\theta_{3}=s .
$$

We can now write down all the $\bar{m}$＇s：

$$
\bar{m}_{12}=\bar{m}_{34}=1-s, \quad \bar{m}_{13}=\bar{m}_{23}=\bar{m}_{14}=\bar{m}_{24}=s .
$$

These equations are correct to the first order of $(1-s)$ ．Substituting them into（3）and （4）we obtain

$$
\begin{aligned}
L_{1} & =-2 N\left[V_{A A}^{\prime}\left(l_{1}\right)+V_{B B}^{\prime}\left(l_{1}\right)-2(1-s) V^{\prime}(l)\right], \\
L_{2} & =-4 N\left[V_{A A}^{\prime}\left(l_{2}\right)+V_{B B}^{\prime}\left(l_{2}\right)-2 s V^{\prime}\left(l_{2}\right)\right] .
\end{aligned}
$$

These are exactly equations（27）in Wilson＇s paper，from which an expression of the degree of tetragonality in agreement with Gorsky＇s measurements ${ }^{2}$ can be obtained．

## 3. THE EFFECT OF THE CHANGE OF LATTICE CONSTANTS ON THE INTERACTION ENERGY

In the alloy CuAu the gold atoms and the copper atoms are in contact when the order is perfect. Since the copper atom is somewhat smaller than the gold atom, the size of the crystal must increase when gold atoms exchange their positions with copper atoms. Thus with increasing disorder the distance between the atoms increases and hence the interaction energies diminish. The disordering process is therefore effected with more ease near the critical temperature than it is at lower temperatures; and we expect the specific heat at constant pressure to possess a steeper and higher maximum at the critical temperature than the specific heat at constant volume.

Now we shall calculate in length the specific heat at constant pressure of the alloy $\beta$-brass, which forms the simplest type of superlattice that can be studied statistically. Bethe's method will be used.

The configurational energy of the crystal is, in Easthope's ${ }^{6}$ notations:

$$
\begin{equation*}
W=-N_{A B} V+\frac{1}{2} N z\left[c\left(V_{A A}-V_{B B}\right)+V_{B B}\right] . \tag{6}
\end{equation*}
$$

Substitution of this expression into (1) gives

$$
0=-\bar{m} V^{\prime}(l)+c\left[V_{A A}^{\prime}(l)-V_{B B}^{\prime}(l)\right]+V_{B B}^{\prime}(l)
$$

when the pressure is put equal to zero. Now the variation of $V$ is not very large, so that to a sufficient approximation we may assume the linear relations

$$
\begin{equation*}
\left[V_{A A}^{\prime}(l)-V_{B B}^{\prime}(l)\right] / V^{\prime}(l)=-K_{0}+K_{1} V \tag{7}
\end{equation*}
$$

and

$$
\begin{equation*}
V_{B B}^{\prime}(l) / V^{\prime}(l)=-J_{0}+J_{1} V . \tag{8}
\end{equation*}
$$

These three last equations give, after eliminating $V_{A A}^{\prime}(l)$ and $V_{B B}^{\prime}(l)$ :

$$
\begin{equation*}
V=\frac{\bar{m}+\left(c K_{0}+J_{0}\right)}{c K_{1}+J_{1}} \tag{9}
\end{equation*}
$$

We have already seen that $V$ increases as $\bar{m}$ increases, hence $c K_{1}+J_{1}$ must be positive. The other constant $c K_{0}+J_{0}$ must also be positive in order that $V$ may be positive with only a relatively small variation.

Eisenschitz ${ }^{7}$ has calculated the specific heat at constant pressure by Bragg-Williams' method. He assumed that the interaction energies depend on a parameter $u$ in the following way:

$$
\frac{1}{2}\left(V_{A A}+V_{B B}\right)=\phi\left[(1-a)+a(1-u)^{2}\right], \quad V_{A B}=\phi b u^{2}
$$

[^10]where $a=.225, b=.203$ and $u$ is of the order of unity．Comparing this with（7）and （8）we see that his assumption is equivalent（approximately）to ours if $\frac{1}{2} K_{0}+J_{0}=1.22$ and $\frac{1}{2} K_{1}+J_{1}=.508 \times 10^{14} \mathrm{erg}^{-1}$ ．But with these values the specific heat at the critical temperature would be too large．In order to make $\left(C_{p}\right)_{T_{c}}=5.1 R$ as given by the measurements of Sykes and Wilkinson ${ }^{8}$ we assume（cf．eq．（12）below）
$$
\frac{1}{2} K_{0}+J_{0}=1.79 .
$$

With this value for $\frac{1}{2} K_{0}+J_{0}$ ，the relative variation of $V$ can be shown to be within 1．3\％．

We can now start from（9）and the equations given by Easthope ${ }^{6}$ for the deter－ mination of $\bar{m}$ as a function of the temperature and $V$ to obtain the specific heat at constant pressure：

$$
\begin{equation*}
C_{p}=\frac{\mathrm{d} W}{\mathrm{~d} T}=\left(\frac{\partial W}{\partial \bar{m}}\right)_{l} \frac{\mathrm{~d} \bar{m}}{\mathrm{~d} x} \frac{\mathrm{~d} x}{\mathrm{~d} T}+\left(\frac{\partial W}{\partial l}\right)_{\bar{m}} \frac{\mathrm{~d} l}{\mathrm{~d} T}=\left(\frac{\partial W}{\partial \bar{m}}\right)_{l} \frac{\mathrm{~d} \bar{m}}{\partial x} \frac{\mathrm{~d} x}{\mathrm{~d} T} . \tag{10}
\end{equation*}
$$

But

$$
\begin{equation*}
\frac{\mathrm{d} x}{\mathrm{~d} T}=\frac{x V / k T^{2}}{1+\frac{x}{k T} \frac{\mathrm{~d} V}{\mathrm{~d}} \frac{\mathrm{~d} \bar{m}}{\mathrm{~d} x}} . \tag{11}
\end{equation*}
$$

Hence by（6）

$$
\begin{equation*}
C_{p}=\frac{\frac{1}{2} N z k x(\log x)^{2}\left(-\frac{\mathrm{d} \bar{x}}{\mathrm{~d} x}\right)}{1+\frac{x \log x}{\bar{m}+\left(c K_{0}+J_{0}\right)}\left(-\frac{\mathrm{d} \bar{x}}{\mathrm{~d} x}\right)} . \tag{12}
\end{equation*}
$$

The value of this expression is calculated for the case $c=\frac{1}{2}$ ，the constant $\frac{1}{2} K_{0}+J_{0}$ being assumed to be 1.79 to make $\left(C_{p}\right)_{T_{c}}=5.1 R$ ．The result is plotted in the accompanying figure together with Bethe＇s curve ${ }^{9}$ for $C_{V}$ and Sykes ad Wilkinson＇s experimental ${ }^{8}$ data．


Fig． 1 Configurational specific heat of $\beta$－brass．

[^11]
## 4. THE EFFECT OF THE ATOMIC DISTRIBUTION ON THE INTERACTION ENERGY

As has already been mentioned, the interaction energy depends in some very complicated manner upon the degree of order. To study the effect of such a dependence Lin ${ }^{4}$ has assumed a linear relationship:

$$
\begin{equation*}
V=V_{0}\left(1+\alpha c+\beta m_{A A}\right) \tag{13}
\end{equation*}
$$

between the interaction energy: $V$ and the fraction of $A-A$ pairs of neighbours: $m_{A A}$. In this section we shall study the general nature of the variation of $V$ in the light of the theory of the free energy in Bethe's approximation given by Wang ${ }^{5}$.

The fundamental equations in Wang's paper are (45), (46) and (39) with $\xi_{\alpha}$ and $\xi_{\beta}$ given by (47), (48), (49) and (50). These equations are still assumed to be valid now $V$ becomes a function of $\theta_{\alpha}, \theta_{\beta}$ and $T$. They may be put into the form:

$$
\begin{gather*}
\frac{\mathrm{d}}{\mathrm{~d} \theta_{\alpha}} \log Q=-N r_{\alpha} \log \xi_{\alpha}=\frac{\partial}{\partial \theta_{\alpha}} \log Q_{0}\left(\theta_{\alpha}, \theta_{\beta}, V / T\right),  \tag{14}\\
\frac{\mathrm{d}}{\mathrm{~d} \theta_{\beta}} \log Q=-N r_{\beta} \log \xi_{\beta}=\frac{\partial}{\partial \theta_{\beta}} \log Q_{0}\left(\theta_{\alpha}, \theta_{\beta}, V / T\right),  \tag{15}\\
E=k T^{2} \frac{\mathrm{~d}}{\mathrm{~d} T} \log Q \tag{16}
\end{gather*}
$$

where $Q_{0}$ is the partition function for the case when $V$ is a constant, if we denote by $\frac{\partial}{\partial \theta_{\alpha}}, \frac{\partial}{\partial \theta_{\beta}}, \frac{\partial}{\partial T}$ and $\frac{\partial}{\partial V}$ differentiations when $\theta_{\alpha}, \theta_{\beta}, T$ and $V$ are regarded as independent of each other, and by $\frac{\mathrm{d}}{\mathrm{d} \theta_{\alpha}}$ the operator $\frac{\partial}{\partial \theta_{\alpha}}+\frac{\mathrm{d} V}{\mathrm{~d} \theta_{\alpha}} \frac{\partial}{\partial V}$. (14) and (15) mean that we have assumed with Lin that the equilibrium values of $\theta_{\alpha}$ and $\theta_{\beta}$ are given by the same equations as in Bethe's approximation. (16) gives the energy of the crystal.

Consistency of (14) and (15) requires

$$
\frac{\mathrm{d}}{\mathrm{~d} \theta_{\alpha}}\left(\frac{\partial}{\partial \theta_{\beta}} \log Q_{0}\right)=\frac{\mathrm{d}}{\mathrm{~d} \theta_{\beta}}\left(\frac{\partial}{\partial \theta_{\alpha}} \log Q_{0}\right),
$$

i.e.

$$
\begin{equation*}
\frac{\mathrm{d} V}{\mathrm{~d} \theta_{\alpha}} \frac{\partial^{2}}{\partial \theta_{\beta} \partial V} \log Q_{0}=\frac{\mathrm{d} V}{\mathrm{~d} \theta_{\beta}} \frac{\partial^{2}}{\partial V \partial \theta_{\alpha}} \log Q_{0} . \tag{17}
\end{equation*}
$$

Upon the hypothesis of nearest neighbour interaction the energy in Wang's paper becomes

$$
E_{0}=k T^{2} \frac{\partial}{\partial T} \log Q_{0}=z N V m_{A A} .
$$

But $Q_{0}$ depends on $T$ and $V$ through $V / T$, so that

$$
\frac{\partial^{2}}{\partial \theta_{\alpha} \partial V} \log Q_{0}=-\frac{T}{V} \frac{\partial^{2}}{\partial T \partial \theta_{\alpha}} \log Q_{0}=-\frac{\partial E_{0}}{\partial \theta_{\alpha}} / k T V
$$

Substituting this eq．and a similar one into（17）we obtain

$$
\begin{equation*}
\frac{\partial E_{0}}{\partial \theta_{\beta}} \frac{\mathrm{d} V}{\mathrm{~d} \theta_{\alpha}}=\frac{\partial E_{0}}{\partial \theta_{\alpha}} \frac{\mathrm{d} V}{\mathrm{~d} \theta_{\beta}}, \tag{18}
\end{equation*}
$$

which becomes，if $\frac{\partial E_{0}}{\partial V} \frac{\mathrm{~d} V}{\mathrm{~d} \theta_{\alpha}} \frac{\mathrm{d} V}{\mathrm{~d} \theta_{\beta}}$ is added to both sides，

$$
\frac{\mathrm{d} E_{0}}{\mathrm{~d} \theta_{\alpha}} \frac{\mathrm{d} V}{\mathrm{~d} \theta_{\beta}}=\frac{\mathrm{d} E_{0}}{\mathrm{~d} \theta_{\beta}} \frac{\mathrm{d} V}{\mathrm{~d} \theta_{\alpha}} .
$$

This shows that $V$ and $E_{0}$ are connected by a relation independent of $\theta_{\alpha}$ and $\theta_{\beta}$ ，i．e．

$$
\begin{equation*}
V=V\left(E_{0}, T\right) \tag{19}
\end{equation*}
$$

A consequence of this result is that the coefficient $\alpha$ in Lin＇s relation（13）must be zero． This makes，however，the maximum critical temperature for the $A B$ type of superlattice to shift to a value of the concentration different from $\frac{1}{2}$ ，which contradicts experimental results．One way out of the difficulty is to make some other assumption regarding the dependence of $V$ on the degree of order，such as

$$
\begin{equation*}
V=V_{0}\left[1+\beta m_{A A}-\frac{\beta(z-1)}{2 c(c z-1)} m_{A A}^{2}\right] . \tag{20}
\end{equation*}
$$

Let us now try to find $E$ in the general case．From（14）and（16）we get

$$
\begin{equation*}
\frac{\mathrm{d} E}{\mathrm{~d} \theta_{\alpha}}=k T^{2} \frac{\mathrm{~d}}{\mathrm{~d} T}\left(\frac{\partial}{\partial \theta_{\alpha}} \log Q_{0}\right)=k T^{2} \frac{\mathrm{~d}\left(\frac{V}{T}\right)}{\mathrm{d} T} \frac{\partial^{2}}{\partial \theta_{\alpha} \partial\left(\frac{V}{T}\right)} \log Q_{0}=-\frac{T^{2}}{V} \frac{\mathrm{~d}\left(\frac{V}{T}\right)}{\mathrm{d} T} \frac{\partial E_{0}}{\partial \theta_{\alpha}} . \tag{21}
\end{equation*}
$$

Similarly

$$
\frac{\mathrm{d} E}{\mathrm{~d} \theta_{\beta}} \quad=-\frac{T^{2}}{V} \frac{\mathrm{~d}\left(\frac{V}{T}\right)}{\mathrm{d} T} \frac{\partial E_{0}}{\partial \theta_{\beta}}
$$

Hence

$$
\frac{\mathrm{d} E}{\mathrm{~d} \theta_{\alpha}} \frac{\partial E_{0}}{\partial \theta_{\beta}}=\frac{\partial E_{0}}{\partial \theta_{\alpha}} \frac{\mathrm{d} E}{\mathrm{~d} \theta_{\beta}} .
$$

Just as（18）leads to（19），this last equation leads to

$$
E=E\left(E_{0}, T\right)
$$

Substituting this into（21）we obtain

$$
\frac{\partial E}{\partial E_{0}}\left(\frac{\partial E_{0}}{\partial \theta_{\alpha}}+\frac{\partial E_{0}}{\partial V} \frac{\partial V}{\partial \theta_{\alpha}}\right)=\frac{\partial E_{0}}{\partial \theta_{\alpha}}\left(1-\frac{T}{V} \frac{\mathrm{~d} V}{\mathrm{~d} T}\right) .
$$

But（19）gives

$$
\frac{\mathrm{d} V}{\mathrm{~d} \theta_{\alpha}}=\frac{\frac{\partial E}{\partial \theta_{\alpha}} \frac{\partial V}{\partial E_{0}}}{1-\frac{\partial V}{\partial E_{0}} \frac{\partial E_{0}}{\partial V}} \quad \text { and } \quad \frac{\mathrm{d} V}{\mathrm{~d} T}=\frac{\frac{\partial V}{\partial T}+\frac{\partial V}{\partial E_{0}} \frac{\partial E_{0}}{\partial T}}{1-\frac{\partial V}{\partial E_{0}} \frac{\partial E_{0}}{\partial V}} .
$$

Hence

$$
\frac{\partial E}{\partial E_{0}}=\left(1-\frac{\partial V}{\partial E_{0}} \frac{\partial E_{0}}{\partial V}\right)\left(1-\frac{T}{V} \frac{\mathrm{~d} V}{\mathrm{~d} T}\right)=1-\frac{\partial V}{\partial E_{0}} \frac{\partial E_{0}}{\partial V}-\frac{T}{V} \frac{\mathrm{~d} V}{\mathrm{~d} T}-\frac{T}{V} \frac{\partial V}{\partial E_{0}} \frac{\partial E_{0}}{\partial T}
$$

Now $E_{0} / V$ is a function of $\theta_{\alpha}, \theta_{\beta}$ and $V / T$, so that

$$
\frac{\partial E_{0}}{\partial V}=-\frac{T}{V} \frac{\partial E_{0}}{\partial T}+\frac{\partial E_{0}}{\partial V}
$$

Hence

$$
\begin{equation*}
\frac{\partial E}{\partial E_{0}}=1-\frac{E_{0}}{V} \frac{\partial V}{\partial E_{0}}-\frac{T}{V} \frac{\partial V}{\partial T} . \tag{22}
\end{equation*}
$$

If $V$ depends on $m_{A A}$ only, and not on $T$, we have

$$
\frac{\partial E}{\partial E_{0}}=1-\frac{E_{0}}{V} \frac{\mathrm{~d} V}{\mathrm{~d} E_{0}}=V \frac{\mathrm{~d}\left(E_{0} / V\right)}{\mathrm{d} E_{0}}
$$

The boundary condition is given by the case when there is no $A$ atoms, i.e. when $\theta_{\alpha}+\theta_{\beta}=0$. In this case $m_{A A}=0, E_{0}=E=0$. Hence

$$
\begin{equation*}
E=\int_{0}^{E_{0}}\left[V \frac{\mathrm{~d}\left(E_{0} / V\right)}{\mathrm{d} E_{0}}\right] \mathrm{d} E_{0}=z N \int_{0}^{m_{A A}} V \mathrm{~d} m_{A A} \tag{23}
\end{equation*}
$$

If the assumption (20) is made, the energy of the crystal is

$$
E=z N V_{0}\left[m_{A A}+\frac{\beta}{2} m_{A A}^{2}-\frac{\beta(z-1)}{6 c(c z-1)} m_{A A}^{3}\right]
$$

When $\beta$ is not large, this differs very little in numerical value from Bethe's original expression. The specific heat is

$$
C_{V}=z N V \frac{\mathrm{~d} m_{A A}}{\mathrm{~d} T}=z N V \frac{\mathrm{~d} m_{A A}}{\mathrm{~d} x} \frac{\frac{x V}{k T^{2}}}{1+\frac{x}{k T} \frac{\mathrm{~d} V}{\mathrm{~d} x}}=z N k x(\log x)^{2} \frac{\mathrm{~d} m_{A A}}{\mathrm{~d} x} \frac{1}{1+\frac{x}{k T} \frac{\mathrm{~d} V}{\mathrm{~d} m_{A A}} \frac{\mathrm{~d} m_{A A}}{\mathrm{~d} x}} .
$$

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# A GENERALIZATION OF THE QUASI－CHEMICAL METHOD IN THE STATISTICAL THEORY OF SUPERLATTICES 

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#### Abstract

The quasi－chemical method introduced by Fowler and Guggenheim for the equilib－ rium distribution of pairs of sites in a superlattice is generalized．It is shown that by considering groups containing large numbers of sites the method may be used to obtain successive approximations of the free energy of the crystal．To analyze the fundamental assumption underlying the method more closely，the hypothesis of the non－interference of local configurations is discussed．The free energy of the crystal is obtained without integration as a closed algebraic expression with the aid of a Legendre transformation． Applications of the results are then made to different approximations for simple and body－centred cubic crystals and for the face－centred cubic crystal $\mathrm{Cu}_{3} A u$ ．In each case the free energy is obtained and discussed．


[^12]
## 1. INTRODUCTION

It was shown by Fowler and Guggenheim ${ }^{1}$ that the quasi-chemical method, originally devised for the theory of regular solutions, applies equally well to the theory of superlattices with long-distance order. The method is, as they have emphasized, definitely one stage further towards an exact theory than Bragg-Williams' method ${ }^{2}$. When compared with Bethe's ${ }^{3}$ or Kirkwood's ${ }^{4}$ method it also distinguishes itself in mathematical simplicity. But to be a method that may lead to a consistent scheme of successive approximations, it must be applicable to the $n$-th approximation in the theory of superlattices. This does not, however, seem possible in the original form of the method given by Fowler and Guggenheim. It is the purpose of the present paper to formulate the quasi-chemical method in a new way which is applicable to high order approximations in the theory of superlattices.

The free energy expression in Bethe's and in the quasi-chemical methods involves an integral. Its evaluation is very complicated and has been carried out ${ }^{1,5}$ so far only in Bethe's approximation for simple and body-centered cubic crystals. In the new formulation of the quasi-chemical method, however, it will be shown that a Legendre transformation helps much in avoiding the mathematical difficulties. (It might be noticed that a similar Legendre transformation is used to essentially the same effect in Fowler's formulation of general statistical mechanics. Cf. Fowler, Statistical Mechanics, second edition, p.188.) The free energy is obtained directly as a closed algebraic expression. Its values are given for Bethe's first and second (modified) approximations and for the face-centered alloy $\mathrm{Cu}_{3} \mathrm{Au}$ in sections 7 and 8 .

To make sure that the quasi-chemical method may actually be used to obtain a series of successively better approximations, we must investigate the free energy in high order approximations and compare it with the partition function of the crystal. This is done in section 5 together with a comparison of the quasi-chemical and Bethe's methods.

Except in the last section we are only concerned with binary alloys with atomic ratio $1: 1$ forming a (quadratic), simple cubic or body-centered cubic lattice. The generalization of the method to the investigation of alloys with other atomic ratios and forming other types of lattices is easy. In fact, the superior power of the quasi-

[^13]chemical method appears to be even more fully revealed when a face－centered lattice is treated．This problem is taken at the end of the paper where an approximate free energy expression for $\mathrm{Cu}_{3} \mathrm{Au}$ is obtained and its critical phenomena discussed．

## 2．REFORMULATION OF THE QUASI－CHEMICAL METHOD

Consider a crystal $A B$ ．Let $2 N$ be the total number of atoms and $z$ the number of nearest neighbours of each．At low temperatures we can distinguish between the so－called $\alpha$－sites and $\beta$－sites for $A$ and $B$ atoms respectively．Denote by $N r$ the number of $A$ atoms on $\alpha$－sites．Let

$$
1-r=w, \quad r-w=s
$$

The partition function of the crystal is

$$
\begin{equation*}
\sum_{r} p(r, T), \tag{1}
\end{equation*}
$$

where $p(r, T)$ is equal to $\sum \exp (-E / k T)$ over all possible configurations of the crystal with the given value of $r$ ．The average energy over all these configurations is

$$
\begin{equation*}
\bar{E}(r, T)=k T^{2} \frac{\partial}{\partial T} \log p(r, T) . \tag{2}
\end{equation*}
$$

But evidently，

$$
\begin{equation*}
p(r, \infty)=g(r)=\left[\frac{N!}{(N r)!(N \omega)!}\right]^{2} . \tag{3}
\end{equation*}
$$

Hence

$$
\begin{equation*}
\log p(r, T)=\log g(r)+\int_{\infty}^{T} \frac{1}{k T^{2}} \bar{E}(r, T) \mathrm{d} T \tag{4}
\end{equation*}
$$

The problem therefore reduces to one of finding $\bar{E}(r, T)$ ．Since a direct solution is very difficult we shall try to find an approximate solution by the quasi－chemical method， which is presented below in a form easily generalizable．

There are in the crystal $z N$ nearest pairs of sites $\alpha-\beta$ ．Among these let there be $\left[q_{\alpha}, q_{\beta}\right]$ with their $\alpha$－sites occupied by $q_{\alpha}(=0,1)$ wrong $(B)$ atoms and their $\beta$－sites by $q_{\beta}(=0,1)$ wrong $(A)$ atoms．For given $r$ the following relations hold：

$$
\begin{align*}
{[0,1]+[0,0]+[1,1]+[1,0] } & =z N, \\
{[1,1]+[1,0] } & =z N w,  \tag{5}\\
{[0,1] \quad+[1,1] } & =z N w .
\end{align*}
$$

Upon the approximation of neighbour interaction the energy of the crystal may be written as

$$
\begin{equation*}
E(r, T)=[0,1] V_{A A}+[0,0] V_{A B}+[1,1] V_{A B}+[1,0] V_{B B}, \tag{6}
\end{equation*}
$$

where the $V$ 's are the interaction energies between a pair of nearest neighbours.
We may give (5) and (6) a different interpretation by imagining $[0,1],[0,0],[1,1]$, $[1,0]$ and $V_{A A}, V_{A B}, V_{A B}, V_{B B}$ to be respectively the numbers and the molecular internal energies of the four different kinds of molecules $X Z, X, X Y Z, X Y$ of a gaseous assembly. The interpretation of (6) is that the assembly has the same internal (nonkinetic) energy as the crystal at the given value of $r$. (5) would mean that there are altogether $z N X$ atoms, $z N w Y$ atoms and $z N w Z$ atoms in the assembly.

The quasi-chemical method consists in taking the averages $\overline{[0,1]}, \overline{[0,0]}, \overline{[1,1]}, \overline{[1,0]}$ of the assembly at any temperature as approximately representing the corresponding averages of the crystal at the same temperature. Whether this approximation is good can only be judged for the present from the results it leads to.

A detailed treatment of the problem of a gaseous assembly has been given by Fowler ${ }^{6}$. We are only interested in our assembly of four different kinds of molecules, for which the results may be summarized as:

$$
\begin{array}{ll}
\overline{[0,1]}=\xi \nu \mathrm{e}^{-V_{A A} / k T}, & \overline{[0,0]}=\xi \mathrm{e}^{-V_{A B} / k T},  \tag{7}\\
\overline{[1,1]}=\xi \mu \nu \mathrm{e}^{-V_{A B} / k T}, & \overline{[1,0]}=\xi \mu \mathrm{e}^{-V_{B B} / k T},
\end{array}
$$

where $\xi, \mu$ and $\nu$ are to be determined from (6). From (7) we get

$$
\begin{equation*}
\frac{\overline{[0,0]} \overline{[1,1]}}{\overline{[0,1]} \overline{[1,0]}}=x^{-2}, \tag{8}
\end{equation*}
$$

where

$$
\begin{equation*}
x=\exp \left[-\frac{1}{2}\left(V_{A A}+V_{B B}-2 V_{A B}\right) / k T\right] . \tag{9}
\end{equation*}
$$

(8) and (6) together form the starting point of Fowler and Guggenheim's work ${ }^{1}$. The subsequent calculations of $\bar{E}(r, T), p(r, T)$ and the free energy of the crystal are straightforward and will not be repeated here. We shall see later how the free energy can be written down directly without actual integration.

## 3. GENERALIZATION TO GROUPS OF FOUR SITES

So far we have fixed our attention on the pairs of nearest neighbours in the crystal and have used the quasi-chemical method to obtain the average numbers of the four different kinds of pairs. Now we shall generalize the whole procedure: we shall study all the groups of sites of an arbitrarily chosen form in the crystal, and classifying these groups according to the way they are occupied by atoms we shall obtain the average number of groups in each class by chemical analogy.

[^14]| $\beta$ | $\alpha$ | $\beta$ | $\alpha$ | $\beta$ |
| :--- | :--- | :--- | :--- | :--- |
| $\alpha$ | $\beta$ | $\alpha$ | $\beta$ | $\alpha$ |
| $\beta$ | $\alpha$ | $\beta$ | $\alpha$ | $\alpha$ |
| $\alpha$ | $\beta$ | $\alpha$ | $\beta$ | $\alpha$ |

Fig． 1

To make this clear let us consider in detail groups of four sites forming squares（as shown）in a quadratic lattice．We classify these groups into $2^{4}=16$ classes denoted by $(0,0,0,0),(0,0,0,1), \cdots,(1,1,1,1)$ respectively，so that all groups in the class $\left(q_{1}, q_{2}, q_{3}, q_{4}\right)$ have $q_{1}$ wrong atoms in their upper $\alpha$－sites，$q_{2}$ wrong atoms in their lower $\alpha$－sites，$q_{3}$ wrong atoms in their upper $\beta$－sites and $q_{4}$ wrong atoms in their lower $\beta$－sites．The total number of these groups is $N$ ．Hence

$$
\begin{equation*}
\sum_{q_{i}=0}^{1}\left[q_{1}, q_{2}, q_{3}, q_{4}\right]=N \tag{10}
\end{equation*}
$$

where $\left[q_{1}, q_{2}, q_{3}, q_{4}\right]$ is an abbreviation for the number of groups in the class $\left(q_{1}, q_{2}, q_{3}, q_{4}\right)$ ． Now the number of all those groups in the crystal with a wrong $(B)$ atom on the upper $\alpha$－site is just the number of $B$ atoms on the $\alpha$－sites．Hence

$$
\begin{equation*}
\sum_{q} q_{i}\left[q_{1}, q_{2}, q_{3}, q_{4}\right]=N w, \quad i=1,2,3,4 \tag{11}
\end{equation*}
$$

Let $\chi\left(q_{1}, q_{2}, q_{3}, q_{4}\right)$ be the energy of each group in the class $\left(q_{1}, q_{2}, q_{3}, q_{4}\right)$ ．It is easy to show that the total energy of the crystal is

$$
\begin{equation*}
\bar{E}(r, T)=\sum_{q} \overline{\left[q_{1}, q_{2}, q_{3}, q_{4}\right]} \chi\left(q_{1}, q_{2}, q_{3}, q_{4}\right) . \tag{12}
\end{equation*}
$$

We may give（10），（11）and（12）an interpretation similar to the one given in section 2 for equations（5）and（6）．The same quasi－chemical method used there to obtain（7） leads now to the following averages（approximate）at a given value of $r$ ：

$$
\begin{equation*}
\overline{\left[q_{1}, q_{2}, q_{3}, q_{4}\right]}=\xi \mu_{1}{ }^{q_{1}} \mu_{2}{ }^{q_{2}} \mu_{3}{ }^{q_{3}} \mu_{4}^{q_{4}} \mathrm{e}^{-\chi\left(q_{1}, q_{2}, q_{3}, q_{4}\right) / k T} . \tag{13}
\end{equation*}
$$

In this expression the parameters $\xi, \mu_{1}, \mu_{2}, \mu_{3}$ and $\mu_{4}$ are to be determined from（10） and（11），which may be written in the form

$$
\begin{equation*}
\xi \frac{\partial \phi}{\partial \xi}=N, \quad \mu_{i} \frac{\partial \phi}{\partial \mu_{i}}=N w \quad(i=1,2,3,4) \tag{14}
\end{equation*}
$$

if we put

$$
\begin{equation*}
\phi\left(\xi, \mu_{1}, \mu_{2}, \mu_{3}, \mu_{4}\right)=\sum_{q} \xi \mu_{1}{ }^{q_{1}} \mu_{2}^{q_{2}} \mu_{3}{ }^{q_{3}} \mu_{4}{ }^{q_{4}} \mathrm{e}^{-\chi\left(q_{1}, q_{2}, q_{3}, q_{4}\right) / k T} . \tag{15}
\end{equation*}
$$

Or again, in the form

$$
\begin{equation*}
\frac{\partial \Psi}{\partial \log \xi}=\frac{\partial \Psi}{\partial \log \mu_{1}}=\frac{\partial \Psi}{\partial \log \mu_{2}}=\frac{\partial \Psi}{\partial \log \mu_{3}}=\frac{\partial \Psi}{\partial \log \mu_{4}}=0, \tag{16}
\end{equation*}
$$

if we put

$$
\begin{equation*}
\Psi=-N \log \xi-\sum_{i} N w \log \mu_{i}+\phi \tag{17}
\end{equation*}
$$

It can be shown ${ }^{7}$ that $\xi$ and $\mu_{i}$ are uniquely determined by (16) at given $r$ and $T$. Their values at $T=\infty$ are

$$
\begin{equation*}
(\xi)_{T=\infty}=N r^{4}, \quad\left(\mu_{i}\right)_{T=\infty}=\frac{w}{r}, \quad i=1,2,3,4, \tag{18}
\end{equation*}
$$

as can be verified by substitution into (14).
To calculate the free energy it is necessary first to evaluate the integral in (4). We shall show that this can be done without first solving (14) for $\xi$ and $\mu_{i}$. For, by (12) and (13) the integrand may be written

$$
\begin{equation*}
\frac{1}{k T^{2}} \bar{E}(r, T)=\frac{1}{k T^{2}} \sum_{q} \overline{\left[q_{1}, q_{2}, q_{3}, q_{4}\right]} \chi\left(q_{1}, q_{2}, q_{3}, q_{4}\right)=\frac{\partial \phi}{\partial T} . \tag{19}
\end{equation*}
$$

In the partial differentiation in $\frac{\partial \phi}{\partial T}, \xi$ and $\mu_{i}$ are treated as independent variables. If, however, we regard them as functions (defined by (14)) of $r$ and $T$, (16) and (17) lead to the following result:

$$
\begin{equation*}
\frac{1}{k T^{2}} \bar{E}(r, T)=\frac{\partial \phi}{\partial T}=\frac{2 \Psi(r, T)}{\partial T} . \tag{20}
\end{equation*}
$$

Mathematically the change of the independent variables from $T, \xi$ and $\mu_{i}$ to $T$ and $r$ is equivalent to the Legendre transformation

$$
\xi, \mu_{1}, \mu_{2}, \mu_{3}, \mu_{4} \rightarrow N, N w, N w, N w, N w
$$

defined by (14). Substituting (20) into (4) we get

$$
\begin{equation*}
\log p(r, T)=\log g(r)+\Psi(r, T)-\Psi(r, \infty) \tag{21}
\end{equation*}
$$

so that the free energy may be written down:

$$
\begin{equation*}
F(r, T)=-k T \log p(r, T)=[\log g(r)+\Psi(r, T)-\Psi(r, \infty)](-k T) . \tag{22}
\end{equation*}
$$

The equilibrium value $\bar{r}$ of $r$ is obtained by minimizing $F$ :

$$
\begin{equation*}
0=\frac{\partial F(\bar{r}, T)}{\partial \bar{r}}=-k T\left[\frac{\mathrm{~d} \log g(\bar{r})}{\mathrm{d} \bar{r}}+\frac{\partial \Psi(\bar{r}, T)}{\partial \bar{r}}-\frac{\partial \Psi(\bar{r}, \infty)}{\partial \bar{r}}\right] . \tag{23}
\end{equation*}
$$

[^15]But by（16）and（17）

$$
\begin{equation*}
\frac{\partial \Psi(r, T)}{\partial r}=\sum_{i} N \log \mu_{i} \tag{24}
\end{equation*}
$$

and by（3）

$$
\frac{\mathrm{d} \log g(r)}{\mathrm{d} r}=2 N \log \frac{w}{r},
$$

so that by（18）

$$
\sum_{i} \log \mu_{i}=-2 \log \frac{\bar{w}}{\bar{r}}+\left[\sum_{i} \log \mu_{i}\right]_{T=\infty}=2 \log \left(\frac{\bar{w}}{\bar{r}}\right)
$$

i．e．

$$
\begin{equation*}
\prod_{i} \mu_{i}=\left(\frac{\bar{w}}{\bar{r}}\right)^{2} \tag{25}
\end{equation*}
$$

It will be shown in the next section that we may put $V_{A A}=V_{B B}, V_{A B}=0$ ，without altering the specific heat of the crystal if $V=\frac{1}{2}\left(V_{A A}+V_{B B}\right)-V_{A B}$ is left unchanged． When this is done，$\phi$ will be symmetrical with respect to $\mu_{1}, \mu_{2}, \mu_{3}$ and $\mu_{4}$ ，and we conclude that all the $\mu$＇s are equal from the facts that（i）equation（14）has only one set of solution ${ }^{7}$ ，and（ii）if the conclusion is true（14）becomes，with all $\mu_{i}$ put equal to $\mu$ ，

$$
\begin{equation*}
\xi \frac{\partial \phi}{\partial \xi}=N, \quad \mu \frac{\partial \phi}{\partial \mu}=4 N w, \tag{26}
\end{equation*}
$$

which does have ${ }^{7}$ a set of solution in $\xi$ and $\mu$ ．Now $\phi$ is given by

$$
\begin{equation*}
\phi=\xi\left[1+4 \mu x^{2}+\left(4 \mu^{2} x^{2}+2 \mu^{2} x^{4}\right)+4 \mu^{3} x^{2}+\mu^{4}\right], \tag{27}
\end{equation*}
$$

where $x$ is defined by（9）．On eliminating $\xi$ from（26）we obtain

$$
\begin{equation*}
(1+s) \mu^{4}+(2+4 s) x^{2} \mu^{3}+2 s x^{2}\left(x^{2}+2\right) \mu^{2}+(4 s-2) x^{2} \mu+(s-1)=0 . \tag{28}
\end{equation*}
$$

The free energy is given by（21）and（18）：
$-\frac{F(r, T)}{2 N k T}=r \log r+w \log w-2 w \log \mu+\frac{1}{2} \log \left(1+4 \mu x^{2}+4 \mu^{2} x^{2}+2 \mu^{2} x^{4}+4 \mu^{3} x^{2}+\mu^{4}\right)$,
and the condition of equilibrium by（25）：

$$
\begin{equation*}
\mu=\sqrt{\frac{1-\bar{s}}{1+\bar{s}}} . \tag{30}
\end{equation*}
$$

To obtain the critical temperature，we expend（28）in powers of $s$ and find after iden－ tifying coefficients

$$
\log \mu=-\frac{1+6 x^{2}+x^{4}}{2+2 x^{2}} s+\kappa s^{3}+\cdots
$$

which is the only real solution for $\log \mu$. Next we expand (30):

$$
\log \mu=-s-\frac{1}{3} s^{3}-\cdots
$$

At the critical value $x_{c}$ of $x$, these last two equations have a multiple solution at $s=0$. Hence

$$
-\frac{1+6 x_{c}{ }^{2}+x_{c}{ }^{4}}{2+2 x_{c}{ }^{2}}=-1,
$$

i.e.

$$
x_{c}=(\sqrt{5}-2)^{1 / 2}=.4858
$$

## 4. GENERAL FORM OF THE QUASI-CHEMICAL METHOD

Let us now take a group of any size and form. Let it have $a \alpha$-sites $b \beta$-sites and $\gamma$ pairs of nearest neighbours. The procedures to obtain an approximate expression for the free energy of the crystal follow exactly the same line as in the special case considered in the last section. Equations (13), (14) and (18) are essentially unchanged:

$$
\begin{gather*}
\overline{\left[q_{1}, q_{2}, \ldots\right]}=\xi \mu_{1}^{q_{1}} \mu_{2}^{q_{2}} \cdots \mathrm{e}^{-\chi / k T}  \tag{31}\\
\phi=\sum_{q} \xi \mu_{1}^{q_{1}} \mu_{2}^{q_{2}} \cdots \mathrm{e}^{-\chi / k T}, \quad \xi \frac{\partial \phi}{\partial \xi}=N, \quad \mu_{i} \frac{\partial \phi}{\partial \mu_{i}}=N w \tag{32}
\end{gather*}
$$

and

$$
\begin{equation*}
\left(\mu_{i}\right)_{T=\infty}=\frac{w}{r} . \tag{33}
\end{equation*}
$$

But (12) should be corrected by a factor $\frac{\gamma}{z}$ to account for the duplications in calculating $E$ from the sum of the energies of all the groups in the crystal:

$$
\begin{equation*}
\bar{E}=\frac{z}{\gamma} \sum_{q} \overline{\left[q_{1}, q_{2}, \ldots\right]} \chi\left(q_{1}, q_{2}, \ldots\right)=\frac{z}{\gamma} k T^{2} \frac{\partial \phi}{\partial T} . \tag{34}
\end{equation*}
$$

Hence (22) becomes*

$$
\begin{equation*}
F(r, T)=-k T\left[\log g(r)+\frac{z}{\gamma} \Psi(r, T)-\frac{z}{\gamma} \Psi(r, \infty)\right] \tag{35}
\end{equation*}
$$

or more explicitly, by (3), (17), and (33):

$$
\begin{equation*}
F(r, T)=-\frac{z N k T}{\gamma}\left[\log N+\left(a+b-\frac{2 \gamma}{z}\right)(r \log r+w \log w)-\log \xi-w \sum_{i} \log \mu_{i}\right] \tag{36}
\end{equation*}
$$

[^16]The derivative is

$$
\begin{equation*}
\frac{\partial}{\partial r} F(r, T)=-\frac{z N k T}{\gamma} \log \left[\left(\prod_{i} \mu_{i}\right)\left(\frac{r}{w}\right)^{a+b-\frac{2 \gamma}{z}}\right] \tag{37}
\end{equation*}
$$

so that the condition of equilibrium is

$$
\begin{equation*}
\prod_{i} \mu_{i}=\left(\frac{\bar{w}}{\bar{r}}\right)^{a+b-\frac{2 \gamma}{z}} \tag{38}
\end{equation*}
$$

In actual calculations the following points may prove helpful：
（i）The free energy is changed by a constant if $V_{A A}$ and $V_{B B}$ are both replaced by $1 / 2\left(V_{A A}+V_{B B}\right)-V_{A B}$ ，and $V_{A B}$ by 0 ．To prove this let $z_{i}$ be the number of sites in the group neighbouring to the site $i$ ．Let $\chi$ be changed into $\chi^{\prime}$ by the replacement．It is evident that

$$
\left.\chi^{\prime}-\chi=-\gamma V_{A B}+\frac{V_{A A}-V_{B B}}{2} \text { (no. of } B-B \text { pairs }- \text { no. of } A-A \text { pairs }\right),
$$

and that

$$
\sum_{\alpha \text {-sites }} q_{i} z_{i}-\sum_{\beta \text {-sites }} q_{i} z_{i}=\text { no. of } B-B \text { pairs }- \text { no. of } A-A \text { pairs. }
$$

Hence

$$
\overline{\left[q_{1}, q_{2}, \ldots\right]}=\xi \mu_{1}^{q_{1}} \mu_{2}^{q_{2}} \cdots \mathrm{e}^{-\chi / k T}=\xi^{\prime} \mu_{1}^{\prime q_{1}} \mu_{2}^{\prime q_{2}} \cdots \mathrm{e}^{-\chi^{\prime} / k T}
$$

if we put

$$
\xi^{\prime}=\xi \mathrm{e}^{-\gamma V_{A B} / k T}, \quad \mu_{i}^{\prime}=\mu_{i} \mathrm{e}^{ \pm z_{i}\left(V_{A A}-V_{B B}\right) / 2 k T}
$$

where the $+\operatorname{sign}$ or the $-\operatorname{sign}$ is to be taken according as the site $i$ is an $\alpha$ or a $\beta$ site． We can now calculate the new free energy and verify the above statement．
（ii）Sites that are symmetrically situated in the group have equal $\mu$＇s irrespective of their nature if $V_{A A}=V_{B B}, V_{A B}=0$ ．This has already been shown in the last section． Since the most troublesome part of the calculations is the elimination of the parameters， much might be gained by choosing a group with a large number of sites symmetrically situated．
（iii）The free energy is a function of $s^{2}$ ，so that（38）is always satisfied at $\bar{w}=\bar{r}=1 / 2$ （i．e．long distance order $=0$ ）．The proof is simple when we have already made $V_{A A}=V_{B B}, V_{A B}=0$ ，so that an interchange of A and B atoms does not alter the energy．Thus

$$
\chi\left(q_{1}, q_{2}, \ldots\right)=\chi\left(1-q_{1}, 1-q_{2}, \cdots\right) .
$$

Putting

$$
\xi^{\prime}=\xi \mu_{1} \mu_{2} \cdots
$$

and

$$
\begin{equation*}
\mu_{i}^{\prime}=\frac{1}{\mu_{i}}, \tag{39}
\end{equation*}
$$

we get

$$
\xi \mu_{1}{ }^{q_{1}} \mu_{2}{ }^{q_{2}} \cdots \mathrm{e}^{-\chi / k T}=\xi^{\prime} \mu_{1}^{\prime 1-q_{1}} \mu_{2}^{\prime 1-q_{2}} \cdots \mathrm{e}^{-\chi / k T} .
$$

Thus if (32) is satisfied

$$
\begin{aligned}
\sum_{q}\left(1-q_{i}\right) \xi^{\prime} \mu_{1}^{\prime 1-q_{1}} \mu_{2}^{\prime 1-q_{2}} \cdots \mathrm{e}^{-\chi / k T} & =\sum_{q} \xi \mu_{1}^{q_{1}} \mu_{2}^{q_{2}} \cdots \mathrm{e}^{-\chi / k T}-\sum_{q} q_{i} \xi \mu_{1}^{q_{1}} \mu_{2}^{q_{2}} \cdots \mathrm{e}^{-\chi / k T} \\
& =N r,
\end{aligned}
$$

i.e. $\xi^{\prime}, \mu_{1}^{\prime}, \mu_{2}^{\prime}$, ...would be the solution of (32) with $r$ substituted for $w$. Hence by (32) and (17)

$$
\Psi(1-r, T)=N-N \log \xi^{\prime}-\sum_{i} N r \log \mu_{i}^{\prime}=\Psi(r, T)
$$

showing that

$$
\begin{equation*}
F(1-r, T)=F(r, T) \tag{40}
\end{equation*}
$$

(iv) The parameter for a corner site is always given by

$$
\begin{equation*}
\epsilon=\frac{1}{1+s}\left(\sqrt{x^{2} s^{2}+\left(1-s^{2}\right)}-s x\right) \tag{41}
\end{equation*}
$$

irrespective of the size of the group, if $V_{A A}=V_{B B}, V_{A B}=0$. By a corner site we mean a site that has only one nearest neighbour in the group. Let $\epsilon$ be the selective variable (parameter) of a corner site, and $\mu_{1}$ that of its only neighbour in the group. If the corner site is dropped, a new group is obtained. We distinguish all quantities referring to this new group by a prime, and obtain at once

$$
\begin{equation*}
\xi^{\prime} \frac{\partial \phi^{\prime}}{\partial \xi^{\prime}}=N, \quad \mu_{i}^{\prime} \frac{\partial \phi^{\prime}}{\partial \mu_{i}^{\prime}}=N w, \quad i=1,2, \cdots . \tag{42}
\end{equation*}
$$

The sites of the primed group are numbered in the same way as in the unprimed group. Introducing the variable $\chi$ defined in (9) we may write

$$
\begin{align*}
\phi & =\sum_{p, q} \xi \epsilon^{p} \mu_{1}^{q_{1}} \mu_{2}^{q_{2}} \cdots \mathrm{e}^{-\chi / k T} \\
& =\sum_{q_{2}, \ldots} \xi(1+\epsilon x) \mu_{2}^{q_{2}} \mu_{3}^{q_{3}} \cdots \mathrm{e}^{-\chi^{\prime} / k T}+\mu_{1} \sum_{q_{2}, \ldots} \xi(\epsilon+x) \mu_{2}^{q_{2}} \cdots \mathrm{e}^{-\chi^{\prime} / k T} . \tag{43}
\end{align*}
$$

Let these two terms be denoted by $\phi_{0}$ and $\phi_{1}$ respectively. Since

$$
\phi=N, \quad \mu_{1} \frac{\partial \phi}{\partial \mu_{1}}=N w,
$$

we have

$$
\begin{equation*}
\phi_{0}=N r, \quad \phi_{1}=N w . \tag{44}
\end{equation*}
$$

Now

$$
\epsilon \frac{\partial \phi_{0}}{\partial \epsilon}=\frac{\epsilon x}{1+\epsilon x} \phi_{0}, \quad \epsilon \frac{\partial \phi_{1}}{\partial \epsilon}=\frac{\epsilon}{\epsilon+x} \phi_{1} .
$$

Hence $\epsilon \frac{\partial \phi}{\partial \epsilon}=N w$ leads to

$$
\begin{equation*}
\frac{\epsilon x}{1+\epsilon x} N r+\frac{\epsilon}{\epsilon+x} N w=N w, \tag{45}
\end{equation*}
$$

or

$$
\begin{equation*}
\frac{w}{r}=\frac{\epsilon(\epsilon+x)}{1+\epsilon x} \tag{46}
\end{equation*}
$$

the solution of which is（41）．Thus the two parameters $\mu$ and $\nu$ in the approximation discussed in section 2 are equal to $\epsilon$ ．
（v）The＂contribution＂to the free energy from a corner atom is such that，in the notations of（iv）．

$$
\begin{equation*}
F(r, T)=\frac{\gamma-1}{\gamma} F^{\prime}(r, T)+\frac{1}{\gamma} F_{0}(r, T), \tag{47}
\end{equation*}
$$

where $F_{0}(r, T)$ is the free energy when $\gamma=1$ ，i．e．the free energy in the approximation discussed in section 2．This is proved as follows．

If we put

$$
\begin{equation*}
\xi=\xi^{\prime \prime} \frac{1}{1+\epsilon x}, \quad \mu_{1}=\mu_{1}^{\prime \prime} \frac{1+\epsilon x}{\epsilon+x}, \quad \mu_{i}=\mu_{i}^{\prime \prime}, \quad i \geq 2 \tag{48}
\end{equation*}
$$

it is evident from（43）that $\phi$ would become a function of $\xi^{\prime \prime}, \mu_{1}^{\prime \prime}, \mu_{2}^{\prime \prime}, \cdots$ satisfying the relations

$$
\begin{equation*}
\xi^{\prime \prime} \frac{\partial \phi}{\partial \xi^{\prime \prime}}\left(=\xi \frac{\partial \phi}{\partial \xi}\right)=N, \quad \mu_{i}^{\prime \prime} \frac{\partial \phi}{\partial \mu_{i}^{\prime \prime}}\left(=\mu_{i} \frac{\partial \phi}{\partial \mu_{i}}\right)=N w, \quad i=1,2, \cdots . \tag{49}
\end{equation*}
$$

It is also evident that $\phi$ is the same function of $\xi^{\prime \prime}, \mu_{1}^{\prime \prime}, \mu_{2}^{\prime \prime}, \cdots$ as $\phi^{\prime}$ is of $\xi^{\prime}, \mu_{1}^{\prime}$ ， $\mu_{2}^{\prime}, \cdots$ ．Now（42）has only one ${ }^{7}$ set of solution in $\xi^{\prime}$ and $\mu_{i}^{\prime}$ ．Hence from（49）we infer that $\xi^{\prime}=\xi^{\prime \prime}, \mu_{i}^{\prime}=\mu_{i}^{\prime \prime}$ ．Thus

$$
\begin{equation*}
\xi=\xi^{\prime} \frac{1}{1+\epsilon x}, \quad \mu_{1}=\mu_{1}^{\prime} \frac{1+\epsilon x}{\epsilon+x}, \quad \mu_{i}=\mu_{i}^{\prime}, \quad i \geq 2 . \tag{50}
\end{equation*}
$$

（41）and（50）give the parameters $\mu_{i}$ in terms of $\mu_{i}^{\prime}$ ．Inserting them into（36）we obtain

$$
\begin{align*}
F(r, T)= & -N k T \frac{z}{\gamma}\left[\log N+\left(a+b-\frac{2 \gamma}{z}\right)(r \log r+w \log w)-\log \xi^{\prime}-w \sum_{i} \log \mu_{i}^{\prime}+\right. \\
& r \log (1+\epsilon x)+w \log (\epsilon+x)-w \log \epsilon] \\
= & \frac{\gamma-1}{\gamma} F^{\prime}(r, T)-N k T \frac{z}{\gamma}\left[\left(1-\frac{2}{z}\right)(r \log r+w \log w)+\right. \\
& \left.r \log (1+\epsilon x)+w \log \frac{\epsilon+x}{\epsilon}\right] . \tag{51}
\end{align*}
$$

If the original (unprimed) group is a pair of nearest neighbours, we have $\gamma=1$, and (51) reduces to the expression for the free energy in the approximation discussed in section 2 :

$$
\begin{equation*}
F_{0}(r, T)=-z N k T\left[\left(1-\frac{2}{z}\right)(r \log r+w \log w)+r \log (1+\epsilon x)+w \log \frac{\epsilon+x}{\epsilon}\right] \tag{52}
\end{equation*}
$$

Inserting this back into (51) we get (47).

## 5. COMPARISON WITH BETHE'S METHOD

The so-called local grand partition function ${ }^{1,3,8}$ in Bethe's approximations with long-distance order is identical in form with our function $\phi$ when all the "interior sites" in the group have the same parameter $\mu$. For the case of equal concentrations for the two kinds of atoms, which is the case so far considered, this parameter has been put equal to unity by Bethe. Since the different terms of the local grand partition function stand for the probabilities of occurrence of the corresponding local groups in the crystal, it is clear that Bethe's method with long-distance order is essentially equivalent to our method plus the assumption that the free energy (35) has a minimum when

$$
\begin{equation*}
(\mu)_{\text {interior sites }}=1 . \tag{53}
\end{equation*}
$$

But as we have shown that (38) gives the condition of a minimum of the free energy, the complete ${ }^{*}$ identification of Bethe's and the quasi-chemical methods in any approximation reduces to the mathematical proof of the equivalence of (38) and (53). While this presents no difficulty at all for Bethe's first approximation (section 7), a general proof is by no means easy. We can only satisfy ourselves with the assertion that the two methods are equivalent for large groups, i.e. groups for which

$$
a+b-\frac{2 \gamma}{z} \ll \gamma .
$$

This follows from the fact that if (53) is true

$$
\left[\left(\prod \mu_{i}\right)\left(\frac{r}{w}\right)^{a+b-\frac{2 \gamma}{z}}\right]^{\frac{1}{\gamma}} \cong\left[\prod(\mu)_{\text {interior sites }}\right]^{\frac{1}{\gamma}}=1
$$

so that by (37)

$$
\frac{\partial}{\partial r} F(r, T)=0 .
$$

[^17]To see how the equilibrium free energy $F(\bar{r}, T)$ varies with $T$ in high order approx－ imations，we substitute（38）into（36）and make use of（32）：

$$
-\frac{F}{z N k T}=\frac{1}{\gamma} \log \left(\sum_{q} \mu_{1}^{q_{1}} \mu_{2}^{q_{2}} \cdots \mathrm{e}^{-\chi / k T}\right)+\frac{1}{\gamma}\left(a+b-\frac{2 \gamma}{z}\right) \log \bar{r} .
$$

The last term is very small for large groups，so that by（53）

$$
-\frac{F}{z N k T}=\frac{1}{\gamma} \log \left(\sum \mathrm{e}^{-\chi / k T}\right) .
$$

## 6．THE NON－CINTERFERENCE OF LOCAL CONFIGURATIONS

Let us return to the fundamental assumption of the quasi－chemical method，i．e． to（31）which gives the average numbers of the different local configurations（so far called groups）in the crystal．This equation expresses the exact distribution law of an assembly of molecules（cf．the example in section 2）which has an energy $\gamma / z$ times as large as the crystal．Distinguishing all quantities referring to the assembly of molecules by a subscript $m$ ，we get

$$
F(r, T)+k T \log g(r)=\frac{z}{\gamma}\left[F_{m}(r, T)+k T \log g_{m}(r)\right],
$$

which is obtained from（4）．But if $H$ is the number of arrangements in the crystal lattice having the given values of $\left[q_{1}, q_{2}, \ldots\right]$ ，

$$
\begin{equation*}
F(r, T)=-k T \log \bar{H}+\bar{E} . \tag{54}
\end{equation*}
$$

Thus

$$
\log \frac{\bar{H}}{g(r)}=\frac{z}{\gamma} \log \frac{\bar{H}_{m}}{g_{m}(r)} .
$$

But＊

$$
\begin{equation*}
H_{m}=\frac{N!}{\prod_{q}\left[q_{1}, q_{2}, \ldots\right]!}, \tag{55}
\end{equation*}
$$

hence dropping the bar we get

$$
\begin{equation*}
H=h(r)\left\{\frac{N!}{\prod_{q}\left[q_{1}, q_{2}, \ldots\right]!}\right\}^{z / \gamma}, \tag{56}
\end{equation*}
$$

where

$$
\begin{equation*}
h(r)=\frac{g(r)}{\left\{g_{m}(r)\right\}^{z / \gamma}} . \tag{57}
\end{equation*}
$$

[^18]Equation (56) has been referred to in Fowler and Guggenheim's paper ${ }^{1}$ as the mathematical expression of the "hypothesis of the non-interference of local configurations", because when $\gamma / z=1$, the number of arrangements in the crystal consistent with the distribution law $\left[q_{1}, q_{2}, \ldots\right]$ for the groups of sites is, except for the factor $h(r)$, equal to

$$
H_{m}=\frac{N!}{\prod_{q}\left[q_{1}, q_{2}, \ldots\right]!},
$$

which is the number of arrangements in the crystal for the given values of $\left[q_{1}, q_{2}, \ldots\right]$ if the $N$ groups in the crystal are imagined to be separated and are filled independently with atoms. The term "non-interference" comes from the fact that actually the $N$ groups are not separated but are interlocked and cannot be filled independently with atoms, i.e. they "interfere" with each other.

To find the value of $g_{m}(r)$ we notice that by definition $g_{m}=\sum H_{m}$. But $\sum H_{m}$ is the number of arrangements in the $N$ separated groups considered above if they are to be so filled with atoms that $N w$ of them have wrong atoms on the sites $i, i=1,2, \ldots$. Among the $N$ sites $i$ of the $N$ groups $\frac{N!}{(N r)!(N w)!}$ different arrangements are possible. Hence*

$$
\begin{equation*}
g_{m}=\sum H_{m}=\sum \frac{N!}{\prod_{q}\left[q_{1}, q_{2}, \ldots\right]!}=\left[\frac{N!}{(N r)!(N w)!}\right]^{a+b} \tag{58}
\end{equation*}
$$

Thus

$$
\begin{equation*}
h(r)=\left[\frac{N!}{(N r)!(N w)!}\right]^{2-(a+b) \frac{z}{\gamma}} . \tag{59}
\end{equation*}
$$

The free energy of the crystal may be obtained from (54), (56) and (59):

$$
\begin{align*}
F(r, T)= & \bar{E}-\frac{z N k T}{\gamma}\left\{\left(a+b-\frac{2 \gamma}{z}\right)(r \log r+w \log w)+\log N-\right. \\
& \frac{1}{N} \sum_{q} \frac{\left.\overline{\left[q_{1}, q_{2}, \ldots\right]} \log \overline{\left[q_{1}, q_{2}, \ldots\right]}\right\}}{} \tag{60}
\end{align*}
$$

which has been obtained above by integration.

[^19]
## 7．SPECIAL CONSIDERATIONS CONCERNING BETHE＇S FIRST AND SECOND APPROXIMATIONS

（i）First Approximation．If an $\alpha$－site together with its $z$ nearest neighbours are taken as our group of interest，all the sites except the central one are corner sites． Hence their selective variables are all equal to the value of $\epsilon$ given in（41）．By successive applications of（47）we see that the free energy is exactly $F_{0}(r, T)$ ，a fact which has already been pointed out by Fowler and Guggenheim ${ }^{1}$ ．The selective variable of the central site is given by successive applications of（50）

$$
\begin{equation*}
\lambda=\frac{w}{r}\left(\frac{1+\epsilon x}{\epsilon+x}\right)^{z} . \tag{61}
\end{equation*}
$$

The factor $w / r$ is the selective variable for the central site when it alone forms the group．The equilibrium condition（38）becomes

$$
\lambda \epsilon^{z}=\left(\frac{\bar{w}}{\bar{r}}\right)^{z-1} .
$$

But by（61）and（45），

$$
\lambda=\left(\frac{w}{r}\right)^{1-z} \epsilon^{z} .
$$

Hence at equilibrium

$$
\begin{equation*}
\lambda=1 . \tag{62}
\end{equation*}
$$

Thus the approximation is completely equivalent to Bethe＇s first approximation，as already mentioned in section 5 ．
（ii）Second Approximation．Now consider the group of sites occurring in Bethe＇s second approximation ${ }^{3}$ ．According to section 4，（iv），the selective variables for the corner sites in the second shell are all equal to $\epsilon$ ，which is given by（41）．But in Bethe＇s original calculations，the selective variables for the corner sites and the medium sites are made equal，and are found to be different from $\epsilon$ ．Thus if we use his original method， equation（32）can not be satisfied．（In other words，the probabilities of occurrence or wrong atoms in the corner and the medium sites would be unequal．）

For simplicity we shall drop the corner sites and take as our group of interest the central site，the first shell sites and the medium sites；with selective variables $\mu, \nu$ and $\lambda$ respectively．（The contribution by the corner sites can be included in the free energy by simple addition as shown in section 4 （v）．）With the notations $n$ ，and $g_{n m}$ of Bethe ${ }^{3}$ we find

$$
\begin{equation*}
\phi=\xi \sum_{n}\left(x^{n}+\mu x^{z-n}\right) P_{n}(x, \nu, \lambda), \tag{63}
\end{equation*}
$$

where

$$
P_{n}(x, \nu, \lambda)=\nu^{n} \sum_{m} g_{n m}[(1+\lambda) x]^{m}\left(x^{2}+\lambda\right)^{\left(\frac{z}{2}-1\right) n-\frac{m}{2}}\left(1+\lambda x^{2}\right)^{\left(\frac{z}{2}-1\right)(z-n)-\frac{m}{2}} .
$$

After eliminating $\xi$ and $\mu$, (32) becomes

$$
\begin{equation*}
z w=\frac{2 \sum_{l, n} x^{l-n}\left(r P_{n} \lambda \frac{\partial}{\partial \lambda} P_{l}+w P_{l} \lambda \frac{\partial}{\partial \lambda} P_{n}\right)}{(z-2)\left(\sum_{n} x^{n} P_{n}\right)\left(\sum_{n} x^{-n} P_{n}\right)}=\frac{\sum_{l, n} x^{l-n}\left(r P_{n} \nu \frac{\partial}{\partial \nu} P_{l}+w P_{l} \nu \frac{\partial}{\partial \nu} P_{n}\right)}{\left(\sum_{n} x^{n} P_{n}\right)\left(\sum_{n} x^{-n} P_{n}\right)} . \tag{64}
\end{equation*}
$$

The free energy is obtained from (36):

$$
\begin{align*}
F(r, T)= & -\frac{N k T}{z-1}\left[\frac{1}{2}\left(z^{2}-4 z+4\right)(r \log r+w \log w)+r \log \sum_{n} x^{n} P_{n}+\right. \\
& \left.w \log \sum_{n} x^{z-n} P_{n}-z w \log \nu-w z\left(\frac{z}{2}-1\right) \log \lambda\right] . \tag{65}
\end{align*}
$$

## 8. APPLICATION TO THE CRYSTAL Cu $\mathrm{C}_{3} \mathrm{Au}$

For the face-centred crystal $\mathrm{Cu}_{3} \mathrm{Au}$, we may of course follow Peierls ${ }^{9}$ and take as our group a central site together with its twelve first shell neighbours. The free energy expression would then contain seven selective variables*, four of which can be eliminated. The resultant expression is very cumbersome and numerical calculations would be laborious. We therefore make a simpler approximation: the group is taken to be four nearest neighbours forming a tetrahedron. A little geometrical consideration assures us that all such tetrahedrons contain an $\alpha$-site (for gold atoms) and three $\beta$-sites (for copper atoms), an interesting conclusion showing that the tetrahedron might be


Fig. 2

[^20]regarded as a sort of＂molecular＂structure in a face－centred lattice with atomic ratio 1：3．Our approximation may thus be reasonably expected to reveal the more important features of order－disorder transformation in such alloys．

Let $\mu$ and $\nu$ be the parameters（for wrong atoms）of the $\beta$－sites and the $\alpha$－sites re－ spectively．Let there be altogether $4 N$ atoms．It is easy to see that there are $8 N$ groups in the crystal．When $N w$ atoms on the $\alpha$－sites are wrong，the equations determining the parameters are

$$
\begin{gather*}
8 N=\phi=\xi\left[x^{3}+3 x^{2} \mu+3 x^{3} \mu^{2}+x^{6} \mu^{3}+\nu\left(x^{6}+3 x^{3} \mu+3 x^{2} \mu^{2}+x^{3} \mu^{3}\right)\right]  \tag{66a}\\
8 N w=\nu \frac{\partial \phi}{\partial \nu}=\xi \nu\left(x^{6}+3 x^{3} \mu+3 x^{2} \mu^{2}+x^{3} \mu^{3}\right) \tag{66b}
\end{gather*}
$$

and

$$
\begin{equation*}
8 N\left(\frac{w}{3}\right)+8 N\left(\frac{w}{3}\right)+8 N\left(\frac{w}{3}\right)=\mu \frac{\partial \phi}{\partial \mu}=3 x^{2} \mu \xi\left[1+2 x \mu+x^{4} \mu^{2}+\nu\left(x+2 \mu+x \mu^{2}\right)\right], \tag{66c}
\end{equation*}
$$

where $x$ is defined by（9）．The energy of the crystal is（cf．（34）），

$$
\begin{equation*}
\bar{E}=\frac{1}{2} k T^{2} \frac{\partial \phi}{\partial T}+\text { constant } ; \tag{67}
\end{equation*}
$$

so that the free energy becomes（cf．（35））

$$
F(w, T)=-k T\left[\log g(w)+\frac{1}{2}(\phi-8 N \log \xi-8 N w \log \nu-8 N w \log \mu)_{T=\infty}^{T}\right]
$$

But

$$
\log g(w)=-N\left\{(1-w) \log (1-w)+w \log w+w \log \frac{w}{3}+(3-w) \log [(3-w) / 3]\right\}
$$

and at $T=\infty$ ，

$$
\nu=\frac{w}{1-w}, \quad \mu=\frac{w}{3-w}, \quad \xi=8 N(1-w)\left(1-\frac{w}{3}\right)^{3} .
$$

Hence

$$
\begin{align*}
-\frac{F(w, T)}{N k T}= & -9 \log 3+4 \log 8 N+6 w \log w+3(1-w) \log (1-w)+ \\
& 3(3-w) \log (3-w)-4 \log \xi-4 w \log \mu-4 w \log \nu \tag{68}
\end{align*}
$$

Since $\xi$ and $\nu$ can be very easily solved from（66），numerical calculations are quite simple．The equilibrium value of $w$ is given by（cf．（37）and（38））

$$
\begin{equation*}
0=-3 \log \frac{(1-\bar{w})(3-\bar{w})}{\bar{w}^{2}}+4 \log \mu \nu \tag{69}
\end{equation*}
$$

This is always satisfied at $\bar{w}=\frac{3}{4}^{*}$ ．Actual calculation shows that the absolute minimum

[^21]of the free energy is or is not at $\bar{w}=\frac{3}{4}$ according as $x \geq .2965$ or $x<.2965$. The value of the free energy is plotted in Fig.3. From the form of the graph it is seen that the crystal has a critical temperature at which the long-distance order and (hence) the energy are discontinuous. The critical temperature $T_{C}$ and the latent heat $Q$ are found to be
$$
T_{C}=.8228 \frac{1}{k}\left[\frac{1}{2}\left(V_{A A}+V_{B B}\right)-V_{A B}\right], \quad Q=.8824 N\left[\frac{1}{2}\left(V_{A A}+V_{B B}\right)-V_{A B}\right] .
$$

In terms of the total energy change from $T=0$ to $T=\infty$ :

$$
E_{0}=3 N\left[\frac{1}{2}\left(V_{A A}+V_{B B}\right)-V_{A B}\right],
$$

these quantities become

$$
\begin{array}{cl}
T_{C}=1.097 E_{0} / R, & \left(T_{C}=2.19 E_{0} / R\right. \text { in Bragg-Williams' approximation and } \\
& \left.T_{C} \cong 1.3 E_{0} / R \text { in Peierls' approximation. }\right) \\
Q=.2941 E_{0}, & \left(Q=.218 E_{0}\right. \text { in Bragg-Williams' approximation and } \\
& \left.Q \cong .36 E_{0} \text { in Peierls' approximation. }\right)
\end{array}
$$

where $R$ stands for $4 N k$.
It will be noticed that due to the lack of a free energy expression Peierls ${ }^{9}$ did not give the exact values of these quantities.

In conclusion, the author wishes to express his thanks to Prof. J. S. Wang for valuable criticism and advice.


Fig. 3

## National Tsing Hua University

INVISTIGGATIONS IN TER STATISTICAL THBORY OF SUPRRIATIICRS

A Dissertation
Submitted to
The Faculty of the Graduate Sohool of Seience
in Candidacy for
The Degree of Master of Seience

By C．N．Yang（楊 振 塞）

Kuming，China
June， 1944

## COPFURNTR

## I. The Variation of the Interrattion Frecgy with Change of Lattiee Constants and Change of the Degree of Order

## II. A Cemeralization of the Quantr-Chumieal Mothod in

 the Statiatieal Theory of Superlattiees
## THE VARIATION OF THE INIURACTION EITKRGY VITH CHANGE OF LATPIIGE CONSTANTS

 AND CHANGE OF THE DIXGREE OF ORDERBy C．N．Yang
National Tsing Hua University， Kunming，China

## ABSTRACT

The change of the lattice oonstants due to the order－disordering proeess in a superlattice is investigated by using the oondition of minimum free energy in Bethe＇s theory．It is found that the interaction energy depends on the degree of order when the eaternal pressure is kept constant．The speoilic heat at constant pressure given by the theory is compared with experiment．Another conkse of the variation of interaction energy is the ohange of atomic arrangements．This is also investigated from the view point of Wang＇s formulation of the free energy in Bethe＇s approximations．

## -1-

## 1. INIRODUCIIION

The binary alloy tuAu is faee-centred oubio when disordered and tetragonal when ordered. This change of lattice form oan be studied thermodymanioally if we know the energy and the entropy of the orystal. Some caleulations along this lind has already been made by Wilson ${ }^{1}$ who used Bethe's method to find the emergy but Bragg-Wilidams' method to find the entropy of the orystal. It will be showm in the present paper that Bethe*s method oan be oarried through in the oaloulationt,making it self-consistent. The results are ocmparable with Gorsky's measurements ${ }^{2}$.

The ohange of lattice constants evidently affects the interaction energy between the atoms, and must oonsequently produce a ahange in the configurational energy and the apeaific heat of the orystal. We shall see that the effeet is in the right direotion to bring the theory into closer agrement with expemiment, beoause it tends to make the energy inorease more rapidly neer the oritioal temperature. An aotual oaloulation of the speoific heat at variable lattioe constant but oonstant emtermal pressure for $\beta$-brass is given in seation 3 .

Now the interaction energy can also be influenced by $\psi_{\text {a }}{ }^{\text {a }}$ ohange of the atomio arrangements. AMott ${ }^{3}$ has shown from a study of the eleotronic distribution in superiattices that the interaction onergy deareases as the degree of order deareases. The actual relation between the two is naturally very complieated. A linear dependence(of the average interactio energy upon the degree of order) has been assured by Lin ${ }^{4}$ in attempting to explain the ocourrence of the madmum oritioal temperature of a faceoentred alloy at the ooncentration ratio 1:3. In order to justify the assumption we shall view the problem from a new angle by the introduc-

[^22]
## －2－

tion of the free energy in Bethe ${ }^{1} s$ approximation ${ }^{5}$ ．In this way it is found that the interaction energy as a funotion of the degree of order must satisfy certain equations obtainedirom a set of conditions of con－ sistency．This same set of conditions of oonsistency makes also possible the calculation of the energy of the arystal without appealing to Bragg－ Williams＇theory as Lin did．

## 2．THE VARTATION OF LATTICE CONSTANTS

We shall form the pertition function at constant lattice constants 1 ， and $l_{2}$ ，and then obtain their equilibrium values py from the equations determinin多 the generalized reaotions．Let $\frac{1}{3}$ zlin be the number of A－B neighbours in the crystal．If $g(m)$ is the number of arrangements of the atoms for the given value of $m$ ，and $W\left(1_{1}, 1_{2}, m\right)$ the configurational energy of the aristal，the configurational partition function is

$$
f\left(m, T, 1_{1}, 1_{2}\right)=g(m) \exp (-W / k T)
$$

The equilibrium value $\bar{n}$ of m is determined from the condition of a maxi－ mum of f ：

$$
\frac{\partial}{\partial m} \log f\left(\bar{m}, T, 1_{2}, 1\right)=0
$$

The generalized reactions are given by

$$
\begin{align*}
L_{i} & =k P \frac{d}{d 1_{i}} \log f\left(\vec{m}, T, 1_{i}, 1_{2}\right)=k T \frac{d \bar{M}}{d 1_{i}} \frac{\partial}{\partial m} \log I+k T \frac{\partial}{\partial 1_{i}} \log f\left(k T \frac{\partial}{\partial 1_{i}} \log f\right. \\
& =-\frac{\partial}{\partial 1_{i}} W\left(I_{i}, L_{i}, \bar{m}\right) \quad . \tag{1}
\end{align*}
$$

To study the change of lattioe form in CuAu we divide the face－ceptred lattice into four simple cubic $\mathcal{Z}$ sublatices $\mathbf{1 , 2 , 3 , 4 ^ { * } \text { ．Let the shortest }}$ the distance between sites of 1 and 2 ，or 3 and 4 be $I_{1}$ ，倠 $\phi \phi \phi$ that between the sites of 1 and 3， 1 and 4， 2 and 3 or 2 and 4 bel $1_{2}$ ，so that the former is the distance between neighbouring Au－Au or Cu－Cu atoms and the latter that between neighbouring Au－Cu atoms when the orystal is perfectly oruered．The interaotion energies $V_{A A}, V_{A B}$ and $V_{B E}$ fure functions of $l_{1}$ and $l_{2}$ ．

Wang，＂Iree Inergy in the Statistioal Theory of Order－Disorder Transfor mations＂，Science Report of National Tsing Hua University，series A， 30－th anniversary Memorial Number（1941），printed but failed to appear．

If the number of sites of each sublattice is $\frac{1 N}{N}$, the number of pairs of sites between sublattices 1 and 2 must be $4\left(\frac{1}{2}\right)$ ilin $2 N$. Denote by $m_{12}$ the fraction of A-B pairs amdng these. Then the number of

$$
\begin{array}{ll}
\text { A-4 pairs is } & \frac{1}{2}\left[4\left(\frac{N}{2} \theta_{1}+\frac{N}{2} \theta_{2}\right)-2 \operatorname{lan}_{2}\right]=\mathbb{N}\left[\theta_{1}+\theta_{2}-m_{12}\right], \\
\text { B-3 pairs is } & \left.\frac{1}{2}\left[4\left(\frac{N}{2}\left\{1-\theta_{\}}\right\}+\frac{N}{2}\left\{1-\theta_{2}\right\}\right)-2 N N n_{3}\right\}=N / 2-\theta_{1}-\theta_{2}-m_{12}\right],
\end{array}
$$

where $\hat{\theta}_{i}$ is the fraction of sites of sublattice $i$ oocupied by $A$ afoms. Thus the osergy of interaction $\beta f$ between the atoms on sublattices 1 and 2 is

$$
N\left[\left(\theta_{1}+\theta_{2}-m_{n 2}\right) V_{A A}\left(1_{1}\right)+2 m_{12} V_{A B}\left(1_{1}\right)+\left(2-\theta_{1}-\theta_{2}-m_{12}\right) V_{B e}\left(1_{1}\right)\right]
$$

Writing $\quad-\frac{1}{4}\left(\theta_{1}+\theta_{2}+\theta_{3}+\theta_{4}\right) \quad$ and $V=\frac{1}{2}\left(V_{A A}+V_{B 8}\right)-V_{A B}$
we get the energy of the whole arystal

$$
\begin{align*}
& +N\left[80 V_{A A}\left(1_{2}\right)+8(1-c) V_{38}\left(1_{2}\right)-2\left(m_{13}+m_{44}+m_{23}+m_{24}\right) V\left(1_{2}\right)\right] \tag{2}
\end{align*}
$$

With this value for ${ }^{W}$, (1) becomes

$$
\begin{align*}
& I_{2}=-N\left[80 V_{A A}{ }^{\prime}\left(I_{2}\right)+8(1-0) V_{2 B}^{\prime}\left(I_{2}\right)-2\left(\bar{m}_{13}+\bar{m}_{14}+\bar{m}_{23}+m_{23}\right) V^{\prime}\left(I_{d}\right)\right] \text {. }  \tag{3}\\
& \text { and } \tag{4}
\end{align*}
$$

To solve for $l_{1}$ and $l_{2}$ as functions of $T$ we must first know the $\boldsymbol{H}^{\boldsymbol{4}} \mathbf{s}_{9}$ which are usually very complicated. Wilson ${ }^{2}$ discussed the values of $I_{l}$ and $1_{2}$ only in the eases when the alloy is disordered and when the order is nearly perfect. We shall also confine our attention to these cases. (1) Disordered. In this ase there is no difierence between the four sublattices so that all the $\overline{H_{j}^{\prime}}$ s are equal to $\bar{m}$. (3) and (4) reduce to

$$
\begin{align*}
& L_{1}=-N\left[4 c V_{A A}^{\prime}\left(L_{1}\right)+4(1-c) V_{B E}^{\prime}\left(1_{1}\right)-4 V_{m}^{\prime}\left(1_{1}\right)\right], \\
& L_{2}=-N\left[8 c V_{A A}^{\prime}\left(1_{2}\right)+8(1-c) V_{B B}^{\prime}\left(1_{2}\right)-8 V_{M}^{\prime}\left(1_{2}\right)\right] . \tag{5}
\end{align*}
$$

If $L_{1}=L_{2}=0$, this shows that $L_{1}=L_{2}$, so that the orystel is cubic.
(ii) oxder neaply perfeat. When omi; and the order is nearly perfect,

$$
\theta_{1}=\theta_{2} \approx 1, \quad \theta_{3}=\theta_{4} \tilde{O}_{0}, \quad \theta_{1}+\theta_{3}=1, \quad \theta_{1}-\theta_{3}=\mathbf{s} .
$$

There are only a few B atoms on sublattices 1 and 2, Honce approximately

$$
\overline{y_{12}}\left(1-\theta_{1}\right)+\left(1-\theta_{2}\right)=2 e_{3}=1-s .
$$

By the ssame reason we can obtain the number of A-A pairs of neighbours
between the sublattices 1 and 3：

$$
N\left(\theta_{1}+\theta_{3}-\bar{M}_{13}\right)=4\left(\frac{1}{2} N \theta_{3}\right)
$$

Thus

$$
\bar{\Gamma}_{3}=\theta_{1}-\theta_{3}=\mathrm{g} .
$$

We can now write down all the $\overline{\text { In }}$＇s：

$$
\bar{\Pi}_{12}=\bar{m}_{34}=1-\mathrm{s} \quad, \quad \overline{\operatorname{H}}_{3}=\bar{I}_{23}={\overline{n_{1}}}^{m}=\overline{H I}_{24}=\mathrm{s} .
$$

These equations are correct to the firgt order of（3－s）．Substituting them into（3）and（4）wo obtein
and

$$
\begin{aligned}
& L_{1}=-2 N_{[ }\left[V_{A A}^{\prime}\left(1_{1}\right)+V_{\theta B}^{\prime}\left(1_{1}\right)-2(1-s) V^{\prime}\left(I_{2}\right)\right] \\
& L_{2}=-4 N\left[V_{A A}^{\prime}\left(I_{2}\right)+V_{B B}^{\prime}\left(I_{2}\right)-2 s V^{\prime}\left(1_{2}\right)\right]
\end{aligned}
$$

These are exactiy equations（27）in Wilson＇s paper，from which an expression of the degree of tetragonality in agreement with forsky＇s measuraments ${ }^{2}$ can be obtained．

3．THE ERFFECT OF THB CHANGS OF LATMIICE CONSTANTS ON THE INLIARACTION ENNGRGY
In the alloy CuAu the gold atons and the copper atoms are in contact when the order is perfect．Since the copper atom is somewhat amaller than the gold atond，the size of the crystal must inorease when gold atoms exchange their positions with copper atoms．Thus with increasing disorder the dis－ tance between the atoms increases and hence the interaction energies aimie nish．The disordering process is therofore offected with more ease near the oritical termperature than it is $\not \propto$ at lower temperatures；and wo expect the specific heat at constant pressure to possess a steeper and higher maximum at the critionl temperature than the specific heat at constant volume．

Now we shall al．culate in length the specific heat at constant pressure of the alloy $\beta$－brass，which forms the sirplest type of suporlattioe that ean be studied statistioslly．Bothe＇s $\not \subset$ method will be used．

The configurational energy of the orystal is，in Easthope＇s $s^{6}$ notations：

$$
\begin{equation*}
W=-N_{A B} T+\frac{1}{2} N z\left\{0\left(V_{A A}-V_{B B}\right)+V_{B B}\right\} . \tag{6}
\end{equation*}
$$

6asthope，Proc．Carb．Phil．Soc．186 33，502（1937）；34，68（1938）．

## -5-

Substitution of this expression into (1) gives

$$
0=-\overline{I I V} V^{\prime}(1)+\sigma\left[V_{A A}(1)-V_{B B}^{\prime}(1)\right)+\left[V_{B B}^{\prime}(1)\right],
$$

when the pressure is put equal to zero. Now the variation of $V$ is not very large, so that to a surfioient approximation we may assume the linear
relations

$$
\begin{equation*}
\left(V_{A A}^{\prime}(1)-V_{B B}^{\prime}(1)\right) / V^{\prime}(1)=-K_{0}+K V \quad, \tag{7}
\end{equation*}
$$

and
$V_{8 B}^{\prime}(1) / V^{\prime}(1)=-J_{0}+J_{1} V$
These three last equations give, after eliminating $V_{A A}{ }^{\prime}(1)$ and $V_{B B}(1)$ :

$$
\begin{equation*}
V=\frac{\overline{\bar{I}}+\left(a K_{K}+J_{J_{0}}\right)}{\alpha K_{1}+J_{1}} \tag{9}
\end{equation*}
$$

We have already seen that $V$ inereases as II increasos, hence $a K,+J$, must be positive. The other constent $\mathrm{a}_{\mathrm{o}}+$ あ must also be positive in orier that V may be positive with only a relatively mall variation.

Bisensohitz ${ }^{7}$ has oalculated the specific heat at constant pressure by Brags-Willians' method. He assumed that the intoraction onergt depend $\%$ on a paraneter ${ }^{u}$ in the following way:

$$
\frac{1}{2}\left(V_{A A}+V_{B B}\right)=\phi\left[(1-a)+a(l-u)^{2}\right], \quad V_{A B}=\phi \mathrm{bu}^{2},
$$

where $a=.225, A x d y=.203$ and $u$ is of the order of unity. Comparing this with (7) and (8) wo see that his assumption is equivalent (approximately) to ours if $K_{0}+J_{0}=1.22$ and $K_{1}+J_{1}=.508 \times 10^{14} \mathrm{erg}^{-1}$. But with those values the specifio heat at the oriticel temperature would be too large. In order to make $16 / Y_{\mathrm{de}} / / / \mathrm{X} \phi / \mathrm{Y}_{\mathrm{Th}}\left(\mathrm{c}_{\mathrm{p}}\right)_{\mathrm{Tb}}=5.1 \mathrm{R}$ as given by the measurements of Sykes and wilkinson ${ }^{3}$ we assume (of. eq. (12) below)

$$
\frac{1}{2} K_{0}+J=1.79
$$

With this value for $\frac{1}{2} K_{2}+J$, the relative variation of $V$ oan be shown to be within $1.3 \%$.

We can now start from (9) and the equations given by Basthope ${ }^{6}$ for the determination of if as a function of ${ }_{\wedge}$ temperature and $V$ to obtain the specific heat at constant pressure:
$\overline{3}$ Sisensehitz, Proc. Roy. Soc. 68, 546(1958).
Syikes and Vilkinson, Inst. Metals J. 61, 223(1937).
－6－

$$
\begin{equation*}
\mathbf{c}_{P}=\frac{d W}{d T}=\left(\frac{\partial W}{\partial \bar{m}}\right)_{l} \frac{d \bar{m}}{d x} \frac{d x}{d T}+\left(\frac{\partial W}{\partial l_{2}} \frac{d Q}{d T}=\left(\frac{\partial W}{\partial \bar{m}}\right)_{l} \frac{d \bar{m}}{d x} \frac{d x}{d T}\right. \tag{10}
\end{equation*}
$$

But

Hence by（6）

The value of this expression is calculated for the case $0=\frac{1}{2}$ ，the oonstant $\frac{1}{2} \bar{F}_{0}+J_{0}$ being assumod to be 1.79 to malke $\left(C_{p}\right)_{T_{0}}=5.1 \mathrm{R}$ ．The result is plotted
 and Syikes and Wiluinson＇s experimental ${ }^{8}$ data．

4．THE KPFPCT OF T


As has already beon ment19ne Temperature in ${ }^{\circ} \mathrm{C}$ ． 500 enengy deponds in some very complicated manus upon the deoreo of ondor．To study the effect of such a dependence $\operatorname{inn}^{4}$ has assumed tás a linear relationship：

$$
\begin{equation*}
V=V_{0}\left(l+\alpha c+\beta m_{4 \alpha}\right) \quad \approx \tag{13}
\end{equation*}
$$

between the interaction onergy：$V$ and the fraction of A－A pairs of noigh－ bours＇ $\mathrm{m}_{M A}$ ．In this section we shall study the general nature of the varia－ tion of V in the light of the theory of the free energy in Bethe＇s appro－ ximation given by Mang ${ }^{5}$ ．

The fundamental equations in Wang＇s paper are（45），（46）and（39）with $\xi_{\alpha}$ and $\xi \beta$ given by $(47),(43),(49)$ and（50）．These equations are still assumed too be valid now V becomes a function of $\theta_{\alpha}, \theta_{\beta}$ and T．They may be put into the form：

$$
\begin{equation*}
\frac{d}{d \theta_{\alpha}} \log \left(--N r_{\alpha} \log \xi_{\alpha}=\frac{\partial}{\partial \phi \alpha_{\alpha}} \log Q_{0}\left(\theta_{\alpha}, q_{\alpha}, V / T\right),\right. \tag{14}
\end{equation*}
$$

$\overline{\mathrm{S}}_{\text {M1x }}$ and Shooklgy，Rev．Hod．Phys．20，1（1958）．

$$
\begin{align*}
& \text {-7- } \\
& \frac{d}{d \theta_{\beta}} \log Q=-\operatorname{Nr} r_{\beta} \log \xi_{\beta}=\frac{\partial}{\partial \theta_{\beta}} \log Q_{0}\left(\theta_{\alpha}, \theta_{z}, V / T\right),  \tag{15}\\
& 3 \mathrm{kr}^{2} \frac{d}{T T} 10 \mathrm{~g}^{6} \tag{18}
\end{align*}
$$

where $Q_{0}$ is the partition function for the oase when $V$ is a constant, if we denote by $\frac{\partial}{\partial \sigma_{\alpha}}, \frac{\partial}{\partial \sigma_{\beta}}, \frac{\partial}{\partial T}$ and $\frac{\partial}{\partial V}$ differentiations when $\sigma_{\mu}, \sigma_{\beta}, T$ and $V$ are regarded as indepondent of each other, and by $\frac{d}{d \sigma_{\alpha}}$ the operator $\frac{\partial}{\partial \sigma_{\alpha}}+\frac{d V}{d \delta_{\alpha}} \frac{\partial}{\partial r}$. (14) and (15) mean that we have assumed with Lin that the equilibrimm values of $\theta_{\alpha}$ and $\theta_{\mu}$ are given by the same equations as in Bethe's approximetion. (26) gives the onergy of the arystal.

Consistency of (14) and (15) requires

$$
\begin{equation*}
\frac{d}{d \theta_{\alpha}}\left(\frac{\partial}{\partial v_{p}} \log Q_{0}\right)=\frac{d}{d \sigma_{s}}\left(\frac{\partial}{\partial \theta_{\alpha}} \log R_{0}\right), \tag{17}
\end{equation*}
$$


Upon the hypothesis of nearest neighbour interaction the energy in Wang's paper beoomes

$$
\mathrm{B}_{0}=k \mathrm{~T}^{2} \frac{\partial}{\partial T} \log \Omega_{0}=2 N V m_{n A}
$$

But $Q_{B}$ depends on $T$ and $V$ through $V / T$, so that

Substituting this $A 0^{\circ} 0^{+}$and a similar one into (17) we obtein $\frac{\partial E_{0}}{\partial V_{\beta}} \frac{d V^{-}}{d Q_{2}}=\frac{\partial E_{0}}{\partial \theta_{\alpha}} \frac{d V}{d V_{\beta}}$,
which bocomes, if $\frac{\partial E_{o}}{\partial V} d V \frac{d V}{d s_{\alpha}}$ is added to both sides,

$$
\frac{d E_{d}}{d \theta_{\alpha}} \frac{d V}{d \theta_{p}}=\frac{d E_{\sigma_{p}}}{d \theta_{\beta}} \frac{d V}{d \theta_{\alpha}}
$$

This shows that $V$ and $B_{0}$ are connected by a rolation independent of $\theta_{\alpha}$ and

$$
\theta_{p}, 1 . \theta_{0} \quad V=v\left(s_{0}, T\right) .
$$

A consoquence of this result is that the coefficient $\alpha$ in Lin's relation (13) must be zero. This makes, however, the maxirum oritical temperature for the $A B$ type of superlattice to shift to a value of the concontration different from 立, which contradicts experinental results. One way out of the dirficuty is to make some other asswaption regarding the dependemoe of $\bar{v}$ on the degree of order, such as

$$
\begin{equation*}
V=V_{0}\left[1+\beta m_{A A}-\frac{\beta(z-1)}{2 c(c z-1)} m_{A A}{ }^{*}\right] . \tag{20}
\end{equation*}
$$

－8－
Let us now try to find F in the general case．From（14）and（16）wo get

$$
\begin{equation*}
\frac{d E}{d E_{d}}=k T^{2} \frac{d}{d T}\left(\frac{\partial}{\partial \theta_{d}} \log e_{0}\right)=\left\{T^{2} \frac{d\left(\frac{v}{T}\right)}{d T} \frac{\partial^{2}}{\partial E_{2} 2\left(\frac{T}{T}\right)} J O Q_{0}=-\frac{T^{2}}{v} \frac{d\left(\frac{v}{T}\right)}{d T} \frac{\partial E_{\mathrm{g}}}{\partial \theta_{\alpha}} .\right. \tag{21}
\end{equation*}
$$

Similarly


Just as（18）leads to（19），this last equation loads to

$$
\mathbb{E}=\mathbb{B}\left(\mathbb{E}_{0}, T\right)
$$

Substituting this into（22）we obtain

$$
\frac{\partial E_{0}}{\partial E_{0}}\left[\frac{\partial E_{e}}{\partial \theta_{\alpha}}+\frac{\partial E_{q}}{\partial V} \frac{\partial V}{\partial \theta_{\alpha}}=\frac{\partial E_{o}}{\partial E_{\alpha}}\left(1-\frac{T}{V} \frac{d v}{d T}\right) .\right.
$$

But（19）gives

Hence $\quad \frac{\partial E_{0}}{\partial E_{0}}=\left(1-\frac{\partial V}{\partial E_{0}} \frac{\partial E_{v}}{\partial V}\right)\left(1-\frac{T}{V} \frac{d V}{d T}\right)=1-\frac{\partial V}{\partial E_{v}} \frac{\partial E_{0}}{\partial V}-\frac{T}{V} \frac{d V}{d T}-\frac{T}{V} \frac{\partial V}{\partial E_{0}} \frac{\partial E_{0}}{\partial T}$
Nov $\mathbb{E}_{0} / V$ is a function of $\mathcal{Q}_{\rho}, \mathcal{N}_{\Omega}$ and $V / P$ ，so that

Hence

$$
\begin{align*}
& \frac{\partial E_{0}}{\partial V}-\frac{T}{V} \frac{\partial E_{P}}{\partial T}+\frac{E_{0}}{V} \\
& \frac{\partial E_{0}}{\partial E_{0}}=1-\frac{E_{V}}{V} \frac{\partial V}{\partial E_{0}}-\frac{T}{V} \frac{\partial V}{\partial T} \tag{22}
\end{align*}
$$

If $V$ depends on $n_{A A}$ only $y$ ，and not on $T$ ，we have

$$
\frac{\partial E_{0}}{\partial E_{0}}=1-\frac{E_{0}}{V} \frac{d V}{d E_{0}}=V \frac{d\left(E_{0} / v\right)}{d E_{0}} .
$$

The boundary condition is given by the ouse when there is no A atoms，i．$e_{0}$ when $\theta_{\alpha}+\theta_{\beta}=0$ ．In this case $m_{A A}=0, \mathcal{F}_{0}=\mathcal{F}=0$ ．Hence

$$
\begin{equation*}
I=\int_{0}^{E_{0}}\left(V \frac{d\left(E_{0} / v\right.}{d E_{0}}\right) d B_{0}=\Sigma d-\log (N / V)=2 N \int_{0}^{m_{A A}} V d n A A . \tag{23}
\end{equation*}
$$

If the assumption（ 20 ）is mede，the energy of the crystal is

$$
\left.3=2 N v_{1}^{[ } m_{A A}+\frac{e^{3}}{2} A_{A A}^{2}-\frac{A(2-1)}{6 c(c z-1)} m_{A A^{3}}^{3}\right]
$$

When $\beta$ is not Inge，this differs very little from Bethe＇s original ex－ pression in numarian value，The specific heat is

The author is very much indebted to Prof．J．S．Wang for suggesting this problem and for helpful aisoussions．

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 STAIISTICAL THEORY OF SUPERLATIICES

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ABSIRACT
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-
The quasi-chemical method introduced by Fowler and Guggenhoin for the equilibriun distribution of pairs of sites in a superlatice is genoralized. It is shown that by considering groups containing large numbers of sites the nethod may be used to obtain successive approximations of the free energy of the orystal. To analfze the fundenental assumption underlying the method nore closely, the hypothesis of the nonInterference of locel configurations is aisoussed. The free energy of the crystal is obtained without integration as a closed algebraic expression with the aid of a Legenare transfomation. Applications of the results are then made to aifferent approximations for simple and body-centred cubic crystals and for the olytu face-centred cubic crystal $\mathrm{Cu}_{\mathrm{g}} \mathrm{Au}$. In each case the free energy is obtained and discussed.

Whesearch Fellow of the China Foundation Por the Promotion of Education and Cul.ture.

## －1－ <br> 1．ITIRODUCIION

It was shown by Fowler and Guggenhein that the quasi－chemical method， originally devised for the theory of regulax solutions，applies equally well to the theory of aupperlatices with long－distence order．The me－ thod is，as they have erphasized，derinitely one stago further tovards an exract theory than Bragg－III11ians＇method ${ }^{2}$ ．When oompared vith Bethe ${ }^{\prime} g^{3}$
 But to be a mothod that my Ioad to a consistent sohan of succeusive approximations，it must be applicabie to the n－th epproxination in the theory of Ajpip superiattices．This does not，hovever，seen possible in the originel fom of the nethod given by Forler and Gugeenhoin．It is the purpoae of the present paper to forinlate the quasi－chenien nethof in a nev way which is appliooble to high orker approxinntions in the theory of superlathices．
the iree energy exprossion in Dethe＇s and in the cuasi－chendon mothods involves an integral．Its ovaluntion is very complicated and has been camied out ${ }^{1,5}$ so far anly in Betheta approximation for simple and body－oentred cubic orystals．In the new formulation of the quest－chomi－ cal mothod，however，it will be show that a Logendre trongrormation helps sugh in avoiding the mathomatioal airrioultios．（ It might be noticea that a sinilas Legendre tronsiomation is used to essentinjy tho same arfect in Fowlorts formalation of genoral statistioal meohenios．of Fovilas，Stetistion Kechantos；second odition，p．193．）．The fiee energy
 ${ }^{2}$ Brask and Vil1ianis，Froc．Roy．Soc．A145，699（1934）；251，540（2935）； $5_{\text {Betho，IToc．Roy．Soc．A150，}} 552(2935)$ ．
4Kiriorood，J．Chat．2hys． $6,70(1.933)$.
5Chang，Iroo．Comb．Phil．Scc．S5， $265(1959)$ ；Kirkwood，J．Chen．Zhyg．日，6S（1940）；Fohg，＂Irao Jnorgy in tho Statiztiont Thoory of 0ndor－ Disordor＂manaformation＂，Soinnco Roport of lational Taing Hua Unimes－ sity，Soriesi， 50 －th Annivarsary liemorios Lurnber（1941），printee，but failed so appear．


#### Abstract

-2- is obtained direotly as a closed algebraic expression. Its values are given for Bethe's Pirgt and second (modified) approdmations and for the face -centred alloy Cught in sections 7 and 8.

To make sure that the quasi-chordical method may actually be usod to obtain a series of successively bettor approximations, we must investigate the iree onergy in high order approximations and compare it with the partition function of the crystal. This is aone in section 5 togother with a comperis on of the quasi-chemical and Bethe'g methods. lixcept in the last section we are only concerned with binary alloys with atomic ratio $1: 1$ Poming a (quadratic), simple cubic or body-centred cubic lattice. The generalization of the method to the investigation of alloys with other atomic ratios and forming other types of lattices is easy. In fact, the superior power of the quasi- chemicel nothod appears to be men more fully revealed when a face-centrod able lattice is traated. This problom is taken at the end of the paperimhere an approximate free onergy expression for $C u_{g A u}$ is obtained and its criticel phenonena discussed.


2. REFORUULATION OF THES GUSI-CHAICAL MUSTIOD

Consider a crystel $A B$. Let $2 N$ be tho total number of atons and $z$ the number of nearest neichbours of each. At low tamperatures we can distinguish betwreen the so-called $\alpha$-sites and the $\beta$-sites for $A$ and $B$ atoms respeetively. Donote by Nr the number of A atoms on $\alpha$ - sites. Let

$$
1-r=w, r-w=5 .
$$

The pertition function of the crystal is

$$
\begin{equation*}
\sum_{r} p(r, T) \tag{1}
\end{equation*}
$$

where $p(r, T)$ is equal to $\Sigma \exp (-\pi / k T)$ over all possible configurations of the cryatal with the given valuo of $r$. The avorage enorgy over all these conrigurations is

$$
\begin{align*}
& \text {-3- } \\
& \bar{E}(r, T)=k T \frac{\partial}{\partial T} \log p(r, T)  \tag{2}\\
& p(r, \infty)=g(r)=\left[\frac{N!}{(N r)!(N *)!}\right]^{2} .  \tag{5}\\
& \text { But ovidently, } \\
& \log p(r, T)=\log g(r)+\int_{0}^{T} \frac{1}{k T^{2}} \bar{E}(r, T) d T \text {. }  \tag{4}\\
& \text { Hence }
\end{align*}
$$ The probler therafore reduces to one or finding $\bar{E}(r, T)$ ．Since a direct solution is very difficult we shall try to find an approximate solutio by the quasi－chemieal method，which is presented below in a fom easily Generalizable．

There are in the crystal $3 N$ noarest pairs of sites $\alpha-\beta$ ．Anong theso let there be $\left[q_{\alpha}, q_{\beta}\right]$ with their $\alpha$－sites occupied by $q_{\alpha}(=0,1)$ wrons $(B)$ atons and their $\beta-s i t e s$ by $q(=0,1)$ wrong $(A)$ atons．For given $r$ the following relations hold：

$$
\begin{align*}
{[0,1]+[0,0]+[1,1]+[1,0] } & =z \mathrm{~N}, \\
{[1,1]+[1,0] } & =\xi \mathrm{Nw}, \tag{5}
\end{align*}
$$

end

$$
[0,1] \quad+[1,1] \quad=z^{N} w .
$$

Upon the approxination of tire neighbour interaction the energy of the crystal may be written as

$$
\begin{equation*}
E(r, T)=[0,1] V_{A A}+[0,0] V_{A B}+[1,1] V_{A B}+[1,0] V_{B B}, \tag{6}
\end{equation*}
$$

whoro the $V^{\prime} s$ are the interaction energtes between a pair of nearest neighbours．

We may give（5）and（6）a different interpretation by inagining $[0,1]$ ， $[0,0],[1,1],[1,0]$ and $V_{A A}, V_{A B}, V_{A B}, V_{B B}$ to be respectively the numbers and the molecular intermal energies of the four different leinds of molecules $X, X, X Y /, X Y$ of an eseembly gasoous assembly．The interpro－ tation of（6）is that the assenbly has the sane internal（non－icinetic） enorgy as the arystal at the given value of $r$ ．（5）would nean that there are altogethor $z N X$ atoms，$z N w^{-} Y$ atoms and $z N w^{-} Z$ atom in the asserbly．

The quasi－chomical method consists in taking the averages $\overline{[0,1]}$ ，
$[\overline{[0,0}],[\overline{1,1]},[\overline{1,0]}$ of the assembly at any temperature as approximately representing the corresponding averages of the crystal at the same terperature. Lother this approxination is good can only be judged for the present fros the results it leads to.

A detail od treatment or the problen of e gaseous assembly has been givon by Powlex ${ }^{6}$. We aro only interested in our easimbly of four dip. ferent leinds of molecules, for which the results may be sumerized as:

$$
\begin{array}{ll}
\overline{[0,1]}=\xi \nu e^{-v_{A A} / k T}, & \overline{[0,0]}=\xi e^{-v_{A B} / A T},  \tag{7}\\
\overline{[1,1]}=\xi \mu \nu e^{-v_{A B} / k T}, & \overline{[1,0]}=\xi \mu e^{-v_{B B} / k T},
\end{array}
$$

where $\xi, \mu$ and $v$ are to be detomined from (6). From (7) we get

$$
\begin{equation*}
\overline{[c, 0]} \overline{[1,1]} / \overline{[0,1]} \overline{[1,0]}=x^{-2}, \tag{8}
\end{equation*}
$$

where

$$
\begin{equation*}
x=\exp \left[-\frac{1}{2}\left(l_{A A}+l_{B B}-2 V_{A B}\right) / k T\right] \tag{9}
\end{equation*}
$$

(8) and (6) together form the starting point of Fowler and Guggenhein's work ${ }^{1}$. The subsequent calculations of $E(r, T), p(r, T)$ and the Iree energy of the crystal are straightforvard and will not be repented here. We shall' see later how the free energy can be written dowm directly vithout actual integration.
3. GHNRRAITZATION TO GROUPS OF ZOUR SITES

So fer we have fixed our attention on the pairs of nearest neighbours in the crystal and have used the quasi-chenical mothod to obtain the average numbers of the four aifferent kinds of pairs. Now we shall generalize the whole procedure: wo shall study all the groups of sites in the cryatal of an arbitrarily chosen form in, and classifying these groups according to the way they are ocoupied by atons we shall obtain the average number of groups in each class by chenical analogy.

To mako this olear let us consider in detail groups of four sites forming squares (as shown) in a quadratic lattice. We classify these groups into $2^{4}=16$ classes 6Fovler, Statistical Mechonias, socond odition, pp.162-165.
denoted by $(0,0,0,0),(0,0,0,1),: \ldots(1,1,1,1)$ respectively，so that all groups in the class $\left(q_{1}, q_{0}, q_{i}, q_{4}\right)$ have $q_{\text {wrong }}$ atons in their upper $\alpha$－sites，$q_{2}$ wrong atoms in their lower $\alpha$－sites，$q_{3}$ vrong atons in． their upper $\beta$－bites and $q 4$ wrong atoms in their lover $\beta$－sites．The total number of ez these groups ie $N^{\prime}$ ．Fience

$$
\begin{equation*}
\sum_{q_{0}}^{\frac{1}{0}}\left[q_{1}, q_{2}, q_{0}, q_{4}\right]=N, \tag{10}
\end{equation*}
$$

where $\left[q_{0}, q_{2}, q_{3}, q_{4}\right]_{i s}$ an abbreviation for＂the number of groups in the class $\left(q, q_{2}, q_{3}, q_{q}\right)$ ．Now the number of all those groups in the exystal with a wrong（ $B$ ）atom on the upper $\alpha$－site\％is just the numbor of $B$ atons on the $\alpha-$－sites．Honce

$$
\begin{equation*}
\sum_{q} q_{i}\left[q_{1}, q_{v}, q_{3}, q_{*}\right]=N W, \quad i=1,2,3,4 . \tag{II}
\end{equation*}
$$

Let $\quad\left(q_{1}, q_{2}, q_{3}, q_{4}\right)$ be the energy of each group in the class $\left(q_{1}, q_{2}, q_{3}, q_{4}\right)$ ． It is easy to show that the total enexgy of the orystal is

$$
\begin{equation*}
E(r, T)=\frac{5}{8} \overline{\left[q_{1}, q_{2}, q_{3}, q_{4}\right]} \times\left(q_{1}, q_{2}, q_{3}, q_{4}\right) . \tag{12}
\end{equation*}
$$

We may give（10），（11）and（12）antideceres interpretation sinilar to the one eiven in section 2 for equations（5）and（6）．The ane quasi－chemical nothod used．there to obtain（7）leads now to the fol－ lowing avorages（approsimate）at a given value of $r$ ：

$$
\begin{equation*}
\overline{\left[q_{1}, q_{2}, q_{3}, q_{4}\right]}=\xi \mu_{1} q_{1} \mu_{2} q_{2} \mu_{3} q_{2} \mu_{4}^{q_{4}} e^{-x\left(q_{1}, q_{2}, q_{3}, q_{4}\right) / k T} \tag{13}
\end{equation*}
$$

In this expression the parameters $\xi, \mu_{1}, \mu_{c}, \mu_{3}$ and $\mu_{4}$ are to be deter－ mined from（10）and（21），which may be written in the form
if we put

$$
\begin{equation*}
\xi \frac{\partial \varphi}{\partial \xi}=N, \quad \mu_{i} \frac{\partial \varphi}{\partial \mu_{i}}=N v \quad(i=1,2,3,4), \tag{14}
\end{equation*}
$$

Or asain，in the form

$$
\begin{equation*}
\frac{\partial \psi}{\partial \log g^{\prime}}=\frac{\partial \psi}{\partial \log \mu_{1}}=\frac{\partial \psi}{\partial \operatorname{kog} \mu_{2}}=\frac{\partial \psi}{\partial \log \mu_{3}}=\frac{\partial \psi}{\partial \log \mu_{4}}=0, \tag{16}
\end{equation*}
$$

if ve put

$$
\begin{equation*}
\psi=-N \log \xi-\sum_{i} N w_{i} \log \mu_{i}+\phi \tag{17}
\end{equation*}
$$

It can be shown ${ }^{7}$ that $\xi$ and $\mu_{i}$ are uniquely determined by（16）at $\overrightarrow{7}_{\text {The }}^{\text {proof }}$ fofownows Lemua 2． 42 of Fowler＇s Statistical Mechanics，second edition．

Givent and $T$. Their values at $T=\infty$ are

$$
\begin{equation*}
(\xi)_{T=\infty}=N r^{4}, \quad\left(\mu_{i}\right)_{T+\infty}=\frac{w}{r}, \quad i=1,2,5,4, \tag{18}
\end{equation*}
$$

as can be verified by substitution into (14).
To calculate the free enorgy it is mest necesuary Plrst to evaluate the intogral in (4). We shall show that this can be done without first solving (14) for $\xi$ and $\mu_{i}$. For, by (12) and (13) the intogrend may be written

$$
\begin{equation*}
\frac{1}{k T^{2}} \vec{E}(r, T)=\frac{1}{k T^{2}} \frac{\sum}{q}\left[q_{1}, q_{2}, q_{v}, q_{4} \overline{]} \chi\left(q_{1}, q_{2}, q_{3}, q_{4}\right)=\frac{\partial \varphi}{\partial T} .\right. \tag{2.9}
\end{equation*}
$$

In the partial differentiation in $\frac{\partial \varphi}{\partial T}$, $\xi$ and $\mu_{i}$ are treated as independont variables. If , however, we rogard them as functions (derined by (14)) of $r$ and $T$, (16) and (17) leads to the follouring rosult:

$$
\begin{equation*}
\frac{1}{\hbar T^{2}} \bar{E}(r, T)=\frac{\partial \varphi}{\partial T}=\frac{\partial \psi(r, T)}{\partial T} . \tag{20}
\end{equation*}
$$

Mathenaticelly the change of the independent variables fron $T$, $\xi$ and $\mu_{i}$ to $T$ and $r$ is equivelent to the Legendre transfomation

$$
\xi, \mu_{1}, \mu_{2}, \mu_{3}, \mu_{4} \longrightarrow N, N w, N w, N w, N w^{-}
$$

derined by (14). Substituting (20) into (4) we get

$$
\begin{equation*}
\log p(r, T)=\log g(r)+4(r, T)-\Psi(r ; \infty),(\omega \tag{21}
\end{equation*}
$$

so that the Iroe energy may be writton down:

$$
\begin{equation*}
F(r, T)=-k T \log p(r, T)=[\log g(r)+\psi(r, T)-\psi(r, \infty)](-k T) . \tag{22}
\end{equation*}
$$

The equilibxiun value $F$ of $r$ is obrainod by mininizing $F$ :

$$
\begin{equation*}
0=\frac{\partial F(\bar{r}, T)}{\partial r^{r}}=-k T\left[\frac{d \log g(\bar{r})}{d \vec{r}}+\frac{\partial \psi(\bar{r}, \tau)}{\partial \bar{r}^{r}}-\frac{\partial \psi(\vec{r}, \infty)}{\partial \tilde{r}}\right] . \tag{23}
\end{equation*}
$$

But by (26) and (17)

$$
\begin{equation*}
\frac{\partial \psi(\gamma, T)}{\partial \gamma}=\sum_{i} N \log \mu_{i}, \tag{24}
\end{equation*}
$$

and by (3)
so that by (13)

$$
\frac{d \log (r)}{d r}=2 N \log \frac{W}{r},
$$

$$
\sum_{i} \log \mu_{i}=-2 \log \frac{\bar{w}}{\bar{r}}+\left[\sum_{i} \log \mu_{i}\right]_{T \rightarrow \infty}=2 \log \left(\frac{\bar{w}}{\bar{r}}\right),
$$

i.e.

$$
\begin{equation*}
\prod_{i} \mu_{i}=\left(\frac{\bar{r}}{\bar{r}}\right)^{2} \tag{25}
\end{equation*}
$$

It will be showm in the next section that we may put $v_{A A}=v_{B B}, v_{A B}=0$, vithout altering the epecilic heat of the crystal if $V=\frac{1}{2}\left(v_{A A}+\tau_{C_{B}}\right) V_{V_{B}}^{2}$

－7－
loft unchangod．When this is done，$\phi$ will be symetrioal vith respect to $\mu_{1}, \mu_{2}, \mu_{3}$ and $\mu_{4}$ ，and we conclude that all the $\mu^{\prime \prime} \mathrm{s}$ are oqual from the facts that（i）epquation（14）has only one set of solution ${ }^{7}$ ， and（1i）if the conclusion is true（14）becones，with all $\mu$ put equal to $\mu$ ，

$$
\begin{equation*}
\xi \frac{\partial \phi}{\partial \xi}=N, \quad \mu \frac{\partial \phi}{\partial \mu}=4 N w . \tag{26}
\end{equation*}
$$

which does have ${ }^{7}$ a set of solution in $\xi$ and $\mu$ ．Lyov $\phi$ is given by

$$
\begin{equation*}
\phi=\xi\left[1+4 \mu x^{2}+\left(4 \mu^{2} x^{2}+2 \mu^{2} x^{4}\right)+4 \mu^{3} x^{2}+\mu^{4}\right], \tag{27}
\end{equation*}
$$

where $x$ is dafinec by（9）．On elininatins $\xi$ from（26）we obtain

$$
\begin{equation*}
(1+5) \mu^{4}+(2+45) x^{2} \mu^{3}+25 x^{2}\left(x^{2}+2\right) \mu^{2}+(45-2) x^{2} \mu+(5-1)=0 . \tag{28}
\end{equation*}
$$

The free energy is given by（21）and（18）：
$-\frac{F(r, T)}{2 N k T}=r \log r+\omega \log \omega-2 \omega \log \mu+\frac{1}{2} \log \left(1+4 \mu x^{2}+4 \mu^{2} x^{2}+z \mu^{2} x^{4}+4 \mu^{3} x^{2}+\mu^{4}\right)^{(29)}$ and the conoition of equilibriun by（25）：

$$
\begin{equation*}
\mu=\sqrt{\frac{1-5}{1+5}} \tag{30}
\end{equation*}
$$

To obtain the critical temperature，we expend（28）in powers of $s$ and find after identifying coerficients

$$
\log \mu=-\frac{1+6 x^{2}+x^{4}}{2+2 x^{2}} s+k s^{3}+\cdots,
$$

which is the only real solution for $\log \mu$ ．Neact we expank（50）：

$$
\log \mu=-s-\frac{1}{3} s^{3}-\cdots
$$

At the critical value $x_{e}$ of $x$ ，these last two equations have a multi－ ple solution at $s=0$ ．Hence
i．e．

$$
-\frac{1+6 x_{c}^{2}+x_{e}^{4}}{2+2 x_{e}^{2}}=-1
$$

$$
x_{c}=(v 5-2)^{1 / 2}=.4858 .
$$

## 4．GRATEAL FORA OF THS GUASI－GHETCAL INEIHDD

Let us now take a group of any size andform．Let it havo a $\alpha-s i t e s$ b $\beta$－sites and $\gamma$ pairs of nearest heighbourst＇The procedures to ob－ tein en approxinate expression for the Iree onorgy of the cryatal fol－ low exactily the same line as in tho speaial eese considered in the

Last section. Bquations (13), (14) and (18) are essentially unchonged:

$$
\begin{align*}
& \overline{\left[q, q_{2} \cdots\right]}=\xi \mu_{1}{ }^{q} \mu_{2} \mu_{2} \cdots e^{-x / k T} \text {, } \tag{31}
\end{align*}
$$

and

$$
\begin{equation*}
\left(\mu_{i}\right)_{T=\infty}=\frac{\boldsymbol{w}}{\boldsymbol{r}} . \tag{38}
\end{equation*}
$$

But (12) should be corrocted by a factor $\frac{\gamma}{y}$ to account for the duplications in oplculating $I$ from the sum of the energios of all the groups in the erystal:

$$
\begin{equation*}
\bar{E}=\frac{3}{\gamma} \frac{z}{2} \overline{\left[q_{1}, q_{2}, \cdots\right]} \times\left(q_{1}, q_{2}, \cdots\right)=\frac{3}{\gamma} k T^{2} \frac{\partial \phi}{\partial T} . \tag{34}
\end{equation*}
$$

Hence (22) becanes*

$$
\begin{equation*}
F(r, T)=-k T\left[\log g(r)+\frac{3}{\gamma} \psi(r, T)-\frac{3}{\gamma} \psi(r, \infty)\right] \text {, } \tag{35}
\end{equation*}
$$

oppore explicitiy, by (3), (17), and(53):

$$
\begin{equation*}
F(r, T)=-\frac{3 N A T}{\gamma}\left[\log N+\left(a+b-\frac{2 r}{3}\right)(r \log r+w \log w)-\log \xi-w>\log \mu i\right] . \tag{56}
\end{equation*}
$$

The dorivative is

$$
\begin{equation*}
\frac{\partial}{\partial r} F(r, T)=-\frac{3 N k T}{\gamma} \log \left[\left(\pi \mu_{i}\right)\left(\frac{r}{w^{2}}\right)^{d+b-\frac{2 x}{\partial x}}\right] \text {, } \tag{57}
\end{equation*}
$$

so that the condition of equilibrium is

$$
\begin{equation*}
\pi \mu_{i}=(\bar{w} / \overline{\mathbf{r}})^{a+b-\frac{2 \gamma}{z}} \tag{58}
\end{equation*}
$$

In actual coloulations the following points may prove helpful:
(1) The free enorsy is changud by a constant if van end $V_{B B}$ are both replacod by $\frac{1}{2}\left(v_{A A}+r_{B B}\right)-v_{A B}$, and $V_{A B}$ by $\left.f\right)^{\prime} \mathrm{O}_{2}$ To prove this $l_{\text {et }} j_{i}$ be the nurber of sites in the group neighbouring to the site i. Let $\chi$ be changed into $\chi$ by the replacenent. It is evident that

$$
x^{\prime}-\chi=-\gamma v_{A B}+\frac{v_{A A}-v_{A}}{2} \text { (ro. of B-B pairs - no. cf. AA pairs), }
$$

and that

Hence
if we put
where the + sign or the -sign is to be taicen according as the site $i$ is on $\alpha$ or a $\beta$ site. We can now calculate the ner free energy and *Care nust be taken whan the thoory is extended to the ease when the atomie ratio is not $1: 1$. Tho function $\Psi$ in ( 35 ) nust then be repleced by ${ }^{\prime} \psi+t y^{\prime}$ where $\psi{ }^{\prime}$ is tho function $\psi$ for the case when the group of interost has the some fozm as the original one but with $\alpha$ enf $f$ sites
interchanged.

## （－9－

verify the above statenent．
（ii）Sites that are sympetifically situatod in the eroup have equal $\mu^{\prime \prime}$ s irrospective of their nature if $V_{W}=Y_{W E}, V_{n g=0}$ ．This has already been showm in the last section．Since the most troublesome part of the cal－ culations is the olintination of the parameters，much night be gained by ohoosing a group with a large number of sites symetrically situated． （iii）The free onergy is a function of $\mathrm{s}^{2}$ ，so that（30）is alvays sa $=$ tigited at $\bar{N}=\bar{r}=\frac{1}{i}$（1．c．long aistance oraer $=0$ ）．The proof is aimple when we have already made $V_{A A}=V_{B B}, V_{A B}=0$ ，so that an interchange of $\Lambda$ and $B$ atons does not alter the energy．Thus

$$
\chi\left(q_{1}, q_{2}, \cdots\right)=\chi\left(1-q_{1}, 1-q_{2}, \cdots\right) .
$$

Putting
\＄ati $\xi^{\prime}=\xi \mu_{1} \mu_{2} \cdots$
and

$$
\begin{equation*}
\mu_{i}^{\prime}=1 / \mu_{i}, \tag{39}
\end{equation*}
$$

we get

$$
\xi \mu_{1}^{g_{1} \mu_{2}}+e^{-\gamma / k T}=\xi^{\prime} \mu_{1}^{\prime-q_{1}} \mu_{2}^{\prime-q_{2}} \cdots e^{-\gamma / \hbar \tau} .
$$

Thus if $\left(\frac{3}{2} \%\right)$ is satisrioa

$$
\sum_{q}\left(1-q_{i}\right) \xi^{\prime} \mu_{1}^{\prime-q_{1}} \mu_{2}^{\prime-q_{2}} \ldots e^{-\chi^{\prime / k T}}=\Sigma_{q} \xi \mu_{1}^{q_{1}} \mu_{2}^{q_{2} \ldots} e^{-\gamma / \beta \pi}-\sum q_{i} \xi \mu_{1}^{q} \mu_{2}^{q_{2}} \ldots e^{-x / k T}=N r \text {; }
$$

1．e．$\xi^{\prime}, \mu_{1}^{\prime}, \mu_{2}^{\prime}, \cdots$ would be the solution or $k \cdots \nmid(52)$ with $r$ substituted for $w$－hence by 174 （52）and（17）

$$
\text { showing that } \quad \begin{align*}
\Psi(1-r, T) & =N-N \log \xi^{\prime}-\sum_{i} N r \log \mu_{i}^{\prime}=\psi(r, T) \\
& F(1-r, T)=F(r, T) . \tag{40}
\end{align*}
$$

（iv）The parometer for a corner site is always given by

$$
\begin{equation*}
\epsilon=\frac{1}{1+5}\left(\sqrt{x^{2} 5^{2}+\left(1-5^{2}\right)}-5 x\right) \tag{4}
\end{equation*}
$$

irrospective of the size of the $G$ roup．if $V_{A A}=V_{B B}, V_{A B}=0$ ，By a cormer site we nean a site that has only one nearest neighbour in the group． Let $\in$ be the selective variable（parameter）of a cornor site，and $\mu_{\text {，}}$ that of its only neighbour in the group．If the comer site is drop－ pod，a now croup is obtained．Wo distinguish all quantities reierring to this new group by a prime，and obtein at once

$$
{\xi^{\prime} \frac{g^{\prime}}{\partial \xi^{\prime}=N}, \quad \mu_{i}^{\prime} \frac{\partial q^{\prime}}{\partial s_{j}}=N w, \quad i=1,2, \ldots}^{2}
$$

The sites of the primed group aro numbered in the same way as in the unprimed group. Introducing the variable $x$ derined in (9), we may write

$$
\phi=\sum_{p, q} \xi \in \mu_{1}{ }^{\$} \mu_{2} q^{2} \ldots e^{-V / k T}
$$


Let these two terms be denoted by $\phi_{0}$ and $\phi_{1}$ respectively. Since


Hence $\epsilon \frac{\partial \phi}{\partial \epsilon}=1 \mathrm{liv}$ Ieads to

$$
\begin{equation*}
\frac{\epsilon x}{1+\epsilon x} 1 I r+\frac{\epsilon}{\epsilon+x} 1 / r m \text {, } \tag{45}
\end{equation*}
$$

or

$$
\begin{equation*}
\frac{w}{T}=\frac{\epsilon(\epsilon+x)}{1+\epsilon x}, \tag{46}
\end{equation*}
$$

the solution of which is (41). Thus the two parametors $\mu$ and $\nu$ in the approsination dioussed in section 2 are equal to $\leqslant$.
(v) The "contribution" to the froe enorgy 险 fron a cormer aton is suoh that, in the notations of (iv).

$$
\begin{equation*}
P(x, T)=\frac{\gamma-1}{\gamma} F^{\prime}(r, T)+\frac{1}{\gamma} \bar{F}_{0}(r, T), \tag{47}
\end{equation*}
$$

where $F_{0}(x, q)$ is the free energy when $\gamma=1$, 1 .e. the free onergy in the approxination aisoussed in section 2. This ie proved as follows. If we put

$$
\begin{equation*}
\xi=\xi^{\prime \prime} \frac{1}{1+\epsilon x}, \mu_{1}=\mu_{1}^{*} \frac{1+\epsilon x}{\epsilon+x}, \mu_{2}=\mu_{i}^{*}, \quad i \geq 2, \tag{48}
\end{equation*}
$$ it is evident from (45) that $\phi$ would becone a function of $\xi^{\prime \prime}, \mu_{1}^{\prime \prime}, \mu_{2}, \cdots$ satisfyine the relations


It is also eviedent that $\phi$ is the sumo function of $\xi^{\prime \prime}, \mu_{1}^{\prime \prime}, \mu_{2}^{\prime \prime}, \cdots$ as $\phi^{\prime}$ ie of $\xi^{\prime}, \mu_{1}^{\prime}, \mu_{2}^{\prime}, \cdots$. Now (42) has only are ${ }^{7}$ set of volution in $\xi^{\prime}$ and $\mu_{i}^{\prime}$. Nonce from (49) we infer that $\epsilon^{\prime} \xi^{\prime} \xi^{\prime \prime}, \mu_{i}^{\prime}-\mu_{i}^{*}$. Whas

$$
\begin{equation*}
\xi=\xi^{\prime} \frac{1}{1+\epsilon x}, \quad \mu_{1}=\mu_{1}^{\prime} \frac{1+\epsilon x}{\epsilon+x}, \mu_{i}=\mu_{i}^{\prime}, \quad i \geq 2 . \tag{50}
\end{equation*}
$$

(42) and (50) cive the paramotors $\mu_{i}$ in toras of $\mu_{i}^{\prime}$. Insarting than into
-11-
（36）we obtain

If the original（unprimed）group is a pair of nearest neighbours，we have $\gamma=1$ ，and（51）reduces to the expression for the free energy in the approximation disoussed in seotion 2 ：

$$
P_{0}(x, T)=-z \mathbb{N} k T\left[\left(1-\frac{2}{3}\right)(r \log r+w \log w)+r \log (1+\epsilon x)+w \log \frac{C+x}{\epsilon}\right] .
$$

Insorting this baok into（51）ve get（47）．

## 5．COMPARISON WITH BIITH＇S LGHHOD

The so－oalled looal grand partition function ${ }^{1,5,8}$ in Bothets approxi－ mations vith long－distance order is idention in form with our funtion $\phi$ when all the＂interior sites＂in the group have the some paxaneter $\mu_{0}$ For the oase of equal ooncentrations for the two kinds of atons，whioh is the aase so far considered，this parameter has been put dequal to unity by Bethe．S1noe the different teanss of the local erand partition funotion stand for the probabilities of oceurance of the corresponding local groups in the orystal，it is olear that Bethe＇s method with long－ aistance oxder is essentially ption that the froe onergy（35）has a mintrawn won

$$
\begin{equation*}
(\mu)_{\text {Interior sites }}=1 \text {. } \tag{53}
\end{equation*}
$$

But as we have shown that（38）gives the condition of a nininum of the free energy，the complete＊identifieation of Bethe＇s and the quasi－ ohemioal mothods in any approximation reduoos to the mathematicel proof of the equivalence of（58）and（53）．While this presents no difficulty at all for Bethe＇s first approximation（section7），a general proof is by no moans easg．We oan only satisif ourselves with the assortion that ＂noomplete＂as far as the probabilities of ocourance of the locel con－ figurations are ooncerned．The energy oaloulations are aifferent in the two nethods．
8ㄱathope，Proe．Camb．Phil．Soo．35，508（1937）．

> -12-
the two mothods are equivalent for large groups, i.e. groups for which

$$
a+b-\frac{2 \gamma}{z} \ll \gamma
$$

This follows from the fact that if (53) is true

$$
\left[\left(\pi \mu_{i}\right)\left(\frac{r}{w}\right)^{a+b-\frac{2 \gamma}{3}}\right]^{\frac{1}{\gamma}} \cong\left[\pi(\mu)_{\text {interior sites }}\right]^{\frac{1}{\gamma}}{ }^{2}=1,
$$

so that by (57)

$$
\frac{\partial}{\partial r} \mathbb{F}(r, T)=0 .
$$

To see hov the equilibriwi free energy $\mathcal{P}(F, T)$ varies with $T$ in high order approxinntions, ve subatitute (38) into (36) and maice use of (32):

$$
-\frac{F}{3 N k T}=\frac{1}{\gamma} \log \left(\sum_{q} \mu_{1}^{q /} \mu_{2}^{q z} \cdots e^{-x / k T}\right)+\frac{1}{\gamma}\left(a+b-\frac{2 \gamma}{3}\right) \log \bar{x} .
$$

The last term is vary mall for large groups, so that by (53)

$$
-\frac{F}{3 N k T}=\frac{1}{\gamma} \log \left(\Sigma e^{-\gamma / k T}\right)
$$

6. THE NON-TWבWRENRMCE OF LOCAL CONTIGURATTONS

Let us return to the funaumental assurption of the quasi-ahemical tho different method, i.e. to (51) which gives the average numbers of loonl conrigu-
 dudatiztelep this equation expresses the exact alstribution law of an assembly of nolecules (of. the exaumle in section 2) whioh hes an enorey $\frac{\gamma}{z}$ times as laxgo as the crystal. Distinguishing all quantities referring to the assambly of moleoules by a subscript $n$, we get

$$
F(x, T)+k T \log g(r)=\frac{g}{\gamma}\left[F_{m}(r, T)+k \log g_{m}(r)\right],
$$

which is obtained from (4). But if H is the number of arrangements in the crystal lattice having the given values of $\left[\mathrm{L}_{1}, \mathrm{~g}_{2}, \cdots\right]$,

Thus

$$
\begin{gather*}
F\left(r, \frac{\eta}{2}\right)=-k 220 \bar{N}+\bar{E} .  \tag{54}\\
\log \frac{\bar{H}}{g(r)}=\frac{3}{\gamma} \log \frac{\overline{M_{m}}}{g_{m}(r)}
\end{gather*}
$$

$$
\begin{aligned}
& \text { But* } \quad H_{\text {m }}=\frac{N!}{H\left[q, q_{2}, \cdots\right]!} \text {, } \\
& \text { hence dropping the bar we get }
\end{aligned}
$$

honce dropping the bar we get
where

$$
\begin{gather*}
H=\operatorname{h}(x)\left\{\frac{N!}{\pi\left[g, q_{2}-j!\right\}^{3} ;}\right.  \tag{56}\\
\mathrm{h}(x)=g(x) /\left\{g_{\mathrm{m}}(x)\right\}^{3 / \gamma} . \tag{57}
\end{gather*}
$$

*rovier; Statistical Mochanics, second edition, sections 2.6 and 5.11 .

## －13－

Equation（56）has been reiferred to in Fowler and Guggenheim＇s paper as the mathematical expression of the＂hypothesis of the non－interference of looal oonfigurations＂，beouuse wen $\frac{\gamma}{z}=1$ ，the number of exrangements in the orystal consistent with tho distribution law $\left[q_{1}, q_{2}, \cdots\right]$ for the groups of sites 1s，except for the factor $h(r)$ ，oqual to ${ }^{\text {wr }}$

$$
F_{n}=\frac{N!}{\Pi_{q}\left[q_{1}, q_{2} \cdots \cdot\right]!},
$$

which is the number of arrangonents in the crystal for the civon values of $\left[q_{1}, q_{2}, \cdots\right]^{\circ}$ if the $N$ groups in the arystal are Impeined to be goparated and are fillod indopentently with atous．The term＂non－intorrorenoe＂is oomes Irom the fact that aotually the N sroups are not semoratod but are interlooked and oannot bo fillea indopondently with atoms，i．e．they ＂interfore＂with each other．

To ifind the value of $g_{\mathrm{m}}(\mathrm{r})$ we notice that by derinftion $g_{m}=\sum H_{i n}$ ．But $\Sigma H_{\mathrm{in}}$ is the number of arrangements in the IN separated groups considered above if thoy are to be so ifilled with atons that 7 mr of them have wrong atons on the sites $i, i=1,2, \cdots$ ．Among the N sites $i$ of tho N Eroups $\frac{N!}{(N N)!(v w)!}$ dirrorent arrangenents ase possible．Hence ${ }^{\text {m／}}$

$$
\begin{equation*}
g_{\mathrm{m}}=\sum H_{22}=\sum \frac{N!}{\Pi\left[q_{1}, q_{2}, \cdots\right]!}=\left[\frac{N!}{(N r)!(N w)!}\right]^{2+b} \tag{58}
\end{equation*}
$$

Thus

$$
\begin{equation*}
\mathbf{h}(\mathbf{r})=\left[\frac{N!}{(n r)!(N w)!}\right]^{(a+b)} \tag{59}
\end{equation*}
$$

The froe energy of the cryatal may be obtained from（ $\mathrm{Na}_{4}^{4}$ ），（ 56 ）and（ N 5 ）： $P(r, T)=\frac{3 N k T}{\gamma}\left\{\left(a+b-\frac{2 \gamma}{j}\right)(r \log r+m \log m)+\log \left[-\frac{1}{N}\left\{\overline{q_{1}}, q_{2}, \cdots\right] \log \left[\overline{\left.q_{1}, q_{2}, 0 \cdots\right]}\right\}\right.\right.$ whioh has been obtained above by integretion．

[^23]
## -14-

7. SPIGIAL, CONETDERAKTONS COHOIRITIG BEMES'S FIRST ADD SENOLD APYROXTMWITONS
(i) Eirgt Approxination. If an $\alpha$-site together with its z nearest noighbours are taken as our croup of interest, all the sites ercoept the eentral one are corner sitos. Hense their selective variables are all oqual to the value of $\epsilon$ given in (41). By successive applications - of (47) we sea that the froe enorgy is exactily $F_{o}(r, T)$, a faot which hes elroedy been pointed out by Fowlor and Guggenhein². The selective variable of the central aite is givon by auecessive applications of(00)

$$
\begin{equation*}
\lambda=\frac{w}{r}\left(\frac{1+\epsilon x}{\epsilon+x}\right)^{z} \tag{61}
\end{equation*}
$$

The factor $W / r$ is the solective variable for the centrel site when it alone forms the group. The aquilibrium oondition ( 53 ) becomes

$$
\begin{align*}
\lambda \epsilon^{z} & =(\bar{w} / \overline{\mathrm{s}})^{z-1} \\
\lambda & =(\mathrm{w} / \mathrm{x})^{1-z} \epsilon^{z} \\
\lambda & =1 . \tag{62}
\end{align*}
$$

But by (61) and (45), Hence at oquilibrium

Thus tho approximation is oupletoly equivalent to Bethets first approxiration, as already mentioned in section 5.
(1i) Second Approximation. Now consider the group of a ites occuring In Bethe's second epproxdnation ${ }^{5}$. iccording to section $4,(1 v)$, the selective veriables for the corner sitos in the second woll are all equal to $\epsilon$, which is given by ( 41 ). But in $7 \phi(\not)$ Bethe's oricinel calculations, the solective variables for the corner sites and the ruediun aites are mede equal, and are found to be different from $\epsilon$. Thus if tue use his orf cinnl method, equation (32) can not be stitisrioc. (In fyff other words, the probillttiee of ocourence of rapong atoms in the correr and would be tho mediun sotes $/ \neq \phi_{n}$ unoque1.)

Por siripliaity we shall drop the cornor gites and take as our eroup of interest the control. site, the firgt ahol2 sites and the nodium
sites；with seleotive variebles $\mu, \nu$ and $\lambda$ respeotively．（The contri－
 frec onorgy by afrple addition as showm in seation 4．（v）．）With the notations $n$ ，wifd and $g_{m m}$ of Bethe ${ }^{3}$ we find，

$$
\begin{equation*}
\phi=\xi \sum_{n}\left(x^{n}+\mu x^{3-n}\right) P_{n}(x, y, \lambda), \tag{63}
\end{equation*}
$$

whera $\quad P_{n}(x, \nu, \lambda)=\nu^{n} \sum_{m} g_{n m}[(1+\lambda) x]^{m}\left(x^{2}+\lambda\right)^{\left(\frac{3}{2}-1\right) n-\frac{m}{2}}(1+\lambda x)^{\left(\frac{3}{2}-1\right)(3-n)-\frac{n}{2}}$ ． at＇vor elininatin；\％end $\mu$ ，（S2）becomes


The isee enorg is obtoince from（36）：

$$
\begin{aligned}
& F(x, Z)=-\frac{N k T}{z-1}\left[\frac{1}{2}\left(z^{2}-4 z+4\right)(x \log x+w \log 3 i)+2 \log x_{n} x^{n} P_{n}+N \log z_{4} x^{3 n} P_{1}-z w \log y-w z^{\frac{3}{2}-1}(65) \log \lambda\right] .
\end{aligned}
$$

Wor the faco－contred crystal $\mathrm{Cu}_{\mathrm{g}}$ bu，we may of course foilow Pelerls ${ }^{9}$ and take as our group a contral site togethor with its twelve flrst ahell．noighbours．The froe onorgy exprewsion would then contain sevon selective veriablest four of which cen be elfminatec．The resultent exprevalon is vexy curbersone and numorioal oalculations would be la－ borious．ie thorefore wake a eimpler approxination：the group is trken to be four neurest neighbours foming a tetrehedron．Aplitile geonetri－ cel consideration assures as that ell such tetrahodrons oontain on
 $\alpha$－aite（ror goll atous）and threo $\beta$－sites（for coppor atoms），an intereating conclusion shoving that the te－ trahodion micht be rogaripd as a sort of＂moleoular＂ structure in a face－oentred lattice with atonic ratio 1：3．Our approximution may thus be reesonably expectod to reveal the more important features of the ondor－disorder transformation in such
＂dodrentrod eroups，three，and fozp－centred，four，paranders exo neco－ ssary．Doth these two kinds of gavops must bo considored baceuse other－ wise the enargy of the erystel oannot be easily obtained irom the enexgy of the groups in the erystel．
$9_{\text {celerdi，Lroc．Roy．Soc．Londor 1154，} 207(1936) .}$
allogs.
Let $\mu$ and $\nu$ be the parazeters (for wrong atous) of thef-sites and the $\alpha$-sites respectivoly. Let there be altogether $\leq i=$ atons. It is ensy to see that thore are ant groups in the orystal. When 1 m atons on the $\alpha$-Eitas are wrong, the equations cotemining the parancters are

$$
\begin{aligned}
& 301=\phi=\xi\left[x^{3}+3 x^{2} \mu+3 x^{3} \mu^{2}+x^{6} \mu^{3}+\nu\left(x^{6}+3 x^{3} \mu+3 x^{2} \mu^{2}+x^{3} \mu^{3}\right)\right], \\
& \operatorname{sen} m \nu=\nu \frac{\partial \varphi}{\partial \nu}=\xi \nu\left(x^{6}+3 x^{3} \mu+3 x^{2} \mu^{2}+x^{3} \mu^{3}\right),
\end{aligned}
$$

and $\operatorname{ari}\left(\frac{v}{3}\right)+\operatorname{ain}\left(\frac{\alpha}{3}\right)+\cos \left(\frac{N}{\xi}\right)=\mu \cdot \frac{\partial q}{\partial \mu}=3 x^{2} \mu \xi\left[1+2 x \mu+x^{4} \mu^{2}+\nu\left(x+2 \mu+x \mu^{2}\right)\right]$,
whero $x$ is fith cofinec by ( 9 ). The enerey of the orystal is (or. (34)),

$$
\begin{equation*}
\bar{I} \frac{1}{2} k T^{2} \frac{\partial \phi}{\partial T}+\text { consitent ; } \tag{67}
\end{equation*}
$$

so thet the frec encrey bocones (er). (:5))

$$
F(w, T)=-k T\left[\log g(w)+\frac{1}{2}(\phi-3 i \log \xi-9 \ln \log \nu-2 \mathrm{wn} \log \mu)_{i=\infty}^{T}=\infty\right] \text {. }
$$

But

$$
\log g(v)=-N\left\{(1-w) \log (1-w)+w \log w+1 \log \frac{w}{3}+(5-w) \log [(5-w) / 5]\right\},
$$ and at $T=\infty \quad \nu=\frac{w}{1-w}, \quad \mu=\frac{T v}{3-w}, \quad \xi=\cos (1-w)\left(1-\frac{w}{3}\right)^{3}$.

 Since $\xi$ and $\nu$ onn be very anstily solved from ( 66 ), numerical onloulations ara guite simple. The equilitorius vilue of vis given by (ef. (37) and( 3 ( 8 )

$$
\begin{equation*}
0=\frac{1}{2} \log \frac{(1-\bar{w})(3-\bar{w})}{\bar{w}^{2}}+4 \log \mu \nu \tag{69}
\end{equation*}
$$

This is alveys getisified ot $\overline{\mathrm{w}}=\frac{3}{4}$ Actual ceneilntion shown that the ebsoof tho froe enerzy luto valuet of the reoe energy is plotted in Pig. 5 . From the foma of the creph it is seon that the orystel has a oritical temperature of which the iongaistance order and.(hence) thip enorcy aro efsoontinnous. The critical terperature $T_{0}$ and the latent hotat $Q$ are found to bo
WIate is not evident fron (09) directiy. But if we divice the thole orystal into $100 r$ eublntitices which are all shaple cubic ant introduce a wr for each sublettioe so that $\mathrm{Mr}_{\mathrm{y}}$ is tho munberp of A atons on the 1-th sublattice $(i=1,2,3,4)$, it is obvious that the inae enercy is ajutaotricol

－17－

In terms of the total energy change from $\mathrm{T}=0$ to $\mathrm{T}=\mathrm{A}$ ：
］ 3 SN $\left[\frac{1}{2}\left(V_{A A}+V_{A B}\right)-T_{A B}\right]$
these quantities beoone
$T_{\mathrm{c}}=1.097 \mathrm{~g} / \mathrm{R},\left(\mathrm{T}_{\mathrm{c}}=2.19 \mathrm{~g} / \mathrm{R}\right.$ in Bragg－ililliams＇approxirution and $\mathrm{T}_{\mathrm{o}}{ }^{\alpha} 1.5 \mathrm{E}_{0} / \mathrm{R}$ in Peierls＇approxinetion．）
 Q²．36：。in Poierlar appioximition．）
wherg E stands for $4 N \mathbb{k}$ ．
It will be noticed that due to tho leok of a Iree enorgy expression Federis ${ }^{9}$ did not give the

Figare

Fig． 3 expet values of these quantities．

In concluaion，the author wishes to express his thanks to Frof．J．S．Wanc for valuable cxitioisn dulyt＇pót and aūice．



[^0]:    产品编号：078177－01

[^1]:    ${ }^{1}$ C．N．Yang．Selected Papers 1945－1980 With Commentary．Freeman and Company（1983），p． 5.
    ${ }^{2}$ C．N．Yang．Selected Papers 1945－1980 With Commentary．Freeman and Company（1983），p． 41.

[^2]:    ${ }^{3}$ C．N．Yang．Selected Papers 1945－1980 With Commentary．Freeman and Company（1983），p． 71.

[^3]:    ${ }^{4}$ C．N．Yang．Selected Papers 1945－1980 With Commentary．Freeman and Company（1983），p． 19.

[^4]:    ${ }^{*}$ Let $C^{\prime} C$ be the resultant operation of first operating $C$ and then $C^{\prime}$ ，we have

    $$
    P_{c^{\prime} c}=P_{c^{\prime}} P_{c}, \quad Z_{c^{\prime} c}=Z_{c^{\prime}} Z_{c}, \quad \text { but } \quad A_{c^{\prime} c}=A_{c} A_{c^{\prime}}
    $$

[^5]:    *We assume here that $Q$ is real. There is probably no difficulty in handling complex coordinates, but they are not necessary unless molecules of symmetry $C_{n}, C_{n h}$ or $S_{n}(n>2)$ are studied.

[^6]:    * From this it is immediately seen that any constraint having the same coefficient for equivalent coordinates contributes 1 to $\operatorname{Spur}\left(\mathscr{D} A_{c} \mathscr{D}^{\prime}\right)$.

[^7]:    ＊cf．§18．

[^8]:    ${ }^{1}$ Wilson，Proc．Camb．Phil．Soc．34，81（1938）．
    ${ }^{2}$ Gorsky，Zeit．f．Phys．50，64（1928）．
    ${ }^{3}$ Mott，Proc．Phys．Soc．49，258（1937）．
    ${ }^{4}$ Lin，Chinese J．Phys．3，182（1939）．
    ${ }^{5}$ Wang，＂Free Energy in the Statistical Theory of Order－Disorder Transformations＂，Science Report of National Tsing Hua University，series A，30－th anniversary Memorial Number（1941），printed but failed to appear．

[^9]:    ${ }^{*}$ Cf. Fig. 27 in Rev. Mod. Phys. 10, 1(1938).

[^10]:    ${ }^{6}$ Easthope, Proc. Camb. Phil. Soc. 33, 502(1937); 34, 68(1938).
    ${ }^{7}$ Eisenschitz, Proc. Roy. Soc. 68, 546(1938).

[^11]:    ${ }^{8}$ Sykes and Wilkinson，Inst．Metals J．61，223（1937）．
    ${ }^{9}$ Nix and Shockley，Rev．Mod．Phys．10，1（1938）．

[^12]:    ${ }^{*}$ Research Fellow of the China Foundation for the Promotion of Education and Culture．

[^13]:    ${ }^{1}$ Fowler and Guggenheim, Proc. Roy. Soc. A174, 189 (1940).
    ${ }^{2}$ Bragg and Williams, Proc. Roy. Soc. A145, 699 (1934); 151, 540 (1935); 152, 231 (1935).
    ${ }^{3}$ Bethe, Proc. Roy. Soc. A150, 552 (1935).
    ${ }^{4}$ Kirkwood, J. Chem. Phys. 6, 70 (1938).
    ${ }^{5}$ Chang, Proc. Camb. Phil. Soc. 35, 265 (1939); Kirkwood, J. Chem. Phys. $\underline{8}, 623$ (1940); Wang, "Free Energy in the Statistical Theory of Order-Disorder Transformation", Science Report of National Tsing Hua University, Series A, 30-th Anniversary Memorial Number (1941), printed but failed to appear.

[^14]:    ${ }^{6}$ Fowler, Statistical Mechanics, second edition, pp. 162-163.

[^15]:    ${ }^{7}$ The proof follows easily (if we put $\mathrm{e}^{\psi}$ to be the function $\Phi$ ) from Lemma 2.42 of Fowler's Statistical Mechanics, second edition.

[^16]:    ${ }^{*}$ Care must be taken when the theory is extended to the case when the atomic ratio is not $1: 1$. The function $\Psi$ in (35) must then be replaced by $\frac{1}{2} \Psi+\frac{1}{2} \Psi^{\prime}$ where $\Psi^{\prime}$ is the function $\Psi$ for the case when the group of interest has the same form as the original one but with $\alpha$ and $\beta$ sites interchanged.

[^17]:    ${ }^{8}$ Easthope, Proc. Camb. Phil. Soc. 33, 502 (1937).
    *"complete" as far as the probabilities of occurrence of the local configurations are concerned. The energy calculations are different in the two methods.

[^18]:    ＊Fowler，Statistical Mechanics，second edition，sections 2.6 and 5．11．

[^19]:    *It might be mentioned in passing that for the special case considered in section 2. (58) gives directly the value of the sum $\sum_{x}$ in equation (8.5) of Fowler and Guggenheim's paper if their $r$ and $q$ are equal. The generalization to the case $r / q$ is however easy. The result is

    $$
    \begin{equation*}
    \sum_{x} \frac{[z N]!}{[z N(r-x)]![z N x]![z N(1-r-q+x)]![z N(q-x)]!}=\frac{[z N]!}{[z N r]![z N(1-r))!!} \frac{[z N]!}{[z N q][z N(1-q)]!} \tag{60}
    \end{equation*}
    $$

    which is exact. The value of $\log \sum_{x}$ given by (60) reduces to the approximate expression that Fowler and Guggenheim obtained by identifying $\sum_{x}$ with its maximum term when $N$ is large.

[^20]:    ${ }^{9}$ Peierls, Proc. Rey. Soc. London A154, 207(1936).

    * For $\alpha$-centred groups, three, and for $\beta$-centred, four, parameters are necessary. Both these two kinds of groups must be considered because otherwise the energy of the crystal cannot be easily obtained from the energy of the groups in the crystal.

[^21]:    ${ }^{*}$ This is not evident from（69）directly．But if we divide the whole crystal into four sublattices which are all simple cubic and introduce a $w$ for each sublattice so that $N w$ is the number of $A$ atoms on the $i$－th sublattice （ $i=1,2,3,4$ ），it is obvious that the free energy is symmetrical in the $w$＇s．From this we infer that（69）is satisfied at $\bar{w}=\frac{3}{4}$ ．

[^22]:    IWilson, Proo. $7 \phi \phi / 1 \$ \phi \phi /$ Camb. Phil. Soc. 34, 81 (2938).
    2Gorsky, Zeit. I. Phys. 50, 64(1928). Suott, Proo. Phys. Soc. $49,258(1937)$. ${ }^{4}$ Lin, Chinese J. Phys. 5, 182 (1939).

[^23]:    ＂It might be montionod in passing that for the spociel case considered in seation $2,(58)$ gives eizectly the vilue of the sum $\Sigma_{x}$ in equation （8．5）of Fowlar and Guggonhaim＇s papen if their $t$ and $q$ are equel．The generriluation to the case If is howover easy．The result is
    $\Sigma_{x} \frac{(z N)!}{[z N(r-x)]![z N x]![z N(1-r-q+x)]![\xi N(q-x)]!}=\frac{[z N]!}{[z N r]![3 N(1-r)]!} \frac{[3 N Q]![3 N(1-q))!}{(60)}$ which is exact．The value of $\log \Sigma_{x}$ given by（ 60 ）reduces to the appro－ ximate expression that lowler and Guggenhein obtained by icentifying $\Sigma_{x}$ with its macirum tam when N is large．

