Evaluation of Integrals over the Brillouin Zone*

II. Gauss-Moment-Singularity Method for Counting Frequencies of Lattice Vibrations

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New approximate formulas for evaluating integrals over the Brillouin zone are reported in this paper. These formulas are formally similar to the Houston type, and can be obtained readily from the Gaussian quadrature formula without solving the matrix equation. Their accuracy is better than that of the Houston's many-term expansion formulas. An application is made to the problems of the lattice vibration to show their feasibility.

I. INTRODUCTION

IN the first paper[1] (referred to as I) of the present series, it has been shown that the Houston method with many terms[2] expansion is very effective to evaluate the integrals over the first Brillouin zone,

$$I=\int F(\mathbf{k})d^3\mathbf{k}=\int_0^{\pi}\sin\theta d\theta\int_0^{2\pi}d\phi J(\theta,\ \phi) \tag{1}$$

with

$$J(\theta,\ \phi)=\int F(k,\ \theta,\ \phi)k^2dk \tag{2}$$

provided that $J(\theta,\phi)$ does not involve the derivatives of k with respective to energy E or to circular frequency[3] ω. When $J(\theta,\phi)$ involves such derivatives of k not too many, that is, when not too many critical points exist in $J(\theta,\phi)$, it is still useful if the technique of modified moment-singularity method is further employed. This technique is a slight variant of the methods due to Phillips[4] and independently to Lax and Lebowitz[5] and to Rosenstock[6]. Thus, if no strong emphasis is placed on the importance of critical points, the Houston method with many terms expansion is never worse than the methods using the large-scale computer, and is rather superior in feasibility.

In this paper we would like to show that approximate formulas formally similar to the Houston type can be obtained readily from the Gaussian quadrature formula without solving the matrix equation. The accuracy of these new formulas is better than that of the Houston type. Then an application is made to the problems of lattice vibrations to show their feasibility.

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(1) J.L. Hwang and C. S. Wang, Chinese J. Phys. *14,* *(1976).*

(2) W. V. Houston, Revs. Modern Phys. 20, 161 (1948); S. P. Singhal, Phys. Rev. **B4**, 2497 (1971); J. Computational Phys. 10, 316 (1972).

(3) $\omega=2\pi\nu$

(4) J.C. Phillips, Phys. Rev. **104**, 1263 (1956).

(5) M. Lax and J. Lebowitz, Phys. Rev. 96, 594 (1954).

(6) H.B. Rosenstock, Phys. Rev. 97, 290 (1955).

II. FORMULAS OF HOUSTON TYPE

As was described in I, the Houston method approximates the integral I (Eqn. (1)) to the form

$$I = 4\pi \int k^2 a_1(k) dk, \tag{3}$$

where a,(k) is the first coefficient of the expansion of the function **F(k)** in terms of the cubic harmonics $K_j(\theta, \phi)$ of van der Lage and Eethe, that is,

$$F(k, \theta, \phi) = \sum_{j=1}^{n} a_j(k) K_j(\theta, \phi). \tag{4}$$

a_j should be determined by solving the matrix equation

$$\mathscr{F}_i = \sum_{j=1}^{n} \mathscr{K}_{ij} a_j, \tag{5}$$

where $\mathscr{K}_{ij} = K_j(\theta_i, \phi_i)$, $\mathscr{F}_i = F(k, \theta_i, \phi_i)$, $i = 1, 2, \cdots, n$, and n is the number of selected directions (θ_i, ϕ_i) along which the secular equation is solved exactly. In general, the n-terms approximation for a_1 obtained from the solution of Eqn. (5) has the form

$$a_1^{(n)} = \sum_{r=1}^{n} C_r F_r(k, l, m), \tag{6}$$

$F_r(k, l, m)$ being the value of the function **F(k)** in the direction [k, l, m]. [k, l, m] can be transformed from the spherical coordinates (k, θ_i, ϕ_i). With Eqs. (1) and (6), the integral I finally becomes

$$I = \sum_{r=1}^{n} C_r \int F(k, \theta_r, \phi_r) k^2 dk, \tag{7}$$

where we have written $F(k, \theta_r, \phi_r)$ instead of $F_r(k, l, m)$.

III. FORMULAS OF HOUSTON TYPE DERIVED FROM THE GAUSSIAN QUADRATURE FORMULA

Now we are going to show that approximate values of the integrals I can be readily obtained from the Gaussian quadrature formula in a form similar to Eqn. (7). The coefficient a_1 need not be determined by solving the matrix equation such as Eqn. (5), and can be evalated directly from the weighting coefficients w_k of the Gaussian formula.

This scheme of calculation is suggested from the following fact: For purposes of illustration, let us merely consider the phonon system, as was done in the paper I. The shape of surfaces of constant frequency in the irreducible first Brillouin zone is not so complicated when they are viewed in a constant θ-plane or in a constant ϕ-plane. In a constant #-plane (or o-plane), if we look contours of constant frequency as a relations between the length of wave vector and the inclination angle θ (or the azimuthal angle ϕ), say k(O) (or $k(\phi)$), then the function ***k(B)*** (or $k(\phi)$) is not so complicated, as may be inferred from the faces of the Brillouin zone. Figs. l(a), (b), (c) show the six faces of the irreducible first Brillouin zone of the simple cubic lattice studied earlier by H. B. Rosenstock and H.M. Rosenstock[7] and the present author(*) (see also the paper I). From this observation, we can assume that $k(\theta)$ (or $k(\phi)$) is at most a polynomial of several degrees (6 or so). On the other hand, it is well known that the Gaussian formula of m associated points

$$\int_{-1}^{1} f(x) dx = \sum_{k=0}^{m-1} w_k f(x_k) \tag{8}$$

(7) H. B. Rosenstock and H. M. Rosenstock, J. Chem. Phys. **21, 1608 (1953).**
(8) J.L. Hwang and C.S. Wang, J. Chem. Phys. 37, 1655 (1962).

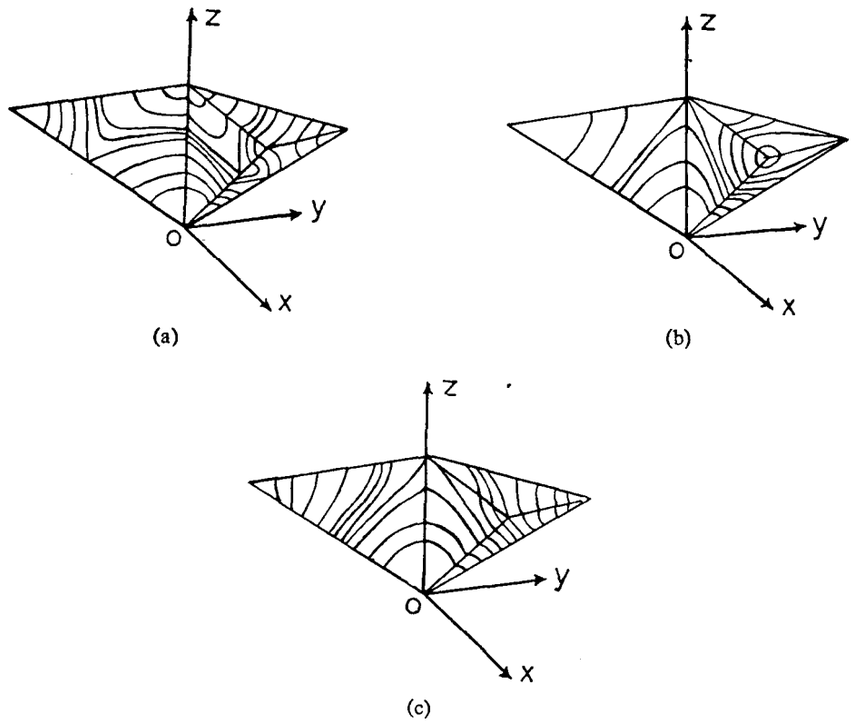

Fig. 1. The contours of constant frequency appearing in the six faces of the irreducible first Brillouin zone of the simple cubic lattice studied by Rosenstock and Rosenstock and the present author. (a) The first branch (the high frequency branch). (b) The second branch (the intermediate frequency branch). (c) The, third branch (the low frequency branch).

involves no approximation if the integrand $f(x)$ is a polynomial of degree $2m-1$ or less. Therefore, the integral with integrand $k(0)$ (or $k(\phi)$) would involve no approximation if the Gaussian formula with 4 associated points or so were used.

For the foregoing reason, it is decided to use the Gaussian formula twice, once for θ and once for ϕ. Then

$$I=\sum_{i=0}^{m-1}\sum_{j=0}^{n-1}u_i u_j \int F(k,\ \theta_i,\ \phi_j)k^2 dk, \tag{9}$$

where $u_i=\Theta w_i \sin\theta_i, u_j=\Phi w_j, \Theta$ and Φ are respectively the range of integration of θ and ϕ, and w_i and w_j are respectively the weighting coefficients of integration over θ and over ϕ. Eqn. (9) has m and n associated points respectively for θ and ϕ, and thus involves mn terms. Eqn. (9) clearly has the same form as Eqn. (7).

As was illustrated in I, the integrated frequency distribution of the lattice considered above is given by

$$N(\omega^2)=48\cdot\int_0^{\pi/4}d\phi\int_0^{\theta(\phi)}\sin\theta d\theta\left(\frac{1}{3}k^3\right) \tag{10}$$

for a branch. To investigate this simple cubic lattice, we calculate the weighting coefficients $u_i u_j$ in Table I for four different schemes(9), $m=2$ and $n=2$ (totally 4 associated points), $m=3$ and $n=3$

(9) These schemes are designed in accordance with the Eqn (10). Therefore, $\Phi=\pi/4, \Theta$ is now a function of ϕ, and then $u_i=\Theta_j w_i \sin\theta_i$.

Table I. The weighting coefficients $u_i u_j \equiv \xi_{ij}$ of the Eqn (9) for different schemes, that is, for $m=n=2$ (totally 4 associated points), $m=n=3$ (totally 9 associated points), $m=n=4$ (16 points) and $m=n=5$ (25 points). (θ,ϕ) represents an associated point, or specifies a direction in the first Brillouin zone.

$m=n=2$

$\theta=0.16743621$ $\phi=0.16597416$ $\xi_{ij}=0.41482690$	$\theta=0.18754000$ $\phi=0.61942400$ $\xi_{ij}=0.51980245$
$\theta=0.62488044$ $\phi=0.16597416$ $\xi_{ij}=1.45614544$	$\theta=0.69990881$ $\phi=0.61942400$ $\xi_{ij}=1.79588616$

$m=n=3$

$\theta=0.08873672$ $\phi=0.08851568$ $\xi_{ij}=0.06765676$	$\theta=0.09297253$ $\phi=0.39269908$ $\xi_{ij}=0.11881682$	$\theta=0.10330236$ $\phi=0.69688248$ $\xi_{ij}=0.09164786$
$\theta=0.39367974$ $\phi=0.08851568$ $\xi_{ij}=0.46855906$	$\theta=0.41247183$ $\phi=0.39269908$ $\xi_{ij}=0.82087717$	$\theta=0.45830007$ $\phi=0.69688248$ $\xi_{ij}=0.62913476$
$\theta=0.69862275$ $\phi=0.08851568$ $\xi_{ij}=0.49102030$	$\theta=0.73197114$ $\phi=0.39269908$ $\xi_{ij}=0.85535177$	$\theta=0.81329778$ $\phi=0.69688248$ $\xi_{ij}=0.64573526$

$m=n=4$

$\theta=0.05458329$ $\phi=0.05453164$ $\xi_{ij}=0.01630388$	$\theta=0.05571080$ $\phi=0.25918884$ $\xi_{ij}=0.03184107$	$\theta=0.05956002$ $\phi=0.52620933$ $\xi_{ij}=0.03639037$	$\theta=0.06462456$ $\phi=0.73086652$ $\xi_{ij}=0.02284968$
$\theta=0.25943430$ $\phi=0.05453164$ $\xi_{ij}=0.14372682$	$\theta=0.26479337$ $\phi=0.25918884$ $\xi_{ij}=0.28056866$	$\theta=0.28308873$ $\phi=0.52620933$ $\xi_{ij}=0.32014071$	$\theta=0.30716048$ $\phi=0.73086652$ $\xi_{ij}=0.20056066$
$\theta=0.52670766$ $\phi=0.05453164$ $\xi_{ij}=0.28163938$	$\theta=0.53758773$ $\phi=0.25918884$ $\xi_{ij}=0.54896492$	$\theta=0.57473126$ $\phi=0.52620933$ $\xi_{ij}=0.62304787$	$\theta=0.62360211$ $\phi=0.73086652$ $\xi_{ij}=0.38736154$
$\theta=0.73155867$ $\phi=0.05453164$ $\xi_{ij}=0.19963796$	$\theta=0.74667030$ $\phi=0.25918884$ $\xi_{ij}=0.38839150$	$\theta=0.79825997$ $\phi=0.52620933$ $\xi_{ij}=0.43781228$	$\theta=0.86613802$ $\phi=0.73086652$ $\xi_{ij}=0.26955330$

$m=n=5$

$\theta=0.03685901$ $\phi=0.03684309$ $\xi_{ij}=0.00510624$	$\theta=0.03723043$ $\phi=0.18124268$ $\xi_{ij}=0.01052429$	$\theta=0.03869817$ $\phi=0.39269908$ $\xi_{ij}=0.01351444$	$\theta=0.04138398$ $\phi=0.60415549$ $\xi_{ij}=0.01300281$	$\theta=0.04402403$ $\phi=0.74855508$ $\xi_{ij}=0.00728369$
$\theta=0.18132101$ $\phi=0.03684309$ $\xi_{ij}=0.05047848$	$\theta=0.18314816$ $\phi=0.18124268$ $\xi_{ij}=0.10402821$	$\theta=0.19036841$ $\phi=0.39269908$ $\xi_{ij}=0.13352694$	$\theta=0.20358076$ $\phi=0.60415549$ $\xi_{ij}=0.12836485$	$\theta=0.21656797$ $\phi=0.74855508$ $\xi_{ij}=0.07184237$
$\theta=0.39286880$ $\phi=0.03684309$ $\xi_{ij}=0.12737575$	$\theta=0.39682769$ $\phi=0.18124268$ $\xi_{ij}=0.26239243$	$\theta=0.41247183$ $\phi=0.39269908$ $\xi_{ij}=0.33623129$	$\theta=0.44109907$ $\phi=0.60415549$ $\xi_{ij}=0.32218291$	$\theta=0.46923851$ $\phi=0.74855508$ $\xi_{ij}=0.17970196$
$\theta=0.60441659$ $\phi=0.03684309$ $\xi_{ij}=0.15907592$	$\theta=0.61050722$ $\phi=0.18124268$ $\xi_{ij}=0.32745258$	$\theta=0.63457526$ $\phi=0.39269908$ $\xi_{ij}=0.41834496$	$\theta=0.67861738$ $\phi=0.60415549$ $\xi_{ij}=0.39854517$	$\theta=0.72190905$ g-O.74855508 $\xi_{ij}=0.22093723$
$\theta=0.74887858$ $\phi=0.03684309$ $\xi_{ij}=0.09433807$	$\theta=0.75642494$ $\phi=0.18124268$ $\xi_{ij}=0.19405514$	$\theta=0.78624550$ $\phi=0.39269908$ $\xi_{ij}=0.24721148$	$\theta=0.84081415$ $\phi=0.60415549$ $\xi_{ij}=0.23420379$	$\theta=0.89445299$ $\phi=0.74855508$ $\xi_{ij}=0.12906921$

Table II. The integrated frequency distributions $N(\omega^2)$ for the first branch of the simple cubic lattice studied by Rosenstock and Rosenstock. Columns 2-5 are the results of Eqn. (9) for 4 different schemes. Columns 6 and 7 are the results calculated by the Singhal's formulas of the Houston method. Column 8 is the results of the graphical interpolation obtained earlier by the present author. The last column is the exact value determined by Rosenstock and Rosenstock.

ω^2	4 direc.	9 direc.	16 direc.	25 direc.	Singhal 12 direc.	Singhal 16 direc.	graphical interpolation	exact (Rosenstock)
0.033	0.0008	0.0008	0.0008	0.0008	0.0008	0.0008	0.0008	0.0008
0.067	0.0024	0.0024	0.0024	0.0024	0.0024	0.0024	0.0024	0.0024
0.100	0.0046	0.0046	0.0046	0.0046	0.0044	0.0044	0.0046	0.0046
0.133	0.0073	0.0073	0.0073	0.0073	0.0070	0.0071	0.0073	0.0073
0.167	0.0104	0.0104	0.0104	0.0104	0.0100	0.0104	0.0104	0.0104
0.200	0.0141	0.0141	0.0141	0.0141	0.0133	0.0136	0.0141	0.0141
0.233	0.0183	0.0183	0.0183	0.0183	0.0173	0.0176	0.0185	0.0185
0.267	0.0231	0.0231	0.0231	0.0231	0.0218	0.0221	0.0231	0.0231
0.300	0.0285	0.0285	0.0285	0.0285	0.0270	0.0273	0.0285	0.0285
0.333	0.0345	0.0345	0.0345	0.0345	0.0325	0.0330	0.0344	0.0345
0.367	0.0413	0.0413	0.0413	0.0413	0.0389	0.0395	0.0412	0.0413
0.400	0.0490	0.0489	0.0489	0.0489	0.0459	0.0467	0.0487	0.0489
0.433	0.0576	0.0574	0.0574	0.0574	0.0541	0.0550	0.0574	0.0575
0.467	0.0673	0.0670	0.0671	0.0670	0.0630	0.0641	0.0670	0.0672
0.500	0.0784	0.0779	0.0780	0.0780	0.0731	0.0743	0.0782	0.0782
0.533	0.0910	0.0904	0.0905	0.0904	0.0845	0.0862	0.0908	0.0906
0.567	0.106	0.105	0.105	0.105	0.0985	0.0999	0.105	0.105
0.600	0.123	0.122	0.122	0.122	0.114	0.116	0.122	0.123
0.633	0.144	0.183	0.180	0.183	0.224	0.179	0.182	0.184
0.667	0.186	0.276	0.280	0.273	0.311	0.313	0.280	0.275
0.700	0.350	0.441	0.414	0.413	0.432	0.453	0.417	0.417
0.733	0.569	0.622	0.570	0.589	0.590	0.605	0.594	0.592
0.767	0.785	0.743	0.714	0.754	0.800	0.732	0.742	0.740
0.800	0.892	0.767	0.829	0.818	0.849	0.817	0.822	0.820
0.833	0.899	0.848	0.906	0.862	0.844	0.902	0.874.	0.870
0.867	0.906	0.939	0.918	0.927	0.935	0.920	0.923	0.923
0.900	0.916	0.980	0.935	0.964	0.939	0.943	0.952	0.954
0.933	0.930	0.983	0.975	0.972	0.982	0.979	0.978	0.978
0.967	0.965	0.988	0.995	0.992	0.994	0.995	0.992	0.993
1.000	0.980	0.999	1.000	1.000	1.000	1.000	1.000	1.000

Table III. The total integrated frequency distribution (the sum of three branches) for the simple cubic lattice studied by Rosenstock and Rosenstock and the present authors.

ω^2	4 direc.	9 direc.	16 direc	25 direc.	graphical interpolation	ω^2	4 direc.	9 direc.	16 direc.	25 direc.	graphical interpolation
0.033	0.0097	0.0098	0.0098	0.0098	0.0098	0.533	1.70	1.68	1.73	1.70	1.71
0.067	0.0288	0.0289	0.0289	0.0289	0.0289	0.567	1.85	1.83	1.86	1.84	1.84
0.100	0.0555	0.0556	0.0556	0.0556	0.0556	0.600	2.07	1.98	1.98	2.01	2.00
0.133	0.0899	0.0902	0.0902	0.0901	0.0902	0.633	2.10	2.16	2.14	2.14	2.15
0.167	0.133	0.133	0.133	0.133	0.133	0.667	2.15	2.27	2.28	2.27	2.27
0.200	0.186	0.186	0.186	0.186	0.186	0.700	2.31	2.44	2.41	2.41	2.42
0.233	0.251	0.252	0.252	0.252	0.252	0.733	2.53	2.62	2.57	2.59	2.60
0.267	0.334	0.334	0.334	0.334	0.334	0.767	2.74	2.74	2.71	2.75	2.74
0.300	0.440	0.439	0.440	0.439	0.440	0.800	2.85	2.77	2.83	2.82	2.82
0.333	0.597	0.591	0.591	0.590	0.591	0.833	2.86	2.85	2.91	2.86	2.87
0.367	0.821	0.804	0.808	0.807	0.808	0.867	3.87	2.94	2.92	2.93	2.93
0.400	1.09	1.06	1.07	1.05	1.06	0.900	2.88	2.98	2.93	2.96	2.95
0.433	1.19	1.25	1.27	1.26	1.26	0.933	2.89	2.98	2.97	2.97	2.97
0.467	1.34	1.49	1.40	1.43	1.43	0.967	2.92	2.99	3.00	2.99	2.99
0.500	1.56	1.58	1.55	1.57	1.56	1.000	2.94	3.00	3.00	3.00	3.00

(totally 9 associatcd points), $m=4$ and $n=4$ (totally 16 points) ard m-5 acd n-5 (totally 25 points). The integrated frequency distributions $N(\omega^2)$ for the first trench thus calculated are tabulated in Table II to compare with those obtained by the Singhal formulas of the Houston methcd. The exact result of Rosenstock and Rosenstock for the first branch and results of the graphical interpolation scheme are also listed in the last two columns. In Table III is listed the total integrated frequency distribution which is a sum of $N(\omega^2)$ for three branches.

Tables II and III clearly show that the accuracy of new scheme Eqn. (9) is better than that of Singhal's formula with the same number of expansion terms. The nine points scheme ($m=n=3$) is already comparable with the sixteen directions scheme of Singhal.

Needless to say, it is not necessary to take $m=n$. For the present illustrating example (Fig. I), the relation $k(\phi)$ is rather simpler than $k(0)$. Therefore, we might take $m>n$, say $m=4$ and $n=2$, or m-5 and $n=3$ etc. The weighting ccefficients $u_t u_j$ such as listed in Table I should be prepared in an analogous manner.

IV. GAUSS-MOMENT-SINGULARITY METHOD FOR DETERMINING FREQUENCY DISTRIBUTIONS

Frequency distributions of lattice vibrations $G(\omega^2)$ are related to the integrated frequency distributions $N(\omega^2)$ by

$$G(\omega^2)=\frac{dN(\omega^2)}{d\omega^2}=48\int_0^{\pi/4}d\theta\int_0^{\theta(\phi)}\sin\theta d\theta\left(k^2\frac{dk}{d\omega^2}\right). \tag{11}$$

Because of the derivatives $dk/d\omega^2$, spurious singularities appear in $G(\omega^2)$ when calculations by the Houston method is made directly via the Eqn. (11). The same situation occur when the Gaussian scheme is applied. However, this drawback may be avoided by calculating $N(\omega^2)$ and its moments. Then the moments of $G(\omega^2)$ are readily derivable from the moments of $N(\omega^2)$, which enable us to determine the shape of $G(\omega^2)$ if incorporating the results of singularity analysis[10]. This process of determination has already described in detail in I.[1] As has been shown is III, no significant difference can be found between the integrated frequency distributions $N(\omega^2)$ calculated by Gaussian scheme ard those calculated by the Houston method with many terms expansion. Therefore, we feel no necessity here to repeat again a demonstration of the process for determining the frequency distributions $G(\omega^2)$.

V. CONCLUDING REMARKS

The illustrative example given above is merely the simple cubic lattice. However, obviously the other kinds of lattices, such as the face-centered cubic, body-centered cubic, hexagonal closed packed lattices, and so on, can be treated in the same manner. The formulas applicable to these lattices will be reported in forthcoming papers of this series.

(10) L. van Hove, Phys. Rev. 89, 1189 (1953).