中 國 物 理 學 報
第 八 卷 第 三 期, 207 頁, 1951 年 12 月

范德伐耳能量對相加律之差異

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如 1, 2, 3 三體之間有互作用，所產生總能量爲 1—2, 2—3, 3—1 各別作用所產生能量之和，該作用謂有相加性。 多數體間相加性作用的定義，可例此類推。 倫敦曾證明范德伐耳吸引作用符合此相加律；證明所用方法係根據量子力學中二次攝動法。 范德伐耳能量起源於原子之間相互電極化作用。 顯然，兩體的相互極化勢必影響對第三體的反應； 故范德伐耳能量相加律實僅近似性的定律。 自倫敦以量子力學方法澈底解明范德伐耳能量的起源，關於該作用的研究雖多，對上述相加律迄無更深切的討論。 本文目的係根據一簡單化的固體模型對此相加定律的差誤作一普遍估計。

本文計算所用基本原則十分簡單。 設想一立方格體 (cubic lattice)，每格點置一點型振動子 (point—oscillator)。 此模型中， 唯一作用能爲范德伐耳能量，蓋各振動子間的互作用端由各體電雙極 (electric dipole) 發生。 故一旦能求得模型中總能量，減去各振動子的原有零點能所獲差數卽該模型的總范德伐耳能量。

根據普通力學，上述模型之運動可分解爲多數不相牽涉的簡諧運動。 故於換用量子力學後，模型中總能量等於各簡諧運動零點能之和。 本文第五節證明相加律的差誤主要由各該簡諧運動頻率與點型振動子原有頻率的差別所決定。第六節中說明，緣此，吾等不需計算各簡諧運動頻率卽可普遍估計相加律的差誤。 第七節中根據數普通固體爲例所計算該項差誤的數值高可達百分之十三。

固體合成能的計算，除范德伐耳能量外，更需用其一，二次微分係數。 此等係數，因相加律所產生差誤估計可達百分之三十五與百分之七十。

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CHINESE JOURNAL OF PHYSICS
Vol. 8, No. 3, 1951, pp. 208–221

DEVIATION OF VAN DER WAALS INTERACTION FROM ADDITIVE RELATIONS

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(Received August 20, 1951)

ABSTRACT

With a lattice of isotropic point-oscillators as an idealized model, the error of the usual additive approximation for the van der Waals interaction in solids is estimated. For a few common crystals, the estimated errors for van der Waals energy and its first and second derivatives have values up to 13%, 34% and 70% respectively.

The model moreover points to the possible importance of the long range dipolar interaction as a mechanism determining the structure of the exciton-band in insulators.

1. INTRODUCTION

Among his classical papers on the attractive van der Waals forces London[1, 2] has given a proof, on the basis of a second order perturbation calculation, that the forces are additive. He did not however omit mentioning that the additivity rule is only of approximate validity. Yet, despite the many investigations[3] on the subject of van der Waals interaction following the works of London no further discussion of the matter appears to have been given. It is the purpose of the present paper to obtain with the help of a simple model an estimate of the order of magnitude of the deviation from the additivity rule in the case of solids.

The method which we shall use is briefly the following: We take as our model a lattice of isotropic point oscillators. Between such oscillators, the only interaction is of the dipolar van der Waals type; the cohesive energy of the lattice may thus be directly identified as the total van der Waals

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1. F. London, *Z. f. Phys.* **63** (1930), 245; R. Eisenschitz & F. London, *Z. f. Phys.* **60** (1930), 492.
2. F. London, *Z. f. Phys. Chemie.* B **11** (1930), 222; *Trans. Faraday Soc.* **33** (1937), 8.
3. See H. Margenau, *Rev. Mod. Phys.* **11** (1939), 1.

interaction energy of the system. It is readily observed that the classical motion of the system resolves into harmonic vibrational modes. The total energy of the lattice in its lowest quantum state may hence be represented as the sum of the zero-point energies of all the vibrational modes. From this, the van der Waals energy is obtained by subtracting the zero point energies of the free point oscillators.*

The lattice model is described in §2 and the corresponding van der Waals energy in the additive approximation given in §3. In §4, the equations determining the classical vibrational modes are deduced. On the basis of these equations, it is shown in §5 that, if the differences between the frequencies of these modes and the frequency of the point-oscillators are regarded as small and the rigorous van der Waals energy is represented as a series expansion in these differences, the rigorous value reduces to the additive approximation upon ignoring third and higher terms of the series. This leads, as shown in §6, to a method of obtaining a rough estimate of the deviation from the additivity rule without actually working out the frequencies of the vibrational modes. Some numerical estimates made on this basis are given in §7. Finally in §8, the relation between the model and the theory of excitons is indicated. It will be seen that the long-range electric interaction, which is usually ignored alone gives rise to an excitation band of considerable width.

2. The Model

An isotropic oscillator with a given circular frequency ω_0 and electric polarizability α can be described in terms of a vectorial coordinate $\boldsymbol{q}$ by the following Lagrangian:

$$L = \frac{1}{2}(\dot{\boldsymbol{q}}^2 - \omega_0^2 \boldsymbol{q}^2) + \omega_0 \sqrt{\alpha}\, \boldsymbol{q} \cdot \boldsymbol{E} \tag{2.1}$$

where $\boldsymbol{E}$ is a uniform field which we may assume to be present. The corresponding Hamiltonian is

$$H = \sum_{\beta=1}^{3} \dot{q}_\beta \left(\frac{\partial L}{\partial \dot{q}_\beta}\right) - L = \frac{1}{2}(\boldsymbol{p}^2 + \omega_0^2 \boldsymbol{q}^2) - \omega_0 \sqrt{\alpha}\, \boldsymbol{q} \cdot \boldsymbol{E} \tag{2.2}$$

where $\boldsymbol{p}$, the conjugate momenta of $\boldsymbol{q}$, is defined in the usual way by

*A similar consideration of van der Waals interaction in terms of zero point energies has been given before by London[2] in the case of two interacting oscillators.

$$p_\beta = \left(\frac{\partial L}{\partial \dot{q}_\beta}\right) = \dot{q}_\beta . \tag{2.3}$$

The dipole moment $\boldsymbol{\mu}$ of the oscillator is obtained by differentiating the Hamiltonian with respect to $-\boldsymbol{E}$:

$$\mu_\beta = -\left(\frac{\partial H}{\partial E_\beta}\right) = \omega_0 \sqrt{\alpha}\, q_\beta . \tag{2.4}$$

We see readily that the oscillator is adequately described in this way. Thus if $\boldsymbol{E}$ vanishes, (2.2) reduces to the standard Hamiltonian of a free isotropic oscillator with the circular frequency ω_0. On the other hand, for static equilibrium ($\boldsymbol{p}=\dot{\boldsymbol{q}}=0$), $\boldsymbol{q}$ is determined by the condition of minimum H, namely,

$$\omega_0^2 q_\beta = \omega_0 \sqrt{\alpha}\, E_\beta , \tag{2.5}$$

the corresponding induced dipole moment (2.4) being thus

$$\boldsymbol{\mu} = \alpha \boldsymbol{E} \tag{2.6}$$

as required.

The use of the Lagrangian (2.1) saves us from contemplating the three independent parameters, namely, the mass, charge and force constant normally required to describe an elastically bound charge. The above description with the two parameters α and ω_0 in fact leaves the spatial extension of the oscillator completely arbitrary. We shall choose it to be a point-oscillator considering its dimensions infinitesimal. This means on the one hand that its field is strictly that of a dipole (2.4) (i.e. no other multipole moments) and on the other hand that $\boldsymbol{E}$ represents the field at the site of the point-oscillator so that its uniformity is no longer in question.

We shall take as our model a simple cubic lattice of such point oscillators and denote the position vectors of the lattice points by $\boldsymbol{x}(l)$, the components of which are $(l_1 a, l_2 a, l_3 a)$ l_1, l_2, l_3 being integers. The oscillator at a lattice point $\boldsymbol{x}(l)$ will be referred to as the oscillator l and its coordinate and dipole moment will be written respectively as $\boldsymbol{q}(l)$ and $\boldsymbol{\mu}(l)$.

3. The Additive Approximation (second order perturbation method)

The field $\boldsymbol{E}$ at a vectorial distance $\boldsymbol{R}$ from a point-dipole has the components:

$$E_\beta = \sum_\gamma \mu_\gamma \frac{\partial^2}{\partial R_\beta \partial R_\gamma}\left(\frac{1}{R}\right) \qquad (\beta, \gamma = 1, 2, 3), \tag{3.1}$$

where R is the scalar magnitude of $\boldsymbol{R}$. The interaction operator between two oscillators $\boldsymbol{q}, \boldsymbol{q}'$ separated by $\boldsymbol{R}$ is thus

$$\begin{aligned} -\sum_\beta \mu'_\beta E_\beta &= -\sum_{\beta\gamma} \mu'_\beta \mu_\gamma \frac{\partial^2}{\partial R_\beta \partial R_\gamma}\left(\frac{1}{R}\right) \\ &= -\omega_0^2 \alpha \sum_{\beta\gamma} q_\beta q_\gamma \frac{\partial^2}{\partial R_\beta \partial R_\gamma}\left(\frac{1}{R}\right). \end{aligned} \tag{3.2}$$

Regarding (3.2) as a perturbation and applying the second order perturbation method to the oscillators each in its ground state, one obtains in a straightforward way the following value for the van der Waals energy:

$$-\frac{3}{4}\hbar\omega_0\alpha^2\frac{1}{R^6}. \tag{3.3}$$

In the same approximation, the van der Waals cohesive energy per oscillator in the lattice model is obtained directly by applying the additivity rule

$$\epsilon_{\text{BDD}} = \frac{1}{2}\sum_l{}' \left\{-\frac{3}{4}\hbar\omega_0\alpha^2\frac{1}{|\boldsymbol{x}(l)|^6}\right\} = -\frac{3}{8}\hbar\omega_0\alpha^2\sum_l{}'\frac{1}{|\boldsymbol{x}(l)|^6}, \tag{3.4}$$

where the prime signifies that $\boldsymbol{x}(0)$ is to be excluded from the summation. The factor 1/2 takes account of the fact that the interaction energy between a pair of oscillators must be considered as shared between the two.

4. The Classical Vibrational Modes

The Lagrangian (2.1) leads to the following equation of motion

$$\ddot{\boldsymbol{q}} = -\omega_0^2\boldsymbol{q} + \omega_0\sqrt{\alpha}\,\boldsymbol{E}. \tag{4.1}$$

Using (3.1), we find that the field components at $\boldsymbol{x}(l)$ due to all the oscillators elsewhere are given by

$$E_\beta = \sum_{l'}{}' \sum_\gamma \mu_\gamma (l') \left\{ \frac{\partial^2}{\partial R_\beta \partial R_\gamma} \left(\frac{1}{R} \right) \right\}_{R=x(l-l')}$$

$$- \sum_{l'}{}' \sum_\gamma \omega_0 \sqrt{a}\, q_\gamma (l') \left\{ \frac{\partial^2}{\partial R_\beta \partial R_\gamma} \left(\frac{1}{R} \right) \right\}_{R=x(l-l')} \tag{4.2}$$

where $l'-l$ stands for l_1-l_1', l_2-l_2', l_3-l_3', and the prime excludes $l'=l$. The equations of motion for the oscillators in the lattice model are hence the following:

$$\ddot{q}_\beta (l) = -\omega_0^2 q_\beta (l) + a\omega_0^2 \sum_{l'}{}' \sum_\gamma \left\{ \frac{\partial^2}{\partial R_\beta \partial R_\gamma} \left(\frac{1}{R} \right) \right\}_{x(l-l')} q_\gamma (l') . \tag{4.3}$$

Owing to the fact that the coefficients in the last term of (4.3) depend only on the differences $l'-l$, the equations have solutions of the following form:

$$q (l) = q (s) \exp \{2\pi i (s_1 l_1 + s_2 l_2 + s_3 l_3) - i\omega t\} . \tag{4.4}$$

Thus upon substituting (4.4) in (4.3) and dividing by

$$\exp \left\{ 2\pi i (s_1 l_1 + s_2 l_2 + s_3 l_3) - i\omega t \right\},$$

we find that the equations (4.3) reduce to

$$(\omega_0^2 - \omega^2)\, q_\beta (l) = \omega_0^2 C_{\beta\gamma} (s)\, q_\gamma (s) , \tag{4.5}$$

where

$$C_{\beta\gamma} (s) = a \sum_{l'}{}' \left\{ \frac{\partial^2}{\partial R_\beta \partial R_\gamma} \left(\frac{1}{R} \right) \right\}_{x(l-l')}$$

$$\exp \left\{ 2\pi i (s_1 (l_1' - l_1) + s_2 (l_2' - l_2) + s_3 (l_3' - l_3) \right\} . \tag{4.6}$$

We observe that the coefficients $C_{\beta\gamma}(s)$ are independent of the value of l, for upon introducing $l-l'=\bar{l}$ as the summation index, we have

$$C_{\beta\gamma}(s) = a \sum_l' \left\{ \frac{\partial^2}{\partial R_\beta \partial R_\gamma} \left(\frac{1}{R} \right) \right\}_{x(l)} \exp\left\{ -2\pi i (s_1 \bar{l}_1 + s_2 \bar{l}_2 + s_3 \bar{l}_3) \right\}$$

$$= \frac{a}{a^3} \sum_l' \left\{ \frac{3 \bar{l}_\beta \bar{l}_\gamma}{(\bar{l}_1^2 + \bar{l}_2^2 + \bar{l}_3^2)^{5/2}} - \frac{\delta_{\beta\gamma}}{(\bar{l}_1^2 + \bar{l}_2^2 + \bar{l}_3^2)^{3/2}} \right\}$$

$$\exp\left\{ -2\pi i (s_1 \bar{l}_2 + s_2 \bar{l}_3 + s_3 \bar{l}_3) \right\}, \tag{4.7}$$

where the prime now excludes $\bar{l}=0$ (i.e. $\bar{l}_1=\bar{l}_2=\bar{l}_3=0$). With values of ω and $q(s)$ so chosen that (4.5) is satisfied, (4.4) is a solution of the equations of motion.

Regarded as homogeneous linear equations in $q_1(s)$, $q_2(s)$, $q_3(s)$, (4.5) is soluble only if the determinant formed from the coefficients vanishes:

$$\begin{vmatrix} \omega_0^2 C_{11}(s) + (\omega^2 - \omega_0^2) & \omega_0^2 C_{12}(s) & \omega_0^2 C_{13}(s) \\ \omega_0^2 C_{21}(s) & \omega_0^2 C_{22}(s) + (\omega^2 - \omega_0^2) & \omega_0^2 C_{23}(s) \\ \omega_0^2 C_{31}(s) & \omega_0^2 C_{32}(s) & \omega_0^2 C_{33}(s) + (\omega^2 - \omega_0^2) \end{vmatrix} = 0. \tag{4.8}$$

(4.8) gives three solutions for ω^2 which we denote by $\omega_j^2(s)$, $(j=1,2,3)$. For any arbitrarily chosen s (i.e. s_1, s_2, s_3), we have thus three vibrational solutions of the form (4.4) with the respective circular frequencies $\omega_1(s)$, $\omega_2(s)$, $\omega_3(s)$, the corresponding value for $q(s)$ being determined by (4.5).

5. Comparison of the rigorous van der Waale energy with the additive approximation

Each of the vibrational solutions is dynamically equivalent to a linear oscillator of the same frequency. When quantized, the system in its lowest state has thus the following energy :

$$\frac{1}{2} \sum_s \sum_j \hbar \omega_j(s). \tag{5.1}$$

In order to normalize the energy to a finite volume, we impose the well-known Born-Kármán condition[4] by requiring $q(l)$ to be periodic with respect to a

4. See, for instance, F. Seitz, *Modern Theory of Solids* (McGraw Hill, New York, 1940).

finite volume, which we choose to be a cube of N^3 cells with N cells along each edge. All distinct vibrations consistent with this condition are obtained if s is restricted to the following N^3 values:

$$(s_1, s_2, s_3) = \frac{n_1}{N}, \frac{n_2}{N}, \frac{n_3}{N} , \tag{5.2}$$

where n_1 n_2 n_3 are integers in the range 0 to $N-1$. In the following, we shall understand that s is restricted to these values. With s so restricted, (5.1) gives the total energy of a finite specimen of N^3 cells so long as N is large enough for an energy of the order of the surface energy to be ignored.

There are, we notice, altogether $3N^3$ terms in (5.1), corresponding to the $3N^3$ vibrational modes comprising three modes each for the N^3 values of s. Hence upon subtracting from (5.1) the zero point energies for N^3 free oscillators ($3\hbar\omega_0/2$ each) and dividing afterwards by N^3, we obtain for the van der Waals cohesive energy per oscillator the following expression:

$$\epsilon = \frac{\hbar}{2N^3} \sum_s \sum (\omega_j(s) - \omega_0) . \tag{5.3}$$

Since (4.8) determines directly $\omega_j^2(s)$ rather than $\omega_j(s)$, let us write

$$\begin{aligned} (\omega_j(s))^2 &= (\omega_0^2 + (\omega_j^2(s) - \omega_0^2))^{1/2} \\ &= \omega_0 \left(1 + \frac{\omega_j^2(s) - \omega_0^2}{\omega_0^2}\right)^{1/2} . \end{aligned} \tag{5.4}$$

Expressing $\omega_j(s)$ in this way in (5.3) and expanding the latter in a series with respect to

$$\frac{\omega_j^2(s) - \omega_0^2}{\omega_0^2} ,$$

we get

$$\epsilon = \frac{\hbar\omega_0}{2N^3} \sum_s \left(\frac{1}{2} \sum_j \frac{\omega_j^2(s) - \omega_0^2}{\omega_0^2} - \frac{1}{8} \sum_j \left(\frac{\omega_j^2(s) - \omega_0^2}{\omega_0^2} \right)^2 + \cdots \right) . \tag{5.5}$$

We shall proceed to show that the first order term in the series vanishes and the second order term is identical with the additive approximative.

It follows from (4.8) that $(\omega_j^2(s)-\omega_0^2)/\omega_0^2$ (j=1,2,3) are equal to the three solutions X_1, X_2, X_3 of the equation:

$$\begin{vmatrix} C_{11}(s)+X & C_{12}(s) & C_{13}(s) \\ C_{21}(s) & C_{22}(s)+X & C_{23}(s) \\ C_{31}(s) & C_{32}(s) & C_{33}(s)+X \end{vmatrix} \equiv (X-X_1)(X-X_2)(X-X_3)=0. \quad (5.6)$$

Expanding the determinant, we obtain from the coefficients of X^2 and X the following relations:

$$X_1+X_2+X_3=-(C_{11}(s)+C_{22}(s)+C_{33}(s)),$$

$$X_2X_3+X_3X_1+X_1X_2=(C_{22}(s)C_{33}(s)+C_{33}(s)C_{11}(s)+C_{11}(s)C_{22}(s) - C_{23}(s)C_{32}(s)-C_{31}(s)C_{13}(s)-C_{12}(s)C_{21}(s)).$$

Using these relations we find that the first and second order terms in (5.5) are given respectively by

$$\epsilon^{(1)}=\frac{\hbar\omega_0}{4N^3}\sum_s\sum_j\frac{\omega_j^2(s)-\omega_0^2}{\omega_0^2}=\frac{\hbar\omega_0}{4N^3}\sum_s(X_1+X_2+X_3)$$

$$=-\frac{\hbar\omega_0}{4N^3}\sum_s\sum_\beta C_{\beta\beta}(s), \quad (5.7)$$

$$\epsilon^{(2)}=-\frac{\hbar\omega_0}{16N^3}\sum_s\sum_j\left(\frac{\omega_j^2(s)-\omega_0^2}{\omega_0^2}\right)^2=-\frac{\hbar\omega_0}{16N^3}\sum_s(X_1^2+X_2^2+X_3^2)$$

$$=-\frac{\hbar\omega_0}{16N^3}\sum_s\left((X_1+X_2+X_3)^2-2(X_2X_3+X_3X_1+X_1X_2)\right)$$

$$=-\frac{\hbar\omega_0}{16N^3}\sum_s\sum_{\beta\gamma}C_{\beta\gamma}^2(s), \quad (5.8)$$

where in (5.8) we have used the fact that $C_{\beta\gamma}(s)=C_{\gamma\beta}(s)$ (see (4.6)).

When the explicit expression (4.7) for the C-coefficients is used in (5.7), we find immediately on carrying out the summation over β that the first order term $\epsilon^{(1)}$ vanishes.

After (4.7) is substituted in (5.7), the second order term becomes

$$\epsilon^{(2)} = -\frac{\hbar\omega_0\alpha^2}{16N^3}\sum_{\beta\gamma}\sum_{l}{}'\sum_{l'}{}'\left(\frac{\partial^2}{\partial R_\beta\partial R_\gamma}\left(\frac{1}{R}\right)\right)_{x(l)}\left(\frac{\partial^2}{\partial R_\beta\partial R_\gamma}\left(\frac{1}{R}\right)\right)_{x(l')}$$

$$\sum_{s}\exp\left\{-2\pi i\left(s_1(l_1+l_1')+s_2(l_2+l_2')+s_3(l_3+l_3')\right)\right\}. \tag{5.9}$$

Upon summing s over the N^3 points (5.2), one finds that the last factor vanishes unless either

$$l_1 + l_1' = l_2 + l_2' = l_3 + l_3' = 0$$

or

$$l_1 + l_1',\quad l_2 + l_2',\quad l_3 + l_3' = \text{integral multiples of } N.$$

The latter cases however make no contribution to (5.9), for at least some of the components of l and l' will have then to be so large ($\sim N$) that the other factors in (5.9) are practically equal to zero. For $l = -l'$, the exponential factor in (5.9) reduces to unity and the summation over s gives a factor N^3. Thus ignoring all except the terms with $l = -l'$ in (5.9), we have

$$\epsilon^{(2)} = -\frac{\hbar\omega_0\alpha^2}{16}\sum_{l}{}'\sum_{\beta\gamma}\left(\frac{\partial^2}{\partial R_\beta\partial R_\gamma}\left(\frac{1}{R}\right)\right)^2_{x(l)} \tag{5.10}$$

Using the explicit expression

$$\frac{\partial^2}{\partial R_\beta\partial R_\gamma}\left(\frac{1}{R}\right) = \frac{3R_\beta R_\gamma}{R^5} - \frac{\delta_{\beta\gamma}}{R^3}, \tag{5.11}$$

we find readily that

$$\sum_{\beta\gamma}\left(\frac{\partial^2}{\partial R_\beta\partial R_\gamma}\left(\frac{1}{R}\right)\right)^2_{x(l)} = \frac{6}{|x(l)|^6}.$$

It is observed that the expression (5.10) for $\epsilon^{(2)}$ reduces exactly to the additive approximation ϵ_{app} given by (3.4).

6. Deviation from the additivity rule

For large N, the s-values (5.2) cover practically a continuum. Thus we can introduce a distribution function $f(\omega^2)$ such that

$$3N^3 f(\omega^2)\, d\omega^2 \tag{6.1}$$

gives the number of vibrational modes with $\omega_j^2(s)$ in the range ω^2 to $\omega^2 + d\omega^2$. Using the distribution function, we can write the van der Waals energy (5.3) alternatively as follows:

$$\epsilon = \frac{3\hbar}{2} \int f(\omega^2)\, (\omega - \omega_0)\, d\omega^2 . \tag{6.2}$$

It is obvious from the discussion in §5 that the order of magnitude of the deviation from the additivity rule in general depends on the magnitude of $(\omega_j^2(s) - \omega_0^2)/\omega_0^2$ which determines the convergence of the series (5.5). Speaking in terms of the distribution function, this means that the deviation depends essentially on the width of the distribution. Thus we should be able to obtain a general estimate of the error of the additive approximation without reference to a particular lattice by taking a simple square distribution:

$$\begin{aligned} f(\omega^2) &= \text{a constant } C, \quad \omega_1^2 < \omega^2 < \omega_2^2 . \\ &= 0 , \qquad\qquad \text{otherwise,} \end{aligned} \tag{6.3}$$

if the width of the distribution:

$$D = \omega_2^2 - \omega_1^2 \tag{6.4}$$

is suitably chosen.

The distribution function must clearly satisfy the normalization condition:

$$\int f(\omega^2)\, d\omega^2 = 1 . \tag{6.5}$$

Moreover the fact that the first order term $\epsilon^{(1)}$ always vanishes can be expressed in terms of the distribution function as follows:

$$\frac{3\hbar\omega_0}{4}\int f(\omega^2)\,\frac{\omega^2-\omega_0^2}{\omega_0^2}\,d\omega^2=0. \tag{6.6}$$

To satisfy (6.5) and (6.6), the square distribution (6.3) must be of the following form:

$$\begin{aligned} f(\omega^2) &= \frac{1}{D},\ \omega_0^2 - D/2 < \omega^2 < \omega_0^2 + D/2, \\ &= 0 \quad \text{otherwise} \end{aligned} \tag{6.7}$$

which contains the width D as the only parameter.

The second order term $\epsilon^{(2)}$ offers a ready means for determining a value for D. Expressed in terms of $f(\omega^2)$, $\epsilon^{(2)}$ can be written as follows:

$$\begin{aligned} \epsilon^{(2)} &= -\frac{3\hbar\omega_0}{16}\int f(\omega^2)\left(\frac{\omega^2-\omega_0^2}{\omega_0^2}\right)^2 d\omega^2 = \frac{-3\hbar}{16\,D\omega_0^3}\int_{-D/2}^{D/2} x^2\,dx \\ &= \frac{-\hbar D^2}{64\,\omega_0^3}, \quad (x=\omega^2-\omega_0^2). \end{aligned} \tag{6.8}$$

We have seen that $\epsilon^{(2)}$ should be equal to the additive approximation (3.4). Thus equating (6.8) to 3.4), we obtain for D:

$$D=\frac{2\omega_0^2\,a\sqrt{6}}{a^3}\left(\sum_l{}' \frac{1}{(l_1^2+l_2^2+l_3^2)^3}\right)^{1/2}. \tag{6.9}$$

Putting in the value 8.4 for the lattice sum[5] we have

$$\frac{D}{\omega_0^2}=14.2\,\frac{a}{v} \qquad (v=\text{volume of lattice cell } a^3) \tag{6.10}$$

a/v can be expressed in terms of the refractive index of the lattice by the well-known formula[6]

$$\frac{a}{v^3}=\frac{3}{4\pi}\left(\frac{n^2-1}{n^2+2}\right) \tag{6.11}$$

5. J. E. Jones and A. E. Ingham, *Proc. Roy. Soc.* A, **107** (1925), 636.
6. See M. Abraham and R. Becker, *Theorie der Elektrizität*, vol. 2, p. 124.

so that (6.10) may also be written as

$$-\frac{D}{\omega_0^2} = 3.4\left(\frac{n^2-1}{n^2+2}\right). \tag{6.12}$$

Once D/ω_0^2 is known, the fractional error of the additive approximation can be estimated readily as follows: For the distribution (6.7), (6.2) reduces to

$$\begin{aligned}\epsilon &= \frac{3\hbar}{2}\,\frac{1}{D}\int_{\omega_0^2-D/2}^{\omega_0^2+D/2}(\omega-\omega_0)\,d\omega^2 \\ &= \frac{\hbar}{D}\left((\omega_0^2+D/2)^{3/2}-(\omega_0^2-D/2)^{3/2}\right)-\frac{3\hbar\,\omega_0}{2}.\end{aligned} \tag{6.13}$$

Subtracting (6.13) from (6.8) ($\epsilon^{(2)}=\epsilon_{app}$) and dividing by the former, we obtain for the fractional error

$$\frac{\epsilon_{app}-\epsilon}{|\epsilon|} = \frac{-\frac{\xi^3}{8}-\left((1+\xi)^{3/2}-(1-\xi)^{3/2}\right)+3\xi}{\left|\left((1+\xi)^{3/2}-(1-\xi)^{3/2}\right)-3\xi\right|} \tag{6.14}$$

where

$$\xi = \frac{D}{2\omega_0^2}. \tag{6.15}$$

7. Numerical estimates

To obtain an idea of the order of magnitude of the error of the additive approximation, we have calculated the fractional error with the help of (6.10) and (6.12) for a few typical alkali halides and some rare gas crystals. The numerical results are given in the adjoining table.

For works on the cohesive energy of crystals, one requires not only the van der Waals energy but also its derivatives with respect to the volume v of the lattice cell[7]. In fact in some cases, the relative stability of alternative crystal structures may depend essentially on the values of these derivatives[8]. Using the square distribution, we can obtain also the expressions for the derivatives of ϵ in this connexion, we need only notice that D/ω_0^2 varies inversely proportional to v. Then by straightforward differentiation of (6.13) we find that

7. See M. Born and J. E. Mayer, *Z. f. Phys.* **25** (1932), 1; M. L. Huggins, *J. Chem. Phys.* **5** (1937), 143.

8. A. May, *Phys. Rev.* **52** (1937), 339.

TABLE

	rare gas crystals*				alkali-halides**		
	A	Kr	Xe		NaCl KBr RbBr	LiBr CsI	LiI
$14.2\ \alpha/v$	0.59	0.79	0.98	$3.4\left(\frac{n^2-1}{n^2+2}\right)=$	1.05	1.38	1.53
$(\epsilon^{(2)}-\epsilon)/\lvert\epsilon\rvert$ (%)	1.65	3.02	4.59		5.50	9.95	12.64
$v\ (d\epsilon/dv)$	2.069	2.128	2.211		2.225	2.499	2.684
Add. Approx.	2	2	2		2	2	2
$v^2d^2\epsilon/dv^2$	-6.351	-6.668	-7.115		-7.328	-8.929	-10.276
Add. Approx.	-6.	-6	-6		-6	-6	-6

* α taken from refractive indices in gaseous state given in Landolt-Börnstein, and v from Wyckoff Tables.
Values of $(n^2-1)/(n^2+2)$ taken from Mayer's paper (J. E. Mayer, *J. Chem. Phys.* **1 (1933), 270.)

$$v\frac{d\epsilon}{dv}=\frac{8}{\xi^3}\left((1+\xi)^{3/2}-(1-\xi)^{3/2}\right)-\frac{12}{\xi^2}\left((1+\xi)^{\frac{1}{2}}+(1-\xi)^{\frac{1}{2}}\right) \qquad (7.1)$$

$$v^2\frac{d^2\epsilon}{dv^2}=\frac{6}{\xi}\left((1+\xi)^{-\frac{1}{2}}-(1-\xi)^{-\frac{1}{2}}\right) \qquad (7.2)$$

where the quantities are given in terms of $\lvert\epsilon^{(2)}\rvert=(\hbar\omega_0/64)(D^2/\omega_0^4)$ as energy unit. Since the additive approximation is inversely proportional to v^2, it is readily seen that in this unit the values for $v(d\epsilon/dv)$ and $v^2(d^2\epsilon/dv^2)$ are respectively 2 and -6 in the additive approximation.

It is seen that the deviations from the additive approximation in the case of solids can be very considerable, particularly as regards the derivatives of the van der Waals energy. Moreover as we have chosen a very symmetric distribution, the third order moment of which vanishes, the above values for the deviations are more likely to be under rather than over-estimates.

8. Relation to the theory of excitation bands

Finally we may remark that if the model is considered as an idealized model for an insulator, the vibrational modes give directly the structure of the excitation band (band of excitons). Thus a mode s,j in its first excited state describes an exciton with the wave number $(s_1/a, s_2/a, s_3/a)$ and the width of the excitation hand is given directly by the spread of the vibrational frequencies. The band width is a measure of the degree of mobility of the excitons; it is now almost as a rule attributed to the atomic overlaps between

neighbouring atoms. In the above model, the band arises through an entirely different mechanism, namely, the transfer of excitation by dipolar interaction. From the numerical values of D/ω_0^2 given in the table, it is observed that the band width in the above model is in all cases comparable with the optical frequency. Thus it is not a priori justifiable to neglect the long range electric interaction in considering the motion of excitons.