DYNAMICAL THEORY OF CRYSTAL LATTICES

BY

MAX BORN

TAIT PROFESSOR OF NATURAL PHILOSOPHY
UNIVERSITY OF EDINBURGH

AND

KUN HUANG

PROFESSOR OF PHYSICS
UNIVERSITY OF PEKING

Classical Coulomb interaction energy U of 2 neutral molecules

$$m_\alpha = \sum_i e_i x_\alpha^i \quad \text{(dipole moments)},$$

$$q_{\alpha\beta} = \sum_i e_i x_\alpha^i x_\beta^i \quad \text{(quadrupole moments)}.$$

$$U = -\sum_{\alpha\beta} m_\alpha^1 m_\beta^2 \left[\frac{\partial^2}{\partial y_\alpha \partial y_\beta} \frac{1}{|\mathbf{y}|}\right]_{\mathbf{y}=\mathbf{R}} -$$

$$-\tfrac{1}{2}\sum_{\alpha\beta\gamma} (m_\alpha^1 q_{\beta\gamma}^2 - m_\alpha^2 q_{\beta\gamma}^1)\left[\frac{\partial^3}{\partial y_\alpha \partial y_\beta \partial y_\gamma} \frac{1}{|\mathbf{y}|}\right]_{\mathbf{y}=\mathbf{R}} +$$

$$+\tfrac{1}{4}\sum_{\alpha\beta\gamma\lambda} q_{\alpha\beta}^1 q_{\gamma\lambda}^2 \left[\frac{\partial^4}{\partial y_\alpha \partial y_\beta \partial y_\gamma \partial y_\lambda} \frac{1}{|\mathbf{y}|}\right]_{\mathbf{y}=\mathbf{R}} - \ldots.$$

The van der Waals interaction is obtained by carrying the perturbation procedure on to the second order. Let us consider the dipole-dipole interaction. If we designate the electronic states of the unperturbed molecules respectively by i, j, and the excited states by i', j', the second-order energy is given by

$$E^{(2)} = {\sum_{i'}}' {\sum_{j'}}' \frac{\left|\sum_{\alpha\beta} \langle i|m_\alpha^1|i'\rangle\langle j|m_\beta^2|j'\rangle\left[\frac{\partial^2}{\partial y_\alpha \partial y_\beta}\frac{1}{|\mathbf{y}|}\right]_{\mathbf{y}=\mathbf{R}}\right|^2}{E_i + E_j - E_{i'} - E_{j'}}, \quad (1.8)$$

where the primes exclude $i' = i$ and $j' = j$. $E_i, E_j, E_{i'}, E_{j'}$ are eigenvalues of the unperturbed molecules, and $\langle i|m_\alpha^1|i'\rangle$, $\langle j|m_\beta^2|j'\rangle$ the matrix elements of the dipoles between the states i, i' in molecule 1 and between the states j, j' in molecule 2. The energy $E^{(2)}$ depends in general not only on the separation between the molecules, but also on the orientation of the molecules with respect to the vector $\mathbf{R}$ joining them. We shall avoid this complication by averaging the expression over various orientations of the molecules. Remembering that the matrix elements transform as vector components when the molecules are rotated, we

$$\overline{E^{(2)}} = -\frac{2B}{3R^6} \quad (R = |\mathbf{R}|),$$

$$B = -{\sum_{i'}}' {\sum_{j'}}' \frac{\left(\sum_\alpha |\langle i|m_\alpha^1|i'\rangle|^2\right)\left(\sum_\beta |\langle j|m_\beta^2|j'\rangle|^2\right)}{E_i + E_j - E_{i'} - E_{j'}}.$$

we obtain London's approximation for the van der Waals l:

$$V(R) = \frac{C}{R^6}, \qquad C = -\tfrac{2}{3}B = -\frac{3}{2}\left(\frac{\Delta_1\Delta_2}{\Delta_1+\Delta_2}\right)\alpha_1\alpha_2. \quad (1.13)$$

α is the molecular polarizability. Δ is the energy of the strongest dipole-allowed electronic excitation.