MOLECULAR QUADRUPOLE MOMENTS

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Introduction.—Any system of electric charges has associated with it a set of *electric multipole moments* (charge, dipole, quadrupole, octopole . . . 2^n-pole . . .). The potential of the electric field at any point outside the distribution of charges, and arising from it, is simply related to these moments, and so is the energy of interaction of the system with an external field. Multipole moments have proved useful in investigations into the nature of intermolecular forces and have therefore helped in the search for an understanding of the properties of imperfect gases, liquids, and solids. Measurements of the dipole and quadrupole moments of molecules are also very important from the structural point of view. The interpretation of dipole moments is well known (see, for example, the books by Debye,[1] Smyth,[2] Le Fèvre,[3] and Smith,[4] and the chapter by Sutton in Braude and Nachod[5]). Similarly, molecular quadrupole moments can lead to important structural information; thus, just as the absence of a dipole must mean that CO_2 is a linear molecule, so the absence of a quadrupole must mean that CH_4 is tetrahedral; also, just as the knowledge that the dipole moment of H_2O is 1.84×10^{-18} e.s.u. (*i.e.*, 1.84 D) leads to conclusions about the charge distribution in the molecule, so too does the quadrupole moment of CO_2 (-3×10^{-26} e.s.u.) tell us much about the C–O bonds in this molecule.

The Electrostatic Potential of Two Point Charges.—Consider the potential ϕ at an arbitrary point P (represented by the polar co-ordinates R, θ) due to charges e_1 and e_2 at points distant z_1 and z_2 from an origin O (see Fig. 1):
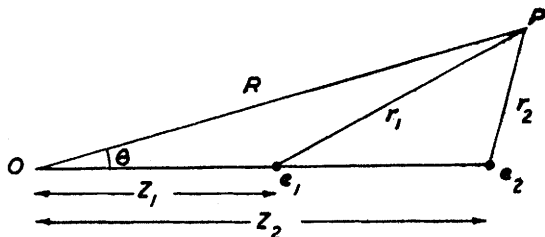

Fig. 1 *The position of the arbitrary point P relative to the origin O and the point charges e_1 and e_2.*

[1] Debye, "Polar Molecules", Chem. Catalog Co., New York, 1929.
[2] Smyth, "Dielectric Behaviour and Structure", McGraw-Hill, New York, 1955.
[3] Le Fèvre, "Dipole Moments", Methuen, London, 1953.
[4] Smith, "Electric Dipole Moments", Butterworths, London, 1955.
[5] Braude and Nachod, "Determination of Organic Structures by Physical Methods", Academic Press Inc., New York, 1955, chap. 9.

$$\phi = \frac{e_1}{r_1} + \frac{e_2}{r_2} = e_1[R^2 - 2Rz_1\cos\theta + z_1{}^2]^{-\frac{1}{2}} + e_2[R^2 - 2Rz_2\cos\theta + z_2{}^2]^{-\frac{1}{2}} \quad\ldots\ldots\quad (1)$$

If R is greater than z_1 and z_2, then the expressions for $r_1{}^{-1}$ and $r_2{}^{-1}$ can be expanded in powers of z_1/R and z_2/R, leading to

$$\phi = \frac{e_1 + e_2}{R} + (e_1z_1 + e_2z_2)\frac{\cos\theta}{R^2} + (e_1z_1{}^2 + e_2z_2{}^2)\frac{3\cos^2\theta - 1}{2R^3} +$$
$$+ (e_1z_1{}^3 + e_2z_2{}^3)\frac{5\cos^3\theta - 3\cos\theta}{2R^4} + \ldots \quad \ldots \ldots \quad (2)$$

$(e_1 + e_2)$ is the zeroth moment (the charge) of the system of two charges, $(e_1z_1 + e_2z_2)$ is its first moment (the dipole moment), $(e_1z_1{}^2 + e_2z_2{}^2)$ its second moment (the quadrupole moment), and $(e_1z_1{}^3 + e_2z_2{}^3)$ its third moment (the octopole moment); all are defined relative to the origin O. ϕ is seen to be equal to the sum of the potentials of a point charge [whose magnitude is $(e_1 + e_2)$] and a point dipole, quadrupole, octopole, ... at O. It should be noted that the charges e_1 and e_2 have a quadrupole and higher moments; thus the name "quadrupole" does not necessarily imply that four or more charges are present.

As is well known, the dipole moment of an uncharged body can be thought of as being formed by separating positive and negative *charges*, the magnitude of the dipole being the product of the charge and the separation. Similarly, the quadrupole moment of a system with zero dipole moment can be thought of as arising from a separation of equal and opposite *dipoles*, the magnitude of the quadrupole being proportional to the product of the dipole moment and the separation. Thus the linear carbon dioxide molecule, which may be supposed to tend towards the structure O–C–O (with charges $\overset{-\ ++\ -}{\text{O–C–O}}$), possesses a quadrupole moment, the two $\overset{+\ -}{\text{C–O}}$ dipoles being opposed to, but separated from, one another.

Unfortunately, several different definitions of the quadrupole and higher moments are in use, so that care is needed in applying formulae in the literature. To clarify the multipole-moment concept, the zeroth, first, and second moments of mass and of charge of a linear array of particles will now be discussed. Let m_i and e_i be the mass and charge of the ith particle distant z_i along the z-axis from the origin O. The zeroth moments are $\sum_i m_i = M$ and $\sum_i e_i = q$ (where $\sum_i$ stands for a summation over all the particles of the array), and are the total mass and total charge of all the particles. The first moments about O are $\sum_i m_iz_i$ and $\sum_i e_iz_i = \mu_z$. If O is the centre of gravity of the system, then $\sum_i m_iz_i$ vanishes. To determine the effect on the moments of a change of origin, consider the dipole moment μ'_z relative to an origin O', where O' is the point $-Z$. Clearly

$$\mu'_z = \sum_i e_i(z_i + Z) = \mu_z + qZ \quad \ldots \ldots \quad (3)$$

so that the dipole moment is independent of the position of the origin only

if q is zero, that is, if the system is electrically neutral. The reason why a centre of mass, but not a centre of charge, can *always* be found is that negative masses do not exist, so that no real system can have $M = 0$: however, eqn. (3) shows that ions will have a centre of charge, but if this
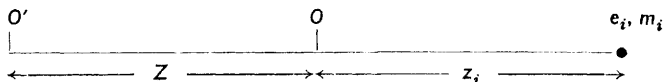

FIG. 2   *The co-ordinate system for the linear array of particles of mass m_i and charge e_i.*

does not correspond to the centre of mass O, then the ion will experience a torque (as well as a force) in a uniform electric field. For convenience, the centre of mass is normally chosen as the origin; thus the hydroxide ion OH^- and the acetate ion $CH_3 \cdot CO_2^-$ will possess dipole moments, although NO_2^+, NH_4^+, and SO_4^{2-} will not.

The second moment of mass of the linear array about O is $\sum_i m_i z_i^2 = I_{zz}$, and is the well-known moment of inertia. Similarly, the second moment of charge about O is $\sum_i e_i z_i^2 = \Theta_{zz}$ and is the quadrupole moment. Only the first non-zero electric multipole moment is independent of the origin, so that Θ_{zz} will be independent of O only if both q and μ_z vanish.

The Interaction of a Charge Distribution with an External Field.— Consider a distribution of charges e_i at points (x_i, y_i, z_i) represented by the vectors $\mathbf{r}_i$ (corresponding to scalars r_i) from the origin O to e_i. Suppose that the distribution is in an external field produced by distant charges. We wish to find the energy of interaction u of the distribution with the external field. If the potential of the *external* field at $\mathbf{r}_i$ is ϕ_i, then

$$u = \sum_i e_i \phi_i \qquad \cdots \cdots \cdots \cdots \quad (4)$$

ϕ_i can be written in terms of the potential and its derivatives at O; thus

$$u = \sum_i e_i \left[\phi_0 + \left\{ \left(\frac{\partial \phi}{\partial x}\right)_0 x_i + \left(\frac{\partial \phi}{\partial y}\right)_0 y_i + \left(\frac{\partial \phi}{\partial z}\right)_0 z_i \right\} + \tfrac{1}{2} \left\{ \left(\frac{\partial^2 \phi}{\partial x^2}\right)_0 x_i^2 + \left(\frac{\partial^2 \phi}{\partial y^2}\right)_0 y_i^2 \right. \right.$$
$$\left. \left. + \left(\frac{\partial^2 \phi}{\partial z^2}\right)_0 z_i^2 + 2\left(\frac{\partial^2 \phi}{\partial x \partial y}\right)_0 x_i y_i + 2\left(\frac{\partial^2 \phi}{\partial y \partial z}\right)_0 y_i z_i + 2\left(\frac{\partial^2 \phi}{\partial z \partial x}\right)_0 z_i x_i \right\} + \ldots \right] (5)$$

The subscript 0 denotes a value at O. Eqn. (5) can be put into a short-hand tensor notation as follows

$$u = \sum_i e_i \left[\phi_0 + \left(\frac{\partial \phi}{\partial r_\alpha}\right)_0 r_{i_\alpha} + \tfrac{1}{2} \left(\frac{\partial^2 \phi}{\partial r_\alpha \partial r_\beta}\right)_0 r_{i_\alpha} r_{i_\beta} \right.$$
$$\left. + \frac{1}{6} \left(\frac{\partial^3 \phi}{\partial r_\alpha \partial r_\beta \partial r_\gamma}\right)_0 r_{i_\alpha} r_{i_\beta} r_{i_\gamma} + \ldots \right] \quad \cdots \quad (6)$$

Greek suffixes denote tensor components (thus r_{i_α} can be x_i, y_i, or z_i) and

repeated suffixes imply a summation over all components (thus $r_{i_\alpha}r_{i_\alpha} = r_i{}^2$ $= x_i{}^2 + y_i{}^2 + z_i{}^2$). On introduction of the parameters

$$
\left.
\begin{aligned}
q &= \sum_i e_i \\
\mu &= \sum_i e_i r_{i_\alpha} \\
Q_{\alpha\beta} &= \sum_i e_i r_{i_\alpha} r_{i_\beta} \\
R_{\alpha\beta\gamma} &= \sum_i e_i r_{i_\alpha} r_{i_\beta} r_{i_\gamma}
\end{aligned}
\right\} \qquad \cdots \cdots \cdots \quad (7)
$$

eqn. (6) becomes

$$
u = q\phi_0 - \mu_\alpha F_\alpha - \tfrac{1}{2} Q_{\alpha\beta} F'_{\alpha\beta} - \tfrac{1}{6} R_{\alpha\beta\gamma} F''_{\alpha\beta\gamma} - \cdots \qquad (8)
$$

where

$$
F_\alpha = - \left(\frac{\partial\phi}{\partial r_\alpha}\right)_0, \ F'_{\alpha\beta} = - \left(\frac{\partial^2\phi}{\partial r_\alpha \partial r_\beta}\right)_0, \ F''_{\alpha\beta\gamma} = - \left(\frac{\partial^3\phi}{\partial r_\alpha \partial r_\beta \partial r_\gamma}\right)_0
$$

Thus F_α is the α-component of the external field at O, $F'_{\alpha\beta}$ the $\alpha\beta$-component of the field gradient at O, etc. Clearly, $F'_{\alpha\beta}$, $F''_{\alpha\beta\gamma}$, ... and $Q_{\alpha\beta}$, $R_{\alpha\beta\gamma}$, ... are symmetric in all suffixes (that is, they are unaffected by interchanging suffixes). Some authors (for example, Condon and Shortley in "The Theory of Atomic Spectra", Cambridge University Press, 1953, p. 85) call $Q_{\alpha\beta}$, $R_{\alpha\beta\gamma}$, ... the quadrupole, octopole, ... moments of the charge distribution, but we shall not do so and our moments describe departures from spherical symmetry ($Q_{\alpha\beta}$ is not zero for a sphere). Eqn. (8) can be simplified by using Laplace's equation $F'_{\alpha\alpha} = F'_{xx} + F'_{yy} + F'_{zz} = 0$, and introducing new tensors:

$$
\left.
\begin{aligned}
\Theta_{\alpha\beta} &= \tfrac{1}{2}(3Q_{\alpha\beta} - Q_{\gamma\gamma}\delta_{\alpha\beta}) = \tfrac{1}{2}\sum_i e_i(3r_{i_\alpha}r_{i_\beta} - r_i{}^2\delta_{\alpha\beta}) \\
\Omega_{\alpha\beta\gamma} &= \tfrac{1}{2}(5R_{\alpha\beta\gamma} - R_{\alpha\delta\delta}\delta_{\beta\gamma} - R_{\beta\delta\delta}\delta_{\gamma\alpha} - R_{\gamma\delta\delta}\delta_{\alpha\beta})
\end{aligned}
\right\} \quad . \ (9)
$$

where $\delta_{\alpha\beta}$ is the substitution tensor ($\delta_{\alpha\beta} = 1$ if $\alpha = \beta$, $\delta_{\alpha\beta} = 0$ if $\alpha \neq \beta$, and $\delta_{\alpha\alpha} = \delta_{xx} + \delta_{yy} + \delta_{zz} = 3$),

$$
u = q\phi_0 - \mu_\alpha F_\alpha - \tfrac{1}{3}\Theta_{\alpha\beta}F'_{\alpha\beta} - \tfrac{1}{15}\Omega_{\alpha\beta\gamma}F''_{\alpha\beta\gamma} - \cdots \qquad . \ (10)
$$

and q is the *charge* of the distribution, μ_α is its *dipole* moment, $\Theta_{\alpha\beta}$ its *quadrupole* moment, and $\Omega_{\alpha\beta\gamma}$ its *octopole* moment. These multipole-moment tensors are symmetric in all suffixes.

As with moments of inertia, it is always possible to find three mutually perpendicular axes such that $\Theta_{\alpha\beta} = 0$ if $\alpha \neq \beta$. There are therefore three principal quadrupole moments Θ_{xx}, Θ_{yy}, Θ_{zz}, but since [from eqn. (9)] $\Theta_{\alpha\alpha} = 0$, only two are independent and need be specified to describe the

interaction of the system with a field gradient. [Eqn. (9) also requires that $\Omega_{\alpha\alpha\beta} = 0$.] From the definitions (7) and (9), it is clear that

$$
\left.
\begin{aligned}
\Theta_{zz} &= \tfrac{1}{2} \sum_i e_i(3z_i{}^2 - r_i{}^2) = \sum_i e_i r_i{}^2 P_2(z_i/r_i) \\
\Theta_{xx} &= \sum_i e_i r_i{}^2 P_2(x_i/r_i), \ \Theta_{yy} = \sum_i e_i r_i{}^2 P_2(y_i/r_i) \\
\Omega_{zzz} &= \tfrac{1}{2} \sum_i e_i(5z_i{}^3 - 3z_i r_i{}^2) = \sum_i e_i r_i{}^3 P_3(z_i/r_i)
\end{aligned}
\right\} \quad . \quad (11)
$$

where P_n is the nth Legendre polynomial. Some authors (for example, Hirschfelder, Curtiss, and Bird[6]) define a quadrupole moment as $2\sum_i e_i r_i{}^2 P_2(z_i/r_i)$, and in nuclear physics the conventional definition is $2e^{-1}\sum_i e_i r_i{}^2 P_2(z_i/r_i)$, where e ($= 4 \cdot 803 \times 10^{-10}$ e.s.u.) is the protonic charge.

For a continuous charge distribution

$$
\Theta_{zz} = \tfrac{1}{2} \int (3z^2 - r^2)\rho \, d\nu = \int r^2 P_2(z/r)\rho \, d\nu \quad . \quad . \quad . \quad (12)
$$

where $\rho \, d\nu$ is the charge in the volume element $d\nu$ at $\mathbf{r}$.

If the charge distribution is symmetric about the z-axis, $\Theta_{xx} = \Theta_{yy} = -\tfrac{1}{2}\Theta_{zz} = -\tfrac{1}{2}\Theta$, and $\Omega_{zxx} = \Omega_{zyy} = -\tfrac{1}{2}\Omega_{zzz} = -\tfrac{1}{2}\Omega$, and eqn. (10) becomes

$$
u = q\phi_0 - \mu F_z - \tfrac{1}{2}\Theta \, F'_{zz} - \tfrac{1}{6}\Omega \, F''_{zzz} - \ldots \quad . \quad (13)
$$

Thus only one dipole, one quadrupole, one octopole, and one multipole of any order[7] are required to specify the interaction of an axially symmetric charge system with an arbitrary electric field.

From eqns. (10) and (13), it can be seen that the energy of a charge system in an electrostatic field is the sum of the energies of a point charge in a potential, a dipole in a uniform field, a quadrupole in a field gradient, and an octopole in the gradient of a field-gradient. In general, there will be a couple acting on a rigid charged body in an electric field, the torque about any point being proportional to the multipole moments about that point as origin.

The Potential produced by a Charge Distribution.—Again consider a distribution of charges e_i at points (x_i, y_i, z_i) represented by the vectors $\mathbf{r}_i$ from an origin O. We wish to find the potential ϕ produced by the charges at an arbitrary point P at (X, Y, Z) denoted by $\mathbf{R}$, where $R > r_i$ for all i. Then

$$
\phi = \sum_i \phi_i = \sum_i e_i R_i{}^{-1} = \sum_i e_i[(X - x_i)^2 + (Y - y_i)^2 +
$$
$$
(Z - z_i)^2]^{-\frac{1}{2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)
$$

[6] Hirschfelder, Curtiss, and Bird, "Molecular Theory of Gases and Liquids", Wiley, New York, 1954, p. 839.
[7] Jansen, *Physica*, 1957, **23**, 599.

where R_i is the distance between the charge e_i and P. We can expand R_i^{-1} in terms of its derivatives with respect to r_{i_α} at O. Thus

$$\phi = \sum_i e_i \left[\frac{1}{R} + \left(\frac{\partial(1/R_i)}{\partial r_{i_\alpha}} \right)_0 r_{i_\alpha} + \frac{1}{2} \left(\frac{\partial^2(1/R_i)}{\partial r_{i_\alpha} \partial r_{i_\beta}} \right)_0 r_{i_\alpha} r_{i_\beta} + \right.$$
$$\left. \frac{1}{6} \left(\frac{\partial^3(1/R_i)}{\partial r_{i_\alpha} \partial r_{i_\beta} \partial r_{i_\gamma}} \right)_0 r_{i_\alpha} r_{i_\beta} r_{i_\gamma} + \dots \right]$$

and since

$$R_i{}^2 = (R_\alpha - r_{i_\alpha})(R_\alpha - r_{i_\alpha})$$

then

$$\left.\begin{aligned}
\left(\frac{\partial(1/R_i)}{\partial r_{i_\alpha}} \right)_0 &= R_\alpha/R^3 \\[4pt]
\left(\frac{\partial^2(1/R_i)}{\partial r_{i_\alpha} \partial r_{i_\beta}} \right)_0 &= (3R_\alpha R_\beta - R^2{}_{\alpha\beta})/R^5 \\[4pt]
\left(\frac{\partial^3(1/R_i)}{\partial r_{i_\alpha} \partial r_{i_\beta} \partial r_{i_\gamma}} \right)_0 &= 3[5R_\alpha R_\beta R_\gamma - R^2(R_{\alpha\delta\beta\gamma} + R_{\beta\delta\gamma\alpha} + R_{\gamma\delta\alpha\beta})] R^7
\end{aligned}\right\} \quad (15)$$

From (7), (9), and (15)

$$\phi = \frac{q}{R} + \frac{\mu_\alpha R_\alpha}{R^3} + \frac{\Theta_{\alpha\beta}}{3R^5}(3R_\alpha R_\beta - R^2 \delta_{\alpha\beta}) +$$
$$\frac{\Omega_{\alpha\beta\gamma}}{5R^7}[5R_\alpha R_\beta R_\gamma - R^2(R_\alpha \delta_{\beta\gamma} + R_\beta \delta_{\gamma\alpha} + R_\gamma \delta_{\alpha\beta})] + \dots \quad (16)$$

For an axially symmetric charge distribution each multipole moment is determined by a single scalar quantity (*viz.*, q, μ, Θ, Ω, ...); for example, $\Theta_{\alpha\beta}$ can be expressed in terms of its principal moments $\Theta_{zz} = \Theta$, $\Theta_{xx} = \Theta_{yy} = -\frac{1}{2}\Theta$, as

$$\Theta_{\alpha\beta} = \frac{1}{2}\Theta [3l_\alpha l_\beta - (l_\alpha l_\beta + m_\alpha m_\beta + n_\alpha n_\beta)] = \frac{1}{2}\Theta [3l_\alpha l_\beta - \delta_{\alpha\beta}]$$

where l_α is a component of the unit vector along the axis of symmetry (the z-axis) and m_α and n_α are unit vectors in the x and y directions. The multipole moment tensors for axially symmetric systems are

$$\left.\begin{aligned}
q &= q \\
\mu_\alpha &= \mu l_\alpha \\
\Theta_{\alpha\beta} &= \frac{1}{2}\Theta (3l_\alpha l_\beta - \delta_{\alpha\beta}) \\
\Omega_{\alpha\beta\gamma} &= \frac{1}{2}\Omega[5l_\alpha l_\beta l_\gamma - l_\alpha \delta_{\beta\gamma} - l_\beta \delta_{\gamma\alpha} - l_\gamma \delta_{\alpha\beta}]
\end{aligned}\right\} \quad \dots \quad (17)$$

so that eqn. (16) becomes

$$\phi = \frac{q}{R} + \frac{\mu \cos \theta}{R^2} + \frac{\Theta}{2R^3}(3 \cos^2 \theta - 1) + \frac{\Omega}{2R^4}(5 \cos^3 \theta -$$
$$3 \cos \theta) + \dots \quad \dots \quad (18)$$

where P is now the point (R, θ) relative to an origin on the axis of the distribution. Eqns. (16) and (18) show that the potential at any point

outside an arbitrary charge distribution is the sum of those due to a charge, a dipole, a quadrupole, an octopole, etc., located at the origin.

Actually, gaseous molecules cannot be completely orientated; if the rotational quantum number of a linear molecule is J, and if the component of its angular momentum in a fixed direction is $Mh/2\pi$, then there is a further component $(J^2 + J - M^2)^{\frac{1}{2}}h/2\pi$ at right-angles to the fixed direction, but its orientation in this plane is uncertain. The potential $\phi_{J,M}$ at the point distant R from the molecule's centre of gravity and at a polar angle σ with the fixed direction is

$$
\phi_{J,M} = \frac{\int\limits_0^{2\pi}\int\limits_0^{\pi} \psi^*_{J,M}\,\phi p\,\psi_{J,M}\sin\xi\,d\xi\,d\eta}{\int\limits_0^{2\pi}\int\limits_0^{\pi} \psi^*_{J,M}\,\psi_{J,M}\sin\xi\,d\xi\,d\eta}
$$

$$
= \frac{q}{R} + \frac{\Theta}{2R^3}\left[\frac{J^2 + J - 3M^2}{(2J-1)(2J+3)}\right](3\cos^2\sigma - 1) + \ldots \quad (19)
$$

where $\cos\theta = \cos\sigma\cos\xi + \sin\sigma\sin\xi\cos\eta$, and $\psi_{J,M} = P^{|M|}_J(\cos\xi)\exp(iM\eta)$ is the rotational wave function. In the states $M = J$ where J is large, the quadrupolar potential of eqn. (19) is approximately minus one-half of the "classical" value given by eqn. (18), with θ replaced by σ; this is because, when it is rapidly rotating, the molecule effectively becomes symmetric about its axis of rotation, and this is at right angles to its own axis of symmetry.

The electric field F at P can be obtained by differentiating eqn. (18). The radial component is F_r and the components at right angles to R are F_s and F_t (see Fig. 3), where
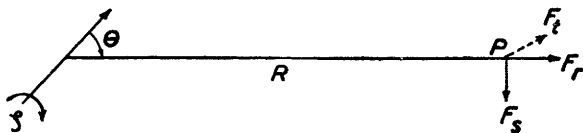

FIG. 3 *The components of the field at a point P due to an axially symmetric charge distribution.*

$$
F_r = -\frac{\partial\phi}{\partial R} = \frac{q}{R^2} + \frac{2\mu\cos\theta}{R^3} + \frac{3\Theta(3\cos^2\theta - 1)}{2R^4}
$$
$$
+ \frac{2\Omega(5\cos^3\theta - 3\cos\theta)}{R^5} + \ldots
$$
$$
F_s = -\frac{1}{R}\frac{\partial\phi}{\partial\theta} = \sin\theta\left[\frac{\mu}{R^3} + \frac{3\Theta\cos\theta}{R^4} + \frac{3\Omega(5\cos^2\theta - 1)}{2R^5} + \ldots\right]
$$
$$
F_t = -\frac{1}{R\sin\theta}\frac{\partial\phi}{\partial\zeta} = 0
$$

$$(20)$$

The fields arising from the various multipoles are illustrated in Fig. 4, where lines of constant F are shown.

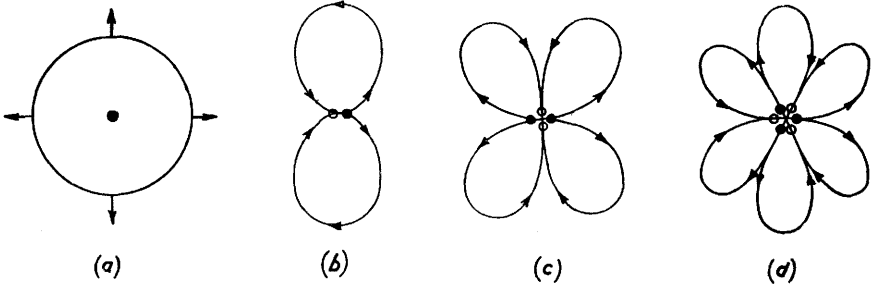(a)   (b)   (c)   (d)

Fig. 4   *Lines of constant electric field strength emanating from*

(a) *a charge, their equation being* $R^{-2} = constant;$
(b) *a dipole,*   ,,   ,,   ,, $(3 \cos^2 \theta + 1)^{\frac{1}{2}}/R^3 = constant;$
(c) *a quadrupole,*   ,,   ,, $(5 \cos^4 \theta - 2 \cos^2 \theta + 1)^{\frac{1}{2}}/R^4 = constant;$
(d) *an octopole,*   ,,   ,, $(175 \cos^6 \theta - 165 \cos^4 \theta + 45 \cos^2 \theta + 9)^{\frac{1}{2}}/R^5$
      $= constant.$

The field gradient $F'_{\alpha\beta}$ at P has the following components

$$
\left.
\begin{aligned}
F'_{rr} &= -\frac{2q}{R^3} - \frac{6\,\mu \cos \theta}{R^4} - \frac{6\,\Theta\,(3 \cos^2 \theta - 1)}{R^5} - \ldots \\[2mm]
F'_{ss} &= \frac{q}{R^3} + \frac{3\,\mu \cos \theta}{R^4} + \frac{3\,\Theta\,(7 \cos^2 \theta - 3)}{2R^5} + \ldots \\[2mm]
F'_{tt} &= \frac{q}{R^3} + \frac{3\,\mu \cos \theta}{R^4} + \frac{3\,\Theta\,(5 \cos^2 \theta - 1)}{2R^5} + \ldots \\[2mm]
F'_{rs} &= -\frac{3\,\mu \sin \theta}{R^4} - \frac{12\,\Theta \sin \theta \cos \theta}{R^5} - \ldots \\[2mm]
F'_{st} &= F'_{tr} = 0
\end{aligned}
\right\}
\qquad (21)
$$

The Interaction Energy of Two Charge Distributions.—Consider two axially symmetric charge distributions 1 and 2 in the relative configuration illustrated in Fig. 5.   The angle ζ is that between the planes formed
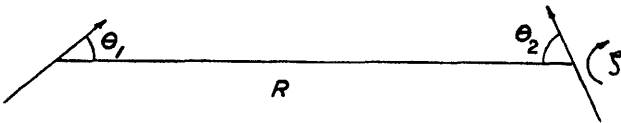

Fig. 5   *A configuration of an interacting pair of axially symmetric charge distributions (the arrows indicate the dipolar directions).*

by the axes of molecules 1 and 2 with the line of centres. If the centres of mass are sufficiently far apart (R must be greater than the sum of the distances of the furthest charges from their origins), the interaction potential energy u_{12} is given by a relation similar to (13), where q, μ, Θ, Ω, ... are the multipole moments of the charge distribution 2, and ϕ, F_s,

F'_{zz}, F''_{zzz}, ... are the potential and its derivatives at the centre of mass of 2 due to the charges of 1; alternatively, the rôles of 1 and 2 could be reversed. Hence

$$u_{12} = q_2 \phi_2 - \mu_2 F_{2_z} - \tfrac{1}{2} \Theta_2 F'_{2_{zz}} - \tfrac{1}{6} \Omega_2 F''_{2_{zzz}} - \dots \qquad . \quad (22)$$

From (18), (20), (21), and (22):

$$u_{12} = \frac{q_1 q_2}{R} + \frac{1}{R^2}[q_1 \mu_2 \cos \theta_2 + q_2 \mu_1 \cos \theta_1] + \frac{1}{2R^3}[q_1 \Theta_2 (3 \cos^2 \theta_2 - 1) +$$

$$q_2 \Theta_1 (3 \cos^2 \theta_1 - 1)] + \frac{\mu_1 \mu_2}{R^3} [2 \cos \theta_1 \cos \theta_2 + \sin \theta_1 \sin \theta_2 \cos \zeta] +$$

$$\frac{1}{2R^4} [q_1 \Omega_2 (5 \cos^3 \theta_2 - 3 \cos \theta_2) + q_2 \Omega_1 (5 \cos^3 \theta_1 - 3 \cos \theta_1)] +$$

$$\frac{3}{2R^4} [\mu_1 \Theta_2 \{\cos \theta_1 (3 \cos^2 \theta_2 - 1) + 2 \sin \theta_1 \sin \theta_2 \cos \theta_2 \cos \zeta \}$$

$$+ \mu_2 \Theta_1 \{\cos \theta_2 (3 \cos^2 \theta_1 - 1) + 2 \sin \theta_1 \sin \theta_2 \cos \theta_1 \cos \zeta \}]$$

$$+ \frac{3 \Theta_1 \Theta_2}{4R^5} [1 - 5 \cos^2 \theta_1 - 5 \cos^2 \theta_2 + 17 \cos^2 \theta_1 \cos^2 \theta_2$$

$$+ 2 \sin^2 \theta_1 \sin^2 \theta_2 \cos^2 \zeta + 16 \sin \theta_1 \sin \theta_2 \cos \theta_1 \cos \theta_2 \cos \zeta] + \dots \quad (23)$$

The favourable relative orientations for charge–dipole, charge–quadrupole, dipole–dipole, dipole–quadrupole, and quadrupole–quadrupole interactions are illustrated in Fig. 6. The structures of molecular crystals are normally determined by the leading multipole moments. The two types of
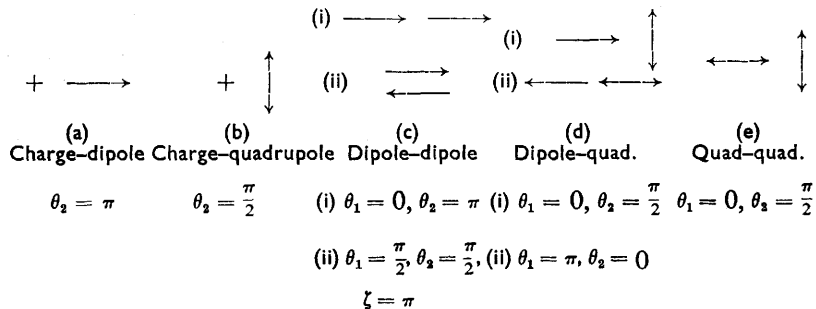

(a)	(b)	(c)	(d)	(e)
Charge–dipole	Charge–quadrupole	Dipole–dipole	Dipole–quad.	Quad.–quad.

$\theta_2 = \pi$ $\theta_2 = \dfrac{\pi}{2}$ (i) $\theta_1 = 0$, $\theta_2 = \pi$ (i) $\theta_1 = 0$, $\theta_2 = \dfrac{\pi}{2}$ $\theta_1 = 0$, $\theta_2 = \dfrac{\pi}{2}$

(ii) $\theta_1 = \dfrac{\pi}{2}$, $\theta_2 = \dfrac{\pi}{2}$, (ii) $\theta_1 = \pi$, $\theta_2 = 0$

$\zeta = \pi$

FIG. 6 *Favourable configurations for various multipolar interactions.*

favourable dipolar interaction are found in (i) ferromagnetic and (ii) antiferromagnetic materials (magnetic dipoles interact similarly to their electric counterparts). There is some evidence[8] that dipole–quadrupole forces are important in the solid hydrogen halides. In molecules where the leading multipole is a quadrupole (*e.g.*, H_2, N_2, CO_2) the structure of the solid may be influenced by quadrupole–quadrupole forces; thus solid CO_2[9] and N_2[10] (in its low-temperature form) have face-centred cubic

[8] Cole and Havriliak, *Discuss. Faraday Soc.*, 1957, **23**, 31.
[9] Keesom and Köhler, *Physica*, 1934, **1**, 167, 655.
[10] Vegard, *Z. Physik,* 1929, **58**, 497.

structures in which the orientations of the molecular axes are such that the quadrupole–quadrupole energy is a minimum—the axes are directed towards the body centres, so that, in CO_2, each oxygen atom approaches three nearest-neighbour carbon atoms (see Fig. 7). The orientations of the molecular axes in solid nitrous oxide[11] and in the α-form of CO[12] (both of which possess small permanent dipole moments) are apparently also determined by quadrupolar forces.
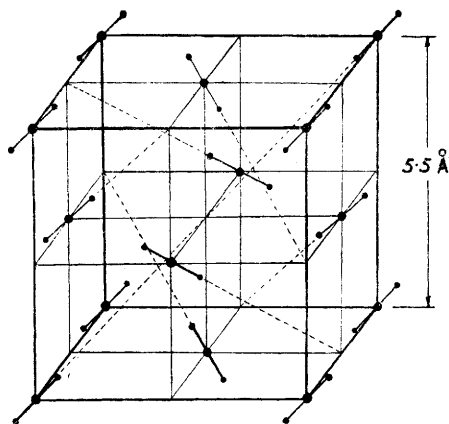

FIG. 7   *The molecular arrangement in solid carbon dioxide.*

The height of the potential barrier opposing free internal rotation in molecules has been attributed[13] to the electrostatic interaction between dipoles and quadrupoles in the bonds. In ethane, the dipole moment of the C–H bond is small (*ca.* 0·4 D) and its quadrupole moment may be the chief cause of the hindered rotation, but owing to the proximity of the interacting C–H bonds, there is some doubt[14,15] about the convergence of the multipole expansion.

The relative orientations of the NH_4^+ ions in the solid ammonium halides is probably determined by the octopole moments of the tetrahedra, but in solids comprised of regular tetrahedral molecules (*e.g.*, CH_4, CCl_4) the packing of nearest neighbours is presumably the most important orientational effect, although the interaction energy of the octopoles will doubtless contribute significantly to the heat of sublimation.

Multipole Moments and Symmetry.—A charge distribution of any shape can be ionic, the magnitude of the net charge being *ne*, where $e = 4·803 \times 10^{-10}$ e.s.u. is the protonic charge and *n* is a positive or negative integer.

[11] Vegard, *Z. Physik*, 1931, **71**, 465.
[12] Jansen, Michels, and Lupton, *Physica*, 1954, **20**, 1235.
[13] Lassettre and Dean, *J. Chem. Phys.*, 1949, **17**, 317.
[14] Oosterhoff, *Discuss. Faraday Soc.*, 1951, **10**, 79.
[15] Wilson, *Proc. Nat. Acad. Sci.*, 1957, **43**, 816.

Molecules with centres of symmetry cannot have permanent dipole or octopole moments (or any multipole of order 2^{2n+1}) but many possess quadrupoles; thus linear molecules (*e.g.*, diatomic ones, CO_2, C_2H_2, etc.) or planar ones (BF_3, C_6H_6) are quadrupolar. Regular tetrahedral molecules like CH_4, $Ni(CO)_4$, etc., have octopoles as their leading multipoles, and octahedral ones like SF_6 possess hexadecapoles (at long-range, the field of a hexadecapole varies as R^{-6}). One can easily determine whether a molecule of known structure has a non-zero multipole of a given order, say a 2^n-pole, by evaluating $\sum_i e_i r_i^n P_n(\cos \theta_i)$ for an ionic model of the molecule; if it is not zero, then the molecule possesses a 2^n-pole. Thus, for the symmetrical planar molecule BF_3, the structure could be written as inset; clearly $\sum_i e_i r_i^n P_n(\cos \theta_i)$ is zero for $n = 0$

and 1, so BF_3 does not have a charge or dipole moment, but $\sum_i e_i(3z_i^2 - r_i^2)/2$ $= 3\delta e l^2/2$ where the z-axis is at right-angles to the paper and l is the B–F bond-length. Since δe is of the order of 10^{-10} e.s.u. and $l \sim 10^{-8}$ cm., molecular quadrupole moments will normally be of the order of 10^{-26} e.s.u. Molecular octopole moments are *ca.* 10^{-34} e.s.u.; thus CH_4 has a single octopole moment component Ω_{xyz}, calculated[16] to be $-1 \cdot 1 \times 10^{-34}$ e.s.u., where the x-, y-, and z-axes are the sides of a cube at whose centre is the carbon atom and at four of whose corners are hydrogen atoms.
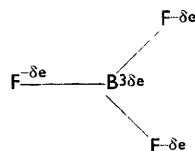
Induced Multipole Moments and Energies of Induction.—It is well known that a uniform field F induces a dipole moment of magnitude αF, where α is the polarizability of the molecule. The induced moment will not in general be parallel to **F**, for anisotropic molecules are more easily polarizable in some directions than in others—α is actually a second-order tensor $\alpha_{\alpha\beta}$. In strong fields the induced dipole moment proportional to F^2 and F^3 can be important.[17,18] The field F can also induce higher-order moments; thus polar molecules will have induced quadrupoles proportional to F, while spherical molecules can only have quadrupoles proportional to F^2 and higher even orders of F.

If it is supposed that the energy u of an uncharged molecule in an external electrostatic field can be written as a power series in $F_\alpha, F'_{\alpha\beta}, \ldots$, where F_α is the α-component of the field at the centre of mass of the molecule and $F'_{\alpha\beta}$ is the field gradient,

$$u = u^{(0)} - \mu_\alpha F_\alpha - \tfrac{1}{2}\alpha_{\alpha\beta}F_\alpha F_\beta - \tfrac{1}{6}\beta_{\alpha\beta\gamma}F_\alpha F_\beta F_\gamma - \tfrac{1}{24}\gamma_{\alpha\beta\gamma\delta}F_\alpha F_\beta F_\gamma F_\delta -$$

$$\tfrac{1}{3}\Theta_{\alpha\beta}F'_{\alpha\beta} - \tfrac{1}{3}A_{\alpha:\beta\gamma} F_\alpha F'_{\beta\gamma} - \tfrac{1}{6}B_{\alpha\beta:\gamma\delta}F_\alpha F_\beta F'_{\gamma\delta} - \tfrac{1}{6}C_{\alpha\beta:\gamma\delta}F'_{\alpha\beta}F'_{\gamma\delta} - \ldots (24)$$

[16] Buckingham and Stephen, *Trans. Faraday Soc.*, 1957, **53**, 884.
[17] Coulson, Maccoll, and Sutton, *Trans. Faraday Soc.*, 1952, **48**, 106.
[18] Buckingham and Pople, *Proc. Phys. Soc.*, 1955, *A*, **68**, 905.

where $u^{(0)}$ is the energy of the molecule in the absence of the field, then it is clear from eqn. (10) that μ_α is the permanent dipole moment and $\Theta_{\alpha\beta}$ the permanent quadrupole moment of the molecule; the nature of the other coefficients can be understood by differentiating u with respect to F_α and to $F'_{\alpha\beta}$. Now where m_α is the α-component of the total dipole moment and $T_{\alpha\beta}$ the $\alpha\beta$-component of the total quadrupole moment of the molecule

$$-\frac{\partial u}{\partial F_\alpha} = m_\alpha, \quad -3\frac{\partial u}{\partial F'_{\alpha\beta}} = T_{\alpha\beta}$$

($\partial/\partial F_\alpha$ means a differentiation with respect to F_α, keeping $F'_{\alpha\beta}$ and higher derivatives of F constant)[†] whence from eqn. (24)

$$m_\alpha = \mu_\alpha + \alpha_{\alpha\beta}F_\beta + \tfrac{1}{2}\beta_{\alpha\beta\gamma}F_\beta F_\gamma + \tfrac{1}{6}\gamma_{\alpha\beta\gamma\delta}F_\beta F_\gamma F_\delta + \tfrac{1}{3}A_{\alpha\,\beta\gamma}F'_{\beta\gamma} + \tfrac{1}{3}B_{\alpha\beta:\gamma\delta}F_\beta F'_{\gamma\delta} + \ldots \quad . \quad (25)$$

$$T_{\alpha\beta} = \Theta_{\alpha\beta} + A_{\gamma:\alpha\beta}F_\gamma + \tfrac{1}{2}B_{\gamma\delta:\alpha\beta}F_\gamma F_\delta + C_{\alpha\beta:\gamma\delta}F'_{\gamma\delta} + \ldots \quad . \quad (26)$$

From eqn. (25), $\alpha_{\alpha\beta}$ can be seen to be the usual polarizability tensor; $\beta_{\alpha\beta\gamma}$ and $\gamma_{\alpha\beta\gamma\delta}$ are "hyperpolarizabilities" describing departures from a linear law (they play a part in the Kerr effect[18]). The tensors $A_{\alpha:\beta\gamma}$ and $B_{\alpha\beta:\gamma\delta}$ describe the quadrupole moment induced in a molecule by a uniform electric field (alternatively, $\tfrac{1}{3}A_{\alpha:\beta\gamma}F'_{\beta\gamma}$ is the dipole moment induced by a field gradient). $C_{\alpha\beta:\gamma\delta}$ is the "field gradient quadrupole polarizability" discussed by Mayer and Mayer,[19] Sternheimer,[20] and Dalgarno and Lewis.[21] Mayer and Mayer extended Born and Heisenberg's[22] idea and showed that the "spectral defects" of the alkali-metal atoms (that is, the splitting of the energies of the states with different values of the orbital quantum number l) were partly dependent on $C_{\alpha\beta:\gamma\delta}$. The tensors $\Theta_{\alpha\beta}$, $\alpha_{\alpha\beta}$, $\beta_{\alpha\beta\gamma}$, and $\gamma_{\alpha\beta\gamma\delta}$ are totally symmetric, as can be seen from eqn. (24); $A_{\alpha:\beta\gamma}$ is symmetric in β and γ, and $B_{\alpha\beta:\gamma\delta}$ and $C_{\alpha\beta:\gamma\delta}$ in α,β and γ,δ; $C_{\alpha\beta:\gamma\delta}$ is also unaffected by interchanging the pairs $\alpha\beta$ and $\gamma\delta$.

For molecules with elements of symmetry, relations between the tensor components exist.[18,23] For molecules with centres of inversion, μ_α,

[†] This can be proved as follows: The Hamiltonian of a molecule in the field is $H = H_0 - m_\alpha F_\alpha - \tfrac{1}{3}T_{\alpha\beta}F'_{\alpha\beta}$, where m_α and $T_{\alpha\beta}$ are the molecular dipole and quadrupole moments for a particular configuration of the nuclei and electrons. Thus if ψ is a normalized eigenfunction, the eigenvalue is $u = (\psi^*|H|\psi)$, whence

$$\frac{\partial u}{\partial F_\alpha} = -(\psi^*|m_\alpha|\psi) + \left(\frac{\partial \psi^*}{\partial F_\alpha}|H|\psi\right) + \left(\psi^*|H|\frac{\partial \psi}{\partial F_\alpha}\right) = -(\psi^*|m_\alpha|\psi),$$

$$\frac{\partial u}{\partial F'_{\alpha\beta}} = -\tfrac{1}{3}(\psi^*|T_{\alpha\beta}|\psi) + \left(\frac{\partial \psi^*}{\partial F'_{\alpha\beta}}|H|\psi\right) + \left(\psi^*|H|\frac{\partial \psi}{\partial F'_{\alpha\beta}}\right) = -\tfrac{1}{3}(\psi^*|T_{\alpha\beta}|\psi);$$

the matrix elements involving first derivatives of ψ and ψ^* with respect to F_α and $F'_{\alpha\beta}$ must vanish, for the derivatives are orthogonal to ψ and to ψ^*.

[19] Mayer and Mayer, *Phys. Rev.*, 1933, **43**, 605.
[20] Sternheimer, *Phys. Rev.*, 1957, **107**, 1565.
[21] Dalgarno and Lewis, *Proc. Roy. Soc.*, 1957, A, **240**, 284.
[22] Born and Heisenberg, *Z. Physik*, 1924, **23**, 388.
[23] Buckingham, *J. Chem. Phys.*, 1959, **30**, 1580.

$\beta_{\alpha\beta\gamma}$, and $A_{\alpha;\beta\gamma}$ must vanish (for u must be unchanged on inverting the molecule), and for spherical molecules in a uniform field

$$\left.\begin{array}{l} m = \alpha F + \tfrac{1}{6}\gamma F^3 + \cdots \\ T = \tfrac{1}{2}BF^2 + \cdots \end{array}\right\} \quad \cdots \quad (27)$$

α is easily measured through dielectric-constant or refractive-index measurements, and the Kerr constant (being a measure of the difference between the polarizabilities of the sphere in the direction of and at right-angles to the field F) is proportional to γ. The quadrupole polarizability B of the ground state of the hydrogen atom has been exactly calculated[24] to be 213/2 atomic units (or -0.487×10^{-38} e.s.u.). The constant B may become measurable through an experiment in which the strong uniform field of the Kerr effect is replaced by a field gradient[23] (see p. 198).

The energy of a hydrogen atom in its ground state interacting with a proton has been evaluated for large R as a power series in $1/R$ by Coulson[25] and is

$$u = -\frac{e^2}{a_0}\left[\frac{1}{2} + \frac{9}{4}\left(\frac{a_0}{R}\right)^4 + \frac{15}{2}\left(\frac{a_0}{R}\right)^6 + \frac{213}{4}\left(\frac{a_0}{R}\right)^7 + \frac{7755}{64}\left(\frac{a_0}{R}\right)^8 + \cdots\right] \quad (28)$$

where a_0 is the Bohr radius (0·5292 Å). It is interesting to compare this expansion with (24). The field F at the hydrogen atom is e/R^2, and the field gradient $F'_{zz} = -2e/R^3$, $F'_{xx} = F'_{yy} = e/R^3$, $F'_{\alpha\beta} = 0$ if $\alpha \neq \beta$. Thus the term in eqn. (28) in R^{-4} is $-\tfrac{1}{2}\alpha F^2 = -\tfrac{1}{2}\alpha e^2/R^4$, whence $\alpha = 9a_0^3/2$. Also, the term in R^{-6} in (28) is $-\tfrac{1}{6}C_{\alpha\beta:\gamma\delta} F'_{\alpha\beta}F'_{\gamma\delta} = -\tfrac{1}{4}C(F'_{zz})^2 = -Ce^2/R^6$, whence $C = 15a_0^5/2$, where $C = C_{zz:zz} - C_{zz:xx} = 2C_{zx:zx}$ (see ref. 23). Similarly, the term in R^{-7} in eqn. (28) is the interaction energy of the quadrupole induced in the hydrogen atom by F, with the field gradient, thus $-\frac{213}{4}e^2 a_0^6 R^{-7} = -\tfrac{1}{4}BF^2 F'_{zz} = \tfrac{1}{2}Be^3/R^7$, so that $B = -213a_0^6/2e$. This term-by-term interpretation of (28) is in fact well based quantum-mechanically.[24]

Little is as yet known of the tensors $\beta_{\alpha\beta\gamma}$ and $A_{\alpha;\beta\gamma}$; the former probably plays a part in the density-dependence of the Lorentz–Lorenz function of a polar substance[26] and possibly in the depolarization of the light scattered by a dense polar fluid,[16] as well as in intermolecular forces.

The energy of induction of a molecule has been equated to $-\tfrac{1}{2}\alpha_{\alpha\beta}F_\alpha F_\beta$ (see, for example, Margenau[27] and p. 984 of ref. 6), but by comparing this expression with (24) it is clear that it is only a part of the *dipole* induction energy—hyperpolarizabilities and induced quadrupoles, octopoles, etc., have been neglected. In the absence of detailed knowledge about the magnitudes of β, γ, A, B, and C, it is not easy to determine how good an

[24] Buckingham, Coulson, and Lewis, *Proc. Phys. Soc.*, 1956, *A*, **69**, 639.
[25] Coulson, *Proc. Roy. Soc. Edinburgh*, 1941, *A*, **61**, 20.
[26] Buckingham, *Trans. Faraday Soc.*, 1956, **52**, 747.
[27] Margenau, *Rev. Mod. Phys.*, 1939, **11**, 1.

approximation $- \frac{1}{2}\alpha_{\alpha\beta}F_\alpha F_\beta$ is in a particular case. However, for guidance, it could reasonably be estimated that for H_2O

$\mu = 1\cdot84 \times 10^{-18}$ e.s.u. $\qquad\qquad \beta = 1 \times 10^{-30}$ e.s.u.

$\alpha = 1\cdot5 \times 10^{-24}$ e.s.u. (cm.³) $\qquad \gamma = 1 \times 10^{-36}$ e.s.u.

(the value for γ is indicated by the fact that for CH_4 $\alpha = 2\cdot6 \times 10^{-24}$ and $\gamma = 2\cdot6 \times 10^{-36}$;[18] the β is the component of $\beta_{\alpha\beta\gamma}$ along the dipolar axis). Thus, for a water molecule whose centre is 2 Å from an Al^{3+} ion and where the dipole μ is directed away from the ion, the dipole energy is $- \mu F = -6\cdot6 \times 10^{-12}$ erg (10^{-12} erg per molecule is equivalent to 14 kcal. mole^{-1}), while $- \frac{1}{2}\alpha F^2 = - 9\cdot7 \times 10^{-12}$, $- \frac{1}{6}\beta F^3 = - 8 \times 10^{-12}$, and $- \frac{1}{24}\gamma F^4 = - 7 \times 10^{-12}$ erg. Thus it is probable that the hyperpolarizabilities β and γ contribute significantly to heats of hydration of aluminium salts (possibly the terms in A, B, C, etc., are also important). Little is known about β, and it may be negative, in which case the induction energies $- \frac{1}{6}\beta F^3$ and $- \frac{1}{24}\gamma F^4$ would tend to cancel. It is clear that much more work is needed before we can understand energies of induction when large fields, or large field gradients, are involved.

Multipole moments can be induced in interacting groups of spherical molecules by the intermolecular perturbations. Thus a pair of atoms in S-states will have an induced quadrupole moment proportional to R^{-6} when R is large, R being the distance between the nuclei; its magnitude is approximately $\Theta = \dfrac{25e\alpha C}{4R^6}$. Each of the atoms will possess a dipole pro-

portional to R^{-7}, but unless they are dissimilar, these will cancel. In the hexagonal arrangement of close-packed spheres (e.g., solid helium), each of the spheres becomes quadrupolar, and the crystal as a whole anisotropic; the magnitude of the induced quadrupoles could possibly be measured by the method discussed on p. 212 in connection with macroscopic quadrupoles.

Methods of Measuring Quadrupole Moments.—Since nuclear dimensions are ca. 10^{-5} of atomic ones, nuclear quadrupole moments are ca. 10^{-36} e.s.u. (for the deuteron, $\Theta_n = 0\cdot66 \times 10^{-36}$ e.s.u.). Nuclei with spin quantum numbers $I \geqslant 1$ possess quadrupole moments, and these give rise to hyperfine structure in the atomic spectrum. Observations of this hyperfine structure[28] or of nuclear resonance spectra[29] lead to information about the magnitude of nuclear quadrupole moments. The field gradient F'_{zz} at the centre of a hydrogen atom in the $2p_z$ state is $1\cdot08 \times 10^{14}$ e.s.u.; thus the nuclear quadrupole contribution to the difference between the energies of the hyperfine states of the $2p_z$ deuterium atom in which the z-components of the nuclear spin are 0 and 1 is ca. 10^4 cycles sec.$^{-1}$. For atoms with complete inner electron shells, it is not possible to determine the nuclear quadrupole moment with precision, for the field of the

[28] Townes and Schawlow, "Microwave Spectroscopy", McGraw-Hill, New York, 1955, p. 130.

[29] Ramsey, "Molecular Beams", Clarendon Press, Oxford, 1956, p. 213.

quadrupolar nucleus induces a substantial, but uncertain, moment in the neighbouring electrons.[30]   Important information about the electronic structure of molecules can be obtained through measurements of nuclear quadrupole resonances; the eigenstates are those corresponding to the various permissible orientations of the nuclear spin relative to the molecular axes.

Although molecular quadrupole moments are normally *ca.* 10^{10} times nuclear moments, they are not easy to measure directly owing to our inability to produce sufficiently large macroscopic field gradients (the biggest values of F'_{zz} obtainable are *ca.* 1000 e.s.u.). Interaction energies of about 10^{-23} erg can be obtained, while for dipoles ($\mu \sim 10^{-18}$ e.s.u.) in fields of 10 e.s.u. (3000 volts cm.$^{-1}$) the energy is *ca.* 10^{-17} erg. At a point a few Ångström units from an ion or polar molecule, the field gradient is *ca.* 10^{14} e.s.u. (its value 2 Å from a univalent ion) whereas the field is *ca.* 10^6 e.s.u.   Thus molecular quadrupoles will contribute significantly to intermolecular forces, and most of the molecular quadrupoles so far "measured" have been determined indirectly by studying the interactions of molecules; however, the values deduced are uncertain, for they depend upon doubtful assumptions concerning the nature of the intermolecular force-field.   The principal methods of this type, as well as others, are discussed below.

(i) *Direct calculation from known wave functions.*   A few molecular quadrupole moments have been computed from accurate wave functions. However, as Θ is sensitive to the outer reaches of the electron cloud this approach is reliable only in a few cases, but conversely if Θ were known, then it would provide a severe test of the accuracy of a trial wave function, and would thus lead to structural information of importance.

For a linear molecule

$$\Theta = \sum_n e_n z_n^2 - \frac{e}{2} \int \psi^*(3z^2 - r^2)\, \psi \, \mathrm{d}v \qquad \cdots \quad (29)$$

where $\sum_n$ is a summation over the nuclear charges e_n and $-e\psi^*\psi$ is the electronic charge density; the origin is at the centre of gravity of the molecule.

ψ is accurately known for one-electron atoms, so that eqn. (29) can be used to compute exact values of Θ for excited hydrogen-like atoms.   If the atom's nuclear charge is Ze

$$\Theta_{n,l,m} = - \frac{n^2\,[5n^2 + 1 - 3l\,(l+1)]\,[l(l+1) - 3m^2]ea_0^2}{2Z^2\,(2l-1)\,(2l+3)} \qquad \cdots \quad (30)$$

where n, l, m are the usual quantum numbers. For np_z states

$$\Theta_{n,1,0} = - \frac{n^2\,(n^2-1)\,ea_0^2}{Z^2} = -2\,\Theta_{n,1,\pm1} \qquad \cdots \quad (31)$$

[30] Sternheimer, *Phys. Rev.*, 1957, **105**, 158.

Hence the well-known dumb-bell shape of a p_z orbital causes the mean value of $(z^2 - x^2)$ to be positive, and Θ to be negative. For the $2p_z$ state of hydrogen, $\Theta = -16 \cdot 14 \times 10^{-26}$ e.s.u. Eqn. (30) shows that one-electron atoms with $l = 3$ and $m = 2$ have zero quadrupole moment.

Exact electronic wave functions are known[31] for one-electron molecules such as $H_2{}^+$. With the mass centre as origin, $\Theta_{H_2{}^+} = 2 \cdot 1 \times 10^{-26}$ e.s.u.,[31] while the best approximate LCAO wave function so far obtained leads to $\Theta_{H_2{}^+} = 1 \cdot 7 \times 10^{-26}$ e.s.u.[31]

A reliable wave function is known for the ground state of H_2, and for this[32] $\Theta = 0 \cdot 60 \times 10^{-26}$ e.s.u. Less precise calculations, one based on a self-consistent field wave function[33] leading to $\Theta = 0 \cdot 78 \times 10^{-26}$ e.s.u., and another on a Wang-type function giving $\Theta = 0 \cdot 34 \times 10^{-26}$, have also been performed.[34]

Elaborate self-consistent LCAO wave functions have been determined for N_2 and CO_2, and these lead to $\Theta_{N_2} = -2 \cdot 5 \times 10^{-26}$,[35] and to $\Theta_{CO_2} = -8 \cdot 6 \times 10^{-26}$ e.s.u.[36] These numbers are probably not accurate, Θ being even more difficult to compute than μ. The calculated quadrupoles of H_2O, NH_3, and HF[37] should also be considered to be only very approximate.

(ii) *A direct method involving induced optical anisotropy.* In the well-known Kerr effect, a gas or liquid becomes doubly refracting in the presence of a strong field F. F acts on the molecular dipoles and anisotropic polarizabilities, partially orienting them and thereby leading to an induced difference $(n_x - n_y)$ between the refractive indices in the directions parallel and perpendicular to F. Fig. 8 shows a cross-section of a Kerr cell; clearly a reversal of F causes no change in $(n_x - n_y)$, so that $(n_x - n_y)$ must be of the second order in F; it has been shown[18] that, hyperpolarizabilities being neglected:

$$n_x - n_y = \frac{2\pi N F^2}{15kT} \left(\alpha_{zz} - \alpha_{xx} \right) \left[\alpha_{zz} - \alpha_{xx} + \frac{\mu^2}{kT} \right] \quad . \quad (32)$$

where N is the number of molecules in unit volume and $(\alpha_{zz} - \alpha_{xx})$ is the difference between the polarizabilities along and at right angles to the axis of a molecule.

If the uniform field of the Kerr cell is replaced by the field gradient $F'_{xx} = -F'_{yy}$ of a four-wire condenser whose cross-section is shown in Fig. 8, then an anisotropy is induced such that[23]

$$n_x - n_y = \frac{4\pi N F'_{xx}}{15} \left[\beta_{\alpha\beta:\alpha\beta} + \frac{\Theta}{kT} \left(\alpha_{zz} - \alpha_{xx} \right) \right] \quad . \quad . \quad (33)$$

[31] Bates and Poots, *Proc. Phys. Soc.*, 1953, *A*, **66**, 784.
[32] James and Coolidge, *Astrophys. J.*, 1938, **87**, 438.
[33] Coulson, *Proc. Camb. Phil. Soc.*, 1938, **34**, 204.
[34] Massey and R. A. Buckingham, *Proc. Roy. Irish Acad.*, 1938, *A*, **45**, 31.
[5] Scherr, *J. Chem. Phys.*, 1955, **23**, 569.
[36] Hamilton, *J. Chem. Phys.*, 1956, **25**, 1283.
[37] Duncan and Pople, *Trans. Faraday Soc.*, 1953, **49**, 217.

so that $(n_x - n_y)$ is of the first-order in the applied field gradient; this can be seen by noting that if the voltages applied to the wires are reversed, $(n_x - n_y)$ must change sign and must therefore be an *odd* function of F'_{xx}.

Both μF and $\Theta F'_{xx}$ are necessarily small compared with kT for eqns. (32) and (33) to be valid, so that although $\Theta F'_{xx} \ll \mu F$ for reasonable values of F and F_{xx} (see p. 197), $\Theta F'_{xx}/kT$ and $(\mu F/kT)^2$ are more nearly comparable. For non-polar anisotropic molecules (*e.g.*, CO_2, C_2H_2, C_6H_6), eqns. (32) and (33) lead, when $B_{\alpha\beta:\alpha\beta}$ is negligible, to

$$\frac{(n_x - n_y)_{F'xx}}{(n_x - n_y)_F} = \frac{2\Theta F'_{xx}}{(\alpha_{zz} - \alpha_{xx})F^2} \quad \cdots \quad (34)$$

and this ratio can be about 0·02 under realistic conditions.[23] Thus there is an excellent chance that this direct method of measuring Θ will lead to accurate quantitative results; both the sign and the magnitude of Θ are obtainable through eqn. (33). Unfortunately, the experiments have not yet been performed, although the relevant equipment is now being assembled in Oxford.
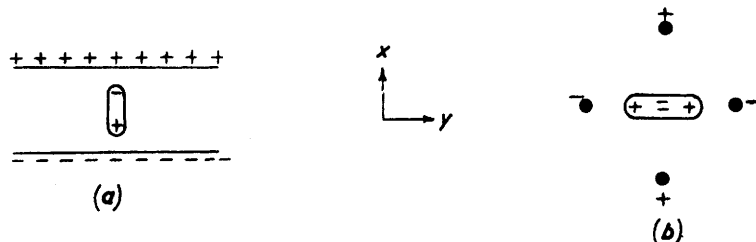

FIG. 8   *Cross-sections of (a) a Kerr cell producing a uniform field F and (b) the four-wire condenser yielding a field gradient $F'_{xx} = - F'_{yy}$ at its centre. $(n_x - n_y)$ is measured by determining the ellipticity induced in a beam of linearly polarized light travelling in the z-direction and with the electric vector at 45° to the x-axis.*

(iii) *Magnetic-susceptibility measurements.* The most accurate measurement of Θ is that on H_2 by Harrick and Ramsey.[38] They utilized the fact that the diamagnetic anisotropy of an axially symmetric molecule is [39]

$$\chi_{zz} - \chi_{xx} = \frac{e^2}{4mc^2} \sum_i (z_i^2 - x_i^2) - \chi_{HF} \quad \cdots \quad (35)$$

where χ_{zz} and χ_{xx} are the molecular susceptibilities parallel and perpendicular to the axis, and the summation is over all the electrons (of mass m); χ_{HF}, the "high-frequency" contribution to χ_{xx}, is only a small part of χ_{xx} in most molecules (in H_2, it is $- 3·7\%$ of χ_{xx}, and $\chi_{xx} = - 6·9 \times 10^{-30}$ erg gauss^{-2}). There is no high-frequency contribution to χ_{zz} (as for atoms). Wick[40] and Ramsey[41] showed that χ_{HF} is related to the rotational magnetic

[38] Harrick and Ramsey, *Phys. Rev.*, 1952, **88**, 228.
[39] Van Vleck, "Theory of Electric and Magnetic Susceptibilities", Oxford Univ. Press, 1932, p. 275.
[40] Wick, *Z. Physik*, 1933, **85**, 25.
[41] Ramsey, *Phys. Rev.*, 1940, **58**, 226; 1952, **87**, 1075.

moment, and this has been measured (it is of the order of a nuclear magneton) for certain states of H_2 and D_2 by observing the radio-frequency spectrum of a molecular beam in a strong magnetic field. χ_{HF} can sometimes be obtained in other ways,[42] and if it is known (or negligible) measurement of $\chi_{zz} - \chi_{xx}$ leads to Θ. Thus

$$\Theta = e \left[\sum_n Z_n \left(z_n{}^2 - x_n{}^2 \right) - \frac{4mc^2}{e^2} \left(\chi_{zz} - \chi_{xx} + \chi_{HF} \right) \right] . \quad (36)$$

where $Z_n e$ is the charge on the nth nucleus at the point (x_n, y_n, z_n). Harrick and Ramsey's[38] observations lead to $\Theta_{H_2} = 0.63 \pm 0.05 \times 10^{-26}$ e.s.u. for the ground state of orthohydrogen, and to $\Theta_{D_2} = 0.63 \pm 0.07 \times 10^{-26}$. Diamagnetic anisotropies are known for a number of molecules,[43] but the difficulties involved in measuring χ_{HF} limit the usefulness of this method of determining Θ.

Anisotropy in the molecular electronic polarizability $\alpha_{\alpha\beta}$ can lead to Θ after some doubtful approximations have been made. Thus

$$\left. \begin{aligned} \alpha_{zz} &= 2e^2 \sum_{ij} {\sum_m}' \frac{(0|z_i|m) (0|z_j|m)}{h\nu_m} \\ \alpha_{xx} &= 2e^2 \sum_{i,j} {\sum_m}' \frac{(0|x_i|m) (0|x_j|m)}{h\nu_m} \end{aligned} \right\} \quad \cdots \quad (37)$$

where $-e(0|z_i|m)$ is the dipole matrix element for the ith electron involving the ground and mth excited states, and $h\nu_m$ is the energy difference between these states; $\sum_m'$ is a summation over all excited states (it excludes the ground state). If $h\nu_m$ is approximated by a constant U (actually the best U for α_{zz} need not be the best for α_{xx}), then

$$\left. \begin{aligned} \alpha_{zz} &= \frac{2e^2}{U} \sum_{i,j} \left[(0|z_i z_j|0) - (0|z_i|0)(0|z_j|0) \right] \\ \alpha_{xx} &= \frac{2e^2}{U} \sum_{i,j} (0|x_i x_j|0) \end{aligned} \right\} \quad \cdots \quad (38)$$

For non-polar molecules $\sum_i (0|z_i|0) = 0$, and for the independent-electron (molecular-orbital) model $\sum_{i,j} (0|z_i z_j|0) = \sum_i (0|z_i{}^2|0)$, and this is presumably an upper limit, since electron correlation will make $\sum_{i,j\neq i} (0|z_i z_j|0)$ negative. With these simplifications, eqn. (38) leads to

$$\alpha_{zz} - \alpha_{xx} = \frac{2e^2}{U} \sum_i (0|z_i{}^2 - x_i{}^2|0) \quad \cdots \cdots \quad (39)$$

Now

$$\chi = \tfrac{1}{3} \left(\chi_{zz} + 2\chi_{xx} \right) = - \frac{e^2}{6mc^2} \sum_i (0|r_i{}^2|0) \tfrac{2}{3}\chi_{HF} \quad (40)$$

[42] Weltner, *J. Chem. Phys.*, 1958, **28**, 477.
[43] Landolt–Börnstein, " Zahlenwerte und Functionen", 1 Band, 3 Teil, Springer, 1951, p. 536.

and if χ_{HF} is negligible relative to $\frac{3}{2}\chi$ (but not necessarily compared with $\chi_{zz} - \chi_{xx}$), then $U = -4mc^2\chi/\alpha$, and

$$\alpha_{zz} - \alpha_{xx} = -\frac{e^2\alpha}{2mc^2\chi} \sum_i (0|z_i^2 - x_i^2|0) \quad . \quad . \quad . \quad (41)$$

whence

$$\Theta = \sum_n Z_n e(z_n^2 - x_n^2) + \frac{6mc^2\kappa\chi}{e} \quad . \quad . \quad . \quad . \quad (42)$$

where the anisotropy $\kappa = (\alpha_{zz} - \alpha_{xx})/3\alpha$; κ is known in many instances from light-scattering or Kerr-constant data (see ref. 43, p. 509); for H_2, $\kappa = 0.117$ [44] and $\chi = -6.6 \times 10^{-30}$ erg gauss^{-2}, [45] so that eqn. (42) leads to $\Theta = 0.64 \times 10^{-26}$ e.s.u., in agreement with the above experimental value.

Two approximations were made in deriving eqn. (42). The first involves the use of a constant excitation energy $U = h\nu_m$, in eqn. (37), but this is probably not serious, for compensation occurs as the same U is used for α in eqn. (41). The second consists in putting $\sum_{i,j}(0|z_i z_j|0) = \sum_i(0|z_i^2|0)$ and $\sum_{i,j}(0|x_i x_j|0) = \sum_i(0|x_i^2|0)$, and therefore neglects electron correlation. If $\sum_{i,j\neq i}(0|z_i z_j - x_i x_j|0) = -g \sum_i (0|z_i^2 - x_i^2|0)$, then g is a number between 0 and 1 describing the extent of electron correlation, and eqn. (42) becomes

$$\Theta = \sum_n Z_n e(z_n^2 - x_n^2) + \frac{6mc^2\kappa\chi}{e(1-g)} \quad . \quad . \quad . \quad (44)$$

If Θ were known, g could be determined and knowledge thereby obtained about the extent of electron correlation. For "inner" electrons, g must be *ca.* 1, for these will nearly balance their equivalent nuclear charges, leading to a zero "inner-shell" quadrupole moment. g computed through eqn. (44) would be an average for all electrons. For CO_2, using $\Theta = -3 \times 10^{-26}$ e.s.u., $\kappa = 0.24$, $\chi = -34.5 \times 10^{-30}$ erg gauss^{-2}, and omitting the K-shell electrons [that is, $Z_n = 6$ for each oxygen atom for which $z_n = \pm 1.163$ Å, $x_n = 0$; actually mean square values of z_n and x_n should be used, but for heavy atoms these are approximately equal to the square of the equilibrium values, although for protons significant differences exist. Thus Hirschfelder, Curtiss, and Bird (ref. 6, p. 1028) incorrectly use the square of the equilibrium nuclear separation in H_2 (0.550 Å²) instead of the mean square value (0.594 Å²), and this leads to an underestimation of Θ of 17%], we obtain $g = 0.896$, indicating that the one-electron molecular-orbital approximation (for which $g = 0$) is limited in its validity in this case. If Θ were zero, g would be 0.891.

(iv) *Indirect methods involving molecular interactions.* Since quadrupole moments contribute significantly to intermolecular forces, estimates of Θ can sometimes be made through observations of the effects of collisions

[44] Ishiguro, Arai, Mizushima, and Kotani, *Proc. Phys. Soc.*, 1952, *A*, **65**, 178.
[45] Havens, *Phys. Rev.*, 1933, **43**, 992.

involving quadrupolar molecules. The measurements may be of several types.

Second virial coefficients. Experimental data on the equation of state of gases at low pressures have been widely used to determine the force constants occurring in approximate intermolecular potential energy functions (see ref. 6, chap 3). In the virial equation of state

$$\frac{PV}{RT} = 1 + \frac{B(T)}{V} + \frac{C(T)}{V^2} + \dots \quad \dots \quad \dots \quad (45)$$

the second virial coefficient $B(T)$ (a function of T but not of the molar volume V) represents an initial deviation from the ideal-gas law, and hence is related to the interaction of molecules in pairs. If u_{12} is the interaction potential energy of two axially-symmetric molecules 1 and 2 in the configuration of Fig. 5, the classical statistical-mechanical expression for $B(T)$ is[46]

$$B(T) = \frac{N}{4} \int_0^\infty R^2 \, dR \int_0^\pi \sin\theta_1 \, d\theta_1 \int_0^\pi \sin\theta_2 \, d\theta_2 \int_0^{2\pi} d\zeta \,[1 -$$
$$\exp(-u_{12}/kT)] \quad \dots \quad \dots \quad (46)$$

If u_{12} is of the central-force type, that is, if $u_{12} = u_{12}^{(0)}(R)$, a function of R only, then eqn. (46) can be evaluated analytically for a number of simple forms of $u_{12}^{(0)}(R)$. For the hard-sphere model (see Fig. 9)

$$u_{12}^{(0)}(R) = u_{HS} = \infty \text{ for } R < R_0, \text{ and } = 0 \text{ for } R > R_0 . \quad \dots \quad (47)$$

$$B(T) = \tfrac{2}{3}\pi N R_0^3 = 4 \times \text{actual volume of the molecules} \quad \dots \quad (48)$$

For the Lennard-Jones 6–12 potential (see Fig. 9)

$$u_{12}^{(0)}(R) = u_{LJ} = 4\epsilon\left[\left(\frac{R_0}{R}\right)^{12} - \left(\frac{R_0}{R}\right)^6\right] \quad \dots \quad \dots \quad (49)$$

where ϵ and R_0 are parameters having the dimensions of energy and length,[47,48]

$$B(T) = \tfrac{2}{3}\pi N R_0^3 F(y) = \tfrac{2}{3}\pi N R_0^3 y^{-2}[H_{12}(y) - \tfrac{1}{2}H_6(y)]. \quad (50)$$

where $y = 2(\epsilon/kT)^{\frac{1}{2}}$ and $F(y)$ is a function that has been tabulated (see ref. 6, p. 1114) and is expressible in terms of the functions $H_n(y)$, introduced by Pople,[49] defined by

$$H_n(y) = 12y^4 R_0^{n-3} \int_0^\infty R^{-n} \exp\left[-y^2\left\{\left(\frac{R_0}{R}\right)^{12} - \left(\frac{R_0}{R}\right)^6\right\}\right] R^2 \, dR$$
$$= y^{(27-n)/6} \sum_{p=0}^\infty \Gamma\left(\frac{6p+n-3}{12}\right)\frac{y^p}{p!} \quad \dots \quad \dots \quad (51)$$

[46] Fowler and Guggenheim, "Statistical Thermodynamics", Cambridge Univ. Press, 1953, chap. 7.
[47] (Lennard-) Jones, *Proc. Roy. Soc.*, 1924, *A*, **106**, 441.
[48] Buckingham and Pople, *Trans. Faraday Soc.*, 1955, **51**, 1173.
[49] Pople, *Proc. Roy. Soc.*, 1954, *A*, **221**, 508.

These functions have been tabulated[48] for all n (since there are recurrence relations) and for $0.6 \leqslant y \leqslant 3.2$.

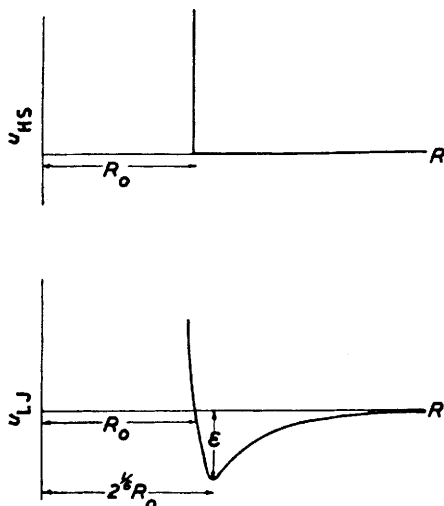Observed values of $B(T)$ lead to the "best" force constants ϵ and R_0

FIG. 9   *The hard-sphere and Lennard-Jones intermolecular potential energy functions.*

by a method due to R. A. Buckingham,[50] and Lennard-Jones potentials are now known for many non-polar molecules (see ref. 6, p. 1110); the potentials obtained through measurements of $B(T)$ are usually in reasonable agreement with those derived from other observables, such as viscosity.

Keesom[51] evaluated eqn. (46) for potentials of the type

$$
\left.
\begin{aligned}
u_{12} &= u_{HS} + u_{\text{dipole–dipole}} \\
u_{12} &= u_{HS} + u_{\text{quadrupole–quadrupole}}
\end{aligned}
\right\} \quad . \quad . \quad . \quad (52)
$$

where $u_{\text{dipole-dipole}}$ and $u_{\text{quadrupole-quadrupole}}$ are the energies proportional to μ^2/R^3 and to Θ^2/R^5 in (23). His result for the quadrupolar case is

$$
B(T) = \frac{2}{3} \pi N R_0^3 \left[1 - \frac{3}{5} \left(\frac{\Theta^2}{R_0^5 kT} \right)^2 + \frac{18}{245} \left(\frac{\Theta^2}{R_0^5 kT} \right)^3 - \frac{639}{4165} \left(\frac{\Theta^2}{R_0^5 kT} \right)^4 + \cdots \right]. \quad . \quad . \quad . \quad . \quad (53)
$$

Keesom erroneously supposed that the forces between inert-gas atoms were of the types (52); the quantum mechanical nature of dispersion forces was proposed some years later by London.[52]

Second-virial data for CO_2 have been obtained over the wide temperature

[50] R. A. Buckingham, *Proc. Roy. Soc.*, 1938, *A*, **168**, 264.
[51] Keesom, *Physikal. Z.*, 1921, **22**, 129.
[52] London, *Trans Faraday Soc.*, 1937, **33**, 8.

range 0—600°c by MacCormack and Schneider,[53] who showed[54] that single values of ϵ and R_0 in u_{LJ} cannot explain their observations over the full range of temperature. They proposed "high" and "low" temperature force-fields, but Pople[49] found that a potential of the form

$$u_{12} = u_{LJ} + u_{\text{quadrupole-quadrupole}} \quad \cdots \quad \cdots \quad (54)$$

leading to the approximate formula (higher powers of Θ^2 being neglected)

$$B(T) = \frac{2}{3} \pi N R_0{}^3 [F(y) - \frac{7}{320} \lambda^2 H_{10}(y)] \quad \cdots \quad (55)$$

where λ is the dimensionless parameter $\Theta^2/\epsilon R_0{}^5$, adequately explained the data over the full range of T. In (54), there are three adjustable parameters, namely, ϵ, R_0, and Θ, and Pople found that $\Theta_{CO_2} = \pm 5.73 \times 10^{-26}$ e.s.u. gave the best agreement [(54) is independent of the sign of Θ, but the negative sign is probably the appropriate one].

Second-virial and crystal data. The molar heat of sublimation H of a crystal at 0°K, and the equilibrium molecular separations, are potential sources of information about intermolecular forces. H is equal to $-E$ minus the zero-point energy, where E is the molar intermolecular potential energy when the molecules are in their equilibrium configurations. The zero-point energy can be obtained through low-temperature specific-heat measurements and is $9Nk\theta_D/8$, where θ_D is the Debye temperature of the crystal. For a face-centred cubic crystal in which all molecules interact with all others according to the Lennard-Jones potential (49),[55]

$$E = -H - 9Nk\theta_D/8 = 2N\epsilon \left[12 \cdot 1318 \left(\frac{R_0}{R} \right)^{12} - 14 \cdot 4539 \left(\frac{R_0}{R} \right)^6 \right] (56)$$

and for the equilibrium separation R_e, $\left(\dfrac{dE}{dR} \right)_{R=R_e} = 0$. These equations adequately describe the properties of the solid inert gases, but for carbon dioxide the calculated H is only 3480 cal.mole^{-1} for the "high", and 3210 cal. mole^{-1} for the "low" temperature potential of MacCormack and Schneider;[54] the experimental value is 6440 cal. mole^{-1}.[49]

Pople's potential (54) leads to [49]

$$E = 2N\epsilon \left[12 \cdot 1318 \left(\frac{R_0}{R} \right)^{12} - 14 \cdot 4539 \left(\frac{R_0}{R} \right)^6 - 5 \cdot 3533 \lambda \left(\frac{R_0}{R} \right)^5 \right] (57)$$

and his parameters $\epsilon/k = 160 \cdot 0$°K, $R_0 = 3 \cdot 80$ Å, $\Theta = \pm 5 \cdot 73 \times 10^{-26}$ e.s.u. to $H = 7330$ cal. mole^{-1}, which, although high, is closer to the experimental result than those obtained from a pure Lennard-Jones potential. There is therefore little doubt that a substantial part of the binding energy of solid carbon dioxide is due to quadrupole-quadrupole

[53] MacCormack and Schneider, *J. Chem. Phys.*, 1950, **18**, 1269.
[54] MacCormack and Schneider, *J. Chem. Phys.*, 1951, **19**, 849.
[55] Lennard-Jones and Ingham, *Proc. Roy. Soc.*, 1925, *A*, **107**, 636.

interactions. Pople's overestimation of H may be due to neglect of induction effects. The principal contributor to the induction energy for large R corresponds to the interaction between the permanent quadrupoles and the dipoles induced in the other molecules; it takes the form

$$u_{\text{induction}} = -\frac{9\alpha\Theta^2}{4R^8}\ [1 - \cos^2\theta_1 - \cos^2\theta_2 + \frac{5}{2}\cos^4\theta_1$$

$$+ \frac{5}{2}\cos^4\theta_2] \quad \ldots \ldots \ldots \quad (58)$$

where $\dot\alpha = \frac{1}{3}\alpha_{\beta\beta}$ is the polarizability (assumed isotropic) of one of the molecules. In the crystal, the symmetry is such that there is no electric field acting on any molecular centre, and $u_{\text{induction}}$ does not contribute to E, but in a gaseous collision all configurations are possible and $u_{\text{induction}}$ will tend to diminish $B(T)$. If $u_{\text{induction}}$ is added to the potential (54), so that

$$u_{12} = u_{\text{LJ}} + u_{\text{quadrupole-quadrupole}} + u_{\text{induction}} \quad \cdots \quad (59)$$

then E is given by (57), and

$$B(T) = \frac{2}{3}\pi N R_0{}^3\ [F(y) - \frac{7}{320}\lambda^2\ H_{10}(y) - \frac{3}{16}\alpha R_0{}^{-3}\ \lambda y^{-2}\ H_8(y)]\ . \quad (60)$$

The parameters ϵ, R_0, and Θ in (59) can be determined from the following three observations: $E = -6530$ cal. mole^{-1}, $R_e = 3.917$ Å,[9] B (60°c) $= -96.9$ cm.^{3} mole^{-1}.[56] They lead to $\epsilon/k = 195.7$ °K, $R_0 = 3.768$ Å, $\Theta = \pm 4.60 \times 10^{-26}$ e.s.u. About 54% of E arises from the quadrupole-quadrupole interactions. This potential leads to B (0°c) $= -146.0$, B (200°c) $= -41.8$, B (600°c) $= 13.0$ cm.^{3} mole^{-1}, and these compare favourably with the observed values[53] of -156.4, -34.1, and 12.1 cm.^{3} mole^{-1}.

The apparent failure[56] of the well-known combination rules $\epsilon_{12} = (\epsilon_1 \epsilon_2)^{\frac{1}{2}}$ and $R_{0_{12}} = \frac{1}{2}(R_{0_1} + R_{0_2})$ for the Lennard-Jones parameters corresponding to the interaction of dissimilar pairs of molecules, is at least partly due to the neglect of quadrupolar effects. In a collision between a quadrupolar molecule 1 and a spherical molecule 2

$$u_{12} = 4\epsilon_{12}\left[\left(\frac{R_{0_{12}}}{R}\right)^{12} - \left(\frac{R_{0_{12}}}{R}\right)^{6}\right] - \frac{9}{8}\frac{\alpha_2\ \Theta_1{}^2}{R^8}\ (1 -$$

$$2\cos^2\theta_1 + 5\cos^4\theta_1)\ . \quad \ldots \ldots \quad (61)$$

and

$$B_{12}(T) = \frac{2}{3}\pi N R_{0_{12}}{}^3\left[F(y_{12}) - \frac{3}{32}\frac{\alpha_2\ \Theta_1{}^2}{\epsilon_{12}\ y_{12}{}^2\ R_{0_{12}}{}^8}\ H_8(y_{12})\right]. \quad (62)$$

The above combination rules, together with the parameters for argon

[56] Cottrell, Hamilton, and Taubinger, *Trans. Faraday Soc.*, 1956, 52, 1310.

(see ref. 6, p. 1110) $\epsilon_2/k = 119\cdot8°\text{K}$, $R_{0_2} = 3\cdot405$ Å, $\alpha_2 = 1\cdot63 \times 10^{-24}$ cm.^{3}, and the above constants for carbon dioxide, lead to

	Calculated (cm.^{3} mole^{-1})	" Experimental "[56] (cm.^{3} mole^{-1})
B_{12} (30°c)	$- 40\cdot1$	$- 32\cdot3$
B_{12} (60°c)	$- 31\cdot3$	$- 26\cdot0$
B_{12} (90°c)	$- 24\cdot2$	$- 19\cdot2$

and this comparison is much more favourable than that obtained on the basis of the pure Lennard-Jones potential.[56]

It has been suggested[57] that the orientation-dependence of the R^{-6} dispersion force potential energy is an important contributor to $B(T)$. However, two opposing effects are involved in both $B(T)$ and E, namely, a coupling between the anisotropic dispersion force and the quadrupole-quadrupole interaction [yielding a positive term proportional to $H_{11}(y)$ in $B(T)$], and the pure anisotropic dispersion effect [leading to a negative term in $H_{12}(y)$]. Thus, the complications caused by using this more accurate form for the dispersion force are probably not justified.

The compressibility of a single crystal, being proportional to $\left(\dfrac{\text{d}^2E}{\text{d}R^2}\right)_{R=R_e}$, is also a potential source of information about inter-molecular forces; presumably the elastic constants relating to shear stresses and strains are closely related to the orientational intermolecular forces—one would expect significant differences between solid argon and solid carbon dioxide; unfortunately, measurements of these kinds do not seem to have been made.

The dielectric constant of an imperfect quadrupolar gas. The total dielectric polarization $_rP$ of a perfect gas of non-dipolar molecules is independent of T. At higher densities, interacting pairs of molecules (which may possess induced dipoles) become significant, and $_rP$ will be temperature-dependent. If the orientation polarization $_oP$ is expanded as a power series in $1/V$, similarly to (45),

$$_oP = \left(\frac{\epsilon - 1}{\epsilon + 2} - \frac{n^2 - 1}{n^2 + 2}\right)V = \mathscr{A}(T) + \frac{\mathscr{B}(T)}{V} + \frac{\mathscr{C}(T)}{V^2} + \cdots \quad (63)$$

where ϵ is the static dielectric constant and $\mathscr{A}(T)$, $\mathscr{B}(T)$, $\mathscr{C}(T)$, $\ldots$, are *dielectric virial coefficients*, then $\mathscr{A}(T) = 4\pi N\mu^2/9kT$, where μ is the per-manent dipole moment of the molecule, and $\mathscr{B}(T)$ is proportional to the mean square dipole moment of an interacting pair of molecules.[58]

[57] Castle, Jansen, and Dawson, *J. Chem. Phys.*, 1956, **24**, 1078.
[58] Buckingham and Pople, *Trans. Faraday Soc.*, 1955, **51**, 1029.

$$\mathscr{B}(T) = \frac{2\pi N^2}{9kT} \ [<m_{12}{}^2 - 2\mu^2> V]_{V=\infty} \quad . \quad . \quad . \quad . \quad (64)$$

where m_{12} is the scalar corresponding to the vector $\boldsymbol{m_{12}} = \boldsymbol{m_1} + \boldsymbol{m_2}$, the dipole moment of the interacting pair of molecules 1 and 2, and the angular brackets denote an average over all configurations. Thus, for axially symmetric molecules with relative co-ordinates as in Fig. 5,

$$\mathscr{B}(T) = \frac{\pi N^2}{9kT} \int_0^\infty R^2 \, dR \int_0^\pi \sin\theta_1 \, d\theta_1 \int_0^\pi \sin\theta_2 \, d\theta_2 \int_0^{2\pi} d\zeta [m_{12}{}^2 - 2\mu^2]$$

$$\exp\left(-u_{12}/kT\right) \quad . \quad . \quad . \quad . \quad . \quad (65)$$

For a pair of molecules quadrupole, $\mu = 0$ and $\boldsymbol{m_1}$ can be approximated by the product of the polarizability of molecule 1 and the electric field $\boldsymbol{F_1}$ (scalar value F_1) at its centre due to the quadrupole moment of molecule 2. Thus, from eqn. (16),

$$m_{1_\alpha} = \alpha_{1_{\alpha\beta}} F_{1_\beta} = -\tfrac{1}{3} \alpha_{1_{\alpha\beta}} \Theta_{2_{\gamma\delta}} \frac{\partial^3}{\partial R_\beta \, \partial R_\gamma \, \partial R_\delta} \left(\frac{1}{R}\right)$$

and if $\alpha_{\alpha\beta}$ is isotropic ($\alpha_{\alpha\beta} = \alpha\delta_{\alpha\beta}$)

$$m_{12}{}^2 = \frac{9\alpha^2\Theta^2}{4R^8} \ [4 - 8\cos^2\theta_1 - 8\cos^2\theta_2 + 5\cos^4\theta_1 + 5\cos^4\theta_2 +$$

$$18\cos^2\theta_1 \cos^2\theta_2 - 8\sin\theta_1 \sin\theta_2 \cos\theta_1 \cos\theta_2 \cos\zeta] \quad . \quad (66)$$

If u_{12} is of the form of (54),[59]

$$\mathscr{B}(T) = \frac{\pi^2 N^2 \alpha^2}{9} \left[\lambda y^{-2} H_8(y) + \frac{1}{10} \lambda^2 H_{13}(y) + \ldots\right] \quad . \quad (67)$$

If $\kappa = (\alpha_{zz} - \alpha_{xx})/3\alpha$ is not zero, then[60,61]

$$<m_1{}^2> \ = \ <m_2{}^2> \ = 3\alpha^2 \ (1 + 2 \kappa^2) \ \Theta^2 \ <R^{-8}>$$

$$<\boldsymbol{m_1} \cdot \boldsymbol{m_2}> \ = -\tfrac{18}{5} \ \alpha^2 \ \kappa^2 \ \Theta^2 \ <R^{-8}>$$

whence

$$<m_{12}{}^2> \ = 6 \ \alpha^2 \ (1 + \tfrac{4}{5} \kappa^2) \ \Theta^2 \ <R^{-8}>$$

and

$$\mathscr{B}(T) = \frac{\pi^2 N^2 \alpha^2 \ (1 + \tfrac{4}{5} \kappa^2)\lambda}{9y^2} \ H_8(y) + O \ (\lambda^2) \quad . \quad . \quad (68)$$

[59] Buckingham, *Trans. Faraday Soc.*, 1956, **52**, 747. [Eqn. (3·11) of this paper erroneously omits a term in λ^2 arising from the cross-term $<\boldsymbol{m_1} \cdot \boldsymbol{m_2}>$.]

[60] Buckingham and Pople, *J. Chem. Phys.*, 1957, **27**, 820.

[61] Jansen, personal communication, 1958, pointing out that $<\boldsymbol{m_1} \cdot \boldsymbol{m_2}>$ does not vanish if $\kappa \neq 0$.

For carbon dioxide, $\epsilon/k = 195\cdot7$ °K, $R_0 = 3\cdot768$ Å, $\Theta = \pm 4\cdot60 \times 10^{-26}$ e.s.u., $\alpha = 2\cdot97 \times 10^{-24}$ cm.^{3}, $\kappa = 0\cdot24$, so that $\mathscr{B}(100°c)$ should be $31\cdot9$ cm.^{6} mole^{-2}; the experimental value deduced[59] from the ϵ and n data of Michels *et al.*[62] is $13\cdot6$ cm.^{6} mole^{-2}.

In compressed carbon dioxide, microwave absorption proportional to p^2, where p is the gas pressure, has been observed and interpreted[63] in terms of transient dipoles induced by the permanent quadrupoles of neighbouring molecules. If the full frequency range of the absorption can be covered, then $\epsilon - n^2$ can be directly measured, and [if $\mathscr{A}(T) = 0$], from (63),

$$\epsilon - n^2 = \frac{3\mathscr{B}(T)}{R^2 T^2} p^2 + O\,(p^3) \quad . \quad . \quad . \quad . \quad . \quad . \quad (69)$$

where $R = Nk$ is the universal gas constant.

Induced vibration and rotation spectra. The general theory of pressure-induced infrared absorption spectra has been developed by van Kranendonk.[64] The induced fundamental vibration–rotation band of H_2 in the pure gas and in mixtures with inert gases has been interpreted[65] in terms of transient dipoles induced both by short-range overlap forces and by quadrupolar fields. At low pressures, only binary interactions are important, and by introducing reasonable assumptions, van Kranendonk[65] deduced from Chisholm and Welsh's[66] spectra for H_2–N_2 mixtures that $\Theta_{N_2} = \pm 1\cdot64 \times 10^{-26}$ e.s.u.

In the case of pressure-induced rotational transitions in H_2,[67] the observed absorption proportional to p^2 can be explained by assuming that the transition dipoles are due to quadrupolar fields; $\Theta_{H_2} = 0\cdot6 \times 10^{-26}$ e.s.u. leads to good agreement with experiment. In hydrogen-argon mixtures, the induced rotational absorption ($\Delta J = 2$) is proportional to the pressure of the inert gas and to the square of its polarizability as well as to $(\Theta_{H_2})^2$.

Pressure broadening in the microwave spectral regions. Spectral lines have a finite width $\Delta\nu$ (the width, in cycles sec.$^{-1}$, at half the maximum intensity) for three reasons, namely, because of the natural line width (related to the uncertainty principle), the Doppler effect (connected with the thermal velocities of the molecules), and pressure broadening (see ref. 28, p. 336, and ref. 6, p. 1020). Only the last is normally significant

[62] Michels and Kleerekoper, *Physica*, 1939, **6**, 586; Michels and Hamers, *Physica*, 1937, **4**, 995.
[63] Birnbaum and Maryott, *Phys. Rev.*, 1954, **95**, 622; Maryott, Wacker, and Birn-baum,, N.B.S. Report (Project 0536), June 1957; Buckingham, "Propiétés optiques et acoustiques des fluides comprimés et actions intermoléculaires", C.R.N.S., Bellevue, France, July 1957, p. 57.
[64] van Kranendonk, *Physica*, 1957, **23**, 825.
[65] van Kranendonk, *Physica*, 1958, **24**, 347.
[66] Chisholm and Welsh, *Canad. J. Phys.*, 1954, **32**, 291.
[67] Colpa and Ketelaar, *Molecular Physics*, 1958, **1**, 343.

in the microwave region of the spectrum, and measurements of $\Delta\nu$ lead to "collision cross-sections" σ by means of the formula

$$\sigma = 2\pi \, \Delta\nu/N\nu \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (70)$$

where N is the number of molecules in unit volume, and ν the mean relative velocity of colliding molecules.

Anderson[68] and Leslie[69] have derived quantum-mechanical formulae relating σ to the intermolecular forces. The most-studied spectral line is the inversion of the $J = 3$, $K = 3$ state of $N^{14}H_3$ at 23,870 Mc./sec. (0·796 cm.$^{-1}$), and the self-broadening of this line has been satisfactorily interpreted in terms of dipole–dipole interactions (see ref. 68, and ref. 28, p. 361).

Smith and Howard[70] were the first to suggest determining molecular quadrupole moments by measuring σ for the broadening of microwave resonance lines (notably the ammonia inversion spectrum) by foreign non-dipolar gases. An approximate theory has been developed by Smith;[71] if the observed σ is considerably larger than the kinetic-theory collision diameter, it is probable that the dipole–quadrupole interaction is dominant in determining σ for collisions between an ammonia molecule and one whose leading multipole is a quadrupole, for its range (R^{-4}) is greatest, but other effects, such as the quadrupole–quadrupole interaction (R^{-5}), are probably also significant. For this reason, the quadrupole moments deduced from pressure-broadening data are not beyond suspicion. Recent measurements[72] of the broadening effect of foreign gases on the $J = 3$, $K = 3$ inversion line of ammonia have led to $\Theta_{CO_2} = \pm 1·7 \times 10^{-26}$ and $\Theta_{N_2} = \pm 0·80 \times 10^{-26}$ e.s.u.

The broadening effect of argon and other spherical molecules on this NH_3 inversion line has been interpreted[73] as arising from the interaction, proportional to R^{-7}, between the permanent NH_3 quadrupole and the dipole induced in the sphere by the field of the permanent NH_3 dipole. Measurements of this effect are consistent with an assumed quadrupole moment $\Theta_{NH_3} = 0·66 \times 10^{-26}$ e.s.u., but this figure should be regarded as only approximate, since all shorter-range interactions (such as exchange and overlap effects, and permanent moment–induced quadrupole terms proportional to $C\mu^2R^{-8}$) have been neglected.

Differences in the heats of solvation of oppositely charged spherical ions of the same size. Although the heats of solvation of salts can easily be measured, the contributions due to the positive and negative ions have not been separated experimentally. However, different authors[74,75] are agreed that

[68] Anderson, *Phys. Rev.*, 1949, **76**, 647.
[69] Leslie, *Phil. Mag.*, 1951, **42**, 37.
[70] Smith and Howard, *Phys. Rev.*, 1950, **79**, 132.
[71] Smith, *J. Chem. Phys.*, 1956, **25**, 510.
[72] Feeny, Madigosky, and Winters, *J. Chem. Phys.*, 1957, **27**, 898.
[73] Anderson, *Phys. Rev.*, 1950, **80**, 511.
[74] Latimer, Pitzer, and Slansky, *J. Chem. Phys.*, 1939, **7**, 108.
[75] Verwey, *Rec. Trav. chim.*, 1942, **61**, 127.

although K^+ and F^- ions are similar in size, their heats of hydration ΔH are different, and are about -75 and -122 kcal. mole^{-1} respectively at 25°c and at infinite dilution.

If it is assumed that the first shell of water molecules is tetrahedrally disposed, with dipoles pointing away from, or directly towards, the ion's centre, and that more distant water molecules interact with the ion as if they formed a continuum having the bulk properties of water, then the difference between K^+ and F^- hydration energies can be explained in terms of the interactions between the ion and the quadrupoles of the water molecules. The charge–dipole energy (R^{-2}) will presumably dominate, and since the field of the ion at a water molecule's centre will change sign on reversing the ionic charge, the molecule will invert in order to preserve the negative sign of the ion–dipole energy (thus, in K^+ the "complex" is

of the type $K^+ \ O\!\!\big<^{\,H}_{\,H}$,while in F^- it is $F^- \ \ ^H\!\!\big>\!O$). However, $\Theta_{\alpha\beta}$ is un-

affected by an inversion, so that the ion-quadrupole energy (R^{-3}) will be equal but opposite in the two cases (it is assumed that the centre of mass of the water molecule is equidistant from the centres of the two ions). There is another small contributor to the hydration energy difference, and this arises from the dipole–quadrupole interactions among the "adsorbed" water molecules; the other significant contributions to ΔH should be identical for the two ions (the ion–octupole interaction will be the same in the two cases). The final result is [76]

$$\Delta H^+ - \Delta H^- = \frac{8N\Theta_{zz}}{R^3}\left[Ze - \frac{135}{128}\left(\frac{2}{3}\right)^{\frac{1}{2}}\frac{\mu}{R}\right] \quad \cdots \quad (71)$$

where Z is the modulus of the charge on the ion ($Z = 1$ for K^+ and F^-), R is the distance from the ion's centre to the centres of gravity of the four nearest solvent molecules ($R = 2 \cdot 73$ Å for K^+ and F^- in water), μ is the permanent dipole moment of a solvent molecule and Θ_{zz} its quadrupole in the direction of the axis of μ. If ($\Delta H^+ - \Delta H^-$) for the K^+, F^- pair in water is 47 kcal. mole^{-1}, then $(\Theta_{zz})_{H_2O} = 2 \cdot 0 \times 10^{-26}$ e.s.u. Similarly, Coulter's figures[77] for the heats of ammonation of the same pair lead to $\Theta_{NH_3} = 1 \cdot 3 \times 10^{-26}$ e.s.u.

It is not easy to assess the accuracy of these Θs; probably the best attitude to adopt is to look upon the model as providing an explanation for any difference that exists between the solvation energies of oppositely charged spherical ions of the same size, and if reliable Θs should become available, then they could be used with the model to determine *absolute* solvation energies from the accurately known *relative* values.

Effects of interactions on nuclear quadrupole resonance frequencies. In the gas phase, the energy differences between the states corresponding to the

[76] Buckingham, *Discuss. Faraday Soc.*, 1957, **24**, 151.
[77] Coulter, *J. Phys. Chem.*, 1953, **57**, 553.

allowed orientations of a quadrupolar nucleus in the field gradient of the other charges of the molecule can be determined through observations of the hyperfine structure of the pure rotational spectrum (see ref. 28, p. 149). In solids, pure quadrupole resonance spectra can be obtained, and the hyperfine energy levels determined through observations of the absorption of radio-waves in the solid.[78,79]   The coupling constant obtainable from both sources is eQq, where $eQ/2 = \Theta_n$ is the nuclear quadrupole moment (actually Θ_n is the moment for the state $M = I$, where I is the nuclear spin and M its component in a fixed direction, so that $Q = \dfrac{1}{e}\int \rho(3z_n{}^2 - r_n{}^2)\mathrm{d}v$,

where z_n is measured along this fixed direction and $\rho\,\mathrm{d}v$ is the nuclear charge in the volume element $\mathrm{d}v$), and $-q = F'_{zz}$ is the electric-field gradient along the molecular axis. Differences between q_{gas} and q_{solid} have been observed;[78,80] in solids comprised of polar molecules, neighbouring dipoles may contribute significantly to q_{solid},[80] but in other cases (e.g., solid D_2 and N_2) it should be possible to use the known crystal structure to relate $(q_{\text{gas}} - q_{\text{solid}})$ to the molecular quadrupole moment Θ.   In a face-centred cubic lattice of the N_2 and CO_2 type (see Fig. 7), the quadrupole moments of neighbouring molecules produce a field gradient $F'_{zz} = 42\cdot83\ \Theta/R_e{}^5$ at each molecular centre [it is F'_{zz} that yields the quadrupolar contribution to E in (57)], and since $F''_{zzz} = 0$ at this point, the field gradient acting on nuclei that are slightly removed from the centre (such as the N nuclei in solid N_2) will be approximately equal to F'_{zz}, so that $(q_{\text{gas}} - q_{\text{solid}}) = 42\cdot83\ \Theta/R_e{}^5$. Since $\Theta/R_e{}^5$ is ca. 10^{11} e.s.u., the quadrupole coupling constants eQq may differ by up to a few kilocycles sec.$^{-1}$ in gases and solids of this type.

If a quadrupolar molecule containing a nucleus with $I \geqslant 1$ is frozen into a matrix of spherical molecules such as CCl_4, then there will be a "reaction field gradient" F'_{zz} at the quadrupolar nucleus, arising from the polarization induced in neighbouring molecules by the field of the molecular quadrupole Θ.   This effect can be evaluated approximately by supposing that F'_{zz} is the field gradient existing at the centre of a spherical cavity of molecular size in a continuum of dielectric constant ϵ, when the cavity contains a quadrupole at its centre.   Arguments similar to those used by Onsager[81] lead to

$$F'_{zz} = q_{\text{gas}} - q_{\text{solid solution}} = \frac{6(\epsilon - 1)}{3\epsilon + 2}\frac{\Theta}{a^5} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (72)$$

where a is the radius of the cavity. Hence, F'_{zz} is ca. 10^{12} e.s.u., so that changes in coupling constants of the order of tens of kilocycles sec.$^{-1}$ could be expected in these cases; if a change of this kind were observed,

[78] Dehmelt, *Discuss. Faraday Soc.*, 1955, **19**, 263.

[79] Orville-Thomas, *Quart. Reviews*, 1957, **11**, 162.

[80] Duchesne, paper presented at the symposium on "Applications of Electron and Nuclear Resonance in Chemistry", Bristol, 1958; *Chem. Soc., Special Publ. No. 12*, p. 235.

[81] Onsager, *J. Amer. Chem. Soc.*, 1936, **58**, 1486.

eqn. (72) would lead to an approximate value of Θ, if Onsager's formula $4\pi N a^3/3 = M/d$, where M is the molecular weight and d the density of the pure quadrupolar liquid or solid, were used for determining a.

(v) *Macroscopic quadrupoles.* Just as electric and magnetic dipoles can be aligned in ferroelectric and ferromagnetic solids, so too can molecular quadrupoles be oriented so that a crystal possesses a large permanent quadrupole moment. Calcite, potassium nitrate, hexamethylbenzene, polyacetylenes, etc., have their molecular quadrupoles parallel and a piece of any of these crystals will behave as a macroscopic quadrupole.

If the molecules are uncharged and non-dipolar (or alternatively, if the unit cell has a centre of inversion) then the total quadrupole moment is

$$\Theta^{(0)}_{\alpha\beta} = \sum_j \Theta^{(j)}_{\alpha\beta} \quad \ldots \ldots \ldots \quad (73)$$

where the summation extends over all molecules in the crystal. For axially symmetric crystals comprised of axially symmetric molecules, eqn. (73) becomes

$$\Theta^{(0)} = \tfrac{1}{2} \Theta \sum_j (3\cos^2\theta_j - 1) \quad \ldots \ldots \ldots \quad (74)$$

where θ_j is the angle between the jth molecular axis and the axis of the sample. For parallel quadrupoles, $\theta_j = 0$ and $\Theta^{(0)} = N\Theta$.

A needle-shaped macroscopic quadrupole will experience a torque in a field gradient, which could be produced either by another macroscopic quadrupole or by a condenser of a suitable shape. If the needle's moment of inertia about an axis is I, its period for small oscillations in the xy plane about its equilibrium position in a field gradient $F'_{xx} = -F'_{yy}$, $F'_{zz} = 0$ (such a field gradient would exist on the line midway between two long parallel wires at a positive potential relative to a large cylinder surrounding them) is

$$\tau = \sqrt{\left(\frac{2\pi^2 I}{\Theta^{(0)} F'_{xx}}\right)} \quad \ldots \ldots \ldots \quad (75)$$

Calcite has a density of 2·711 g. cm.$^{-3}$ at 25°, and the unit cell (see Fig. 10) contains two $CaCO_3$ units. The quadrupole moment of a unit cell is approximately $\Theta = [-146 \times 10^{-26} + 2\,\Theta_{CO_3{}^{2-}}]$, and for an ionic structure ${}^-O\!-\!C\!\!\underset{\diagdown O^-}{\overset{\diagup O^-}{<}}\!\!+$ (which is isoelectronic with BF_3) $\Theta_{CO_3{}^{2-}} = 12 \times$ 10^{-26} e.s.u., as the C–O bond length is 1·31 Å; thus, the total quadrupole moment of a unit cell is probably about -120×10^{-26} e.s.u., and the moment of a crystal weighing 1 g. is *ca.* $3·6 \times 10^{-3}$ e.s.u. For $I \sim 1$ g. cm.^{2}, and $F'_{xx} \sim 100$ e.s.u., eqn. (75) leads to a period $\tau \sim 7$ seconds. This should be a reasonable period to measure, so that $\Theta^{(0)}$, and hence Θ (or in the case of calcite, $\Theta_{CO_3{}^{2-}}$) might be measurable by this means.
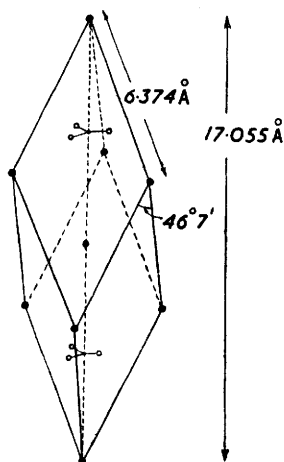
FIG. 10   *The structure and dimensions of the unit rhombohedral cell of calcite.*

Quadrupole Radiation.—Allowed transitions take place between eigen-states $\psi^{(1)}$ and $\psi^{(2)}$ if a non-zero electric dipole moment matrix element $(\psi^{(1)}|\mu|\psi^{(2)})$ exists, and the transition probability is proportional to the square of this transition moment. The symmetry of $\psi^{(1)}$ and $\psi^{(2)}$ is often such that the matrix element vanishes, and the transition is then said to be *forbidden*. However, spectral lines corresponding to forbidden transitions are sometimes observed (usually they are weak), and they may arise from: (*a*) perturbation of the wave functions by external influences, such as electric fields[82] or collisions with other molecules, (*b*) a non-zero magnetic dipole transition moment, (*c*) a non-zero quadrupole transition moment $(\psi^{(1)}|\Theta|\psi^{(2)})$. Effects (*b*) and (*c*) normally lead to intensities only $\sim 10^{-5}$ and $\sim 10^{-8}$ respectively of that of an allowed transition, but they have been observed.[83]

For the electronic ground state of H_2, all dipole vibrational transition moments vanish, but Θ will vary with the internuclear distance R (James

and Coolidge[32] calculated that $\left(\dfrac{d\Theta}{dR}\right)_{R=R_\theta} = 0.8 \times 10^{-18}$ e.s.u.) and

vibration–rotation bands have been observed by Herzberg,[84] using a multipath infrared spectrometer of total path length 5.5 kilometres at 10 atm. The selection rule for vibration–rotation transitions in homo-nuclear diatomic molecules is $\Delta v = \pm 1$, $\Delta J = 0, \pm 2$ (except that $J = 0 \rightarrow J = 0$ is forbidden).[83] It was suggested[85] that these H_2 spectra were

[82] Condon, *Phys. Rev.*, 1932, **41**, 759.
[83] Herzberg, "Spectra of Diatomic Molecules", D. van Nostrand, New York, 1950, p. 277.
[84] Herzberg, *Nature*, 1949, **163**, 170.
[85] Crawford, Welsh, and Locke, *Phys. Rev.*, 1949, **75**, 1607.

in fact due to intermolecular collisions (and hence proportional to the square, rather than to the first power, of the H_2 pressure) but owing to the sharpness of the lines, this suggestion was later shown to be incorrect.[86]

Bond Quadrupole Moments.—When values of molecular quadrupole moments become known, there will be a need for the development of the relationships between the moments and molecular structural features. Empirical bond dipoles have proved very useful, and so too have bond polarizabilities.[87] Similarly, "bond quadrupole moments" should also be of considerable importance. If the bonds are axially symmetric (most are approximately so), the molecular quadrupole has components

$$\Theta_{xx} = \tfrac{1}{2} \sum_j \Theta_j (3 \cos^2 \theta_{jx} - 1)$$
$$\Theta_{yy} = \tfrac{1}{2} \sum_j \Theta_j (3 \cos^2 \theta_{jy} - 1) \qquad [\Theta_{xx} + \Theta_{yy} + \Theta_{zz} = 0] \quad . \quad . \quad (76)$$
$$\Theta_{zz} = \tfrac{1}{2} \sum_j \Theta_j (3 \cos^2 \theta_{jz} - 1)$$

where Θ_j is the quadrupole moment of the jth bond and $\theta_{j\alpha}$ is the angle between its axis and the α-axis of the molecule. Thus bond quadrupoles are simpler to handle than bond polarizabilities, for the latter have components along and perpendicular to the bond; if the perpendicular components were always zero, the rules for deriving molecular quadrupoles from bond parameters would be identical to those used for obtaining molecular polarizabilities from the appropriate bond constants.[87]

A Table of Molecular Quadrupole Moments.—The Table lists the most probable values (deduced from the meagre present data) of the molecular quadrupole moments of simple molecules. The last seven entries are based on microwave pressure-broadening data (incorporating the correction recently deduced by Smith[71]), but as explained on p. 209, these may sometimes be unreliable.

Numerical values of quadrupole moments

Substance	$10^{26}\Theta_{zz}$ (e.s.u.)	Substance	$10^{26}\Theta_{zz}$ (e.s.u.)
deuteron	0.66×10^{-10}	NH_3	1
$2p_z$ H atom	-16.14	O_2	$> -0.3, < 0.3$
$3d_{z^2}$ H atom	-48.4	NO	± 1
H_2	0.63	CO	± 1
D_2	0.63	CS_2	-2
N_2	± 1.5	N_2O	-2.5
CO_2	-3	C_2H_2	3
H_2O	2	C_2H_4	± 1

[86] Welsh, Crawford, and Locke, *Phys. Rev.*, 1949, **76**, 580.
[87] Le Fèvre and Le Fèvre, *Rev. Pure Appl. Chem.*, 1955, **5**, 261.