But by the divergence theorem, the first term may be converted to a surface integral that vanishes because the field and the potential both vanish at infinity. To evaluate the second term, we use (3.7) and Gauss's law to get

$$W = \frac{1}{2} \int \rho(\mathbf{r}) \Phi(\mathbf{r}) \, d^3\mathbf{r} = \frac{1}{2} \iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{4\pi \varepsilon_0 |\mathbf{r} - \mathbf{r}'|} \, d^3\mathbf{r} \, d^3\mathbf{r}' \tag{3.27}$$

That is, the total energy is half the potential energy of each of the charges in the field of all the other charges. We see from the last form of the integral that the factor $\frac{1}{2}$ appears because the integral "double counts" the interaction of each charge with the other charges.

For point charges we run into some difficulty, because the potential Φ is infinite at the position of the point charge. That is, point charges have infinite self-energy in the electric field. For now, we ignore the (infinite) self-energy of the particles and calculate the energy of interaction in the following way. If we begin with a charge q_1 at position $\mathbf{r}_1$ and bring up another charge q_2 from infinity to position $\mathbf{r}_2$, the amount of work done on charge q_2 is just the potential energy of charge q_2 in the field of charge q_1,

$$W_2 = \frac{q_1 q_2}{4\pi \varepsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|} \tag{3.28}$$

If we now bring up, in succession, charges q_3, q_4, and so on, the work done on each charge is

$$W_i = \sum_{j<i} \frac{q_i q_j}{4\pi \varepsilon_0 |\mathbf{r}_i - \mathbf{r}_j|} \tag{3.29}$$

where the sum is over the previous charges $j < i$, and the total work done is

$$W = \sum_i \sum_{j<i} \frac{q_i q_j}{4\pi \varepsilon_0 |\mathbf{r}_i - \mathbf{r}_j|} = \frac{1}{2} \sum_i \sum_{j \neq i} \frac{q_i q_j}{4\pi \varepsilon_0 |\mathbf{r}_i - \mathbf{r}_j|} \tag{3.30}$$

when we "double count" the interactions. Therefore, the total energy of the assembly of point charges, relative to their energy at infinite separation, may be expressed in the form

$$W = \frac{1}{2} \sum_i q_i \Phi_i \tag{3.31}$$

where the potential at position $\mathbf{r}_i$,

$$\Phi_i = \sum_{j \neq i} \frac{q_j}{4\pi \varepsilon_0 |\mathbf{r}_i - \mathbf{r}_j|} \tag{3.32}$$

is due to all the other charges. These expressions are analogous to (3.27), except that they discard the (infinite) self-energy of the point charges.

3.1.3 Multipole Moments

For localized charge distributions, such as atoms and nuclei, the field at a point far from the charges may be expanded in inverse powers of the distance from the charges, and the coefficients in this expansion are called the multipole moments of the charge distribution. The interaction of the charge distribution with externally applied fields can also be expressed in terms of the same multipole moments, making them convenient for a variety of different problems. For example, the hydration of ions in water is the result of the interaction
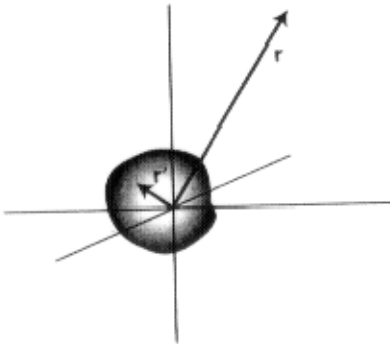
Figure 3.2 Potential surrounding a charge distribution.

between the charge on the ion and the dipole moments of the water molecules. Also, the observation of a finite electric quadrupole moment for a deuteron shows that it is prolate, or egg-shaped, rather than spherically symmetric.

As we have seen, the potential at point $\mathbf{r}$ due to a charge distribution $\rho(\mathbf{r}')$ is

$$\Phi(\mathbf{r}) = \frac{1}{4\pi\varepsilon_0} \int \frac{\rho(\mathbf{r}')\,d^3\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|} \tag{3.33}$$

If the source is localized near the origin and the field point $\mathbf{r}$ is a large distance away, as shown in Figure 3.2, it is useful to Taylor expand the reciprocal of the radius

$$f(\mathbf{r}') = \frac{1}{|\mathbf{r}-\mathbf{r}'|} = \frac{1}{\sqrt{(x-x')^2 + (y-y')^2 + (z-z')^2}} \tag{3.34}$$

as a function of $\mathbf{r}'$ for $r' \ll r$. The Taylor series for a function of three variables may be expressed in the form

$$f(\mathbf{r}') = f\Big|_{\mathbf{r}'=0} + \sum_{i=1}^{3} r_i' \frac{\partial f}{\partial r_i}\Big|_{\mathbf{r}'=0} + \frac{1}{2} \sum_{i,j=1}^{3} r_i' r_j' \frac{\partial^2 f}{\partial r_i' \partial r_j'}\Big|_{\mathbf{r}'=0} + \cdots \tag{3.35}$$

If we differentiate (3.34) we find, after some algebra, that

$$f(\mathbf{r}')\Big|_{\mathbf{r}'=0} = \frac{1}{r} \tag{3.36}$$

$$\frac{\partial f}{\partial r_i'}\Big|_{\mathbf{r}'=0} = \frac{r_i}{r^3} \tag{3.37}$$

$$\frac{\partial^2 f}{\partial r_i' \partial r_j'}\Big|_{\mathbf{r}'=0} = \frac{3r_i r_j - r^2 \delta_{ij}}{r^5} \tag{3.38}$$

and so on. Therefore, at large distances from the localized charge distribution the potential is

$$\Phi(\mathbf{r}) = \int \frac{1}{r} \rho(\mathbf{r}')\,d^3\mathbf{r}' + \int \sum_{i=1}^{3} \frac{r_i r_i'}{r^3} \rho(\mathbf{r}')\,d^3\mathbf{r}'$$

$$+ \int \frac{1}{2} \sum_{i,j=1}^{3} \frac{3r_i r_j - r^2 \delta_{ij}}{r^5} r_i' r_j' \rho(\mathbf{r}')\,d^3\mathbf{r}' + \cdots \tag{3.39}$$

But the summations and all factors of $\mathbf{r}$ may be moved outside the integrals over $\mathbf{r}'$. We also note that for $i = j$ the last term vanishes since

$$\sum_{i=1}^{3} (3r_i r_i - r^2) = 0 \tag{3.40}$$

for any $\mathbf{r}$. Therefore, in the third term of (3.39) we may add to the factor $r_i' r_j'$ inside the integral anything multiplied by δ_{ij}. Specifically, we add $\frac{1}{3} r'^2 \delta_{ij}$ to symmetrize the dependence of this term on $\mathbf{r}$ and $\mathbf{r}'$. We then find that the potential is given by the series

$$\Phi(\mathbf{r}) = \frac{1}{4\pi \varepsilon_0} \left[\frac{Q}{r} + \sum_{i=1}^{3} \frac{Q_i r_i}{r^3} + \frac{1}{6} \sum_{i,j=1}^{3} \frac{Q_{ij}(3r_i r_j - r^2 \delta_{ij})}{r^5} + \cdots \right] \tag{3.41}$$

where the multipole moments of the charge distribution are

$$Q = \int \rho(\mathbf{r}') \, d^3 \mathbf{r}' \tag{3.42}$$

$$Q_i = \int r_i' \rho(\mathbf{r}') \, d^3 \mathbf{r}' = p_i \tag{3.43}$$

$$Q_{ij} = \int (3r_i' r_j' - r'^2 \delta_{ij}) \rho(\mathbf{r}') \, d^3 \mathbf{r}' \tag{3.44}$$

and so on. The first term, the monopole moment, is just the total charge. The second term is called the dipole moment $\mathbf{p}$, and the third is the quadrupole moment. Of the nine components of the quadrupole moment, only five are independent. Symmetry ($Q_{ij} = Q_{ji}$) reduces the number of independent components to six, and since the trace vanishes,

$$\sum_{i=1}^{3} Q_{ii} = \sum_{i=1}^{3} \int (3r_i' r_i' - r'^2) \rho(\mathbf{r}') \, d^3 \mathbf{r}' = 0 \tag{3.45}$$

by (3.40), we see that the third diagonal component is dependent on the other two. Beyond the quadrupole moment the multipole expansion (3.41) becomes increasingly cumbersome.

In addition to using a multipole expansion to calculate the potential outside a localized charge distribution, the multipole expansion can be used to compute the energy $W = \int \rho(\mathbf{r}) \Phi(\mathbf{r}) \, d^3 \mathbf{r}$ of a localized charge distribution in an externally applied potential Φ. Near the origin, the potential Φ may be Taylor expanded in the form

$$\Phi(\mathbf{r}) = \Phi \bigg|_{\mathbf{r}=0} + \sum_{i=1}^{3} r_i \frac{\partial \Phi}{\partial r_i} \bigg|_{\mathbf{r}=0} + \frac{1}{2} \sum_{i,j=1}^{3} r_i r_j \frac{\partial^2 \Phi}{\partial r_i \, \partial r_j} \bigg|_{\mathbf{r}=0} + \cdots \tag{3.46}$$

But the externally applied potential (the potential in the absence of the local charge distribution) satisfies the Laplace equation

$$\sum_{i=1}^{3} \frac{\partial^2 \Phi}{\partial r_i \, \partial r_i} = 0 \tag{3.47}$$

so in the third term of (3.46), we may add to the factor $r_i r_j$ anything multiplied by δ_{ij} and the sum is unchanged. Specifically, we add $\frac{1}{3} r^2 \delta_{ij}$, in which case the energy of the charge

distribution in the externally applied field becomes

$$W = \int \Phi(\mathbf{r})\rho(\mathbf{r})\,d^3\mathbf{r} = Q\Phi\Big|_{r=0} + \sum_{i=1}^{3} Q_i \frac{\partial \Phi}{\partial r_i}\Big|_{r=0} + \frac{1}{6}\sum_{i,j=1}^{3} Q_{ij} \frac{\partial^2 \Phi}{\partial r_i\,\partial r_j}\Big|_{r=0} + \cdots \tag{3.48}$$

In terms of the applied electric field $\mathbf{E} = -\nabla\Phi$, this becomes

$$W = Q\Phi(0) - \mathbf{p}\cdot\mathbf{E}(0) - \frac{1}{6}\sum_{i,j=1}^{3} Q_{ij} \frac{\partial E_j}{\partial r_i}\Big|_{r=0} + \cdots \tag{3.49}$$

We see from this that the total charge Q interacts with the potential at the origin, the dipole moment $\mathbf{p}$ interacts with the electric field, and the quadrupole moment Q_{ij} interacts with the gradient of the field. The net force on a rigid charge distribution, such as a quantum-mechanical atom or molecule, is found from the gradient of the energy. Thus,

$$F_k = -\frac{\partial W}{\partial r_k} = Q E_k(0) + \sum_{i=1}^{3} p_i \frac{\partial E_i}{\partial r_k}\Big|_{r=0} + \frac{1}{6}\sum_{i,j=1}^{3} Q_{ij} \frac{\partial^2 E_j}{\partial r_i\,\partial r_k}\Big|_{r=0} + \cdots \tag{3.50}$$

The net force on a localized charge distribution is proportional to the total charge times the electric field, the dipole moment times the derivative of the electric field, the quadrupole moment times the second derivative of the electric field, and so on. If the charge distribution is not perfectly rigid, so that a dipole or higher order moment can be induced by the external field, then the situation becomes more complex. This is discussed in Chapters 6 and 7.

Some examples can make these notions clearer. Consider the interaction of two dipoles, $\mathbf{p}_1$ and $\mathbf{p}_2$, the first at the origin and the second at point $\mathbf{r}$, as shown in Figure 3.3. The potential at point $\mathbf{r}$ due to the dipole $\mathbf{p}_1$ at the origin is

$$\Phi(\mathbf{r}_2) = \frac{1}{4\pi\varepsilon_0} \frac{\mathbf{p}_1\cdot\mathbf{r}}{r^3} \tag{3.51}$$

and the electric field is

$$\mathbf{E} = -\nabla\Phi = \frac{1}{4\pi\varepsilon_0}\left(3\frac{\mathbf{p}_1\cdot\mathbf{r}}{r^5}\mathbf{r} - \frac{\mathbf{p}_1}{r^3}\right) \tag{3.52}$$

The energy of interaction is then

$$W = -\mathbf{E}\cdot\mathbf{p}_2 = \frac{1}{4\pi\varepsilon_0}\left[\frac{\mathbf{p}_1\cdot\mathbf{p}_2}{r^3} - 3\frac{(\mathbf{p}_1\cdot\mathbf{r})(\mathbf{p}_2\cdot\mathbf{r})}{r^5}\right] \tag{3.53}$$
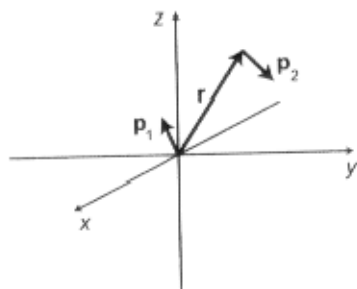
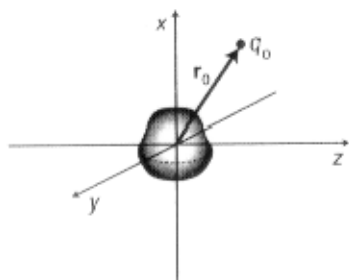**Figure 3.3** Interaction between two dipoles.

Figure 3.4 Interaction of a charge distribution with a point charge.

The energy is lowest when the dipoles are both oriented in the same direction parallel or antiparallel to the vector **r** that separates them.

As another example, we consider the interaction of a charge distribution located near the origin with a point charge q_0 located at position $\mathbf{r}_0$, as shown in Figure 3.4. We assume in the following that the total charge and dipole moment of the localized charge distribution vanish, so the quadrupole components are the first nonvanishing moments. If we make the distribution symmetric about the x axis and use the fact that the trace of Q_{ij} vanishes, then the quadrupole moments are

$$Q_{11} = \int (3x^2 - r^2)\rho(\mathbf{r})\, d^3\mathbf{r} \tag{3.54}$$

$$Q_{22} = Q_{33} = -\tfrac{1}{2}Q_{11} \tag{3.55}$$

$$Q_{ij} = 0, \qquad \text{for } i \neq j \tag{3.56}$$

For any other orientation of the charge distribution, the quadrupole moment matrix can be found by a rotation of coordinates, if desired. However, this is not necessary, since the energy clearly depends only on the angle θ between the axis of the spheroid and the radius vector $\mathbf{r}_0$. From (3.48) we see that the dominant term in the interaction energy (the quadrupole term) is

$$W = -\frac{1}{6}\sum_{i,j=1}^{3} Q_{ij}\frac{\partial E_j}{\partial r_i}\bigg|_{\mathbf{r}=0} = -\frac{Q_{11}}{6}\left(\frac{\partial E_x}{\partial x} - \frac{1}{2}\frac{\partial E_y}{\partial y} - \frac{1}{2}\frac{\partial E_z}{\partial z}\right) \tag{3.57}$$

But

$$\mathbf{E} = \frac{q_0}{4\pi\varepsilon_0}\frac{\mathbf{r} - \mathbf{r}_0}{|\mathbf{r} - \mathbf{r}_0|^3} \tag{3.58}$$

so

$$\frac{\partial E_i}{\partial r_i} = -\frac{q_0}{4\pi\varepsilon_0}\left(\frac{3r_{0i}^2}{r_0^5} - \frac{1}{r_0^3}\right) \tag{3.59}$$

and the interaction energy is

$$W = \frac{Q_{11}q_0}{16\pi\varepsilon_0}\frac{3x_0^2 - r_0^2}{r_0^5} = \frac{Q_{11}q_0}{4\pi\varepsilon_0}\frac{3\cos^2\theta - 1}{r_0^3} \tag{3.60}$$

To make this example more concrete, we consider an atomic system consisting of a positively charged nucleus at the origin (effectively a point charge) surrounded by a negative

charge distribution created by the electrons. If the negative charge distribution of the elec-
trons is prolate (egg shaped), then the quadrupole moment of the atom is negative,
$Q_{11} < 0$. In this case the lowest energy occurs for $\theta = 0$ and $\theta = \pi$, so the atom tends to
line up parallel to the electric field of the point charge. If the charge distribution is oblate
(pancake shaped), then $Q_{11} > 0$. In this case the lowest energy occurs for $\theta = \pi/2$, and the
atom tends to align its symmetry axis normal to the field.

EXERCISE 3.3

Molecular interactions are frequently interpreted in terms of multipoles.

(a) What is the energy of interaction between a dipole and a point charge?
(b) It is found experimentally (in molecular-beam experiments) that the bond energy
between a water molecule ($p = 6.2 \times 10^{-30}$ C-m) and a Mg^+ ion is 1.7×10^{-19} J,
with a bond length of 2.0×10^{-10} m. How does this compare to the charge–dipole
interaction? Draw a graph of the interaction energy as a function of the bond length
including the expected short-range repulsion, and use this to explain the difference
between the charge–dipole interaction energy and the measured bond energy.

EXERCISE 3.4

Consider a molecule at the the origin with axial symmetry about the x axis having no net
charge or dipole moment, but a quadrupole moment Q_{11}. The molecule interacts with a
charge q_0 at point $\mathbf{r}_0 = (r_0, \theta_0, \phi_0)$.

(a) Show that the force on the quadrupole is

$$F = -\frac{3q_0 Q_{11}}{16\pi \varepsilon_0 r_0^4}[(1 + 5\cos^2 \theta_0)\hat{\mathbf{r}}_0 - 2\cos \theta_0 \hat{\mathbf{x}}] \tag{3.61}$$

(b) Show that the torque on the quadrupole is

$$\tau = \frac{3q_0 Q_{11}}{8\pi \varepsilon_0 r_0^3} \cos \theta_0 \sin \theta_0 \tag{3.62}$$

EXERCISE 3.5

When a spherically symmetric atom is placed in an electric field, the charge distribution
distorts to form a dipole moment. In the linear approximation, the induced dipole moment is

$$p = \alpha E \tag{3.63}$$

where α is the atomic polarizability.

(a) Show that relative to infinity (where the externally applied field is assumed to
vanish), the energy of the atom in the electric field E is

$$W = -\tfrac{1}{2}\varepsilon_0 E^2 V \tag{3.64}$$

where $\frac{1}{2}\varepsilon_0 E^2$ is the energy density of the electric field and

$$V = \frac{\alpha}{\varepsilon_0} \tag{3.65}$$

is a volume that is typically of the order of the volume of the atom. Thus, neutral atoms are drawn into regions where the electric field is highest.

(b) The atom can be represented crudely by a nucleus surrounded by a rigid, uniform, spherical distribution of negative charge of radius a, such that the nucleus can be pulled off center by the externally applied electric field against the restoring force of the spherical charge distribution itself. Compute the restoring electric field felt by the nucleus inside the uniform negative charge distribution, and show that for this simple atomic model the polarizability is

$$\alpha = 4\pi \varepsilon_0 a^3 \tag{3.66}$$

EXERCISE 3.6

The long-range interaction between atoms and molecules is dominated by the electrostatic interactions between their multipole moments. In the case of neutral, spherically symmetric atoms or molecules, the interaction is called the van der Waals attraction and has an r^{-6} dependence on the separation r between the atomic centers. Classically, this is interpreted as the interaction between a fluctuating dipole moment in one atom that induces a dipole moment in the other atom, and vice versa. Although the average fluctuating dipole moment of a spherically symmetric atom vanishes, the mean square fluctuation does not.

(a) Show that the instantaneous electric field of dipole 1 (located at the origin) is

$$\mathbf{E}_1(\mathbf{r}) = -\nabla \Phi_1 = \frac{1}{4\pi \varepsilon_0 r^3}[3(\mathbf{p}_1 \cdot \hat{\mathbf{r}})\hat{\mathbf{r}} - \mathbf{p}_1] \tag{3.67}$$

The dipole moment induced in atom 2 (located at $\mathbf{r}$) is then $\mathbf{p}_2 = \alpha_2 \mathbf{E}_1(\mathbf{r})$, where α_2 is the molecular polarizability.

(b) The energy of the induced dipole in the electric field of atom 1 is $W = -\mathbf{p}_2 \cdot \mathbf{E}_1(\mathbf{r})$. Show that the instantaneous energy of the dipole–dipole interaction is

$$W = \frac{-\alpha_2}{(4\pi \varepsilon_0)^2 r^6}[\mathbf{p}_1 \cdot \mathbf{p}_1 + 3(\mathbf{p}_1 \cdot \hat{\mathbf{r}})^2] \tag{3.68}$$

(c) Average this over a time that is long compared with the fluctuations of $\mathbf{p}_1$, and add the effects of the fluctuating dipole moment of atom 2 on atom 1 to show that the total interaction energy is

$$\langle W \rangle_{\text{total}} = -\frac{\alpha_2 \langle p_1^2 \rangle + \alpha_1 \langle p_2^2 \rangle}{8\pi^2 \varepsilon_0^2 r^6} \tag{3.69}$$

where the brackets indicate a time average. This is negative, showing that the van der Waals interaction is attractive.