

Electrostatic Multipoles

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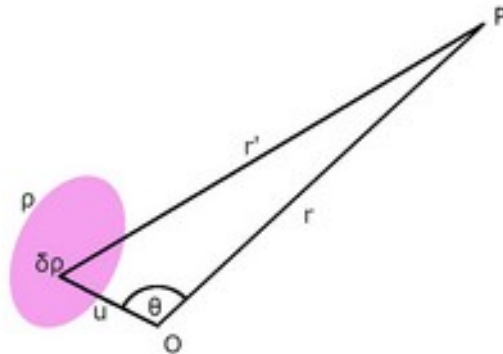


Figure 1. The potential due to a continuous charge density distribution ρ .

This note describes the determination of the electrostatic potential at a point P at a position \vec{r} from the origin of coordinates at O , due to a finite, continuous charge density distribution $\rho(\vec{u})$ at position \vec{u} as shown in Figure 1. (Note that it is not necessary to pay attention to the *form* of $\rho(\vec{u})$ in what follows.)

Cartesian Multipoles

Our first description is based on Cartesian coordinates. We begin by defining an element of charge $\delta\rho$ as

$$\delta\rho = \rho(\vec{u}) dv, \quad (1)$$

where δv is the volume of the element $\delta\rho$, and $\rho(\vec{u})$ is the charge density function shown in Figure 1. At a distance $u = |\vec{u}|$ from the origin of coordinates at O the potential $\delta\Phi$ at a point P is given by Coulomb's law as

$$\delta\Phi = \frac{1}{4\pi\epsilon_0} \frac{\delta\rho}{r'}, \quad (2)$$

where r' is the distance between $\delta\rho$ and the point P (see Figure 1). The total potential at P is therefore

$$\Phi = \frac{1}{4\pi\epsilon_0} \int_V \frac{\rho(\vec{u})}{r'} dv, \quad (3)$$

in which the integral is over the volume of the distribution $\rho(\vec{u})$. With reference to Figure 1 and using the cosine formula we may write:

$$\frac{1}{r'} = \frac{1}{(r^2 + u^2 - 2ru\cos\theta)^{1/2}}, \quad (4)$$

where θ is the angle between vectors \vec{r} and \vec{u} in Figure 1.

We note (for later use) that $\cos(\theta)$ can be expressed as the scalar product

$$\cos(\theta) = \frac{\vec{r} \cdot \vec{u}}{ru}. \quad (5)$$

Equation (4), may be rewritten as

$$\frac{1}{r'} = \frac{1}{r} (1 + \epsilon)^{-1/2}, \quad (6)$$

where

$$\epsilon = \left(\frac{u^2}{r^2} - \frac{2u}{r} \cos \theta \right). \quad (7)$$

We now make the stipulation that $r \gg u$, or equivalently $\epsilon \ll 1$, which means that the charge distribution is small in relation to the distance r . Then we note that the binomial theorem gives a well known expansion for the form $(1 + \epsilon)^n$:

$$(1 + \epsilon)^n = 1 + n\epsilon + \frac{n(n-1)}{2} \epsilon^2 + \frac{n(n-1)(n-2)}{3!} \epsilon^3 + \frac{n(n-1)(n-2)(n-3)}{4!} \epsilon^4 + O(\epsilon^5), \quad (8)$$

which we may use with $n = -1/2$, giving

$$(1 + \epsilon)^{-1/2} = 1 - \frac{1}{2} \epsilon + \frac{3}{8} \epsilon^2 - \frac{5}{16} \epsilon^3 + \frac{105}{384} \epsilon^4 + O(\epsilon^5), \quad (9)$$

where we have arbitrarily truncated the series at the fourth power of ϵ .

Using the form of ϵ given in equation (7) we can write the powers of ϵ as follows.

$$\begin{aligned} \epsilon^2 &= \frac{u^4}{r^4} - 4 \frac{u^3}{r^3} \cos(\theta) + 4 \frac{u^2}{r^2} \cos^2(\theta), \\ \epsilon^3 &= \frac{u^6}{r^6} - 6 \frac{u^5}{r^5} \cos(\theta) + 12 \frac{u^4}{r^4} \cos^2(\theta) - 8 \frac{u^3}{r^3} \cos^3(\theta) \\ \epsilon^4 &= \frac{u^8}{r^8} - 8 \frac{u^7}{r^7} \cos(\theta) + 24 \frac{u^6}{r^6} \cos^2(\theta) - 32 \frac{u^5}{r^5} \cos^3(\theta) + 16 \frac{u^4}{r^4} \cos^4(\theta). \end{aligned} \quad (10)$$

Inserting these expansions into equation (9) and gathering terms in powers of (u/r) leads to the following equation.

$$(1 + \epsilon)^{-1/2} = 1 + \cos(\theta) \frac{u}{r} + \frac{1}{2} [3 \cos^2(\theta) - 1] \left(\frac{u}{r} \right)^2 + \frac{1}{2} [5 \cos^3(\theta) - 3 \cos(\theta)] \left(\frac{u}{r} \right)^3 + O\left(\frac{u^4}{r^4} \right) \quad (11)$$

From (11) it transpires that the coefficients of powers of u/r have the form of Legendre polynomials $P_l(z)$ (with $z = \cos(\theta)$), which are derived from the formula

$$P_l(z) = \frac{1}{2^l l!} \frac{d^l}{(dz)^l} (z^2 - 1)^l \quad (12)$$

where l is an integer index. Table 1 below presents a list of Legendre polynomials.

Table 1. Legendre polynomials up to $l=3$.

l	$P_l(z)$	$P_l(\cos(\theta))$
0	1	1
1	z	$\cos(\theta)$
2	$(3z^2 - 1)/2$	$(3 \cos^2(\theta) - 1)/2$
3	$(5z^3 - 3z)/2$	$(5 \cos^3(\theta) - 3 \cos(\theta))/2$

So equation (11) can be written as

$$(1+\epsilon)^{-1/2} = P_0(\cos(\theta)) + P_1(\cos(\theta))\frac{u}{r} + P_2(\cos(\theta))\frac{u^2}{r^2} + P_3(\cos(\theta))\frac{u^3}{r^3} + O\left(\frac{u^4}{r^4}\right). \quad (13)$$

We thus infer that the infinite series (without truncation) is

$$(1+\epsilon)^{-1/2} = \sum_{l=0}^{\infty} P_l(\cos(\theta)) \left(\frac{u^l}{r^l}\right). \quad (14)$$

Substituting (14) back into equation (6) permits us to rewrite equation (3) as

$$\Phi = \frac{1}{4\pi\epsilon_0} \sum_{l=0}^{\infty} \left(\frac{1}{r^{l+1}}\right) \int_{\rho} \rho(\vec{u}) u^l P_l(\cos(\theta)) dv, \quad (15)$$

which is the formal solution for the potential at point P due to the distributed charge density ρ . Equation (15) is known as the *multipole expansion*. Each term in the series, indicated by the integer index l , represents a contribution to the potential at P due to a particular multipole of the charge distribution. In practice the series converges rapidly provided the region ρ is small in relation to r (as stipulated above) and is therefore usually truncated at some low level multipole.

We may now examine the potential due to some common multipoles.

i) The monopole term ($l=0$):

In this case the contribution to the potential Φ is

$$\Phi_q = \frac{1}{4\pi\epsilon_0} \left(\frac{1}{r}\right) \int_{\rho} \rho(\vec{u}) dv. \quad (16)$$

From this it is evident that the integral in the term defines the *scalar charge* q (17).

$$q = \int_{\rho} \rho(\vec{u}) dv \equiv \int_{\rho} \rho(u_x, u_y, u_z) du_x du_y du_z. \quad (17)$$

In a system that is electrically charged, this is the dominant contributor to the potential at P .

ii) The dipole term ($l=1$):

Here the potential contribution is

$$\Phi_d = \frac{1}{4\pi\epsilon_0} \left(\frac{1}{r^2}\right) \int_{\rho} \rho(\vec{u}) u \cos(\theta) dv, \quad (18)$$

where we have used the Legendre function $P_1(\cos(\theta))$ from Table 1. Using the scalar product (5) this can be written as

$$\begin{aligned} \Phi_d &= \frac{1}{4\pi\epsilon_0} \left(\frac{1}{r^2}\right) \int_{\rho} \rho(\vec{u}) u \left(\frac{\vec{r} \cdot \vec{u}}{ru}\right) dv, \\ &= \frac{1}{4\pi\epsilon_0} \left(\frac{1}{r^3}\right) \vec{r} \cdot \int_{\rho} \rho(\vec{u}) \vec{u} dv. \end{aligned} \quad (19)$$

From which it is evident that the integral defines a 3 component vector, which is called the *dipole* \vec{d} (20).

$$\vec{d} = \int_{\rho} \rho(\vec{u}) \vec{u} dv. \quad (20)$$

In the absence of an overall system charge, the dipole term is dominant.

iii) The quadrupole term ($l=2$):

Taking the Legendre polynomial $P_2(\cos(\theta))$ from Table 1 and proceeding as before, the quadrupole contribution to the potential is

$$\begin{aligned}
\Phi_Q &= \frac{1}{4\pi\epsilon_0} \left(\frac{1}{r^3} \right) \int_{\rho} \rho(\vec{u}) u^2 \frac{1}{2} [3\cos^2(\theta) - 1] dv \\
&= \frac{1}{4\pi\epsilon_0} \left(\frac{1}{r^3} \right) \int_{\rho} \rho(\vec{u}) u^2 \frac{1}{2} \left[3 \frac{(\vec{r} \cdot \vec{u})^2}{(ru)^2} - 1 \right] dv \\
&= \frac{1}{4\pi\epsilon_0} \left(\frac{1}{r^5} \right) \int_{\rho} \rho(\vec{u}) \frac{1}{2} [3(\vec{r} \cdot \vec{u})^2 - (ru)^2] dv \\
&= \frac{1}{4\pi\epsilon_0} \left(\frac{1}{r^5} \right) [\vec{r} \vec{r}] : \int_{\rho} \rho(\vec{u}) \frac{1}{2} [3[\vec{u} \vec{u}] - \mathbf{I} u^2] dv.
\end{aligned} \tag{21}$$

In which $[\vec{r} \vec{r}]$ and $[\vec{u} \vec{u}]$ define square 3x3 matrices of the form

$$[\vec{r} \vec{r}] = \begin{bmatrix} xx & xy & xz \\ yx & yy & yz \\ zx & zy & zz \end{bmatrix} \quad \text{and} \quad [\vec{u} \vec{u}] = \begin{bmatrix} u_x u_x & u_x u_y & u_x u_z \\ u_y u_x & u_y u_y & u_y u_z \\ u_z u_x & u_z u_y & u_z u_z \end{bmatrix}. \tag{22}$$

We also define the scalar product of matrices \mathbf{A} and \mathbf{B} as

$$\mathbf{A} : \mathbf{B} = \sum_i \sum_j A_{ij} B_{ij}. \tag{23}$$

The matrix \mathbf{I} is the unit matrix, which may be defined by its components:

$$I_{\alpha\beta} = \delta_{\alpha\beta}, \tag{24}$$

where $\delta_{\alpha\beta}$ is the Dirac delta function, which is unity when the indices α and β are identical and zero otherwise.

The final integral in (21) thus defines a 3x3 matrix called the quadrupole \mathbf{Q} (25).

$$\mathbf{Q} = \int_{\rho} \rho(\vec{u}) \frac{1}{2} [3[\vec{u} \vec{u}] - \mathbf{I} u^2] dv. \tag{25}$$

The quadrupole term is dominant where no overall charge or dipole is present.

iv) The octupole term ($l=3$):

In this case the contribution to the potential has the form

$$\Phi_O = \frac{1}{4\pi\epsilon_0} \left(\frac{1}{r^4} \right) \int_{\rho} \rho(\vec{u}) u^3 \frac{1}{2} [5\cos^3(\theta) - 3\cos(\theta)] dv, \tag{26}$$

which includes the expansion for $P_3(\theta)$ from Table 1. Working through as before we get

$$\begin{aligned}
\Phi_O &= \frac{1}{4\pi\epsilon_0} \left(\frac{1}{r^4} \right) \int_{\rho} \rho(\vec{u}) u^3 \frac{1}{2} \left[5 \frac{(\vec{r} \cdot \vec{u})^3}{(ru)^3} - 3 \frac{(\vec{r} \cdot \vec{u})}{(ru)} \right] dv, \\
&= \frac{1}{4\pi\epsilon_0} \left(\frac{1}{r^7} \right) \int_{\rho} \rho(\vec{u}) \frac{1}{2} [5(\vec{r} \cdot \vec{u})^3 - 3(\vec{r} \cdot \vec{u})(ru)^2] dv, \\
&= \frac{1}{4\pi\epsilon_0} \left(\frac{1}{r^7} \right) [\vec{r} \vec{r} \vec{r}] : \int_{\rho} \rho(\vec{u}) \frac{1}{2} [5[\vec{u} \vec{u} \vec{u}] - 3\mathbf{U} u^2] dv.
\end{aligned} \tag{27}$$

In which $[\vec{r} \vec{r} \vec{r}]$ is a rank 3 tensor with 27 elements $\{\vec{r} \vec{r} \vec{r}\}_{\alpha\beta\gamma}$ of the form

$$\{\vec{r} \vec{r} \vec{r}\}_{\alpha\beta\gamma} = r_{\alpha} r_{\beta} r_{\gamma}. \tag{28}$$

so each element is a product of x , y or z . The tensor \mathbf{U} is also of rank 3, with 27 elements of the form

$$U_{\alpha\beta\gamma} = \delta_{\alpha\beta} u_\gamma. \quad (29)$$

The elements $U_{\alpha\beta\gamma}$ are zero unless indices α and β are identical, and u_γ is one of u_x , u_y or u_z in order. We also define the scalar product of two rank 3 tensors as (cf. (23))

$$\mathbf{A} : \mathbf{B} = \sum_i \sum_j \sum_k A_{ijk} B_{ijk}. \quad (30)$$

The final integral in (27) defines a rank 3 tensor of dimension 3x3x3 called the octupole \mathbf{O} (31).

$$\mathbf{O} = \int \rho(\vec{u}) \frac{1}{2} [5[\vec{u}\vec{u}\vec{u}] - 3\mathbf{U}u^2] dv. \quad (31)$$

The octupole is least commonly encountered in practice, but in the absence of an overall charge, dipole or quadrupole, it is the main contributor to the potential Φ .

The charge q , dipole \vec{d} , quadrupole \mathbf{Q} and octupole \mathbf{O} are the most likely encountered of the multipoles in practice. Thus the potential (15) may be approximated by the following series, truncated with the octupole.

$$\Phi \approx \frac{1}{4\pi\epsilon_0} \left(\frac{q}{r} + \frac{\vec{r} \cdot \vec{d}}{r^3} + \frac{[\vec{r}\vec{r}]:\mathbf{Q}}{r^5} + \frac{[\vec{r}\vec{r}\vec{r}]:\mathbf{O}}{r^7} \right) \quad (32)$$

Note that the increasing powers of r in the denominator of each term ensures that successive terms in the series decrease rapidly in importance.

The above description of the multipoles is termed cartesian due to its dependence on the cartesian components u_x , u_y and u_z . However, there is a drawback to the cartesian description on that the number of terms in each successive multipole grows exponentially and soon becomes unwieldy (despite the equivalence of many components). Fortunately there is an alternative description possible that makes use of spherical harmonic functions $Y_{lm}(\theta, \phi)$ which requires far fewer components per multipole. We now explore this possibility.

Spherical Harmonic Multipoles

Spherical harmonics arise naturally in physics, for example in the solution of the atomic Schroedinger equation, or the Laplace equation in electrostatics, whenever polar coordinates are chosen for a solution. Mathematically they are set of functions $Y_{lm}(\theta, \phi)$ of the polar angles θ and ϕ (with ranges $0 \leq \theta \leq \pi$ and $0 \leq \phi \leq 2\pi$ respectively), which represent the angular components of polar coordinates (r, θ, ϕ) . The indices l and m associated with each spherical harmonic are integers in the ranges: $0 \leq l < \infty$ and $-l \leq m \leq +l$.

The spherical harmonics have the functional form

$$Y_{lm}(\theta, \phi) = \Theta_{|l|m}(\theta) \Phi_m(\phi), \quad (33)$$

where $|m|$ refers to the absolute value of m . $\Theta_{|l|m}(\theta)$ is a *normalised* function, meaning that when multiplied by itself and integrated over the range $0 \leq \theta \leq \pi$ it returns a value of unity. The function is closely related to the Legendre polynomials described in the previous section and is known as an *associated Legendre polynomial*, normally written as $P_l^{|m|}(z)$, where $z = \cos(\theta)$. Examples of normalised functions $P_l^{|m|}(z)$ and $\Theta_{|l|m}(\theta)$ are presented in Table 2 below.

Table 2. The normalised functions $P_l^{|m|}(z)$ and $\Theta_{l|m|}(\theta)$ up to $l=3$.

l	$ m $	$P_l^m(z)$	$\Theta_{l m }(\theta)$	*
0	0	$(1/2)^{1/2}$	$(1/2)^{1/2}$	e
1	0	$(3/2)^{1/2}z$	$(3/2)^{1/2}\cos(\theta)$	o
1	1	$(3/4)^{1/2}(1-z^2)^{1/2}$	$(3/4)^{1/2}\sin(\theta)$	e
2	0	$(5/8)^{1/2}(3z^2-1)$	$(5/8)^{1/2}(3\cos^2(\theta)-1)$	e
2	1	$(15/4)^{1/2}z(1-z^2)^{1/2}$	$(15/4)^{1/2}\cos(\theta)\sin(\theta)$	o
2	2	$(15/16)^{1/2}(1-z^2)$	$(15/16)^{1/2}\sin^2(\theta)$	e
3	0	$(7/8)^{1/2}(5z^3-3z)$	$(7/8)^{1/2}(5\cos^3(\theta)-3\cos(\theta))$	o
3	1	$(21/32)^{1/2}(1-z^2)^{1/2}(5z^2-1)$	$(21/32)^{1/2}\sin(\theta)(5\cos^2(\theta)-1)$	e
3	2	$(105/16)^{1/2}(1-z^2)z$	$(105/16)^{1/2}\sin^2(\theta)\cos(\theta)$	o
3	3	$(35/32)^{1/2}(1-z^2)^{3/2}$	$(35/32)^{1/2}\sin^3(\theta)$	e

* indicates $P_l^{|m|}(z)$ is even or odd over the interval $[-1 \leq z \leq 1]$ (see below).

The function $\Phi_m(\phi)$ can be written in a *complex* or *real* representation. It is also normalised, in this case over the range $0 \leq \phi \leq 2\pi$, and has the form:

$$\Phi_m(\phi) = \frac{1}{(2\pi)^{1/2}} \exp(im\phi) \quad (34)$$

in the complex representation, and the form

$$\begin{aligned} \Phi_m^+(\phi) &= \frac{1}{(4\pi)^{1/2}} (\exp(i|m|\phi) + \exp(-i|m|\phi)) \quad \text{if } m > 0, \\ \Phi_m^-(\phi) &= \frac{-i}{(4\pi)^{1/2}} (\exp(i|m|\phi) - \exp(-i|m|\phi)) \quad \text{if } m < 0, \end{aligned} \quad (35)$$

in the real representation. Alternatively (35) may be written in a trigonometric form:

$$\begin{aligned} \Phi_m^+(\phi) &= \pi^{-1/2} \cos(|m|\phi) \quad \text{if } m > 0, \\ \Phi_m^-(\phi) &= \pi^{-1/2} \sin(|m|\phi) \quad \text{if } m < 0. \end{aligned} \quad (36)$$

Note that for both real and complex representations

$$\Phi_0(\phi) = (2\pi)^{-1/2}. \quad (37)$$

Some typical *real* spherical coordinates for low values of l appear in Table 3.

The spherical harmonics form an orthonormal set of functions, meaning they are both normalised and orthogonal to each other and therefore obey the relation:

$$\int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} Y_{lm}(\theta, \phi) Y_{l'm'}^*(\theta, \phi) \sin(\theta) d\theta d\phi = \delta_{ll'} \delta_{mm'}. \quad (38)$$

This orthonormality property means that any angular function $F(\theta, \phi)$ can be expressed as a sum of spherical harmonics (39):

$$F(\theta, \phi) = \sum_{l=0}^{\infty} \sum_{m=-l}^l A_{lm} Y_{lm}(\theta, \phi), \quad (39)$$

Table 3. Spherical harmonics (real) $Y_{lm}(\theta, \phi)$ up to $l=3$.

l	m	$Y_{lm}(\theta, \phi)$.
0	0	$(2\pi)^{-1/2}$
1	-1	$(3/4\pi)^{1/2} \sin(\theta) \sin(\phi)$
1	0	$(3/4\pi)^{1/2} \cos(\theta)$
1	1	$(3/4\pi)^{1/2} \sin(\theta) \cos(\phi)$
2	-2	$(15/4\pi)^{1/2} \sin^2(\theta) \sin(\phi) \cos(\phi)$
2	-1	$(15/4\pi)^{1/2} \cos(\theta) \sin(\theta) \sin(\phi)$
2	0	$(5/16\pi)^{1/2} (3\cos^2(\theta) - 1)$
2	1	$(15/4\pi)^{1/2} \cos(\theta) \sin(\theta) \cos(\phi)$
2	2	$(15/16\pi)^{1/2} \sin^2(\theta) (\cos^2(\phi) - \sin^2(\phi))$
3	-3	$(35/32\pi)^{1/2} \sin^3(\theta) \sin(\phi) (3\cos^2(\phi) - \sin^2(\phi))$
3	-2	$(105/4\pi)^{1/2} \cos(\theta) \sin^2(\theta) \sin(\phi) \cos(\phi)$
3	-1	$(21/32\pi) (5\cos^2(\theta) - 1) \sin(\theta) \sin(\phi)$
3	0	$(7/16\pi)^{1/2} (5\cos^3(\theta) - 3\cos(\theta))$
3	1	$(21/32\pi) (5\cos^2(\theta) - 1) \sin(\theta) \cos(\phi)$
3	2	$(105/16\pi)^{1/2} \cos(\theta) \sin^2(\theta) (\cos^2(\phi) - \sin^2(\phi))$
3	3	$(35/32\pi)^{1/2} \sin^3(\theta) \cos(\phi) (\cos^2(\phi) - 3\sin^2(\phi))$

where the coefficient A_{nm} is obtained from the integral

$$A_{lm} = \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} F(\theta, \phi) Y_{lm}^*(\theta, \phi) \sin(\theta) d\theta d\phi. \quad (40)$$

A useful consequence of the expansion (39) is the *addition theorem* for spherical harmonics, which is as follows.

Given two unit vectors \hat{a} and \hat{b} defining unit displacements from the origin of coordinates, we have that

$$\hat{a} \cdot \hat{b} = \cos(\theta_{ab}), \quad (41)$$

where θ_{ab} is the angle between the two vectors. The addition theorem states that for any Legendre polynomial $P_l(\cos(\theta_{ab}))$ the following expansion holds:

$$P_l(\cos(\theta_{ab})) = \frac{4\pi}{(2l+1)} \sum_{m=-l}^l Y_{lm}(\hat{a}) Y_{lm}^*(\hat{b}). \quad (42)$$

In which

$$Y_{lm}(\hat{a}) \equiv Y_{lm}(\theta_a, \phi_a) \quad \text{and} \quad Y_{lm}(\hat{b}) \equiv Y_{lm}(\theta_b, \phi_b), \quad (43)$$

meaning the value of the spherical harmonic in the *direction* of \hat{a} or \hat{b} .

We may use (42) in conjunction with equation (15) for the electrostatic potential if we replace the vectors \hat{a} and \hat{b} with the unit vectors \hat{u} and \hat{r} directed along \vec{u} and \vec{r} respectively. This allows (15) to be written as

$$\Phi = \frac{1}{4\pi\epsilon_0} \sum_{l=0}^{\infty} \left(\frac{1}{r^{l+1}} \right) \frac{4\pi}{(2l+1)} \sum_{m=-l}^l \int_{\rho} \rho(\vec{u}) u^l Y_{lm}^*(\hat{u}) Y_{lm}(\hat{r}) dv. \quad (44)$$

The integral in (44) is over the range of the charge density $\rho(\vec{u})$ i.e. over the range of the vector \vec{u} . So we may define the spherical harmonic multipole M_{lm} as

$$M_{lm} = \frac{4\pi}{(2l+1)} \int_{\rho} \rho(\vec{u}) u^l Y_{lm}^*(\hat{u}) dv, \quad (45)$$

or equivalently, using the polar coordinates (u, θ, ϕ) of vector \vec{u} ,

$$M_{lm} = \frac{4\pi}{(2l+1)} \int_{\rho} \rho(\vec{u}) u^{l+2} Y_{lm}^*(\theta_u, \phi_u) \sin(\theta_u) du d\theta_u d\phi_u. \quad (46)$$

This result allows us to write (44) as

$$\Phi = \frac{1}{4\pi\epsilon_0} \sum_{l=0}^{\infty} \left(\frac{1}{r^{l+1}} \right) \sum_{m=-l}^l M_{lm} Y_{lm}(\hat{r}). \quad (47)$$

Equation (47) is the expansion of the potential in terms of spherical harmonic multipoles. This is a more convenient expansion than the cartesian form (15) since, at each level of the index l there are only $2l+1$ terms to evaluate compared with the 3^l terms of cartesian expansion.

We note that (47) is commonly written as

$$\Phi = \frac{1}{4\pi\epsilon_0} \sum_{l=0}^{\infty} \left(\frac{1}{r^{l+1}} \right) \sum_{m=-l}^l M_{lm} Y_{lm}(\theta, \phi), \quad (48)$$

which is consistent with the charge distribution $\rho(\vec{u})$ being at, or extremely close to, the origin of coordinates. We may indeed assume that the origin of the coordinates is at some convenient point in the charge distribution, such as its centre of mass. Lastly we note that equations (38) to (48) are also valid for the real spherical harmonics, except that there is no distinction between a normal spherical harmonic $Y_{lm}(\theta, \phi)$ and its complex conjugate $Y_{lm}^*(\theta, \phi)$.

Obtaining Multipoles from Molecular Orbital Calculations

Multipoles may be calculated using molecular orbital theory. The formal expression of the calculation of a multipole M_{lm} is given by the *expectation value*

$$M_{lm} = \langle \Psi^* | \hat{M}_{lm} | \Psi \rangle, \quad (49)$$

in which Ψ is the *molecular wavefunction* and \hat{M}_{lm} is the so called *multipole operator* which is a sum of single-electron multipole operators

$$\hat{M}_{lm} = \sum_{j=1}^{2N_o} \hat{M}_{lm}(j). \quad (50)$$

It is assumed here that we are dealing with a *closed-shell* system (which applies to most molecules) and there are N_o electrons of alpha spin and N_o of beta spin, making $2N_o$ electrons in all. The sum over j in (50) ranges over all electrons. The operator $\hat{M}_{lm}(j)$ is the multipole operator for the j 'th electron, which we may write as

$$\hat{M}_{lm}(j) = \frac{4\pi}{(2l+1)} u_j^l Y_{lm}^*(\theta_j, \phi_j), \quad (51)$$

where the variables (u_j, θ_j, ϕ_j) are the polar coordinates of the electron's position vector \vec{u}_j , defined with respect to some convenient origin. The fact that all electrons

are equivalent means that we need evaluate the integral (49) for just one indexed electron (e.g. $j=1$) and write

$$M_{lm} = 2N_o \langle \Psi^* | \hat{M}_{lm}(1) | \Psi \rangle \quad (52)$$

To go further, we must expand Ψ into a molecular orbital representation i.e. into molecular orbitals: $\{\psi_i: i=1, \dots, N_o\}$, where each orbital is occupied by two electrons of opposite spin. Here on, we will use the notation: ψ_i and $\bar{\psi}_i$ to indicate the alpha and beta spin components of the i 'th molecular orbital (these are known as *spin orbitals*).

The standard form for Ψ is

$$\Psi = \eta \sum_p^{(2N_o)!} (-1)^p P \{ \psi_1 \bar{\psi}_1 \dots \psi_{N_o} \bar{\psi}_{N_o} \}, \quad (53)$$

which is a sum of antisymmetric permutations of the $2N_o$ electrons between the N_o molecular orbitals. The antisymmetry is signalled by the factor $(-1)^p$ and is necessary to satisfy the Pauli exclusion principle. This is the so-called Slater determinant form of the molecular wavefunction. The normalisation constant η has the value $\eta = (2N_o!)^{-1/2}$.

Inserting (53) into (52) results in a loss of many integration terms, because the different permutations in (53) will have at least two electrons in different spin orbitals and the integration over the coordinates of these electrons means the term has to be zero. The final result is that (52) collapses to

$$M_{lm} = 2 \sum_{i=1}^{N_o} M_{lm}^i, \quad (54)$$

in which the index i refers to a molecular orbital ψ_i and M_{lm}^i is the integral

$$M_{lm}^i = \int \psi_i^*(1) \hat{M}_{lm}(1) \psi_i(1) d\tau_1, \quad (55)$$

in which the element $d\tau_1$ indicates that the integration is over both the spatial and spin coordinates of the electron. Equations (54) and (55) formally represent the solution to calculating any required molecular multipole M_{lm} , but it is not practical without knowledge of the form of the molecular orbitals ψ_i .

In the LCAO (Linear Combination of Atomic Orbitals) approximation, the molecular orbitals are assumed to resemble a sum of the atomic orbitals of the atoms of the molecule. Thus we have

$$\psi_i = \sum_{\mu=1}^N c_{\mu i} \chi_{\mu}, \quad (56)$$

where χ_{μ} is an atomic orbital, $N \geq N_o$ is the number of atomic orbitals available to participate in the molecular orbitals and $c_{\mu i}$ is a coefficient describing the degree to which the atomic orbital χ_{μ} contributes to the molecular orbital ψ_i . Inserting (56) into (55) gives the result

$$M_{lm}^i = \sum_{\mu=1}^N \sum_{\nu=1}^N c_{\mu i}^* c_{\nu i} M_{lm}^{\mu\nu}, \quad (57)$$

where

$$M_{lm}^{\mu\nu} = \int \chi_{\mu}^*(1) \hat{M}_{lm}(1) \chi_{\nu}(1) d\tau_1. \quad (58)$$

This integral represents the multipole arising from a charge distribution $\chi_\mu^*(1)\chi_\nu(1)$ and its definition is independent of the molecular orbital ψ_i since it is a purely *atomistic* integral. But note χ_μ and χ_ν may, in general, reside on different atoms.

Inserting equation (57) into (54) gives

$$M_{lm} = 2 \sum_{\mu=1}^N \sum_{\nu=1}^N \sum_{i=1}^{N_o} c_{\mu i}^* c_{\nu i} M_{lm}^{\mu\nu}, \quad (59)$$

where we have moved the sum over index i inside the sums over μ and ν , which allows us to define the so called *population matrix* $P_{\mu\nu}$ as

$$P_{\mu\nu} = 2 \sum_{i=1}^{N_o} c_{\mu i}^* c_{\nu i}, \quad (60)$$

which is a sum over all the occupied molecular orbitals in the molecule. It follows that equation (59) may be written as

$$M_{lm} = \sum_{\mu=1}^N \sum_{\nu=1}^N P_{\mu\nu} M_{lm}^{\mu\nu}. \quad (61)$$

Molecular orbital calculations based on the LCAO approximation provide the coefficients $c_{\mu i}$ from which the population matrix $P_{\mu\nu}$ may be calculated. A knowledge of the set of atomic orbitals $\{\chi_\mu\}$ allows the calculation of integrals (58) (at least in principle) of the multipole terms $M_{lm}^{\mu\nu}$, thus solving equation (61). Inevitably, the calculations are non-trivial and approximations are advantageous.

There are two main issues. Firstly, the result (61) is the multipole for an entire molecule, which may be useful for a small molecule but less so for a large one, where a set of *distributed multipoles* placed at different sites in the molecule might be a better option for, for instance, calculating intermolecular interactions by classical methods. Secondly, it is common in molecular orbital calculations to reduce the computational burden by neglect of those integrals which actually make a negligible contribution to the overall result. The computational saving this enables makes this a very attractive option.

One approach that addresses both issues is to neglect any integral involving two atomic orbitals on different atoms. This means all the surviving multipole terms $M_{lm}^{\mu\nu}$, are necessarily single atom integrals. Applying this idea to (61) leads to

$$M_{lm}^A = \sum_{\mu=1}^{\text{on } A} \sum_{\nu=1}^{\text{on } A} P_{\mu\nu} M_{lm}^{\mu\nu}, \quad (62)$$

in which M_{lm}^A is a site multipole on atom A and all the contributing integrals $M_{lm}^{\mu\nu}$ involve atomic orbitals χ_μ and χ_ν sited on atom A . Note that in (62) it is logical to put the origin of coordinates on the atom for which the site multipole is being calculated. Only if the molecule is small, may we approximate the molecular multipole by a sum of the site multipoles, as in

$$M_{lm} = \sum_{A=1}^{N_A} M_{lm}^A, \quad (63)$$

in which N_A is the number of atoms in the molecule.