Supplement 6

Curvilinear Coordinates

Applications of quantum mechanics to atomic structure require expressions for the volume element and the Laplacian operator in spherical polar coordinates. We can actually derive more general results applicable to all systems of orthogonal curvilinear coordinates. Consider therefore a set of curvilinear coordinates (q_1, q_2, q_3) such that the elements of length in the three coordinate directions are given by $ds_i = Q_i\, dq_i$ for $i = 1, 2, 3$, as shown in Fig. 1. The element of volume is then given by

$$d\tau = Q_1 Q_2 Q_3\, dq_1 dq_2 dq_3 \tag{1}$$

where the Q_i can be functions of q_1, q_2 and q_3.

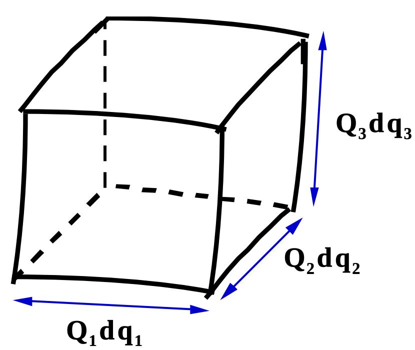

Figure 1. Volume element in curvilinear coordinates.

The components of the gradient vector represent directional derivatives of a function. For example, the change in the function $f(q_1, q_2, q_3)$ along the q_1-direction is given by the ratio of df to the element of length $Q_1\, dq_1$. Thus the gradient in curvilinear coordinates can be written

$$\nabla f = \frac{\mathbf{\hat{u}_1}}{Q_1}\frac{\partial f}{\partial q_1} + \frac{\mathbf{\hat{u}_2}}{Q_2}\frac{\partial f}{\partial q_2} + \frac{\mathbf{\hat{u}_3}}{Q_3}\frac{\partial f}{\partial q_3} \tag{2}$$

where the $\mathbf{\hat{u}_i}$ are unit vectors in the q_i directions.

The divergence $\nabla \cdot \mathbf{A}$ represents the limiting value of the net outward flux of the vector quantity $\mathbf{A}$ per unit volume. Referring to Fig. 2, the net flux of the component A_1 in the q_1-direction is given by the difference bet-

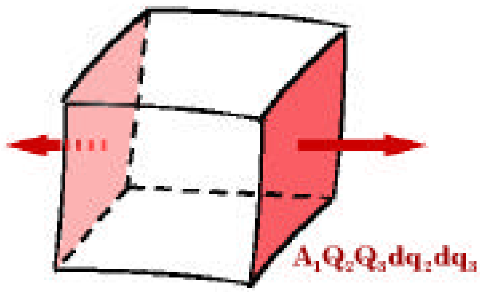

Figure 2. Evaluation of divergence in curvilinear coordinates.

ween the *outward* contributions $Q_2 Q_3 A_1\, dq_2 dq_3$ on the two shaded faces. As the volume element approaches a point, this reduces to

$$\frac{\partial (Q_2 Q_3 A_1)}{\partial q_1} dq_1 dq_2 dq_3$$

Adding the analogous contributions from the q_2- and q_3-directions and diving by the volume $d\tau$, we obtain the general result for the divergence in curvilinear coordinates

$$\nabla \cdot \mathbf{A} = \frac{1}{Q_1 Q_2 Q_3} \left[\frac{\partial}{\partial q_1} Q_2 Q_3 A_1 + \frac{\partial}{\partial q_2} Q_3 Q_1 A_2 + \frac{\partial}{\partial q_3} Q_1 Q_2 A_3 \right] \tag{3}$$

The Laplacian is the divergence of the gradient:

$$\nabla^2 f = \nabla \cdot \nabla f$$

Thus, substitution of (2) into (3) gives the operator relation

$$\nabla^2 = \frac{1}{Q_1 Q_2 Q_3} \left[\frac{\partial}{\partial q_1} \frac{Q_2 Q_3}{Q_1} \frac{\partial}{\partial q_1} + \frac{\partial}{\partial q_2} \frac{Q_3 Q_1}{Q_2} \frac{\partial}{\partial q_2} + \frac{\partial}{\partial q_3} \frac{Q_1 Q_2}{Q_3} \frac{\partial}{\partial q_3} \right] \tag{4}$$

For spherical polar coordinates, we identify

$$q_1 = r,\ q_2 = \theta,\ q_3 = \phi$$

and

$$Q_1 = 1,\ Q_2 = r,\ Q_3 = r \sin\theta$$

Therefore, we obtain the volume element

$$d\tau = r^2 \sin\theta\, dr d\theta d\phi \tag{5}$$

and the Laplacian operator

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{1}{r^2 \sin\theta} \frac{\partial}{\partial \theta} \sin\theta \frac{\partial}{\partial \theta} + \frac{1}{r^2 \sin^2\theta} \frac{\partial^2}{\partial \phi^2} \tag{6}$$