Appendix EE

The Radial Equation for Hydrogen

The operators describing atomic electrons can generally be separated into radial and angular parts. As we have seen in Appendix AA, the angular part of the Laplacian operator is related to the angular momentum operator $\mathbf{l}^2$. Equation (AA.11) expresses the Laplacian operator in terms of its radial and angular parts.

We consider now the effect of the Laplacian operator (AA.11) upon the wave function of the hydrogen atom. Using the form of the atomic wave function and the spherical harmonics introduced in Section 4.1.3, the wave function of hydrogen can be written

$$\psi(r,\theta,\phi) = \frac{P(r)}{r} Y_{lm_l}(\theta,\phi). \tag{EE.1}$$

The spherical harmonic $Y_{lm_l}(\theta,\phi)$ is an eigenfunction of the angular momentum operator $\mathbf{l}^2$ corresponding to the eigenvalue $l(l+1)\hbar^2$.

We consider first the effect of the first term on the right-hand side of Eq. (AA.11) upon the wave function (EE.1). Taking the partial derivate with respect to r does not affect the spherical harmonic. So we must evaluate the result of operating successively upon the function $P(r)/r$ with the partial derivative, then with r^2 and the partial derivative, and finally multiplying with $1/r^2$. Operating upon $P(r)/r$ with the partial derivative gives

$$\frac{\partial}{\partial r}\left(\frac{P}{r}\right) = \frac{\partial(r^{-1}P)}{\partial r} = \frac{1}{r}\frac{\mathrm{d}P}{\mathrm{d}r} - \frac{1}{r^2}P. \tag{EE.2}$$

Multiplying this equation by r^2 and taking the partial derivative with respect to r, then gives

$$\frac{\partial}{\partial r}\left[r^2 \frac{\partial}{\partial r}\left(\frac{P}{r}\right)\right] = r\frac{\mathrm{d}^2P}{\mathrm{d}r^2}. \tag{EE.3}$$

Finally, dividing by r^2, we obtain

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2 \frac{\partial}{\partial r}\left(\frac{P}{r}\right)\right] = \frac{1}{r}\frac{\mathrm{d}^2P}{\mathrm{d}r^2}. \tag{EE.4}$$

Operating with the first term on the right-hand side of Eq. (AA.11) upon the wave function (EE.1) thus gives

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)\psi(r,\theta,\phi) = \frac{1}{r}\frac{\mathrm{d}^2P}{\mathrm{d}r^2}\, Y_{lm_l}(\theta,\phi). \tag{EE.5}$$

Similarly, operating with the second term on the right-hand side of Eq. (AA.11) upon the wave function (EE.1) and taking advantage of the fact that $Y_{lm_l}(\theta,\phi)$ is an eigenfunction of $\mathbf{l}^2$ corresponding to the eigenvalue $l(l+1)\hbar^2$, we obtain

$$-\frac{\mathbf{l}^2}{\hbar^2\, r^2}\,\psi(r,\theta,\phi) = -\frac{l(l+1)}{r^2}\,\frac{P(r)}{r}Y_{lm_l}(\theta,\phi). \tag{EE.6}$$

The effect of multiplying the Laplacian operator (AA.11) upon the hydrogen wave function (EE.1) can be evaluated using Eqs. (EE.5) and (EE.6). This leads to the result

$$\nabla^2\,\psi(r,\theta,\phi) = \frac{1}{r}\frac{\mathrm{d}^2P}{\mathrm{d}r^2}\, Y_{lm_l}(\theta,\phi) - \frac{l(l+1)}{r^2}\,\frac{P(r)}{r}Y_{lm_l}(\theta,\phi). \tag{EE.7}$$

The Schrödinger equation for the electron of a hydrogen atom is given by Eq. (4.2). Substituting the hydrogen wave function (EE.1) into the Schrödinger equation and using Eq. (EE.7) to evaluate the effect of the Laplacian operator upon the wave function, we obtain

$$-\frac{\hbar^2}{2m}\frac{1}{r}\frac{d^2P}{dr^2}\,Y_{lm_l}(\theta,\phi)+\frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\,\frac{P(r)}{r}Y_{lm_l}(\theta,\phi)-\frac{1}{4\pi\epsilon_0}\,\frac{Ze^2}{r}\,\frac{P(r)}{r}Y_{lm_l}(\theta,\phi)=E\frac{P(r)}{r}Y_{lm_l}(\theta,\phi). \quad \text{(EE.8)}$$

The radial equation (4.5) is obtained from the above equation by deleting $(1/r)Y_{lm_l}(\theta,\phi)$ from each term.