Continuum wave functions

1 Normalization

1.1 Basics

The most basic implementation of the normalization of continuum eigenfunctions is as follows. Let an observable $\hat{A}$ have discrete eigenvalues a_n and continuum eigenvalues a, with respective eigenfunctions $\psi_n(\mathbf{r})$ and $\psi_a(\mathbf{r})$. An arbitrary wave function $\psi(\mathbf{r})$ can be expanded as

$$\psi(\mathbf{r}) = \sum_n c_n \, \psi_n(\mathbf{r}) + \int c_a \, \psi_a(\mathbf{r}) \, da, \tag{1}$$

where the sum is taken over the discrete spectrum and the integral over the continuous spectrum. in Dirac notation,

$$|\psi\rangle = \sum_n c_n \, |\psi_n\rangle + \int da \, c_a \, |\psi_a\rangle. \tag{2}$$

Since the sum of the probability of all possible values of A must be equal to one, we have

$$\sum_n |c_n|^2 + \int |c_a|^2 \, da = 1. \tag{3}$$

We can obtain the coefficients from the wave function by means of

$$c_n = \langle \psi_n | \psi \rangle \equiv \int \psi_n^*(\mathbf{r}) \, \psi(\mathbf{r}) \, d^3r, \tag{4}$$

$$c_a = \langle \psi_a | \psi \rangle \equiv \int \psi_a^*(\mathbf{r}) \, \psi(\mathbf{r}) \, d^3r. \tag{5}$$

The normalization conditions are

$$\langle \psi_{n'} | \psi_n \rangle \equiv \int \psi_{n'}^*(\mathbf{r}) \, \psi_n(\mathbf{r}) \, d^3r = \delta_{n'n}, \tag{6}$$

$$\langle \psi_{n'} | \psi_a \rangle \equiv \int \psi_{n'}^*(\mathbf{r}) \, \psi_a(\mathbf{r}) \, d^3r = 0, \tag{7}$$

$$\langle \psi_{a'} | \psi_a \rangle \equiv \int \psi_{a'}^*(\mathbf{r}) \, \psi_a(\mathbf{r}) \, d^3r = \delta(a' - a). \tag{8}$$

One expresses the last normalization condition by saying that the continuum eigenfunctions are normalized on the a scale. The continuum eigenfunctions are orthogonal to the discrete eigenfunctions. The completeness relation is

$$\sum_n \psi_n(\mathbf{r}) \, \psi_n^*(\mathbf{r}') + \int \psi_a(\mathbf{r}) \, \psi_a^*(\mathbf{r}') \, da = \delta(\mathbf{r}' - \mathbf{r}). \tag{9}$$

In Dirac notation,

$$\sum_n |\psi_n\rangle \langle \psi_n| + \int da \, |\psi_a\rangle \langle \psi_a| = 1. \tag{10}$$

The expectation value of each operator in the left hand side on a state $|\psi\rangle$ gives the probability of having the respective eigenvalue in state $|\psi\rangle$. Thus the probability to have eigenvalue a_n in state $|\psi\rangle$ is

$$\text{Prob}(a_n;\psi) = \langle\psi|\psi_n\rangle\,\langle\psi_n|\psi\rangle = |\langle\psi_n|\psi\rangle|^2, \tag{11}$$

and the probability to have eigenvalue in the range $(a,\, a+da)$ is

$$\text{Prob}(a;\psi) = \langle\psi|\psi_a\rangle\,\langle\psi_a|\psi\rangle\, da = |\langle\psi_a|\psi\rangle|^2\, da. \tag{12}$$

The completeness relation can be taken as the basic relation from which the other normalization conditions can be derived. For example, multiply Eq. (10) by $\langle\psi_{a'}|$ to obtain

$$\int da\,\langle\psi_{a'}|\psi_a\rangle\,\langle\psi_a| = \langle\psi_{a'}|, \tag{13}$$

from which

$$\langle\psi_{a'}|\psi_a\rangle = \delta(a'-a) \tag{14}$$

follows.

1.2 Other normalizations

The continuum eigenfunctions can also be parametrized by a variable α related to the eigenvalue a in a one-to-one manner. For example, using the energy in place of the magnitude of the momentum, or the wave number in place of the momentum. In this case, one wants to change the integration in da to an integration in $d\alpha$. At the same time one may or may not change the normalization of the continuum eigenfunctions. There is often ambiguity of notation. The fundamental relation that must not change is the completeness relation (10). One must have, for example,

$$\int da\,|\psi_a\rangle\,\langle\psi_a| = \int d\alpha\,\frac{da}{d\alpha}\,|\psi_{a(\alpha)}\rangle\,\langle\psi_{a(\alpha)}|, \tag{15}$$

where $|\psi_{a(\alpha)}\rangle = |\psi_a\rangle$ denotes the continuum eigenfunction $|\psi_a\rangle$ (no change in normalization) with the eigenvalue a expressed in terms of the parameter α. One can split the term $da/d\alpha$ into a factor μ_α attached to the integration measure $\mu_\alpha\, d\alpha$, and a (real-valued) factor N_α that changes the normalization of the continuum eigenfunctions. Thus

$$\frac{da}{d\alpha} = \mu_\alpha\, N_\alpha, \tag{16}$$

$$|\psi_\alpha\rangle = \sqrt{N_\alpha}\,|\psi_{a(\alpha)}\rangle, \tag{17}$$

$$\int da\,|\psi_a\rangle\,\langle\psi_a| = \int d\alpha\,\mu_\alpha\,|\psi_\alpha\rangle\,\langle\psi_\alpha|. \tag{18}$$

The following relations follow.

$$\sum_n |\psi_n\rangle\,\langle\psi_n| + \int d\alpha\,\mu_\alpha\,|\psi_\alpha\rangle\,\langle\psi_\alpha| = 1, \tag{19}$$

$$\langle\psi_{\alpha'}|\psi_\alpha\rangle = \frac{1}{\mu_\alpha}\,\delta(\alpha'-\alpha), \tag{20}$$

$$|\psi\rangle = \sum_n c_n\,|\psi_n\rangle + \int d\alpha\,\mu_\alpha\, c_\alpha\,|\psi_\alpha\rangle. \tag{21}$$

$$c_\alpha = \langle\psi_\alpha|\psi\rangle. \tag{22}$$

From the completeness relation in Eq. (19), one obtains the probability to have eigenvalue a_n in state $|\psi\rangle$ as

$$\mathrm{Prob}(a_n;\psi) = \langle\psi|\psi_n\rangle\,\langle\psi_n|\psi\rangle = |\langle\psi_n|\psi\rangle|^2, \tag{23}$$

and the probability that the parameter α is in the range $(\alpha,\,\alpha+d\alpha)$ as

$$\mathrm{Prob}(\alpha;\psi) = \langle\psi|\psi_\alpha\rangle\,\langle\psi_\alpha|\psi\rangle\,\mu_\alpha\,d\alpha = |\langle\psi_\alpha|\psi\rangle|^2\,\mu_\alpha\,d\alpha. \tag{24}$$

If $\mu_\alpha = 1$, one says that the eigenfunctions $|\psi_\alpha\rangle$ are normalized on the α scale, $\langle\psi_{\alpha'}|\psi_\alpha\rangle = \delta(\alpha'-\alpha)$. The most common normalizations use the momentum scale, the wave number scale (also called the k scale), the reduced wave number scale (called the $k/2\pi$ scale), and the energy scale.

2 Normalization by means of the asymptotic form

Given some unnormalized continuum eigenfunctions $X_\alpha(\mathbf{r})$, it may be rather complicated to compute the normalization integral

$$\int X^*_{\alpha'}(\mathbf{r})\,X_\alpha(\mathbf{r})\,d^3r. \tag{1}$$

In one-dimensional problems and in problems with central potentials, the following method is available for normalizing continuum eigenfunctions that behave sinusoidally at large distances directly from their asymptotic expression at large values of $R = |\mathbf{r}|$ (Landau–Lifshitz, section 21).

The normalization integral diverges as $R \to \infty$, and to find the normalization constant one can replace $X_\alpha(\mathbf{r})$ by its asymptotic form at large R, and perform the integration in r taking as lower limit any finite value of r, say zero. This amounts to neglecting a finite quantity in comparison with an infinite one. Suppose for example that the asymptotic behavior of the unnormalized eigenfunction in a central potential is

$$X_{klm}(r,\theta,\phi) \approx \frac{A_{kl}}{r}\,\sin(kr-\varphi_l)\,Y_{lm}(\theta,\phi). \tag{2}$$

Introduce the normalized eigenfunction

$$\psi_{klm} = C_{kl}\,X_{klm}. \tag{3}$$

Then

$$\int \psi^*_{k'l'm'}(\mathbf{r})\,\psi_{klm}(\mathbf{r})\,d^3r = \delta_{ll'}\,\delta_{mm'}\,C^*_{k'l}\,C_{kl}\,A^*_{k'l}A_{kl}\int_0^\infty \sin(k'r-\varphi_l)\,\sin(kr-\varphi_l)\,dr. \tag{4}$$

We are interested only in values of k' close to k. Writing $\sin x$ in terms of $e^{\pm ix}$ and keeping only terms that diverge for $k' = k$ (in other words, omitting terms that contain the factor $e^{\pm i(k+k')r}$),

$$\int_0^\infty \sin(k'r-\varphi_l)\,\sin(kr-\varphi_l)\,dr = \int_0^\infty \frac{e^{ik'r-i\varphi_l}-e^{-ik'r+i\varphi_l}}{2i}\,\frac{e^{ikr-i\varphi_l}-e^{-ikr+i\varphi_l}}{2i}\,dr \tag{5}$$

$$= \frac{1}{4}\int_0^\infty \left[e^{i(k'-k)r}+e^{-i(k'-k)r}\right]\,dr \tag{6}$$

$$= \frac{1}{4}\left[\int_0^\infty e^{i(k'-k)r}\,dr + \int_{-\infty}^0 e^{i(k'-k)r}\,dr\right] \tag{7}$$

$$= \frac{1}{4}\int_{-\infty}^\infty e^{i(k'-k)r}\,dr \tag{8}$$

$$= \frac{\pi}{2}\,\delta(k'-k). \tag{9}$$

Thus

$$\int \psi^*_{k'l'm'}(\mathbf{r})\,\psi_{klm}(\mathbf{r})\,d^3r = \delta_{ll'}\,\delta_{mm'}\,|C_{kl}A_{kl}|^2\,\frac{\pi}{2}\,\delta(k'-k) \tag{10}$$

Thus eigenfunctions normalized on the $k/2\pi$ scale,

$$\int \psi^*_{k'l'm'}(\mathbf{r})\,\psi_{klm}(\mathbf{r})\,d^3r = \delta_{ll'}\,\delta_{mm'}\,2\pi\,\delta(k'-k), \tag{11}$$

are

$$\psi_{klm}(\mathbf{r}) = \frac{2}{A_{kl}}\,X_{klm}(\mathbf{r}), \tag{12}$$

with asymptotic form

$$\psi_{klm}(\mathbf{r}) \approx \frac{2}{r}\,\sin(kr-\varphi_l)\,Y_{lm}(\theta,\phi). \tag{13}$$

For reference, eigenfunctions normalized on the k scale are

$$\int \psi^{k\text{-scale}*}_{k'l'm'}(\mathbf{r})\,\psi^{k\text{-scale}}_{klm}(\mathbf{r})\,d^3r = \delta_{ll'}\,\delta_{mm'}\,\delta(k'-k), \tag{14}$$

are

$$\psi^{k\text{-scale}}_{klm}(\mathbf{r}) = \frac{1}{\sqrt{2\pi}}\,\psi_{klm}(\mathbf{r}) \tag{15}$$

with asymptotic form

$$\psi^{k\text{-scale}}_{klm}(\mathbf{r}) \approx \sqrt{\frac{2}{\pi}}\,\frac{1}{r}\,\sin(kr-\varphi_l)\,Y_{lm}(\theta,\phi). \tag{16}$$

And eigenfunctions ψ_{Elm} normalized on the energy scale $E = k^2\hbar^2/(2m)$,

$$\int \psi^*_{E'l'm'}(\mathbf{r})\,\psi_{Elm}(\mathbf{r})\,d^3r = \delta_{ll'}\,\delta_{mm'}\,\delta(E'-E), \tag{17}$$

are

$$\psi_{Elm}(\mathbf{r}) = \frac{1}{\sqrt{2\pi\hbar v}}\,\psi_{klm}(\mathbf{r}), \tag{18}$$

where $v = k\hbar/m$, with asymptotic form

$$\psi_{klm}(\mathbf{r}) \approx \sqrt{\frac{2}{\pi\hbar v}}\,\frac{1}{r}\,\sin(kr-\varphi_l)\,Y_{lm}(\theta,\phi). \tag{19}$$

3 Energy eigenfunctions for a free particle

3.1 Eigenfunctions of energy and linear momentum (plane waves)

Eigenfunctions of energy and linear momentum are parametrized by the 3-momentum $\mathbf{p}$ or the wave vector $\mathbf{k} = \mathbf{p}/\hbar$. They are commonly normalized according to one of the following scales.

On the momentum scale: $\psi_{\mathbf{p}} = \frac{1}{(2\pi\hbar)^{3/2}}\,e^{i\mathbf{p}\cdot\mathbf{r}/\hbar}$, $\int \psi^*_{\mathbf{p}'}\,\psi_{\mathbf{p}}\,d^3r = \delta(\mathbf{p}'-\mathbf{p})$. (1)

On the reduced wave number scale: $\psi_{\mathbf{k}} = e^{i\mathbf{k}\cdot\mathbf{r}}$, $\int \psi^*_{\mathbf{k}'}\,\psi_{\mathbf{k}}\,d^3r = (2\pi)^3\,\delta(\mathbf{k}'-\mathbf{k})$. (2)

Since momentum eigenfunctions with momenta $\mathbf{p}$ and $-\mathbf{p}$ correspond to the same energy $E = p^2/(2m)$, any of their linear combinations is an energy eigenfunction with eigenvalue E. In particular, so are the real functions

$$\cos(\mathbf{k}\cdot\mathbf{r}) = \mathrm{Re}\, e^{i\mathbf{k}\cdot\mathbf{r}} = \frac{e^{i\mathbf{k}\cdot\mathbf{r}} + e^{-i\mathbf{k}\cdot\mathbf{r}}}{2}, \tag{3}$$

$$\sin(\mathbf{k}\cdot\mathbf{r}) = \mathrm{Im}\, e^{i\mathbf{k}\cdot\mathbf{r}} = \frac{e^{i\mathbf{k}\cdot\mathbf{r}} - e^{-i\mathbf{k}\cdot\mathbf{r}}}{2i}. \tag{4}$$

Of course,

$$e^{i\mathbf{k}\cdot\mathbf{r}} = \cos(\mathbf{k}\cdot\mathbf{r}) + i\,\sin(\mathbf{k}\cdot\mathbf{r}). \tag{5}$$

When the time dependence is reinserted, the functions $e^{i\mathbf{k}\cdot\mathbf{r}-i\omega t}$, where $E = \hbar\omega$, have surfaces of constant phase ("wave fronts") moving in the direction of $\mathbf{k}$ with phase velocity ω/k, while the functions $\cos(\mathbf{k}\cdot\mathbf{r})$ and $\sin(\mathbf{k}\cdot\mathbf{r})$ have stationary wave fronts ("standing waves").

3.2 Eigenfunctions of energy and angular momentum (spherical waves)

Free particle wave functions in spherical coordinates are presented for example in Section 33 of Landau & Lifshitz. They are

$$\psi_{klm}(r,\theta,\phi) = R_{kl}(r)\, Y_{lm}(\theta,\phi), \tag{6}$$

where in the $k/2\pi$ scale

$$R_{kl}(r) = 2k j_l(kr). \tag{7}$$

Here k is the wave number, related to the energy as $E = k^2\hbar^2/(2m)$, and $j_l(x)$ is the spherical Bessel function

$$j_l(x) = \sqrt{\frac{\pi}{2x}}\, J_{l+1/2}(x), \tag{8}$$

where $J_\alpha(x)$ is the Bessel function of the first kind. The first few spherical Bessel functions are

$$j_0(x) = \frac{\sin x}{x}, \qquad j_1(x) = \frac{\sin x}{x^2} - \frac{\cos x}{x}, \qquad j_3(x) = \left(\frac{3}{x^3} - \frac{1}{x}\right)\sin x - \frac{3\cos x}{x^2}. \tag{9}$$

The asymptotic form of the radial wave functions at large r is

$$R_{kl} \approx \frac{2\sin(kr - \frac{1}{2}l\pi)}{r} = \frac{e^{ikr - \frac{i}{2}l\pi} - e^{-ikr + \frac{i}{2}l\pi}}{r} \tag{10}$$

In analogy to "standing" and "moving" plane waves for energy and momentum eigenfunctions, one introduces "outgoing" and "incoming" spherical waves with asymptotic behavior e^{ikr} and e^{-ikr}, respectively. In the reduced momentum scale they are given by

$$R^+_{kl}(r) = k h_l^{(1)}(kr), \qquad R^-_{kl}(r) = k h_l^{(2)}(kr), \tag{11}$$

respectively, where $h_l^{(1)}(x)$ and $h_l^{(2)}(x)$ are the spherical Hankel functions of the first and second kind. The first few spherical Hankel functions are

$$h_0^{(1)}(x) = -i\frac{e^{ix}}{x}, \quad h_1^{(1)}(x) = -\frac{(x+i)e^{ix}}{x^2}, \quad h_2^{(1)}(x) = i\frac{(x^2 - 3 + 3ix)e^{ix}}{x^3}; \tag{12}$$

$$h_0^{(2)}(x) = i\frac{e^{-ix}}{x}, \quad h_1^{(2)}(x) = -\frac{(x-i)e^{-ix}}{x^2}, \quad h_2^{(2)}(x) = -i\frac{(x^2 - 3 - 3ix)e^{-ix}}{x^3}. \tag{13}$$

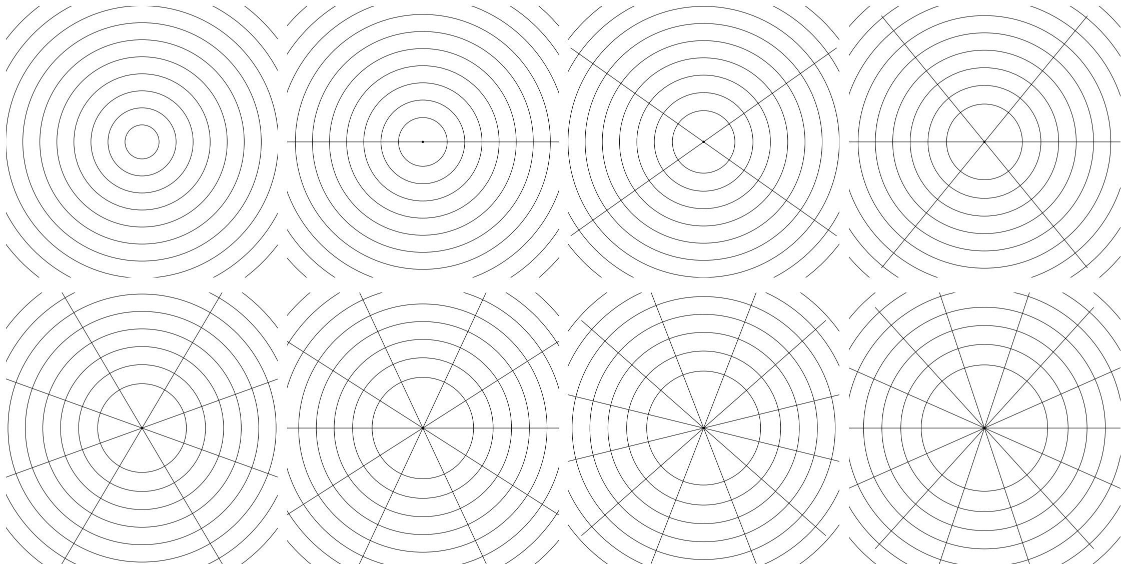

Figure 1: Nodes of the free particle standing waves R_{kl0} for $l = 0, \ldots, 7$ (from top left) in the xz plane.

For real x, one has $j_l(x) = \mathrm{Re}\, h_l^{(1)}(x)$ and $h_l^{(2)}(x) = [h_l^{(1)}(x)]^*$. Thus $R_{kl} = \mathrm{Re}\, R_{kl}^+$. The imaginary part of R_{kl}^+ is singular at $r = 0$ and does not appear as a solution for the free particle. It appears however in scattering problems off a finite-range central potential, in which free-particle spherical waves are used outside the region with nonzero potential.

4 Energy eigenfunctions for a Coulomb potential

In a Coulomb potential $V = -Ze^2/(4\pi\epsilon_0 r)$, there are discrete energy eigenstates (bound states) and continuum energy eigenstates (scattering states).

Bound state wave functions in spherical coordinates for the n-th energy level $E_n = E_1/n^2$ (with $E_1 = -mc^2\alpha^2/2$ where $\alpha = e^2/(4\pi\hbar c) \simeq 1/137$ is the fine structure constant) are of the form

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r)\, Y_{lm}(\theta, \phi). \tag{1}$$

The bound state radial wave functions are

$$R_{nl}(r) = \frac{2}{a_0^{3/2} n^2 (2l+1)!} \sqrt{\frac{(n+l)!}{(n-l-1)!}}\, \rho^l\, e^{-\rho/2}\, {}_1F_1(-n+l+1; 2l+2; \rho), \tag{2}$$

$$= \frac{2}{a_0^{3/2} n^2} \sqrt{\frac{(n-l-1)!}{(n+l)!}}\, e^{-\rho/2}\, \rho^l\, L_{n-l-1}^{2l+1}(\rho), \tag{3}$$

Here $\rho = (2r)/(na_0)$, $a_0 = \hbar/(mc\alpha)$. (For the hydrogen atom, the quantity a_0 is equal to the Bohr radius). The functions $L_n^m(\rho)$ are the associated Laguerre polynomials. The function ${}_1F_1(\alpha; \gamma; z)$ is the confluent hypergeometric function

$${}_1F_1(\alpha; \gamma; z) = 1 + \frac{\alpha}{1!\gamma} z + \frac{\alpha(\alpha+1)}{2!\gamma(\gamma+1)} z^2 + \cdots . \tag{4}$$

Continuum wave functions in spherical coordinates are presented for example in Section 36 of Landau & Lifshitz. They are

$$\psi_{klm}(r, \theta, \phi) = R_{kl}(r)\, Y_{lm}(\theta, \phi), \tag{5}$$

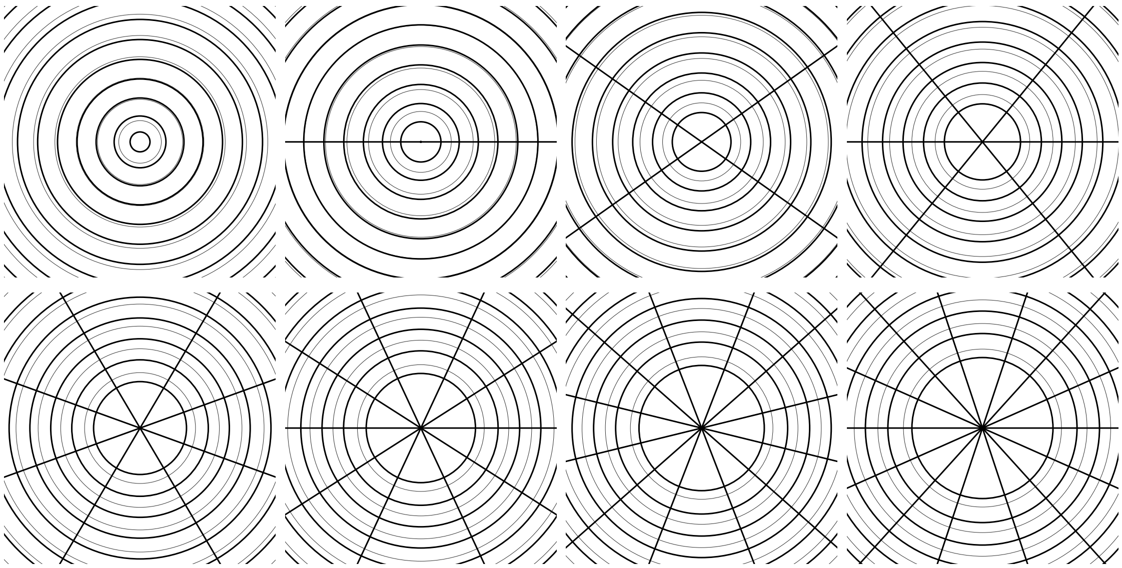

Figure 2: Nodes of the Coulomb standing waves R_{kl0} (in black) for $k = 1/a$ (i.e., $\eta = 1$) and $l = 0, \ldots, 7$ (from top left) in the xz plane, compared with the nodes of the free particle standing waves with the same k and l (in gray). The nodes of the Coulomb waves are closer to the center (attractive potential).

where

$$R_{kl}(r) = \frac{C_{kl}}{(2l+1)!} (2kr)^l e^{-ikr} {}_1F_1(l+1+i\eta; 2l+2; 2ikr). \tag{6}$$

Here k is the wave number, related to the energy as $E = k^2\hbar^2/(2m)$, with m the reduced mass, and $\eta = Z/(ka_0)$. In the $k/2\pi$ scale,

$$C_{kl} = 2ke^{\eta\pi/2}|\Gamma(l+1-i\eta)| = 2k\sqrt{\frac{2\pi\eta}{1-e^{-2\pi\eta}}} \prod_{s=1}^{l} \sqrt{s^2+\eta^2}, \tag{7}$$

where for $l = 0$ the product is replaced by unity. The asymptotic expression of R_{kl} at large r is

$$R_{kl} \approx \frac{2}{r} \sin\left(kr + \eta\log(2kr) - \tfrac{1}{2}l\pi + \delta_l\right), \tag{8}$$

where the Coulomb phase shift is

$$\delta_l = \arg\Gamma(l+1-i\eta). \tag{9}$$

When $\eta \to 0$, one recovers the free particle radial wave functions,

$$R_{kl}(r) = 2kj_l(kr) \qquad (\eta = 0). \tag{10}$$

Here we used the identity

$$j_l(z) = \frac{l!}{(2l+1)!} (2z)^l e^{-iz} {}_1F_1(l+1; 2l+2; 2iz). \tag{11}$$

Incoming and outgoing spherical Coulomb waves can also be defined by their asymptotic $e^{\mp ikr}$ behavior. One has incoming Coulomb waves

$$R_{kl}^{-} = C_{kl} \, \frac{e^{-\pi\eta/2}}{\Gamma(l+1-i\eta)} \, \frac{e^{-i[kr-(l+1)\pi/2+\eta\log(2kr)]}}{kr} \, {}_2F_0(l+1+i\eta, i\eta-l; \tfrac{i}{2kr}), \tag{12}$$

and outgoing Coulomb waves

$$R_{kl}^{+} = C_{kl} \, \frac{e^{-\pi\eta/2}}{\Gamma(l+1+i\eta)} \, \frac{e^{+i[kr-(l+1)\pi/2+\eta\log(2kr)]}}{kr} \, {}_2F_0(l+1-i\eta, -i\eta-l; -\tfrac{i}{2kr}). \tag{13}$$

Here ${}_2F_0(\alpha, \beta; z)$ is the generalized hypergeometric function

$${}_2F_0(\alpha, \beta; z) = 1 + \frac{\alpha\beta}{1!} z + \frac{\alpha(\alpha+1)\beta(\beta+1)}{2!} z^2 + \cdots . \tag{14}$$

References

Landau, L.D. & Lifshitz, E.M. *Quantum Mechanics: Non-Relativistic Theory* (Pergamon Press, 3rd ed.,1977). Section 5 contains a lucid description of the normalization of operator eigenfunctions in the continuum. Sections 21 and 33 contain the method of normalizing the wave functions using their asymptotic form at large radii. Section 33 deals with radial wave functions for a free particle. Section 36 is about radial wave functions in a Coulomb potential in spherical coordinates.

Sakurai, J.J. & Napolitano, J. *Modern Quantum Mechanics* (Addison-Wesley, 2nd ed., 2010).