Free-Particle Continuum Density

W. R. Johnson

March 5, 2003

1 Bound and Continuum States

Let us suppose that the orbital wave functions for an electron in a potential $V(r)$ are given by

$$\begin{aligned} \phi_{nlm\sigma}(\vec{r}) &= \frac{1}{r}\, P_{nl}(r)\, Y_{lm}(\hat{r})\, \chi_\sigma \qquad \text{bound} && (1) \\ \phi_{\epsilon lm\sigma}(\vec{r}) &= \frac{1}{r}\, P_{\epsilon l}(r)\, Y_{lm}(\hat{r})\, \chi_\sigma \qquad \text{continuum} && (2) \end{aligned}$$

where the radial functions are normalized as

$$\begin{aligned} \int_0^\infty dr P_{nl}(r)\, P_{n'l}(r) &= \delta_{nn'} && (3) \\ \int_0^\infty dr P_{\epsilon l}(r)\, P_{\epsilon' l}(r) &= \delta(\epsilon - \epsilon'). && (4) \end{aligned}$$

For the free-particle case, we may write

$$P_{\epsilon l}(r) = \sqrt{\frac{2m}{\pi p}}\, pr\, j_l(pr) \qquad (5)$$

with $p = \sqrt{2m\epsilon}$.

Now let us consider the density, $\rho(\vec{r})$ assumed to be spherically symmetric $\rho(\vec{r}) \equiv \rho(r)$. The contribution to the density from bound states is

$$4\pi r^2 \rho_{\text{bound}}(r) = \sum_{nl} \frac{2(2l+1)}{1 + e^{(\epsilon_{nl} - \mu)/kT}}\; P_{nl}^2(r), \qquad (6)$$

and similarly, the contribution from continuum states is

$$4\pi r^2 \rho_{\text{contin}}(r) = \sum_l \int_0^\infty d\epsilon\, \frac{2(2l+1)}{1 + e^{(\epsilon - \mu)/kT}}\; P_{\epsilon l}^2(r). \qquad (7)$$

1.1 Free-Particle Continuum

Assuming that the continuum wave functions are approximated as free-particle states, them we may write

$$4\pi r^2 \rho_{\rm contin}(r) \approx \sum_l \int_0^\infty d\epsilon \, \frac{2(2l+1)}{1+e^{(\epsilon-\mu)/kT}} \, \frac{2m\,(pr)^2}{p\pi} j_l^2(pr) \tag{8}$$

$$= \frac{4mr^2}{\pi} \int_0^\infty p\, d\epsilon \, \frac{1}{1+e^{(\epsilon-\mu)/kT}} \, \sum_l (2l+1) j_l^2(pr) \tag{9}$$

$$= \frac{2r^2(2mkT)^{3/2}}{\pi} \int_0^\infty y^{1/2} dy \, \frac{1}{1+e^{y-x}} \tag{10}$$

where $y = \epsilon/kT$ and $x = \mu/kT$, and where we have used the identity

$$\sum_l (2l+1) j_l^2(pr) = 1. \tag{11}$$

This corresponds to a constant density

$$\rho_{\rm contin}(r) = \frac{(2mkT)^{3/2}}{2\pi^2} I_{1/2}(x), \tag{12}$$

with $x = \mu/kT$. The Thomas-Fermi expression for the density is Eq. (12) with

$$x \to x(r) = [\mu - V(r)]/kT. \tag{13}$$

Blenski and Ishikawa [2] recommend that one evaluate the continuum contribution as

$$\rho_{\rm contin} = \frac{1}{4\pi r^2} \sum_l \int_0^\infty d\epsilon \, \frac{2(2l+1)}{1+e^{(\epsilon-\mu)/kT}} \, \left[P_{\epsilon l}^2(r) - P_{\epsilon l \, {\rm free}}^2(r)\right] + \frac{(2mkT)^{3/2}}{2\pi^2} I_{1/2}(x). \tag{14}$$

They assert that the partial wave sum in the first term in this expression converges rapidly.

1.2 Nonrelativistic Problem

Let's start with the radial Schrödinger equation

$$\frac{d^2 P_l}{dr^2} + 2\left(E - V(r) - \frac{l(l+1)}{2r^2}\right) P_l = 0 \tag{15}$$

In the field-free region, $V = 0$, we may rewrite this equation as

$$\frac{d^2 P_l}{dr^2} + \left(p^2 - \frac{l(l+1)}{r^2}\right) P_l = 0, \tag{16}$$

where we express the energy in terms of momentum through $E = p^2/2$. Two independent solutions to this equation are $P_l(r) = pr\, j_l(pr)$ and $P_l(r) = pr\, y_l(pr)$, where j_l and y_l are spherical Bessel and Hankel functions, respectively [1]. The general solution to the radial equation in the field-free region may be written as a linear combination of the two independent solutions:

$$P_l(r) = \mathcal{N}_l \; [pr\, j_l(pr) \cos\delta_l - pr\, y_l(pr) \sin\delta_l] \,. \tag{17}$$

This solution has the asymptotic limit

$$\lim_{r\to\infty} P_l(r) = \mathcal{N}_l \cos\Big(pr + \delta_l - (l+1)\frac{\pi}{2}\Big), \tag{18}$$

and leads to the interpretation of δ_l as the continuum wave phase shift.

We integrate the radial Schrödinger equation outward from the origin to the cavity boundary $r = R$ and match the solution and it's derivative to the corresponding free-particle radial wave function and derivative:

$$P_l(R) \;=\; \mathcal{N}_l \Big[x\, j_l(x) \cos\delta_l - x\, y_l(x) \sin\delta_l\Big] \tag{19}$$

$$\frac{1}{p} Q_l(R) \;=\; \mathcal{N}_l \Big[\frac{d[x\, j_l(x)]}{dx} \cos\delta_l - \frac{d[x\, y_l(x)]}{dx} \sin\delta_l\Big], \tag{20}$$

where $x = pR$. Solving, we find

$$\mathcal{N}_l \sin\delta_l \;=\; \frac{d[x\, j_l(x)]}{dx} P_l(R) - x\, j_l(x) \frac{1}{p} Q_l(R) \tag{21}$$

$$\mathcal{N}_l \cos\delta_l \;=\; \frac{d[x\, y_l(x)]}{dx} P_l(R) - x\, y_l(x) \frac{1}{p} Q_l(R), \tag{22}$$

where we have made use of the identity

$$x\, j_n(x)\, \frac{d[x\, y_n(x)]}{dx} - x\, y_n(x)\, \frac{d[x\, j_n(x)]}{dx} = 1. \tag{23}$$

If we define

$$\begin{aligned} S_l &= \frac{d[x\, j_l(x)]}{dx} P_l(R) - x\, j_l(x) \frac{1}{p} Q_l(R) \\ &= (l+1) j_l(x) P_l(R) - x \left[j_{l+1}(x) P_l(R) + j_l(x) \frac{1}{p} Q_l(R) \right] \end{aligned} \tag{24}$$

$$\begin{aligned} C_l &= \frac{d[x\, y_l(x)]}{dx} P_l(R) - x\, y_l(x) \frac{1}{p} Q_l(R) \\ &= (l+1) y_l(x) P_l(R) - x \left[y_{l+1}(x) P_l(R) + y_l(x) \frac{1}{p} Q_l(R) \right], \end{aligned} \tag{25}$$

where we have used the identity

$$\frac{d[x f_l(x)]}{dx} = (l+1) f_l(x) - x f_{l+1}(x),$$

which holds for both $f_l(x) = j_l(x)$ and $f_l(x) = y_l(x)$. We find

$$\tan \delta_l = \frac{S_l}{C_l}, \tag{26}$$

and

$$\mathcal{N}_l = \sqrt{S_l^2 + C_l^2}. \tag{27}$$

The later result can be used to insure that the radial wave function is properly normalized on the energy scale. To do this, we multiply $P_l(r)$ and $Q_l(r)$ for all r by the factor

$$A = \frac{1}{\mathcal{N}_l}\sqrt{\frac{2}{\pi p}}.$$

The resulting wave function has the desired asymptotic limit

$$\lim_{r\to\infty} P_l(r) = \sqrt{\frac{2}{\pi p}} \cos\left(pr + \delta_l - (l+1)\frac{\pi}{2}\right) \tag{28}$$

1.3 Relativistic Problem

Let's start with the radial Dirac equations

$$\left(V + mc^2\right) G_\kappa + c\left(\frac{d}{dr} - \frac{\kappa}{r}\right) F_\kappa = EG_\kappa \tag{29}$$

$$-c\left(\frac{d}{dr} + \frac{\kappa}{r}\right) G_\kappa + \left(V - mc^2\right) F_\kappa = EF_\kappa. \tag{30}$$

In the field-free region, $V = 0$, we may express F_κ in terms of G_κ through the relation

$$F_\kappa = -\frac{c}{E + mc^2}\left(\frac{d}{dr} + \frac{\kappa}{r}\right) G_\kappa. \tag{31}$$

This leads to

$$-\frac{c^2}{E + mc^2}\left(\frac{d}{dr} - \frac{\kappa}{r}\right)\left(\frac{d}{dr} + \frac{\kappa}{r}\right) G_\kappa - \left(E - mc^2\right) G_\kappa = 0, \tag{32}$$

or, equivalently,

$$\left(\frac{d^2}{dr^2} - \frac{\kappa(\kappa+1)}{r^2}\right) G_\kappa + p^2 G_\kappa = 0. \tag{33}$$

We introduce the independent variable $x = pr$ and note that $\kappa(\kappa+1) = l(l+1)$, where $l = l(\kappa)$. We then write $G_\kappa(r) = x f_l(x)$. We find that $f_l(x)$ satisfies

$$x^2\frac{d^2 f_l}{dx^2} + 2x\frac{df_l}{dx} + \left[x^2 - l(l+1)\right] f_l = 0. \tag{34}$$

The solutions to this equation are spherical Bessel functions: $j_l(x)$ or $y_l(x)$. Now, let us look at the small-component of the wave function. We write

$$\begin{aligned}
F_\kappa(r) &= -\frac{cp}{E+mc^2}\left(\frac{d}{dx}+\frac{\kappa}{x}\right)xf_l(x) && (35)\\
&= -\sqrt{\frac{E-mc^2}{E+mc^2}}\;x\left(\frac{df_l}{dx}+\frac{1+\kappa}{x}f_l\right) && (36)\\
&= -\sqrt{\frac{E-mc^2}{E+mc^2}}\;x\left(\frac{df_l}{dx}+\frac{l+1}{x}f_l\right) \qquad \text{for } \kappa = l && (37)\\
&= -\sqrt{\frac{E-mc^2}{E+mc^2}}\;x\left(\frac{df_l}{dx}-\frac{l}{x}f_l\right) \qquad \text{for } \kappa = -l-1 && (38)\\
&= -\sqrt{\frac{E-mc^2}{E+mc^2}}\;xf_{l-1}(x) \qquad \text{for } \kappa = l && (39)\\
&= \sqrt{\frac{E-mc^2}{E+mc^2}}\;xf_{l+1}(x) \qquad \text{for } \kappa = -l-1 && (40)\\
&= -\mathrm{Sgn}(\kappa)\sqrt{\frac{E-mc^2}{E+mc^2}}\;xf_{l'}(x), && (41)
\end{aligned}$$

where $l' = l(-\kappa)$.

Generally, in the potential-free region, we may write

$$G_\kappa(r) = \mathcal{N}_\kappa\, pr\left[\cos\delta_\kappa j_l(pr) - \sin\delta_\kappa y_l(pr)\right], \qquad (42)$$

where $\mathcal{N}_\kappa$ is a suitably chosen normalization and δ_κ is a corresponding phase shift. Let us look at the asymptotic form of this function. We have

$$\begin{aligned}
xj_l(x) &\rightarrow \cos\left(pr-(l+1)\frac{\pi}{2}\right) && (43)\\
xy_l(x) &\rightarrow \sin\left(pr-(l+1)\frac{\pi}{2}\right) && (44)
\end{aligned}$$

Therefore,

$$G_\kappa(r) \rightarrow \mathcal{N}_\kappa \cos\left(pr+\delta_\kappa-(l+1)\frac{\pi}{2}\right). \qquad (45)$$

The general small-component wave function is

$$\begin{aligned}
F_\kappa(r) &= -\mathrm{Sgn}(\kappa)\sqrt{\frac{E-mc^2}{E+mc^2}}\;\mathcal{N}_\kappa\, pr\left[\cos\delta_\kappa j_{l'}(pr) - \sin\delta_\kappa y_{l'}(pr)\right] && (46)\\
&\rightarrow \sqrt{\frac{E-mc^2}{E+mc^2}}\;\mathcal{N}_\kappa \sin\left(pr+\delta_\kappa-(l+1)\frac{\pi}{2}\right). && (47)
\end{aligned}$$

On the (relativistic) energy scale, one chooses

$$\mathcal{N}_\kappa = \sqrt{\frac{E+mc^2}{2E}}\sqrt{\frac{2E}{\pi c^2 p}} \qquad (48)$$

then the wave function in the field free region is

$$\left[\begin{array}{c} G_\kappa(r) \\ F_\kappa(r) \end{array}\right] = \sqrt{\frac{2E}{\pi c^2 p}} \left[\begin{array}{r} \sqrt{\frac{E+mc^2}{2E}}\ pr\ \Big(\cos\delta_\kappa j_l(pr) - \sin\delta_\kappa y_l(pr)\Big) \\ -\mathrm{Sgn}(\kappa)\sqrt{\frac{E-mc^2}{2E}}\ pr\ \Big(\cos\delta_\kappa j_{l'}(pr) - \sin\delta_\kappa y_{l'}(pr)\Big) \end{array}\right] \tag{49}$$

Asymptotically, this becomes

$$\left[\begin{array}{c} G_\kappa(r) \\ F_\kappa(r) \end{array}\right] \to \sqrt{\frac{1}{\pi c^2 p}} \left[\begin{array}{c} \sqrt{E+mc^2}\cos\left(pr+\delta_\kappa-(l+1)\frac{\pi}{2}\right) \\ \sqrt{E-mc^2}\sin\left(pr+\delta_\kappa-(l+1)\frac{\pi}{2}\right) \end{array}\right] \tag{50}$$

We suppose that at the boundary $r = R$ the numerically generated solution to the radial Dirac equation has the form

$$A\left[\begin{array}{c} G_\kappa(R) \\ F_\kappa(R) \end{array}\right]$$

where the radial functions $G_\kappa(r)$ and $F_\kappa(r)$ are the properly normalized free-field functions given in Eq. (49). It follows that

$$A\left[\begin{array}{c} G_\kappa(R) \\ F_\kappa(R) \end{array}\right] = \left[\begin{array}{r} \sqrt{\frac{E+mc^2}{\pi c^2 p}}\ pR\ \Big(\cos\delta_\kappa j_l(pR) - \sin\delta_\kappa y_l(pR)\Big) \\ -\mathrm{Sgn}(\kappa)\sqrt{\frac{E-mc^2}{\pi c^2 p}}\ pR\ \Big(\cos\delta_\kappa j_{l'}(pR) - \sin\delta_\kappa y_{l'}(pR)\Big) \end{array}\right] \tag{51}$$

These equations can be solved to give A and $\tan\delta_\kappa$:

$$A = 1/\sqrt{S_\kappa^2 + C_\kappa^2} \tag{52}$$

$$\tan\delta_\kappa = S_\kappa/C_\kappa, \tag{53}$$

where

$$S_\kappa = pR\left[\mathrm{Sgn}(\kappa)\sqrt{\frac{\pi c^2 p}{E+mc^2}} G_\kappa(R) j_{l'}(pR) + \sqrt{\frac{\pi c^2 p}{E-mc^2}} F_\kappa(R) j_l(pR)\right] \tag{54}$$

$$C_\kappa = pR\left[\mathrm{Sgn}(\kappa)\sqrt{\frac{\pi c^2 p}{E+mc^2}} G_\kappa(R) y_{l'}(pR) + \sqrt{\frac{\pi c^2 p}{E-mc^2}} F_\kappa(R) y_l(pR)\right] \tag{55}$$

References

[1] *Handbook of Mathematical Functions*, Ed. M. Abramowitz and I. A. Stegun, National Bureau of Standards Applied Mathematics Series 55, (USGPO, Washington, 1964), Chap. 10.

[2] T. Blenski and K. Ishikawa, Phys. Rev. E **51**, 4869 (1995).