Numerical Integration of Radial Wave Function

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For $\psi(r,\theta,\varphi) = [\chi_\ell(r)/r]\, Y_\ell^m(\theta,\varphi)$,

$$\left\{\frac{d^2}{dr^2} + \left[\frac{2m}{\hbar^2}(E_{n\ell} - V(r)) - \frac{\ell(\ell+1)}{r^2}\right]\right\}\chi_{n\ell}(r) = 0 \qquad (1)$$

We shall normalize the length by the Bohr radius

$$a = \frac{\hbar^2}{me^2} \qquad (2)$$

and the energy by the Rydberg unit

$$Ry = \frac{e^2}{2a} = \frac{me^4}{2\hbar^2} \sim 13.6\,eV \qquad (3)$$

$r = ar'$, $E = \frac{e^2}{2a}E'$

$$\left\{\frac{d^2}{a^2 dr'^2} + \left[\frac{\cancel{2}m}{\hbar^2}\frac{e^2}{\cancel{2}a}{}^{\frac{1}{a}}(E'_{n\ell} - V'(r')) - \frac{\ell(\ell+1)}{a^2 r'^2}\right]\right\}\chi_{n\ell}(r') = 0$$

$$\cancel{\frac{1}{a^2}}\left\{\frac{d^2}{dr'^2} + \left[E'_{n\ell} - V(r') - \frac{\ell(\ell+1)}{r'^2}\right]\right\}\chi_{n\ell}(r') = 0$$

In the Bohr-Rydberg unit,

$$\boxed{\left\{\frac{d^2}{dr^2} + \left[E_{n\ell} - V(r) - \frac{\ell(\ell+1)}{r^2}\right]\right\}\chi_{n\ell}(r) = 0} \qquad (4)$$

– Logarithmic Mesh

To efficiently represent both oscillations at $r \sim 1$ and evanscent behavior for $r \gg 1$, we use a logarithmic mesh, i.e., equispaced points in $x = \log r$.

$$\boxed{\begin{cases} r \equiv \exp(x) & (5) \\ \chi_{nl}(r) \equiv \sqrt{r}\,\phi_{nl}(x) & (6) \end{cases}}$$

$$\frac{d}{dr} = \overbrace{\frac{dx}{dr}}^{(\frac{dr}{dx})^{-1} = e^{-x}}\frac{d}{dx} = e^{-x}\frac{d}{dx}$$

$$e^{-x}\frac{d}{dx}e^{-x}\frac{d}{dx}\overbrace{e^{\frac{x}{2}}}^{\sqrt{r}}\phi_{nl}(x) + \left[E_{nl} - V(r) - \frac{l(l+1)}{r^2}\right]e^{\frac{x}{2}}\phi_{nl}(x) = 0$$

$$\frac{1}{2}e^{x/2}\phi + e^{x/2}\phi'$$

$$= e^{x/2}\left(\frac{1}{2}\phi + \phi'\right)$$

$$e^{-x/2}\left(\frac{1}{2}\phi + \phi'\right)$$

$$-\frac{1}{2}e^{-x/2}\left(\frac{1}{2}\phi + \phi'\right) + e^{-x/2}\left(\frac{1}{2}\phi' + \phi''\right)$$

$$= e^{-x/2}\left(-\frac{1}{4}\phi - \cancel{\frac{1}{2}\phi'} + \cancel{\frac{1}{2}\phi'} + \phi''\right)$$

$$e^{-3/2x}\left(-\frac{1}{4}\phi + \phi''\right)$$

$$\therefore \cancel{e^{-\frac{3}{2}x}}\left(\phi''_{nl} - \frac{1}{4}\phi_{nl}\right) + \cancel{e^{x/2}}\left[E_{nl} - V(r) - \frac{l(l+1)}{r^2}\right]\phi_{nl} = 0 \qquad e^{2x} = r^2$$

$$\phi''_{nl} + \left[-\frac{1}{4} + r^2(E_{nl} - V(r)) - l(l+1)\right]\phi_{nl} = 0$$

$$\boxed{\frac{d^2}{dx^2}\phi_{nl}(x) + \underbrace{\left[-\frac{1}{4} + r^2(E_{nl} - V(r)) - l(l+1)\right]}_{-g(r)}\phi_{nl}(x) = 0} \qquad (7)$$

— Numerov Integration

Consider equispaced mesh points

$$x_n = nh \qquad (n = 1, 2, \cdots, M) \tag{8}$$

$$\phi(x \pm h) = \phi(x) \pm h\phi'(x) + \frac{h^2}{2}\phi''(x) \pm \frac{h^3}{6}\phi'''(x) + \frac{h^4}{24}\phi''''(x) \pm O(h^5) + O(h^6) \tag{9}$$

$$\phi(x+h) + \phi(x-h) = \cancel{2}\left[\phi(x) + \frac{h^2}{\cancel{2}}\phi''(x) + \frac{h^4}{\underset{12}{\cancel{24}}}\phi''''(x) + O(h^6)\right]$$

$$\therefore \frac{\phi_{n+1} - 2\phi_n + \phi_{n-1}}{h^2} = \phi_n'' + \frac{h^2}{12}\phi_n'''' + O(h^4) \tag{10}$$

Let's discretize the wave equation to estimate ϕ_n'''',

$$\frac{d^2}{dx^2}\left(\phi'' - g\phi\right) = 0$$

$$\phi'''' = \underbrace{\frac{d^2}{dx^2} g\phi}_{\frac{g_{n+1}\phi_{n+1} - 2g_n\phi_n + g_{n-1}\phi_{n-1}}{h^2} + O(h^2)}$$

$$\therefore \phi_n'''' = \frac{g_{n+1}\phi_{n+1} - 2g_n\phi_n + g_{n-1}\phi_{n-1}}{h^2} + O(h^2) \tag{11}$$

Substituting Eq. (11) in (10),

$$\frac{\phi_{n+1} - 2\phi_n + \phi_{n-1}}{h^2} = \phi_n'' + \frac{h^2}{12}\frac{1}{h^2}\left(g_{n+1}\phi_{n+1} - 2g_n\phi_n + g_{n-1}\phi_{n-1}\right) + O(h^4)$$

$$\therefore \phi_n'' = \frac{\left(1-\frac{h^2}{12}g_{n+1}\right)\phi_{n+1} - 2\left(1-\frac{h^2}{12}g_n\right)\phi_n + \left(1-\frac{h^2}{12}g_{n-1}\right)\phi_{n-1}}{h^2} + O(h^4) \tag{12}$$

Substituting this discrete approximation to Eq. (7),

$$\frac{\left(1-\frac{h^2}{12}g_{n+1}\right)\phi_{n+1} - 2\left(1-\frac{h^2}{12}g_n\right)\phi_n + \left(1-\frac{h^2}{12}g_{n-1}\right)\phi_{n-1}}{h^2} - g_n\phi_n = O(h^4)$$

Multiplying both side by h^2,

$-2+\frac{2h^2}{12}-\frac{12}{12}h^2 = -2-\frac{10}{12}h^2$

$$\left(1-\underbrace{\frac{h^2}{12}g_{n+1}}_{\equiv G_{n+1}}\right)\phi_{n+1} - 2\left(1+\frac{5h^2}{12}g_n\right)\phi_n + \left(1-\frac{h^2}{12}g_{n-1}\right)\phi_{n-1} = O(h^6) \tag{13}$$

or

$$\phi_{n+1} = \frac{2\left(1+5h^2G_n\right)\phi_n - \left(1-h^2G_{n-1}\right)\phi_{n-1}}{1-h^2G_{n+1}} + O(h^6) \tag{14}$$

where

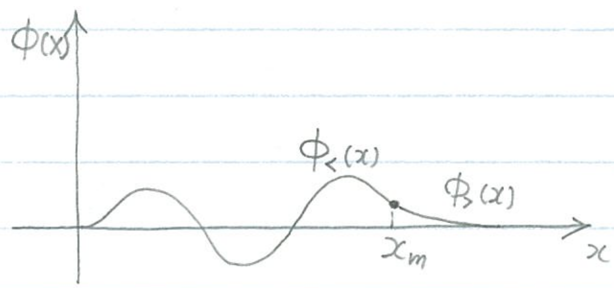
$$\phi_n = \phi_{n\ell}(x_n) \tag{15}$$

$$G(x) = \frac{1}{12}\left[\frac{1}{4} - r^2\left(E_{n\ell}-V(r)\right) + \ell(\ell+1)\right] \tag{16}$$

Shooting Method.

Because of admixture of $e^{\kappa x}$ and $e^{-\kappa x}$ solutions, integration "into" a classically forbidden region is likely to be inaccurate.

We perform the Numerov recursion starting from $x = 0$ outward, $\phi_<(x)$, and also from $x = x_{max} = x(Mh)$ inward, $\phi_>(x)$. The matching point is chosen to be the classical turning point, $G(x_m) = 0$.



For $x \geq x_m$, the solution $\phi_>(x)$ is not oscillatory so that there is no node. Therefore, $\phi_<(x)$ must have $n' = n - l - 1$ nodes!

– Boundary conditions

For $r \to 0$, the centrifugal potential is most singular:

$$\left[\frac{d^2}{dr^2} - \frac{\ell(\ell+1)}{r^2}\right] \chi_{n\ell}(r) \sim 0$$

Assuming that the leading term is r^α,

$$\alpha(\alpha-1) r^{\alpha-2} - \ell(\ell+1) r^{\alpha-2} \sim 0 \quad \to \quad \alpha = \ell + 1$$

$$\therefore \quad \chi_{n\ell}(r) \sim r^{\ell+1} \qquad (r \to 0) \tag{17}$$

(see p.8 for the next term)

or

$$\phi_{n\ell}(x) \sim r^{\ell+\frac{1}{2}} \qquad (r \to 0) \tag{18}$$

Cf. hydrogenic atom

$$\begin{cases} \chi_{10}(r) = \left(\frac{Z}{a}\right)^{3/2} 2 r e^{-Zr/a} \sim r \\ \chi_{21}(r) = \left(\frac{Z}{2a}\right)^{3/2} \frac{Z r^2}{\sqrt{3}a} e^{-Zr/2a} \sim r^2 \end{cases}$$

For $r \to \infty$, all potentials vanish:

$$\left(\frac{d^2}{dr^2} + E_{n\ell}\right) \chi_{n\ell}(r) = 0$$

$$\therefore \quad \chi_{n\ell}(r) \sim \exp\left(-\sqrt{-E_{n\ell}}\, r\right) \qquad (r \to \infty) \tag{19}$$

or

$$\phi_{n\ell}(x) \sim \exp\left(-\sqrt{-E_{n\ell}}\, r\right) / \sqrt{r} \qquad (r \to \infty) \tag{20}$$

- Normalization

$$1 = \int_0^\infty dr\, \cancel{r^2} \frac{\chi_{n\ell}^2(r)}{\cancel{r^2}} \underbrace{\int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\varphi\, |Y_\ell^m(\theta,\varphi)|^2}_{1}$$

$$\therefore \int_0^\infty dr\, \chi_{n\ell}^2(r) = 1 \qquad (21)$$

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Boundary condition at the origin

The $r \to 0$ limit of the wave function can generally be expressed as

$$\chi_{nl}(r) \propto r^{\alpha} \exp(1 + ar + br^2 + O(r^3)) \tag{22}$$

i.e., the leading term is r^{α} and the exponential function is introduced only to simplify the algebra for the homogeneous differential equation.

$$\chi' = \alpha r^{\alpha-1} \exp + r^{\alpha}(a+2br)$$

$$\chi'' = \alpha(\alpha-1) r^{\alpha-2} \exp + 2\alpha r^{\alpha-1}(a+2br) \exp + r^{\alpha}(a+2br)^2 \exp$$

$$= \left[\frac{\alpha(\alpha-1)}{r^2} + \frac{2a\alpha}{r} + (a^2 + 4b\alpha)\right] \exp(1+ar+br^2) \tag{23}$$

Note that for $r \to 0$, the screening is not effective so that

$$V(r) = -\frac{2Z}{r}$$ Rydberg

$$\therefore \left\{\frac{d^2}{dr^2} + \left[E_{nl} + \frac{2Z}{r} - \frac{l(l+1)}{r^2}\right]\right\} \chi_{nl}(r) = 0 \tag{24}$$

Substituting Eq. (23) in (24),

$$\left\{\frac{\alpha(\alpha-1) - l(l+1)}{r^2} + \frac{2(a\alpha+Z)}{r} + (a^2 + 4b\alpha + E_{nl})\right\} \chi_{nl}(r) = 0$$

To make the two leading term 0 (for the third term, screening may not be ignored),

$$\alpha = l+1.$$

$$a\alpha + Z = 0 \quad \to \quad a = -\frac{Z}{\alpha} = -\frac{Z}{l+1}$$

$$\therefore \quad \boxed{\chi_{nl}(r) \propto r^{l+1} \exp\left(1 - \frac{Z}{l+1} r\right)} \tag{25}$$