Logarithmic-Derivative/Charge Sum Rule

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Since the radial Schrödinger equation is a second-order differential equation, $R_l(r)$ and dR_l/dr at a radius, r_c, completely determines the entire function. Or, its logarithmic derivative, $(dR_l/dr)/R_l$, determines uniquely the wave function except for a scaling factor.

A norm-conserving pseudopotential matches the logarithmic derivative (for each angular momentum, l) of the eigenstate, E_l, between all-electron and pseudoorbital calculations.

If, in addition, the charge within a cutoff length, r_c, beyond which the pseudo- and all-electron potentials are identical, is identical, the energy dependence of the logarithmic derivative (upto the linear term) is also conserved, i.e., all-electron- and pseudopotentials produce same wavefunctions for E near E_l.

- Sum rule

$$\chi_{l,E}(r)\times \quad -\frac{\hbar^2}{2m}\frac{d^2}{dr^2}\chi_{l,E+\Delta}(r) + \left[V(r) + \frac{\hbar^2 l(l+1)}{2mr^2}\right]\chi_{l,E+\Delta}(r) = (E+\Delta)\chi_{l,E+\Delta}(r)$$

$$\chi_{l,E+\Delta}(r)\times \quad -\frac{\hbar^2}{2m}\frac{d^2}{dr^2}\chi_{l,E}(r) + \left[V(r) + \frac{\hbar^2 l(l+1)}{2mr^2}\right]\chi_{l,E}(r) = E\,\chi_{l,E}(r)$$

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$$-\frac{\hbar^2}{2m}\underbrace{\left(\chi_E\frac{d^2}{dr^2}\chi_{E+\Delta} - \chi_{E+\Delta}\frac{d^2}{dr^2}\chi_E\right)}_{\frac{d}{dr}\left(\chi_E\frac{d}{dr}\chi_{E+\Delta}\right) - \cancel{\chi_E'\chi_{E+\Delta}'} - \frac{d}{dr}\left(\chi_{E+\Delta}\frac{d}{dr}\chi_E\right) + \cancel{\chi_E'\chi_{E+\Delta}'}} = \Delta\,\chi_{E+\Delta}\chi_E$$

Integrating this equation from $\emptyset$ to r_c,

$$-\frac{\hbar^2}{2m}\underbrace{\int_0^{r_c} dr\,\frac{d}{dr}\left(\chi_E\frac{d}{dr}\chi_{E+\Delta} - \chi_{E+\Delta}\frac{d}{dr}\chi_E\right)}_{\left[\chi_E\frac{d}{dr}\chi_{E+\Delta} - \chi_{E+\Delta}\frac{d}{dr}\chi_E\right]_{\cancel{\emptyset}}^{r_c}} = \Delta\int_0^{r_c} dr\,\overset{\chi_{E+\Delta}}{(r R_{E+\Delta})}\overset{\chi_E}{(r R_E)}$$

$$\cancel{\emptyset} \rightarrow \chi_l(r) \propto r^{l+1} \rightarrow 0$$

$$\therefore -\frac{\hbar^2}{2m}\underbrace{\left(\chi_E\frac{d}{dr}\chi_{E+\Delta} - \chi_{E+\Delta}\frac{d}{dr}\chi_E\Big|_{r=r_c}\right)}_{r R_E\frac{d}{dr}r R_{E+\Delta} - r R_{E+\Delta}\frac{d}{dr}r R_E} = \Delta\int_0^{r_c} dr\,r^2 R_{E+\Delta}R_E$$

$$= \cancel{r R_E R_{E+\Delta}} + r^2 R_E R_{E+\Delta}' - \cancel{r R_{E+\Delta}R_E} - r^2 R_{E+\Delta}R_E'$$

$$= r^2 R_E R_{E+\Delta}\left(\frac{R_{E+\Delta}'}{R_{E+\Delta}} - \frac{R_E'}{R_E}\right)$$

$$\therefore -\frac{\hbar^2}{2m}r_c^2 R_E R_{E+\Delta}\,\frac{1}{\Delta}\left[\frac{R_{E+\Delta}'}{R_{E+\Delta}} - \frac{R_E'}{R_E}\right]_{r=r_c} = \int_0^{r_c} dr\,r^2 R_{E+\Delta}R_E$$

By setting $\Delta \to 0$,

$$-\frac{\hbar^2}{2m} r_c^2 R_E^2(r_c) \frac{d}{dE} \left. \frac{dR_E/dr}{R_E} \right|_{r_c} = \int_0^{r_c} dr\, r^2 R_E^2(r)$$

or

$$\boxed{\begin{aligned} -\frac{\hbar^2}{2m} r_c^2 R_{\ell,E}^2(r_c) \frac{d}{dE} \frac{dR_{\ell,E}/dr_c}{R_{\ell,E}(r_c)} &= \frac{1}{4\pi} \int_0^{r_c} 4\pi r^2 dr\, R_{\ell,E}^2(r) \\ &= \frac{1}{4\pi} \rho(r<r_c) \end{aligned}} \qquad (1)$$

where $\rho(r<r_c)$ is the charge enclosed in the sphere with radius r_c. If this charge is correct, the (linear) energy dependence of the logarithmic derivative is also correct.

Logarithmic Derivative

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$$\begin{cases} R_{nl}(r) = \dfrac{1}{\sqrt{r}}\,\phi_{nl}(X) & (1) \\[2ex] r = \exp(X) & (2) \end{cases}$$

$$\left(\frac{dr}{dx}\right)^{-1} = \frac{1}{r}$$

$$\frac{dR}{dr} = \frac{\frac{dx}{dr}\frac{d\phi}{dx}}{\sqrt{r}} - \frac{\phi}{2r\sqrt{r}}$$

$$= \frac{1}{r\sqrt{r}}\left(\frac{d\phi}{dx} - \frac{1}{2}\phi\right)$$

$$\frac{1}{R}\frac{dR}{dr} = \frac{1}{r\cancel{\sqrt{r}}}\left(\frac{d\phi}{dx} - \frac{1}{2}\phi\right) \times \frac{\cancel{\sqrt{r}}}{\phi} = \frac{1}{r}\left(\frac{1}{\phi}\frac{d\phi}{dx} - \frac{1}{2}\right)$$

$$\therefore \frac{1}{R_{nl}(r)}\frac{dR_{nl}}{dr} = \frac{1}{r}\left(\frac{d\phi_{nl}/dX}{\phi_{nl}(X)} - \frac{1}{2}\right) \qquad (3)$$

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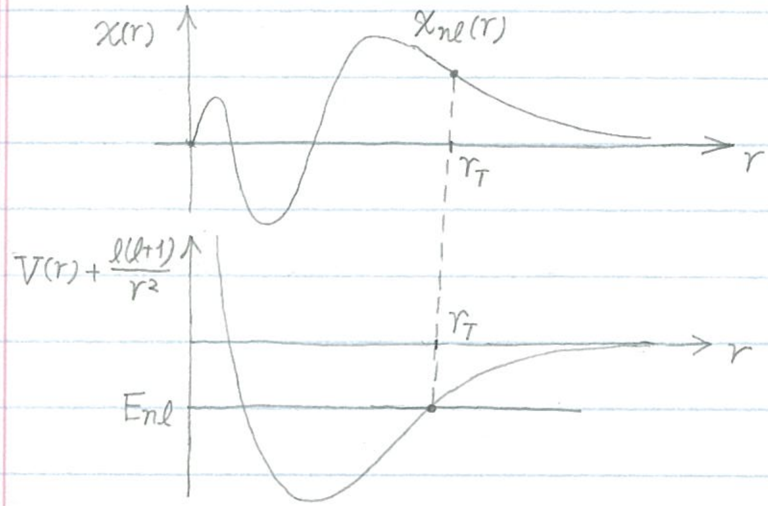
Logarithmic derivative and eigenenergy



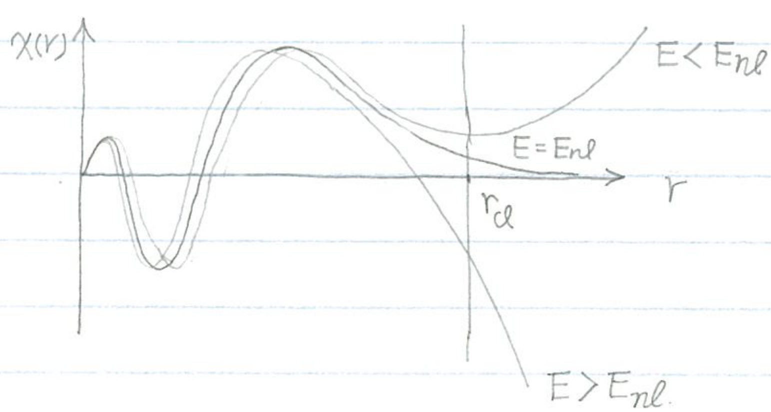
Consider logarithmic derivative at $r = r_{c\ell}$, where the cutoff radius, $r_{c\ell}$, is near the classical turning point, r_T, which is defined through $E_{n\ell} - V(r_T) - \ell(\ell+1)/r_T^2 = 0$.

We choose $r_{c\ell}$ beyond the classical turning point for all the energy range under consideration,

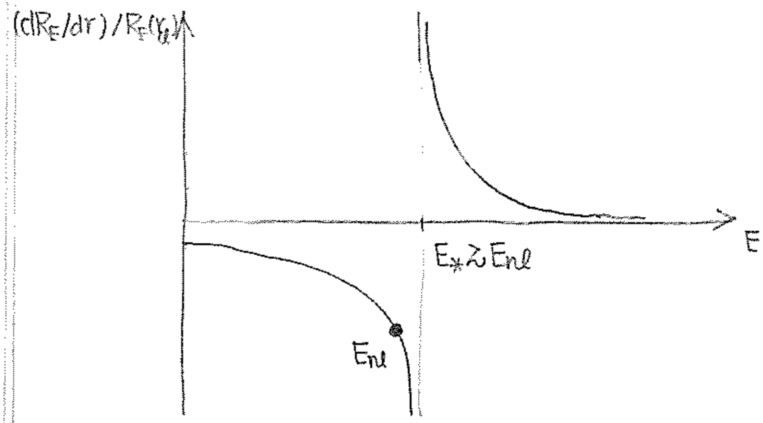
$$r_{c\ell} > r_T(E \text{ under consideration}); \quad E - V(r_T(E)) - \ell(\ell+1)/r_T^2(E) = 0$$

Then, beyond $r_{c\ell}$, the wave function is not oscillatory, and exponentially decaying / growing.

Let's consider $(dR/dr)/R$ around the eigenenergy $E_{n\ell}$.



At E slightly larger, $E \gtrsim E_{n\ell}$, $R_E(r_{c\ell}) \to 0$ and the logarithmic derivative diverges



Therefore, a $1/(E-E_*)$ singularity in the logarithmic derivative in the "asymptotic radial region" signifies the existence of an eigenenergy.