Logarithmic-Derivative/Charge Sum Rule

Since the radial Schrödinger equation is a second-order differential equation, \( R_e(r) \) and \( \frac{dR}{dr} \) at a radius \( r_c \), completely determines the entire function. Or, its logarithmic derivative, \( \frac{dR}{dr}/R_e \), 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**

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

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

- \[
\frac{\hbar^2}{2m} \left(\chi_{E}^{E} \frac{d^2}{dr^2} \chi_{E+\Delta} - \chi_{E+\Delta} \frac{d^2}{dr^2} \chi_{E}^{E}\right) = \Delta \chi_{E+\Delta} \chi_{E}
\]

\[
\frac{d}{dr} \left(\chi_{E}^{E} \frac{d}{dr} \chi_{E+\Delta} - \chi_{E+\Delta} \frac{d}{dr} \chi_{E}^{E}\right) = \frac{d}{dr} \left(\chi_{E+\Delta} \frac{d}{dr} \chi_{E}^{E}\right) + \chi_{E}^{E} \chi_{E+\Delta}
\]

Integrating this equation from 0 to \(r_c\),

\[
- \frac{\hbar^2}{2m} \int_0^{r_c} dr \left(\chi_{E}^{E} \frac{d}{dr} \chi_{E+\Delta} - \chi_{E+\Delta} \frac{d}{dr} \chi_{E}^{E}\right) = \Delta \int_0^{r_c} dr \left(r R_{E+\Delta}(r) R_E\right)
\]

\[
\left[\chi_{E}^{E} \frac{d}{dr} \chi_{E+\Delta} - \chi_{E+\Delta} \frac{d}{dr} \chi_{E}^{E}\right]_{r=0}^{r=r_c} \rightarrow \chi_{E}^{E}(r) \sim r^{l+1} \rightarrow 0
\]

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

\[
= r R_E R_{E+\Delta} + r^2 R_E R_{E+\Delta} - r R_{E+\Delta} R_E - r^2 R_{E+\Delta} R_E
\]

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

\[
\frac{\hbar^2}{2m} \int_0^{r_c} dr \left[r R_{E+\Delta}(r) R_E\right]_{r=r_c} = \int_0^{r_c} dr \left[r R_{E+\Delta}(r) R_E\right]
\]
By setting $\Delta \to 0$,
\[-\frac{h^2}{2m} r_c^2 R_E^2(r_c) \frac{d}{dE} \left. \frac{dR_{\ell E}}{dE} \right|_{r_c} = \int_0^{r_c} dr \, r^2 R_E^2(r)\]

or
\[-\frac{h^2}{2m} r_c^2 R_{\ell E}(r_c) \frac{d}{dE} \frac{dR_{\ell E}}{dE} = \frac{1}{4\pi} \int_0^{r_c} 4\pi r^2 dr \, R_{\ell E}^2(r) = \frac{1}{4\pi} \rho(r < r_c) \tag{1}\]

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

\[
R_{nl}(r) = \frac{1}{\sqrt{r}} \phi_{nl}(x) \tag{1}
\]

\[r = \exp(x)\]  \tag{2}

\[
\frac{dR}{dr} = \frac{\sqrt{r} \frac{d\phi}{dx} \frac{dx}{dr} + \phi}{\sqrt{r}} - \frac{\phi}{2r\sqrt{r}}
\]

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

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

\[
\frac{1}{R} \frac{dR}{dr} = \frac{1}{r \left( \phi_{nl}(x) - \frac{1}{2} \right)}\]

\[
\frac{1}{R_{nl}(r)} \frac{dR_{nl}}{dr} = \frac{1}{r} \left( \frac{d\phi_{nl}/dx}{\phi_{nl}(x)} - \frac{1}{2} \right)\]  \tag{3}
Consider logarithmic derivative at \( r = r_{cl} \), where the cutoff radius, \( r_{cl} \), is near the classical turning point, \( r_T \), which is defined through \( E_{nl} - V(r_T) - l(l+1)/r_T^2 = 0 \).

We choose \( r_{cl} \) beyond the classical turning point for all the energy range under consideration,

\[ r_{cl} > r_T(E \text{ under consideration}); \quad E - V(r_{cl}) - l(l+1)/r_{cl}^2 = 0 \]

Then, beyond \( r_{cl} \), the wave function is not oscillatory, and exponentially decaying/growing.

Let's consider \((dR/dr)/R\) around the eigenenergy \( E_{nl} \).
At \( E \) slightly larger, \( E \geq E_{nl} \), \( R_E(r_{nl}) \rightarrow 0 \) and the logarithmic derivative diverges.

\[
\frac{(dP/dE)/P_{nl}}{E} \rightarrow E \geq E_{nl} \quad \text{End}
\]

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