Generalized Logarithmic Derivative = Surface Green Function

7/8/03

[J.E. Inglesfield, J. Phys. C 14, 3795 ('81)]

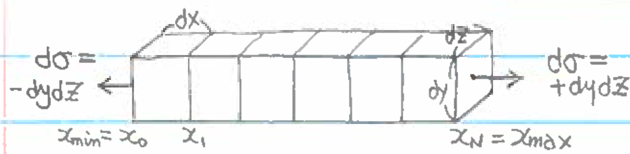
Preliminary: Green's theorem

(Gauß's theorem)

$$\int_V d\tau\, \nabla\cdot \mathbf{v} = \int_S d\boldsymbol{\sigma}\cdot\mathbf{v} \tag{1}$$

$d\tau$ ↳ volume element; $\mathbf{v}$ ↳ vector field; $d\boldsymbol{\sigma}$ ↳ outgoing surface element

☺ This is just a telescopic technique:



$$\overbrace{\sum_{i=1}^{N} \frac{\partial}{\partial x} v_x(x_i)\, dx\,dy\,dz}$$

$$= \sum_{i=1}^{N} [v_x(x_i) - v_x(x_{i-1})]\, dy\,dz$$

$$= [-v_x(x_0) + \cancel{v_x(x_1)} - \cancel{v_x(x_1)} + \cancel{v_x(x_2)} - \cdots - \cancel{v_x(x_{N-1})} + v_x(x_N)]\, dy\,dz$$

$$= [v_x(x_N) - v_x(x_0)]\, dy\,dz$$

$$= v_x(x_{max})\underbrace{(+dy\,dz)}_{d\sigma} + v_x(x_{min})\underbrace{(-dy\,dz)}_{d\sigma} \quad //$$

(Green's theorem)

Note, for scalar fields u & v,

$$\nabla\cdot(u\nabla v - v\nabla u) = u\nabla^2 v - v\nabla^2 u \tag{2}$$

$\int_V d\tau \times$ Eq. (2)

$$\int_V d\tau\, \nabla\cdot(u\nabla v - v\nabla u) = \int_V d\tau\, (u\nabla^2 v - v\nabla^2 u)$$

Applying Gauß's theorem to the l.h.s.,

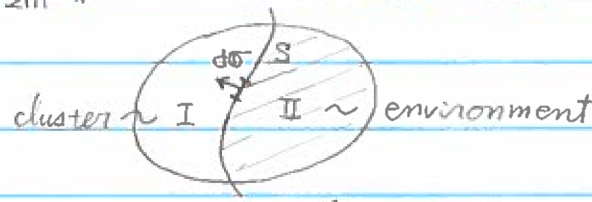
$$\int_S d\boldsymbol{\sigma}\cdot(u\nabla v - v\nabla u) = \int_V d\tau\, (u\nabla^2 v - v\nabla^2 u) \tag{3}$$

Or, using the surface-normal derivative,

$$\int_S d^2r_s \left(u\frac{\partial}{\partial n_s} v - v\frac{\partial}{\partial n_s} u\right) = \int_V d^3r\, (u\nabla^2 v - v\nabla^2 u) \tag{4}$$

– Generalized logarithmic derivative

$$\begin{cases} \left[-\frac{\hbar^2}{2m}\nabla_{\mathbf{r}'}^2 + V(\mathbf{r}') - \varepsilon\right]\psi(\mathbf{r}') = 0 & \mathbf{r} \in \mathrm{I} \quad (5) \\ \left[-\frac{\hbar^2}{2m}\nabla_{\mathbf{r}'}^2 + V(\mathbf{r}') - \varepsilon\right]G(\mathbf{r},\mathbf{r}';\varepsilon) = \delta(\mathbf{r}-\mathbf{r}') & \mathbf{r},\mathbf{r}' \in \mathrm{II} \quad (6) \end{cases}$$



$$\int_{\mathrm{II}} d^3r' \, G(\mathbf{r},\mathbf{r}';\varepsilon) \times \text{Eq.}(5) - \int_{\mathrm{II}} d^3r' \, \psi(\mathbf{r}') \times \text{Eq.}(6)$$

$$\int_{\mathrm{II}} d^3r' \Big\{ G(\mathbf{r},\mathbf{r}';\varepsilon)\left(-\frac{\hbar^2}{2m}\nabla_{\mathbf{r}'}^2\right)\psi(\mathbf{r}') + \cancel{[V(\mathbf{r}')-\varepsilon]G(\mathbf{r},\mathbf{r}';\varepsilon)\psi(\mathbf{r}')}$$

$$- \psi(\mathbf{r}')\left(-\frac{\hbar^2}{2m}\nabla_{\mathbf{r}'}^2\right)G(\mathbf{r},\mathbf{r}';\varepsilon) - \cancel{[V(\mathbf{r}')-\varepsilon]\psi(\mathbf{r}')G(\mathbf{r},\mathbf{r}';\varepsilon)} \Big\} = \underbrace{-\int_{\mathrm{II}} d^3r' \, \psi(\mathbf{r}')\,\delta(\mathbf{r}-\mathbf{r}')}_{-\psi(\mathbf{r})}$$

$$-\frac{\hbar^2}{2m}\int_{\mathrm{II}} d^3r' \, \nabla_{\mathbf{r}'} \cdot \left[G(\mathbf{r},\mathbf{r}';\varepsilon)\nabla_{\mathbf{r}'}\psi(\mathbf{r}') - \psi(\mathbf{r}')\nabla_{\mathbf{r}'}G(\mathbf{r},\mathbf{r}';\varepsilon)\right] = -\psi(\mathbf{r})$$

Using Green's theorem,

$$+\frac{\hbar^2}{2m}\int_S d^2r_S \left[G(\mathbf{r},\mathbf{r}_S;\varepsilon)\frac{\partial\psi(\mathbf{r}_S)}{\partial n_S} - \psi(\mathbf{r}_S)\frac{\partial}{\partial n_S}G(\mathbf{r},\mathbf{r}_S;\varepsilon)\right] = -\psi(\mathbf{r})$$

※ Here, we have defined the surface-normal derivative, "out-going from region I".

If we define $G(\mathbf{r},\mathbf{r}';\varepsilon)$ with the boundary condition that $\partial G/\partial n_S = 0$ on S, then

$$\psi(\mathbf{r}) = -\frac{\hbar^2}{2m}\int_S d^2r_S \, G(\mathbf{r},\mathbf{r}_S;\varepsilon)\frac{\partial\psi(\mathbf{r}_S)}{\partial n_S} \qquad (7)$$

Putting $\mathbf{r}$ on S,

$$\psi(\mathbf{r}_S) = -\frac{\hbar^2}{2m}\int_S d^2r_S' \, G(\mathbf{r}_S,\mathbf{r}_S';\varepsilon)\frac{\partial\psi(\mathbf{r}_S')}{\partial n_S} \qquad (8)$$

Inverting Eq.(8),

$$\frac{\partial \psi(\mathbf{r}_s)}{\partial n_s} = -\frac{2m}{\hbar^2}\int_S d^2r_s'\, G^{-1}(\mathbf{r}_s,\mathbf{r}_s';\varepsilon)\,\psi(\mathbf{r}_s') \qquad (9)$$

Since Eq.(9) connects the wave function value and its derivative on the boundary surface, G^{-1} is a generalization of the logarithmic derivative, $L(\varepsilon) = (dR/dr)/R(r)\,|_{r=r_c}$.

Note the inverse Green's function is expressed in terms of the energy eigenstates as

$$G^{-1}(\mathbf{r},\mathbf{r}';\varepsilon) = \sum_n \langle \mathbf{r}|n\rangle(\varepsilon-\varepsilon_n)\langle n|\mathbf{r}'\rangle \qquad (10)$$

$$= \sum_n \psi_n(\mathbf{r})(\varepsilon-\varepsilon_n)\,\psi_n^*(\mathbf{r}') \qquad (11)$$

Wave-Function-Derivative Discontinuity Energy

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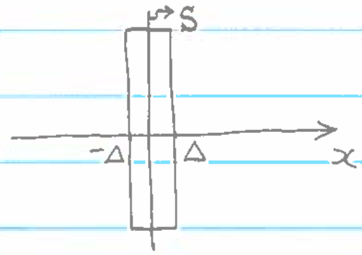

$$E = \int d\mathbf{r}_\perp \int_{-\Delta}^{\Delta} dx\, \phi^*(x, \mathbf{r}_\perp) \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\right) \phi(x, \mathbf{r}_\perp)$$

$$= -\frac{\hbar^2}{2m}\int d\mathbf{r}_\perp \int_{-\Delta}^{\Delta} dx \left\{ \frac{\partial}{\partial x}\left[\phi^*(x,\mathbf{r}_\perp)\frac{\partial}{\partial x}\phi(x,\mathbf{r}_\perp)\right] - \frac{\partial}{\partial x}\phi^*(x,\mathbf{r}_\perp)\frac{\partial}{\partial x}\phi(x,\mathbf{r}_\perp)\right\}$$

$$= -\frac{\hbar^2}{2m}\int d\mathbf{r}_\perp \left\{ \underbrace{\left[\phi^*(x,\mathbf{r}_\perp)\frac{\partial}{\partial x}\phi(x,\mathbf{r}_\perp)\right]_{-\Delta}^{\Delta}}_{\phi^*(x,\mathbf{r}_\perp)\left[\frac{\partial}{\partial x}\phi(x,\mathbf{r}_\perp)\right]_{x-0}^{x+0}} - \underbrace{\int_{-\Delta}^{\Delta} dx \frac{\partial}{\partial x}\phi^*(x,\mathbf{r}_\perp)\frac{\partial}{\partial x}\phi(x,\mathbf{r}_\perp)}_{O(\Delta)}\right\}$$

$$= -\frac{\hbar^2}{2m}\int_S d^2r_S\, \phi^*(\mathbf{r}_S)\left[\frac{\partial}{\partial n_S}\phi_+(\mathbf{r}_S) - \frac{\partial}{\partial n_S}\phi_-(\mathbf{r}_S)\right] \qquad (1)$$

(Bottomline) Discontinuity in the first derivative of a wave function has a finite contribution to the energy through the kinetic energy.