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Kinetic-Energy Expectation Values with Discontinuous Approximate Wave Functions*

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The Schlosser-Marcus stationary principle for discontinuous approximate wave functions is shown to be the "finite part" of the energy expectation value. The divergent terms in the expectation value of the kinetic energy are second order in the discontinuity, which explains why the energy expression obtained when they are omitted remains stationary.

Energy eigenfunctions must be continuous and have continuous first derivatives. Approximate eigenfunctions may have discontinuous first derivatives or even be discontinuous themselves, *if* suitable formulas are used for kinetic-energy matrix elements.[1–4] This paper is to clarify some confusion concerning the justification of these "suitable formulas."

When ψ is continuous but has jump discontinuities in its first derivatives, the kinetic-energy expectation value is correctly given by[1]

$$\langle \psi | -\tfrac{1}{2}\nabla^2 | \psi \rangle = \tfrac{1}{2}\int (\nabla\psi)^* \cdot (\nabla\psi)\, dV \,. \tag{1}$$

It is not always appreciated that

$$\langle \psi | -\tfrac{1}{2}\nabla^2 | \psi \rangle = -\tfrac{1}{2}\int \psi^* \nabla^2 \psi\, dV \tag{2}$$

is also correct if $\nabla^2\psi$ *is evaluated correctly*.

Consider for simplicity one dimension. Let the first derivative of $\psi = \psi(x)$ have a jump discontinuity $[\psi'(x_0+0) - \psi'(x_0-0]$ at x_0, where $\psi'(x)$ denotes $(d/dx)\psi(x)$. Let $\hat{\psi}''(x_0) = 0$ and $\hat{\psi}''(x) = (d/dx)^2\psi(x)$ when $x \neq x_0$; then the *correct* formula for $(d/dx)^2 \times\psi(x)$ involves a Dirac δ function[5]:

$$\left(\frac{d}{dx}\right)^2 \psi(x) = \hat{\psi}''(x) + [\psi'(x_0+0) - \psi'(x_0-0)]\,\delta(x-x_0)\,. \tag{3}$$

Thus we have

$$-\tfrac{1}{2}\int_{-\infty}^{\infty} \psi^* \left(\frac{d}{dx}\right)^2 \psi\, dx$$

$$= -\tfrac{1}{2}\left(\int_{-\infty}^{x_0-0} + \int_{x_0+0}^{\infty}\right) \psi^* \left(\frac{d}{dx}\right)^2 \psi\, dx$$

$$-\tfrac{1}{2}\psi^*(x_0)\,[\psi'(x_0+0) - \psi'(x_0-0)]\,. \tag{4}$$

The three-dimensional version is[2]

$$-\tfrac{1}{2}\int \psi^* \nabla^2 \psi\, dV = -\tfrac{1}{2}\int_{V_i+V_o} \psi^* \nabla^2\psi\, dV$$

$$-\tfrac{1}{2}\int_S \psi^* (\nabla\psi_o - \nabla\psi_i)\cdot d\vec{S}\,, \tag{5}$$

where $\int_{V_i+V_o} dV$ denotes the integral over the volume excluding the surface of discontinuity S, and $(\nabla\psi_o - \nabla\psi_i)$ denotes the discontinuity in the gradient across the surface and represents the "strength" of the δ function obtained by differentiating the discontinuous function $\nabla\psi$ across the surface. By integration by parts (Green's theorem), the right-hand side of Eq. (5) is $-\tfrac{1}{2}\int(\nabla\psi)^*\cdot(\nabla\psi)\,dV$. Hence Eqs. (1) and (2) are equivalent when Eq. (5) is used to evaluate the right-hand side of Eq. (2). Q.E.D.

By way of example, the augmented-plane-wave method of Slater[1,6,7] uses continuous wave functions with discontinuous first derivatives. Slater[1] clearly understood the content of Eqs. (2)–(5), which he stated[1] more or less in words (also see Ref. 2). (Indeed, the rigorous mathematical theory of δ functions came several years later.[5])

If ψ itself is discontinuous, the kinetic-energy expectation value is infinite, but the infinity is easily identified and removed. The essence of this exorcism is revealed by the following heuristic (but decidedly nonrigorous) considerations. (The integral of a discontinuous function times a δ function which appears below is irreconcilably outside the theory of generalized functions.) The analogs of Eqs. (3) and (4) are

$$\left(\frac{d}{dx}\right)^2 \psi(x) = \hat{\psi}''(x) + [\psi'(x_0+0) - \psi'(x_0-0)]\,\delta(x-x_0) + [\psi(x_0+0)-\psi(x_0-0)]\,\delta^{(1)}(x-x_0)\ , \qquad (6)$$

$$-\tfrac{1}{2}\int_{-\infty}^{\infty} \psi^* \left(\frac{d}{dx}\right)^2 \psi dx = -\tfrac{1}{2}\left(\int_{-\infty}^{x_0-0} + \int_{x_0+0}^{\infty}\right) \psi^* \left(\frac{d}{dx}\right)^2 \psi dx - \tfrac{1}{2}\psi^*(x_0)[\psi'(x_0+0)-\psi'(x_0-0)] + \frac{1}{2}\left[\left(\frac{d}{dx}\right)\psi^*\right]_{x=x_0} [\psi(x_0+0)-\psi(x_0-0)]\ , \qquad (7)$$

where $\delta^{(1)}(x-x_0) = (d/dx)\delta(x-x_0)$. Because of the discontinuity, $\psi^*(x_0)$ and $[(d/dx)\psi^*]_{x=x_0}$ have no meaning, but heuristically we interpret them as averages (a and c are arbitrary numbers):

$$\psi^*(x_0) = c^*\psi^*(x_0-0) + (1-c^*)\psi^*(x_0+0)\ , \qquad (8)$$

$$\left[\left(\frac{d}{dx}\right)\psi^*\right]_{x=x_0} = (1-a)\psi'^*(x_0-0) + a\psi'^*(x_0+0) + [\psi(x_0+0)-\psi(x_0-0)]^*\,[\delta(x-x_0)]_{x=x_0}\ . \qquad (9)$$

With Eqs. (8) and (9), Eq. (7) has three parts: (i) a "volume" integral excluding the "surface" of discontinuity; (ii) two "surface" terms involving arbitrary constants a and c; (iii) an infinite term, $\frac{1}{2}|\psi(x_0+0)-\psi(x_0-0)|^2[\delta(x-x_0)]_{x=x_0}$. The "volume" and "surface" terms are the one-dimensional version of the kinetic-energy part of the Schlosser-Marcus expression,[3]

$$-\tfrac{1}{2}\int \psi^*\nabla^2\psi\, dV = -\tfrac{1}{2}\int_{V_i+V_o} \psi^*\nabla^2\psi\, dV + \tfrac{1}{2}\int_S d\vec{S}\cdot[a^*\nabla\psi_o + (1-a^*)\nabla\psi_i]^*(\psi_o-\psi_i) - \tfrac{1}{2}\int_S [(1-c)\psi_o + c\psi_i]^*(\nabla\psi_o - \nabla\psi_i)\cdot d\vec{S}\ . \qquad (10)$$

The infinite term is proportional to $|\psi(x_0+0)-\psi(x_0-0)|^2$ (in three dimensions, $|\psi_o-\psi_i|^2$), which is second order in $|\psi-\psi_{\text{exact}}|$, since

$$|\psi(x_0+0)-\psi(x_0-0)| \le |\psi(x_0+0)-\psi_{\text{exact}}| + |\psi(x_0-0)-\psi_{\text{exact}}|\ . \qquad (11)$$

Thus, the Schlosser-Marcus expression is the finite part of the energy expectation value, and it is stationary because the omitted infinite part is of second order.

There is no question[8] of the validity of the Schlosser-Marcus expression [Eq. (10) above], and the above derivation serves to tie the formula to the more familiar energy expectation value.

The above result can be derived rigorously[9] by first smoothing ψ ($\to\psi_\epsilon$), then letting the smoothed ψ_ϵ approach the discontinuous ψ. The values of a and c depend on the details of the smoothing process. One new feature arises: If $\psi_\epsilon \to \psi$ in $\langle\psi_\epsilon| -\frac{1}{2}\nabla^2|\psi_\epsilon\rangle$, then $a=c$ (always) and Eq. (10) is real; if ψ_ϵ and $\psi_{\epsilon'}$ approach ψ at different rates in $\langle\psi_\epsilon| -\frac{1}{2}\nabla^2|\psi_{\epsilon'}\rangle$, then $a\ne c$ is the rule, and Eq. (10) is not necessarily real.

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