E833: Application of Green's Theorem

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The problem:

A particle in a box has eigenvalues E_n, and eigenfunctions $\psi^n(x)$. A weak potential $V(x) = V_0$ is turned on in a certain domain inside the box. At the rest of the box the potential is zero. In order to calculate the pertubated energies we need the matrix elements V_{nm}. Show that one can calculate these matrix elements by an integral on the boundry of the domain.

The solution:

Introduction to Green's Theorem.
If u and v are two scalar functions, we have the identities

$$\nabla \cdot (u\nabla v) = u\nabla^2 v + (\nabla u)(\nabla v)$$

$$\nabla \cdot (v\nabla u) = v\nabla^2 u + (\nabla v)(\nabla u)$$

Subtracing the second equation from the first, integrating over a volume (u, v and their derivatives, assumed continuous), and applying Gauss's theorem we obtain

$$\int_V \left(u\nabla^2 v - v\nabla^2 u\right) dV = \oint_S (u\nabla v - v\nabla u)\cdot \hat{n} ds$$

where $\hat{n}$ is a unit vector normal to the surface.
This is Green's theorem.
Back to our problem. The matrix elements of the potential are

$$V_{n,m} = \left\langle \psi^n_{(r)} | V | \psi^m_{(r)} \right\rangle$$

Because the potentail is constant we can rewrite the matrix elements

$$V_{n,m} = V_0 \int_V \psi_n^* \psi_m dr$$

Shreodinger equations for ψ_n^* and ψ_m are

$$-\frac{\hbar^2}{2m}\nabla^2\psi_n^* + V_0\psi_n^* = E_n\psi_n^*$$

$$-\frac{\hbar^2}{2m}\nabla^2\psi_m + V_0\psi_m = E_m\psi_m$$

After multiplying the first equation with ψ_m and the second equation with ψ_n^* from the left and rearranging we get

$$-\frac{\hbar^2}{2m}\psi_m\nabla^2\psi_n^* = (E_n - V_0)\,\psi_n^*\psi_m$$

$$-\frac{\hbar^2}{2m}\psi_n^*\nabla^2\psi_m = (E_m - V_0)\,\psi_n^*\psi_m$$

Subtracing the second equation from the first we obtain

$$\psi_n^*\psi_m = \frac{\hbar^2}{2m}\frac{1}{(E_n - E_m)}\left[\psi_n^*\nabla^2\psi_m - \psi_m\nabla^2\psi_n^*\right]$$

And the matrix elements of the potential are

$$V_{n,m} = \frac{\hbar^2}{2m}\frac{V_0}{(E_n - E_m)}\int_V \left[\psi_n^*\nabla^2\psi_m - \psi_m\nabla^2\psi_n^*\right] dr$$

Apllying Green's theorem we get

$$V_{n,m} = \frac{\hbar^2}{2m} \frac{V_0}{(E_n - E_m)} \oint_S [\psi_n^* \nabla \psi_m - \psi_m \nabla \psi_n^*] \cdot \hat{n} ds$$

We can define $\partial \psi = \nabla \psi \cdot \hat{n}$ and than we have

$$V_{n,m} = \frac{\hbar^2}{2m} \frac{V_0}{(E_n - E_m)} \oint_S [\psi_n^* \partial \psi_m - \psi_m \partial \psi_n^*] \, ds$$