A Minimum Flux Surface

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The flux operator which has been introduced by Miller[1] has following form in one dimension;

$$\mathbf{F}(x_0)=\frac{\bar{h}}{2mi}\{\delta(x-x_0)\frac{d}{dx}+\frac{d}{dx}\delta(x-x_0)\} \qquad (1)$$

where x_0 is the position at which the flux is measured. Calculation of thermal rate constant, k(T), either by the flux-flux autocorrelation function method[2] or by the quantum transition state theory (QTST)[2,3] requires evaluation of the flux $< E|\mathbf{F}(x_0)|E' >$ between any two continuum states $|E >$ and $|E' >$ with energies E and E' respectively. Thermal rate constants by the flux-flux autocorrelation method in principle are known to be independent of the position of the dividing surface x_0 because the dynamics of a process is kept followed until the change is completed.[1,2] In practical applications, however, Rom *et al.*[4] has shown that k(T) by the method depends on the position of x_0. This does also apply to the rate constants by QTST, which is regarded as the short time approximation of the flux-flux autocorrelation method,[3] since the barrier recrossing is not taken into account. Determination of the minimum flux surface is thus frequently sought in actual calculations. In this work, we determine the position of the dividing surface for minimum flux.

In order to determine x_0 for minimum flux between two states, we need following conditions;

$$\begin{aligned}&\frac{d}{dx_0}|\langle E|F(x_0)|E'\rangle|^2\\&=\frac{d}{dx_0}\left(\frac{\bar{h}}{2m}\right)^2|\psi^*_E(x_0)\psi'_{E'}(x_0)-\psi^{*\prime}_E(x_0)\psi_{E'}(x_0)|^2\\&=0\end{aligned} \qquad (2a)$$

$$\begin{aligned}&\frac{d^2}{dx_0^2}|\langle E|F(x_0)|E'\rangle|^2\\&=\frac{d^2}{dx_0^2}\left(\frac{\bar{h}}{2m}\right)^2|\psi^*_E(x_0)\psi'_{E'}(x_0)-\psi^{*\prime}_E(x_0)\psi_{E'}(x_0)|^2>0\end{aligned} \qquad (2b)$$

where ′ denotes differentiation with respect to x_0. Define $W_{EE'}(x_0)$ as below;

$$W_{EE'}(x_0)\equiv\psi^*_E(x_0)\psi'_{E'}(x_0)-\psi^{*\prime}_E(x_0)\psi_{E'}(x_0) \qquad (3)$$

and Eqs. (2a) and (2b) become as follows respectively;

$$\begin{aligned}\frac{d}{dx_0}|W_{EE'}|^2&=(W'_{EE'}W^*_{EE'}+W_{EE'}W^{*\prime}_{EE'})\\&=\frac{2m}{\bar{h}^2}(E-E')\left[|\psi_E|^2\frac{d}{dx_0}|\psi_{E'}|^2-|\psi_{E'}|^2\frac{d}{dx_0}|\psi_E|^2\right]\\&=0\end{aligned} \qquad (4a)$$

$$\begin{aligned}\frac{d^2}{dx_0^2}|W_{EE'}|^2=2\left(\frac{2m}{\bar{h}^2}\right)&\left[\frac{2m}{\bar{h}^2}(E-E')^2|\psi_E\psi_{E'}|^2\right.\\&\left.+(E-E')(|\psi_E\psi'_{E'}|^2-|\psi_{E'}\psi_{E'}|^2)\right]>0\end{aligned} \qquad (4b)$$

Eq. (4a) yields following condition for x_0 of minimum flux for two states with different energies E and E';

$$\frac{\frac{d}{dx_0}|\psi_E(x_0)|^2}{|\psi_E(x_0)|^2}=\frac{\frac{d}{dx_0}|\psi_{E'}(x_0)|^2}{|\psi_{E'}(x_0)|^2} \qquad (5)$$

which shows that if the ratio $\dfrac{\frac{d}{dx_0}|\psi_E(x_0)|^2}{|\psi_E(x_0)|^2}$ is constant for any E at certain x_0, then this point may be the position for minimum flux. Inequality in Eq. (4b) is satisfied for any finite x_0 since at $x_0\rightarrow\pm\infty$, $(d^2/dx_0^2)|W_{EE'}|^2$ becomes zero as $\psi_E(x_0)\rightarrow e^{\pm ikx_0}$ due to the cancellation of the first term by the second term. For finite x_0, $\psi_E(x_0)\sim e^{\pm i\int^{x_0}k(x')dx'}$ and $k(x)\le k$ since $k=\sqrt{2mE}/\bar{h}$ is the wave vector where V(x) =0. Then the second term would be $(E-E')(|k'(x_0)|^2-|k(x_0)|^2)|\psi_E\psi_{E'}|^2$ which is greater than $-2mE/\bar{h}(E-E')^2|\psi_E\psi_{E'}|^2$ and $\psi_E(x_0)$ satisfies Eq. (4b). Therefore a finite x_0 which meets Eq. (4a) will be the position of minimum flux.

We apply Eq. (4a) for a given potential V(x) to find out x_0. To do this, we consider two cases where a) V(x) is symmetric; and b) V(x) is not with respect to x.

a) symmetric V(x). Since the parity operator commutes with the Hamiltonian of a system with symmetric V(x), four eigensolutions such as $\psi_E(\pm x)$ and $\psi^*_E(\pm x)$ are possible for a given E. Among these, only two solutions are linearly independent and the following relations hold between them;

$$\psi_E(-x)=\pm\psi_E(x) \qquad (6a)$$

$$\psi^*_E(-x)=\pm\psi_E(x) \qquad (6b)$$

where Eq. (6a) represents the definite parity of the eigenfunctions. Definite parity functions satisfy the condition of Eq. (5) since $|\psi_E|^2$ from these functions is even with respect to $x_{\max}$, the position of barrier maximum, and $d/dx_0|\psi_E|(x_0)|^2_{x_{\max}}$ equals to 0. However these functions yield $W_{EE'}$ of Eq. (3) to be 0 at $x_{\max}$ which is trivial. On the contrary, $|\psi_E|^2$ from functions of Eq. (6b) meets the condition of Eq. (5) because $|\psi_E|^2$ is even with respect to $x_{\max}$ while the flux from these functions is not equal to 0 at this point. These functions also satisfy Eq. (4b) for condition of the minimum flux according to the argument stated above. Therefore $x_{\max}$ is a minimum flux surface. At $x_0 \to \pm\infty$, both $d/dx_o|W_{EE'}|^2$ and $d^2/dx_o^2|W_{EE'}|^2$ become zero while $W_{EE'}$ does not as the asymptotic solutions behave like $e^{\pm ikx_o}$. Accordingly $x_0 \to \pm\infty$ may be inflection points. The result shows why the position of barrier maximum is often chosen as the dividing surface for symmetric systems.[3]

b) nonsymmetric V(x). Eigenfunctions for nonsymmetric systems do not have definite parities and the position of barrier maximum may not be a minimum flux surface in general. However, for V(x) with a slight asymmetry, the eigenfunctions possess approximate parities and $x_{\max}$ would be a minimum flux surface for this system. For systems with V(x) of a strong asymmetry, $x_{\max}$ will not be a minimum flux point while $x_0 \to \pm\infty$ are inflection points which was shown numerically.[4] The analysis may be extended to higher dimensions since the flux operator can be expressed approximately in an appropriate one dimensional form.

References

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