Theory of tunneling splitting in symmetric double well systems - Equivalence of the two state approximation and the Herring formula

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Abstract

The computation of tunneling splitting in physical systems such as molecular systems, qubits and more, is still quite challenging because of its very small magnitude, as compared with the typical ~~vibrational~~ spacing between doublet levels. Thus, it is important to understand and develop methods that can reproduce the physics of the tunneling splitting in a simple and direct way. Herring's formula is probably the most popular expression in this sense. To shed light on the implications of this formula, which was first proposed by C. Herring, Rev. Mod. Phys. 34, 631 (1962), we investigate the connection between the two state approximation, as employed for non-adiabatic induced tunneling splitting, and the Herring formula, which is relevant to adiabatic tunneling splitting. We will show that the two state approximation, and the Herring formula which may be derived as a weak value of the flux operator and is a derivative result, are identical for a symmetric double well potential. This unveils the physics underlying Herring's formula and provides further justification for the two state approximation for the nonadiabatic tunneling splitting estimate. We conclude that when Herring's formula is used with approximate eigenfunctions, it will not be accurate when the two state approximation is not valid, i.e. when the energy splitting is comparable to the eigen-energy spacing. More generally, Herring's formula will fail when the two state approximation fails. We also show how the identity between the integral two state approximation form and Herring's formula may be used to obtain analytic expressions for some non-trivial integrals.

I. INTRODUCTION

It is almost a century since tunneling splitting was discovered by Hund in symmetric molecules [1]. The computation of the magnitude even today is challenging, due to the very small splitting energy as compared to other ~~vibrational molecular~~ energy scales. The numerical computation in one dimensional models is straightforward, however as the number of degrees of freedom increases, the computation becomes increasingly more difficult. A popular approximate methodology is based on semiclassics [2–5]. One class of semiclassical methods is based on steepest descent estimates of thermal averages [6, 7]. Another semiclassical approach is to obtain the semiclassical limit of what is known as the Herring formula [8–11] which shows that the splitting is proportional to the spatial derivative of the ~~molecular~~ system density, typically at the barrier location.

To prevent any misunderstanding, we set the terminology as used when studying transitions between electronic levels rather than its use in thermodynamics. The word adiabatic as used here refers to approximations such as the Born-Oppenheimer approximation [12], in which electronic motion is fast compared to nuclear motion and therefore the electronic states does not change when the nuclei evolve in time. Nonadiabatic refers to a situation which enables transitions between electronic states. The word diabatic refers to an approach in which a certain configuration of the heavy masses is kept fixed, i.e. the electronic character of the system, whether neutral or ionic. The adiabatic-diabatic nomenclature is discussed extensively for example in Refs. [13–15].

Tunneling splitting is not limited to motion on a single adiabatic double well potential. It may also be induced due to nonadiabatic interactions [16]. The two mechanisms are related, but not identical, especially when the nonadiabatic interaction energy is small as compared to the typical spacing between energy levels. Recently we have shown [17] that a robust method for computation of nonadiabatic induced tunneling splitting is based on a two diabatic state approximation [19–21], where each state is relevant to one of the two wells which give the tunneling splitting. The two state approximation provides an efficient route for numerical evaluation of the tunneling splitting.

It thus becomes natural to question whether there is any connection between the two state approximation as used for non-adiabatic induced tunneling splitting and the Herring formula, which is employed for adiabatic tunneling splitting. This is the topic of this paper.

We will show that the two state approximation and the Herring formula lead to identical results. This gives insight into the physics underlying the Herring formula, and serves as a further justification for the use of the two state approximation when considering nonadiabatic tunneling splitting energies.

In Section II we review the two state approximation as applied to nonadiabatic tunneling splitting. In Section III we rederive the Herring formula for adiabatic tunneling splitting, showing among others that it may be reformulated as a weak value [22, 23] of the flux operator. Then in Section IV we show how the multi-dimensional two state approximation reduces to the multidimensional Herring formula demonstrating that the two state approach may be considered as an integral form of the Herring formula which is the derivative form. We end with a Discussion and implications for future work on tunneling splitting, paying special attention to generalization to asymmetric tunneling.

II. THE TWO STATE APPROXIMATION

Consider a system with two orthogonal electronic states such that the Hamiltonian has the form

$$\hat{H} = \hat{H}_1 \left|L\right\rangle\left\langle L\right| + \hat{H}_2 \left|R\right\rangle\left\langle R\right| + \hat{V}\left[\left|L\right\rangle\left\langle R\right| + \left|R\right\rangle\left\langle L\right|\right] \tag{2.1}$$

where $\hat{H}_1, \hat{H}_2$ and $\hat{V}$ depend on the "nuclear" coordinates. The matrix representation of the "nuclear" Hamiltonian in this diabatic electronic basis set is

$$\hat{H} = \begin{pmatrix} \hat{H}_1 & \hat{V} \\ \hat{V} & \hat{H}_2 \end{pmatrix}. \tag{2.2}$$

Symmetry implies that the diabatic Hamiltonians are mirror images (in the sense that the potentials in the Hamiltonians have mirror symmetry, in one dimension $V(x) = V(-x)$) and have a complete set of discrete eigenstates states with real normalized eigenfunctions:

$$\hat{H}_i|\psi_{ij}\rangle = E_j|\psi_{ij}\rangle, \quad i = 1, 2. \tag{2.3}$$

Here, the index j runs over the eigenstates of each separate well. When the nonadiabatic coupling operator is "small" the two equal energy levels with the same quantum numbers of the diabatic Hamiltonians will be slightly shifted -this is the energy level splitting which is here of interest.

The matrix representation of the full Hamiltonian using only the two mirror image states $|\psi_{1j}\rangle$ and $|\psi_{2j}\rangle$ to estimate the energies of the j-th pair of eigenstates takes the form

$$\left\langle \hat{H} \right\rangle = \begin{pmatrix} \langle\psi_{1j}|\hat{H}_1|\psi_{1j}\rangle & \langle\psi_{1j}|\hat{V}|\psi_{2j}\rangle \\ \langle\psi_{1j}|\hat{V}|\psi_{2j}\rangle & \langle\psi_{2j}|\hat{H}_2|\psi_{2j}\rangle \end{pmatrix} = \begin{pmatrix} E_j & \langle\psi_{1j}|\hat{V}|\psi_{2j}\rangle \\ \langle\psi_{1j}|\hat{V}|\psi_{2j}\rangle & E_j \end{pmatrix} . \tag{2.4}$$

This Hermitian Hamiltonian has 2 eigenvalues and associated eigenfunctions. Using the notation

$$V_{jj} = \langle\psi_{1j}|\hat{V}|\psi_{2j}\rangle \tag{2.5}$$

one readily finds that the eigenvalues are the solutions of a quadratic equation such that

$$\lambda_{\pm} = E_j \pm V_{jj}. \tag{2.6}$$

The energy splitting is then estimated as

$$\Delta\lambda = |\lambda_+ - \lambda_-| = 2\,|V_{jj}|\,. \tag{2.7}$$

In this two diabatic state approximation, all that is needed is the expectation value of the nonadiabatic coupling operator using the mirror image eigenfunctions of the diabatic Hamiltonian. This approximation has been described and analyzed in some detail in Ref. [17]. The challenge is to show that a two state approximation may be useful also when considering the energy splitting due to a single adiabatic double well potential.

III. WEAK VALUE OF THE FLUX AND HERRING'S FORMULA

Weak values of operators have been formulated to express the results of many weak measurements which do not disturb the quantum system significantly yet provide important information when pre and post selecting the quantum states of the system. Further information on weak values may be found for example in Ref. [24]. We will show that the starting point of the derivation of Herring's formula is the reformulation of the difference in energy between two eigenvalues as a weak value of the flux operator in terms of their respective (normalized) eigenstates. To simplify we consider here one dimensional systems. The multidimensional version of the Herring formula is given in Section IV. Consider a one dimensional Hamiltonian operator such that

$$\langle x|\hat{H}|\psi_j\rangle = \left[-\frac{\hbar^2}{2M}\frac{d^2}{dx^2} + V\left(x\right)\right]\langle x|\psi_j\rangle = E_j\langle x|\psi_j\rangle. \tag{3.1}$$

The overlap of the two states $\langle\psi_j|\psi_k\rangle$ is of course zero. However, the partial overlap defined as

$$\langle\psi_j|\psi_k\rangle^* = \int_{-\infty}^{x^*} dx\psi_k(x)\,\psi_j(x) \equiv S_{jk}(x^*) \tag{3.2}$$

does not necessarily vanish. Here, the coordinate value x^* is in principle arbitrary. Below, we will choose this to be the value of the coordinate at the barrier. With this definition one readily has that

$$\langle\psi_k|\theta(x^*-\hat{x})\,\hat{H}|\psi_j\rangle = E_j S_{jk}(x^*) \tag{3.3}$$

$$\langle\psi_j|\theta(x^*-\hat{x})\,\hat{H}|\psi_k\rangle = E_k S_{kj}(x^*) = E_k S_{jk}(x^*). \tag{3.4}$$

where the last line equality follows from the fact that for bound states, the eigenfunctions are pure real.

The energy difference between two eigenstates may then be written as

$$\begin{aligned}\Delta E_{kj} &\equiv E_k - E_j = \frac{\langle\psi_k|\theta(x^*-\hat{x})\,\hat{H}|\psi_j\rangle - \langle\psi_j|\theta(x^*-\hat{x})\,\hat{H}|\psi_k\rangle}{S_{jk}(x^*)} \\ &= -\frac{\hbar^2}{2MS_{jk}(x^*)}\left[\langle\psi_k|\theta(x^*-\hat{x})\frac{d^2}{dx^2}|\psi_j\rangle - \langle\psi_j|\theta(x^*-\hat{x})\frac{d^2}{dx^2}|\psi_k\rangle\right].\end{aligned} \tag{3.5}$$

where the last line is due to the fact that the potential operator $V(\hat{x})$ commutes with the step function projection operator $\theta(x^*-\hat{x})$. Using the fact that the eigenfunctions vanish as $x \to \pm\infty$ and integrating twice by parts, one readily finds that

$$\begin{aligned}&\langle\psi_j|\theta(x^*-\hat{x})\frac{d^2}{dx^2}|\psi_k\rangle \\ &= \psi_j(x^*)\frac{d\psi_k(x)}{dx}|_{x=x^*} - \psi_k(x^*)\frac{d\psi_j(x)}{dx}|_{x=x^*} + \int_{-\infty}^{x^*} dx\psi_k(x)\frac{d^2\psi_j(x)}{dx^2}.\end{aligned} \tag{3.6}$$

Inserting this result into Eq. 3.5 enables rewriting the energy difference as

$$\Delta E_{kj} = \frac{\hbar^2}{2MS_{jk}(x^*)}\left[\psi_j(x^*)\frac{d\psi_k(x)}{dx}|_{x=x^*} - \psi_k(x^*)\frac{d\psi_j(x)}{dx}|_{x=x^*}\right] \tag{3.7}$$

The matrix element of the flux operator at the point x^* is by definition

$$\begin{aligned}\langle\psi_j|\hat{F}(x^*)|\psi_k\rangle &= \langle\psi_j|\frac{\hat{p}}{2M}\delta(x^*-\hat{x}) + \delta(x^*-\hat{x})\frac{\hat{p}}{2M}|\psi_k\rangle \\ &= -\frac{i\hbar}{2M}\left[\psi_j(x^*)\frac{d\psi_k(x)}{dx}|_{x=x^*} - \psi_k(x^*)\frac{d\psi_j(x)}{dx}|_{x=x^*}\right]\end{aligned} \tag{3.8}$$

so that the energy difference may be reformulated exactly as a weak value of the flux operator [18]

$$\Delta E_{kj} = i\hbar \frac{\langle \psi_j | \hat{F}(x^*) | \psi_k \rangle}{\langle \psi_j | \psi_k \rangle^*}. \tag{3.9}$$

This result is valid for any finite point x^*.

Thus far the discussion was very general, applicable to any pair of non-degenerate eigenvalues. We now specify to the case of symmetric tunneling splitting. Denoting the exact normalized symmetric and antisymmetric eigenfunctions of a given doublet as $\psi_{n,\pm}(x)$ one may always define normalized left and right wavefunctions as the sum and difference of the two eigenfunctions (the factor of 2 in the denominator multiplying $S_{jk}(0)$ is due to the fact that $S_{jk}(0)$ is the integral from $-\infty$ to 0 and not the integral from $-\infty$ to $+\infty$, see Eq. 3.2)

$$\psi_{n,\pm}(x) = \frac{\psi_{n,L}(x) \pm \psi_{n,R}(x)}{\sqrt{2\left(1 \pm 2S_{jk}(0)\right)}}. \tag{3.10}$$

Since the potential is assumed to be a symmetric double well potential, the barrier will be located at $x = 0$ so we choose $x^* = 0$. Using Eq. 3.8 and the definitions of the right and left functions as in Eq. 3.10 gives

$$\begin{aligned} E_{n,a} - E_{n,s} &= \frac{\hbar^2}{2M} \frac{\left[\psi_{n,+}(0)\,\psi'_{n,-}(0) - \psi'_{n,+}(0)\,\psi_{n,-}(0)\right]}{S_{jk}(0)} \\ &= \frac{\hbar^2}{2M} \frac{\psi_{n,R}(0)\,\psi'_{n,L}(0) - \psi_{n,L}(0)\,\psi'_{n,R}(0)}{S_{jk}(0)\sqrt{\left(1 - 4S_{jk}^2(0)\right)}} \end{aligned} \tag{3.11}$$

Due to symmetry

$$\psi_{n,R}(0) = \psi_{n,L}(0), \quad \psi'_{n,R}(0) = -\psi'_{n,L}(0) \tag{3.12}$$

so that the final exact result for the tunneling splitting in the case of a symmetric potential is

$$E_a - E_s = \frac{\hbar^2}{M} \frac{\psi_{n,L}(0)\,\psi'_{n,L}(0)}{S_{jk}(0)\sqrt{\left(1 - 4S_{jk}^2(0)\right)}}. \tag{3.13}$$

Using the definition of the overlap $S_{jk}(0)$ between the symmetric and antisymmetric eigenfunctions of the doublet and the localized left and right functions as in Eq. 3.10, one readily finds that

$$\begin{aligned} S_{jk}(0)\sqrt{\left(1 - 4S_{jk}^2(0)\right)} &= \frac{1}{2}\int_{-\infty}^{x^*=0} dx \left[\psi_{n,L}(x)\,\psi_{n,L}(x) - \psi_{n,R}(x)\,\psi_{n,R}(x)\right] \\ &\simeq \frac{1}{2} \end{aligned} \tag{3.14}$$

since the right side function is almost negligible on the left side of the barrier and the left function is almost completely localized on the left side. The final result then is Herring's formula for the symmetric case

$$E_a - E_s \simeq \frac{2\hbar^2}{M} \psi_{n,L}(0)\, \psi'_{n,L}(0)\,. \tag{3.15}$$

It is instructive to recapitulate the derivation. If the symmetric-antisymmetric pair of eigenstates is known exactly, then Eq. 3.13 is exact. The only approximation made in deriving Herring's result is that the left and right functions are localized on the left and right sides, leading to Eq. 3.15. In practice, the eigenfunctions are typically not known and then one resorts to approximations. A common and useful one is the semiclassical approach as discussed for example in Ref. [9].

IV. HERRING'S FORMULA AND THE TWO STATE APPROXIMATION

A. Preliminaries

We assume the existence of a Hamiltonian operator in $N+1$ dimensions

$$\hat{H} = \sum_{j=0}^{N} \frac{\hat{p}_j^2}{2M_j} + V(\hat{x}_0, \hat{\mathbf{x}}) \tag{4.1}$$

where $\hat{\mathbf{x}}$ denotes the coordinate operators $\hat{x}_1, \hat{x}_2, ..., \hat{x}_N$ conjugate to the momentum operators $\hat{p}_1, \hat{p}_2, ..., \hat{p}_N$ of the stable normal modes while $\hat{p}_0$ and $\hat{x}_0$ are the momentum and coordinate operators associated with the unstable mode at the saddle point of the potential ($x_0 = x_1 = ,,, = x_N = 0$). We are interested in the tunneling splitting due to symmetrically placed wells, on each side of the saddle point. Without loss of generality, we assume that the coordinate x_0 is the reaction coordinate and the symmetry is with respect to inversion of the reaction coordinate, that is

$$V(\hat{x}_0, \hat{\mathbf{x}}) = V(-\hat{x}_0, \hat{\mathbf{x}})\,. \tag{4.2}$$

We may then define mirror image potentials centered to the left and right of the saddle point such that:

$$V_L(\hat{x}_0, \hat{\mathbf{x}})\,\theta(-\hat{x}_0) \;=\; V(\hat{x}_0, \hat{\mathbf{x}})\,\theta(-\hat{x}_0) \tag{4.3}$$

$$V_R(\hat{x}_0, \hat{\mathbf{x}})\,\theta(\hat{x}_0) \;=\; V(\hat{x}_0, \hat{\mathbf{x}})\,\theta(\hat{x}_0) \tag{4.4}$$

The left and right potentials are shown schematically in Fig. 1. Note that the left (right) potential is arbitrary for positive (negative) x_0 and may be defined such that the spectrum associated with the left and right potentials is complete. The associated Hamiltonians are

$$\hat{H}_{L,R} = \sum_{j=0}^{N} \frac{\hat{p}_j^2}{2M_j} + V_{L,R}\left(\hat{x}_0, \hat{\mathbf{x}}\right). \tag{4.5}$$

and by construction

$$V\left(\hat{x}_0, \hat{\mathbf{x}}\right) = V_L\left(\hat{x}_0, \hat{\mathbf{x}}\right)\theta\left(-\hat{x}_0\right) + V_R\left(\hat{x}_0, \hat{\mathbf{x}}\right)\theta\left(\hat{x}_0\right). \tag{4.6}$$

We may then assume that the left and right Hamiltonians have eigenfunctions and eigenvalues such that

$$\hat{H}_L|\Psi_{\mathbf{n},L}\rangle = \bar{E}_{\mathbf{n}}|\Psi_{\mathbf{n},L}\rangle, \quad \hat{H}_R|\Psi_{\mathbf{n},R}\rangle = \bar{E}_{\mathbf{n}}|\Psi_{\mathbf{n},R}\rangle \tag{4.7}$$

where $\mathbf{n}$ stands for the quantum numbers $n_0, n_1, ..., n_N$ and the bar on the energy is to denote that these are the eigenvalues of the left and right Hamiltonians, not the exact eigenvalues.

B. The adiabatic two state approximation

In the two state approximation we set up the matrix equation for the eigenvalues of the $\mathbf{n}$-th state using the two states $|\Psi_{\mathbf{n},L}\rangle$ and $|\Psi_{\mathbf{n},R}\rangle$ only. These two functions are not orthogonal, we denote their (small) overlap as

$$S_{\mathbf{n}} = \langle\Psi_{\mathbf{n},L}|\Psi_{\mathbf{n},R}\rangle. \tag{4.8}$$

The diagonal elements of the full Hamiltonian are by symmetry

$$\begin{aligned}
&\langle\Psi_{\mathbf{n},L}|\hat{H}|\Psi_{\mathbf{n},L}\rangle = \langle\Psi_{\mathbf{n},R}|\hat{H}|\Psi_{\mathbf{n},R}\rangle \\
&= \bar{E}_{\mathbf{n}} + \langle\Psi_{\mathbf{n},L}|\left[V_R\left(\hat{x}_0, \hat{\mathbf{x}}\right) - V_L\left(\hat{x}_0, \hat{\mathbf{x}}\right)\right]\theta\left(\hat{x}_0\right)|\Psi_{\mathbf{n},L}\rangle \equiv \bar{E}_{\mathbf{n}} + \langle\Psi_{\mathbf{n},L}|\Delta V|\Psi_{\mathbf{n},L}\rangle \\
&= \bar{E}_{\mathbf{n}} + \langle\Psi_{\mathbf{n},R}|\left[V_L\left(\hat{x}_0, \hat{\mathbf{x}}\right) - V_R\left(\hat{x}_0, \hat{\mathbf{x}}\right)\right]\theta\left(-\hat{x}_0\right)|\Psi_{\mathbf{n},R}\rangle
\end{aligned} \tag{4.9}$$

The off-diagonal elements are

$$\langle\Psi_{\mathbf{n},L}|\hat{H}|\Psi_{\mathbf{n},R}\rangle = \langle\Psi_{\mathbf{n},R}|\hat{H}|\Psi_{\mathbf{n},L}\rangle = \bar{E}_{\mathbf{n}}S_{\mathbf{n}} + \langle\Psi_{\mathbf{n},L}|\Delta V\left(\hat{x}_0, \hat{\mathbf{x}}\right)|\Psi_{\mathbf{n},R}\rangle. \tag{4.10}$$

The two state representation of the Schrödinger equation is thus

$$\begin{pmatrix} \bar{E}_{\mathbf{n}} + \langle\Psi_{\mathbf{n},L}|\Delta\hat{V}|\Psi_{\mathbf{n},L}\rangle & \bar{E}_{\mathbf{n}}S_{\mathbf{n}} + \langle\Psi_{\mathbf{n},L}|\Delta\hat{V}|\Psi_{\mathbf{n},R}\rangle \\ \bar{E}_{\mathbf{n}}S_{\mathbf{n}} + \langle\Psi_{\mathbf{n},L}|\Delta\hat{V}|\Psi_{\mathbf{n},R}\rangle & \bar{E}_{\mathbf{n}} + \langle\Psi_{\mathbf{n},L}\Delta|\hat{V}|\Psi_{\mathbf{n},L}\rangle \end{pmatrix} = \lambda \begin{pmatrix} 1 & S_{\mathbf{n}} \\ S_{\mathbf{n}} & 1 \end{pmatrix} \tag{4.11}$$

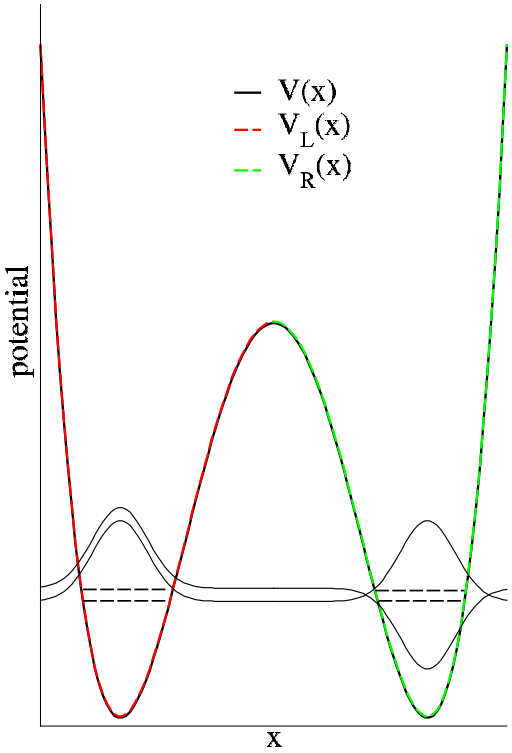

FIG. 1: Schematic figure of left (red dashed line) and right (green dashed line) potentials as defined in Eqs. 4.3 and 4.4. The black line is the full double well potential. The (dashed black) horizontal lines denote the ground state doublet. Also sketched are the doublet symmetric and antisymmetric eigenfunctions (continuous black lines).

and this leads again to a quadratic equation for the eigenvalues whose solutions are

$$\lambda_{\pm} = \bar{E}_{\mathbf{n}} + \frac{\langle \Psi_{\mathbf{n},L}|\Delta\hat{V}|\Psi_{\mathbf{n},L}\rangle \mp \langle \Psi_{\mathbf{n},L}|\Delta\hat{V}|\Psi_{\mathbf{n},R}\rangle}{(1 \mp S_{\mathbf{n}})} \tag{4.12}$$

The doublet mean energy is

$$\begin{aligned} \bar{\lambda}_{\mathbf{n}} &= \frac{\lambda_+ + \lambda_-}{2} \\ &= \bar{E}_{\mathbf{n}} + \frac{\langle \Psi_{\mathbf{n},L}|\Delta\hat{V}|\Psi_{\mathbf{n},R}\rangle - S_{\mathbf{n}}\langle \Psi_{\mathbf{n},L}|\Delta\hat{V}|\Psi_{\mathbf{n},L}\rangle}{(1 - S_{\mathbf{n}}^2)} \end{aligned} \tag{4.13}$$

while the energy splitting is

$$\begin{aligned} \Delta\lambda_n &= \lambda_- - \lambda_+ \\ &= \frac{2\langle \Psi_{\mathbf{n},L}|\Delta\hat{V}|\Psi_{\mathbf{n},R}\rangle - 2S_{\mathbf{n}}\langle \Psi_{\mathbf{n},L}|\Delta\hat{V}|\Psi_{\mathbf{n},L}\rangle}{(1 - S_{\mathbf{n}}^2)} \end{aligned} \tag{4.14}$$

The associated normalized symmetric and antisymmetric eigenvectors are

$$|\Psi_{\mathbf{n},\pm}\rangle = \frac{|\Psi_{\mathbf{n},L}\rangle \pm |\Psi_{\mathbf{n},\mathbf{R}}\rangle}{\sqrt{2\left(1 \pm S_{\mathbf{n}}\right)}} \tag{4.15}$$

Eqs. 4.13 and 4.14 provide a "practical route" for estimating energies and energy splitting in double well potentials. The only approximation used thus far is diagonalizing the Hamiltonian with only two states.

The numerator of Eq. 4.14 has two terms. The term $S_{\mathbf{n}}\langle\Psi_{\mathbf{n},L}|\Delta\hat{V}_L|\Psi_{\mathbf{n},L}\rangle$ will usually be negligible since the left-right overlap $S_{\mathbf{n}}$ is typically exponentially small and the left function is exponentially small to the right of the barrier so that the term is a product of two exponentially small components. Similarly, in the denominator, the term $S_{\mathbf{n}}^2$ may be ignored so that to a good approximation one may write the energy splitting as

$$\Delta\lambda_n \simeq 2\langle\Psi_{\mathbf{n},L}|\hat{V}_L|\Psi_{\mathbf{n},R}\rangle. \tag{4.16}$$

and we relate to this as the two state approximation to the adiabatic tunneling splitting.

C. Derivation of Herring's formula from the two state approximation

The two state approximation for the tunneling splitting, as expressed in Eq. 4.16 may be rewritten as

$$\begin{aligned}
\Delta\lambda_n &\simeq 2\langle\Psi_{\mathbf{n},L}|\left[V_R\left(\hat{x}_0,\hat{\mathbf{x}}\right) - V_L\left(\hat{x}_0,\hat{\mathbf{x}}\right)\right]\theta\left(\hat{x}_0\right)|\Psi_{\mathbf{n},R}\rangle \\
&= 2\langle\Psi_{\mathbf{n},L}|\theta\left(\hat{x}_0\right)\left[\sum_{j=0}^{N}\frac{\hat{p}_j^2}{2M_j} + V_R\left(\hat{x}_0,\hat{\mathbf{x}}\right) - \sum_{j=0}^{N}\frac{\hat{p}_j^2}{2M_j} - V_L\left(\hat{x}_0,\hat{\mathbf{x}}\right)\right]|\Psi_{\mathbf{n},R}\rangle \\
&= 2\bar{E}_{\mathbf{n}}\langle\Psi_{\mathbf{n},L}|\theta\left(\hat{x}_0\right)|\Psi_{\mathbf{n},R}\rangle - 2\langle\Psi_{\mathbf{n},L}|\theta\left(\hat{x}_0\right)\left[\sum_{j=0}^{N}\frac{\hat{p}_j^2}{2M_j} + V_L\left(\hat{x}_0,\hat{\mathbf{x}}\right)\right]|\Psi_{\mathbf{n},R}\rangle
\end{aligned} \tag{4.17}$$

Using two integrations by parts and the vanishing of the function at $\pm\infty$ gives

$$\begin{aligned}
&\langle\Psi_{\mathbf{n},L}|\theta\left(x_0\right)\left[\frac{\hat{p}_0^2}{2M_0}\right]|\Psi_{\mathbf{n},R}\rangle = -\frac{\hbar^2}{2M_0}\int_{-\infty}^{\infty}d\hat{\mathbf{x}}\int_0^{\infty}dx_0\Psi_{\mathbf{n},L}\left(x_0,\hat{\mathbf{x}}\right)\frac{\partial^2}{\partial x_0^2}\Psi_{\mathbf{n},R}\left(x_0,\hat{\mathbf{x}}\right) \\
= \frac{\hbar^2}{2M_0}\int_{-\infty}^{\infty}d\hat{\mathbf{x}}&\left(\Psi_{\mathbf{n},L}\left(0,\hat{\mathbf{x}}\right)\left[\frac{\partial}{\partial x_0}\Psi_{\mathbf{n},R}\left(x_0,\hat{\mathbf{x}}\right)\right]_{x_0=0} - \Psi_{\mathbf{n},R}\left(0,\hat{\mathbf{x}}\right)\left[\frac{\partial}{\partial x_0}\Psi_{\mathbf{n},L}\left(x_0,\hat{\mathbf{x}}\right)\right]_{x_0=0}\right) \\
-\frac{\hbar^2}{2M_0}&\int_{-\infty}^{\infty}d\hat{\mathbf{x}}\int_0^{\infty}dx_0\Psi_{\mathbf{n},R}\left(x_0,\hat{\mathbf{x}}\right)\frac{\partial^2}{\partial x_0^2}\Psi_{\mathbf{n},L}\left(x_0,\hat{\mathbf{x}}\right).
\end{aligned} \tag{4.18}$$

and therefore

$$\Delta\lambda_n \simeq \frac{\hbar^2}{M_0}\int_{-\infty}^{\infty} d\hat{\mathbf{x}}\left(\Psi_{\mathbf{n},R}\left(0,\hat{\mathbf{x}}\right)\left[\frac{\partial}{\partial x_0}\Psi_{\mathbf{n},L}\left(x_0,\hat{\mathbf{x}}\right)\right]_{x_0=0} - \Psi_{\mathbf{n},L}\left(0,\hat{\mathbf{x}}\right)\left[\frac{\partial}{\partial x_0}\Psi_{\mathbf{n},R}\left(x_0,\hat{\mathbf{x}}\right)\right]_{x_0=0}\right). \tag{4.19}$$

Due to symmetry

$$\frac{\partial}{\partial x_0}\Psi_{\mathbf{n},R}\left(x_0,\hat{\mathbf{x}}\right) = -\frac{\partial}{\partial x_0}\Psi_{\mathbf{n},L}\left(x_0,\hat{\mathbf{x}}\right) \tag{4.20}$$

so that

$$\Delta\lambda_n \simeq 2\frac{\hbar^2}{M_0}\int_{-\infty}^{\infty} d\hat{\mathbf{x}}\Psi_{\mathbf{n},R}\left(0,\hat{\mathbf{x}}\right)\left[\frac{\partial}{\partial x_0}\Psi_{\mathbf{n},L}\left(x_0,\hat{\mathbf{x}}\right)\right]_{x_0=0} \tag{4.21}$$

this is precisely the multidimensional form of Herring's formula and reduces to Eq. 3.15 since at the barrier point 0, $\Psi_L = \Psi_R$.

It is of interest to consider the two state derivation, vs Herring's derivation. If one knows the exact symmetric and antisymmetric eigenfunctions of a given doublet, then the two state approximation expression can be exact, since the left and right functions are defined as an orthogonal transformation of the exact eigenfunctions. The approximation leading from Eq. 3.13 to Eq. 3.15 is the same as the one used in Eqs. 4.14 and 4.16. In this sense one may consider the two state approximation as given in Eq. 4.16 as an integral approximation, while the Herring formula may be considered as a differential form. In practice, since the exact eigenfunctions are not known, it is not clear at this point, which formula would give a better approximation. However, as shown in the Appendix, this identity may be used to derive new analytic formulae for integrals involving Gauss-Hermite functions and other orthogonal polynomials which are eigenfunctions of a Hamiltonian.

V. DISCUSSION

The relationship of Herring's formula for the tunneling splitting in a symmetric double well potential has been related to a two state approximation for the same property. The two state approximation may be considered as an integral approximation while Herring's formula is the derivative result. From the derivation it becomes clear that the Herring formulation will not be valid when the tunneling splitting energy becomes similar to the level spacing between doublets, since in this case, the two state approximation will no longer be valid.

The effect of tunneling on energy levels in asymmetric systems has been considered in the past by a number of authors, see for example Refs. [25–27]. Especially the approach of Song

[27] is relevant in this context. For the two state approximation to be relevant, one must assume that there are two energy levels which are closer to each other than the energy gap to other states. In the integral approximation, the two energy levels are the eigenvalues of a 2 dimensional matrix. When the energy distance between the two eigenvalues is much larger than the coupling term $\langle \Delta V \rangle$ then the change in the energy eigenvalues will go as $\langle \Delta V \rangle^2$. When the energy distance is much smaller than $\langle \Delta V \rangle$ the energy will change linearly with the coupling element. The matrix element $\langle \Delta V \rangle$ is readily evaluated with either the integral or the derivative form. In the semiclassical limit, the exponential action term involved will be the Euclidean action for going from the left to the right adiabatic turning point. When the effect on the energy levels goes as $\langle \Delta V \rangle^2$ then the semi-classically one will have the full action as one goes from left to right and back to left [28] in the exponent. In the linear dependence case it will be only half the same. One can then use either the two state approximation or Herring's formula (Eq. 3.9) to estimate the effect of tunneling on spectra in asymmetric systems. The integral form as coming from the two state approximation also helps in understanding the limitations. Herring's formula will fail when the two state approximation fails.

The derivation based on two partial integrations also opens up a path for obtaining analytic estimates of integrals involving a product of eigenfunctions of a given Hamiltonian, as exemplified in Appendix A for the cusped harmonic double well potential.

Appendix A: Some analytic results

Let us consider a harmonic cusped double well potential model

$$V(q) = \frac{M\omega^2}{2} \left(|q| - q_0 \right)^2 \tag{A.1}$$

so that

$$V_L(q) = V_R(-q) = \frac{M\omega_0^2}{2} \left(q + q_0 \right)^2 . \tag{A.2}$$

Using the notation

$$\theta = \frac{M\omega}{\hbar} q_0^2 \tag{A.3}$$

for the reduced action, we know that the eigenfunctions of the left oscillator are the Gauss-Hermite polynomials. At the crossing point

$$\varphi_{n,L}(0) = \varphi_{n,R}(0) = \left(\frac{M\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{2^n n!}} \exp\left(-\frac{\theta}{2}\right) H_n\left(\sqrt{\theta}\right). \tag{A.4}$$

The resulting symmetrized and antisymmetrized functions and their derivatives at the crossing point are

$$\psi_s(0) = \frac{2\varphi_{n,L}(0)}{\sqrt{2\left(1+S_{nn}(\infty)\right)}}, \psi_a(0) = 0 \tag{A.5}$$

$$\psi_s'(0) = 0, \psi_a'(0) = \frac{2\varphi_{n,L}'(0)}{\sqrt{2\left(1+S_{nn}(\infty)\right)}} \tag{A.6}$$

and therefore:

$$\begin{aligned} \langle\psi_s|\psi_a\rangle^* &= \int_{-\infty}^{0} dq \frac{\left[\varphi_{n,L}(q)+\varphi_{n,R}(q)\right]}{\sqrt{2\left(1+S_{nn}(\infty)\right)}} \frac{\left[\varphi_{n,L}(q)-\varphi_{n,R}(q)\right]}{\sqrt{2\left(1-2S_{nn}(\infty)\right)}} \\ &\simeq \frac{1}{2\sqrt{\left(1-S_{nn}^2(\infty)\right)}} \simeq \frac{1}{2} \end{aligned} \tag{A.7}$$

where as in the Herring approximation, the contribution from $\varphi_{n,R}(q)$ may be neglected for $q \leq 0$. Similarly the contribution from $\varphi_{n,L}(q)$ may be neglected for $q \geq 0$. Using the Herring formula (Eq. 3.15) and the dimensionless energy variable

$$\varepsilon = \frac{2E}{\hbar\omega_0} \tag{A.8}$$

implies that

$$\Delta\varepsilon_n = \frac{(E_a - E_s)}{\frac{\hbar\omega}{2}} = \frac{4}{\sqrt{\pi}} \frac{1}{2^n n!} \exp(-\theta) H_n\left(\sqrt{\theta}\right) \left[\sqrt{\theta} H_n\left(\sqrt{\theta}\right) - H_n'\left(\sqrt{\theta}\right)\right]. \tag{A.9}$$

The same may be derived from the two state tunneling splitting expression. With the choices given in Eq. A.2, we have that

$$\Delta V(q) = -\theta(q)\, 2M\omega_0^2 q q_0. \tag{A.10}$$

Using the dimensionless energy (Eq. A.8) and the reduced coordinate

$$z = \sqrt{\frac{M\omega_0}{\hbar}} q \tag{A.11}$$

we readily find that the two state result for the tunneling splitting as given in Eq. 2.7 is

$$\begin{aligned}\Delta\varepsilon_n &= \frac{4}{\hbar\omega_0}\langle\varphi_{n,L}(q)|\Delta V(q)|\varphi_{n,R}(q)\rangle \\ &= -\sqrt{\frac{\theta}{\pi}}\frac{8}{2^n n!}\exp(-\theta)\int_0^\infty z\exp\left(-z^2\right)H_n\left(z+\sqrt{\theta}\right)H_n\left(z-\sqrt{\theta}\right)dz. \quad \text{(A.12)}\end{aligned}$$

Inspection of the "standard" Tables of integrals does not give the analytic result for the integral.

The exercise is then an example of how one may use physics to derive an analytic expression for an integral. Using the definitions of the left and right Gauss Hermite eigenfunctions we note that

$$\begin{aligned}&2\sqrt{\theta}\int_0^\infty z\exp\left(-z^2\right)H_n\left(z+\sqrt{\theta}\right)H_n\left(z-\sqrt{\theta}\right)dz \\ &= 2^n n!\sqrt{\pi}\exp(\theta)\int_0^\infty\left(2z\sqrt{\theta}\right)\varphi_{n,L}(z)\varphi_{n,R}(z)\,dz \\ &= 2^n n!\sqrt{\pi}\exp(\theta)\int_0^\infty\left[\frac{1}{2}\left(z+\sqrt{\theta}\right)^2-\frac{1}{2}\left(z-\sqrt{\theta}\right)^2\right]\varphi_{n,L}(z)\varphi_{n,R}(z)\,dz \\ &= 2^n n!\sqrt{\pi}\exp(\theta)\int_0^\infty\varphi_{n,R}(z)\left[-\frac{1}{2}\frac{d^2}{dz^2}+\frac{1}{2}\left(z+\sqrt{\theta}\right)^2\right]\varphi_{n,L}(z)\,dz \\ &\quad -2^n n!\sqrt{\pi}\exp(\theta)\int_0^\infty\varphi_{n,R}(z)\left[-\frac{1}{2}\frac{d^2}{dz^2}+\frac{1}{2}\left(z-\sqrt{\theta}\right)^2\right]\varphi_{n,L}(z)\,dz \quad \text{(A.13)}\end{aligned}$$

But as before, integrating twice by parts

$$\begin{aligned}&\int_0^\infty dz\varphi_{n,R}(z)\left[-\frac{1}{2}\frac{d^2}{dz^2}\right]\varphi_{n,L}(z) \\ &= \frac{1}{2}\left[\varphi_{n,R}(0)\varphi'_{n,L}(0)-\varphi'_{n,R}(0)\varphi_{n,L}(0)\right]-\frac{1}{2}\int_0^\infty dz\varphi''_{n,R}(z)\varphi_{n,L}(z) \quad \text{(A.14)}\end{aligned}$$

implies that

$$\begin{aligned}&2\sqrt{\theta}\int_0^\infty dzz\exp\left(-z^2\right)H_n\left(z+\sqrt{\theta}\right)H_n\left(z-\sqrt{\theta}\right) \quad \text{(A.15)} \\ &= -2^n n!\sqrt{\pi}\exp(\theta)\varphi_{n,L}(0)\varphi'_{n,L}(0) = H_n(z_0)\left[\sqrt{\theta}H_n(z_0)-H'_n(z_0)\right]\end{aligned}$$

so that we have the identity

$$\int_0^\infty dzz\exp\left(-z^2\right)H_n\left(z+\sqrt{\theta}\right)H_n\left(z-\sqrt{\theta}\right)=\frac{1}{2}H_n\left(\sqrt{\theta}\right)\left[H_n\left(\sqrt{\theta}\right)-\frac{1}{\sqrt{\theta}}H'_n\left(\sqrt{\theta}\right)\right] \quad \text{(A.16)}$$

demonstrating the equivalence of the integral and differential forms for the two state splitting energy as well as providing an analytic result for the integral on the left hand side.

Table 1: Tunneling splitting energies for the symmetric cusped double well potential with a high barrier			
n,$\theta = 16$	$\Delta\varepsilon_n$ (exact)	$\Delta\varepsilon_n$ (2 state)	$\Delta\varepsilon_n$ (semiclassical)
0	$1.018 \cdot 10^{-6}$	$1.01588 \cdot 10^{-6}$ (0.2%)	$9.3747 \cdot 10^{-7}$ (7.9%)
1	$3.0534 \cdot 10^{-5}$	$3.04758 \cdot 10^{-5}$ (0.2%)	$2.93837 \cdot 10^{-5}$ (3.8%)
2	$4.26514 \cdot 10^{-4}$	$4.25137 \cdot 10^{-4}$ (0.3%)	$4.13468 \cdot 10^{-4}$ (3.2%)
3	$3.665754 \cdot 10^{-3}$	$3.64321 \cdot 10^{-3}$ (0.6%)	$3.54968 \cdot 10^{-3}$ (3.3%)

Appendix B: Some numerical results

Finally, it is worthwhile to provide some numerics. The WKB approximation [28] as applied to the cusped double well potential gives the following results for the (reduced) energy splitting:

$$\Delta\varepsilon_n = \frac{1}{\pi} \exp\left(-2\int_{-z_n}^{0} dz \sqrt{\left[\left(z+\sqrt{\theta}\right)^2 - (2n+1)\right]}\right) \tag{B.1}$$

with

$$z_n = -\sqrt{\theta} + \sqrt{(2n+1)}. \tag{B.2}$$

The numerically exact results are taken from Table 3 of Ref. [29]. Inspection of the Tables shows that the two state approximation is quantitative and superior to the semiclassical one. The first Table is for a deep potential well, the second more moderate and the third shallow. The numbers in parentheses denote the relative error in the approximate results.

It should be stressed that the high quality of the 2 state or equivalently Herring approximation is related to the fact that the eigenfunctions of the left and right Hamiltonians are known in this case exactly. For other models, such as a quartic double well potential one may expect the semiclassical WKB approximation to be superior to the Herring formula, since it has the correct structure of the wave function in the deep tunneling region. This is no longer true if for example one approximates the left and right potential as harmonic oscillators only.

Table 2: Tunneling splitting energies for the symmetric cusped double well potential with a medium barrier			
n,$\theta = 9$	$\Delta\varepsilon_n$ (exact)	$\Delta\varepsilon_n$ (2 state)	$\Delta\varepsilon_n$ (semiclassical)
0	$8.3950 \cdot 10^{-4}$	$8.3552 \cdot 10^{-4}$ (0.5%)	$7.6616 \cdot 10^{-4}$ (9.6%)
1	$1.3518 \cdot 10^{-2}$	$1.3368 \cdot 10^{-2}$ (1.1%)	$1.2760 \cdot 10^{-2}$ (5.9%)
2	$9.4297 \cdot 10^{-2}$	$9.2325 \cdot 10^{-2}$ (2.1%)	$8.8214 \cdot 10^{-2}$ (6.9%)
3	$3.5149 \cdot 10^{-1}$	$3.5092 \cdot 10^{-1}$ (0.2%)	$3.2920 \cdot 10^{-1}$ (6.8%)

Table 3: Tunneling splitting energies for the symmetric cusped double well potential with a shallow barrier			
n,$\theta = 4$	$\Delta\varepsilon_n$ (exact)	$\Delta\varepsilon_n$ (2 state)	$\Delta\varepsilon_n$ (semiclassical)
0	0.084345	0.082668 (2.0%)	0.074368 (13.4%)
1	0.48798	0.49601 (1.6%)	0.44769 (9.0%)

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