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A simple and accurate approximation for a coupled system-bath: locally propagating gaussians

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Abstract

A simple method that incorporates coupling between bath and system and between individual bath modes is proposed. In the new locally propagating gaussian (LPG) approximation, the bath is modeled by Gaussians at each system site that propagate in time. Each site couples to others by the overlap of their Gaussians. In a test case with weak but non-negligible coupling, LPG is nearly as rapid as TDSCF but more closely follows exact calculations. LPG can be extended to larger simulations. Strongly coupled system coordinates will be treated with a grid-type calculation and weakly coupled bath modes will be handled by LPG.

1. Introduction

In quantum mechanical simulations accuracy and speed have to be balanced. For an accurate fully-quantum rovibrational dynamical solution the computational effort grows exponentially with the number of coupled degrees of freedom, restricting full simulations to small systems. There are a number of approximations for this problem. A notable one is the time dependent self-consistent field approximation (TDSCF), which only couples the average fields of each degree of freedom (Ref. [1]: U. Peskin, private communication). Other techniques which incorporate correlations in dynamical simulations include, e.g., path-integral and semi-classical methods [2–10], matrix-transfer approaches [11,12], and coupled channel techniques [13–16].

In this article we present a new technique which allows the inclusion of correlations between system and bath as well as modification of the bath-modes. The method is based on the following observations. First, typically in chemical reactions there are several degrees of freedom which are strongly anharmonic (the system) while the rest of the degrees of freedom (the bath) are generally harmonic. For purely harmonic potentials, a very convenient approach is to use Gaussian wavepackets [17–21]. The wavepackets preserve their shape and are simple to model. Furthermore, in multidimensional systems, a Gaussian wavepacket may be influenced by correlations that shift its tensor width. However, the coupling between the system and bath is a function of the system position. Thus, we are led to a very natural and inexpensive approach. We describe the bath by a set of Gaussians, and let the Gaussian position, momentum, and (tensor) width parameters be dependent on its site in the system. We label this approach as locally propagating gaussians (LPG). This ap-

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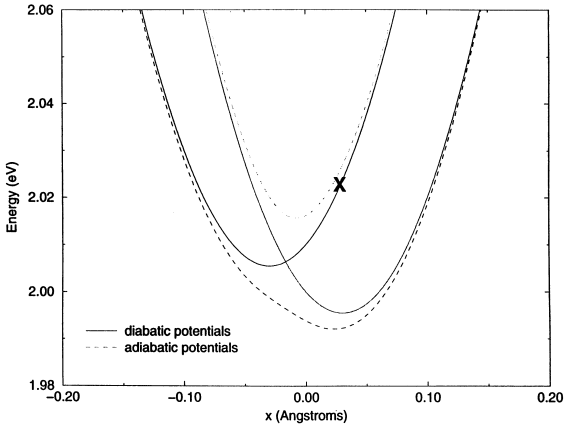

Fig. 1. Potential curves used for cases II and III, showing both the adiabatic and diabatic representations. $\boldsymbol{X}$ marks the placement of the initial Gaussian wavepacket ($\bar{x}$) in case III.

proach is clearly related to both an approach by Makri [22] where the bath is represented by a product of system-dependent TDSCF modes, and to the large amount of work on frozen Gaussians in multi-dimensions [17–21]. In the present approach very little computational resources are necessary for the bath part, so that very large systems can be handled; further, inter-bath correlations are handled (within the Gaussian approximation) by letting the Gaussian tensor width parameters be site and time dependent.

This is a presentation and preliminary test case of the method. Because of the speed of this method, large systems can be handled; however, for this first model calculation and comparison with more extensive treatments, we begin with a generic system of electron transfer between two valence atoms. This is a well known example of curve crossing (Fig. 1). In Section 2, the methodology is discussed. Section 3 compares LPG, TDSCF and full quantum calculations. In Section 4, future extension are proposed and Section 5 concludes.

2. Methodology

Consider a system and bath combination, with the general Hamiltonian:

$$H = H_{\text{bath}} + H_{\text{system}} + H_{\text{mix}}, \tag{1}$$

where we introduce the system, bath and mixing Hamiltonians (for specific forms, see below). We denote the number of bath degrees of freedom by N and define a vector $\boldsymbol{x}$, of N dimensions, for the bath degrees of freedom. Similarly, we label the system states by $|i\rangle$. The number of the system states (sites) may vary from 2, as in two site electron transfer, to a much larger number for a system comprised of several quasi-continuous degrees of freedom.

The LPG approximation for the total wavefunction is:

$$\Psi(i,\boldsymbol{x},t) = \frac{(\det M)^{1/2}}{(\pi)^{N/4}} \exp\Big[-\tfrac{1}{2}(\boldsymbol{x}-\bar{\boldsymbol{x}}_i)\cdot\boldsymbol{M}_i \cdot(\boldsymbol{x}-\bar{\boldsymbol{x}}_i) + i\bar{\boldsymbol{p}}_i\cdot\boldsymbol{x}\Big]\psi(i,t), \tag{2}$$

where the bath's variables $\bar{\boldsymbol{x}}_i$, $\bar{\boldsymbol{p}}_i$ and M_i are respectively the average position, average momentum and the tensor width, all of which are time and system-site dependent. (Note the exact meaning of $\bar{\boldsymbol{x}}_i$. It is a vector of N variables, $\bar{x}_{ni}(t)$, where $\bar{x}_{ni}(t)$ refers to the average position of the nth bath degree of freedom for system site i.)

For simplicity, we have used the case of local linear coupling to a bath of harmonic oscillators; therefore, the Hamiltonian is:

$$H_{\text{bath}} = \frac{\boldsymbol{p}^2}{2m} + \frac{\boldsymbol{x}\cdot\boldsymbol{\kappa}\cdot\boldsymbol{x}}{2} \equiv \sum_n \frac{p_n^2}{2m} + \sum_{ln}\frac{x_n\kappa_{ln}x_l}{2}, \tag{3}$$

$$H_{\text{system}} = \sum_{i,j} |i\rangle h_{ij}\langle j|, \tag{4}$$

$$H_{\text{mix}} = \sum_i \boldsymbol{\Delta}_i\cdot\boldsymbol{x}|i\rangle\langle i|, \tag{5}$$

where i and j are indices for system-sites, l and n are are the indices for the dimensions. m is the oscillators' mass (chosen as the same for all oscillators with no loss of generality), $\boldsymbol{\kappa}$ is the force constant tensor taken here as diagonal (κ_n), and h_{ij} is the matrix element of the system Hamiltonian (including, e.g., the off diagonal kinetic term in an adiabatic representation or the diagonal and off-diagonal terms in a diabatic representation). The mixing term ($\boldsymbol{\Delta}_i\cdot\boldsymbol{x} \equiv \sum_n \Delta_{in}x_n$) is assumed to be local in the system site coordinates (i.e., it does not explicitly couple different sites $|i\rangle$ and $|j\rangle$). Other more general forms than Eqs. (3)–(5) (e.g., non-local and non-linear system-bath mixing) are easily inserted.

For this initial report we make the simplifying assumption that M is time independent. In that case it can be made diagonal and we denote the vector of its eigenvalues by $\{1/\sigma_n^2\}_{n=1}^N$ (σ_n is most naturally taken to be the natural width, $(\kappa_n m)^{1/4}$, for each Harmonic oscillator). The equations of motion for ψ_i, $\bar{x}_i$ and $\bar{p}_i$ are most conveniently obtained from the Frenkel Variational Principle [23], i.e., by varying the functional A defined as:

$$A = \int_0^\infty \langle \Psi | H - i\frac{\partial}{\partial t} | \Psi \rangle \mathrm{d}t, \tag{6}$$

where $|\Psi\rangle$ is defined in (2) and $\hbar = 1$. Specifically, the equation for $\partial\psi_i/\partial t$ is derived by by taking derivative of A with respect to ψ_i^* and setting it equal to zero. The process is then repeated with respect to $\bar{x}_i$ to give $\partial\bar{p}_i/\partial t$. However, before $\partial A/\partial\bar{p}_i$ is taken to find $\partial\bar{x}_i/\partial t$, a canonical transformation needs to be done. By multiplying the Gaussian by $\exp(i\bar{x}_i\bar{p}_i)$, the time dependent term in A with $\bar{x}_i\dot{\bar{p}}_i$ transforms to $\dot{\bar{x}}_i\bar{p}_i$. The equations of motion eventually become (for local coupling):

$$\frac{\partial\psi_i}{\partial t} = -i\left\{\left(\bar{x}_i\cdot\frac{\partial\bar{p}_i}{\partial t} + \bar{E}_i + \bar{x}_i\cdot\boldsymbol{\Delta}_i\right)\psi_i + \sum_{j=1}^{\text{sites}} W_{ij}h_{ij}\psi_j\right\}, \tag{7}$$

$$\frac{\partial\bar{x}_i}{\partial t} = \frac{\bar{p}_i}{m} + \mathrm{Re}\left[\frac{1}{\psi_i}\sum_{j=1}^{\text{sites}} h_{ij}\psi_j W_{ij}\left[\sigma^2\left(\bar{p}_j - \bar{p}_i\right) - i\left(\bar{x}_j - \bar{x}_i\right)\right]\right], \tag{8}$$

$$\frac{\partial\bar{p}_i}{\partial t} = -\left\{\bar{x}_i\cdot\boldsymbol{\kappa} + \boldsymbol{\Delta}_i + \mathrm{Re}\left[\frac{1}{\psi_i}\sum_{j=1}^{\text{sites}} h_{ij}\psi_j W_{ij} \times\left[\frac{1}{\sigma^2}\left(\bar{x}_j - \bar{x}_i\right) + i\left(\bar{p}_j - \bar{p}_i\right)\right]\right]\right\}. \tag{9}$$

Here, $\bar{E}_i$ is the sum of the oscillator energies relative to the minimum for site i and is calculated as $\bar{p}_i^2/2m + \bar{x}_i\cdot\boldsymbol{\kappa}\cdot\bar{x}_i/2 + \sum_n\omega_n/2$, with $\omega_n = \sqrt{\kappa_n/m_n}$. We also introduce the overlap term between two Gaussians on sites i and j:

$$W_{ij} = \exp\left[-\frac{1}{4\sigma^2}\left(\bar{x}_i - \bar{x}_j\right)^2 - \frac{\sigma^2}{4}\left(\bar{p}_i - \bar{p}_j\right)^2 + \frac{i}{2}\left(\bar{x}_i + \bar{x}_j\right)\cdot\left(\bar{p}_i - \bar{p}_j\right)\right]. \tag{10}$$

These equations are very efficient, since the number of real variables is just $2 + 2N$ per system site. Note that the off-diagonal terms define the coupling in Eq. (7) and are vanishing if the Gaussians have very small overlap (i.e., if $W_{ij} \cong 0$: further note the $1/\psi_i$ term in Eqs. (8) and (9). We found that this term poses no numerical difficulties in practice, even for small ψ_i).

It is interesting to compare the LPG equations to the exact and TDSCF equations. The exact wavefunction propagates as:

$$\frac{\partial\Psi(i,\boldsymbol{x},t)}{\partial t} = -i\left\{\left(\frac{\boldsymbol{p}^2}{2m} + \frac{\boldsymbol{x}\cdot\boldsymbol{\kappa}\cdot\boldsymbol{x}}{2} + \boldsymbol{x}\cdot\boldsymbol{\Delta}_i\right) \times\Psi(i,\boldsymbol{x},t) + \sum_{j=1}^{\text{sites}} h_{ij}\Psi(j,\boldsymbol{x},t)\right\}. \tag{11}$$

In the TDSCF approach the equation for the system part $\psi_i(t)$ is:

$$\frac{\partial\psi_i}{\partial t} = -i\left\{\left(\bar{\boldsymbol{x}}\cdot\frac{\partial\bar{\boldsymbol{p}}}{\partial t} + \bar{E} + \bar{\boldsymbol{x}}\cdot\boldsymbol{\Delta}\right)\psi_i + \sum_{j=1}^{\text{sites}} h_{ij}\psi_j\right\}, \tag{12}$$

where $\bar{\boldsymbol{x}}$ and $\bar{\boldsymbol{p}}$ describe the (site-independent) position of the Gaussian describing the bath in TDSCF (U. Peskin, private communication). Thus among these approaches the overlap terms are unique to LPG (see also Ref. [22]).

3. Model application

3.1. Model system

Our model study is a standard 2-site electron-transfer coupled to a simple Harmonic oscillator. The system is the electronic part with no mixing (i.e. no vibrations) and the bath is defined as the single ($N = 1$) vibrational mode. The Hamiltonian for local coupling has the simple form:

$$H = \begin{bmatrix}1 & 0\\ 0 & 1\end{bmatrix}\left(\frac{p^2}{2m} + \frac{\kappa x^2}{2}\right) + \begin{bmatrix}\epsilon_1 & \Gamma\\ \Gamma & \epsilon_2\end{bmatrix} + \begin{bmatrix}\Delta & \\ & -\Delta\end{bmatrix}x. \tag{13}$$

where the matrix notation refers to the electronic sites.

3.2. Results

In the case of weak coupling, the results of LPG closely mimic a full quantum calculation for three or more vibrational periods. The conditions chosen are shown in Table 1. For all runs Δ was chosen as 0.03 eV. The reason Δ is chosen to be small is that in future simulations when the system is expanded to many sites, the LPG approximation will only be used for coordinates (x_n) with small mixing values Δ_{in}. The strongly mixed modes will be part of a larger, full description.

At $t = 0$, we placed a wavepacket ψ on diabat 1, with $\bar{p}_i = 0$. The oscillator mass was 17 amu and $\omega =$ 0.05 eV (for numerical reason the actual placement on diabat is $\psi_1 = \sqrt{0.99}$ and the remaining portion, 0.01, on diabat 2. This was done since the equations require that ψ_i never be strictly vanishing). We varied H_{elec} and the initial $\bar{x}_i$ starting position. A Runge-Kutte differential solver was used to propagate Eqs. (7)–(9).

The LPG results were compared to the exact simulations (Eq. (11)) and TDSCF (Eq. (12)). We first examined the probability for the electron to remain on the initial site, which we denote simply by $|\Psi_1|^2$ (formally referring to $\int |\Psi(i=1,x,t)|^2 \, \mathrm{d}x$). This probability closely matches the full calculation for several vibrational periods, as shown below.

In Fig. 2, the LPG far outperforms the TDSCF results. Each vibrational period is 53 fs, so that the probability rates are very reasonable for about five vibrational periods. Eventually the pure Gaussian assumption in LPG breaks down. Qualitatively, if the wavepacket were followed exactly a new Gaussian would appear at each occurrence of the curve crossing, so that the total wavepacket on each curve would be a summation of progressively more Gaussians. But for several vibrations LPG is reasonable.

Table 1
Parameters for three test cases

Case	I	II	III
ϵ_1 (eV)	2.00	2.01	2.01
ϵ_2 (eV)	2.00	2.00	2.00
Γ (eV)	0.01	0.01	0.01
$\bar{x}_{1,2}$ (Å)	0.15	0.15	0.03

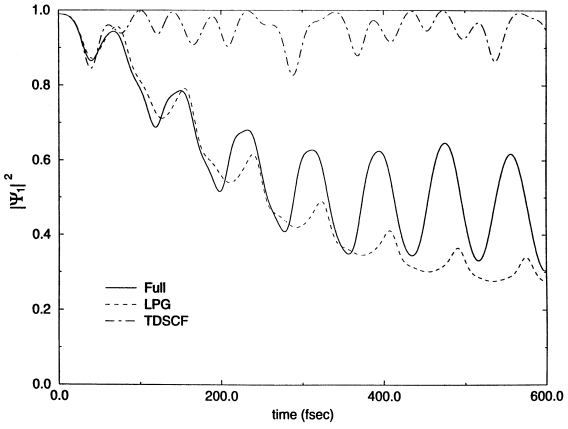

Fig. 2. Comparison of $|\Psi_1|^2$ as a function of time for two potentials of equal energy, with $\bar{x}$ at 0.15 Å. Shown are the and exact (full), LPG and TDSCF results.

In the second case (Fig. 3) the two diabats no longer have the same minimum, but are offset by 0.01 eV. Again the approximation closely follows the complete full calculation for about 230 fs.

In the third case (Fig. 4), even when $|\Psi_1|^2$ oscillates in a very non-regular fashion, LPG follows the full calculation very well, especially in comparison with TDSCF.

We also compared the Fourier transform of the correlation function defined as:

$$c(\omega) = \int_0^\infty \langle \Psi(0) | \Psi(t) \rangle e^{-i\omega t} e^{-\gamma^2 t^2} \mathrm{d}t. \qquad (14)$$

We set $\gamma = 0.0025\,\text{eV} = (263\,\text{fs})^{-1}$. Because the LPG does so well for the first several oscillations, the

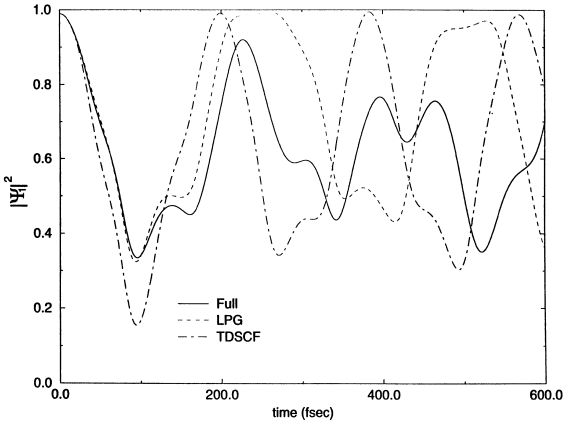

Fig. 3. Comparison of $|\Psi_1|^2$ as a function of time for $\epsilon_1 - \epsilon_2 =$ 0.01 eV and $\bar{x}$ at 0.15 Å.

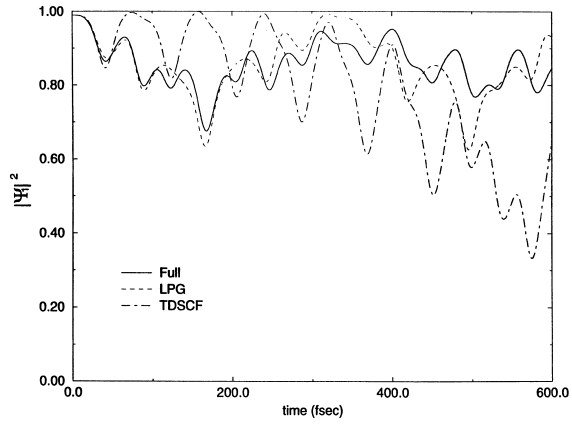

Fig. 4. Comparison of $|\Psi|^2$ as a function of time for $\epsilon_1 - \epsilon_2 = 0.01$ eV and $\bar{x}$ at 0.03 Å.

Fourier transform closely follows the exact results. Fig. 5 shows a typical result. The LPG shows excellent correspondence with the full calculation. It has some difficulty getting the exact intensity and resolving the tunneling splitting, but it shows significant improvement over TDSCF. The low energy wiggles at below -2.0 eV are the result of placing a small amount of the initial wavepacket on diabat 2.

All the cases shown correspond to weak site-site coupling. In the case (not shown) of strong coupling (Γ), the mean field and the LPG have comparable results in relation to the full calculation.

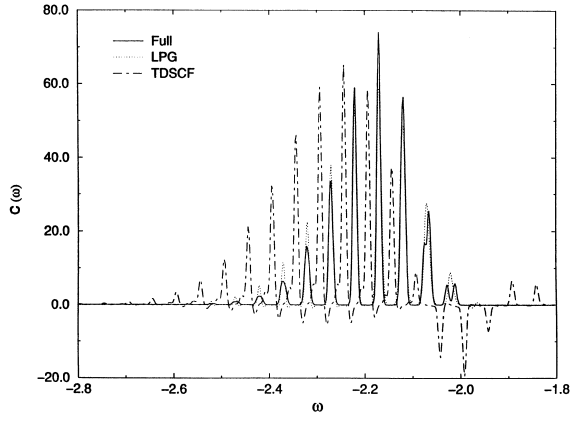

Fig. 5. Comparison of the Fourier transform of the correlation function $(c(\omega) = \int_0^\infty \langle \Psi(0)|\Psi(t)\rangle \exp(-i\omega t)\exp(-\gamma^2 t^2)\mathrm{d}t$ with $\gamma = 0.0025$ eV) for case I ($\Delta\epsilon = 0$ and $\bar{x}$ initially at 0.15 Å).

4. Future extensions

Because of its speed and ability to handle weakly coupled systems, LPG should be ideal for calculating quantum dynamics of large systems. Examples are large-scale electron transfer problems and chemical reactions on a single (or multiple) Born Oppenheimer surface(s), with several floppy (or reacting) degrees of freedom. In these cases, fully quantum calculations are not feasible because of their size, and TDSCF can break down. In this window, the LPG is an excellent candidate for quantum propagations. The system wavefunction will then be expanded from the two site model to a general multidimensional continuous coordinate.

Currently we have only used a constant for the tensor-width **M** matrix (frozen-Gaussians). In the more general equations, **M** will be time dependent. This expansion will be done in future work .

5. Conclusions

We presented a method, LPG, that accurately mimics a fully quantum propagation for several vibrational periods for weakly coupled systems without requiring extensive computational effort. The method assumes that the wavefunction at each site is (and remains) a Gaussian, but unlike the mean field approximation, explicit system dependence on the Gaussian form is incorporated. This method has been tested on only a two site problem, but it can be expanded to a much larger system. The strongly coupled system modes will still need to be done with an explicit grid-type calculation, but the bath can accurately be treated with LPG. This will extend the types of problems with correlations that can be done quantum mechanically, including many body chemical reactions and electron transfer on either surfaces or large molecules. We will be investigating these applications in the future.

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