**Published paper**
Shalashilin, D.V. and Burghardt, I. (2008) *Gaussian-based techniques for quantum propagation from the time-dependent variational principle: Formulation in terms of trajectories of coupled classical and quantum variables,* Journal of Chemical Physics, Volume 129 (8), 084104.

# Gaussian-based techniques of quantum propagation from variational principle describing dynamics by trajectories of coupled classical and quantum variables

Dmitrii V. Shalashilin

*School of Chemistry, University of Leeds, Leeds LS2 9JT, UK*

Irene Burghardt

*D'epartement de Chimie, Ecole Normale Supérieure, 24 rue Lhomond, F–75231 Paris cedex 05, France*

*In this article two existing methods of quantum propagation, namely Coupled Coherent States (CCS) and Gaussian-based Multiconfigurational Time Dependent Hartree (G-MCTDH), are put on the same formal footing and derived from variational principle in Lagrange form, which treats identically oscillations of classical motion and oscillations of quantum amplitudes. We also suggest a new approach named here as Coupled Coherent States Trajectories (CCST), which completes the family of Gaussain-based methods. Using the same formalism for all related techniques allows their systematization, easy comparison of detailed mathematical structure and cost, and transfer of important computational tricks between them.*

**Introduction**

It is well known that the time dependence of a wave function $\Psi(\alpha_1,\alpha_2,...,\alpha_n)$ is simply that of its parameters, and equations for the "trajectories" $\alpha_n(t)$ can be worked out from the variational principle

$$\delta S = 0 \tag{1}$$

by minimizing the action $S = \int L dt$ of the Lagrangian

$$L(\alpha^*_1,\alpha^*_2,...,\alpha^*_n,\alpha_1,\alpha_2,...,\alpha_n) = \left\langle \Psi(\alpha^*_1,\alpha^*_2,...,\alpha^*_n) \middle| i\frac{\hat{\partial}}{\partial t} - \hat{H} \middle| \Psi(\alpha_1,\alpha_2,...,\alpha_n) \right\rangle \tag{2}$$

with respect to the parameters of the wave function [1,2]. Everywhere in this article the time derivative operator

$$i\frac{\hat{\partial}}{\partial t} = \frac{i}{2}\left(\frac{\vec{\partial}}{\partial t} - \frac{\overleftarrow{\partial}}{\partial t}\right) \tag{3}$$

is taken as a half sum of two parts acting on the ket $i\frac{\vec{\partial}}{\partial t}$ or on the bra $-i\frac{\overleftarrow{\partial}}{\partial t}$, respectively.

The variational principle (1) straightforwardly leads to the Lagrange equations of motion

$$\frac{\partial L}{\partial \alpha_l} - \frac{d}{dt}\frac{\partial L}{\partial \dot{\alpha}_l} = 0 \quad , \tag{4}$$

and an adjoint equation for the complex conjugate, $\frac{\partial L}{\partial \alpha_l *} - \frac{d}{dt}\frac{\partial L}{\partial \dot{\alpha}_l *} = 0$.

As shown in Refs. [2], a remarkable fact is that the dynamical equations obtained from the Lagrangian exhibit a symplectic structure, similarly to the equations of classical mechanics. Perhaps the most compact and elegant way to represent the equation of motion (4) is to rewrite the Lagrange equation in the Hamilton's form by introducing the generalised momenta [2]

$$p_{\alpha_l}(\alpha *_1,...,\alpha *_n,\alpha_1,...,\alpha_n) = 2\frac{\partial L}{\partial \dot{\alpha}_l} = i\left\langle \Psi(\alpha *_1,...,\alpha *_n)\middle|\frac{\partial}{\partial \alpha_l}\Psi(\alpha_1,...,\alpha_n)\right\rangle, \tag{5}$$

and similarly for the complex conjugate $p_{\alpha_l^*} = 2\frac{\partial L}{\partial \dot{\alpha}_l *} = -i\left\langle \frac{\partial}{\partial \alpha_l *}\Psi \middle| \Psi \right\rangle$. Then the equation of motion has the usual Hamilton's form

$$\dot{\alpha}_l = \frac{\partial\langle H\rangle}{\partial p_{\alpha_l}} = \sum_j \frac{\partial\langle H\rangle}{\partial \alpha *_j}\frac{\partial \alpha *_j}{\partial p_{\alpha_l}} \quad . \tag{6}$$

with the complication that the Hamiltonian

$$\left\langle \hat{H} \right\rangle = \left\langle \Psi(\alpha^*_1, \alpha^*_2, ..., \alpha^*_n) \middle| \hat{H} \middle| \Psi(\alpha_1, \alpha_2, ..., \alpha_n) \right\rangle \tag{7}$$

is not an explicit function of the momenta. Therefore its partial derivative with respect to the momenta must be expressed through the elements of the matrix $\frac{\partial \alpha^*_j}{\partial p_{\alpha_l}} = \left(D^{-1}\right)_{lj}$ obtained by inverting the matrix

$$D_{jl} = \frac{\partial p_{\alpha_i}}{\partial \alpha^*_j} = i\left\langle \frac{\partial}{\partial \alpha^*_j} \Psi(\alpha^*_1, \alpha^*_2, ..., \alpha^*_n) \middle| \frac{\partial}{\partial \alpha_l} \Psi(\alpha_1, \alpha_2, ..., \alpha_n) \right\rangle \tag{8}$$

defined by (5).

Variational Gaussian wavepacket dynamics is certainly the most straightforward example for the application of the time dependent variational principle to a parametrized wavefunction. While the construction of variationally evolving Gaussian basis sets can be traced back to the work of Sawada, Heather, Jackson and Metiu [1] and perhaps even further, the elegant analogy of the quantum equations of motion with the Lagrange and Hamilton's equations of classical mechanics noticed in [2] has rarely been pointed out in these applications.

The goal of this article is to systematically apply the variational principle (1,2) and the Lagrange equations (4) to the wave function expressed as a superposition of Frozen Gaussian (FG) wave packets also known as Coherent States (CS). Beginning with the work of Heller [3], FG wave packets have a long history of use in quantum and semiclassical simulations. CS provide a very convenient analog of the classical phase space point, following classical trajectory motion, and ensembles of CS have been extensively used within the semiclassical Herman-Kluk propagator formulation [4,5] (see

for example the reviews [6-10]). Recently a number of quantum methods have emerged, such as multiple spawning (MS) by Martinez [11-14] and Coupled Coherent States (CCS) by Shalashilin and Child [15-20], which employ grids of FG Coherent States guided by classical trajectories in [11-14], and by classical trajectories with a quantum corrected Hamiltonian in [15-20]. Here, the CS provide a basis set for quantum propagation without making any semiclassical approximations. FG basis sets were also employed by Burghardt and Worth in the G-MCTDH method [21,22], which is a variant of the multiconfiguration time-dependent Hartree (MCTDH) method [31] that relies on nonclassically evolving Gaussians guided by equations determined from the Dirac-Frenkel variational principle. Although the G-MCTDH method in principle allows for changes of the Gaussian width parameter (and several application based on such "Thawed Gaussians" have been carried out [22]), Frozen Gaussians are numerically more robust and are therefore employed in the majority of applications. If used as an all-Gaussian method and restricted to an FG basis set, the method is referred to as vMCG (variational multiconfigurational Gaussian approach). A related approach, denoted LCSA (local coherent state approximation) has recently been developed by Martinazzo et al. [23] who demonstrated that harmonic bath modes can be very efficiently described with CS guided by nonclassical trajectories derived from a variational principle.

There are several advantages associated with CS basis sets: (i) They constitute moving basis sets composed of localized functions that are guided by the dynamics (or a classical approximation to the true dynamics), (ii) CS initial conditions can be chosen randomly thus providing a good scaling with the number of degrees of freedom (dimensionality), (iii) classical mechanics provides clear guidance for importance

sampling, which results in huge gains in efficiency. A number of multidimensional calculations have been performed with the above methods, showing that basis sets of Frozen Gaussian CS are a useful tool. G-MCTDH applications for high-dimensional system-bath type situations show that the method converges to the exact result, even for highly anharmonic problems involving conical intersections [22].

*In this article we put the existing Gaussian based methods on the same formal footing, which allows easy systematization and comparison of their structure and cost. First we derive the equations of G-MCTDH using full variational principle and the coherent-state notation previously employed in Refs. [15-20]. Second we show that CCS technique uses full variational principle only for the amplitudes but predetermined trajectories of classical oscillators are optimal (i.e. determined from variational principle) for single CS only. Then we notice that we also the time dependence of quantum amplitudes a can be predetermined with variation principle yielding the trajectories of classical parameters z. This suggests a new technique denoted Coupled Coherent States Trajectories (CCST), which completes the family of Gaussian based methods. Using the same formalism for three different techniques allows easy comparison of their cost. We show that the number of variational parameters in CCST is almost the same as in full variation method of G-MCTDH but the computational cost of CCST should be much smaller. In addition we demonstrate how numerical tricks can be transferred between related methods and suggest a variant of the G-MCTDH method showing how its solution can be factorized into an oscillating exponent and a smooth preexponential factor, an idea used previously within the CCS approach to achieve a*

*larger time step. Therefore we provide a systematic view of the family of Gaussian based method.*

## 2.Theory

### *2.1 Coherent States*

In quantum mechanics the ket and bra coherent states of the harmonic oscillator

$$\hat{H}_{HO} = \hbar\omega\left(\hat{a}^{+}\hat{a} + \frac{1}{2}\right) \tag{8}$$

are eigenfunctions of the annihilation an creation operators, respectively,

$$\hat{a}|z\rangle = z|z\rangle \qquad \langle z|\hat{a}^{+} = \langle z|z^{*} \tag{9}$$

In the coordinate representation coherent states are Gaussian wave packets

$$\langle x|z\rangle = \left(\frac{\gamma}{\pi}\right)^{\frac{1}{4}} \exp\left(-\frac{\gamma}{2}(x-q)^{2} + \frac{i}{\hbar}p(x-q) + \frac{ipq}{2\hbar}\right) \tag{10}$$

where $q$ the position of the wave packet and its momentum $p$ are given by

$$z = \frac{\gamma^{\frac{1}{2}}q + i\hbar^{-1}\gamma^{-\frac{1}{2}}p}{\sqrt{2}} \qquad z^{*} = \frac{\gamma^{\frac{1}{2}}q - i\hbar^{-1}\gamma^{-\frac{1}{2}}p}{\sqrt{2}} \tag{11}$$

and the Eq.(10), written for one-dimensional CS, can easily be generalized for many dimensions.

Thus the CS represents a phase space point "dressed" with a finite width. In Eqs.(11) $\gamma = \frac{m\omega}{\hbar}$ determines the coordinate space width of the wave packet. For notational simplicity everywhere below it is assumed that the units are such that the Plank constant $\hbar$ and width parameter $\gamma$ are equal to one.

$$\hbar = 1 \qquad \gamma = 1 \tag{12}$$

In classical mechanics, the equations of motion can easily be written in the ($q$, $p$) variables of (11) yielding the classical Lagrange or Hamilton's equations.

Although Coherent States originate from the harmonic oscillator problem, they can be used to represent a generic Hamiltonian, which is not necessarily that of Eq.(8). Using operator relationship similar to the above Eq.(11)

$$\hat{a} = \frac{\hat{q} + i\hat{p}}{\sqrt{2}} \qquad \hat{a}^{+} = \frac{\hat{q} - i\hat{p}}{\sqrt{2}} \tag{13}$$

a generic Hamiltonian (not only that of the simple harmonic oscillator Eq.(8)) can be represented as

$$H(\hat{p},\hat{q}) = H(\hat{a},\hat{a}^{+}) = H_{ord}(\hat{a}^{+},\hat{a}) \tag{14}$$

where in the "ordered" form $H_{ord}$, creation and annihilation operators are reordered such that the powers of $\hat{a}^{+}$ precede those of $\hat{a}$ [24,30]. Operator reordering is simply a

convenient way of calculating matrix elements of the Hamiltonian, which can now be obtained by replacing the creation operator $\hat{a}^+$ with z and the annihilation operator $\hat{a}$ with $z^*$ and multiplying by the overlap of coherent states $\langle z_l | z_j \rangle$

$$\langle z_l | \hat{H} | z_j \rangle = \langle z_l | z_j \rangle H_{ord}(z_l^*, z_j) \tag{15}$$

The reordered form of the Hamiltonian differs from the classical Hamiltonian and contains additional terms resulting from the non-commutativity of the creation and annihilation operators.

Coherent States are not orthogonal and their overlap is given as

$$\langle z_l | z_j \rangle = \Omega_{lj} = \exp\left( z^*_l z_j - \frac{z^*_l z_l}{2} - \frac{z^*_j z_j}{2} \right) \tag{16}$$

A finite basis set of CS can be characterized by the identity operator

$$\hat{I} = \sum_{l,j} |z_l\rangle \Omega^{-1}_{lj} \langle z_j| \tag{17}$$

where $\Omega^{-1}_{lj}$ is the matrix elements of the inverse of the overlap matrix. More information about Coherent States can be found for example in [24,30].

### *2.2 Variational principle for classical dynamics of Coherent States*

In classical mechanics equations of motion can be obtained from the variational principle (1) with the Lagrangian $L = p\dot{q} - H(p,q)$ or $L = \frac{p\dot{q} - q\dot{p}}{2} - H(p,q)$ by the standard variation (1). In classical CS coordinates $z = \frac{q + ip}{\sqrt{2}}$ $z^* = \frac{q - ip}{\sqrt{2}}$ the Lagrangian can be written as

$$L = \frac{p\dot{q} - q\dot{p}}{2} - H(p,q) = \frac{i}{2}\left(\dot{z}z^* - \dot{z}^* z\right) - H(z,z^*) \tag{18}$$

and its variation (1) results in the classical Hamilton's equations.

$$\dot{z}^* = i\frac{\partial H(z,z^*)}{\partial z} \tag{19}$$

and the complex conjugate $\dot{z} = -i\frac{\partial H(z,z^*)}{\partial z^*}$ which can also be written in the Lagrange Form

$$\frac{\partial L}{\partial z} - \frac{d}{dt}\frac{\partial L}{\partial \dot{z}} = 0 \quad . \tag{20}$$

Indeed from the Lagrangian (18), one obtains

$$\frac{\partial L}{\partial z^*} - \frac{d}{dt}\frac{\partial L}{\partial \dot{z}^*} = \left(-\frac{\partial H(z,z^*)}{\partial z^*} + \frac{i}{2}\dot{z}\right) + \left(\frac{i}{2}\dot{z}\right) = 0 \tag{21}$$

which yields (19).

### *2.3 Variational principle for quantum dynamics of a single CS*

Now consider a wave function expressed by a single frozen Gaussian CS as

$$|\Psi\rangle = a|z\rangle \tag{22}$$

The Lagrangian then becomes

$$\begin{aligned} L = \langle \Psi | i\frac{\hat{\partial}}{\partial t} - \hat{H} | \Psi \rangle = \\ i\left[\frac{a^*\dot{a}}{2} - \frac{a\dot{a}^*}{2}\right]\langle z|z\rangle + i\left[\frac{z^*\dot{z}}{2} - \frac{z\dot{z}^*}{2}\right]a^*a - a^*a\,H_{ord}(z,z^*) \end{aligned} \tag{23}$$

where $\langle z|z\rangle = 1$, and according to (15)

$$\langle \Psi|\hat{H}|\Psi\rangle = \langle az|\hat{H}|az\rangle = a^*a\langle z|z\rangle H_{ord}(z,z^*) = a^*a\,H_{ord}(z,z^*). \tag{24}$$

The Lagrangian (23) is a very convenient object in which the classical coordinate $z, z^*$ and quantum amplitude $a, a^*$ enter in an absolutely similar fashion and therefore can be

treated on the same footing. Then the equations of motion are simply those of (4) with the parameter α being either $z$ or $a$, yielding correspondingly

$$\frac{\partial L}{\partial z^*} - \frac{d}{dt}\frac{\partial L}{\partial \dot{z}^*} = a^* a\left[ i\dot{z} - \frac{\partial H_{ord}(z^*, z)}{\partial z^*}\right] + \frac{iz}{2}\frac{d(a^* a)}{dt} = 0 \tag{25}$$

$$\frac{\partial L}{\partial a^*} - \frac{d}{dt}\frac{\partial L}{\partial \dot{a}^*} = \left[ i\frac{\dot{z}z^* - \dot{z}^* z}{2} - H_{ord}(z, z^*)\right] a + i\frac{da}{dt} = 0 \tag{26}$$

and similar equations for the complex conjugates. The solution of (25,26) is

$$a = a(0)\exp(iS) \tag{27}$$

where

$$S = \int\left[ i\frac{\dot{z}z^* - \dot{z}^* z}{2} - H_{ord}(z, z^*)\right] dt \tag{28}$$

with the CS trajectory given by the Hamilton equation

$$\dot{z} = -i\frac{\partial H_{ord}(z, z^*)}{\partial z^*} \tag{29}$$

which includes quantum corrections in the Hamiltonian $H_{ord}(z, z^*)$. It is easy to verify that for a harmonic oscillator with the Hamiltonian (8) the solution for $z$ is simply a CS orbiting the zero and the oscillating amplitude

$$z(t) = z(0)\exp(-i\omega t) \qquad a(t) = a(0)\exp\left(-\frac{i\omega t}{2}\right) \tag{30}$$

Therefore, from the above example of the variational principle (1) applied to the wave function (22) we can conclude that :

(1) The quantum Lagrangian (2) can be written as a function of the CS parameters { α } which are the CS phase space position $z$ and quantum amplitude $a$, so that the Lagrange equations yields time dependent "trajectories" for both $z$ and $a$, which determine the evolution of the quantum wave function.

(2) The evolution of the "classical oscillator" $z$ parameter of the wave function (22) represented by a single CS is given by the classical motion of the CS guided by the Hamiltonian $H_{ord}(z, z^*)$ which is a quantum average of the Hamiltonian operator over the CS $|z\rangle$.

(3) The Lagrange equation and variational principle also give rise to the "Frozen Gaussian" solution (27,28) for the amplitude, which is a product of a constant prefactor and an oscillating exponent of the classical action. The solution for the "quantum oscillation" becomes particularly simple for the harmonic Hamiltonian (30).

(4) The preexponential factor in (27) has the meaning of a classical constant of motion or invariant.

### *2.4 Variational principle for quantum dynamics in CS basis: full variation*

Now let us consider a more generic wave function represented as a superposition of several CS

$$\left|\Psi\right\rangle = \sum_{l=1,N} a_l \left|z_l\right\rangle \tag{31}$$

The Lagrangian then becomes

$$\begin{aligned} L = \left\langle \Psi \left| i\frac{\hat{\partial}}{\partial t} - \hat{H} \right| \Psi \right\rangle = \sum_{l,j} \{ & \frac{i}{2}\left[ a_l * \dot{a}_j - a_j \dot{a}_l * \right] \left\langle z_l \left| z_j \right\rangle + \right. \\ & \frac{i}{2}\left[ \left( \left(z_l * - z * _j\right)\dot{z}_j + \frac{\dot{z}_j z * _j}{2} - \frac{z_j \dot{z}_j *}{2} \right) - \left( \left(z_j - z_l\right)\dot{z} *_l + \frac{z_l \dot{z} *_l}{2} - \frac{\dot{z}_l z * _l}{2} \right) \right] \\ & \left. a_l * a_j \left\langle z_l \left| z_j \right\rangle - a_l * a_j \left\langle z_l \left| z_j \right\rangle H_{ord}\left(z * _l, z_j\right) \right\} \right. \end{aligned} \tag{32}$$

and the Lagrange equations from the variation of amplitudes $a^*$ and phase space positions $z^*$ yield, respectively,

$$\begin{aligned} \sum_j \; & i\dot{a}_j \left\langle z_l \left| z_j \right\rangle - \left\langle z_l \left| z_j \right\rangle H_{ord}\left(z * _l, z_j\right) a_j + \right. \right. \\ & \left. \left. i\left[ \left(z_l * - z * _j\right)\dot{z}_j + \frac{\dot{z}_j z * _j}{2} - \frac{z_j \dot{z}_j *}{2} \right] \left\langle z_l \left| z_j \right\rangle a_j = 0 \right. \right. \end{aligned} \tag{33}$$

and

$$\sum_j a_l^* a_j \left[ i\dot{z}_j - \frac{\partial H_{ord}(z_l^*, z_j)}{\partial z_i^*} \right] \langle z_l | z_j \rangle +$$
$$\sum_j i a_l^* \dot{a}_j (z_j - z_l) \langle z_l | z_j \rangle +$$
$$\sum_j a_l^* a_j (z_j - z_l) \langle z_l | z_j \rangle \left\{ i \left( (z^*_l - z^*_j) \dot{z}_j + \frac{\dot{z}_j z^*_j}{2} - \frac{z_j \dot{z}^*_j}{2} \right) - H_{ord}(z^*_l, z_j) \right\} +$$
$$a_l^* \left( \frac{z_l}{2} \right) \sum_j \left[ a_j \langle z_l | z_j \rangle \left\{ i \left( (z^*_l - z^*_j) \dot{z}_j + \frac{\dot{z}_j z^*_j}{2} - \frac{z_j \dot{z}^*_j}{2} \right) - H_{ord}(z^*_l, z_j) \right\} + i \dot{a}_j \langle z_l | z_j \rangle \right] +$$
$$a_l \left( \frac{z_l}{2} \right) \sum_j \left[ a^*_j \langle z_j | z_l \rangle \left\{ i \left( (z_l - z_j) \dot{z}^*_j + \frac{\dot{z}^*_j z_j}{2} - \frac{z^*_j \dot{z}_j}{2} \right) + H_{ord}(z^*_j, z_l) \right\} + i \dot{a}^*_j \langle z_j | z_l \rangle \right]$$
$$= 0 \tag{34}$$

The latter can be simplified greatly by noticing that according to (33) the last two sums in (34) are zero. Therefore, (34) becomes:

$$\sum_j a_l^* a_j \left[ i\dot{z}_j - \frac{\partial H_{ord}(z_l^*, z_j)}{\partial z_l^*} \right] \langle z_l | z_j \rangle + \sum_j i a_l^* \dot{a}_j (z_j - z_l) \langle z_l | z_j \rangle +$$
$$\sum_j a_l^* a_j (z_j - z_l) \langle z_l | z_j \rangle \left\{ i \left( (z^*_l - z^*_j) \dot{z}_j + \frac{\dot{z}_j z^*_j}{2} - \frac{z_j \dot{z}^*_j}{2} \right) - H_{ord}(z^*_l, z_j) \right\} = 0 \tag{35}$$

The Equations (33,35) are simply a system of linear equations for the derivatives of the wave function parameters $\alpha = \{a, z\}$, noting that interdependent equations are obtained for these derivatives. If, e.g., Eq. (33) is used to eliminate the derivative of the *a* coefficients from Eq. (35), a matrix form

$$A\dot{\alpha} = b$$

is obtained. In the appendix we verify that apart from notation, Eqs. (33,35) are equivalent to those introduced by Burghardt et al. in the G-MCTDH approach [21]. In order to produce time derivatives of the wave function parameters, the solution of the linear equations (33,35) is required at each step of the propagation. This is a difficult task. For a system with M dimensions represented on a basis set of N CS (31) the vector of wave function parameters $\alpha$ is comprised of N×M complex numbers $z$ describing the positions of N basis CS in M-dimensional phase space plus N CS amplitudes $a$. A numerical scheme to solve these equations in the framework of the G-MCTDH approach has been presented in [22]. Apart from the matrix inversion required to solve Eqs. (33,35), another difficulty noticed by Burghardt and Worth [22] is that the amplitudes are highly oscillatory, which requires small time steps. This problem can be coped with by introducing a suitable multi-scale integration scheme [22]. Apart from this, modifications in the formulation of the dynamical equations could lead to improvement. This issue will be addressed in Section 2.7 where a smoothing of G-MCTDH equations will be suggested. But first simplifications to the Eqs.(33,35) will be considered in Sections 2.5 and 2.6.

The conclusions of this section are:

(1) The equations of [21,22] are Lagrange equations for coupled classical and quantum oscillators.

(2) The oscillations of quantum ($a$) and classical ($z$) degrees of freedom can be treated on the same footing, as degrees of freedom of a complicated "pseudo-classical" Lagrangian (32).

### *2.5 Variation of the amplitudes a only. The method of CCS*

Let us now notice that we are not obliged to apply the variational principle to all parameters of the wave function (28). While an "optimal" time evolution will only be obtained for the subset of variational parameters, reasonable assumptions can be introduced for the remaining set of non-variational parameters. For example, we are free to choose the CS trajectories $z_i(t)$ and obtain Lagrange equations of motion to the amplitudes only. Then we do not need to solve Eqs.(35) but only Eqs.(33) with a chosen time dependence of $z_i(t)$. One for example may choose $z_l(t) = const$ and end up with a familiar system of equations for quantum amplitudes on a static grid of CS,

$$\sum_j \langle z_l | z_j \rangle \dot{a}_j = -i \sum_j \langle z_l | H | z_j \rangle a_j \tag{37}$$

where $\langle z_l | H | z_j \rangle = \langle z_l | z_j \rangle H_{ord}(z^*_l, z_j)$ is the matrix of the Hamiltonian, see Ref.[20].

A better option however would be to choose trajectories $z_i(t)$ which are optimal for a single CS, from the Hamilton's equation (29) obtained by applying the variational principle to the single CS wave function (22). It is also convenient to present the amplitudes as

$$a_j = d_j \exp(iS_j) \tag{38}$$

where

$$S_j = \int \left[ i \left( \frac{\dot{z}_j z^*{}_j}{2} - \frac{z_j \dot{z}_j^*}{2} \right) - H_{ord}\left(z_j^*, z_j\right) \right] dt \,. \tag{39}$$

and write the equations (33) for a smooth preexponential factor *d* rather than for the rapidly oscillating amplitude *a*. The result are the familiar equations of the CCS theory (see, e.g., Eq.(85) in Ref. [20] ),

$$\sum_j \left\langle z_l \middle| z_j \right\rangle \dot{d}_j \exp\left(iS_j\right) = -i \sum_j \Delta^2 H'_{lj} d_j \exp\left(iS_j\right) \tag{40}$$

where

$$\Delta^2 H'_{lj} = \left\langle z_l \middle| z_j \right\rangle \delta^2 H'_{lj} \tag{41}$$

and

$$\delta^2 H'_{lj} = \left[ H_{ord}\left(z^*{}_l, z_j\right) - H_{ord}\left(z^*{}_j, z_j\right) - i\left(z^*{}_l - z^*{}_j\right)\dot{z}_j^* \right] \tag{42}$$

which in CCS becomes

$$\delta^2 H'_{lj} = \left[ H_{ord}\left(z^*{}_l, z_j\right) - H_{ord}\left(z^*{}_j, z_j\right) - \left(z^*{}_l - z^*{}_j\right) \frac{\partial H\left(z_j^*, z_j\right)}{\partial z_j^*} \right] \tag{43}$$

From the CCS theory the coupling matrix $\Delta^2 H'_{lj}$ is known to be small, sparse and traceless because the overlap $\left\langle z_l \middle| z_j \right\rangle$ is small for remote $z_l$ , $z_j$ and $\delta^2 H'_{lj}$ is small for $z_l$ , $z_j$ close to each other. Therefore the preexponential factor is changing slowly. It is no longer a constant of motion like the one in Eq.(27) but rather an adiabatic invariant.

For the simple harmonic Hamiltonian (8) the solution of (40) is again given by Eq.(30). Our experience with applications of Eqs.(37) and (40) to more complicated anharmonic systems shows that the latter is a lot more efficient and requires much fewer CS to converge. The reason is that the trajectory (29) provides a good approximation to the one determined from the full variation i.e. by the solution of the system (33,35).

The main conclusions of this section are:

(1) The CCS theory simplifies the full variational equations by avoiding variation of z but using simple solution for $z$(t), which is optimal for a single CS wave function.

(2) The gain is huge. Instead of dealing with large (M+1)×N vectors and corresponding matrices we get away with the vector of N amplitudes only and much smaller N×N matrixes. Therefore CCS can afford a much bigger basis set then G-MCTDH, which however comes at a price of having a less flexible wave function.

(3) CCS is still a formally exact quantum theory which follows from the quantum time dependent variational principle

(4) In (38) the slowly changing prefactor is a mechanical adiabatic invariant.

### *2.6 Variation of z only. The method of Coupled Coherent State Trajectories*

Now let us as introduce another possible simplification to the full variational equations (33,35). Instead of choosing CS trajectories $z_i(t)$ and applying the variational principle to the amplitudes let us now assume certain "trajectories" $a_i(t)$ for the amplitude

oscillations and apply the variational principle to the CS phase space positions $z_i$ only. Let us assume that the amplitudes are given by the single CS solution $a_i = d_i \exp(iS_i)$ with a constant prefactor $d_l = const$ (like in Eq.(27)). Then the system of equations for $\dot{z}_l$ which follows from the Lagrange equation becomes

$$\begin{aligned}
&\frac{\partial L}{\partial z_l^*} - \frac{d}{dt}\frac{\partial L}{\partial \dot{z}_l^*} = \\
&d_l^* d_l \left[ i\dot{z}_l - \frac{\partial H_{ord}(z_l^*, z_j)}{\partial z_l^*} \right] + \\
&\sum_{j\neq l} d_l^* d_j \exp\left(i(S_j - S_l)\right)\left[ i\dot{z}_j - \frac{\partial H_{ord}(z_l^*, z_j)}{\partial z_l^*} \right]\langle z_l | z_j \rangle - \\
&\sum_{j\neq l} d_l^* d_j \exp\left(i(S_j - S_l)\right)(z_j - z_l)\langle z_l | z_j \rangle \delta^2 H'_{lj} + \\
&\sum_{j\neq l} d_l^* d_j \exp\left(i(S_j - S_l)\right)\left(\frac{z_l}{2}\right)\langle z_l | z_j \rangle \delta^2 H'_{lj} + \\
&\sum_{j\neq l} d_l d^*_j \exp\left(i(S_l - S_j)\right)\left(\frac{z_l}{2}\right)\langle z_j | z_l \rangle \delta^2 H'^*_{lj} = 0
\end{aligned} \tag{44}$$

One must remember that $\delta^2 H'_{ij}$ contains $\dot{z}_j$ (see (42)) but still Eq. (44) is once again simply a system of linear equations for the derivatives $\dot{z}_j$. Again it is easy to see that for the harmonic oscillator (8) the solution of (44) is (30). For anharmonic system we can notice that all terms except for the first one contain oscillatory exponents as well as overlaps, which are small for remote $z_l$, $z_j$. If $z_l$, $z_j$ are close to each other then in the vicinity of classical trajectory both $\delta^2 H'_{lj}$ and $\left[ i\dot{z}_j - \frac{\partial H_{ord}(z_l^*, z_j)}{\partial z_l^*} \right]$ are small. Therefore the solution should not be very far away from the Frozen Gaussian solution

$$\dot{z}_l = -i\frac{\partial H_{ord}(z_l, z_l^*)}{\partial z_l^*} \tag{45}$$

which is not surprising because since the work of Heller [3] the Frozen Gaussian approximation is known to be remarkably accurate.

*The computational advantage of the Eq.(44) is that although it was obtained by variation of N×M parameters of the wave function (i.e. N M-dimensional complex vectors $z_j$) , which is almost the same as N×(M+1) in the full variation, the linear equations for the derivatives $\dot{z}_j$ in each dimension are independent and the solution of N linear equations for N coupled components of the vectors $\dot{z}_j$ repeated M times is required, which is a much easier task then solving the whole system (33,35) of N×(M+1) equations. The computational cost of CCST is proportional to $N^2 \times M$ as opposed to $N^2 \times (M+1)^2$ in G-MCTDH. The trajectories $z_l(t)$ found in this technique, which we call Coupled Coherent States Trajectories are non-classical. They "push" each other with complicated quantum forces coming from the last three sums in the Eq.(44).*

In summary this section:

(1) demonstrates a peculiar possibility to make the Frozen Gaussian approximation [3] exact at the expense of coupling trajectories via equations obtained from the variation of the classical *z* variable only.

(2) shows that this can be done by imposing the "trajectories" of the quantum amplitudes, using solutions that would be optimal for a single CS wave function,

and then applying the variational principle to $z$ only. This is opposite to the CCS approach, where the trajectories of the classical oscillators were set and the variational principle was applied to the amplitudes.

### *2.7 Full variation again. Smoothing of the amplitude equations.*

As pointed out in Section 2.4, the solution of (33,35) features rapidly oscillating phase terms which may require small time steps. Therefore it appears useful to take some oscillations out of the solution and once again rewrite the equations not for the amplitudes but for preexponential factors , see the discussion of Sec. 2.5. This yields for Eq.(36) for the amplitudes

$$\sum_{j\neq l}\left\langle z_l \middle| z_j \right\rangle \dot{d}_j \exp\left(iS_j\right) + i\sum_{j\neq i}\left\langle z_l \middle| z_j \right\rangle \delta^2 H'_{lj}\, d_j \exp\left(iS_j\right) = 0 \tag{46}$$

with

$$\delta^2 H'_{lj} = \left[ H_{ord}\left(z^*_l, z_j\right) - H_{ord}\left(z^*_j, z_j\right) - i\left(z^*_l - z^*_j\right)\dot{z}_j \right] \tag{47}$$

Note that unlike CCS (43) theory $\dot{z}_j$ is not given by the Hamilton's equation. Eq.(35) for $\dot{z}$ now becomes

$$\begin{aligned} & d_l^* d_l \left[ i\dot{z}_l - \frac{\partial H_{ord}\left(z_l^*, z_l\right)}{\partial z_l^*} \right] + \\ & \sum_{j\neq l} d_l^* d_j e^{i\left(S_j - S_l\right)} \left[ i\dot{z}_j - \frac{\partial H_{ord}\left(z_l^*, z_j\right)}{\partial z_l^*} \right] \left\langle z_l \middle| z_j \right\rangle + \\ & \sum_{j\neq l} i d_l^* \left(z_j - z_l\right) \left[ \left\langle z_l \middle| z_j \right\rangle \dot{d}_j\, e^{i(S_j - S_l)} + i\left\langle z_l \middle| z_j \right\rangle \delta^2 H'_{lj}\, d_j e^{i(S_j - S_l)} \right] = 0 \end{aligned} \tag{48}$$

Again one can verify that for the harmonic oscillator the solution of (46,48), is the same as in previous sections, i.e. the Frozen Gaussian solution (30). Indeed, for harmonic oscillator $\delta^2 H'_{lj} = 0$ and $\frac{\partial H_{ord}(z_l^*, z_j)}{\partial z_l^*} = \omega z_l$ . In a generic anharmonic system the Frozen Gaussian solution again will be not very far from the exact one at least for a short time because as we know from the CCS theory and from the previous sections the terms including time derivatives of $d$ and the product $\langle z_l | z_j \rangle \delta^2 H'_{lj}$ are small near the classical trajectory and the terms $\left[ i \dot{z}_j - \frac{\partial H_{ord}(z_l^*, z_j)}{\partial z_l^*} \right] \langle z_l | z_j \rangle$ entering into the first sum in (48) are also small (see previous sections). Of course, at longer times deviations from classical dynamics will accumulate making trajectories more and more nonclassical.

In principle the system of equations (46,48) for determining the derivatives of $d$ and $z$ is equivalent to those obtained in the Ref.[21] and used in the Ref.[22]. However the advantage is that similarly to the CCS technique, oscillatory exponents have been eliminated, which should allow for significantly larger time steps.

**3. Discussion and Conclusions**

In this article we used the variational principle Eq. (1) to derive various forms of equations for the evolution of the parameters of the wave function. The wave function has been chosen to be a superposition of Frozen Gaussian Coherent States carrying quantum amplitude. Then CS phase space positions $z$ and their quantum amplitudes $a$

were treated on the same footing as "quasi-classical" variables. Their trajectories were determined from Lagrange equations.

The idea that the oscillations of quantum amplitudes are mathematically equivalent to those of a system of coupled classical oscillators is not new (see for instance [25]), but in the present approach the quantum oscillations of $a$ are also coupled with the oscillations of the classical variables $z$. This slightly unorthodox view may lead us in new directions. For example, it is appealing to apply the methods of classical statistical mechanics to the Hamilton's equation (6) in which classical and quantum "oscillators" are treated at the same classical-like level of description, determined by the symplectic structure of the variational parameter dynamics [2]. Further, a mixed quantum-classical approach can be naturally formulated in this framework *and various combinations of Gaussian based techniques can be used*.

Previously Gaussian wave packets with parameters determined from a variational principle have been used predominantly in the context of the single Gaussian approximation with the position and the width of the wavepacket determined from the variational principle [26,27,28] - somewhat similar to the famous Thawed Gaussian approach [29]. Here, our wave packets are Frozen Gaussians (FG) with constant width but the wavefunction is a superposition of several FG so that the spreading of the wave function is mimicked by the FG motion like in the original FG semiclassical approach [3]. The approaches discussed here are closely related to the variational multiconfigurational FG methods of G-MCTDH [21,22] and LCSA [23].

The existing techniques of CCS and G-MCTDH have been derived from Lagrange equations for the parameters of the wave functions. While G-MCTDH

represents the most general variational scheme, comprising the variation of both the amplitude coefficients and FG parameters, CCS uses a non-variational moving CS basis. Building upon the elimination of oscillatory phase factors in CCS, a similar scheme is suggested here for G-MCTDH, which might lead to smoother numerical solutions.

Finally, a new approach denoted Coupled Coherent State Trajectories (CCST) has been suggested, which is based on the variation of $z$ only, with the amplitudes chosen to be those of the FG approximation (ref.[3] and Eq.(27)).

A family of FG-based approaches can thus be derived from the variational principle. In this article two existing and one new technique has been derived using the same formalism. *This allowed us to compare their mathematical structure and related computational cost, as well as to transfer numerical tricks between them.* Future applications of the considered techniques should provide a detailed assessment of these variants, and comparisons of the numerical efficiency.

**Acknowledgements**

This project is supported by EPSRC and by ANR project No. ANR-NT05-3-42315. We thank Fausto Martelli for many useful discussions.

**Appendix**

In this appendix, we show that the dynamical equations for the coefficients $a_j$ and coherent states $z_j$, Eqs. (33) and (35), can be obtained in the framework of the G-MCTDH method [21]. G-MCTDH uses variational equations of motion for a multiconfigurational wavefunction involving parametrized time-dependent basis functions; the method has been applied, in particular, to a moving Gaussian basis. For the purpose of the present discussion, we consider a wavefunction (31) which is represented as a superposition of coherent states,

$$|\Psi\rangle = \sum_{l=1,N} a_l |z_l\rangle = \sum_{l=1,N} a_l \exp(\mu_l) \|z_l\rangle \tag{A1}$$

where we have introduced the Bargmann states $\|z_l\rangle$, i.e., non-normalized coherent states defined as [30]

$$\|z_l\rangle = \exp\left(\frac{|z_l|^2}{2}\right) |z_l\rangle \tag{A2}$$

The complex phase parameter $\mu_l$ is initially taken to be an independent parameter, as in the general G-MCTDH scheme [21], but will later on be fixed at the value $\mu_l = -\frac{|z_l|^2}{2}$ ("coherent state gauge"). The advantage of using Bargmann states lies in the fact that these are analytic functions of $z_l$, in contrast to the conventional coherent states $|z_l\rangle$ [30]. This property was not explicitly required for the derivation presented in

the main part of the manuscript, but is important when introducing the derivative matrix elements of Eqs. (A5)-(A6) below.

We will use the G-MCTDH equations in a form that involves coupled equations for the coefficient derivatives and coherent-state derivatives. Following Ref. [21], an equation of motion is obtained from the variation with respect to the $\{a_j\}$ coefficients (see Eq. (15) of Ref. [21]),

$$i\sum_l S_{jl}\dot{a}_l = \sum_l H_{jl}a_l - i\sum_l\sum_\alpha S_{jl}^{(0\alpha)}\dot{\lambda}_{l\alpha}a_l \tag{A3}$$

and a second equation results from the variation with respect to the Gaussian parameters $\{\lambda_{l\alpha}\}=\{z_l,\mu_l\}$ (see Eq. (17) of Ref. [21]),

$$i\sum_l \rho_{jl}\left(\sum_l S_{jl}^{(\alpha\beta)}\dot{\lambda}_{l\beta}\right) = \sum_l\left(\rho_{jl}H_{jl}^{(\alpha o)} - i\sum_l a^*{}_j\,\dot{a}_l S_{jl}^{(\alpha 0)}\right) \tag{A4}$$

In Eqs. (A3)--(A4), the density matrix elements $\rho_{jl}=a^*{}_j\,a_l$ have been introduced, along with several types of overlap matrix matrix elements,

$$\begin{aligned} S_{jl} &= \langle z_j | z_l \rangle \\ S_{jl}^{(\alpha 0)} &= \frac{\partial}{\partial \lambda^*{}_{j\alpha}}\langle z_j | z_l \rangle \\ S_{jl}^{(\alpha\beta)} &= \frac{\partial}{\partial \lambda^*{}_{j\alpha}\,\partial\lambda_{l\beta}}\langle z_j | z_l \rangle \end{aligned} \tag{A5}$$

which are closely related to the quantities introduced in Eqs. (5) and (8). Further, the Hamiltonian matrix elements are given as

$$H_{jl} = \langle z_j | H | z_l \rangle = H_{ord}(z^*_j, z_l)\langle z_j | z_l \rangle$$
$$H^{(\alpha 0)}_{jl} = \frac{\partial}{\partial \lambda^*_{j\alpha}} \langle z_j | H | z_l \rangle \tag{A6}$$

From Eq. (A3), we obtain

$$i\sum_l \langle z_j | z_l \rangle \dot{a}_l = \sum_l H_{ord}(z^*_j, z_l)\langle z_j | z_l \rangle a_l - i\sum_l \left(S^{(\alpha z)}_{jl}\dot{z}_l + S^{(\alpha \mu)}_{jl}\dot{\mu}_l\right)a_l =$$
$$= \sum_l H_{ord}(z^*_j, z_l)\langle z_j | z_l \rangle a_l - i\sum_l \left( \left(z^*_j - z^*_l\right)\dot{z}_l + \frac{1}{2}\left(\dot{z}_l z^*_l - z_l \dot{z}^*_l\right)\right)\langle z_j | z_l \rangle a_l \tag{A7}$$

where we used $S^{(0z)}_{jl} = z^*_j \langle z_j | z_l \rangle$ $S^{(0\mu)}_{jl} = S_{jl} = \langle z_j | z_l \rangle$. In addition, the complex phase parameter is now set to the value $\mu_l = -\frac{1}{2}|z_l|^2$ such that

$$\dot{\mu}_l = -\dot{z}_l z^*_l + \frac{1}{2}\left(\dot{z}_l z^*_l - z_l \dot{z}^*_l\right) \tag{A8}$$

Eq. (A7) is in agreement with Eq. (33) of the main manuscript text. From Eq. (A4), we obtain with the choice $\alpha = z_j$ :

$$i\sum_l a^*_j a_l \left(S^{(zz)}_{jl}\dot{z}_l + S^{(z\mu)}_{jl}\dot{\mu}_l\right) = \sum_l \left(a^*_j a_l H^{(z0)}_{jl} - i a^*_j \dot{a}_l S^{(z0)}_{jl}\right) \tag{A9}$$

This corresponds to:

$$i\sum_l a^*_j a_l \left(\left(1 + z^*_j z_l\right)\dot{z}_l + z_l \dot{\mu}\right) =$$
$$\sum_l \left( a^*_j a_l \left( H_{ord}(z^*_j, z_l) z_l + \frac{\partial H_{ord}(z^*_j, z_l)}{\partial z^*_j}\right)\langle z_j | z_l \rangle - i a^*_j \dot{a}_l z_l \langle z_j | z_l \rangle \right) \tag{A10}$$

where we used $S_{jl}^{(z\mu)} = z_l \left\langle z_j \middle| z_l \right\rangle$ as well as the following equalities which follow from Eqs. (A5)-(A6) and involve some commutation relations [30]:

$$\begin{aligned} S_{jl}^{(zz)} &= \left\langle z_j \middle| \hat{a}\hat{a}^+ \middle| z_l \right\rangle = \left(1 + z^*_j \, z_l\right) \left\langle z_j \middle| z_l \right\rangle \\ H_{jl}^{(z0)} &= \exp\left(\mu_j + \mu_l\right) \left\langle z_j \middle\| \hat{a}\hat{H} \middle\| z_l \right\rangle = H_{ord}\left(z^*_j, z_l\right) z_l + \frac{\partial H_{ord}\left(z^*_j, z_l\right)}{\partial z^*_j} \left\langle z_j \middle| z_l \right\rangle \end{aligned} \tag{A11}$$

Finally, when inserting again the relation Eq. (A8) for $\dot{\mu}_l$, the following form is obtained:

$$\begin{aligned} & i \sum_l a^*_j \, a_l \left( \dot{z}_l + z_l \left(z^*_j - z^*_l\right) \dot{z}_l + \frac{1}{2} z_l \left(\dot{z}_l z^*_l - z_l \dot{z}^*_l\right) \right) \left\langle z_j \middle| z_l \right\rangle = \\ & \quad \sum_l \left( a^*_j \, a_l \left( H_{ord}\left(z^*_j, z_l\right) z_l + \frac{\partial H_{ord}\left(z^*_j, z_l\right)}{\partial z^*_j} \right) \left\langle z_j \middle| z_l \right\rangle - i a^*_j \, \dot{a}_l \left\langle z_j \middle| z_l \right\rangle \right) \end{aligned} \tag{A12}$$

This equation is identical to Eq. (35) of the manuscript, which can be seen by recognizing that the following sum of terms is zero (from the equation for the $a_j$ coefficients):

$$\begin{aligned} 0 = & \, i \sum_l a^*_j \, \dot{a}_l \left(- z_j\right) \left\langle z_j \middle| z_l \right\rangle + \\ & \sum_l a^*_j \, a_l \left(- z_j\right) \left\langle z_j \middle| z_l \right\rangle \left\{ i \left[ \left(z^*_j - z^*_l\right) \dot{z}_l + \frac{1}{2} \left(\dot{z}_l z^*_l - z_l \dot{z}^*_l\right) \right] - H_{ord}\left(z^*_j, z_l\right) \right\} \end{aligned} \tag{A13}$$

and interchanging the indexes *j* and *l*.

**References**

1. S.I. Sawada, R. Heather, B. Jackson, H. Metiu, J.Chem.Phys., **83** 3009 (1985), S.I. Sawada, H. Metiu, J.Chem.Phys., **84** 227 (1986).

2. P. Kramer and M. Saraceno, Geometry of the Time-Dependent Variational Principle in Quantum Mechanics (Springer, NewYork, 1981), A. K. Kerman and S. E. Koonin, Ann. Phys. **100**, 332 (1976), D. J. Rowe, A. Ryman, and G. Rosensteel, Phys. Rev. **A, 22**, 2362 (1980), J. Broeckhove, L. Lathouwers, E. Kesteloot, and P. V. Leuven, Chem. Phys. Lett., **149**, 547 (1988), A. D. McLachlan, Mol. Phys. **8**, 39 (1964).

3. E.J. Heller, J.Chem.Phys., **75** 2923 (1981).

4. M.F. Herman and E. Kluk, Chem.Phys., **91**, 27 (1984).

5. E. Kluk, M.F. Herman, and H.L. Davis, J.Chem.Phys., **84**, 326 (1986).

6. M.F. Herman, Ann. Rev. Phys. Chem., **45**, 83 (1994).

7. F. Grossmann, Comments At. Mol. Phys. **34**, 141 (1999).

8. D. J. Tannor and S. Garashchuk, Ann. Rev. Phys. Chem.,. **51**, 553 (2000).

9. W. H. Miller, J. Phys. Chem., **A105**, 2942 (2001).

10. K.G.Kay, Ann.Rev.Phys.Chem., **56**, 255 (2005).

11. T.Martinez and R.D.Levine Chem.Phys.Lett. **259**, 252 (1996); J.Chem.Phys. **105**, 6334 (1996).

12. M.Ben-Nun and T.Martinez, J.Chem.Phys. **104**, 5161 (2000), ibid **108**, 7244 (1998); ibid **110**, 4134 (1999),ibid **112**, 6113 (2003).

13. T.Martinez, M.Ben-Nun, J.Chem.Soc.Faraday Trans. **93**, 940 (1997).

14. M. Ben-Nun and T. J. Martinez in Adv.Chem.Phys., **121**, 439, ed. I.Prigogine and S.A.Rice (John Wiley & Sons, Inc. 2002).

15. D. V. Shalashilin and M. S. Child, J. Chem. Phys., **113**, 10028 (2000).

16. D. V. Shalashilin and M. S. Child, J. Chem. Phys., **114**, 9296 (2001).

17. D. V. Shalashilin and M. S. Child, J. Chem. Phys., **115**, 5367 (2001).

18. D. V. Shalashilin and M. S. Child, J. Chem. Phys., **121**, 3563 (2004).

19. P.A.J. Sherratt, D.V. Shalashilin, and M.S. Child, Chem. Phys., **322**, 127 (2006).

20. D. V. Shalashilin and M. S. Child, Chem. Phys., **304**, 103 (2004).

21. I.Burghardt, H.-D.Meyer, and L.S.Cederbaum, J.Chem.Phys., **111**, 2927 (1999).

22. G.A.Worth and I.Burghardt, Chem.Phys.Lett. **368**, 502 (2003), I. Burghardt, M. Nest, and G.A. Worth, J.Chem.Phys. **119**, 5364 (2003), I. Burghardt, K. Giri, and G. A. Worth, to be submitted.

23. R. Martinazzo, M. Nest, P. Saalfrank, and G. F. Tantardini, J. Chem. Phys. **125**, 194102 (2006).

24. J.R.Klauder, B.S.Skagerstam, Coherent States (World Scientific, Singapore, 1985).

25. F.Remacle, R.D. Levine, J.Chem. Phys. **113**, 4515 (2000}.

26. V. Buch, J.Chem.Phys., **112**, 6113 (2000).

27. P. Frantsuzov, A.Neumaier, V.A. Mandelshtam, Chem.Phys.Lett., **381**, 117 (2003).

28. P.A.Frantsuzov and V.A. Mandelshtam, J.Chem.Phys., **121**, 9247 (2004).

29. E. J. Heller, J. Chem. Phys., **62**, 1544 (1975).

30. C.W. Gardiner, Quantum Noise, Springer, Berlin, Heidelberg, (1991).

31. H.-D. Meyer, U. Manthe, and L. S. Cederbaum, Chem. Phys. Lett. **165**, 73 (1990), M. H. Beck, A. Jackle, G. A. Worth, and H.-D. Meyer, Phys. Rep. **324**, 1 (2000).