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# The Generalized Coherent State Ansatz: Application to Quantum Electron-Vibrational Dynamics

Raffaele Borrelli<sup>a</sup>, Maxim F. Gelin<sup>b</sup>

<sup>a</sup>DISAFA, Università di Torino, I-10095 Grugliasco, Italy. <sup>b</sup>Departement of Chemistry, Technische Universität München, D-85747 Garching, Germany.

## Abstract

A new *ansatz* for molecular vibronic wave functions based on a superposition of time-dependent generalized coherent states is developed and analysed. The methodology is specifically tailored to describe the time evolution of the wave function of a system in which several interacting electronic states are coupled to a bath of harmonic oscillators. The equations of motion for the wave packet parameters are obtained by using the Dirac-Frenkel timedependent variational principle. The methodology is used to describe the quantum dynamical behaviour of a model polaron system and its scaling and convergence properties are discussed and compared with numerically exact results.

## 1. Introduction

One of the simplest ways to describe the motion of nuclei in molecular systems is based on the use of complex Gaussian wave packets, *i.e.* coherent states. Heller was among the first to recognize the primary role of such a simple approximation of the nuclear wave function in the study of chemico-physical problems, mainly focusing his work on semiclassical theories. [1, 2, 3, 4] At the same time Davydov used coherent states to study energy transport in biochemical systems, though with a different theoretical approach. [5] Since then a number of extensions of these methods has been proposed for dealing with multidimensional systems and non-adiabatic processes, *i.e.* for the treatment of electronic transitions.

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<sup>\*</sup>Corresponding author

Email address: raffaele.borrelli@unito.it (Raffaele Borrelli) Preprint submitted to Elsevier

Among others the Gaussian based-multiconfiguration time-dependent Hartree (G-MCTDH), the direct dynamics variational multi-configurational Gaussian (DD-vMGC), and the ab initio multiple spawning (AIMS), are extremely general and powerful methodologies that utilize, in different ways, linear combinations of Gaussian wave packets to define a time-dependent set of orthonormal basis functions which are then used to describe the wavefunction of the entire nuclear system. [6, 7, 8, 9, 10] Coherent states, combined with a time-dependent DVR representation are employed in methodologies such as the Local Coherent State Approximation (LCSA)[11], and the multiconfigurational Ehrenfest (MCE).[12, 13] The so-called Davydov ansatz and its extensions, which have been extensively used in the study of polaron and spin-boson dynamics are also based on the use of superposition of coherent states [14, 15, 16, 17, 18, 19, 20] or multiple coherent states.[21] Heller was also the first to suggest that a significant improvement of the semiclassical description based on Gaussian wavepackets could have been obtained by introducing a polynomial prefactor to the wave function. [1, 2] Hagedorn later recognized that the natural extension of the description of quantum dynamics by Gaussian wavepacket was the use of generalized Gauss-Hermite functions [22, 23, 24, 25] known in the quantum optics literature as Generalized Coherent States (GCS)[26], and in molecular dynamics as Hagedorn's wavepackets. [27, 28] A similar technique was developed later by Billing [29, 30, 31, 32] in the framework of semiclassical mechanics as well as non-adiabatic transitions.[33] Though a generalized form of non spreading, *i.e.* coherent, wave-packets was first introduced by Senitzky in the fifties [34], as pointed out by other authors, [35] they have not yet received the due attention.

Here we propose and develop a new type of *ansatz* to represent the time evolution of molecular vibronic states using GCSs. Following a very recent approach for the study of quantum dynamics of chemico-physical systems [36] we employ the time-dependent Dirac-Frenkel variational principle to derive a new set of equations in which position and momentum of the coherent states are dynamically coupled to the evolution of the expansion coefficients of the basis functions.

The methodology is applied to the study of a one-dimensional Holstein polaron model where N electronic sites are coupled to local phonons, and its results are compared with numerically exact MCTDH calculations.[37]

#### 2. The Generalized Coherent State method

GCSs where described for the first time in fifties by Senitzky[34] and later generalized by Nieto[38] in the form of squeezed number states. In their basic form GCSs can be obtained by applying the translation operator to any harmonic oscillator eigenstate  $|n\rangle$ [39]

$$|n,\alpha\rangle = D(\alpha)|n\rangle \tag{1}$$

where

$$D(\alpha) = \exp(\alpha a^+ - \bar{\alpha}a),$$

a and  $a^+$  are boson annihilation and creation operators, and  $\alpha$  is a complex number. When n = 0 standard Glauber coherent states are obtained.[40] Unlike the latter, GCSs are not eigenstates of the annihilation operator. It can be easily verified that

$$a|n,\alpha\rangle = \sqrt{n}|n-1,\alpha\rangle + \alpha|n,\alpha\rangle$$
 (2)

$$a^{\dagger}|n,\alpha\rangle = \sqrt{n+1}|n+1,\alpha\rangle + \bar{\alpha}|n,\alpha\rangle.$$
 (3)

GCS have the coordinate representation [41]

$$\varphi_n(x,q,p) = 2^{-n/2} (n!)^{-1/2} \pi^{-1/4} e^{-(x-q)^2/2 + ip(x-q/2))} H_n[(x-q)]$$
(4)

where the two real variables, q, p are related to the complex variable  $\alpha$  by

$$\alpha = \frac{q + ip}{\sqrt{2}}.$$

Finally, it is possible to give the number state expansion of a GCS in the form

$$\left|n,\alpha\right\rangle = \frac{e^{-|\alpha|^{2}/2}}{(n!)^{1/2}} \sum_{k=0}^{\infty} (-1)^{n+k} (k!)^{1/2} L_{k}^{n-k} (|\alpha^{2}|) (\bar{\alpha})^{n-k} \left|k\right\rangle \tag{5}$$

 $L_n^{n-k}(\cdot)$  being the associated Laguerre polynomials of order n. For n = 0,  $|0, \alpha\rangle \equiv |\alpha\rangle$ , and we recover the formula for Glauber coherent states.[40]

Without loosing any generality we can write the vibronic wave function in the form

$$\left|\Psi(t)\right\rangle = \sum_{l,K} C_{lK}(t) \left|K, \alpha_l(t)\right\rangle \left|l\right\rangle \tag{6}$$

where  $|l\rangle$  specifies electronic states (l = 1, 2, ..., N), K is a multi-index  $K = (k_1, k_2, ..., k_d) \in \mathbb{N}_0^d$ , and the  $|K, \alpha_l(t)\rangle$  are a set of *time-dependent* GCS defined as the product of d one-dimensional GCS

$$|K, \alpha_l(t)\rangle \equiv |k_1 \cdots k_d, \alpha_{l1}(t), \cdots, \alpha_{ld}(t)\rangle = \prod_{i=1}^d |k_i, \alpha_{li}(t)\rangle.$$
 (7)

It is well known that the number of coefficients of expansion 6 is subject to an exponential growth, and cannot be used for practical purposes as such. On the other hand, by introducing an explicit time-dependent basis functions and using the Dirac-Frenkel variational approach the quantum dynamical problem is formulated on a Hilbert bundle, and the basis set is locally adapted to provide the "best" approximation to the Schrödinger equation on the parameters manifold. It is therefore physically sound that a truncation of the above expansion to a relatively small subset of states already provides a good description of the state of the system.

The approach developed in this work is based on the idea of partitioning the entire Hilbert space in a set of subspaces which differ in the number of vibrations which are allowed to be simultaneously excited. Thus the entire Hilbert space  $\mathscr{H}$  spanned by the Hamiltonian of Eq. 13 can be partitioned as

$$\mathscr{H} = \bigcup_{c} S_{c}$$

where  $S_c$  is the space spanned by the states in which only c basis functions are simultaneously excited, *i.e.* have a non-zero value of  $k_i$ . Of course for any practical purposes the basis is truncated to a maximum quantum number. Since in a system with d vibrational degrees of freedom there will be  $\binom{d}{c}$ distinct combinations having c excited modes, using such a partition the wavefunction of Eq. 6 can be written in the form

$$\Psi(x,t) = \sum_{l=1}^{N} \left[ \sum_{c=0}^{d} \sum_{i_{1}...i_{C}}^{\binom{d}{c}} \sum_{k_{i_{1}}...k_{i_{c}}=1}^{w_{i_{1}}...w_{i_{c}}} C_{lk_{i_{1}}...k_{i_{c}}}(t) |k_{i_{1}}, \alpha_{li_{1}}(t)\rangle \dots |k_{i_{c}}, \alpha_{li_{c}}(t)\rangle \right] |l\rangle$$
$$= \sum_{l=1}^{N} \left[ C_{l}(t) |\alpha_{l}(t)\rangle + \sum_{i=1}^{d} \sum_{k_{i}=1}^{w_{i}} C_{lk_{i}}(t) |k_{i}, \alpha_{li}(t)\rangle |\alpha_{l}'(t)\rangle + \sum_{i,j=1}^{\binom{d}{2}} \sum_{k_{i}=1}^{w_{i}} \sum_{k_{j}=1}^{W_{j}} C_{lk_{i}k_{j}}(t) |k_{i}, \alpha_{li}(t)\rangle |k_{j}, \alpha_{lj}(t)\rangle |\alpha_{l}''(t)\rangle + \dots \right] |l\rangle, \quad (8)$$

where we have partitioned the  $\alpha_l$  as  $\alpha_l = (\alpha'_l, \alpha_{li})$  in the first summation and  $\alpha_l = (\alpha''_l, \alpha_{li}, \alpha_{lj})$  in the second summation. An analogous partition has been performed for the quantum numbers K, and indices of the expansion coefficients with value zero are omitted;  $w_i$  represent the maximum quantum number on the *i*-th mode. Using partition 8 it is possible to reduce the size of the basis set by limiting its combinatorial explosion. Indeed, if each mode is allowed to have w basis functions then a combination with c simultaneously excited modes will introduce  $w^c$  new basis states, and since there are  $\binom{d}{c}w^c$ . Thus, for c = 1 we will have d possible combinations and dw basis states, for c = 2 we will have  $\binom{d}{2}w^2$  states and so on. This type of partitioning has been recently applied by the authors, to the study of electron superxchange in molecular chains.[42]

Numerical convergence can, in principle, be tested by letting c vary until no significant variations of the properties of interest (*i.e.* electronic population or coherences) are observed. However, our main purpose is to study the result of low order approximations up to c = 2, which are the most appealing for treating systems with a large number of degrees of freedom. Therefore, in the following we will restrict our discussion to the *ansatz* 8 truncated to the excitation levels c = 1, 2.

More specifically in the following we will refer to the equations 9 and 10 below

$$\Psi^{\text{GCS1}}(x,t) = \sum_{l=1}^{N} \left[ C_{l}(t) |\alpha_{l}(t)\rangle + \sum_{i=1}^{d} \sum_{k_{i}=1}^{w_{i}} C_{lk_{i}}(t) |k_{i}, \alpha_{li}(t)\rangle |\alpha_{l}'(t)\rangle \right] |l\rangle \quad (9)$$

$$\Psi^{\text{GCS2}}(x,t) = \sum_{l=1}^{N} \left[ C_{l}(t) |\alpha_{l}(t)\rangle + \sum_{i=1}^{d} \sum_{k_{i}=1}^{w_{i}} C_{lk_{i}}(t) |k_{i}, \alpha_{li}\rangle |\alpha_{l}'(t)\rangle + \sum_{i,j=1}^{d} \sum_{k_{i}=1}^{w_{j}} C_{lk_{i}}(t) |k_{i}, \alpha_{li}(t)\rangle |\alpha_{l}''(t)\rangle |\alpha_{l}''(t)\rangle \right] |l\rangle \quad (10)$$

as GCS-1 and GCS-2 approximation respectively.

It is worth noticing that the so called Davydov D1 ansatz correspond to truncating the above expansion at the excitation level c = 0. The equations of motion for the parameters  $(C_{lK}(t), q_{li}(t), p_{li}(t))$  can be derived by using the standard machinery of the Dirac-Frenkel time-dependent variational principle with the Lagrangian

$$L = \frac{i}{2} [\langle \Psi | \dot{\Psi} \rangle - \langle \dot{\Psi} | \Psi \rangle] - \langle \Psi | H | \Psi \rangle.$$

In the following we adopt a mathematical formulation in which all the parameters of the wave function are real hence we split each coefficient in its real and imaginary part,  $C_{lK}(t) = r_{lK}(t) + is_{lK}(t)$ . This leads to the set of differential equations [43, 44, 45]

$$\sum_{j} \eta_{ij} \dot{y}_j = \partial_{y_i} \mathcal{H} \tag{11}$$

where y denotes the set of parameters  $(r_{lK}, s_{lK}, q_{li}, p_{li})$ ,  $\eta_{ij}$  is a real antisymmetric tensor, and  $\mathcal{H}$  is the Hamiltonian function:

$$\eta_{ij} = i[\langle \partial_{y_i} \Psi | \partial_{y_j} \Psi \rangle - \langle \partial_{y_j} \Psi | \partial_{y_i} \Psi \rangle] = -2 \operatorname{Im} \langle \partial_{y_i} \Psi | \partial_{y_j} \Psi \rangle \tag{12}$$

$$\mathcal{H} = \left\langle \Psi \middle| H \middle| \Psi \right\rangle = \mathcal{H}(r_{lK}, s_{lK}, q_{li}, p_{li}).$$
<sup>(13)</sup>

After carrying out the calculations (see appendix A) the tensor  $\eta$  can be written in the form

$$\eta_{r_{lK}s_{mJ}} = -2\delta_{lm}\delta_{KJ} \tag{14a}$$

$$\eta_{r_{lK}q_{mh}} = \delta_{lm} [p_{lh}r_{lK} - \sqrt{2} \left( s_{l(K-1_h)} \sqrt{k_h} - s_{l(K+1_h)} \sqrt{k_h + 1} \right)]$$
(14b)

$$\eta_{s_{lK}q_{mh}} = \delta_{lm} [p_{lh}s_{lK} + \sqrt{2} \left( r_{l(K-1_h)}\sqrt{k_h} - r_{l(K+1_h)}\sqrt{k_h + 1} \right)]$$
(14c)

$$\eta_{r_{lK}p_{mh}} = -\delta_{lm} [q_{lh}r_{lK} + \sqrt{2} \Big( r_{l(K-1_h)}\sqrt{k_h} + r_{l(K+1_h)}\sqrt{k_h+1} \Big)]$$
(14d)

$$\eta_{s_{lK}p_{mh}} = -\delta_{lm} [q_{lh}s_{lK} + \sqrt{2} \left( s_{l(K-1_h)}\sqrt{k_h} + s_{l(K+1_h)}\sqrt{k_h + 1} \right)]$$
(14e)

$$\eta_{q_{lj}p_{mh}} = -\delta_{lm}\delta_{hj}\sum_{K} (r_{lK}^2 + s_{lK}^2).$$
(14f)

From the above metric tensor the final equations of motion take the form

of the implicit system

$$2\dot{r}_{lK} + \sum_{i}^{d} \eta_{s_{lK}q_{li}} \dot{q}_{li} + \sum_{i}^{d} \eta_{s_{lK}p_{li}} \dot{p}_{li} = \partial_{s_{lK}} \mathcal{H}$$
(15a)

$$2\dot{s}_{lK} - \sum_{i}^{a} \eta_{r_{lK}q_{li}}\dot{q}_{li} - \sum_{i}^{a} \eta_{r_{lK}p_{li}}\dot{p}_{li} = -\partial_{r_{lK}}\mathcal{H}$$
(15b)

$$\dot{q}_{li}\sum_{K}(r_{lK}^2 + s_{lK}^2) - \sum_{K}\eta_{r_{lK}p_{li}}\dot{r}_{lK} - \sum_{K}\eta_{s_{lK}p_{li}}\dot{s}_{lK} = \partial_{p_{li}}\mathcal{H}$$
(15c)

$$\dot{p}_{li}\sum_{K}(r_{lK}^2 + s_{lK}^2) + \sum_{K}\eta_{r_{lK}q_{li}}\dot{r}_{lK} + \sum_{K}\eta_{s_{lK}q_{li}}\dot{s}_{lK} = -\partial_{q_{li}}\mathcal{H}$$
(15d)  
with  $K = 1, ..., K_{\max}$   $i = 1, ..., d$   $l = 1, ..., N$ 

We notice that the metric tensor,  $\eta$ , does not directly couple the variables of two different electronic states because the electronic wavefunction is not parametrized, however, the equations are coupled by the "quantum forces"  $\partial_{y_i} \mathcal{H}$ . On the other hand the metric directly couples the  $(q_{li}, p_{li})$  variables of the GCS with the coefficients of the expansion. Equations 15a-15d constitutes a set of  $2 \sum_{l}^{N} (N_l + d)$  differential equations where N is the number of electronic states,  $N_l$  is the size of the basis set in the electronic state l, and d is the number of nuclear degrees of freedom.

The numerical solution of the set of differential equations 15 is not an easy task. Indeed, when the number of variables is small a pseudo-inverse of the tensor  $\eta$  can be computed, *e.g.* by singular value decomposition, and the system can be solved using standard methods for ordinary differential equations. On the other hand for problems with a large number of degrees of freedom computing a pseudo-inverse of  $\eta$  is not feasible and methods for implicit differential equations[46] must be used. Here we have used a specifically tailored approach which combines a Newton-Raphson method, and an explicit fourth-order Runge-Kutta integration. Details about the numerical implementation will be given elsewhere.

## 3. Numerical applications: polaron dynamics

One of the simplest theoretical model describing a set of electronic states interacting with environmental phonons is certainly the so-called Holstein polaron Hamiltonian. Its widespread applications in the study of charge and energy transport in solids and soft matter make it an excellent test for the GCS methodology. Here we focus on the study of the one-dimensional Holstein polaron Hamiltonian[47, 48]

$$H = \sum_{i}^{N} \epsilon_{i} c_{i}^{\dagger} c_{i} - J \sum_{i} (c_{i+1}^{\dagger} c_{i} + \text{H.c.}) + \sum_{i}^{N} \omega_{i} a_{i}^{\dagger} a_{i} + g \sum_{i}^{N} c_{i}^{\dagger} c_{i} (a_{i} + a_{i}^{\dagger})$$
(16)

where  $a_i^{\dagger}$ ,  $a_i$  and  $c_i^{\dagger}$ ,  $c_i$  are boson and fermion creation and annihilation operators, g is is the strength of the electron-phonon coupling,  $\omega_i$  are the boson frequencies and  $\epsilon_i$  are the site energies. We notice that in this case the number of electronic states N is equal to the number of vibrational degrees of freedom d and are both labelled as N. Furthermore in our model system the first and last sites are coupled, *i.e.* we consider a molecular ring.

In the following, for the sake of simplicity, we will assume that all the bosons have the same optical frequency  $\omega$ , and all the sites have the same energy ( $\epsilon_i = 0$ ). We will describe the site population dynamics both in the non-adiabatic regime ( $|J/\omega| < 1$ ) and in the adiabatic regime ( $|J/\omega| > 1$ ), and as a function of the electron-phonon coupling strength g.

Using the properties of GCSs described in appendix A we can easily compute the Hamiltonian function,  $\mathcal{H}$ , as

$$\mathcal{H}(p,q,r,s) = \mathcal{H}^{\circ} + \mathcal{V}$$

where (see appendix B)

$$\begin{aligned} \mathcal{H}^{\circ} &= \sum_{l,i,K} \left\{ \left[ \epsilon_{l} + \frac{\omega}{2} (p_{li}^{2} + q_{li}^{2}) + gq_{li} + \omega k_{i} \right] (r_{lK}^{2} + s_{lK}^{2}) \right\} \\ &+ \sum_{l,i,K} (\omega q_{li} + g) \sqrt{2(k_{i} + 1)} (r_{lK+1_{i}} r_{lK} + s_{lK+1_{i}} s_{lK}) \\ &+ \sum_{l,i,K} \omega p_{li} \sqrt{2(k_{i} + 1)} (r_{lK} s_{lK+1_{i}} - r_{lK+1_{i}} s_{lK}) \\ \mathcal{V} &= 2J \operatorname{Re} \{ \sum_{l \geq m,K,J} \bar{C}_{lK} C_{mJ} \langle K, \alpha_{l} | J, \alpha_{m} \rangle \}. \end{aligned}$$

The derivatives  $\partial_{y_i} \mathcal{H}$  can be obtained analytically as described in appendix B.

The zero-th order Hamiltonian  $\mathcal{H}^{\circ}$  includes a classical-like energy part that depends explicitly on the wavepacket positions and momenta  $(q_{li}(t), p_{li}(t))$ , and a purely quantum contribution that depends on the quantum numbers  $(k_1, ..., k_d)$ . The terms  $\langle K, \alpha_l | J, \alpha_m \rangle$  appearing in the potential energy  $\mathcal{V}$  are Franck-Condon type integrals and depend on time through the variables  $(q_{li}(t), p_{li}(t))$ . Their evaluation is a critical step of the time propagation and can be performed analytically using the recurrence relations described in the appendix. In all the calculations reported below the initial conditions are  $C_l(0) = \delta_{l1}$ , *i.e.* the exciton is localized on one site.

Figure 1a shows the population dynamics in the non-adiabatic regime for  $q/\omega = 0.5$ . In this case the zero-th order model (*i.e.* the Davydov D1 ansatz) is accurate only for the first 100 fs, and cannot reproduce the beatings which characterize the dynamics between 100 and 300 fs. The addition of single mode excitations, *i.e.* the GCS-1 ansatz, provides almost exact results, as can be seen by comparison with converged MCTDH calculations. This result if of major importance since from a numerical perspective adding single mode excitations increases only marginally the overall computational cost. It is also worth noticing that the description of the wave function using MCTDH requires about 85000 expansion coefficients, while the GCS-1 methodology requires only 1200 variables. With this set of parameters the results of the GCS-1 and GCS-2 ansätze are practically undistinguishable. Increasing the coupling strength the differences between the different levels of approximations become more evident (see figure 1b). The D1 ansatz becomes quite inaccurate both at short and long times. The GCS-1 approach provides a significant improvement over the D1. The results are almost quantitative, and show a somewhat larger deviation only after 500 fs. The GCS-2 results are in quantitative agreement with numerically exact MCTDH.

Figures 2a-b show the population dynamics when  $J = 1.5\omega$  that is in the adiabatic regime for two different values of the coupling strength. For  $g = 0.5\omega$  the D1 ansatz cannot reproduce the correct behaviour of the population dynamics, showing large deviations from the exact results after the very first initial decay (about 5 fs). The GCS-1 ansatz provides a good description of the dynamics though the overall accuracy worsen after the first 50 fs. In this regime GCS-2 dynamics is in quantitative agreement with the exact MCTDH. Upon increasing the electron-phonon coupling strength the D1 ansatz becomes quite inaccurate. The GCS-1 ansatz, while not quantitative, allows to reproduce most of the dynamical features of the systems, although the overall agreement with the exact results worsen at longer times. The GCS-2 population dynamics is almost exact for the first 50 fs, and in qualitatively agreement with MCTDH for longer times.



Figure 1: Population of the initial electronic state as a function of time in a molecular ring with 11 electronic states. The parameters of the model are  $J = 100 \text{ cm}^{-1}$ ,  $\omega = 1000 \text{ cm}^{-1}$ ; a)  $g = 0.2\omega$ , b)  $g = \omega$ . The number of bath modes is N = 11; the maximum number of state per mode is w = 4 in both GCS-1 and GCS-2. Dash-dotted line  $(-\cdot)$  excitation levels of the N electronic states c = 0 (D1); dashed line (- ) c = 1; full line (-) c = 2; (×) MCTDH result.



Figure 2: Population of the initial electronic state as a function of time in a molecular ring with 11 electronic states. The parameters of the model are  $J = 1500 \text{ cm}^{-1}$ ,  $\omega = 1000 \text{ cm}^{-1}$ ; a)  $g = 0.2\omega$ , b)  $g = \omega$ . The number of bath modes is N = 11; the maximum number of state per mode is w = 4 in both GCS-1 and GCS-2. Dash-dotted line  $(-\cdot)$  excitation levels of the N electronic states c = 0 (D1); dashed line (- ) c = 1; full line (-) c = 2; (×) MCTDH result.

## 4. Discussion and conclusion

The GCS methodology provides a new *ansatz* for the vibronic wave function of a molecular system with electronic inter-state couplings. The partitioning of the Hilbert space into subspaces with different levels of excitations appears quite effective in selecting the active space. Increasing the number of simultaneously excited vibrations allows to achieve, at least in principle, converged results, however this procedure can be applied only to small systems and more advanced truncation schemes must be developed.

In the cases considered here GCS-1 and GCS-2 methodologies provide a significant improvement over the widely used D1 *ansatz*. On the basis of the results discussed in the preceding section the GCS-1 methodology is ideal to study systems in the non-adiabatic or intermediate regime even with large electron-phonon coupling strengths. GCS-2 can be used to have quantitative results both in the non-adiabatic and in the adiabatic regime, and for a wider range of coupling-strength. This result is of primary importance since the computational cost of the GCS-1 method is not much higher that the D1. It is worth mentioning that very recently Zhao Yang and coworkers have suggested a generalisation of the D1 *ansatz* using multiple coherent states which provides a significant improvement over the D1 approach, and extend its applicability range.[17, 21]

On the other hand, as in any basis set methodology the number of independent coefficients in the wave function expansion is of main concern. While we have not yet investigated the possibility of contraction or projection schemes[49, 50, 51] the methodology could be easily extended to handle such techniques.

From a numerical point of view, the evaluation of the derivatives of the potential energy is the most crucial step of the numerical integration scheme. Indeed, it requires the calculation of Franck-Condon type integrals between pairs of time-dependent basis functions. Here we have developed new recurrence formulae to efficiently compute this type of integrals, that are akin to the well-known recurrence relations for FC integrals between harmonic oscillators wavefunctions.[52, 53, 54, 55, 56] Furthermore, the explicit time-dependent basis and the multi-set formulation allows to strongly reduce the number of primitive functions in the calculations, which, from a numerical perspective, implies very low computer memory requirements.

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#### Appendix A. The metric tensor

The determination of the metric tensor  $\eta$  requires the evaluation of the derivatives of the wavefunction  $\Psi(x,t)$  and its complex conjugate  $\Psi^*(x,t)$  with respect to the set of real parameters  $\{r_{lK}, s_{lK}, q_{li}, p_{li}, K \in \mathbb{N}^d\}$ . The derivatives of  $\Psi$  with respect to the expansion coefficients are straightforward and not reported here. Starting from the properties of the one-dimensional displacement operator  $D(\alpha)$ 

$$\frac{\partial}{\partial \alpha} D(\alpha) = a^{\dagger} D(\alpha) - \frac{\bar{\alpha}}{2} D(\alpha) = D(\alpha) a^{\dagger} + \frac{\bar{\alpha}}{2} D(\alpha)$$
(A.1)

$$\frac{\partial}{\partial\bar{\alpha}}D(\alpha) = -aD(\alpha) + \frac{\alpha}{2}D(\alpha) = -D(\alpha)a - \frac{\alpha}{2}D(\alpha)$$
(A.2)

we easily obtain

$$\frac{\partial}{\partial q}D(\alpha) = \frac{(a^{\dagger} - a)}{\sqrt{2}}D(\alpha) + i\frac{p}{2}D(\alpha) = D(\alpha)\frac{(a^{\dagger} - a)}{\sqrt{2}} - i\frac{p}{2}D(\alpha)$$
(A.3)

$$\frac{\partial}{\partial p}D(\alpha) = i\frac{(a^{\dagger}+a)}{\sqrt{2}}D(\alpha) - i\frac{q}{2}D(\alpha) = iD(\alpha)\frac{(a^{\dagger}+a)}{\sqrt{2}} + i\frac{q}{2}D(\alpha) \quad (A.4)$$

and

$$\frac{\partial}{\partial q}D^{\dagger}(\alpha) = -\frac{(a^{\dagger} - a)}{\sqrt{2}}D^{\dagger}(\alpha) + i\frac{p}{2}D^{\dagger}(\alpha) = \left(\frac{\partial}{\partial q}D(\alpha)\right)^{\dagger}$$
(A.5)

$$\frac{\partial}{\partial p}D^{\dagger}(\alpha) = -i\frac{(a^{\dagger}+a)}{\sqrt{2}}D^{\dagger}(\alpha) - i\frac{q}{2}D^{\dagger}(\alpha) = \left(\frac{\partial}{\partial p}D(\alpha)\right)^{\dagger}$$
(A.6)

from which we derive the relations

$$\partial_{q_{lh}}\Psi = -i\frac{p_{lh}}{2}\sum_{K}C_{lK}|K,\alpha_l\rangle + \sum_{K}C_{lK}\left[\sqrt{\frac{k_h+1}{2}}|K+1_h,\alpha_l\rangle - \sqrt{\frac{k_h}{2}}|K-1_h,\alpha_l\rangle\right]$$

$$(A.7a)$$

$$\partial_{p_{lh}}\Psi = i\frac{q_{lh}}{2}\sum_{K}C_{lK}|K,\alpha_l\rangle + i\sum_{K}C_{lK}\left[\sqrt{\frac{k_h+1}{2}}|K+1_h,\alpha_l\rangle + \sqrt{\frac{k_h}{2}}|K-1_h,\alpha_l\rangle\right].$$

$$(A.7b)$$

where we remind that  $q_{lh} = \sqrt{2} \operatorname{Re} \alpha_{lh}$ ,  $p_{lh} = \sqrt{2} \operatorname{Im} \alpha_{lh}$ , and  $\partial_{q_{lh}} = (\partial_{\alpha_{lh}} + \partial_{\bar{\alpha}_{lh}})/\sqrt{2}$ ,  $\partial_{p_{lh}} = i(\partial_{\alpha_{lh}} - \partial_{\bar{\alpha}_{lh}})/\sqrt{2}$ .

Using the above rule for the derivatives of the displacement operator deriving explicit formulae for the metric tensor elements is quite easy. Here we outline the derivation of the  $\eta_{q_{il}p_{hm}}$  element. First of all we notice that  $\eta_{q_{il}p_{hm}} = 0$  if  $l \neq m$ . From the definition of the metric tensor we have

$$\eta_{q_{il}p_{hl}} = -2 \operatorname{Im} \sum_{KJ} \bar{C}_{lK} \langle K \big| \partial_{q_{il}} D^{\dagger}(\alpha_l) \partial_{p_{hl}} D(\alpha_l) \big| J \rangle C_{lJ}$$
(A.8)

The expression above is the imaginary part of a quadratic form and is the anti-Hermitian part of the operator

$$X = \partial_{q_{il}} D^{\dagger}(\alpha_l) \partial_{p_{hl}} D(\alpha_l) = -i \frac{(a_i^{\dagger} - a_i)(a_h^{\dagger} + a_h)}{2} - i \frac{a_i^{\dagger} - a_i}{2\sqrt{2}} q_i - p_h \frac{(a_h + a_h^{\dagger})}{2\sqrt{2}} - \frac{q_i p_h}{4}$$
(A.9)

which has been derived by using formulae A.5 and A.4, whence

$$\eta_{q_{il}p_{hl}} = -\sum_{KJ} \bar{C}_{lK} \langle K | X - X^{\dagger} | J \rangle C_{lJ}.$$
(A.10)

If  $i \neq h$  the operator X is Hermitian thus the corresponding metric tensor element is zero. If i = h it can be easily verified that  $X - X^{\dagger} = [a_i, a_i^{\dagger}] = 1$ . Thus, considering the orthonormality relation  $\langle K|J \rangle = \delta_{KJ}$ , we have

$$\eta_{q_{il}p_{il}} = -\sum_{K} |C_{lK}|^2 = -\sum_{K} (r_{lK}^2 + s_{lK}^2).$$
(A.11)

The term  $\eta_{q_{il}p_{il}}$  represents the overall population of the *l*-th electronic state with negative sign.

## Appendix B. The Hamiltonian function

The Hamiltonian function  ${\mathcal H}$  can be easily obtained by using the unitary transformations

$$D^{\dagger}(\alpha)\omega_{i}a_{i}^{\dagger}a_{i}D(\alpha) = \omega_{i}a_{i}^{\dagger}a_{i} + \omega_{i}|\alpha_{i}|^{2} + \omega_{i}(\alpha_{i}a_{i}^{\dagger} + \bar{\alpha}_{i}a_{i})$$
(B.1)  
$$D^{\dagger}(\alpha)g_{i}q_{i}D(\alpha) = D^{\dagger}(\alpha)\frac{g_{i}}{\sqrt{2}}(a_{i}^{\dagger} + a_{i})D(\alpha) = \frac{g_{i}}{\sqrt{2}}(a_{i}^{\dagger} + a_{i}) + \frac{g_{i}}{\sqrt{2}}(\bar{\alpha}_{i} + \alpha_{i})$$
(B.2)

from which, using the orthonormality of the basis functions  $|K, \alpha_l\rangle$ , we have

$$\mathcal{H} = \sum_{miK} \left\{ \left[ \epsilon_m + \omega (|\alpha_{mi}|^2 + k_i) + \frac{g}{\sqrt{2}} (\bar{\alpha}_{mi} + \alpha_{mi}) \right] |C_{mK}|^2 \right\}$$
(B.3)  
$$+ \sum_{miK} [\omega \alpha_{mi} + \frac{g}{\sqrt{2}}] \sqrt{k_i + 1} \bar{C}_{mK+1_i} C_{mK}$$
  
$$+ \sum_{miK} [\omega \bar{\alpha}_{mi} + \frac{g}{\sqrt{2}}] \sqrt{k_i} \bar{C}_{mK-1_i} C_{mK}$$
  
$$+ J \sum_{lmKJ} \bar{C}_{lK} C_{mJ} \langle K, \alpha_l | J, \alpha_m \rangle + \text{H.c..}$$

Splitting each parameter into its real and imaginary component, the Hamiltonian can be rewritten in the form

$$\mathcal{H} = \mathcal{H}^{\circ} + \mathcal{V} \tag{B.4}$$

with

$$\mathcal{H}^{\circ} = \sum_{miK} \left\{ \left[ \epsilon_{m} + \omega(p_{mi}^{2} + q_{mi}^{2})/2 + \omega k_{i} + gq_{mi} \right] (r_{mK}^{2} + s_{mK}^{2}) \right\}$$
(B.5)  
+ 
$$\sum_{miK} (\omega q_{mi} + g) \sqrt{2(k_{i} + 1)} (r_{mK+1_{i}} r_{mK} + s_{mK+1_{i}} s_{mK}) + \sum_{miK} \omega p_{mi} \sqrt{2(k_{i} + 1)} (r_{mK+1_{i}} s_{mK} - s_{mK+1_{i}} r_{mK})$$
(B.5)  
$$\mathcal{V} = J \sum_{lmKJ} \bar{C}_{lK} C_{mJ} \langle K, \alpha_{l} | J, \alpha_{m} \rangle = 2J \sum_{JK} \sum_{m>l} \left[ (r_{lK} r_{mJ} + s_{lK} s_{mJ}) \operatorname{Re} \langle K, \alpha_{l} | J, \alpha_{m} \rangle \right]$$
(B.6)  
- 
$$(r_{lK} s_{mJ} - s_{lK} r_{mJ}) \operatorname{Im} \langle K, \alpha_{l} | J, \alpha_{m} \rangle \right]$$
15

The integrals  $\langle K, \alpha_l | J, \alpha_m \rangle$  are complex numbers, that can be evaluated by using the recurrence relations described in appendix C. The calculation of the derivatives of the Hamilton function with respect to  $(r_{lK}, s_{lK}, q_{li}, p_{li})$  follows from standard differentiation rules

The calculation of the derivatives of  $\mathcal{V}$  is quite lengthy but straightforward. By rewriting the overalp integrals between GCSs in the form

$$\langle K, \alpha_l | J, \alpha_m \rangle = \langle K | D(-\alpha_l) D(\alpha_m) | J \rangle$$
 (B.8)

and using equations A.3 and A.4 we obtain

$$\partial_{q_{ni}} \mathcal{V} = 2 \sum_{lKJ} V_{ln} (r_{lK} r_{nJ} + s_{lK} s_{nJ}) \times \left[ \sqrt{\frac{j_i + 1}{2}} \operatorname{Re}\langle K, \alpha_l | J + 1_i, \alpha_n \rangle - \sqrt{\frac{j_i}{2}} \operatorname{Re}\langle K, \alpha_l | J - 1_i, \alpha_n \rangle + \frac{p_{ni}}{2} \operatorname{Im}\langle K, \alpha_l | J, \alpha_n \rangle \right] \\ - 2 \sum_{lKJ} V_{ln} (r_{lK} s_{nJ} - s_{lK} r_{nJ}) \times \left[ \sqrt{\frac{j_i + 1}{2}} \operatorname{Im}\langle K, \alpha_l | J + 1_i, \alpha_n \rangle - \sqrt{\frac{j_i}{2}} \operatorname{Im}\langle K, \alpha_l | J - 1_i, \alpha_n \rangle - \frac{p_{ni}}{2} \operatorname{Re}\langle K, \alpha_l | J, \alpha_n \rangle \right]$$
(B.9)

and

$$\partial_{p_{ni}} \mathcal{V} = -2 \sum_{lKJ} V_{ln} (r_{lK} r_{nJ} + s_{lK} s_{nJ}) \times \left[ \sqrt{\frac{j_i + 1}{2}} \operatorname{Im} \langle K, \alpha_l | J + 1_i, \alpha_n \rangle + \sqrt{\frac{j_i}{2}} \operatorname{Im} \langle K, \alpha_l | J - 1_i, \alpha_n \rangle + \frac{q_{ni}}{2} \operatorname{Im} \langle K, \alpha_l | J, \alpha_n \rangle \right] \\ + 2 \sum_{lKJ} V_{ln} (r_{lK} s_{nJ} - s_{lK} r_{nJ}) \times \left[ \sqrt{\frac{j_i + 1}{2}} \operatorname{Re} \langle K, \alpha_l | J + 1_i, \alpha_n \rangle + \sqrt{\frac{j_i}{2}} \operatorname{Re} \langle K, \alpha_l | J - 1_i, \alpha_n \rangle + \frac{q_{ni}}{2} \operatorname{Re} \langle K, \alpha_l | J, \alpha_n \rangle \right]$$
(B.10)

# Appendix C. Franck-Condon integrals

The one-dimensional Franck-Condon integrals  $\langle K, \alpha_l | J, \alpha_m \rangle$  can be computed by recurrence formulae. [54, 56, 55] Indeed we first observe that

$$\langle K, \alpha_l | J, \alpha_m \rangle = \langle K \big| D^{\dagger}(\alpha_l) D(\alpha_m) \big| J \rangle = e^{\operatorname{Im}(\bar{\alpha}_l \alpha_m)} \langle K \big| D(\gamma) \big| J \rangle$$
(C.1)

where  $\gamma = \alpha_m - \alpha_l$ , then, using the generating function[57]

$$G(\bar{\rho},\tau) = \sum_{m,n} D_{mn}(\gamma) \frac{\bar{\rho}^m \tau^n}{\sqrt{m!n!}} = \exp(-|\gamma|^2/2) \exp(\bar{\rho}\tau + \bar{\rho}\gamma - \tau\bar{\gamma}) \quad (C.2)$$

and applying well known mathematical procedures [54, 56, 55, 58, 59, 52] it is possible to derive the recurrence formulae

$$\sqrt{m+1}D_{m+1,n} = \gamma D_{mn} + \sqrt{n}D_{m,n-1} \tag{C.3}$$

$$\sqrt{n+1}D_{m,n+1} = -\bar{\gamma}D_{mn} + \sqrt{m}D_{m-1,n},$$
 (C.4)

with

$$D_{00}(\gamma) = \exp(-|\gamma|^2/2),$$
 (C.5)

which allow to compute FC integrals for any pair of quantum numbers.[60, 52]

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