

Grid implementation of the electron nuclear dynamics theory: a coherent states chemistry

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ABSTRACT: We report our ongoing implementation of the electron nuclear dynamics (END) theory as a multi domain grid service involving Globus toolkit, Avaki compute grid, and Avaki data grid. END provides a genuine quantum dynamics but recast in a generalized classical Hamiltonian format via coherent states (CS) parameterization. END simulations of chemical reactions demand several trajectory calculations in quantum phase space and naturally call for a grid solution. The current grid implementation is based on the suite of programs CSTechG, which has been tested for various architectures under different conditions involving file staging and several queuing techniques. Different components and services of the application and sample calculations for the $H^+ + CH \equiv CH$ reaction system are also presented.

1 INTRODUCTION: COHERENT STATES FOR CHEMICAL SIMULATIONS

The final challenge in the field of quantum chemistry is to achieve direct, real-time simulations of chemical reactions. However, even with the present computer technology, full quantum mechanics descriptions of large molecular systems remain unfeasible and recurrences to less costly classical mechanics treatments are inescapable. A realistic treatment of large molecules should employ a generalized hybrid quantum/classical approach (Warshel & Levitt 1976) where some molecular degrees of freedom and/or some molecular regions are partitioned into quantum and classical descriptions. Degrees of freedom for which a quantum treatment is less critical [e.g. translational, rotational (Morales, Deumens et al. 1999) and vibrational (Morales, Diz et al. 1995) motions] and/or molecular regions not undergoing chemical reactions (e.g. the bulk solvent surrounding a solute) can be treated via classical mechanics with added quantum corrections on top (Miller 2001). Conversely, regions where quantum phenomena occur (e.g. tunneling) must be described quantum-mechanically. An ideal Q/C methodology should permit that the transition from quantum to classical mechanics be realized at any desired level of accuracy and in a continuous way. Such flexibility can be obtained by exploiting the properties of coherent states (CS) functions (Klauder & Skagerstam 1985). Conceptually speaking, CS are sets of genuine quantum states that permits expressing full quantum dynamical equations in a classical format

in terms of generalized positions q_i and generalized conjugate momenta p_i (Kramer & Saraceno 1981). More formally, the states $|z_i\rangle$, depending upon the complex parameters $z_i = q_i + ip_i$, make a set of CS if they satisfy the following two conditions (Klauder & Skagerstam 1985): (1) continuity with respect to z_i , and (2) resolution to unity: $1 = \int d\mu(z_i, z_i^*) |z_i\rangle\langle z_i|$ with positive measure $d\mu(z_i, z_i^*) \geq 0$ and $\langle z_i | z_i \rangle \neq 0$ (i.e. a non-orthogonal and over-complete basis set). Some CS are also quasi-classical (Morales, Deumens et al. 1999) in the sense that there exists a Hamiltonian \hat{H} so that the CS average positions $\langle \hat{x}_i \rangle = q_i(t) = \langle z_i(t) | \hat{x}_i | z_i(t) \rangle$ and momenta $\langle \hat{p}_i \rangle = p_i(t) = \langle z_i(t) | \hat{p}_i | z_i(t) \rangle$ evolve in time with \hat{H} according to Hamilton classical equations: $\dot{q}_i = \partial H(q_i, p_i) / \partial p_i$ and $\dot{p}_i = -\partial H(q_i, p_i) / \partial q_i$, with $H(q_i, p_i) = \langle z_i(t) | \hat{H} | z_i(t) \rangle$. A CS-expressed dynamics is fully quantum but in the closest possible form to classical mechanics; if the CS is also quasi-classical then a classical dynamics with a quantum state is obtained. The most common way to construct CS is by following the group-related Perelomov prescription (PP). Illustrating with the quantum harmonic oscillator quasi-classical Glauber CS, PP involves (Klauder & Skagerstam 1985): (1) finding adequate sets of Lie-algebra generators [here, the Weyl algebra creation (annihilation) a^\dagger (a) operators] and then (2) applying an associated Lie-group irreducible unitary representation $\hat{U}(z, z^*)$ onto a fiducial state $|0\rangle$ to generate the CS: $|z\rangle = \hat{U}(z, z^*)|0\rangle = \exp(za^\dagger - z^*a)|0\rangle$. PP is simple in outline but its application to construct CS for chemical problems is far from being trivial. Furthermore, PP does not nec-

essarily generate quasi-classical CS and departures from the group treatment are inevitable to obtain such a property (Morales, Deumens et al. 1999). So far, almost all the chemical research on CS has only dealt with the Glauber CS to only describe nuclear dynamics (Miller 2002). Contrastingly, our group is developing a unifying CS approach where novel or unusual types of CS (Morales, Diz et al. 1995; Morales, Deumens et al. 1999) for all types of particles (nuclei and electrons) and for all types of dynamics (translational, rotational, vibrational, and electronic) are used. This unifying CS approach with its grid implementation is explained below.

2 THE ELECTRON NUCLEAR DYNAMICS THEORY

A general scheme for a CS dynamics is the electron nuclear dynamics (END) theory (Deumens, Diz et al. 1994). Herein, we will briefly outline our own version of END. For a molecular system with N_{Nucl} nuclei and N_{el} electrons, the total wavefunction ψ_{Total} is the product of nuclear ψ_{Nucl} and electronic ψ_{el} parts: $\psi_{Total} = \psi_{Nucl} \psi_{el} \cdot \psi_{Nucl}$ is a product of $3N_{Nucl}$ frozen Gaussian wave packets $\psi_{Nucl} = \prod_i \exp\{-\lambda_i (X_i - R_i)^2 + iP_i (X_i - R_i)\}$ with positions R_i and momenta P_i . ψ_{Nucl} is also factorized into translational, rotational and vibrational parts: $\psi_{Nucl} = \psi_{Trans} \psi_{Rot} \psi_{Vib} \cdot \psi_{Trans}$ is a 3-D CS wave packet describing quasi-classically the center of mass (CM) motion (Morales, Deumens et al. 1999). ψ_{Rot} is the almost quasi-classical Morales rotational CS (Morales, Deumens et al. 1999) $\psi_{Rot} = |\alpha\beta\gamma\rangle$ formulated by a departure from the PP treatment of the $SO(3) \otimes SO(3) \otimes A$ Lie group. ψ_{Vib} is a product of $3N_{Nucl} - 6$ quasi-classical Glauber CS (Morales, Diz et al. 1995) $\psi_{Vib} = \prod_i |z_i\rangle$. For ψ_{el} , K fermion creation (annihilation) operators b_i^\dagger (b_i) of N_{el} occupied and $K - N_{el}$ virtual orthogonal molecular orbitals (MO) generate pair-holes operators $b_p^\dagger b_h$ of the $U(K)$ Lie group (Klauder & Skagerstam 1985). Taking as fiducial state the Fermi vacuum $|0\rangle = b_{N_{el}}^\dagger \dots b_1^\dagger |vac\rangle$, the non quasi-classical, single-determinant Thouless electronic CS (Klauder & Skagerstam 1985) is $\psi_{el} = |\mu\rangle = \exp(\sum_p \sum_h \mu_{ph} b_p^\dagger b_h) |0\rangle$. Hartree-Fock (HF) (Szabo & Ostlund 1989) MO are currently used but both Kohn-Sham (KS) density functional theory (DFT) (Parr & Yang 1989), and semiempirical Austin Model 1 (AM1) (Zerner 1991) MO will be implemented. Thouless CS contains the ground and excited electronic states with their non-adiabatic coupling terms. With ψ_{Total} CS-formulated, the quantum Lagrangian is $\mathcal{L} = \langle \psi_{Total} | [(1/2)i(\bar{\partial}/\partial t - \bar{\partial}/\partial t) - \hat{H}] | \psi_{Total} \rangle / \langle \psi_{Total} | \psi_{Total} \rangle$. By imposing stationary to the quantum action A , $\delta A = \delta \int \mathcal{L}(t) dt = 0$ (Kramer & Saraceno 1981; Deumens, Diz et al. 1994), the END dynamical equations for the CS parameters $R_i, P_i, \mu_{ph}, \mu_{ph}^*$ are obtained :

$$\begin{bmatrix} i\mathbf{C} & \mathbf{0} & i\mathbf{C}_R & \mathbf{0} \\ \mathbf{0} & -i\mathbf{C}^* & -i\mathbf{C}_R^* & \mathbf{0} \\ i\mathbf{C}_R^\dagger & -i\mathbf{C}_R^T & i\mathbf{C}_{RR} & -\mathbf{I} \\ \mathbf{0} & \mathbf{0} & \mathbf{I} & \mathbf{0} \end{bmatrix} \begin{bmatrix} \frac{d\mu}{dt} \\ \frac{d\mu^*}{dt} \\ \frac{d\mathbf{R}}{dt} \\ \frac{d\mathbf{P}}{dt} \end{bmatrix} = \begin{bmatrix} \frac{\partial E_{Total}}{\partial \mu^*} \\ \frac{\partial E_{Total}}{\partial \mu} \\ \frac{\partial E_{Total}}{\partial \mathbf{R}} \\ \frac{\partial E_{Total}}{\partial \mathbf{P}} \end{bmatrix} \quad (1)$$

where the left matrix is related to Hamilton symplectic matrix and the total energy is $E_{total} = \langle \psi_{Total} | \hat{H} | \psi_{Total} \rangle$. The dynamics described by Eq. (1) is fully quantum but expressed in a generalized classical Hamiltonian format and even quasi-classical for the CM wave packet and the rotational and vibrational CS. Eq. (1) treats simultaneously both electron and nuclei and provides a direct dynamics not requiring pre-calculated potential energy surfaces to run. The CS parameters $R_i, P_i, \mu_{ph}, \mu_{ph}^*$ evolving in time determine different reaction trajectories in a CS quantum phase space. In a simulation, reactants are prepared with initial positions, momenta and electronic state: R_i^0, P_i^0, μ_{ph}^0 , and μ_{ph}^{0*} (Fig.1) to define the initial wavefunction: $\psi_{Total}^i = \psi_{Total}^0$. A chemical reaction simulation is advanced by integrating Eq. (1) over time. At final time, the evolved wavefunction ψ_{Total}^f can be projected onto selected reaction products eigenstates $\psi_{Total}^f = \psi_{Trans}^f \psi_{Rot}^f \psi_{Vib}^f \psi_{el}^f$ so that the quantum probability amplitude CS S-matrix for the transition $\psi_{Total}^i \rightarrow \psi_{Total}^f$ is $S_{CS}^{i \rightarrow f} = \langle \psi_{Total}^f | \psi_{Total}^i \rangle = A_{Trans}^{i \rightarrow f} A_{Rot}^{i \rightarrow f} A_{Vib}^{i \rightarrow f} A_{el}^{i \rightarrow f} \exp(iA)$ where each $A_{Degree}^{i \rightarrow f}$ is a reaction transition probability amplitude per degree. All the relevant properties of a chemical reaction (e.g. differential and integral cross sections, rate constants) can be directly calculated from $S_{CS}^{i \rightarrow f}$.

3 CSTECHG GRID IMPLEMENTATION

The simulation of one single chemical reaction requires myriads of trajectories in the CS quantum phase space. To avoid tail-backing sequential trajectory calculations, the CS END dynamics can be naturally implemented for simultaneous trajectory runs on a compute grid. Our grid implementation of the CS END dynamics is based on the suite of programs CSTechG developed for several operating systems (Microsoft Windows®, Red Hat Linux®, and IRIX® *inter alia*) from the ENDyne 2.7 and 2.8 codes (Deumens 1997). From an algorithmic point of view, a CS END grid service should be capable of performing the following tasks: (1) define the reaction initial conditions from any grid node, (2) submit all the trajectory jobs from those initial conditions via the grid bootstrap to run them in parallel on any of the available grid nodes; this implies using the

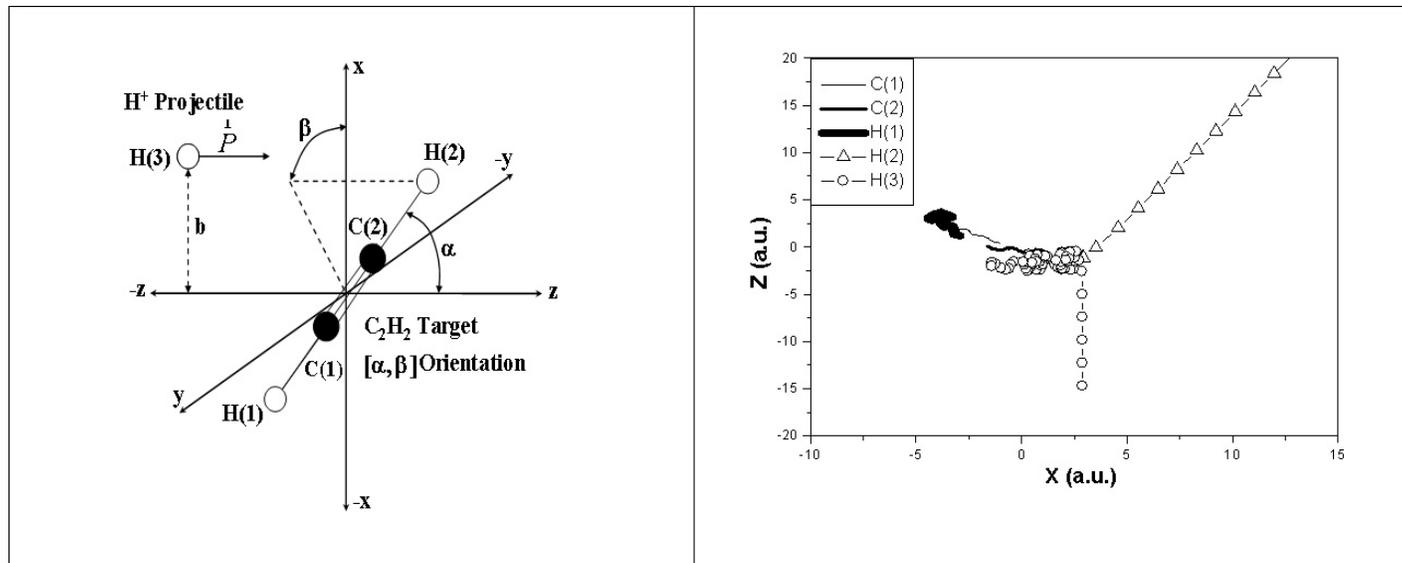


Figure 1: Simulation of the $H^+ + C_2H_2 \rightarrow$ reaction with the CS END grid implementation at the HF/STO-3G level. Left Panel: Reactants CS initial conditions; balls represent the CS wave packets describing the nuclei and carrying the CS electronic wavefunction; b = projectile impact parameter and $[\alpha, \beta]$ = target angular orientation. Right Panel: CS wave packets trajectory on the X-Z plane predicting the reaction: $CH \equiv CH + H^{+*} \rightarrow CH \equiv CH^+ + H^+$ (hydrogen rearrangement) from the $[112.5^\circ, 0.0^\circ]$ orientation.

CSTechG executable corresponding to the nodes architectures and operating systems; (3) collect all the trajectories outputs and calculate relevant chemical properties.

An efficient grid solution for the previously outlined tasks should necessarily satisfy the following sets of requirements: (1) shared resources allowing transparent communication amongst the different grid sites; (2) encrypted data transfer to individual computer nodes and different sites; (3) homogenous implementation of all features; and (4) rescheduling and salvaging of dropped jobs using a restart repository. The first three requirements are similar to many grid services (Foster, Kesselman et al. 2002). However, the CSTechG implementation is essentially centered on deploying jobs on different platforms at various sites with controlled access to data repository, dynamic file staging, and tunneling through different queuing systems. Our current implementation is based on a global grid framework from the Globus webpage (www.globus.org) that enables transparent access to resources on public network via secure communication.

These features are maintained as objects of different administrative domains. Avaki data and Avaki compute grid (Avaki location independent objects) together with Globus are implementations tested for the current application. The services finally used or under development include: (1) *CSTechG Restart*: This service deals with lost jobs that have stopped reporting and restarts them on different resources. (2) *CSTechG Deploy*: This service dynamically deploys the CSTechG executable on a compute resource; (3) *CSTechG Monitor*: This service takes

care of currently deployed CSTechG services and jobs at various sites and on different compute resources; (4) *CSTechG Reschedule*: This service keeps track of current jobs and triggers a restart from a CSTechG.rst file; (5) *CSTechG Migrate*: This service moves jobs to different resources when triggered by resource usage expiration limit; and (6) *CSTechG HTTP*: An http implementation to deploy CSTechG job. The identified services interact with each other to perform the tasks that were initiated by the CSTechG executable. Users will have the ability to run jobs from the web interface using any web browser. Also, users can currently register their version of the CSTechG implementation, schedule and deploy jobs, and import and export data to various devices.

Single point authentication and non availability of multicast networks have been taken into account; therefore, dynamic resource binding has not been implemented in the current version. The CSTechG implementation makes use of the service architecture, which is flexible in many ways. The same version of the implementation could be deployed on geographically different administrative domains. This makes the task of the CSTechG administrator less complicated for redeploying in case of application upgrade. Additionally, different versions of CSTechG can coexist for testing purpose.

4 SAMPLE CALCULATIONS

Reactions of proton H^{+*} projectiles with acetylene $CH \equiv CH$ molecular targets at collisional energy $E_{lab} = 30$ eV are ideal candidates to illustrate the pre-

sent implementation and to test the accuracy of the CS END dynamics. In those reactions, the H^{+*} can probe all the energetically accessible channels (chemical reactions) in the collisional system $CH \equiv CH + H^{+*} \rightarrow$, *i.e.*, non-transfer scattering: $\rightarrow CH \equiv CH + H^{+*}$; charge transfer scattering: $\rightarrow CH \equiv CH^+ + H^{0*}$; hydrogen rearrangement: $\rightarrow CH \equiv CH^* + H^+$, H_2 formation: $\rightarrow CH \equiv C^+ + HH^*$; C-H dissociation $\rightarrow CH \equiv C + H^0 + H^{+*}$, and C=C dissociation: $\rightarrow CH + CH + H^{+*}$. CS END calculations (Addepalli, Maiti et al. 2004) for this system at the HF/STO-3G minimal basis set level (Szabo & Ostlund 1989) correctly described all the mentioned processes (*e.g.* hydrogen rearrangement is shown in Fig. 1), and predicted both charge-transfer integral cross section and total differential cross section (Addepalli, Maiti et al. 2004) in good agreement with experimental results (Aristov, Niedner Schatteburg et al. 1991). In a CS END dynamics, the different reactions channels along with the details in their chemical kinetics mechanism can be discerned from the calculated trajectories in the CS quantum phase space. In addition, the simulated reactions can be readily visualized with computer animation software.

5 SUMMARY AND CONCLUSIONS

The dynamics of both electrons and nuclei in a molecular system can be expressed in a generalized classical Hamiltonian format via coherent states. The resulting END equation of motion demands the calculation of several trajectory calculations in the CS quantum phase space to describe a single chemical reaction. We present an efficient solution for this problem that works on multiple grid architectures and uses geographically dispersed compute resources. Those resources were classified and controlled by different services demonstrating the interoperability between Avaki and Globus grid architectures. Sample calculations to the $H^+ + CH \equiv CH$ collision system could describe several chemical reactions and agreed well with available experimental results. Present efforts are concentrated on using this new capability to study other proton collision reactions with different targets.

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