

Time dependent quantum scattering using non orthogonal coordinates

Parallel approach to the benchmark collinear $A + BC \rightarrow AB + C$

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Introduction. The calculation of the detailed state-to-state quantum reactive probabilities for atom-diatom systems requires either the stationary or time dependent Schrödinger equation for the nuclei wavefunction to be integrated step by step from reactants to products along a continuity variable. From a direct or indirect comparison of the system wavefunction of the reactants with that of the products, one can compute the elements of the scattering S matrix from which all the scattering properties of the system can be derived [1, 2]. In this work the use of Jacobi coordinates as well as of the less conventional [3] Bond Length (BL) and Bond Order (BO) ones is made for the description of the reactive events on parallel machines. Jacobi coordinates are orthogonal coordinates and because of their arrangement based nature make the formulation of the Hamiltonian extremely simple and asymptotically uncoupled. For the same reason, however, a transformation from reactant to product arrangement formulation is needed at some length during the process. Next in complexity are the hyperspherical coordinates, that, despite being orthogonal, because of their spherical nature make the formulation of the Hamiltonian more complex and, depending on their specific formulation, bear an arrangement dependence that needs some reformulation in going from reactants to products. BL and BO coordinates are non orthogonal coordinates; as such they bear a more complicated formulation of the Hamiltonian. Yet they are process coordinates and therefore describe reactions better than traditional orthogonal coordinates without requiring a reformulation in going from reactants to products. Moreover, Bond Order coordinates (derived from the homonym concept introduced by Pauling [4]) have the appealing feature of deforming the space in terms of the strengths of the acting forces making the related space inverted (with respect to the distance one) and limited.

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Figure 1: The ABC collinear system in the reactant (left) and product (right) arrangement. Reactant (R , r) and product (R' , r') Jacobi coordinates are shown together with the process BL coordinates r_{AB} and r_{BC} .

The real wavepacket approach. In order to assess the features of the usage of alternative sets of coordinates we focus first on time dependent methods. For this a parallel code has been developed for the simple $A + BC$ collinear reaction where the real wavepacket propagation method [2] has been employed. In our scheme [5], inspired by the work of Ref [2], only the real part $q(\mathbf{w}, t) = \text{Re}[\psi(\mathbf{w}, t)]$ of the wavepacket (depending on the nuclear coordinates collectively denoted by \mathbf{w} and on time) is considered and a scaled Hamiltonian $\hat{H}_s = a_s \hat{H} + b_s$ (such that its spectrum lies within the interval $[-1, 1]$) is used. In this case, the simple three term recursion scheme

$$q_{t+\tau}(\mathbf{w}) = -q_{t-\tau}(\mathbf{w}) + 2\hat{H}_s q_t(\mathbf{w})$$

can be used for the wavepacket time evolution after applying a first special iteration (simply involving a Hamiltonian application):

$$q_\tau(\mathbf{w}) = \hat{H}_s q_0(\mathbf{w}).$$

The collocation of the initial wavepacket (written as the product of a translational Gaussian function and a vibrational ϕ_v diatomic function) on the \mathbf{w} grid involves the diagonalization of a real symmetric matrix to solve the reactant diatomic problem (here referenced to as $\hat{H}_r \phi_v$), while the product diatomic problem ($\hat{H}_{r'} \phi'_v$) has to be solved for the final state to state analysis. Employing as usual when needing state to state information the product Jacobi coordinates (R', r' in Fig 1) grid, the evaluation of the kinetic parts ($\hat{T}_{R'}$ and $\hat{T}_{r'}$) of the Hamiltonian (the potential part is multiplicative and therefore straightforward and fast) involves 1D-Fourier transforming the wavepacket four times:

$$\begin{aligned} [\hat{T}_{R'} + \hat{T}_{r'}] q_t(R', r') &= -\frac{\hbar^2}{2\mu_{R'}} \mathbf{FT}_{R'}^{-1} \left[-k_{R'}^2 \mathbf{FT}_{R'} [q_t(R', r')] \right] \\ &\quad -\frac{\hbar^2}{2\mu_{r'}} \mathbf{FT}_{r'}^{-1} \left[-k_{r'}^2 \mathbf{FT}_{r'} [q_t(R', r')] \right]. \end{aligned}$$

Parallel implementation. A coarse grain model, based on functional decomposition, and a fine grain model, based on domain decomposition have been implemented using a message passing interface. In the first model, $\hat{T}_{R'}$ and $\hat{T}_{r'}$ are evaluated concurrently; in the latter one, portions of the wavepacket

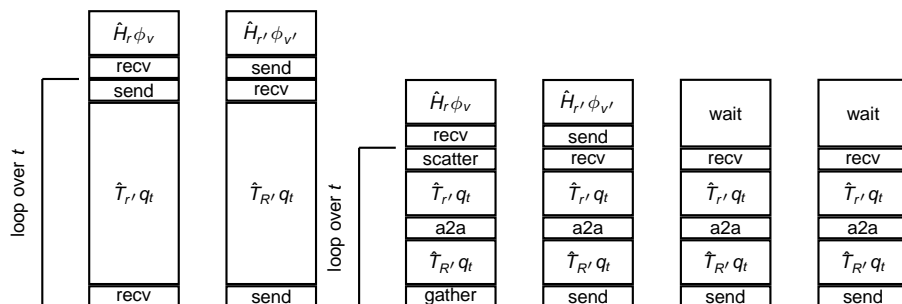


Figure 2: Main blocks of computation for a coarse grain (left panel, involving two concurrent tasks) and a fine grain (right panel, involving four concurrent tasks) parallel implementation. Inter-task communications are also shown.

are processed concurrently. The main blocks of computation are schematized in Fig 2 for both models.

The alternative BL (non orthogonal coordinates) formulation. The adoption of non orthogonal coordinates involves a reformulation of the Hamiltonian leading to the presence of mixed derivative terms. In the case of Bond Length coordinates (see Fig 1) one has

$$\hat{H} = -\frac{\hbar^2}{2\mu_{BC}} \frac{\partial^2}{\partial r_{BC}^2} - \frac{\hbar^2}{2\mu_{AB}} \frac{\partial^2}{\partial r_{AB}^2} + \frac{\hbar^2}{m_B} \frac{\partial^2}{\partial r_{BC} \partial r_{AB}} + V(r_{BC}, r_{AB}),$$

that requires an adaptation of the computational algorithms and of the parallel models designed for the Jacobi formalism.

Detailed state to state probabilities for two benchmark symmetric reactions ($\text{H} + \text{H}_2$ and $\text{N} + \text{N}_2$) obtained using a Bond Length formalism (and the LSTH and LEPS potentials, respectively) are shown in Fig 3.

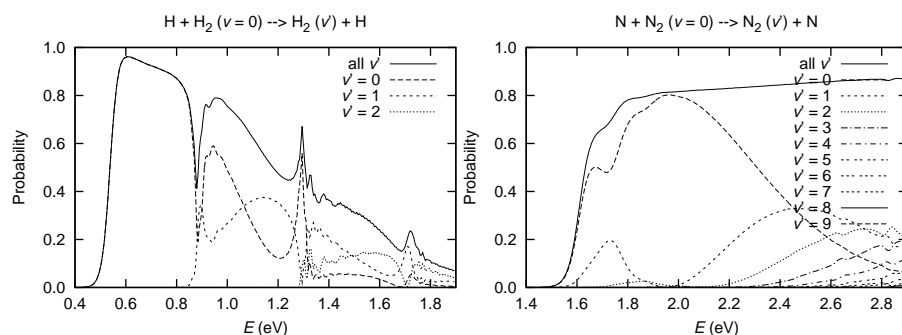


Figure 3: $J = 0$ collinear state to state reactive probabilities plotted as a function of the total energy calculated using BL coordinates.

The BO formulation. BO coordinates are defined as

$$n_{BC} = e^{-\beta_{BC}(r_{BC}-r_{eqBC})}$$

$$n_{AB} = e^{-\beta_{AB}(r_{AB}-r_{eqAB})}$$

where β and r_{eq} are system specific parameters related to the reactant and product diatomic vibrational equilibrium and force constant properties.

As already pointed out, the original feature of the BO coordinates is that they provide an inverted physical space (the zero of the BO coordinate corresponds to an infinite bond length while large BO values correspond to short bond lengths) and, more appealing, confined into a finite volume.

The related Hamiltonian reads

$$\hat{H} = -\frac{\hbar^2 \beta_{BC}^2}{2\mu_{BC}} \left(n_{BC}^2 \frac{\partial}{\partial n_{BC}^2} + n_{BC} \frac{\partial}{\partial n_{BC}} \right) - \frac{\hbar^2 \beta_{AB}^2}{2\mu_{AB}} \left(n_{AB}^2 \frac{\partial}{\partial n_{AB}^2} + n_{AB} \frac{\partial}{\partial n_{AB}} \right) + \frac{\hbar^2 \beta_{BC} \beta_{AB}}{2m_B} n_{BC} n_{AB} \frac{\partial^2}{\partial n_{BC} n_{AB}} + V(n_{BC}, n_{AB}).$$

Accordingly, further modifications with respect to the computational algorithms and parallel models adopted in the Jacobi coordinates treatment have been introduced. Though the reactive probabilities calculation is still in a test phase, the use of the BO approach has shown to be advantageously applicable to wavepacket treatments (a graphical illustration of the results is shown in Fig 4).

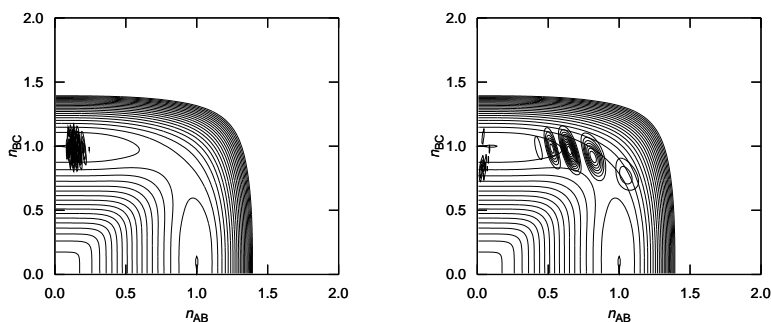


Figure 4: Contours of the square modulus $|q(n_{AB}, n_{BC})|^2$ of the real wavepacket on a Bond Order grid for the H + H₂ system at the initial and an evolved stage. Contours of the LSTH PES are also shown.

Perspectives. This work describes a first step towards the use of Bond Order representations for quantum reactive scattering. BO coordinates appear to be more a natural choice to represent forces driven molecular processes, as the strength of a chemical bond can be associated with the exponential of the

displacement of the internuclear distance from equilibrium. Parallelization has also been considered, as the computational effort will result even heavier when a third degree of freedom (of rotation) will be introduced. In the near future, the advantages of an angular reaction coordinate given by a polar representation of Bond Order coordinates (HYBO) will also be explored.

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