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Quantum hydrodynamics with trajectories: The nonlinear conservation form mixed/discontinuous Galerkin method with applications in chemistry

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ABSTRACT

We present a solution to the conservation form (Eulerian form) of the quantum hydrodynamic equations which arise in chemical dynamics by implementing a mixed/discontinuous Galerkin (MDG) finite element numerical scheme. We show that this methodology is stable, showing good accuracy and a remarkable scale invariance in its solution space. In addition the MDG method is robust, adapting well to various initial-boundary value problems of particular significance in a range of physical and chemical applications. We further show explicitly how to recover the Lagrangian frame (or pathline) solutions.

1. Introduction

Quantum hydrodynamics (QHD) has engendered substantial activity in the field of theoretical chemical dynamics, where one may refer to Wyatt et al. [40] for a comprehensive introductory overview of the numerous recent results emerging from this blossoming field.

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The basic idea emerging from quantum chemistry in the context of QHD is to employ the time-dependent Schrödinger equation (TDSE) to solve for the dynamical properties (probability densities, "particle" velocities, etc.) of chemical systems. In the same spirit in which the de Broglie–Bohm interpretation (see [17,5,6]) of quantum mechanics may be used to recover "trajectories" of individual fluid elements along the characteristics of motion of the solution, the QHD equations of Madelung and Bohm are derived as formally equivalent to the TDSE and thus comprise an alternative route to solutions which generate quantum trajectories that follow particles along their respective paths (see [40,19] for a comprehensive overview).

These solutions hold particular significance, where, in the context of the QHD formulation, it is possible to resolve the chemical dynamics of a vast number of reaction mechanisms known to have pathways dominated by quantum tunneling regimes. Some of these systems include proton transfer reactions (for example see Fig. 1), conformational inversions, biologically important redox reactions in enzymatic catalysis reactions (see Fig. 2), and proton-coupled electron transfer reactions (refer to [28,27]). It is not yet clear if these types of methods may also have application at higher energies, for example in the halo nuclei tunneling occurring in fusion reactions (as seen, for example, in [18]).

Substantial research has been done in quantum hydrodynamics to find the best and fastest computational methodology for solving this system of equations. In the standard methodology presented using the quantum trajectory method (QTM), for example, solutions to the QHD equations are found by transforming the system of equations, which is generally posited in the Eulerian fixed coordinate framework (see [25,19,15,14]), into the same set of equations in the Lagrangian coordinate framework, which effectively follows solutions along particle trajectories; or along so-called "Bohmian trajectories." The transformation from the Eulerian to the Lagrangian frame leads to a set of coupled equations which solve for two unknowns: the *quantum action* $S(t,\vec{r})$ and the probability density or *quantum amplitude* $\sqrt{\varrho(t,\vec{r})} = R(t,\vec{r})$ along the trajectories $\vec{r}(t,\boldsymbol{x})$ (e.g. see [40] box 1.2). The obvious advantage of the Lagrangian framework is reduced computational times, since solutions are only computed along a set of chosen trajectories; while clearly the disadvantage is the possibility of obscuring structure hidden within the continuum of the full solution, which may only emerge properly in convergent numerical schemes, and also the increased complications of transposing into more complicated settings: such as with functional or time dependencies on the potential term V, or including dissipative or rotational vector fields.

In addition, the numerical solutions to the above mentioned Lagrangian formulations have demonstrated characteristic behaviors which introduce certain technical difficulties at the level of formal analysis. First, the system of equations are *stiff*, which is to say, solutions to the system may locally or globally vary rapidly enough to become numerical unstable without reducing numerically to extremely small timesteps. Furthermore, there exists the so-called "node problem," which is characterized by singularity formation (see [40] for characterization of node types) along particle trajectories. Another issue which arises is obtaining unique solutions, since there is not a unique choice of trajectories in the Lagrangian formulation (see for example Section 6 and Appendix A). And finally, boundary data is often treated without regard to the (often substantial) numerical residuals introduced in the weak entropy case, or taking into account consistency between the TDSE and the QHD system of equations (see for example [30] and Section 3).

We introduce an alternative formulation to the standard solutions described above in ϱ and S and tracked with respect to the Lagrangian coordinate frame which is motivated by work of Gardner, Cockburn, et al. (see [15,16,8]). Instead, we keep the system in its conservation form (instead of in a primitive variable form) in the Eulerian coordinate system (see [25]), and solve for the density $\varrho = \varrho(t,\boldsymbol{x})$ and the particle *velocity* $\boldsymbol{v} = \boldsymbol{v}(t,\boldsymbol{x})$ (instead of the *quantum action* S). We show that these solutions may be used to easily recover the variables S and ψ in a single step; and may with little difficulty be transformed into their Lagrangian coordinate frame counterpart solutions $\varrho(t,\vec{r}), \boldsymbol{v}(t,\vec{r}), S(t,\vec{r})$ and $\psi(t,\vec{r})$, using the conservation equation (continuity equation), or by solving for pathlines in the sense of classical mechanics, or by any number of alternative so-called "offset methods." Additionally, our solutions demonstrate a type of resolution invariance, which is to say that the behavior of our solutions are qualitatively equivalent at varying spatial resolutions, and compare favorably with solutions to the formally equivalent TDSE. As a consequence, our conservation-based formulation is computationally competitive with Lagrangian formulations, up to a type of "formal accuracy" in the trajectory solutions.

Our solutions, as the Lagrangian formulated solutions mentioned above, still demonstrate a *stiff* behavior. However, also as the Lagrangian solutions above, and similarly to the classical CFL condition in fluid mechanics, we consider this a prohibitive but not insurmountable computational difficulty. On the other hand, our solutions to the conservation form of QHD do not demonstrate the node problem (at least on Gaussian wavepackets) as expected, as the only type of node our formulation

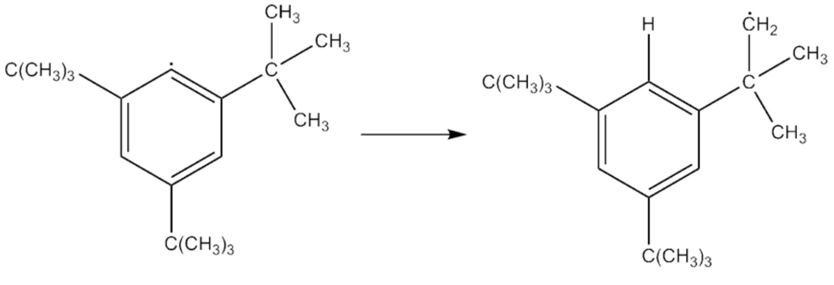

Fig. 1. Here we have the intramolecular rearrangement of the aryl radical 2,4,6-tri-tert-butylephenyl to 3,5-di-*tert*-butylneophyl (see [7] for details).