

Exact many-electron simulation method for bond-breaking reactions in liquids

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Scientific background

Chemical reactions involve the formation and breaking of bonds between atoms and much of the field of chemistry is concerned with how chemical reactions progress and how one can alter the path of a reaction to produce a desired molecule. Although ultrafast laser spectroscopic techniques have progressed to a level where one can probe the elementary steps of a reaction in real time, for systems containing anything more than simple molecules, spectroscopy simply does not yield enough information to be able to back out what individual atoms are doing.

It has thus been a goal of computational chemistry to be able to simulate chemical reactions so that one can follow the path of every atom involved in the reaction. This is challenging because chemical bonds involve the sharing of electrons between atoms, therefore to deal with bond breaking and making processes one must explicitly include at least the bonding electrons in the simulation and since electrons are light particles one must invoke quantum mechanics, *i.e.* solve Schrödinger's Equation (SE). Furthermore, one would like to use a simulation method that uses no experimentally derived parameters but rather is based on first principles physics so that the simulation method is transferable and predictive *i.e.* it can be accurately applied to many different types of system, including model systems and those that are not experimentally accessible.

The current state-of-the-art simulation methods that meet these criteria are called ***ab initio* molecular dynamics** (AIMD) methods, and they involve the coupling of an algorithm that propagates the nuclei, which are usually treated via classical mechanics, with a method that simultaneously (approximately) solves SE for the electrons; such methods have been successfully applied to study bond breaking/making processes involving tens of atoms *e.g.* see reference [1]. However, the class of reactions that we are interested in, **condensed-phase photodissociation reactions**, require a whole new set of computational methods. These reactions involve using light to break chemical bonds in molecules dissolved in liquids. This class of reaction has been extensively studied experimentally, and investigations of the photodissociation of small molecules serve as a paradigm to understand the influence of the surrounding medium (and its dynamics) on the bond-breaking dynamics of a molecule. These studies are of fundamental importance because most chemical reactions occur in solution. Unfortunately, this class of reaction has been hard to simulate for the following reasons:

- 1) The liquid phase involves many degrees of freedom – typically requiring hundreds or thousands of atoms for a reasonable simulation cell.
- 2) Photodissociation reactions necessarily involve electronically excited species, ruling out the use of ground-state only quantum mechanical theories (*e.g.* density functional theory).
- 3) Electronic energy gaps are typically small enough for solvent or solute nuclear motions to induce population transfer between electronic states (radiationless transition) so that the adiabatic approximation is no longer valid, greatly increasing the complexity of solving SE.

Rather than follow the path of AIMD that treats all electrons on an equal footing, our approach has been to focus on the chemically most important electrons: those that make up the bond being broken (for now just two electrons, limiting the quantum mechanical problem to six dimensions), whilst treating all other particles as classical objects. This mixed quantum/classical approach drastically reduces the number of degrees of freedom that need to be treated at a high level and solves problem 1). To tackle problems 2) and 3), we have

focused on two-electron systems and developed a new algorithm by which we can *exactly* solve the time-independent SE (TISE). Our algorithm is right at the limit of computational feasibility, and help with improving the speed of the algorithm would provide a significant advance in the field of condensed-phase chemical dynamics.

Our algorithm works as follows:

Algorithm

The TISE for two electrons in an arbitrary potential reads:

$$(\hat{V} + \hat{T} + \hat{r}_{12}^{-1})\Psi(\vec{r}_1, \vec{r}_2) = E\Psi(\vec{r}_1, \vec{r}_2)$$

where \hat{V} is the external potential energy operator (due to the field of the classical particles) for both electrons, \hat{T} is the kinetic energy operator for both electrons and \hat{r}_{12}^{-1} is the electron-electron coulomb operator. Solving this equation yields energy eigenvalues, E , and six dimensional wavefunctions, $\Psi(\vec{r}_1, \vec{r}_2)$, for the two electrons.

The TISE is transformed into a matrix equation by discretizing the two electron wavefunction on a regular 6D real-space grid:

$$\Psi(\vec{r}_1, \vec{r}_2) = \sum_{i,j} c_{ij} g(\vec{r}_i) g(\vec{r}_j)$$

Where $g(\vec{r}_i)$ is a Dirac delta function at grid point position \vec{r}_i and without loss of generality we choose the wavefunction coefficients, c_{ij} , to be real valued.

Since we require only the lowest few eigenvalues of the matrix we use a subspace iterative matrix diagonalization algorithm based on the Jacobi-Davidson method described elsewhere [2]. An advantage of this method is that it requires computing only the action of the matrix on a vector so the full Hamiltonian matrix does not need to be stored (avoiding a memory bottleneck). Instead, the Hamiltonian matrix is broken into two pieces: the potential energy terms (which are diagonal in real-space) and the kinetic energy terms (which are diagonal in reciprocal space). Thus the Hamiltonian matrix is completely described by two diagonal matrices so that its operation on a vector involves simply multiplications in either real or reciprocal space. To transform vectors between real-space and reciprocal space we use six dimensional fast fourier transforms (FFT) using the FFTW package [3].

Bottlenecks

It is the diagonalization described above that provides the major computational bottleneck in our algorithm. The typical number of real-space grid points that we use is 16^6 , and after taking advantage of a symmetry, our algorithm involves finding the lowest few eigenvectors of a ~ 8 million by 8 million matrix at every timestep in our simulation! Despite this enormous size, we have achieved a timing of roughly two minutes per timestep on a single processor of the CNSI2 cluster when solving for just the lowest eigenvector. However, when solving for multiple excited states (which is where all the interesting chemistry takes place) the timings are less favorable: around 30 minutes per timestep for ten eigenvectors. We therefore would like assistance in speeding up the diagonalization by means of:

- a) Serial code improvements & optimizations – alternative diagonalization algorithms.
- b) Making use of matrix preconditioning techniques (which we are currently not using).
- c) Getting the diagonalization algorithm to use threads (which is built into the package).
- d) Reusing the subspace used to diagonalize the Hamiltonian from previous timesteps.

Objective:

We therefore have a single objective: to speed up the diagonalization routine sufficiently to allow the calculation of more excited states (10 minutes/timestep is acceptable) and/or allow the use of more grid points in the quantum basis (e.g. 20^6). If such a speed-up were achieved it would open an entirely new realm of the exact simulation of chemical bond dynamics in solution, marking a milestone in condensed-phase physical chemistry.

References

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