A Temperature-Dependent Hartree Approach for Excess Proton Transport in Hydrogen-Bonded Chains

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ABSTRACT

We develop a temperature-dependent Hartree (TeDH) approach to solving the $N$-dimensional Schrödinger equation, based on the time dependent Hartree (TDH) approximation, where the $N$-dimensional Schrödinger equation is approximated as $N$ one-dimensional equations with a time dependent Hamiltonian arising from the mean field potentials. The TeDH method uses the temperature-dependent analog of the TDH method to efficiently obtain the approximate ground state wavefunction. The TeDH is formulated with the goal of describing the dynamics of an excess proton in a hydrogen-bonded chain, as found in biological systems. A quantum description of all the protons involved in making and breaking hydrogen bonds of the chain must be used; hence the utility of a SCF approximation whose computational cost scales linearly with the number of quantum degrees of freedom. We show by comparison with numerically exact results that the TeDH scheme gives accurate ground state wavefunctions for chains with up to three protons. (Comparison with longer chains was not possible due to the computational requirements of numerically exact solutions). Sharing of a proton between flanking heavy atoms, as well as “split” protons, respectively corresponding to proton potential surfaces with one and two, symmetric wells are properly described by the TeDH method.
I. Introduction

The proteins and enzymes of photosynthesis and respiration have optimized structures that utilize energy gathered along a charge separating network to drive a proton pump, which results in a transmembrane chemical potential that provides the energy for the synthesis of complex biomolecules. A common theme in these exquisitely engineered systems is the possibility of rapid translocation of protons. One mechanism for proton translocation is via chains of hydrogen bonded waters, using a “proton wire” concept that has its origin in the Grotthuss mechanism. The speed is attributed to an excess proton “hopping” along the water chain by a series of making and breaking hydrogen bonds, which does not require the slow process of molecular diffusion. Membrane spanning water chains of varying lengths are found in a number of systems including bacteriorhodopsin and the photosynthetic reaction center of Rhodobacter sphaeroides. Internal waters in conjunction with titratable amino acid residues are thought to be responsible for proton uptake in cytochrome c oxidase.

In this paper we develop a methodology that should be capable of describing the real-time dynamics of proton translocation in hydrogen bonded chains. A problem that arises in characterizing a water chain with an excess proton, where the transport mechanism is the formation and breaking of hydrogen bonds throughout the chain, is the necessity for a quantum description of the protons that take part in the transport. For example, in the \( H_{11}O_5^+ \) chain shown in Fig. 1a, there are five protons that are involved in hydrogen bonds whose dynamics must be described quantum mechanically. (On a relatively short time scale, we may disregard the rotations of the chain that would involve the other protons.) The protons that are to be treated quantum mechanically will be referred to as the *active* protons. Furthermore, the heavy atom motion of the chain and the coupling to the surrounding medium that modifies the chain dynamics produces the
generic problem of a mixed quantum/classical treatment. As the number of quantum degrees of freedom increase, such mixed quantum/classical treatments become increasingly time consuming from a computational point of view. Thus efficient methods of handling the quantum part must be sought.

There are three main issues that need to be addressed in proton chain calculations: the construction of an appropriate potential energy surface, the incorporation of the quantum nature of the protons involved in the transport, that is noted above, and the influence of the medium in driving the proton transport. In principle, \textit{ab initio} calculations can provide the surface as a function of all the active proton’s coordinates, but as the chain becomes long this becomes a high-dimensional function that is 1) expensive to evaluate and 2) expensive to use once evaluated. A second problem that arises is how to deal with many quantum degrees of freedom in an efficient manner. It is this issue that is the focus of the work described in this article. Once the quantum properties of the chain parametric on the state of the other, heavy nuclear degrees of freedom can be handled, the task is to couple to the dynamics of these other degrees of freedom. This task can be handled by known methods based on propagating molecular dynamics with forces from the quantum degrees of freedom obtained with use of the Hellmann-Feynman theorem.

A great number of approaches to mixed quantum/classical of treatments of single proton transfer reactions have appeared.\textsuperscript{16-38} For multiple proton transfers, there are Feynman path integral-based methods that are limited to equilibrium properties and use transition state theory to obtain dynamical information,\textsuperscript{18,31-33,39-42} or use centroid molecular dynamics to probe dynamics.\textsuperscript{43-46} Another general approach when there are multiple quantum degrees of freedom coupled to classical degrees of freedom relies on SCF and multi-configuration SCF methods to characterize real time dynamics.\textsuperscript{47-63}
Closest in spirit yet distinct from the work presented herein are the simulations of proton chains by Pomès and Roux\textsuperscript{41,64} and Hammes-Schiffer and co-workers.\textsuperscript{23,24,65-67} Both these works used the PM6 effective potential model\textsuperscript{68,69} to describe a water chain with an excess proton. The PM6 model is based on H\textsuperscript{+} and O\textsuperscript{2-} ions, and permits dissociation of water molecules into ionic fragments. Pomès and Roux use discretized path integral simulations to treat protonated water chains of various lengths. The nature of the single-proton wavefunctions reflecting the quantized proton as a function of chain configuration was studied. In particular, they investigated the potential role of oxygen-oxygen distance fluctuations in providing a proton transport mechanism. While suggestive, these path integral simulations can not directly probe real time dynamics. Hammes-Schiffer and co-workers have developed MC-SCF methods to treat the real time dynamics of proton chains. They have studied up to a protonated water tetramer (three active protons).\textsuperscript{66} An advantage of their method is its ability to treat nonadiabatic transitions as implemented by surface hopping algorithms.\textsuperscript{21,22} The effects of a surrounding medium were modeled by use of an external electric field.\textsuperscript{67} This approach shows great promise but it is computationally intensive, especially if longer proton chains are of interest, and explicit medium effects are to be incorporated.

Another approach that has been applied to bulk water\textsuperscript{70,71}, protonated water\textsuperscript{72,73}, ion channels\textsuperscript{74} and model proton wires\textsuperscript{75} is \textit{ab initio} (Carr - Parrinello)\textsuperscript{76} molecular dynamics (CPMD). In the CPMD method the electronic structure is obtained “on the fly” by the density functional theory (DFT) method, parametric on the nuclear degrees of freedom. The forces required to advance the nuclear degrees of freedom are obtained with use of the Hellmann-Feynman theorem. The electronic structure and nuclear dynamics are obtained by MD with the electronic orbitals following a fictitious adiabatic “dynamics”. A great advantage of the method is
the evaluation of the electronic structure “on the fly” in contrast to other methods that require first
the evaluation of a potential energy surface and, subsequently, its use. However, consequently, the
time step required in the CPMD method is dictated by the electronic degrees of freedom, making it
computationally intensive. To incorporate nuclear quantum effects from e.g. protons\textsuperscript{75} the nuclei
can be quantized with use of the Feynman path integral method\textsuperscript{77}, (a PI-CPMD method). To the
extent that DFT methods give an accurate description of an excess proton in a chain of hydrogen
bonded water molecules, the method should be the most accurate of those noted. Predictions of
the DFT method have been compared with experimental data for small protonated clusters.\textsuperscript{71,78}
The PI-CPMD method is limited to equilibrium properties and is computationally demanding.

The approach we shall develop is predicated on the assumption that the active protons are
always in their ground state configuration, as contributions from excited states to the dynamics of
the chain may be neglected. The reasoning is illustrated in Fig. 2. If we construct an active
proton’s potential energy surface for a fixed oxygen-oxygen distance $r_{OO}$ then, if $r_{OO}$ is large,
there will be a double well potential surface with a large barrier (cf. Fig. 2a). If the double well is
(instantaneously) symmetric, a proton on the “left” side can tunnel through the barrier to become
right localized. A coupling to solvent fluctuations is required to stabilize the so-obtained right-
localized state; otherwise, only delocalized states would exist. Tunneling of this kind is a slow
process as it requires fluctuations to provide a symmetrized surface (an activation energy factor)
and once symmetrized the tunnel matrix element will be extremely small for a large barrier.\textsuperscript{79} For
most configurations of the solvent, the proton potential surface will be quite asymmetric, as in Fig.
2b, the levels will be far apart, and only the ground state will be required for the dynamics. When
the $r_{OO}$ distance is smaller, then tunnel doublet states do not exist when the potential is symmetric
as the lowest state may be above the barrier (Fig. 2c) and, if not, the energy difference between the
two lowest levels will still be much larger than $k_B T$. Most of the time the potential surface will not be symmetric (Fig. 2d). For the situations schematized in Figs. 2b-2d: 1) the transfer of the proton from left to right can be very fast and 2) it will be a ground-state process because the excited states are much further than $k_B T$ above the ground state. Note that the time scale is set by the chain’s heavy atom and the medium’s fluctuations for the ground state proton dynamics, according to the Born-Oppenheimer principle. Thus, when $r_{OO}$ is large, if tunneling does occur the proton dynamics is slow and when $r_{OO}$ is small the transport can be fast. These shorter distances will dominate the overall dynamics, and the calculation can be approached by a ground state (adiabatic) approach. We note that ground state dominance has been found in the simulations of Pomes and Roux\textsuperscript{64} and Hammes-Schiffer and co-workers\textsuperscript{66}.

With this assumption we can adapt an adiabatic simulation method (ASM) that was used to discuss the properties of an excess electron in liquids\textsuperscript{80-84} to describe proton chains. The active protons are quantum objects whose state, using the Born-Oppenheimer separation, is parametric on the nuclear configuration of the rest of the proton chain and the surrounding medium. For a given nuclear configuration, the time dependent Schrödinger equation could be solved for the active protons’ ground state wavefunction. While it is certainly possible do so, from previous ASM work on electron localization in fluids problems it is known that solution of the Schrödinger equation in imaginary time ($t \to -i \beta \hbar$) can be used to obtain ground states reliably and efficiently\textsuperscript{80-84}. The wavefunction can be represented on a spatial grid and propagated by using fast Fourier transform methods\textsuperscript{85-88}. This procedure avoids the use of basis set representations and matrix diagonalization methods. The nuclear configuration is then updated by e.g. Molecular Dynamics (MD), where the time scale for the MD step is the nuclear time scale. The forces for the MD step are obtained from the sum of the classical medium/heavy-atom chain potential energy and the
quantum force that the active protons exert on the nuclear degrees of freedom. The above procedure is iterated for a sufficient MD time interval to extract the desired information.

To apply the ASM method to a proton chain is straightforward in principle, granting the assumed ground state dominance, but daunting in practice. A chain with $N$ quantum protons would require a $(\text{number of basis functions})^N$ calculation. Clearly, this is computationally demanding. From the formative years of quantum mechanics\textsuperscript{89} to the present\textsuperscript{47-63,90,91}, schemes under the general rubric of self-consistent field (SCF) approximations have been proposed to turn this difficult scaling with $N$ into a $N^\#(\text{number of basis functions})$ problem. These schemes write the overall wavefunction as a product wavefunction and differences among the methods provide different optimizations of the product form. Central to these approaches is the construction of an approximate Hamiltonian that incorporates the expectation values of parts of the Hamiltonian. The Hamiltonian then depends on the wavefunction; hence, the requirement for an SCF solution. One class of such schemes is the time dependent Hartree (TDH) approximation.\textsuperscript{92,93} We shall formulate a version of this method that we will refer to as a temperature-dependent Hartree (TeDH) approximation.

A goal of our approach to proton chains is to base the description of the active protons and their framework on the results of \textit{ab initio} (or other) quantum chemical calculations. While current information is limited regarding \textit{ab initio} results\textsuperscript{94}, as advances in algorithms and computational power progress, the advantage of a formulation based on potentials is that it should still apply without modification to more refined potentials. A intrinsic problem with potential energy based methods is the range of correlation in the proton chain. The potential surface then is an $N$ dimensional surface for $N$ active protons, for a fixed heavy-atom framework. Cooperative effects are important for extended hydrogen-bonded assemblies. However, most of the correlation should
be contained in a finite range of interaction. For example, in an *ab initio* study of water chains with up to seven waters, and clusters, contributions from one, two and three-body terms are required to capture essentially the total interaction energy. Non-additive three body contributions are required to provide accurate potentials for molecular dynamics simulations of liquid water. Developments of many-body potentials directed toward excess proton transport in water include valence bond force fields. For water clusters with an excess proton, it is not clear whether higher than three body terms will be required, as comparison with high-level *ab initio* data is only feasible for small clusters. Our initial focus is on extended hydrogen bonded chains, as opposed to protonated water. Extended chains should be less demanding with regard to the potential energy surface’s correlations than water with an excess proton. Therefore, for the purposes of this investigation, we formulate the Hamiltonian appropriate to *N* active protons with a sum of one, two and three particle contributions, and work out the corresponding TeDH equations of motion. It is straightforward both analytically and computationally to extend the method to higher order correlations, though it should be noted that both the parametrization of the potential surface and its computational expense may become problematic.

The focus of this paper is the validation of the TeDH method. As it is a new method, we provide a careful exploration of its validity, and of its practicality as an algorithm for long proton chains. Specific applications are deferred to future work. The plan of the remainder of this paper follows: In Sec. II, the TeDH approximation is formulated and we introduce a solution method based on the symmetric split operator propagation scheme. We show that the method can be extended to apply to the TeDH equations where the Hamiltonian is now a temperature-dependent operator. In Sec. III, we show that the TeDH equations do provide an accurate solution of the many active proton problem. We do so by comparison of the TeDH solutions with an exactly
soluble two degree of freedom problem. We shall also compare the TeDH solutions with those obtained by explicit two and three-dimensional solutions for model two and three active proton chains whose potential function for the two active proton chain is a fit to \textit{ab initio} derived data.

Section IV presents our concluding remarks.

II. A Temperature-Dependent Hartree (TeDH) approximation

A rationale for why a TDH or TeDH scheme should be reasonable for the proton chain application can be stated in general terms.\textsuperscript{91} Consider for simplicity but without loss of generality two quantum protons. If the wavefunctions $\psi_{i}^{bg} (i=1,2)$ of the protons are localized initially between their respective flanking groups, and if over some time interval they remain localized, then a semiclassical approximation is warranted. The bonding of the protons will of course prevent the protons from delocalizing away from their respective flanking groups. Then, the potential felt by e.g. proton one is very nearly the potential due to a classical particle with position $x_{2}^{bg}$ interacting with proton one via the potential $V_{c_{1},x_{2}}^{bgch}$. Since $\psi_{2}^{bg} \approx \psi_{1}^{bg}$ will be a good approximation the more classical the particles, and the protons are well-localized between their flanking groups, they are reasonably suited to a SCF scheme that uses mean field potentials, $V_{c_{1},x_{2}}^{bgch}$.

The time dependent Schrödinger equation with the replacement $t \rightarrow -i\beta\hbar$ is

$$-\frac{\partial \Psi}{\partial \beta} = H \Psi, \quad (2.1a)$$

where $H = H_{0} + V$, with

$$H_{0} = \sum_{i} a_{i} V_{i} b_{g} b_{g} + \sum_{i} H_{i} b_{g}$$

and
We have decomposed the total potential for the degrees of freedom that we shall treat quantum mechanically (the “active” protons) in terms of one, two and three body contributions. As noted in the Introduction, this decomposition should be sufficient to approximately characterize \textit{ab initio} based potential surfaces for the active protons. If a greater range of correlation is required, appropriate terms may be added on to the decomposition of Eq. (2.1c). The errors of the approach then will be controlled by the ability to fit these potential surfaces to suitably parametrized functions and, of course, limited by the accuracy of the TeDH methodology.

The temperature-dependent Hartree equations of motion are obtained by writing \( \Psi = \prod_i \Psi_i \), and multiplying the Schrödinger equation by \( \Pi \psi \beta \) to obtain (we use real wavefunctions throughout, as appropriate to the solution of Eq. (2.1))

\[
-\partial_t \psi_{i,\beta} = e_{\beta} \mu_{\beta} \epsilon_{\beta} \psi_{i,\beta} \tag{2.2}
\]

The terms on the right hand side of Eq. (2.2) have the following meanings: The one body contributions to Eq. (2.2) pass through unchanged from Eq. (2.1b) of course. Let us define \( \beta \) dependent normalization constants \( N_i^2_{\beta} \) that will be important to the proper formulation of a TeDH approximation, along with energies \( \epsilon_{i,\beta} \) and \( \gamma_{i,\beta} \), and the convenient definitions of \( \mu_{i,\beta} \) and \( \mu^i_{\beta} \):
The two and three body potentials contribute a term \( \langle V_i \rangle_{bg} \) that is defined by the expectation values

\[
\langle V_i \rangle_{bg} = \sum_{j \neq i} \sum_{k \neq i < \ell \neq i} \langle V_{jk} \rangle_{bg} + \sum_{j \neq i} \sum_{k \neq i < \ell \neq i} \langle V_{jk\ell} \rangle_{bg}
\]

(2.4)

The last term is the temperature and coordinate dependent one:

\[
\bar{V}_i \beta g = \sum_{j \neq i} \bar{V}_{i,j} \beta g + \sum_{j \neq i} \bar{V}_{i,j,k} \beta g
\]

(2.5a)

where

\[
\bar{V}_{i,j} \beta g = \int \psi_j \psi_{j,k} \beta \psi_{j,k} \psi_{j,k} \beta \psi_{j,k} \psi_{j,k} \beta / N_j^2 N_k^2
\]

\[
\bar{V}_{i,j,k} \beta g = \int \psi_j \psi_{j,k} \beta \psi_{j,k} \psi_{j,k} \beta \psi_{j,k} \psi_{j,k} \beta \psi_{j,k} \psi_{j,k} \beta / N_j^2 N_k^2 N_{j,k}^2
\]

(2.5b)

An interesting identity can be obtained by multiplying Eq. (2.2) by \( \psi_i \) and integrating over \( x_i \):

\[
\sum_{i} ^b g + \gamma_i g - \sum_{i} \langle V_i \rangle_{i} \equiv -\langle V \rangle.
\]

(2.6)

For the purposes of the TeDH, we have not found this identity to be particularly useful, as is the case for the analogous one in the time-dependent Hartree theory. Now define
Then, Eq. (2.2) may be written as
\[ \frac{\partial \phi_{i,\beta}}{\partial \beta} = H^{i}_{\beta} \phi_{i,\beta} + \psi_{i,\beta} \]  
(2.8)

and
\[ \Psi = e^{i} \sum_{i} \prod_{i} \phi_{i,\beta} \]  
(2.9)

The right-hand side of Eq. (2.9) is the TeDH approximation to \( \Psi \). The wavefunctions \( \phi_{i,\beta} \) obtained from Eq. (2.7) are sufficient to construct \( \Psi \), as we will always normalize the wavefunction. This means that, at each step in the quench (the solution of Eq. (2.8) as an initial value problem starting from \( \beta = 0 \) and terminating at some sufficiently large \( \beta \) value), the quantities
\[ \bar{V}_{i,j} = \int d\psi_{j,\beta} \bar{V}_{ij} d\psi_{j,\beta} \beta / N_{j}^{2} \equiv \int d\psi_{j,\beta} \bar{V}_{ij} d\psi_{j,\beta} \beta \]  
(2.10a)
and
\[ \bar{V}_{i,j,k} = \int d\psi_{k,\beta} \bar{V}_{ijk} d\psi_{k,\beta} \beta / N_{k}^{2} \]  
(2.10b)
are to be evaluated, where \( \bar{\psi}_{j,\beta} \) denotes the normalized version of \( \psi_{j,\beta} \). Since \( \psi_{j,\beta} \) and \( \phi_{j,\beta} \) differ by just a \( \beta \)-dependent quantity according to Eq. (2.7), normalization ensures that we only need to solve the \( \phi_{i,\beta} \) equations of Eq. (2.8). The solutions of the \( \beta \)-Schrödinger equation lead to real wavefunctions, assuming a real initial \( \beta = 0 \) trial wavefunction.

The formal solution of Eq. (2.1) using a basis set \( \{ e_{n}^{N}(x) \} \) is
\[
\psi^{N,\beta} = \sum_{n=0} a_n e^{-\beta E_n} \phi_n \psi^N
\]

(2.11)

and, for \( \beta b_1 - E_0 g > 1 \),

\[
\psi^{N,\beta} = a_0 e^{-\beta E_0} \phi_0 \psi^N
\]

(2.12)

The normalized ground-state wavefunction, \( \overline{\phi}_0 \psi^N \), then is obtained by normalizing the numerically-obtained \( \psi^{N,\beta} \) in Eq. (2.12). The method we use to solve the Schrödinger equation is based on the symmetrically split operator fast Fourier transform (FFT) technique developed by Feit, Fleck and Steiger. Using this method, the solution of Eq. (2.1) proceeds by propagating the Hamiltonian over some small \( \Delta \beta \) step and accumulating enough steps to ensure \( \beta b_1 - E_0 g > 1 \). A more efficient procedure that we shall refer to as a “decimation” quench, starts with a relatively large \( \Delta \beta \) and tests convergence of the energy (the expectation value of \( H \)) to some tolerance. Then, \( \Delta \beta \) is halved and the same procedure of quenching and energy convergence is iterated until \( \Delta \beta \) is less than some small quantity.

Applying an analogous method to the TeDH-approximated equations in Eq. (2.8) requires some development. Since wavefunctions contribute to the Hamiltonian via the \( \mathcal{V}_{xbg} \), \( \beta bg \) terms, a propagation algorithm that accounts for a \( \beta \)-dependent Hamiltonian has to be used. The formal solution of Eq. (2.8) involves a \( \beta \)-ordered exponential operator as \( [\hat{H},\beta_1,\beta_2] \neq 0 \) for \( \beta_1 \neq \beta_2 \). Of concern too is the order of the error term of the method. The symmetric split operator method for a \( \beta \)-independent Hamiltonian is accurate to \( O(\Delta \beta)^3 \). In Appendix A we show that for a Hamiltonian \( \hat{H} \), \( \beta \in \hat{T} \mathcal{V} \), \( \mathcal{V}_{xbg} \), \( \beta bg \) the one-step propagator:

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\[
\psi = \beta_0 + \Delta \beta \gamma \left( e^{-\hat{H}(x, \beta_0) \Delta \beta} \right) \psi \beta_0 \gamma \\
\approx e^{-\hat{T}_x \Delta \beta/2} - c_{bg} \beta \gamma \left( e^{-\hat{T}_x \Delta \beta/2} \right) \psi \beta_0 \gamma \left( \Delta \beta \right)^3
\]

has, as indicated, the same order of error as the usual method. Therefore, in principal, application of a quench method of solution to the TeDH equations should also be an efficient method of solution of Eq. (2.8).

The issue arises of how to carry out the quench with regard to the convergence to the ground state. There no longer is a formal eigenvalue-eigenvector decomposition as in Eq. (2.11) for the $\beta$-dependent Hamiltonian to provide guidance. The situation is similar to “SCF” problems that are solved with a basis set by using a trial wavefunction where matrix elements of the Hamiltonian depend on the wavefunction. There, iteration between the trial wavefunction and the Schrödinger equation is carried out until convergence is achieved. We will apply the quench method as described above and use Eq. (2.13) for the propagation. The solutions of Eq. (2.8) for all the degrees of freedom are simultaneously advanced over a $\Delta \beta$ interval as all the wavefunctions are required to construct the $V_{ij}$, $\beta g$. A choice must be made regarding an “energy” test. The simplest procedure is to use the total (sum over all degrees of freedom) expectation value of the Hamiltonian. To summarize, we solve the TeDH equations of Eq. (2.8) using repeated application of the propagator in Eq. (2.13) with use of the decimation quench method based on the expectation value of the Hamiltonian. As shown in the next Section, using this method leads to reliable results.

III. TeDH procedure validation

The accuracy of the TeDH method can be assessed by comparison either with analytic solutions or numerically exact solutions for the wavefunctions arising from two (or higher) dimensional Hamiltonians. In this section we first consider a quadratic form Hamiltonian where
analytic solution is possible, and then consider a realistic model of a proton chain, to compare with the TeDH generated solutions. For the numerically exact solution of a two and three dimensional Hamiltonian we use a “conventional” quench method. That is, the two (three) dimensional Schrödinger equation is solved using the same Fourier transform methodology as in the TeDH discussed in Section II using of course a 2D (3D) Fourier transform. The overhead associated with constructing the $\beta$-dependent potential energies $V_{\beta}^{x_{ii}}, \beta_{bg}$ at each step in the quench is gone of course, but it is certainly true that the TeDH is much faster than the numerically exact two and three dimensional calculations. We could detect no difference in quench efficiency between using the split operator method with the $\beta$-dependent Hamiltonian required in the TeDH solution versus the split operator method for a $\beta$-independent Hamiltonian. This indicates the correctness of the argument made in Appendix A showing that the split operator method’s error term is not increased by having to deal with a $\beta$-dependent Hamiltonian.

A. A Harmonic Model

An exactly soluble model that will illustrate the accuracy of the TeDH method for obtaining the ground state wavefunction is readily constructed from a quadratic form Hamiltonian with potential energy

$$V = \frac{1}{2} k \delta x_1^2 + \frac{1}{2} k \delta x_2^2 - ax_1 x_2$$

where $\delta x_i = x_i - x_i^e$ ($i=1,2$), $k$ is a force constant for the uncoupled system and $a$ a coupling strength. For symmetry, choose $x_2^e = -x_1^e = x^e$ with $x^e > 0$, denoting equilibrium positions of the uncoupled system. The coupled system equilibrium positions $x_{1,2}^n$ are

$$x_{1,2}^n = \pm \frac{1}{1 + a} x^e,$$
and we define the equilibrium shifts induced by the coupling $a$ as $\delta x'_{1,2} = x'_{1,2} - x''_{1,2}$:

$$\delta x'_{1,2} = \pm \frac{a}{1 + a} x''$$  \hspace{1cm} (3.2b)

Using the dimensionless coordinates $X = \frac{1}{\sqrt{2}} h + x_2 g$, $x = \frac{1}{\sqrt{2}} b - x_1 g$ where $x_{1,2} \rightarrow x_{1,2} / \ell$

with $\ell = \sqrt{\hbar/m\omega}$, the Hamiltonian is

$$H = \frac{d^2}{dx^2} + \frac{d^2}{dX^2} + \frac{1}{2} b \cdot g + \frac{1}{2} (1 - a) \cdot g$$  \hspace{1cm} (3.3)

The solution in terms of the coordinates $\delta x'_{i,n} = x_i - x''_{i}$ ($i=1,2$) is

$$\psi_{\delta x'_{1,n}, \delta x'_{2,n}} \cdot \frac{\pi^2}{\sqrt{1 + a \sqrt{1 - a}}} \cdot e^{-\frac{1}{4} \frac{1}{2} \left( \frac{\sqrt{1 + a} + \sqrt{1 - a}}{2} \right) \delta x'^2_{1,n} + \delta x'^2_{2,n}} \cdot e^{-\frac{1}{2} \left( \frac{\sqrt{1 - a} - \sqrt{1 + a}}{2} \right) \delta x'^2_{1,n} \delta x'^2_{2,n}}$$  \hspace{1cm} (3.4)

The correlation between the degrees of freedom appears in the last exponentiated term. A TeDH approach cannot capture this correlation. However, if we are interested in the wavefunctions $\psi_{\delta x'_{1,n}}$ and $\psi_{\delta x'_{2,n}}$ then what must be captured by the TeDH approximation is the shift in the position of the wavefunctions $\psi_{\delta x'_{1,n}}$ and $\psi_{\delta x'_{2,n}}$ arising from the coupling term, $a$.

The wavefunctions $\psi_{\delta x'_{1,n}}$ and $\psi_{\delta x'_{2,n}}$ were obtained using the TeDH method, as explained in Section II, and compared with the exact solution $\psi_{\delta x'_{1,n}}$ obtained by numerical integration of Eq. (3.4). (By symmetry, the two wavefunctions are identical, so we need only examine one of them.) In Fig. 3 we display the results of this comparison. Clearly, the TeDH method does an excellent job of capturing the shift in the wavefunction induced by the coupling.

Note that a value of $a = 0.5$ is a rather large coupling, yet the method still yields excellent results. Unfortunately, the expression for the wavefunction $\psi_{\delta x'_{1,n}}$ obtained by integration of Eq. (3.4)
over \( x_2 \) is too complicated to be revealing. However, examination of the behavior of the integral over coordinate \( x_2 \) of the second exponential term, relative to the factor 
\[
\exp \left[ \frac{1}{4} \right] + a + \sqrt{1 - a} i \int_{-\infty}^{\infty} \frac{dx}{4J} \]
obtained by \( x_2 \) integration of the first term, shows that the first term is dominant. Thus, it is not a surprise that the TeDH procedure will be accurate for this model Hamiltonian.

**B. A model proton chain**

In this subsection we summarize some known potential energy surfaces appropriate to proton chains. The coordinate system we adopt for the proton chain is shown in Fig. 1. The \( i \)th active proton’s coordinate \( r_{iH} \) is referenced to the \( i \)th oxygen on its “left”, as this permits ready expression of the notion that an excess proton is injected from the left side of a membrane and will exit from the other, “right”, side of the membrane. Oxygen-Oxygen distances are denoted as \( r_{i,i+1} \) where \( i = 1 \) denotes the left-most oxygen in the chain. When a specific oxygen pair, such as the one-two pair, is designated, we refer to its distance as \( r_{12} \). Referencing the active proton distances as defined above will let us plot the respective wavefunctions on a common axis, as each proton’s origin is on its left-side oxygen.

We start with \( H_2O^+ \), a “chain” with one active proton. Scheiner has fit the results of \textit{ab-initio} calculations of the active proton potential energy surface, parametric on the oxygen-oxygen distance \( r_{12} \), to various functional forms.\textsuperscript{101,102} A Morse-based representation that works well is

\[
V_{1H} = -D \left[ e^{-\alpha (r_{1H} - r_{He})} + e^{-\alpha (r_{1H} - r_{He})} + 2e^{-\alpha (r_{He} - r_{12})} \right] \tag{3.5}
\]

where the last term serves to set the zero of energy of \( V_{1H} \) at the minimum-energy point(s) for the proton surface. The characteristic features of many hydrogen-bonded interfaces are found for this
water cation; namely, a double-well form of the proton potential for larger \( r_{12} \) values, with a large barrier that rapidly drops as \( r_{12} \) decreases yielding a single minimum potential surface for sufficiently short \( r_{12} \). The Morse parameters of the potential are given in Table 1. For a chain \( \text{H}_2\text{O}_3^+ \) with two active protons, \textit{ab-initio} calculations were fit to the form

\[
V_{TOT} = V_{1H} c_{1H} r_{12}^2 + V_{2H} c_{2H} r_{23}^2 + V_{12} c_{1H} c_{2H} r_{12} r_{23} + V_{12} c_{1H} c_{2H} r_{12}^2 r_{23}^2 \tag{3.6}
\]

where

\[
V_{12} = -k (1 + b_1 - r_{1He} - r_{2He}) \tag{3.7}
\]

This expression is the result of a fit with \( \eta_2 = \eta_{23} \); thus the lack of an explicit dependence on \( r_{23} \) in Eq. (3.7). The value of the interaction constant \( k \) is given in Table 1.

A contour plot of this \( V_{TOT} \) is shown in Fig. 4. The oxygen distances, \( r_{12} = r_{23} = 2.7 \) Å, provide double minimum potential surfaces in the \( r_{1H} \) and \( r_{2H} \) coordinate directions, with barrier heights around 5 kcal/mol. The absolute minimum corresponds to proton 1 having transferred and proton 2 at its initial state, assuming that both protons were initially “left” localized. The other two minima are of equal energy and are about 1.1 kcal/mol higher in energy than the true minimum. The interaction term, \( V_{12} \), strongly disfavors the doubly-charged state where \( r_{1H} \approx 1.0 \) Å and \( r_{2H} \approx 1.7 \) Å, in accord with chemical principles. The harmonic proton frequency, \( \omega_{1H} \), based on expanding, e. g., \( V_{1H} c_{1H} r_{12}^2 \) around \( r_{1He} \) is \( \omega_{1H} \approx 3,000 \) cm\(^{-1} \), implying a zero point energy around 5 kcal/mol. In this situation, the solvation coming from the environment can provide a path for proton motion, where the first proton can transfer and then the second may transfer. As will be shown below, the protons are both localized around the absolute minimum for this potential surface. When the oxygen-oxygen distances are reduced to \( r_{12} = r_{23} = 2.4 \) Å, the potential surface
exhibits a single minimum, with no subsidiary minima as shown in Fig. 5. The one-dimensional surfaces $V_{1H}$ and $V_{2H}$ also only have one minimum in accord with the short oxygen-oxygen distance. Again, the doubly charged state is strongly disfavored by the $V_{12}$ term.

The above potential energy formulation can be applied to chains with more than two protons, by returning to the pair and triplet decomposition of the potential introduced in Eq. (2.1c). For the purposes of this work, we shall use just the pair terms, as the \textit{ab-initio} data has only been obtained for chains with two active protons. Of course, as more refined potential data becomes available, it will be straightforward to incorporate such three-proton correlations into the formalism.

\textbf{C Validation of the TeDH approximation on the two proton chain.}

We shall consider three $r_{12} = r_{23}$ distances to illustrate the accuracy and potential difficulties of the TeDH method. First, for $r_{12} = r_{23} = 3.0$ Å a caution can be found. The two dimensional potential surface is shown in Fig. 6. The large barriers (25 kcal/mol) along the $r_{1H}$ and $r_{2H}$ directions suggest that the initial condition of the quench method for the TeDH is crucial, as with this approximation it may not be possible to find the correct ground state of the system with a poor initial choice. If the wavefunction is “trapped” in a local minimum, it may not be able to tunnel out through a large barrier and find the true ground state. For a two dimensional surface it is not clear from the shape of the surface where the ground state is when the minima are rather close in energy. So, we first find the ground state by using the numerically exact two dimensional split operator quench method applied directly to the two dimensional Hamiltonian with potential given in Eqs. (3.5-3.7). The results as a function of the initial wavefunction choice are displayed in Table 2.
All the initial wavefunctions for both protons are Gaussians; oscillator ground states with widths appropriate to a harmonic oscillator with frequency chosen as the local well frequency. The initial quench step is $\Delta \beta = 0.1$, the energy convergence condition is set to 0.0001 and $\Delta \beta$ is halved until $\Delta \beta < 0.01$. (These quantities are in dimensionless internal units of $\hbar \omega_{1H} / 2$ where 1 unit $\sim 5$ kcal/mol). The notation for the wavefunctions is shown in Fig. 1b, except for the designation $|SH_1 \rangle |SH_2 \rangle$. Here, the origin of each oscillator wavefunction is chosen half-way between the two equilibrium positions of the protons. This ensures a much better chance of converging to the correct ground state. Indeed, the energies show that the $|RH_1 \rangle |LH_2 \rangle$ state is the ground state, even though the surface around the $|LH_1 \rangle |LH_2 \rangle$ and $|RH_1 \rangle |RH_2 \rangle$ minima are lower in energy by about 0.88 kcal/mol than around $|RH_1 \rangle |LH_2 \rangle$. (The units of energy in the table are internal units and the 0.127 energy difference is around 0.6 kcal/mol.) Thus, the energies are quite close when measured against the barrier height of 25 kcal/mol. For the initial state $|LH_1 \rangle |LH_2 \rangle$ of the quench where both protons are on the left, the final state in the 2D quench is predicted to be on the left. Thus, for this difficult case of a very large barrier and two close-to-degenerate states, a poor choice of initial wavefunction can miss the ground state. Starting on the correct side with $|RH_1 \rangle |LH_2 \rangle$ verifies the correctness of the ground state assignment. Note that when the correct ground state is found, irrespective of the initial wavefunction, the energy is very consistently predicted. The number of iterations in the decimation quenches show that starting with a poorer guess requires a greater number of iterations. In particular, the initial state designated as $|L'H_1 \rangle |LH_2 \rangle$, which indicates that we have shifted the origin of the wavefunction of proton 1 over by about 0.1 Å toward the right, converges to the correct ground state but requires a large number of quench steps.
Turning now to the TeDH results, it is gratifying that they are in accord with the 2D results with the exception of the just-noted $|L'H_1\rangle|LH_2\rangle$ case. Here, the TeDH does not obtain the correct ground state. We also tried broader initial wavefunctions, centered around the same positions as used in constructing Table 2 to see if they would give correct results. The wavefunctions to accomplish this have to be so broad that they are essentially flat. Nevertheless, as the choice of initial wavefunction is under our control, it is always the case that the TeDH will give the same result as the numerically exact 2D method. We do not display the wavefunctions but just note that the 2D and TeDH ones are coincident for the correct ground state. (Wavefunctions for more realistic $r_{ij}s$ are displayed below.) It is important to note that while we report an “energy” in the TeDH method, it is not an energy in the sense of an eigenstate. The TeDH (and TDH) methods cannot give eigenstate energies.

The oxygen-oxygen distances of 3.0 Å are much too large to be major contributors to proton chains, at least if fast transport is anticipated. A more representative distance is $r_{12} = r_{23} = 2.7$ Å. The protons’ potential surface is displayed in Fig. 4. The surface around $|RH_1\rangle|LH_2\rangle$ now is lower in energy by about 1 kcal/mol than around $|LH_1\rangle|LH_2\rangle$ and $|RH_1\rangle|RH_2\rangle$. The barriers between the one dimensional proton paths are about 5 kcal/mol. Note that the local oscillator frequency around the various minima corresponds to an energy around 5 kcal/mol. Thus, these barriers are of the same order as the sum of the zero point energies of the two protons. Again, it is not evident from the potential surface where the ground state is. Table 3 summarizes the results of the 2D and TeDH quenches. The ground state is at $|RH_1\rangle|LH_2\rangle$. The 2D results show that for this more forgiving case all the initial wavefunctions we examined go to the correct ground state. The initial wavefunction denoted as $|L'H_1\rangle|LH_2\rangle$ ($|L''H_1\rangle|LH_2\rangle$) shifts the origin
of proton one’s wavefunction 0.1 Å to the right (left) relative to the \(|LH_1\rangle\langle LH_2|\) initial choice. The TeDH quench is not correct for the initial choices \(|LH_1\rangle\langle LH_2|\) and \(|L''H_1\rangle\langle LH_2|\), but moving the origin of proton one 0.1 Å to the right (the \(|L'H_1\rangle\langle LH_2|\) initial wavefunction) corrects this. Furthermore, if we slightly broaden the initial wavefunction from its harmonic oscillator width, in units scaled by the length \(\ell = \sqrt{\hbar/m\omega}\), \(\psi_{1bg} \approx \exp(-x^2/2j)\), to \(\psi_{1bg} \exp(-0.8x^2/2j)\), then the TeDH again predicts the correct ground state.

The individual proton probabilities are displayed in Fig. 7. As the probabilities will be used in evaluating the quantum forces for the MD evolution, it is important that the TeDH represent them accurately, and it does. The probabilities displayed in Fig. 7 have much more weight toward the centers than the extremities of the surfaces. Therefore, as the exploration of different initial wavefunctions in Table 3 and our observation about using slightly wider initial choices indicates, the TeDH method should be capable of yielding the correct ground state when the wavefunctions from a previous MD configuration are used as the initial wavefunctions for the current configuration’s quench.

When the oxygen-oxygen distances are short, e.g. \(r_{12} = r_{23} = 2.4\) Å, single well surfaces are obtained. The surface displayed in Fig. 5 shows that now there is only one minimum, in accord with the single proton coordinate potential surfaces. Starting from initial states \(|SH_1\rangle\langle SH_2|\) or \(|LH_1\rangle\langle LH_2|\) for both 2D and TeDH methods lead to the same ground state. Both protons are shared between their respective flanking groups. For these short oxygen-oxygen distances where the ground state is unambiguous, any reasonable initial wavefunction will converge to the correct one, for both 2D and TeDH methods.
In the examples above, the oxygen-oxygen distances were set equal, since these symmetric cases are the most demanding of the TeDH method. Naturally, proton chains with their heavy atom vibrational motion and coupling to a medium will not often have equal oxygen-oxygen distances. We have explored a number of cases where the \( r_{12} \) and \( r_{23} \) distances range from 2.4 to 2.7 Å and find that in these asymmetric situations the TeDH method gives essentially the exact results starting from the same initial wavefunctions as used for the exact quench method.

D Validation of the TeDH approximation on the three proton chain.

The potential surface for a three active proton chain with the assumption of only pair order terms in the potential is given by the first sum in Eq. (2.1c). We stress that the use of only pair order terms is a consequence of the available potential surface; it is not a limitation of the TeDH method. Note that the relative CPU time between the 3D and the TeDH methods is about a factor of 1200 when 64 points are used for the FFT grid. Even for a 3 proton chain, the numerically exact 3D method would not be feasible in the context of an MD simulation where the quench would have to be carried out for several thousand MD steps.

A new feature does arise in a three proton chain that is not present for a two proton chain. Examination of the potential surface for \( r_{1H} = r_{12} - b_{He} - s \) and \( r_{3H} = r_{3He} + s \) as a function of \( r_{2H} \) yields a symmetric double well for proton two. This is evident from the symmetry of the chain when all oxygen-oxygen distances are the same; for a symmetric arrangement of protons one and three relative to the chain’s bisector, proton two will experience a symmetric potential. Indeed, using the above symmetry related coordinates for \( r_{1H} \) and \( r_{3H} \),

\[
V_{12} + V_{23} = -k_1 q_{12} - 2r_{1He} g
\]

showing that the summed correlation potential is a constant (with respect to \( r_{2H} \)) that depends on the value of \( s \). The correlation parts cancel and, if the oxygen-oxygen distances are sufficiently
The total potential will be a double well from the one-body $V_2$ term. It is then important that the initial wavefunction span the wells in order to converge to the correct ground state. In Table 4 we display the results of the numerically exact calculations for different initial conditions when there is a double well for proton two ($r_{12} = r_{23} = r_{34} = 2.7 \text{ Å}$). The ground state probabilities of the protons is shown in Fig. 8. Unless the initial wavefunctions are distributed over all the wells, $|SH_1\rangle|SH_2\rangle|SH_3\rangle$, or the initial wavefunctions are qualitatively the same as the corrects ones, $|RH_1\rangle|SH_2\rangle|LH_3\rangle$ (the second proton is distributed over the double well), then the wrong ground state will result. The corresponding results for the TeDH are also shown in Table 4. It has no difficulty in producing the split probability for proton two. The TeDH is still an accurate procedure, though now the differences between the exact and TeDH are evident.

For smaller oxygen-oxygen distances, around 2.5 Å and shorter, the double well for proton two, when protons one and three are symmetrically disposed, is essentially gone. Both the numerically exact and TeDH methods will converge to the ground state as shown in Fig. 9, and the initial wavefunction can be e.g. left localized. That is, the initial state $|LH_1\rangle|LH_2\rangle|LH_3\rangle$ now does go to the correct ground state. Again, there is some difference between the probabilities in the 3D and TeDH methods. We would anticipate, for this easier case, where there are no double wells to contend with, that the agreement between 3D and TeDH approaches might be better. Unfortunately, we were not able to use a $128^3$ grid for the 3D calculation, as the memory requirements were too large. However, the agreement certainly is sufficiently good to consider the method reliable. Note that the quantum force is an integral over the probability weighted by the solvent - proton potential, and integration will smooth out small errors in the probabilities.
IV. Concluding Remarks

In this work we have formulated a temperature-dependent Hartree approximation for obtaining the ground state solution of the $N$-dimensional Schrödinger equation. The method was shown to be accurate for predicting the ground state probabilities of up to three coupled protons by comparing the TeDH with the numerically exact solutions. As the TeDH method scales linearly with the number of quantum degrees of freedom, it will be possible to treat problems with many coupled protons as relevant to proton chains in biological settings. While not explored here, it should be noted that the TeDH method should be capable of obtaining excited states also, as is the case for solutions of the Schrödinger equation for temperature independent Hamiltonians. The applications we contemplate must focus on ground states because dynamics based on a mixed quantum/classical evolution scheme such as the adiabatic simulation method are only correct for ground state evolution.\textsuperscript{80-84} In this regard, once it is assumed that ground state dynamics are dominant in a particular problem, the ASM method provides a complete solution for the dynamics.

The Introduction provided a rationale for why fast proton chain dynamics will be dominated by ground state protons. Qualitatively, one may think of the overall rate of proton transfer as a thermal average over the varying heavy atom distances. The shorter distance configurations, with their faster dynamics, will dominate the overall rate. Thus an adiabatic theory, appropriate to these shorter flanking atom distances, should be used to characterize fast proton transport phenomena. Then, the crucial issue for obtaining a practical scheme for treating proton chains dynamics is validation of the TeDH method, and this is what we have shown herein. Because a three proton chain has contributions from both flanking protons of the middle proton in the TeDH scheme, validation of the TeDH at this level should then give confidence that it will also
be accurate for longer chains. That is fortunate, as validation of the TeDH method by comparison with exact numerical solution of a four proton chain would be computationally challenging.

We stress that an analytic proof of the TeDH’s correctness has not been obtained. Once the eigenvalue-eigenvector decomposition of the governing differential equations in Eq. (2.8) is no longer available, as it is for a temperature independent Hamiltonian, (cf. Eqs. (2.11) and (2.12)), it is only suggestive that a quench method of solution will provide the correct ground state. In part, this is why we have carried out the extensive numerical comparisons reported in this work. Having demonstrated numerically that correct ground states are predicted by the TeDH method, we explored the sensitivity of the quench method to the choice of the initial wavefunctions. Section III shows, with a few exceptions, that the TeDH method performs as well as the numerically exact method. The role of the initial, trial wavefunction is of particular importance when the ASM scheme is being carried out. Clearly, one wants to use the wavefunctions determined on a previous MD step as the initial wavefunction for the quench on the succeeding MD step. The hope is that by doing so the number of iterations in the quench will be minimal. The data reported in Tables 2-4 do show that when the initial wavefunction is relatively like the true one, the number of iterations in the quench are reduced. However, caution will have to be used in the initial wavefunction choice when the oxygen-oxygen distances are large, or when a split wavefunction can arise as in the three proton chain for e.g. \( r_{12} = r_{23} = r_{34} = 2.7 \text{ Å} \) (cf. Sec. IIID).

In the absence of the interaction terms \( V_{ij} \) there are, for sufficiently large \( r_{ij} \) distances, degenerate minima in each proton’s surface. These could be the origin of tunneling states. They are precluded by the \( V_{ij} \) terms. When a solvent is included, the active protons’ potential surface could be symmetrized even in the presence of the \( V_{ij} \) terms. For chains where the \( r_{ij} \) values are
rather large on average, so that there would be below barrier localized states, such symmetric potential surfaces could lead to a proton transfer tunneling mechanism (cf. Fig. 2a). For these configurations, the ASM method would have to be modified to account for nonadiabatic transitions. Effects of nonadiabatic transitions can be accommodated by surface hopping\textsuperscript{103,104} and allied \textsuperscript{105-107} techniques. However, as noted in the Introduction, the rates associated with these events would be very small, and would be dominated by the transport mechanism characterized by adiabatic events. Furthermore, these large $r_{ij}$ values should be very rare. Indeed, we note that the equilibrium oxygen-oxygen values for \textit{ab initio} calculations always correspond to chains where the one dimensional surfaces are single minima.\textsuperscript{94} The chains collapse in to short distances. In a membrane this cannot be the case.\textsuperscript{108} Otherwise, it would be difficult to envisage a mechanism where the excess proton could be transported by a hopping mechanism. Recognizing this difficulty, a constraining potential has be added to the results of the \textit{ab initio} calculations that represent the effect of the surrounding medium on the chain geometry.\textsuperscript{109} We postpone the details of this addition until our simulations with a solvent are presented. Here we just remark that it is possible to construct such a potential that doesn’t significantly influence the active proton potentials, it just biases the $r_{ij}$ values to sufficiently large values to give “left-right” localized proton states.

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Appendix A

The time-dependent Hartree approximation to the Schrödinger equation for any of the
degrees of freedom is

$$i \hbar \frac{\partial \phi}{\partial t} = \hat{H} \phi$$  \hspace{1cm} (A.1)

We shall use the more conventional time version for this analysis and obtain the temperature
version by the substitution, $t = -i \beta \hbar$. As a reminder of the operator nature of the Hamiltonian, we
use a $^\dagger$ on it. In contrast with the exact Schrödinger equation with its time independent $\hat{H}$, the
propagator $U_{t_0 t}$ must be expressed as an ordered exponential

$$U_{t_0 t} = T e^{-i \int_{t_0}^{t} ds \hat{H}} = 1 + b g_{t_0} ds \hat{H} + b g_{t_0} ds \hat{H} + \cdots$$  \hspace{1cm} (A.2)

that is properly time ordered because $s_2 < s_1$. The issue here is to assess the error made in using
the Trotter formula in the form of the second-order split exponential operator formula. If the error
is no worse than the $0(\Delta t)^3$ error of this split operator formula for a time-independent
Hamiltonian, then we anticipate that the method will be a fast and reliable method to obtain
the ground-state wavefunction.

For the step from $t_0 \rightarrow t_0 + \Delta t$, we may write a second order midstep expression,

$$\hat{H} g_{t_0} \hat{H} \frac{s-t_0}{2} g_{s-t_0} + \Delta t/2 \hat{H} \frac{s-t_0}{2} + \Delta t/2 \hat{H} \frac{s-t_0}{2} + \Delta t/2 \hat{H} \frac{s-t_0}{2}$$  \hspace{1cm} (A.3)

with $t_0 < s < t_0 + \Delta t$. Using this expression in Eq. (A.1) and evaluating all the terms shows that
the error term is still of $0(\Delta t)^3$, and is the same error as for a time independent $\hat{H}$. The non-
commutativity arising from the time dependent Hamiltonian, $[\hat{H}_{s_1}, \hat{H}_{s_2}] \neq 0; (s_1 \neq s_2)$, does not contribute to the error to $0(\Delta t)^3$. Another approach is to expand about $t_0$, the beginning of the interval. When this is done, the error term is $\hat{H}_{s_1} \hat{H}_{s_2} \Delta t^2$ and is of the same order as that of the time-independent split-operator form. While a half-step formalism for the split-operator method can be developed, the overhead incurred in such a formula seems not to be worth the effort, since the error of the standard split-operator formula arising from the non-commutativity $[\hat{T}, \hat{V}] \neq 0$ is of the same order as that incurred in the $\hat{H}_{bg}$ case with expansion about $t_0$. Unless there were an unfavorable numerical coefficient that would significantly reduce its accuracy, the above error estimate indicates that the expansion about $t_0$ should be used, and we do so in this work. Thus a working formula for a Hamiltonian schematized as $\hat{H}_{bg} = \hat{T} + V_0 + V_{bg}$, based on Eq. (A.1) and the above considerations is

$$\psi_{t_0 + \Delta t} = e^{-i[H_{bg}(t_0), \Delta \hat{T}]/\hbar} e^{-i[H_{bg}(t_0), \Delta \hat{V}]/\hbar} \psi_{t_0}$$

As the wavefunction is known at time $t_0$, the expectation value $\langle V \rangle_{t_0}$ is available to propagate to $t_0 + \Delta t$. The substitution $t = -i \beta \hbar$ then yields Eq. (2.13).
References


Figures

Fig. 1a. A proton chain $\text{H}_{11}\text{O}_5^+$ with one excess proton. The active protons’ coordinates $r_{1H}$, $r_{2H}$,... are referenced to the oxygen atoms to their respective left; and the inter-oxygen distances are denoted as $r_{12}$, $r_{23}$,... The HOH angle is $112^\circ$.\textsuperscript{101,102} The excess proton can migrate from left to right by a “hopping” mechanism (cf. Introduction). 1b) A proton chain $\text{H}_9\text{O}_4^+$ with one excess proton. The proton ground state locations are denoted as $|UH_1\rangle|UH_2\rangle|UH_3\rangle...$ with $U$ denoting a left ($L$) or right ($R$) localized proton.

Fig. 2. Some potential surfaces for protons. a) Tunnel states—symmetric potential surface with close lying even (ground) and odd (excited) states. b) Asymmetric double well with well separated levels. c) Symmetric double well with barrier low enough that both lowest levels are above the barrier and well separated in energy ($>k_BT$). d) Asymmetric double well with well separated levels ($>k_BT$). The b)-d) situations are suited to the adiabatic simulation method that assumes only protonic ground states contribute to the dynamics of the proton chain. The nonadiabatic dynamics associated with a) would be much slower.

Fig. 3. Ground state probability $\psi_1^2$ as predicted by the numerically exact 2D quench and the TeDH approximation for the exactly soluble model Hamiltonian of Eq. (3.1).

Fig. 4. Contour plot of $V_{TOT}$ with the functional form in Eq. (3.6) and parameters given in Table 1, for $r_{12} = r_{23}=2.7$ Å. The minimum of the potential is at $|RH_1\rangle|LH_2\rangle = b_g$ with energy $0.2265$ kcal/mol. The two other subsidiary minima are $|LH_1\rangle|LH_2\rangle = b_g$ and $|RH_1\rangle|RH_2\rangle = b_g$ with energy $1.293$ kcal/mol. There is a “path” for proton motion...
that, starting with both protons on the “left” ($r_{1H} \approx r_{2H} \approx 1.0$ Å), will first transfer proton one and then transfer proton two.

Fig. 5. Contour plot of $V_{TOT}$ for $r_{12} = r_{23} = 2.4$ Å with the parameters in Table 1. There is only one minimum in this surface around $r_{1H} = 1.279$ Å, $r_{2H} = 1.121$ Å.

Fig. 6. Contour plot of $V_{TOT}$ for $r_{12} = r_{23} = 3.0$ Å with the functional form in Eq. (3.6) and parameters in Table 1. The barriers along the $r_{1H}$ and $r_{2H}$ directions are about 25 kcal/mol. The absolute minima of the potential surface are at $|RH_1\rangle|RH_2\rangle = b_{091,2,093}g$ Å and $|LH_1\rangle|LH_2\rangle = b_{098,091}g$ Å, with energy $-0.856$ kcal/mol. There is a local minimum at $|RH_1\rangle|LH_2\rangle = b_{030,097}g$ Å with energy $-0.0275$ kcal/mol. Even though the potential surface is higher in energy around $|RH_1\rangle|LH_2\rangle$, the ground state is located here.

Fig. 7. Ground state probabilities $\psi_{iH}^2$ ($i = 1,2$) as predicted by the numerically exact 2D quench and the TeDH approximation. The oxygen-oxygen distances are $r_{12} = r_{23} = 2.7$ Å. The TeDH approximation is clearly of excellent quality.

Fig. 8. Ground state probabilities $\psi_{iH}^2$ ($i = 1-3$) as predicted by the numerically exact 3D quench and the TeDH approximation. The oxygen-oxygen distances are $r_{12} = r_{23} = r_{34} = 2.7$ Å. The TeDH approximation is of good quality, though the difference with the exact result is evident. The second proton’s wavefunction is symmetrically split, reflecting the cancellation of the two interaction terms when proton one and three are symmetrically disposed with respect to the midpoint of the chain, and the oxygen-oxygen distance is sufficiently large that proton two’s one-body potential is a (symmetric) double well (see the discussion in Section III.D).
Fig. 9. Ground state probabilities $\psi_{i}^{2}b_{i}g_{i=1-3}$ as predicted by the numerically exact 3D quench and the TeDH approximation. The oxygen-oxygen distances are $r_{12} = r_{23} = r_{34} = 2.5\ \text{Å}$. The TeDH approximation is of good quality, though the difference with the exact result is evident. The second proton is between its oxygens reflecting the cancellation of the two interaction terms when proton one and three are symmetrically disposed with respect to the midpoint of the chain, and the oxygen-oxygen distance is sufficiently short that proton two’s one-body potential is a single well (see the discussion in Section III.D).