

**Wavepacket *Ab Initio* Dynamics:
Generalizations to Higher Dimensions**

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Introduction – Atom-centered Density Matrix Propagation (ADMP)^{1,5,6} is a relatively new development in the field of *ab-initio* molecular dynamics. The most attractive feature about this method is that it is computationally inexpensive compared to other common molecular dynamics algorithms, such as Born-Oppenheimer Molecular Dynamics (BOMD). This is because BOMD has a computational scaling problem. The size of the system it can analyze is limited, since it must solve an expensive eigenvalue problem – the Schrödinger equation via the Self-Consistent Field (SCF) approximation (for a review, see reference 9). In BOMD, this expensive problem must be solved every time the nuclei move in order to calculate the new electronic energy of the system. ADMP, on the other hand, solves for the electronic energy only once and propagates this energy via the density matrix along with the nuclei. Thus, the computational time scales linearly with the size of the problem, making ADMP faster than BOMD.¹

Another attractive feature of ADMP is that it uses atom-centered basis functions to calculate electronic energies. Another method that has a similar scaling, the Carr-Parrinello method², uses sines and cosines (plane waves) as basis functions to describe the electrons. Atom centered basis sets, i.e. Gaussian bell curves, are intuitively smarter choices for molecular systems, since the electron density increases closer to and decreases further from the nucleus. Since Gaussians exhibit the same boundary conditions, a small number are required to accurately represent the electron density. On the other hand, a large combination of plane waves is needed for a similar description.

ADMP and BOMD, however, are not able to describe all types of dynamics

encountered in chemistry. One thing they lack is an ability to handle dynamics that can only be explained with full quantum mechanics. Proton tunneling, for example, is a purely quantum effect that can play an important role in the evolution of a system. It is completely overlooked by ADMP. This is due to the classical nature of ADMP, which will be explained in the following section. The reasons why BOMD neglects these effects will also be discussed in section II. However, improvements have recently been made to allow both molecular dynamics schemes to account for quantum effects by allowing a quantum particle to be propagated via the full Time-Dependent Schrödinger Equation (TDSE). This new method is called wavepacket *ab-initio* molecular dynamics³, since it propagates the quantum particle as a wavepacket. This scheme, however, is not completely general. In particular, it will currently only propagate a particle along one dimension, limiting the scope of the methodology. The purpose of this C500 project has been to generalize the method to full dimensionality.

The rest of this report is divided into the following parts: section II gives the necessary theory behind ADMP and wavepacket *ab-initio* molecular dynamics, section III explains the theory of the C500 project and discusses the results and difficulties, and section IV ends the report with conclusions and future directions.

Section II – We will start the theoretical discussion with the TDSE:

$$i\hbar \frac{\partial}{\partial t} \psi(r,R;t) = H \psi(r,R;t), \quad (1)$$

where H is the nuclear-electron Hamiltonian and $\psi(r,R;t)$ is the function that describes the system at time t . The TDSE can be approximated by breaking it into three parts:

$$i\hbar \frac{\partial}{\partial t} \psi_1(\mathbf{R}_{\text{QM}};t) = H_1 \psi_1(\mathbf{R}_{\text{QM}};t), \quad (2)$$

$$i\hbar \frac{\partial}{\partial t} \psi_2(\mathbf{R}_C;t) = H_2 \psi_2(\mathbf{R}_C;t), \quad (3)$$

$$i\hbar \frac{\partial}{\partial t} \psi_3(\mathbf{r};t) = H_3 \psi_3(\mathbf{r};t), \quad (4)$$

where ψ_1 is the quantum particle with position \mathbf{R}_{QM} , ψ_2 represents the nuclei with position \mathbf{R}_C and ψ_3 represents the electrons and \mathbf{r} denotes their position. This approximation is only valid if each subsystem acts independently. These equations are coupled in the sense that each system interacts with the others in an average way via the Time-Dependent Self-Consistent Field Method (TDSCF)⁹. This means that H_1 is defined as

$$\langle \psi_2 \psi_3 | H | \psi_2 \psi_3 \rangle. \quad (5)$$

H_2 and H_3 are defined in a similar manner.

To propagate the nuclei, we would enforce the classical limit ($\hbar \rightarrow 0$) on (3), which gives rise to the Hamilton-Jacobi equation⁴, another form of Newton's $F = ma$. This means the nuclei are classical particles and are treated as such. The electronic portion, ψ_3 , is treated by assuming a stationary state approximation of the wavefunction, i.e. space-time separation.⁴ This allows the electronic energies to be calculated via the Time-Independent Schrödinger Equation (TISE), $H\psi_3 = E\psi_3$. Using these two equations, one classical and one quantum, BOMD propagates the system according to the algorithm discussed in the previous section.

ADMP, however, works differently. It is an extended Lagrangian scheme, similar to the CP method. Lagrangian dynamics is an alternate formalism of normal

Newtonian mechanics. The difference is that Lagrangian equations allow for constraints. The Lagrangian we use is the kinetic energy *minus* the potential energy ($L = T - V$). It can be shown, see refs. 1 and 5, that in ADMP,

$$L = \frac{1}{2} \text{Tr}[\mathbf{V}^T \mathbf{M} \mathbf{V}] + \frac{1}{2} \text{Tr}[(\underline{\mu}^{1/4} \mathbf{W} \underline{\mu}^{1/4})^2] - E(\mathbf{R}, \mathbf{P}) - \text{Tr}[\Lambda(\mathbf{P}\mathbf{P} - \mathbf{P})], \quad (6)$$

where \mathbf{M} and \mathbf{V} represent the nuclear, i.e. classical, mass and velocity; $\underline{\mu}$ and \mathbf{W} are the fictitious mass tensor^{5,6} and density matrix velocity, which describe the electronic degrees of freedom; E is the potential energy, which depends on the nuclear positions, \mathbf{R} , and the density matrix, \mathbf{P} ; and the last term is a Lagrange multiplier which constrains the density matrix to be idempotent, i.e. $\mathbf{P}^2 = \mathbf{P}$, and so that the trace of \mathbf{P} is the number of electrons. These two conditions are known as N representability, and if they are met, then there exists an N -particle wavefunction for \mathbf{P} . It can be shown via extensive derivations which will not take place here but can also be found in refs. 1 and 3, that

$$\mathbf{M} \frac{d^2 \mathbf{R}}{dt^2} = - \langle \psi_1 | \frac{\partial E(\{\mathbf{R}_C, \mathbf{P}\}, \mathbf{R}_{QM})}{\partial \mathbf{R}_C} | \psi_1 \rangle \quad (7)$$

$$\underline{\mu}^{1/2} \frac{d^2 \mathbf{P}}{dt^2} \underline{\mu}^{1/2} = - \langle \psi_1 | \frac{\partial E(\{\mathbf{R}_C, \mathbf{P}\}, \mathbf{R}_{QM})}{\partial \mathbf{P}} |_{\mathbf{R}_C} - [\Lambda \mathbf{P} + \mathbf{P} \Lambda - \Lambda] | \psi_1 \rangle. \quad (8)$$

The gradient of the potential energies, $\frac{\partial E(\{\mathbf{R}_C, \mathbf{P}\}, \mathbf{R}_{QM})}{\partial \mathbf{R}_C}$ and $\frac{\partial E(\{\mathbf{R}_C, \mathbf{P}\}, \mathbf{R}_{QM})}{\partial \mathbf{P}}$, are averaged over ψ_1 , the quantum system. Careful inspection of these two equations will reveal that equation (7) is $F = ma$, since the negative gradient of the potential energy is force. Equation (8) is similar in form, since $\underline{\mu}$ is the fictitious electron mass and \mathbf{P} is similar to the electronic position, but the content is quantum mechanical. The last

term of equation (8) is the N representability constraint. Because equations (7) and (8) compute classical trajectories, ADMP cannot account for quantum effects.

Whether quantum wavepacket dynamics is being performed with ADMP or BOMD, one equation, (2), remains untouched:

$$i\hbar \frac{\partial}{\partial t} \psi_1(\mathbf{R}_{QM};t) = \left[-\frac{\hbar^2}{2M_{QM}} \tilde{\mathcal{N}}^2_{ROM} + E(\{\mathbf{R}_C, \mathbf{P}\}, \mathbf{R}_{QM}) \right] \psi_1(\mathbf{R}_{QM};t). \quad (9)$$

The energy functional, $E(\{\mathbf{R}_C, \mathbf{P}\}, \mathbf{R}_{QM})$, depends on the coordinates of all three subsystems. It can be represented by any single particle method, including all Density Functional Theory (DFT) functionals, or other formalisms like Hartree-Fock (HF) or semiempirical methods. More explicitly, it is

$$E = \text{Tr}[h\mathbf{P} + \frac{1}{2} \mathbf{G}(\mathbf{P})\mathbf{P}] + E_{xc} + V_{NN}, \quad (10)$$

where h is the one electron matrix and G is the two-electron matrix for HF methods but the coulomb potential for DFT methods. E_{xc} is the DFT exchange correlation functional (in HF, $E_{xc} = 0$), and V_{NN} is the nuclear repulsion.¹ Equation (9) is used to propagate one particle, i.e. proton or electron, and the rest of the system is propagated according to the ADMP or BOMD equations.

The quantum system is propagated according the solution of equation (2):

$$i\hbar \frac{\partial}{\partial t} \exp\left\{-\frac{iH_1 t}{\hbar}\right\} \varphi(\mathbf{R}_{QM};0) = H_1 \exp\left\{-\frac{iH_1 t}{\hbar}\right\} \varphi(\mathbf{R}_{QM};0), \quad (11)$$

where $\exp\left\{-\frac{iH_1 t}{\hbar}\right\} \varphi(\mathbf{R}_{QM};0) = \varphi(\mathbf{R}_{QM};t)$ and $\exp\left\{-\frac{iH_1 t}{\hbar}\right\}$ is called the quantum propagator. The propagator is an operator that moves the system in time. It is this propagator that we use to evolve the quantum subsystem in our new method and it is

the approximation of this propagator that comprises the majority of the theory behind the methodology.

The first step towards representing the propagator is to approximate it using a kinetic reference symmetric split operator approach:³

$$\exp\left\{-\frac{iHt}{\hbar}\right\} = \exp\left\{-\frac{iVt}{2\hbar}\right\} \exp\left\{-\frac{iKt}{\hbar}\right\} \exp\left\{-\frac{iVt}{2\hbar}\right\} + O(t^3), \quad (12)$$

where K is the kinetic energy operator in equation (9), V is the potential energy operator and the final term arises because the error inherent in this form of the operator scales as $O(t^3)$, i.e. as a cubic function of time. This error arises since K and V do not commute. The potential energy part of the propagator is trivial to represent if the potential is local, as its matrix representation is diagonal in the coordinate representation. The kinetic energy portion of the propagator, known as the free propagator, is not diagonal in the coordinate representation. Thus, a suitable approximation must be found.

The free propagator can be calculated by a number of methods, including using fast Fourier transforms to represent it in the momentum representation, where it is diagonal, and implementing Feynman path integrals.³ However, we represent it with an analytical banded Distributed Approximating Functional (DAF)⁷ for reasons that will soon become clear. The free propagator is represented analytically as³:

$$\begin{aligned} & \int R'_{QM} \langle R_{QM} | \exp\left\{-\frac{iK\Delta t_{QM}}{\hbar}\right\} | R'_{QM} \rangle \varphi(R'_{QM}; t) \\ &= \frac{1}{\sigma(0)} \exp\left\{-\frac{(R_{QM} - R'_{QM})^2}{2\sigma(\Delta t_{QM})^2}\right\} \sum_{n=0}^{M/2} \left(\frac{\sigma(0)}{\sigma(\Delta t_{QM})}\right)^{2+1} \\ & \quad \left(-\frac{1}{4}\right)^n \frac{1}{n!} (2\pi)^{-1/2} H_{2n}\left(\frac{R_{QM} - R'_{QM}}{\sqrt{2}\sigma(\Delta t_{QM})}\right) \varphi(R'_{QM}; t), \end{aligned} \quad (13)$$

where

$$\{\sigma(\Delta t_{QM})\}^2 = \sigma(0)^2 + \frac{i\Delta t_{QM}\hbar}{M_{QM}}. \quad (14)$$

This expression comes from the familiar expression of the free propagation of a Gaussian function,³

$$\exp\left\{-\frac{iK\Delta t_{QM}}{\hbar}\right\} \exp\left\{-\frac{x^2}{2\sigma(0)^2}\right\} = \frac{\sigma(0)}{\sigma(\Delta t_{QM})} \exp\left\{-\frac{x^2}{2\sigma(\Delta t_{QM})^2}\right\} \quad (15)$$

and from the fact that Hermite functions can be generated from Gaussians:

$$H_{2n}(x) \exp\left\{-\frac{x^2}{2\sigma^2}\right\} = (-1)^n \frac{d^n}{dx^n} \exp\left\{-\frac{x^2}{2\sigma^2}\right\}. \quad (16)$$

Equation (13) is in a continuous form. In order to implement it in a feasible algorithm, it must be discretized. Thus, the evolution of the wavepacket, $\varphi(R_{QM};t)$, is

$$\begin{aligned} \varphi(R^i_{QM};t+\Delta t) &= \frac{\Delta x}{\sigma(0)} \sum_j \exp\left\{-\frac{(R^i_{QM} - R^j_{QM})^2}{2\sigma(\Delta t_{QM})^2}\right\} \sum_{n=0}^{M/2} \left(\frac{\sigma(0)}{\sigma(\Delta t_{QM})}\right)^{2+n} \\ &\quad \left(-\frac{1}{4}\right)^n \frac{1}{n!} (2\pi)^{-1/2} H_{2n}\left(\frac{R^i_{QM} - R^j_{QM}}{\sqrt{2}\sigma(\Delta t_{QM})}\right) \varphi(R^j_{QM};t). \end{aligned} \quad (17)$$

It is this form of the propagator that the DAF approximates. This particular propagation takes place along a one dimensional grid (a line) with spacing of Δx . M and σ are parameters that, when chosen correctly, will give the DAF an optimum accuracy.³ Now that the form of the DAF propagator is known, one can see why this choice of approximation provides some advantages. In particular, the elements of the DAF matrix depend only on $(R^i_{QM} - R^j_{QM})^2$. This means we only need to store the first row of this matrix, since it contains all of the information we need. Another advantage is that the scaling of the DAF propagation scheme is $O\{(2W+1)(N - W) - W^2\}$, where N is the number of grid points and W depends on the choice of the

parameters M and σ .² Because N does not depend on W , the scaling goes as $O(N)$, i.e. linearly, for large grids.

Section III – Since the propagation discussed in section II of this work is one-dimensional, the multidimensional propagation must be derived. We will only present a three-dimensional scheme since it is the most useful and, by using it as a model, the derivation of a multi-dimensional scheme can easily be extrapolated. It is this portion of the C500 project that has been taken close to completion.

The derivation begins with the free propagator, $\exp\{-\frac{iK\Delta t_{QM}}{\hbar}\}$. To generalize the scheme into three dimensions, the direct product form of the propagator is used

$$\exp\{-\frac{iK\Delta t_{QM}}{\hbar}\} = \exp\{-\frac{iK_x\Delta t_{QM}}{\hbar}\} \exp\{-\frac{iK_y\Delta t_{QM}}{\hbar}\} \exp\{-\frac{iK_z\Delta t_{QM}}{\hbar}\}, \quad (18)$$

where $K_{x/y/z}$ is the momentum operator along the $x/y/z$ -axis. This splitting can be done in an exact manner since all three operators commute. The continuous form of the operator is

$$\begin{aligned} \varphi(R_x, R_y, R_z; t + \Delta t) = & \int dR_x' \langle R_x | \exp\{-\frac{iK_x\Delta t_{QM}}{\hbar}\} | R_x' \rangle \int dR_y' \langle R_y | \exp\{-\frac{iK_y\Delta t_{QM}}{\hbar}\} | R_y' \rangle \\ & \int dR_z' \langle R_z | \exp\{-\frac{iK_z\Delta t_{QM}}{\hbar}\} | R_z' \rangle \varphi(R_x', R_y', R_z'; t). \end{aligned} \quad (19)$$

It is easy to see that each dimension of this equation is the continuous form of equation (17). Thus, equation (19) is approximated by:

$$\varphi(R_x^i, R_y^j, R_z^k; t + \Delta t) = DAF_{x_i} DAF_{y_j} DAF_{z_k} \varphi(R_x^i, R_y^j, R_z^k; t), \quad (20)$$

where each DAF is calculated according to equation (17). Although the derivation of the multi-dimensional propagation scheme is relatively straight forward, the actual implementation is not.

The first hurdle in implementing a higher-dimensional methodology is to write an algorithm that generates a multi-dimensional grid. This grid is laid out according to the researcher's specifications (i.e. orientation, length, grid spacing, etc). The challenge posed, and the challenge met, was to make this grid completely general to size, spacing, and dimensionality. After the grid was laid out, the new propagation algorithm needed to be written and tested for accuracy.

Table I. The propagation error computed according to $\Sigma(\varphi_{\text{DAF}} - \varphi_{\text{Exact}})^2$. The appropriate σ value was chosen for each value of M for maximum accuracy.

	$\Delta t=0$	$\Delta t=10$
M = 10	0.02608	0.02610
(- 2 pts)	7.652×10^{-11}	8.219×10^{-11}
M = 60	.018397	.018402
(-5 pts)	1.807×10^{-9}	1.812×10^{-9}

Table I displays the results of the propagation of a proton along a 100 x 100 x 100 grid – the wavepacket is propagated over one-million points! Because we have chosen to represent the wavepacket as a Gaussian, measuring the accuracy of the propagation is straight-forward, since the analytical answer is well known (equation (15)). t (~25 attoseconds), along with the other variables in equations (17) and (15) is in atomic units. The first and third rows show the error of the propagation according to $\sum_i^N (\varphi(i)_{\text{DAF}} - \varphi(i)_{\text{Exact}})^2$, where the summation takes place over all of the grid points. The second and fourth rows show the error summed over all but the first two and five grid points along each dimension. It can be seen from the data that the bulk of the errors occur in the first few points for M = 60 and M = 10, which is expected due to the banded nature of the propagator (i.e. the first few points are expected to be less accurate). The second column shows that the propagation is stable over 0.25

femtoseconds. Further tests demonstrating stability over longer time scales (~10 picoseconds) are currently underway.

The final step is to successfully enter the code into a development version of Gaussian03.⁸ This presents its own set of challenges, since the insertion of a small algorithm into a large program requires that changes are made in both the new and old portions of the code. To date, this insertion has been partly successful. The multidimensional grid algorithm works well. Including the propagation scheme is currently in progress.

Section IV - Considerable progress has been made towards generalizing quantum wavepacket dynamics to higher dimensions. The new multi-dimensional grid algorithm functions both in and out of Gaussian. The propagation scheme has been shown to be accurate.

Once the full scheme functions properly, tests will be performed to show accuracy and to ensure that energy is conserved during the propagation. Suitable applications, such as an electron transfer through a molecular wire, will then be treated to demonstrate the power of this novel method. Finally, one last adjustment must be implemented before the method is feasible for large grid sizes.

In order to properly move the quantum particle, the potential energy felt by the quantum particle must be calculated at every grid point. This calculation quickly becomes a bottleneck when both grid size and dimension increase. In order to avoid this potentially large computational expense, a multi-dimensional interpolation scheme must be implemented that will allow points to be left out during these

calculations. To date, a one-dimensional scheme has been implemented and is being tested.

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