Complex Quantum Dynamics Driven by Lasers: Quantum Control Theory and Optimization in the Large Multiple-Particle Regime

Calvin Chen

October 2016

1 Introduction

High-order Harmonic Generation (HHG) in plasmas is an area of research that is of broad fundamental and practical interest. As the oscillatory modes of ionized particles resulting from excitation by a laser pulse could reveal valuable insights into the properties of such ions and their states, HHG remains not only a fertile area of interest, but also a valuable experimental tool. However, I took a more generalized focus in my work during the summer under Professor Herschel Rabitz and the Program in Plasma Science and Technology (PPST). While HHG is a phenomenon that occurs in laser driven plasmas, there is a growing body of inquiry concentrated upon the effects of lasers at various intensities and frequencies upon molecules in general – specifically, upon the potential for lasers to alter the Hamiltonian of a system in order to optimize the wave function in a desired way. One immediate application of such methods, known as quantum control theory (QCT), would be the ability for photons to act as "photonic reagents" within various chemical reactions, including with ionized products.

However, while a significant amount of literature concerning quantum control theory has been developed in recent decades, there remains a scarcity of work regarding the theory when applied to many-particle systems. Therefore, this summer I studied QCT in the large multiple-particle regime. It is my expectation that after the theory is developed beyond the control of few-particle systems, not only would the practical applications of quantum control with photonic reagents be enabled, the manipulation and evolution of the Hamiltonians of many-particle systems would also emerge as a broad field of study. The HHG phenomena seen in plasmas will thus be subsumed into the larger regime of molecular- and atomic-scale transformations possible with the quantum control of many-particle systems.

To address the many-particle control challenge above, several theoretical and computational methods have been developed, which I will build on in my research, and upon which I will further expand. Although the Hamiltonians and wave functions for many-particle systems become extraordinarily difficult to calculate as the complexity of a system increases, the Hartree-Fock method has proved to be an extremely effective method of approximation outside of the field of control. More specifically, and more relevant to my work, adaptation of the multi-configuration time-dependent Hartree (MCTDH) method would be extremely useful in improving the speed and efficiency of the calculations required to evolve the relevant wavefunctions, without sacrificing much accuracy. Once we have established the effectiveness of the TDH approximation, we can begin to implement it in the DMORPH optimization algorithm as a direct application to QCT.

2 Preliminaries

Quantum optimal control theory (OCT) generally concerns the problem of is to optimize an objective functional $J[\epsilon(\cdot)]$ (usually the expectation value of an observable) through a control function/field $\epsilon(\cdot)$.

Several quantum OCT problems concern wavefunctions $\Psi(\overrightarrow{r_1}, \overrightarrow{r_2}, \ldots)$ that describe systems of several particles interacting with the external control field $\epsilon(\cdot)$ and possibly with each other, as described by a Hamiltonian

$$\hat{H} = \hat{H}_0^{[2]} + \hat{H}_1^{[2]}(\Psi(\overrightarrow{r}), \Psi(\overrightarrow{r})^*, \epsilon(t)) \tag{1}$$

, where

$$\hat{H}_0^{[2]} = \sum_i -\frac{h^2}{2M_i}\nabla_i^2 + V(\overrightarrow{r_i}, \ldots, \overrightarrow{r_j}) \tag{2}$$

is the free-field Hamiltonian and $\hat{H}_1^{[2]}(\Psi(\overrightarrow{r}), \Psi(\overrightarrow{r})^*, \epsilon(t))$ is the (generally non-linear) control field Hamiltonian.

3 The time-dependent Hartree (TDH) approximation

In order to simplify calculations involved in the determination of the wavefunction $\Psi(\overrightarrow{r_1}, \overrightarrow{r_2}, \ldots)$ describing the behavior of systems of several interacting particles, we employ the approximation of the time-dependent Hartree (TDH) ansatz:

$$|\Psi(t)\rangle \approx a(t) \prod_i |\Psi_i(t)\rangle \tag{3}$$

where $a(t)$ is a global phase term that can absorb the phases of each individual single-particle wavefunction $\Psi(\overrightarrow{r_i})$ such that $|a(t)|^2 = 1$.

Given a Hamiltonian $\hat{H}$, and gauging the phase by setting $\langle\Psi_i| \frac{\partial}{\partial t} |\Psi_i\rangle = 0$ we then have the Schrödinger equation:

$$i\hbar\frac{\partial}{\partial t}\left|\Psi\right\rangle = \hat{H}\left|\Psi\right\rangle \tag{4}$$

$$i\hbar\frac{\partial}{\partial t}a(t)\prod_i\left|\Psi_i\right\rangle = a(t)\hat{H}\prod_i\left|\Psi_i\right\rangle \tag{5}$$

$$i\hbar[\frac{\partial a(t)}{\partial t}\prod_i\left|\Psi_i\right\rangle + a(t)\sum_i(\frac{\partial\left|\Psi_i\right\rangle}{\partial t}\prod_{j\neq i}\left|\Psi_j\right\rangle)] = a(t)\hat{H}\prod_i\left|\Psi_i\right\rangle \tag{6}$$

Taking the inner product with $\prod_i\left\langle\Psi_i\right|$ we have:

$$i\hbar\frac{\partial a(t)}{\partial t} = a(t)\prod_i\left\langle\psi_i\right|\hat{H}\prod_i\left|\psi_i\right\rangle \tag{7}$$

Taking the inner product with $\prod_{j\neq i}\left\langle\Psi_j\right|$ we have:

$$i\hbar[\frac{\partial a(t)}{\partial t}\left|\Psi_i\right\rangle + a(t)\frac{\partial\left|\Psi_i\right\rangle}{\partial t}] = (\prod_{j\neq i}\left\langle\Psi_j\right|\hat{H}\prod_{j\neq i}\left|\Psi_i\right\rangle)\left|\Psi_i\right\rangle \tag{8}$$

$$i\hbar\frac{\partial\left|\Psi_i\right\rangle}{\partial t} = (\prod_{j\neq i}\left\langle\Psi_j\right|\hat{H}\prod_{j\neq i}\left|\Psi_i\right\rangle)\left|\Psi_i\right\rangle - \prod_j\left\langle\Psi_j\right|\hat{H}\prod_j\left|\Psi_j\right\rangle\left|\Psi_i\right\rangle \tag{9}$$

$$\begin{aligned} i\hbar\frac{\partial\left|\Psi_i\right\rangle}{\partial t} &= (1-\left|\Psi_i\right\rangle\left\langle\Psi_i\right|)(\prod_{j\neq i}\left\langle\Psi_j\right|\hat{H}\prod_{j\neq i}\left|\Psi_j\right\rangle)\left|\Psi_i\right\rangle \\ &= (1-\left|\Psi_i\right\rangle\left\langle\Psi_i\right|)\hat{\hat{H}}_i^{[1]}\left|\Psi_i\right\rangle \end{aligned} \tag{10}$$

where $\hat{\hat{H}}_i^{[1]} \equiv \prod_{j\neq i}\left\langle\Psi_j\right|\hat{H}\prod_{j\neq i}\left|\Psi_j\right\rangle$ and $(1-\left|\Psi_i\right\rangle\left\langle\Psi_i\right|)\hat{\hat{H}}_i^{[1]}$ is to be defined as the effective Hamiltonian for $\left|\Psi_i\right\rangle$

$$i\hbar\frac{\partial\left|\Psi_i\right\rangle}{\partial t} = (1-\left|\Psi_i\right\rangle\left\langle\Psi_i\right|)\hat{\hat{H}}_i^{[1]}\left|\Psi_i\right\rangle \tag{11}$$

is thus the TDH equation of motion for $\left|\Psi_i\right\rangle$.

4 The D-MORPH method

The D-MORPH (diffeomorphic modulation under observable-response-preserving homotopy) method is an optimization algorithm by which one may evolve an initial Hamiltonian $H(\hat{\epsilon(t)})$, which depends on a control function $\epsilon(t)$, into a final Hamiltonian $H\prime$ that optimizes the objective functional J of the control problem, by introducing a homotopy parameter s to the control function $\epsilon(s,t)$. The homotopy upon the control function $\epsilon(s,t)$ is defined by the ansatz:

$$\frac{\partial\epsilon(s,t)}{\partial s} = \frac{\delta J[\epsilon(s,t)]}{\delta\epsilon(s,t)} \tag{12}$$

This ansatz allows for the variation in $J[\epsilon(s,t)]$ provided by the D-MORPH method to be monotonically convergent as:

$$\begin{aligned}\frac{dJ}{ds} &= \int_0^{t_f} \frac{\delta J[\epsilon(s,t)]}{\delta\epsilon(s,t)} \frac{\partial\epsilon(s,t)}{\partial s} dt \\ &= \int_0^{t_f} (\frac{\delta J[\epsilon(s,t)]}{\delta\epsilon(s,t)})^2 dt \\ &\geq 0\end{aligned} \tag{13}$$

Given an initial state of the system $t = 0$, $|\Psi(0)\rangle$, a co-state $|\lambda(t_f)\rangle = \hat{A}\,|\Psi(t_f)\rangle$ for some operator $\hat{A}$ to be determined, both of which are approximated by the TDH ansatz 3 evolve under an effective Hamiltonian $\tilde{H}(\epsilon\hat{(}s,t)$ (cf. **??**):

$$i\hbar\,|\Psi(t)\rangle = \hat{\tilde{H}}_i(\epsilon(s,t)\,|\Psi(t)\rangle \tag{14}$$

$$i\hbar\,|\lambda(t)\rangle = \hat{\tilde{H}}_i(\epsilon(s,t)\,|\lambda(t)\rangle \tag{15}$$

and given a sufficiently dense grid of time points $t = 0, \Delta t, 2\Delta t, \ldots, N_t\Delta t$, where $N_t = t_f/\Delta t$ and homotopy parameter points $s = 0, \Delta s, 2\Delta s, \ldots$, each iteration of the general D-MORPH method for each $s = k\Delta s$ proceeds as follows:

1. Integrate forward $|\Psi(t)\rangle$ from $i\Delta t$ to $(i+1)\Delta t$ under 14 subject to the initial condition $|\Psi(0)\rangle$.
2. Integrate backward $|\lambda(t)\rangle$ from $i\Delta t$ to $(i-1)\Delta t$ under 15 subject to a terminal condition $|\lambda(t_f)\rangle$.
3. Use $|\Psi(t)\rangle$ and $|\lambda(t)\rangle$ to compute the gradient $\frac{\delta J[\epsilon(s,t)]}{\delta\epsilon(s,t)}$
4. Integrate $\frac{\partial\epsilon(s,t)}{\partial s} = \frac{\delta J[\epsilon(s,t)]}{\delta\epsilon(s,t)}$ from $k\Delta s$ to $(k+1)\Delta s$ to update $\epsilon(k\Delta s, t)$ to $\epsilon((k+1)\Delta s, t)$

This algorithm continues until the optimal condition ($\frac{\partial\epsilon(s,t)}{\partial s} = \frac{\delta J[\epsilon(s,t)]}{\delta\epsilon(s,t)} = 0$) is reached.

5 Example 1: Controlling the orientation of a single dipole rotor confined to a plane

We now turn our attention to implementing the D-MORPH method in the case of the orientation of a single dipole rotor interacting with a control field $\epsilon(t)$. Given moment of inertia I and a dipole moment of μ, we have a Hamiltonian (in the angular representation):

$$H = -\frac{\hbar^2}{2I}\frac{\partial^2}{\partial\phi^2} - \mu\epsilon(t)\cos(\phi) \tag{16}$$

We define our objective functional $J[\epsilon(t)]$ to be:

$$J_\alpha \equiv \langle\Psi(\phi)|\cos(\theta)|\Psi(\phi)\rangle+\alpha\int_0^{t_f}\epsilon(t)^2dt+\int_0^{t_f}(\langle\lambda(t)|\,(\frac{\partial}{\partial t}-\hat{H})\,|\Psi(t)\rangle+\langle\Psi(t)|\,(\frac{\partial}{\partial t}-\hat{H})\,|\lambda(t)\rangle)dt \tag{17}$$

Taking the gradient $\frac{\delta J[\epsilon(s,t)]}{\delta\epsilon(s,t)}$, we find:

$$\delta J[\epsilon(s,t)]/\delta\epsilon(s,t) = -\mu\epsilon(t)(\langle\lambda(t)|\cos(\Phi)\,|\Psi(t)\rangle + \langle\Psi(t)|\cos(\Phi)\,|\lambda(t)\rangle)$$

6 Example 2: Controlling the orientation of two coupled dipole rotors confined to a plane

6.1 The TDH equations of motion

In the case of a pair of coupled dipole rotors confined to a plane, the Hamiltonian $\hat{H}^{[2]}$ becomes (in the angular representation):

$$\begin{aligned}
H^{[2]} &= \sum_{i=1}^{2} -\frac{\hbar^2}{2I}\frac{\partial^2}{\partial\phi_i^2} + \frac{\mu_1\mu_2}{4\pi\varepsilon_0 R^3}[\cos(\phi_1-\phi_2) - 3\cos(\phi_1-\theta)\cos(\phi_2-\theta)] \\
&- \sum_{i=1}^{2}\mu_i\epsilon(t)\cos\phi_i \\
&= \sum_{i=1}^{2} -\frac{\hbar^2}{2I}\frac{\partial^2}{\partial\phi_i^2} + \frac{\mu_1\mu_2}{4\pi\varepsilon_0 R^3}[(1-3\cos^2\theta)\cos\phi_1\cos\phi_2 + (1-3\sin^2\theta)\sin\phi_1\sin\phi_2 \\
&- 3\cos\theta\sin\theta(\cos\phi_1\sin\phi_2 + \sin\phi_1\cos\phi_2)] - \sum_{i=1}^{2}\mu_i\epsilon(t)\cos\phi_i
\end{aligned} \tag{18}$$

The TDH ansatz and the corresponding wavefunction thus become:

$$|\Psi(t)\rangle \approx a(t)\,|\Psi_1(t)\rangle\,|\Psi_1(t)\rangle \tag{19}$$

$$\begin{aligned}
\Psi(\phi_1,\phi_2,t) &= \langle\phi_2|\,\langle\phi_1|\Psi(t)\rangle \\
&= a(t)\Psi_1(\phi_1,t)\Psi_2(\phi_2,t)
\end{aligned} \tag{20}$$

The TDH ansatz thus satisfies the follow equations of motion:

$$i\hbar\frac{\partial\,|\Psi_1\rangle}{\partial t} = (1-|\Psi_1\rangle\,\langle\Psi_1|)\,\langle\Psi_2|H|\Psi_2\rangle\,|\Psi_1\rangle \tag{21}$$

$$i\hbar\frac{\partial\,|\Psi_2\rangle}{\partial t} = (1-|\Psi_2\rangle\,\langle\Psi_2|)\,\langle\Psi_1|H|\Psi_1\rangle\,|\Psi_2\rangle \tag{22}$$

or, expressed in terms of wavefunctions:

$$i\hbar\frac{\partial\Psi_1}{\partial t} = (\,\langle\Psi_2|H|\Psi_2\rangle - \,\langle\Psi_1\Psi_2|H|\Psi_1\Psi_2\rangle)\Psi_1 \tag{23}$$

$$i\hbar\frac{\partial\Psi_2}{\partial t} = (\,\langle\Psi_1|H|\Psi_1\rangle - \,\langle\Psi_1\Psi_2|H|\Psi_1\Psi_2\rangle)\Psi_2 \tag{24}$$

Our goal is to express 23 and 24 as matrix equations for computational purposes:

$$i\hbar\frac{\partial\mathbf{\Psi_1}}{\partial t} = \mathbf{\tilde{H}_1\Psi_1} \tag{25}$$

$$i\hbar\frac{\partial\mathbf{\Psi_2}}{\partial t} = \mathbf{\tilde{H}_2\Psi_2} \tag{26}$$

where:

$$\partial\mathbf{\Psi_i} = \begin{bmatrix} \vdots \\ c_{-2_i} \\ c_{-1_i} \\ c_{0_i} \\ c_{1_i} \\ c_{2_i} \\ \vdots \end{bmatrix} \tag{27}$$

where $c_{m_i} = \langle m_i|\Psi_i\rangle$ and where each $|m_i\rangle$ is an eigenstate of the free-field Hamiltonian $H_{0i} = -\frac{\hbar^2}{2I}\frac{\partial^2}{\partial\phi_i^2}$ such that

$$\langle\phi_i|m_i\rangle = \frac{1}{\sqrt{2\pi}}e^{im\phi_i} \tag{28}$$

and:

$$\tilde{H}_{1m_1,m_1'} = \langle m_1|\,(\,\langle\Psi_2|H|\Psi_2\rangle - \,\langle\Psi_1\Psi_2|H|\Psi_1\Psi_2\rangle)\,|m_1'\rangle \tag{29}$$

$$\tilde{H}_{2m_2,m_2'} = \langle m_2|\,(\,\langle\Psi_1|H|\Psi_1\rangle - \,\langle\Psi_1\Psi_2|H|\Psi_1\Psi_2\rangle)\,|m_2'\rangle \tag{30}$$

We have:

$$
\begin{aligned}
\langle m_1|\,\langle \Psi_2|H|\Psi_2\rangle\,|m_1'\rangle &= \sum_{m_2,m_2'} c_{m_2}^* c_{m_2'}\,\langle m_1|\,\langle m_2|\,H\,|m_2'\rangle\,|m_1'\rangle \\
&= \sum_{m_2,m_2'} c_{m_2}^* c_{m_2'}\,\langle m_1|\,\langle m_2|\,(\sum_{i=1}^{2} -\frac{\hbar^2}{2I}\frac{\partial^2}{\partial\phi_i^2} \\
&+ \frac{\mu_1\mu_2}{4\pi\varepsilon_0 R^3}[(1-3\cos^2\theta)\cos\phi_1\cos\phi_2 + (1-3\sin^2\theta)\sin\phi_1\sin\phi_2 \\
&- 3\cos\theta\sin\theta(\cos\phi_1\sin\phi_2 + \sin\phi_1\cos\phi_2)] \\
&- \sum_{i=1}^{2}\epsilon(t)\cos\phi_i)\,|m_2'\rangle\,|m_1'\rangle \\
&= \sum_{m_2,m_2'} c_{m_2}^* c_{m_2'}\Bigg[\frac{\hbar^2}{2I}(m_1'^2 + m_2'^2)\delta_{m_1,m_1'}\delta_{m_2,m_2'} \\
&+ \frac{\mu_1\mu_2}{16\pi\varepsilon_0 R^3}[(1-3\cos^2\theta)(\delta_{m_1,m_1'+1} + \delta_{m_1,m_1'-1})(\delta_{m_2,m_2'+1} + \delta_{m_2,m_2'-1}) \\
&- (1-3\sin^2\theta)(\delta_{m_1,m_1'+1} - \delta_{m_1,m_1'-1})(\delta_{m_2,m_2'+1} - \delta_{m_2,m_2'-1}) \\
&+ i3\cos\theta\sin\theta((\delta_{m_1,m_1'+1} + \delta_{m_1,m_1'-1})(\delta_{m_2,m_2'+1} - \delta_{m_2,m_2'-1}) \\
&+ (\delta_{m_1,m_1'+1} - \delta_{m_1,m_1'-1})(\delta_{m_2,m_2'+1} + \delta_{m_2,m_2'-1}))] \\
&+ \frac{1}{2}\epsilon(t)[\mu_1\delta_{m_1,m_1'}(\delta_{m_2,m_2'+1} + \delta_{m_2,m_2'-1}) \\
&+ \mu_2(\delta_{m_1,m_1'+1} + \delta_{m_1,m_1'-1})\delta_{m_2,m_2'}]\Bigg] \\
&= \sum_{m_2}\Bigg[\frac{\hbar^2}{2I}(m_1'^2 + m_2^2)\delta_{m_1,m_1'}|c_{m_2}|^2 \\
&+ \frac{\mu_1\mu_2}{16\pi\varepsilon_0 R^3}[(1-3\cos^2\theta)(\delta_{m_1,m_1'+1} + \delta_{m_1,m_1'-1})(c_{m_2}^* c_{m_2-1} + c_{m_2}^* c_{m_2+1}) \\
&- (1-3\sin^2\theta)(\delta_{m_1,m_1'+1} - \delta_{m_1,m_1'-1})(c_{m_2}^* c_{m_2-1} - c_{m_2}^* c_{m_2+1}) \\
&+ i3\cos\theta\sin\theta((\delta_{m_1,m_1'+1} + \delta_{m_1,m_1'-1})(c_{m_2}^* c_{m_2-1} - c_{m_2}^* c_{m_2+1}) \\
&+ (\delta_{m_1,m_1'+1} - \delta_{m_1,m_1'-1})(c_{m_2}^* c_{m_2-1} + c_{m_2}^* c_{m_2+1}))] \\
&+ \frac{1}{2}\epsilon(t)[\mu_1(\delta_{m_1,m_1'+1} + \delta_{m_1,m_1'-1})|c_{m_2}|^2] \\
&+ \mu_2\delta_{m_1,m_1'}(c_{m_2}^* c_{m_2-1} + c_{m_2}^* c_{m_2+1})]\Bigg]
\end{aligned}
\tag{31}
$$

We also have:

$$
\begin{aligned}
\langle m_1| \langle \Psi_1\Psi_2|H|\Psi_1\Psi_2\rangle |m_1'\rangle &= \sum_{m_1'',m_1''',m_2,m_2'} c^*_{m_1''} c_{m_1'''} c^*_{m_2} c_{m_2'} \langle m_1| \langle m_1''| \langle m_2| H |m_2'\rangle |m_1'''\rangle |m_1'\rangle \\
&= \sum_{m_1'',m_1''',m_2,m_2'} c^*_{m_1''} c_{m_1'''} c^*_{m_2} c_{m_2'} \delta_{m_1,m_1'} (\langle m_1''| \langle m_2| H |m_2'\rangle |m_1'''\rangle) \\
&= \delta_{m_1,m_1'} \sum_{m_1'',m_1''',m_2,m_2'} c^*_{m_1''} c_{m_1'''} c^*_{m_2} c_{m_2'} \left[\frac{\hbar^2}{2I}(m_1'^2 + m_2'^2)\delta_{m_1'',m_1'''}\delta_{m_2,m_2'} \right. \\
&+ \frac{\mu_1\mu_2}{16\pi\varepsilon_0 R^3}[(1-3\cos^2\theta)(\delta_{m_1'',m_1'''+1} + \delta_{m_1'',m_1'''-1})(\delta_{m_2,m_2'+1} + \delta_{m_2,m_2'-1}) \\
&- (1-3\sin^2\theta)(\delta_{m_1'',m_1'''+1} - \delta_{m_1'',m_1'''-1})(\delta_{m_2,m_2'+1} - \delta_{m_2,m_2'-1}) \\
&+ i3\cos\theta\sin\theta((\delta_{m_1'',m_1'''+1} + \delta_{m_1'',m_1'''-1})(\delta_{m_2,m_2'+1} - \delta_{m_2,m_2'-1}) \\
&+ (\delta_{m_1'',m_1'''+1} - \delta_{m_1'',m_1'''-1})(\delta_{m_2,m_2'+1} + \delta_{m_2,m_2'-1}))] \\
&+ \frac{1}{2}\epsilon(t)[\mu_1(\delta_{m_1'',m_1'''+1} + \delta_{m_1'',m_1'''-1})\delta_{m_2,m_2'} \\
&\left. + \mu_2\delta_{m_1'',m_1'''}(\delta_{m_2,m_2'+1} + \delta_{m_2,m_2'-1})] \right] \\
&= \delta_{m_1,m_1'} \sum_{m_1'',m_2} \left[\frac{\hbar^2}{2I}(m_1''^2 + m_2^2)|c_{m_1''}|^2 |c_{m_2}|^2 \right. \\
&+ \frac{\mu_1\mu_2}{16\pi\varepsilon_0 R^3}[(1-3\cos^2\theta)(c^*_{m_1''}c_{m_1''-1} + c^*_{m_1''}c_{m_1''+1})(c^*_{m_2}c_{m_2-1} + c^*_{m_2}c_{m_2+1}) \\
&- (1-3\sin^2\theta)(c^*_{m_1''}c_{m_1''-1} - c^*_{m_1''}c_{m_1''+1})(c^*_{m_2}c_{m_2-1} - c^*_{m_2}c_{m_2+1}) \\
&+ i3\cos\theta\sin\theta((c^*_{m_1''}c_{m_1''-1} + c^*_{m_1''}c_{m_1''+1})(c^*_{m_2}c_{m_2-1} - c^*_{m_2}c_{m_2+1}) \\
&+ (c^*_{m_1''}c_{m_1''-1} - c^*_{m_1''}c_{m_1''+1})(c^*_{m_2}c_{m_2-1} + c^*_{m_2}c_{m_2+1}))] \\
&+ \frac{1}{2}\epsilon(t)[\mu_1(c^*_{m_1''}c_{m_1''-1} + c^*_{m_1''}c_{m_1''+1})|c_{m_2}|^2 \\
&\left. + \mu_2|c_{m_1''}|^2(c^*_{m_2}c_{m_2-1} + c^*_{m_2}c_{m_2+1})] \right]
\end{aligned}
\tag{32}
$$

Whew. Thus, we have:

$$
\begin{aligned}
\tilde{H}_{1m_1,m_1'} = \sum_{m_2} \Bigg[& \frac{\hbar^2}{2I}(m_1^2 + m_2^2)\delta_{m_1,m_1'}|c_{m_2}|^2 \\
& + \frac{\mu_1\mu_2}{16\pi\varepsilon_0 R^3}[(1 - 3\cos^2\theta)(\delta_{m_1,m_1'+1} + \delta_{m_1,m_1'-1})(c^*_{m_2}c_{m_2-1} + c^*_{m_2}c_{m_2+1}) \\
& - (1 - 3\sin^2\theta)(\delta_{m_1,m_1'+1} - \delta_{m_1,m_1'-1})(c^*_{m_2}c_{m_2-1} - c^*_{m_2}c_{m_2+1}) \\
& + i3\cos\theta\sin\theta((\delta_{m_1,m_1'+1} + \delta_{m_1,m_1'-1})(c^*_{m_2}c_{m_2-1} - c^*_{m_2}c_{m_2+1}) \\
& + (\delta_{m_1,m_1'+1} - \delta_{m_1,m_1'-1})(c^*_{m_2}c_{m_2-1} + c^*_{m_2}c_{m_2+1}))] \\
& + \frac{1}{2}\epsilon(t)[\mu_1(\delta_{m_1,m_1'+1} + \delta_{m_1,m_1'-1})|c_{m_2}|^2] \\
& + \mu_2\delta_{m_1,m_1'}(c^*_{m_2}c_{m_2-1} + c^*_{m_2}c_{m_2+1})] \\
& - \delta_{m_1,m_1'}\sum_{m_1''}\Bigg[\frac{\hbar^2}{2I}(m_1''^2 + m_2^2)|c_{m_1''}|^2|c_{m_2}|^2 \\
& + \frac{\mu_1\mu_2}{16\pi\varepsilon_0 R^3}[(1 - 3\cos^2\theta)(c^*_{m_1''}c_{m_1''-1} + c^*_{m_1''}c_{m_1''+1})(c^*_{m_2}c_{m_2-1} + c^*_{m_2}c_{m_2+1}) \\
& - (1 - 3\sin^2\theta)(c^*_{m_1''}c_{m_1''-1} - c^*_{m_1''}c_{m_1''+1})(c^*_{m_2}c_{m_2-1} - c^*_{m_2}c_{m_2+1}) \\
& + i3\cos\theta\sin\theta((c^*_{m_1''}c_{m_1''-1} + c^*_{m_1''}c_{m_1''+1})(c^*_{m_2}c_{m_2-1} - c^*_{m_2}c_{m_2+1}) \\
& + (c^*_{m_1''}c_{m_1''-1} - c^*_{m_1''}c_{m_1''+1})(c^*_{m_2}c_{m_2-1} + c^*_{m_2}c_{m_2+1}))] \\
& + \frac{1}{2}\epsilon(t)[\mu_1(c^*_{m_1''}c_{m_1''-1} + c^*_{m_1''}c_{m_1''+1})|c_{m_2}|^2 \\
& + \mu_2|c_{m_1''}|^2(c^*_{m_2}c_{m_2-1} + c^*_{m_2}c_{m_2+1})]\Bigg]\Bigg]
\end{aligned}
\tag{33}
$$

and

$$
\begin{aligned}
\tilde{H}_{2m_2,m_2'} = \sum_{m_1} \Bigg[& \frac{\hbar^2}{2I}(m_2^2 + m_1^2)\delta_{m_2,m_2'}|c_{m_1}|^2 \\
& + \frac{\mu_1\mu_2}{16\pi\varepsilon_0 R^3}[(1 - 3\cos^2\theta)(\delta_{m_2,m_2'+1} + \delta_{m_2,m_2'-1})(c^*_{m_1}c_{m_1-1} + c^*_{m_1}c_{m_1+1}) \\
& - (1 - 3\sin^2\theta)(\delta_{m_2,m_2'+1} - \delta_{m_2,m_2'-1})(c^*_{m_1}c_{m_1-1} - c^*_{m_1}c_{m_1+1}) \\
& + i3\cos\theta\sin\theta((\delta_{m_2,m_2'+1} + \delta_{m_2,m_2'-1})(c^*_{m_1}c_{m_1-1} - c^*_{m_1}c_{m_1+1}) \\
& + (\delta_{m_2,m_2'+1} - \delta_{m_2,m_2'-1})(c^*_{m_1}c_{m_1-1} + c^*_{m_1}c_{m_1+1}))] \\
& + \frac{1}{2}\epsilon(t)[\mu_2(\delta_{m_2,m_2'+1} + \delta_{m_2,m_2'-1})|c_{m_1}|^2] \\
& + \mu_1\delta_{m_2,m_2'}(c^*_{m_1}c_{m_1-1} + c^*_{m_1}c_{m_1+1})] \\
& - \delta_{m_2,m_2'}\sum_{m_2''}\Bigg[\frac{\hbar^2}{2I}(m_2''^2 + m_1^2)|c_{m_2''}|^2|c_{m_1}|^2 \\
& + \frac{\mu_1\mu_2}{16\pi\varepsilon_0 R^3}[(1 - 3\cos^2\theta)(c^*_{m_2''}c_{m_2''-1} + c^*_{m_2''}c_{m_2''+1})(c^*_{m_1}c_{m_1-1} + c^*_{m_1}c_{m_1+1}) \\
& - (1 - 3\sin^2\theta)(c^*_{m_2''}c_{m_2''-1} - c^*_{m_2''}c_{m_2''+1})(c^*_{m_1}c_{m_1-1} - c^*_{m_1}c_{m_1+1}) \\
& + i3\cos\theta\sin\theta((c^*_{m_2''}c_{m_2''-1} + c^*_{m_2''}c_{m_2''+1})(c^*_{m_1}c_{m_1-1} - c^*_{m_1}c_{m_1+1}) \\
& + (c^*_{m_2''}c_{m_2''-1} - c^*_{m_2''}c_{m_2''+1})(c^*_{m_1}c_{m_1-1} + c^*_{m_1}c_{m_1+1}))] \\
& + \frac{1}{2}\epsilon(t)[\mu_2(c^*_{m_2''}c_{m_2''-1} + c^*_{m_2''}c_{m_2''+1})|c_{m_1}|^2 \\
& + \mu_1|c_{m_2''}|^2(c^*_{m_1}c_{m_1-1} + c^*_{m_1}c_{m_1+1})]\Bigg]\Bigg]
\end{aligned} \tag{34}
$$

Keeping the normalization of the wavefunctions $\sum_{m_i}|c_{m_i}|^2 = |\Psi_i|^2 = 1$, in mind, we arrive at the simplified form:

$$
\begin{aligned}
\tilde{H}_{1m_1,m_1'} &= \delta_{m_1,m_1'}\frac{\hbar^2}{2I}[m_1^2 - \sum_{m_1''}(m_1''^2|c_{m_1''}|^2)] \\
&+ \frac{1}{2}\epsilon(t)\mu_1[(\delta_{m_1,m_1'+1} + \delta_{m_1,m_1'-1}) - \delta_{m_1,m_1'}\sum_{m_1''}(c^*_{m_1''}c_{m_1''-1} + c^*_{m_1''}c_{m_1''+1})] \\
&+ \frac{\mu_1\mu_2}{16\pi\varepsilon_0 R^3}\sum_{m_2}[(1-3\cos^2\theta)[(\delta_{m_1,m_1'+1} + \delta_{m_1,m_1'-1}) \\
&- \delta_{m_1,m_1'}\sum_{m_1''}(c^*_{m_1''}c_{m_1''-1} + c^*_{m_1''}c_{m_1''+1})](c^*_{m_2}c_{m_2-1} + c^*_{m_2}c_{m_2+1}) \\
&- (1-3\sin^2\theta)[(\delta_{m_1,m_1'+1} - \delta_{m_1,m_1'-1}) \\
&- \delta_{m_1,m_1'}\sum_{m_1''}(c^*_{m_1''}c_{m_1''-1} - c^*_{m_1''}c_{m_1''+1})](c^*_{m_2}c_{m_2-1} - c^*_{m_2}c_{m_2+1}) \\
&+ i3\cos\theta\sin\theta([(\delta_{m_1,m_1'+1} + \delta_{m_1,m_1'-1}) \\
&- \delta_{m_1,m_1'}\sum_{m_1''}(c^*_{m_1''}c_{m_1''-1} + c^*_{m_1''}c_{m_1''+1})](c^*_{m_2}c_{m_2-1} - c^*_{m_2}c_{m_2+1}) \\
&+ [(\delta_{m_1,m_1'+1} - \delta_{m_1,m_1'-1}) - \delta_{m_1,m_1'}\sum_{m_1''}(c^*_{m_1''}c_{m_1''-1} - c^*_{m_1''}c_{m_1''+1})](c^*_{m_2}c_{m_2-1} + c^*_{m_2}c_{m_2+1}))]
\end{aligned}
\tag{35}
$$

$$
\begin{aligned}
\tilde{H}_{2m_2,m_2'} &= \delta_{m_2,m_2'}\frac{\hbar^2}{2I}[m_2^2 - \sum_{m_2''}(m_2''^2|c_{m_2''}|^2)] \\
&+ \frac{1}{2}\epsilon(t)\mu_2[(\delta_{m_2,m_2'+1} + \delta_{m_2,m_2'-1}) - \delta_{m_2,m_2'}\sum_{m_2''}(c^*_{m_2''}c_{m_2''-1} + c^*_{m_2''}c_{m_2''+1})] \\
&+ \frac{\mu_1\mu_2}{16\pi\varepsilon_0 R^3}\sum_{m_1}[(1-3\cos^2\theta)[(\delta_{m_2,m_2'+1} + \delta_{m_2,m_2'-1}) \\
&- \delta_{m_2,m_2'}\sum_{m_2''}(c^*_{m_2''}c_{m_2''-1} + c^*_{m_2''}c_{m_2''+1})](c^*_{m_1}c_{m_1-1} + c^*_{m_1}c_{m_1+1}) \\
&- (1-3\sin^2\theta)[(\delta_{m_2,m_2'+1} - \delta_{m_2,m_2'-1}) \\
&- \delta_{m_2,m_2'}\sum_{m_2''}(c^*_{m_2''}c_{m_2''-1} - c^*_{m_2''}c_{m_2''+1})](c^*_{m_1}c_{m_1-1} - c^*_{m_1}c_{m_1+1}) \\
&+ i3\cos\theta\sin\theta([(\delta_{m_2,m_2'+1} + \delta_{m_2,m_2'-1}) \\
&- \delta_{m_2,m_2'}\sum_{m_2''}(c^*_{m_2''}c_{m_2''-1} + c^*_{m_2''}c_{m_2''+1})](c^*_{m_1}c_{m_1-1} - c^*_{m_1}c_{m_1+1}) \\
&+ [(\delta_{m_2,m_2'+1} - \delta_{m_2,m_2'-1}) - \delta_{m_2,m_2'}\sum_{m_2''}(c^*_{m_2''}c_{m_2''-1} - c^*_{m_2''}c_{m_2''+1})](c^*_{m_1}c_{m_1-1} + c^*_{m_1}c_{m_1+1}))]
\end{aligned}
\tag{36}
$$

Then, the equations of motion become:

$$
\begin{aligned}
i\hbar\frac{\partial c_{m_1}}{\partial t} &= \sum_{m_1'} \tilde{H}_{1m_1,m_1'} c_{m_1'} \\
&= \sum_{m_1'} \Bigg[\delta_{m_1,m_1'} \frac{\hbar^2}{2I}[m_1^2 - \sum_{m_1''}(m_1''^2 |c_{m_1''}|^2)] \\
&+ \frac{1}{2}\epsilon(t)[\mu_1(\delta_{m_1,m_1'+1} + \delta_{m_1,m_1'-1}) - \delta_{m_1,m_1'} \sum_{m_1''}(c^*_{m_1''} c_{m_1''-1} + c^*_{m_1''} c_{m_1''+1})] \\
&+ \frac{\mu_1\mu_2}{16\pi\varepsilon_0 R^3} \sum_{m_2} [(1 - 3\cos^2\theta)[(\delta_{m_1,m_1'+1} + \delta_{m_1,m_1'-1}) \\
&- \delta_{m_1,m_1'} \sum_{m_1''}(c^*_{m_1''} c_{m_1''-1} + c^*_{m_1''} c_{m_1''+1})](c^*_{m_2} c_{m_2-1} + c^*_{m_2} c_{m_2+1}) \\
&- (1 - 3\sin^2\theta)[(\delta_{m_1,m_1'+1} - \delta_{m_1,m_1'-1}) \\
&- \delta_{m_1,m_1'} \sum_{m_1''}(c^*_{m_1''} c_{m_1''-1} - c^*_{m_1''} c_{m_1''+1})](c^*_{m_2} c_{m_2-1} - c^*_{m_2} c_{m_2+1}) \\
&+ i3\cos\theta\sin\theta([(\delta_{m_1,m_1'+1} + \delta_{m_1,m_1'-1}) \\
&- \delta_{m_1,m_1'} \sum_{m_1''}(c^*_{m_1''} c_{m_1''-1} + c^*_{m_1''} c_{m_1''+1})](c^*_{m_2} c_{m_2-1} - c^*_{m_2} c_{m_2+1}) \\
&+ [(\delta_{m_1,m_1'+1} - \delta_{m_1,m_1'-1}) - \delta_{m_1,m_1'} \sum_{m_1''}(c^*_{m_1''} c_{m_1''-1} - c^*_{m_1''} c_{m_1''+1})](c^*_{m_2} c_{m_2-1} + c^*_{m_2} c_{m_2+1}))]\Bigg] c_{m_1'}
\end{aligned}
\tag{37}
$$

$$
\begin{aligned}
i\hbar\frac{\partial c_{m_2}}{\partial t} &= \sum_{m_2'} \tilde{H}_{2m_2,m_2'} c_{m_2'} \\
&= \sum_{m_2'} \Bigg[\delta_{m_2,m_2'}\frac{\hbar^2}{2I}[m_2^2 - \sum_{m_2''}(m_2''^2|c_{m_2''}|^2)] \\
&+ \frac{1}{2}\epsilon(t)\mu_2[(\delta_{m_2,m_2'+1}+\delta_{m_2,m_2'-1}) - \delta_{m_2,m_2'}\sum_{m_2''}(c^*_{m_2''}c_{m_2''-1}+c^*_{m_2''}c_{m_2''+1})] \\
&+ \frac{\mu_1\mu_2}{16\pi\varepsilon_0 R^3}\sum_{m_1}[(1-3\cos^2\theta)[(\delta_{m_2,m_2'+1}+\delta_{m_2,m_2'-1}) \\
&- \delta_{m_2,m_2'}\sum_{m_2''}(c^*_{m_2''}c_{m_2''-1}+c^*_{m_2''}c_{m_2''+1})](c^*_{m_1}c_{m_1-1}+c^*_{m_1}c_{m_1+1}) \\
&- (1-3\sin^2\theta)[(\delta_{m_2,m_2'+1}-\delta_{m_2,m_2'-1}) \\
&- \delta_{m_2,m_2'}\sum_{m_2''}(c^*_{m_2''}c_{m_2''-1}-c^*_{m_2''}c_{m_2''+1})](c^*_{m_1}c_{m_1-1}-c^*_{m_1}c_{m_1+1}) \\
&+ i3\cos\theta\sin\theta([(\delta_{m_2,m_2'+1}+\delta_{m_2,m_2'-1}) \\
&- \delta_{m_2,m_2'}\sum_{m_2''}(c^*_{m_2''}c_{m_2''-1}+c^*_{m_2''}c_{m_2''+1})](c^*_{m_1}c_{m_1-1}-c^*_{m_1}c_{m_1+1}) \\
&+ [(\delta_{m_2,m_2'+1}-\delta_{m_2,m_2'-1}) - \delta_{m_2,m_2'}\sum_{m_2''}(c^*_{m_2''}c_{m_2''-1}-c^*_{m_2''}c_{m_2''+1})](c^*_{m_1}c_{m_1-1}+c^*_{m_1}c_{m_1+1}))]\Bigg] c_{m_2'}
\end{aligned} \tag{38}
$$

Note that in the limit where $R \to \infty$, the equations of motion for each rotor become uncoupled from those of the other rotor, as is expected:

$$
\begin{aligned}
i\hbar\frac{\partial c_{m_1}}{\partial t} &= \sum_{m_1'} \tilde{H}_{1m_1,m_1'} c_{m_1'} \\
&= \sum_{m_1'} \Bigg[\delta_{m_1,m_1'}\frac{\hbar^2}{2I}[m_1^2 - \sum_{m_1''}(m_1''^2|c_{m_1''}|^2)] \\
&+ \frac{1}{2}\epsilon(t)[\mu_1(\delta_{m_1,m_1'+1}+\delta_{m_1,m_1'-1}) - \delta_{m_1,m_1'}\sum_{m_1''}(c^*_{m_1''}c_{m_1''-1}+c^*_{m_1''}c_{m_1''+1})]\Bigg] c_{m_1'}
\end{aligned} \tag{39}
$$

$$
\begin{aligned}
i\hbar\frac{\partial c_{m_2}}{\partial t} &= \sum_{m_2'} \tilde{H}_{2m_2,m_2'} c_{m_2'} \\
&= \sum_{m_2'} \Bigg[\delta_{m_2,m_2'} \frac{\hbar^2}{2I}[m_2^2 - \sum_{m_2''}(m_2''^2|c_{m_2''}|^2)] \\
&+ \frac{1}{2}\epsilon(t)\mu_2[(\delta_{m_2,m_2'+1} + \delta_{m_2,m_2'-1}) - \delta_{m_2,m_2'} \sum_{m_2''}(c^*_{m_2''}c_{m_2''-1} + c^*_{m_2''}c_{m_2''+1})]\Bigg] c_{m_2'}
\end{aligned} \tag{40}
$$

Keep in mind also that the term $\delta_{m_1,m_1'}b_1(t)$, where:

$$
b_1(t) \equiv -(\sum_{m_1''}(m_1''^2|c_{m_1}''|^2) + \sum_{m_1''}(c^*_{m_1''}c_{m_1''-1} + c^*_{m_1''}c_{m_1''+1}) + \frac{\mu_1\mu_2}{16\pi\varepsilon_0 R^3}\sum_{m_2}[(1-3\cos\theta^2)\cdots] \tag{41}
$$

in 37 and 39 result in an overall global phase of $U_1(t)^{-1} \equiv e^{-\frac{i}{\hbar}\int b_1(t)dt}$ in Ψ_1, and the term $\delta_{m_2,m_2'}b_2(t)$, where:

$$
b_2(t) \equiv -(\sum_{m_2''}(m_2''^2|c_{m_2}''|^2) + \sum_{m_2''}(c^*_{m_2''}c_{m_2''-1} + c^*_{m_2''}c_{m_2''+1}) + \frac{\mu_1\mu_2}{16\pi\varepsilon_0 R^3}\sum_{m_1}[(1-3\cos\theta^2)\cdots] \tag{42}
$$

in 38 and 40 result in an overall global phase of $U_2(t)^{-1} \equiv e^{\frac{i}{\hbar}\int b_2(t)dt}$ in Ψ_2. Thus, if we apply the unitary transformations that will yield the same expectation values:

$$
|\Phi_1\rangle \equiv \hat{U}_1 |\Psi_1\rangle \tag{43}
$$

$$
|\Phi_2\rangle \equiv \hat{U}_2 |\Psi_2\rangle \tag{44}
$$

and let $\tilde{c}_{m_1} \equiv \langle m_1|\Phi_1\rangle$ and $\tilde{c}_{m_2} \equiv \langle m_2|\Phi_2\rangle$, we have the following, much-simplified, differential equations:

$$
\begin{aligned}
i\hbar\frac{\partial \tilde{c}_{m_1}}{\partial t} &= \sum_{m_1'} \tilde{H}'_{1m_1,m_1'} \tilde{c}_{m_1'} \\
&= \sum_{m_1'} \Bigg[\delta_{m_1,m_1'} \frac{\hbar^2}{2I} m_1^2 + \frac{1}{2}\epsilon(t)\mu_1(\delta_{m_1,m_1'+1} + \delta_{m_1,m_1'-1}) \\
&+ \frac{\mu_1\mu_2}{16\pi\varepsilon_0 R^3}\sum_{m_2}[(1-3\cos^2\theta)(\delta_{m_1,m_1'+1} + \delta_{m_1,m_1'-1})(\tilde{c}^*_{m_2}\tilde{c}_{m_2-1} + \tilde{c}^*_{m_2}\tilde{c}_{m_2+1}) \\
&- (1-3\sin^2\theta)(\delta_{m_1,m_1'+1} - \delta_{m_1,m_1'-1})(\tilde{c}^*_{m_2}\tilde{c}_{m_2-1} - \tilde{c}^*_{m_2}\tilde{c}_{m_2+1}) \\
&+ i3\cos\theta\sin\theta((\delta_{m_1,m_1'+1} + \delta_{m_1,m_1'-1})(\tilde{c}^*_{m_2}\tilde{c}_{m_2-1} - \tilde{c}^*_{m_2}\tilde{c}_{m_2+1}) \\
&+ (\delta_{m_1,m_1'+1} - \delta_{m_1,m_1'-1})(\tilde{c}^*_{m_2}\tilde{c}_{m_2-1} + \tilde{c}^*_{m_2}\tilde{c}_{m_2+1}))]\Bigg] \tilde{c}_{m_1'}
\end{aligned} \tag{45}
$$

$$
\begin{aligned}
i\hbar\frac{\partial \tilde{c}_{m_2}}{\partial t} &= \sum_{m_2'} \tilde{H}'_{2 m_2, m_2'} \tilde{c}_{m_2'} \\
&= \sum_{m_2'} \Bigg[\delta_{m_2,m_2'} \frac{\hbar^2}{2I} m_2^2 + \frac{1}{2}\epsilon(t)\mu_2(\delta_{m_2,m_2'+1} + \delta_{m_2,m_2'-1}) \\
&+ \frac{\mu_1\mu_2}{16\pi\varepsilon_0 R^3} \sum_{m_1} [(1-3\cos^2\theta)(\delta_{m_2,m_2'+1} + \delta_{m_2,m_2'-1})(\tilde{c}^*_{m_1}\tilde{c}_{m_1-1} + \tilde{c}^*_{m_1}\tilde{c}_{m_1+1}) \\
&- (1-3\sin^2\theta)(\delta_{m_2,m_2'+1} - \delta_{m_2,m_2'-1})(\tilde{c}^*_{m_1}\tilde{c}_{m_1-1} - \tilde{c}^*_{m_1}\tilde{c}_{m_1+1}) \\
&+ i3\cos\theta\sin\theta((\delta_{m_2,m_2'+1} + \delta_{m_2,m_2'-1})(\tilde{c}^*_{m_1}\tilde{c}_{m_1-1} - \tilde{c}^*_{m_1}\tilde{c}_{m_1+1}) \\
&+ (\delta_{m_2,m_2'+1} - \delta_{m_2,m_2'-1})(\tilde{c}^*_{m_1}\tilde{c}_{m_1-1} + \tilde{c}^*_{m_1}\tilde{c}_{m_1+1}))] \Bigg] \tilde{c}_{m_2'}
\end{aligned} \tag{46}
$$

Or:

$$
\begin{aligned}
i\hbar\frac{\partial \Phi_1}{\partial t} &= \tilde{H}'_1 \Phi_1 \\
i\hbar\frac{\partial \Phi_2}{\partial t} &= \tilde{H}'_2 \Phi_2
\end{aligned} \tag{47}
$$

Note that, had we not included the global phase in our original TDH Ansatz, we could have implemented similar unitary transformations as above in the subsequent derivation to arrive at identical equations of motion.

6.2 Numerical methods

There are several numerical methods we can employ to implement the above equations of motion derived from the TDH ansatz. For purposes of efficiency and speed, we have elected the split-operator approximation method to solve for and evolve our wavefunction, following the example provided by Hongling Yu, rather than the more exact short-time propagator and Runge-Kutta. As we shall see, for cases in which the TDH ansatz is valid, this approximation method does not sacrifice much accuracy. In this section, we shall discuss the two alternatives to the more cumbersome Runge-Kutta ODE solver: the short-time propagator and the split-operator method. In the next section, we shall compare the results given by the TDH ansatz to the Exact solution for the coupled dipole wavefunctions.

6.2.1 Short-time propagator

Given the Hermitian Hamiltonian operators $\tilde{H}'_i$ in equations 45 and 46, and letting $\tilde{H}'_i$ be diagonalized by the unitary matrix A_i such that for:

$$\tilde{H}''_i = A_i^\dagger \tilde{H}'_i A_i$$

where the j-th row vector A_{i_j} is the orthogonal eigenvector corresponding to the j-th eigenvalue $\lambda_j = \tilde{H}''_{i\,j,j}$ of $\tilde{H}'_i$.

Thus, if we split our propagation time T into increments of dt such that $T/dt = n$, $\{0, dt, 2dt, \ldots, ndt\}$, the short-time propagator proceeds by incrementing:

$$\Phi_1(t+dt) = A_1 e^{-\frac{i}{\hbar}\tilde{H}''_1 dt} A_1^\dagger \Phi_1(t)$$
$$\Phi_2(t+dt) = A_2 e^{-\frac{i}{\hbar}\tilde{H}''_2 dt} A_2^\dagger \Phi_2(t)$$

6.2.2 Split-operator approximation

Given the Hamiltonian operators $\tilde{H}'_i$ in equations 45 and 46, we can deconstruct it as follows:

$$\tilde{\mathrm{H}}'_i = H_{0i} + V_i$$

where

$$H_{0_{i_{m_i,m'_i}}} = \delta_{m_i,m'_i}\frac{\hbar^2}{2I}m_i^2 + \frac{1}{2}\epsilon(t)\mu_1(\delta_{m_i,m'_i+1} + \delta_{m_i,m'_i-1}) \tag{48}$$

and V_i are the respective potentials/interaction terms for each dipole rotor. Then, letting H_{0_i} and V_i be diagonalized by the unitary matrices B_i and C_i such that:

$$\mathrm{H}''_{0_i} = B_i^\dagger H_{0_i} B_i$$
$$\mathrm{V}''_i = C_i^\dagger V_i C_i$$

where the j-th row vector B_{i_j} is the orthogonal eigenvector corresponding to the j-th eigenvalue $\lambda_j = H''_{0_i\,j,j}$ of H_{0_i} and the j-th row vector C_{i_j} is the orthogonal eigenvector corresponding to the j-th eigenvalue $\lambda_j = V''_{i\,j,j}$ of V_i.

Thus, if we split our propagation time T into increments of dt such that $T/dt = n$, $\{0, dt, 2dt, \ldots, ndt\}$, the short-time propagator proceeds by incrementing:

$$\Phi_1(t+dt) = ((B_1 e^{-\frac{i}{2\hbar}H_{0_1}dt} B_1^\dagger)(C_1 e^{-\frac{i}{\hbar}V_1 dt} C_1^\dagger)(B_1 e^{-\frac{i}{2\hbar}H_{0_1}dt} B_1^\dagger))\Phi_1(t)$$
$$\Phi_2(t+dt) = ((B_2 e^{-\frac{i}{2\hbar}H_{0_2}dt} B_2^\dagger)(C_2 e^{-\frac{i}{\hbar}V_2 dt} C_2^\dagger)(B_2 e^{-\frac{i}{2\hbar}H_{0_2}dt} B_2^\dagger))\Phi_2(t)$$

6.3 Comparing the accuracy of the TDH ansatz to the exact solution

6.3.1 The exact solution

The exact solution for the state of the combined wavefunction of the two rotors is as follows:

$$|\Psi_1\Psi_2\rangle = \sum_{m_1}\sum_{m_2} c_{m_1,m_2}\,|m_1\rangle \otimes |m_2\rangle$$

The Hamiltonian $\hat{H}^{[2]}$ governing $|\Psi_1\Psi_2\rangle$ is given by (in the angular representation):

$$\mathrm{H}^{[2]} = -\frac{h^2}{2I}\left(\frac{\partial^2}{\partial\phi_1^2} \otimes 1 + 1 \otimes \frac{\partial^2}{\partial\phi_2^2}\right) - \epsilon(t)(\mu_1 \cos\phi_1 \otimes 1 + 1 \otimes \mu_2 \cos\phi_2)$$
$$+ \frac{\mu_1\mu_2}{4\pi\epsilon_0 R^3}[(1 - 3\cos^2\theta)\cos\phi_1 \otimes \cos\phi_2 + (1 - 3\sin^2\theta)\sin\phi_1 \otimes \sin\phi_2$$
$$+ 3\cos\theta\sin\theta(\cos\phi_1 \otimes \sin\phi_2 + \sin\phi_1 \otimes \cos\phi_2)]$$

Then:

$$\mathrm{i}\hbar\frac{\partial}{\partial t}|\Psi_1\Psi_2\rangle = \hat{H}^{[2]}|\Psi_1\Psi_2\rangle$$

The exact solution to these equations of motion was given by Hongling Yu by constructing out of the elements of the $2{*}m{+}1$-by-$2{*}m{+}1$ tensor representation of $|\Psi_1\Psi_2\rangle$ a $(2*m+1)^2$ vector, and out of $H^{[2]}$ a corresponding $(2*m+1)^2$-by-$(2*m+1)^2$ matrix. The solution is then given by iterating a split-operator method similar to that described in 6.2.2.

6.3.2 Comparison

We now compare the results given by the TDH ansatz as solved by the split-operator method to those given by the TDH ansatz as solved by the short-time propagator and Runga-Kutta, as well as the exact solution introduced above. The following figures show the time evolution of the wavefunctions (manifested by the evolution of the expected value $\langle\cos\phi_1|\Psi_1|\cos\phi_1\rangle + \langle\cos\phi_2|\Psi_2|\cos\phi_2\rangle$) of two rotors with the identical rotational constant of $B = 4.033e - 17J$, dipole moment $\mu = 0.709e - 18J/T$, orientation $\theta = \pi/2$ over 10 rotational periods ($T = 2\pi\frac{\hbar}{B} = 1.6430e - 10s$), over a range of separations r. The control field is:

$$\epsilon(t) = a_0[0.2\cos(w_1 t) + 0.3\cos(w_2 t) + 0.5\cos(w_3 t)]e^{(-(t-5T)^2/(8T^2))} \qquad (49)$$

where $a_0 = 1e13\ V/m$, and $w_1 = B/\hbar$, $w_2 = 3B/\hbar$, $w_3 = 4B/\hbar$.

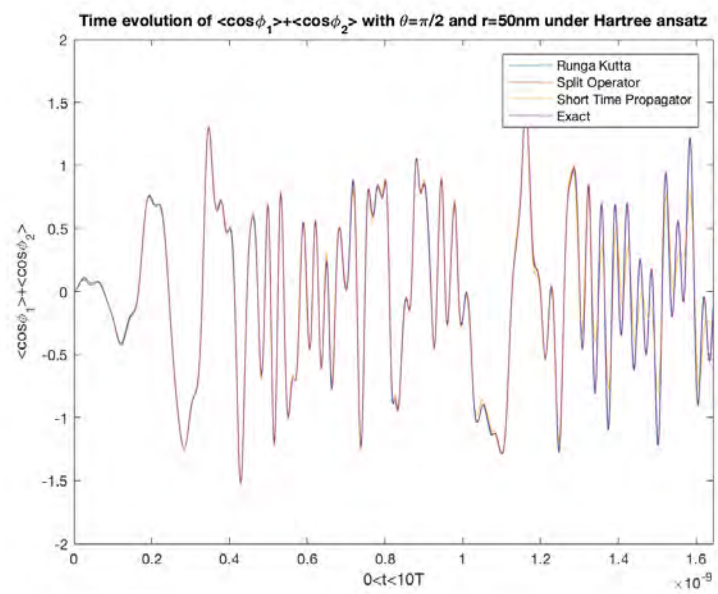

Figure 1: 50 nm

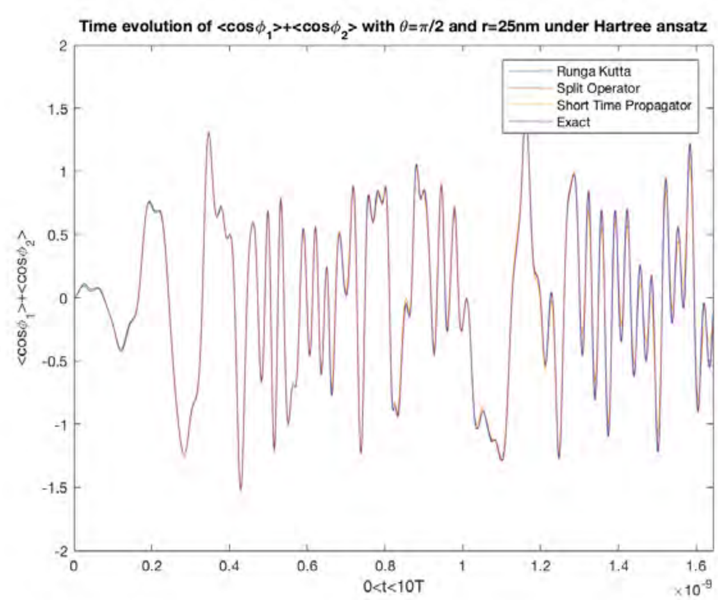

Figure 2: 25 nm

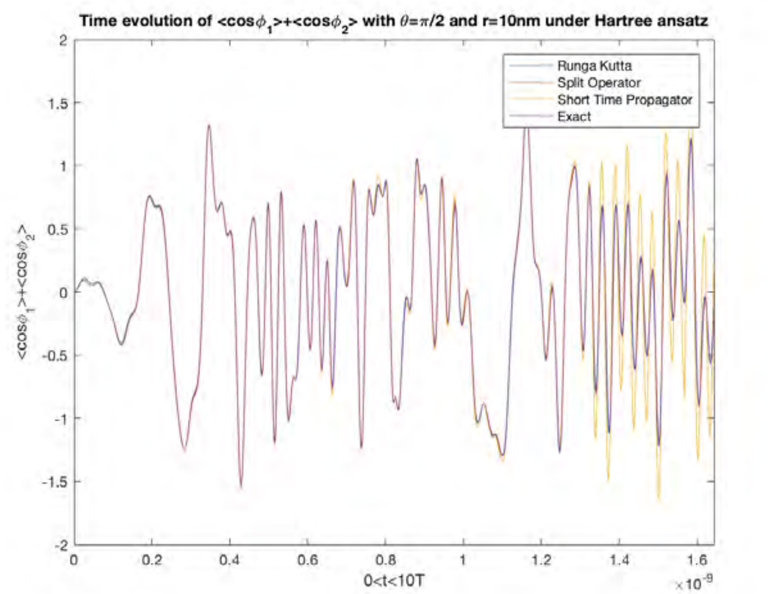

Figure 3: 10 nm

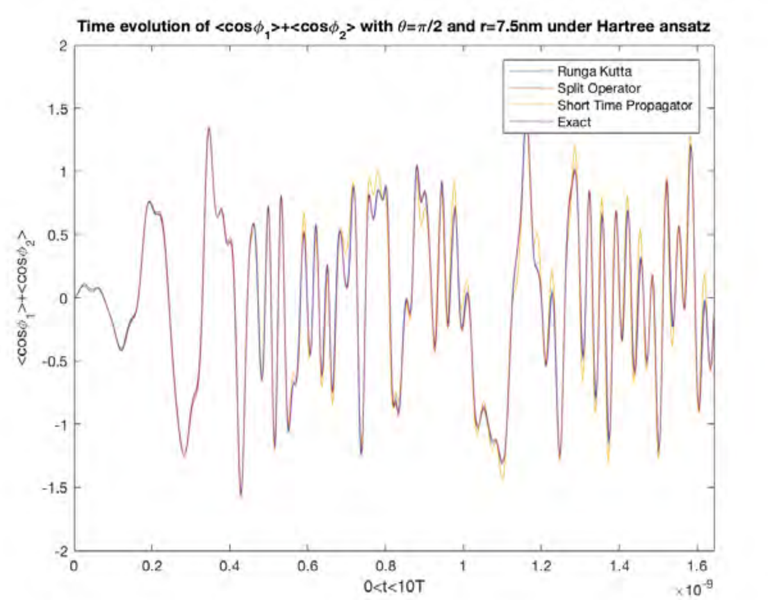

Figure 4: 7.5 nm

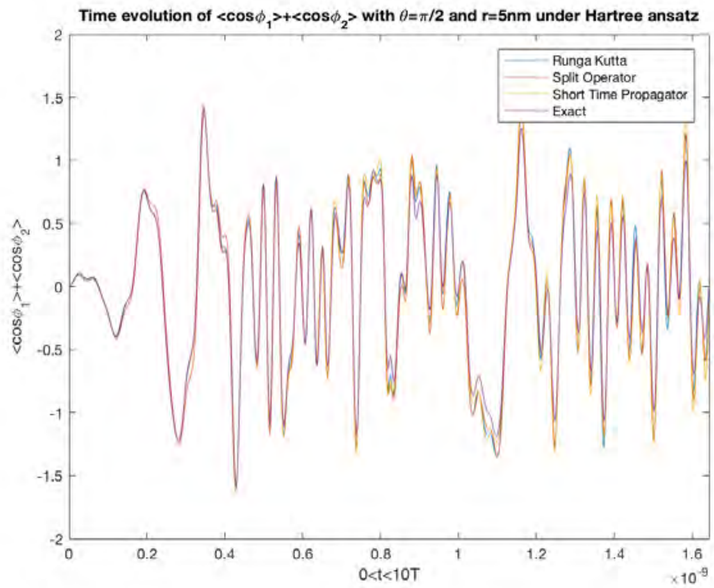

Figure 5: 5 nm

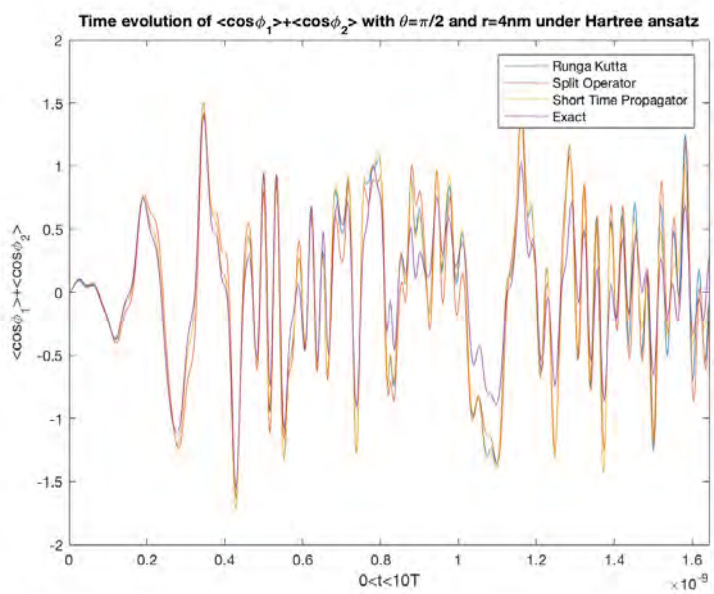

Figure 6: 4 nm

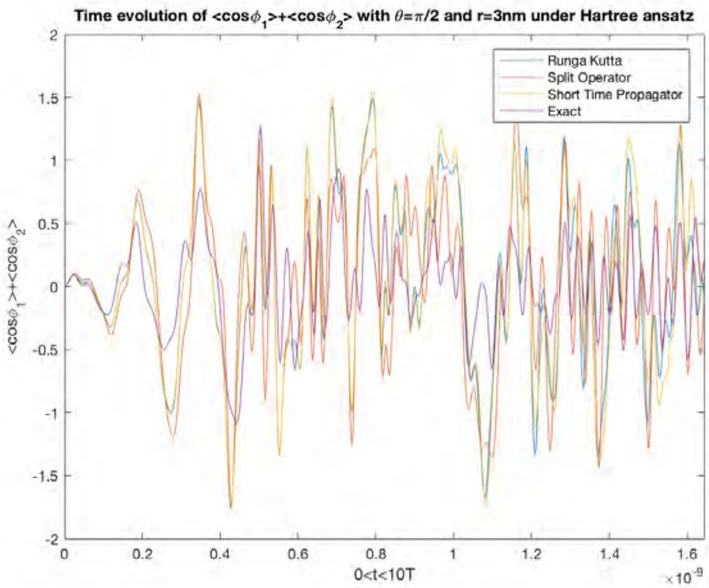

Figure 7: 3 nm

Clearly, the split operator method agrees with the more accurate Runga-Kutta and short-time-propagator methods in the region where the interaction term does not dominate the Hamiltonian ($r \geq 3\ nm$). In addition, for distances where the interaction term becomes negligible ($r \geq 6\ nm$), the TDH ansatz and the exact solution agree almost completely. Small departures from the exact solution in the TDH ansatz solution only become manifested, thus, as the interaction term becomes stronger and strong in the region of interest ($3\ nm < r < 6\ nm$), before the approximation completely breaks down.

7 Conclusion

Having established the applicability and utility of the TDH ansatz in solving the equations of motion, our next step would be to implement it within the DMORPH scheme outlined earlier in Section 4. However, several computational issues still persist within the evaluation of the gradient. As of now, we have determined that operators involved in evolving the Laplace multiplier costate $|\lambda\rangle$ are not Hermitian. However, methods still exist for diagonalizing them in order to facilitate fast calculations of their corresponding unitary operators. The focus of our research right now lies in examining and implementing these methods.

After we have successfully used TDH to reduce the calculation time required to optimize the objective functional through DMORPH in the two-rotor case, the flexibility and efficiency of TDH will allow us to immediately adapt this method for the three-rotor case. Afterwards, we will also be able to examine systems that involve entanglement, as well as generalizing to systems possessing other potentials.