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I, Matt Ellis, confirm that the work presented in this thesis is my own. Where information has been derived from other sources, I confirm that this has been indicated in the work.

Abstract

My research is about stuff.

It begins with a study of some stuff, and then some other stuff and things.

There is a 300-word limit on your abstract.

Acknowledgements

Acknowledge all the things!

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Chapter 1

Introduction

1.1 Charge Transport in Organic Semiconductors

1.1.1 Organic Semiconductors

Conductive polymers were first discovered in 1977 by Shirakawa et al^{1,2} for which they were awarded the Nobel prize in Chemistry. Recently these materials have become ubiquitous in many technologies, such as in organic solar cells³, organic field-effect transistors (OFET)⁴ and organic light-emitting diodes (OLED)⁵. While the other two technologies lag behind their inorganic counterparts, uptake of OLED screens is becoming ubiquitous -especially in the smartphone and television market due to their flexibility, better colour representation and lower energy consumption than standard backlit LCD displays. OLEDs have also found uses in lighting with their efficiency rivalling that of fluorescent tubes^{6,7}. Although, industry has made large strides in fabricating and using these materials the exact nature of the charge transport is still poorly understood. Conventional hopping and band theories break down in the regime of partial delocalisation of the charge carriers and atomistic simulations are required for a realistic picture.

Typically charge carrier mobilities in ‘good’ organic semiconductors (OSCs) fall between 1-10 cm²V⁻¹s⁻¹⁸. This is beyond the range of hopping model validity (~ 1 cm²V⁻¹s⁻¹) and below that of band theory (> 50 cm²V⁻¹s⁻¹)⁹. In this intermediate regime the charge carriers are typically not completely delocalised at the valence band edges (band regime) or localised to a single site/molecule (hopping regime) but delocalised over a

few/tens of molecules. Without any analytic approaches currently being valid in this regime many computational approaches have been developed to investigate the underlying charge transport mechanisms¹⁰.

1.2 Atomistic Simulations of Nonadiabatic Processes

In simulating processes involving electronic transfers a key approximation used in conventional molecular dynamics (MD) breaks down. That is the Born-Oppenheimer or adiabatic approximation¹¹. This approximation, relied upon for almost a century¹², hinges on the fact that nuclei are more massive than electrons and are approximately stationary with respect to electron movement¹³. This results in nuclear evolution that is governed by a single, adiabatic, potential energy surface. However, in many interesting processes, such as the proton coupled electron transfer in photosynthesis and respiration^{14,15}, non-radiative decay and photochemical processes, electronic transitions between adiabatic potential energy surfaces occur¹⁶. Simulating these processes requires non-adiabatic molecular dynamics (NAMD) techniques to be developed, to correctly capture dynamical properties.

There have been many techniques proposed for use in NAMD such as the quantum classical Liouville equation¹⁷, multiple spawning¹⁸ or nonadiabatic Bohmian dynamics¹⁹. However, two of the most popular are trajectory surface hopping²⁰ and mean-field approaches²¹. This is probably due to their relative simplicity to implement, efficiency for large systems and proven efficacy in a wide variety of situations²². In these approaches the general aim is to treat as much of the system as possible with (computationally cheaper) classical mechanics. While handling all necessary parts with quantum mechanics²³. In Surface Hopping, Ehrenfest and Coupled-Trajectory Mixed Quantum-Classical molecular dynamics (CTMQC) one treats the nuclear subsystem classically and the electronic one quantum mechanically. The nuclei are propagated using a velocity verlet algorithm according to Newton's laws. The electrons are propagated using a fourth order Runge

Kutta algorithm according to the time-dependent Schrödinger equation. This is normally expanded as a linear combination of adiabatic or diabatic states. The nuclei and electrons can also interact. Taking account of this interaction is where these different atomistic simulation techniques differ. Both trajectory surface hopping (SH) and Ehrenfest have significant downsides that the new algorithm CTMQC aims at overcoming with minimal computational overheads. In this project I will be developing an efficient implementation of CTMQC within the CP2K code.

1.2.1 Surface Hopping and Ehrenfest Dynamics

An important technique in the field of mixed quantum classical nonadiabatic molecular dynamics is Ehrenfest dynamics. Assuming we treat the nuclei classically the Ehrenfest equations can be rigorously derived from the electronic Schrödinger equation. This is done by assuming that the nuclei's motion is provided by a single population weighted average potential energy surface. This average is taken from the adiabatic potential energy surfaces (eigenvalues of the Hamiltonian) where weights are provided by the populations of each adiabatic state. This effective potential energy surface is shown in fig 1.1. In this way the electronic subsystem influences the propagation of the nuclei. The propagation of the forces and the electrons are controlled by equations (1.1) and (1.2).

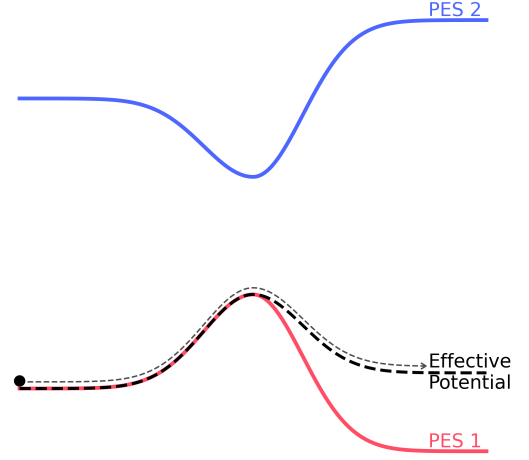


Figure 1.1: An example of a typical Ehrenfest simulation near an avoided crossing. The black lines represent the adiabatic potential energy surface due to the ground (PES 1) and excited (PES 2) state. The red line represents the population weighted average potential the nuclei travel on.

$$F_v^{Ehren} = \sum_i^{N_{st}} |C_i|^2 \nabla_v E_i + \sum_{i,j}^{N_{st}} C_i^* C_j (E_j - E_i) d_{ij,v} \quad (1.1)$$

$$i\hbar \vec{C}_m = C_m E_m - i\hbar \sum_n^{N_{st}} C_n d_{mn}^{ad} \quad (1.2)$$

In the above equations C_i is the adiabatic expansion coefficient for state i , E_m is the energy of adiabatic state m , $d_{mn,v}^{ad}$ is the nonadiabatic coupling (in the adiabatic basis) between states m and n for atom v . The d_{mn}^{ad} are the nonadiabatic coupling elements expressed in the adiabatic basis. Although the Ehrenfest method has been applied with success in many systems^{24–26} it has a number of key shortcomings. Namely, its inability to capture the branching of the nuclear wavefunction as propagation occurs on only a single potential energy surface and its poor account of the decoherence of the electronic and

nuclear subsystem after an avoided crossing. Ehrenfest also violates detailed balance by populating all adiabatic states evenly^{11,27}. In the limit of infinite states this results in infinite electronic temperature²⁸.

Possibly the most popular technique in NAMD is trajectory surface hopping. In trajectory surface hopping the shape of the potential energy surface is determined by a series of discrete stochastic hops between adiabatic potential energy surfaces²⁷. See fig 1.2. The probability of these hops is determined by the non-adiabatic coupling between states. A swarm of trajectories are used and the probability a hop (non-adiabatic coupling) determines how many of these change state. The nuclear dynamics are dictated by the shape of the energy surface they are travelling on. This method can capture the branching of nuclear wavepacket unlike Ehrenfest. However, it still suffers from a number of issues. The original ‘fewest switches surface hopping’ proposed by John Tully suffered from

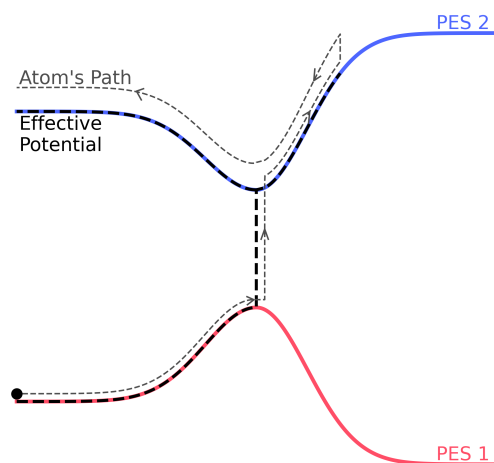


Figure 1.2: An example of a typical Surface Hopping simulation near an avoided crossing. The black lines represent the adiabatic potential energy surface due to the ground (PES 1) and excited (PES 2) state. The red line represents the discontinuous effective potential the nuclei travel on.

bad overcoherence of the nuclear and electronic subsystems. That is the electronic and nuclear motion was coupled long after the region of high non-adiabatic coupling (crossing region). The fact that the hops are instant leads to discontinuities and methods need to be implemented to fix these such as velocity re-scaling. Finally, perhaps the most important shortcoming is that this technique has not been derived from first principles and cannot be guaranteed to work generally. These problems have lead to a number of other techniques being developed. One of these, CTMQC, is the subject of this report.

Chapter 2

CTMQC applied to the Tully Models

The Tully models, first proposed by John Tully in 1990²⁹, are a collection of simple 1 dimensional model systems. They were designed to be simple enough to obtain accurate quantum results to benchmark new nonadiabatic molecular dynamics (NAMD) methods against. Originally there were 3, 1 dimensional, 1 atom models. However, in this work an extra model has been introduced with parameters taken from Gossel, 18³⁰. This is to allow a full comparison of my implementation of CTMQC with the literature. In this chapter my implementation of CTMQC will be tested using these model systems and by comparing my results with those in the literature.

In each of the Tully models the (diabatic) Hamiltonian is a function of nuclear positions and is a 2×2 matrix that takes the form:

$$\hat{H} = \frac{\hat{P}^2}{2M} + \begin{pmatrix} H_{11}(\mathbf{R}) & H_{12}(\mathbf{R}) \\ H_{21}(\mathbf{R}) & H_{22}(\mathbf{R}) \end{pmatrix} \quad (2.1)$$

The nuclear mass has been set to 2000 a.u.. This was set to be very close to the proton's mass of 1836 a.u. so we can expect significant quantum effects that classical theory couldn't replicate. The values of the Hamiltonian matrix elements are set to produce systems that resemble common features in a typical nonadiabatic simulation such as avoided crossings and regions of extended coupling. The parameters used in each systems' Hamiltonian were taken from Gossel, 18³⁰ in order to compare the 2 implementations. These can be found in appendix A.

In order to propagate dynamics in the adiabatic basis we need to calculate various quantities from the hamiltonian at each timestep. These are, for Ehrenfest, the (adiabatic) nonadiabatic coupling vector ($\mathbf{d}_{lk}^{(I)}$) and the adiabatic energies ($E_l^{(I)}$). In the full CTMQC simulations we must also calculate the adiabatic momentum term $\mathbf{f}_l^{(I)}$ from the Hamiltonian. The adiabatic energies are the eigenvalues of the Hamiltonian. The adiabatic NACV can be calculated via an (explicit Euler) finite difference method and equation (2.2) below.

$$\mathbf{d}_{lk}^{(I)} = \langle \psi_l^{(I)} | \nabla \psi_k^{(I)} \rangle \quad (2.2)$$

Where $\psi_l^{(I)}$ is the adiabatic electronic basis function. This is given by the eigenvector of the Hamiltonian, on replica I, corresponding to state l. Illustrations of these 2 properties can be found below in fig 2.1 for each of the 4 models systems.

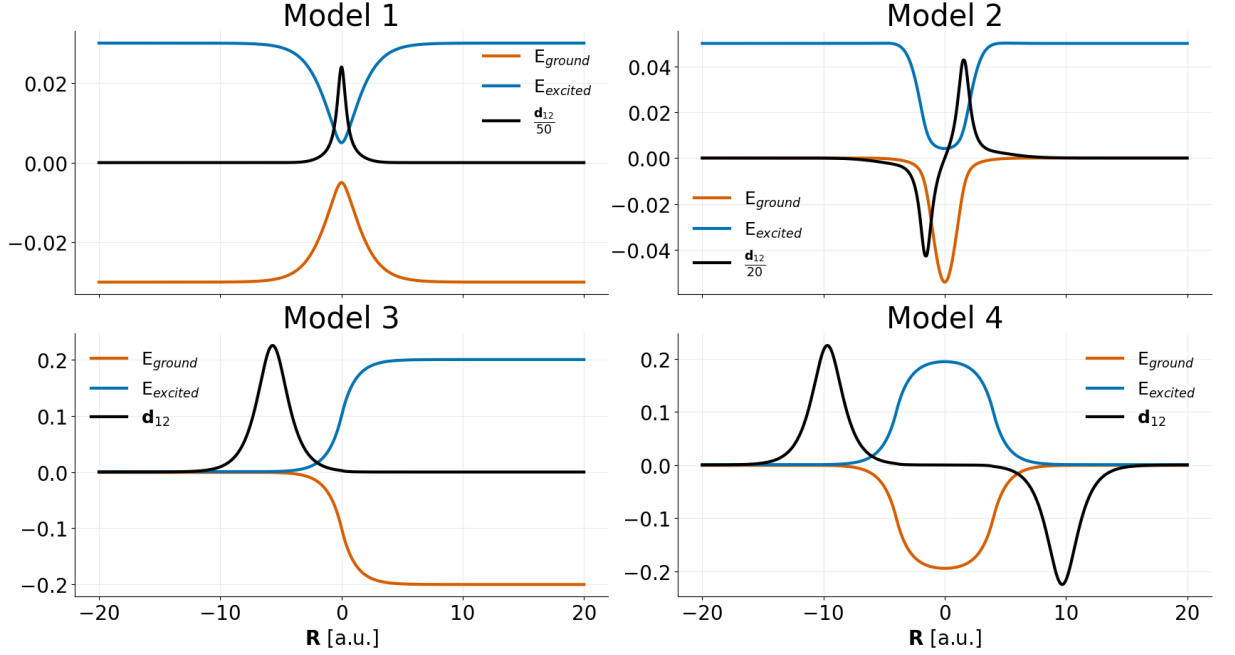


Figure 2.1: Adiabatic potential energy surfaces (orange and blue) and element 1, 2 of the nonadiabatic coupling vector (black) for the 4 model systems. For parameters see appendix A.

In order to initialise the simulations coordinates and velocities were sampled from the Wigner phase-space distribution of a gaussian nuclear wavepacket given by equation (2.3). A derivation of this can be found in appendix B.

$$\chi(R,0) = \frac{1}{(\pi\mu^2)^{\frac{1}{4}}} e^{-\frac{(R-R_0)^2}{2\mu^2} + ik_0(R-R_0)} \quad (2.3)$$

The adiabatic coefficients were initialised purely on the ground state and the initial width of the nuclear wavepacket was set to $\mu = \sqrt{2}$ bohr. 2 values of initial momenta k_0 were chosen for each model, 1 low value and another higher one. Full details of all input parameters can be found in appendix A.

Chapter 3

CTMQC applied to molecular systems

Chapter 4

Extending surface hopping

Fragment-orbital based surface hopping (FOB-SH) is a technique developed within the Blumberger group³¹ designed to simulate large molecular systems. It has had much success in the study of organic crystalline materials^{32,33}. Most notably the electron/hole mobilities of a variety of common organic semi-conducting materials were measured within a factor of 2 of experimental measurements. However, in order to study very large amorphous and semi-crystalline systems some more memory/computation optimisations were required and electrostatic interactions (which weren't important in previous systems) needed to be accounted for. In this chapter I outline some minor improvements I implemented within the surface hopping code as well as the method used to implement the electrostatic interactions.

4.1 Code Optimisations

4.2 Electrostatics interaction within FOB-SH

FOB-SH is a variant of Tully's original fewest switches surface hopping (ref John Tully 1990 original surface hopping paper). The electron and nuclear dynamics are dictated by the Hamiltonian, where the spatial derivative of the diagonal elements (site-energies) give the nuclear forces which come from a classical forcefield and the off-diagonal elements (electron couplings) are proportional to the overlap of the diabatic wavefunctions. Each site-energy, $H_{\gamma\gamma}$, is defined as the potential energy of the system where the excess charge is localised on a single molecule, γ . The input parameters such as the charge distribution or the strength of the bonds are different for molecule γ than the other molecules,

resulting in different forces/potentials. The different potentials from each permutation of the charge state are saved as the site-energies, the forces are saved in a different array of size $(N_{states}, N_{atoms}, 3)$. To implement electrostatic interactions the potential and the forces within the surface hopping framework will have to be altered.

To calculate the electrostatic contribution from each atom to the forces and potential the standard Ewald method was chosen, with some additional tricks to reduce the computational cost. The Ewald method, first published by Paul Ewald in 1921 (NEED REF), is a near ubiquitous method used to evaluate the potential and forces from a set of point charges. This is equivalent to carrying out the much slower to converge (NEED REF) and conditionally convergent traditional coulomb sum. The Ewald method relies on separating the traditional coulomb summation into 2 quickly converging parts; a long range term and short range term. The short range term is carried out in real space and the long range term is carried out in reciprocal space

Chapter 5

Surface hopping applied to large systems

Chapter 6

General conclusions

Appendix A

Tully Model Paramters

A.1 Model 1 -Single Avoided Crossing

Hamiltonian Paramters:

$$H_{11}(\mathbf{R}) = A \tanh(B\mathbf{R})$$

$$H_{12}(\mathbf{R}) = Ce^{-D\mathbf{R}^2}$$

$$H_{21}(\mathbf{R}) = H_{12}(\mathbf{R})$$

$$H_{22}(\mathbf{R}) = -H_{11}(\mathbf{R})$$

Where A = 0.03, B = 0.4, C = 0.005 and D = 0.3

Quantity	Value	Unit
Initial Position	-20	a.u.
Initial Velocities	15.0, 25.0	a.u.
Initial Adiab Pop	ground state	-
Simulation Time	6000, 4000	a.u.
$\sigma_v^{(I)}$	0.5	a.u.
M (σ constant)	40	-
$\Delta t_{\text{nuclear}}$	0.1	fs
$\Delta t_{\text{electronic}}$	0.01	fs
$\frac{\delta \mathbf{R}_{lk,v}^{(I)}}{\delta t}$ threshold	0.15	a.u.
N_{rep}	200	-

A.2 Model 2 -Dual Avoided Crossing

	Quantity	Value	Unit
Hamiltonian Paramters:	Initial Position	-8	a.u.
	Initial Velocities	16.0, 30.0	a.u.
$H_{11}(\mathbf{R}) = 0$	Initial Adiab Pop	ground state	-
$H_{12}(\mathbf{R}) = Ce^{-D\mathbf{R}^2}$	Simulation Time	2500, 1500	a.u.
$H_{21}(\mathbf{R}) = H_{12}(\mathbf{R})$	$\sigma_v^{(I)}$	0.5	a.u.
$H_{22}(\mathbf{R}) = -Ae^{-B\mathbf{R}^2} + E$	M (σ constant)	40	-
	$\Delta t_{\text{nuclear}}$	0.1	fs
Where A = 0.1, B = 0.28, C = 0.015, D =	$\Delta t_{\text{electronic}}$	0.01	fs
0.06 and E = 0.05	$\frac{\delta \mathbf{R}_{lk,v}^{(I)}}{\delta t}$ threshold	0.15	a.u.
	N_{rep}	200	-

A.3 Model 3 -Extended Coupling

	Quantity	Value	Unit
Hamiltonian Paramters:	Initial Position	-15	a.u.
	Initial Velocities	10, 30	a.u.
$H_{11}(\mathbf{R}) = A$	Initial Adiab Pop	ground state	-
$H_{12}(\mathbf{R}) = \begin{cases} Be^{C\mathbf{R}}, & R \leq 0 \\ B(2 - e^{-C\mathbf{R}}), & R > 0 \end{cases}$	Simulation Time	5000, 1500	a.u.
$H_{21}(\mathbf{R}) = H_{12}(\mathbf{R})$	$\sigma_v^{(I)}$	0.5	a.u.
$H_{22}(\mathbf{R}) = -H_{11}(\mathbf{R})$	M (σ constant)	40	-
	$\Delta t_{\text{nuclear}}$	0.1	fs
	$\Delta t_{\text{electronic}}$	0.01	fs
Where A = 6×10^{-4} , B = 0.1 and C = 0.9	$\frac{\delta \mathbf{R}_{lk,v}^{(I)}}{\delta t}$ threshold	0.15	a.u.
	N_{rep}	200	-

A.4 Model 4 -Dual Arch

Hamiltonian Paramters:

$$H_{11}(\mathbf{R}) = A$$

$$H_{12}(\mathbf{R}) = \begin{cases} B \left[-e^{C(\mathbf{R}-D)} + e^{C(\mathbf{R}+D)} \right] & R \leq -D \\ B \left[e^{-C(\mathbf{R}-D)} - e^{-C(\mathbf{R}+D)} \right] & R \geq D \\ B \left[2 - e^{C(\mathbf{R}-D)} - e^{-C(\mathbf{R}+D)} \right] & -D < R < D \end{cases}$$

$$H_{21}(\mathbf{R}) = H_{12}(\mathbf{R})$$

$$H_{22}(\mathbf{R}) = -H_{11}(\mathbf{R})$$

Where $A = 6 \times 10^{-4}$, $B = 0.1$ and $C = 0.9$

Quantity	Value	Unit
Initial Position	-20	a.u.
Initial Velocities	10, 40	a.u.
Initial Adiab Pop	ground state	-
Simulation Time	6000, 2000	a.u.
$\sigma_v^{(I)}$	0.5	a.u.
M (σ constant)	40	-
$\Delta t_{\text{nuclear}}$	0.1	fs
$\Delta t_{\text{electronic}}$	0.01	fs
$\frac{\delta \mathbf{R}_{lk,v}^{(I)}}{\delta t}$ threshold	0.15	a.u.
N_{rep}	200	-

Appendix B

Wigner Distribution Derivation

The nuclear wavepacket (at time 0) is given by:

$$\chi(R) = \frac{1}{(\pi\mu^2)^{\frac{1}{4}}} e^{-\frac{(R-R_0)^2}{2\mu^2} + ik_0(R-R_0)} \quad (\text{B.1})$$

The Wigner quassprobability function for momentum and position (p, R) is given by:

$$W(p, R) = \frac{1}{\pi\hbar} \int_{-\infty}^{\infty} \chi^*(R+y) \chi(R-y) e^{\frac{2ipy}{\hbar}} dy \quad (\text{B.2})$$

However, both Ehrenfest and CTMQC require atomic positions as input so we must extract the position and velocity probability densities from this. We get these from the marginal integrals of the Wigner distribution i.e.

$$|f(R)|^2 = \int_{-\infty}^{\infty} W(R, p) dp \quad (\text{B.3})$$

$$|f(p)|^2 = \int_{-\infty}^{\infty} W(R, p) dR \quad (\text{B.4})$$

In order to calculate these marignal integrals we must first crunch through the maths of equation (B.2). Substituting eq (B.1) into (B.2):

$$W(p, R) = \frac{1}{\pi\hbar} \int_{-\infty}^{\infty} \frac{1}{\mu\sqrt{\pi}} e^{-\frac{(R+y-R_0)^2}{2\mu^2} - 2ik_0y - \frac{(R-y-R_0)^2}{2\mu^2}} e^{\frac{2ipy}{\hbar}} dy \quad (\text{B.5})$$

Simplifying the 2 quadratic equations (equation (B.5)) we get:

$$W(p, R) = \frac{1}{\pi\hbar} \int_{-\infty}^{\infty} \frac{1}{\mu\sqrt{\pi}} e^{-\mu^{-2}(y^2 - 2ik_0 y \mu^2 + (R - R_0)^2)} e^{\frac{2ipy}{\hbar}} dy \quad (\text{B.6})$$

We can now take the expressions not dependant on y outside of the integral and combine the exponents.

$$W(p, R) = \frac{1}{\pi\sqrt{\pi}\mu\hbar} e^{-\frac{(R-R_0)^2}{\mu^2}} \int_{-\infty}^{\infty} e^{-\frac{y^2 + 2iy\mu^2(\frac{p}{\hbar} - k_0)}{\mu^2}} dy \quad (\text{B.7})$$

Integrating we get:

$$\int e^{-\frac{y^2 + 2iy\mu^2(\frac{p}{\hbar} - k_0)}{\mu^2}} dy = \frac{\sqrt{\pi}\mu}{2} e^{-\frac{\mu^2}{\hbar^2}(p - \hbar k_0)^2} \text{erf} \left[\frac{y}{\mu} + i \left(\frac{p\mu}{\hbar} - \mu k_0 \right) \right] \quad (\text{B.8})$$

Applying limits we get:

$$\int_{-\infty}^{\infty} e^{-\frac{y^2 + 2iy\mu^2(\frac{p}{\hbar} - k_0)}{\mu^2}} dy = \sqrt{\pi}\mu e^{-\frac{\mu^2}{\hbar^2}(p - \hbar k_0)^2} \quad (\text{B.9})$$

Substituting this back into the Wigner distribution (equation (B.2)) we finally get:

$$W(p, R) = \frac{1}{\pi\hbar} e^{-\frac{(R-R_0)^2}{\mu^2}} e^{-\frac{(p - \hbar k_0)^2}{\hbar^2/\mu^2}} \quad (\text{B.10})$$

Taking the maringal integrals we get the position and velocity probability distributions:

$$|f(R)|^2 = \frac{2}{\mu\sqrt{\pi}} e^{-\frac{(R-R_0)^2}{\mu^2}} \quad (\text{B.11})$$

$$|f(p)|^2 = \frac{2}{\frac{\hbar}{\mu}\sqrt{\pi}} e^{-\frac{\mu^2}{\hbar^2}(p - \hbar k_0)^2} \quad (\text{B.12})$$

The above distributions are randomly sampled to get initial atomic velocities and positions for each simulation.

Appendix C

Colophon

This is a description of the tools you used to make your thesis. It helps people make future documents, reminds you, and looks good.

(example) This document was set in the Times Roman typeface using L^AT_EX and BibT_EX, composed with the Atom text editor.

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