Chapter 3

Quantum Dynamics

This chapter sets out to solve the time-dependent Schrödinger equation (TDSE). The discussion begins with the derivation of the equations of motion for a time-independent Hamiltonian. Subsequently, the formal solution for transforming the wave function from an initial time to some further time will be given for a time-independent and a time-dependent Hamiltonian. The succeeding section focuses on the concepts needed to simulate UV absorption spectra, where the Hamiltonian, in this case, is time-independent. The methodology used for transferring population from one state to another via laser-matter interaction is described, thereafter, the equations of motion are revisited for inclusion of this perturbation. The last section introduces a numerical solution, the split-operator technique, which when implemented, allows for a simulation of a wavepacket over discretized time steps.

3.1   Time-dependent Nuclear Schrödinger Equation

The intent of this section is to derive a general equation of motion for the nuclear wave function. The nuclear wave function evolves along the potential energy surface, by solving the equations of motion, and describes the vibrational behavior of the molecular system. To derive these equations we start with the TDSE

$$i\hbar\frac{\partial}{\partial t}|\Psi(t)\rangle = \hat{\mathbf{H}}_{\mathrm{el,nu}}|\Psi(t)\rangle \tag{3.1}$$

where the nuclear Hamiltonian

$$\hat{\mathbf{H}}_{\text{el,nu}} = \hat{\mathbf{T}}_{\text{nu}}(\mathbf{R}_A) + \hat{\mathbf{V}}_{\text{el}}(\mathbf{R}_A) \tag{3.2}$$

is a sum of the nuclear kinetic energy operator $\hat{\mathbf{T}}_{\text{nu}}(\mathbf{R}_A)$ and the electronic potential energy $\hat{\mathbf{V}}_{\text{el}}(\mathbf{R}_A)$ both of which depend on the nuclear coordinates, as the electronic energy has already been calculated at each nuclear configuration. Considering a single electronic state, the time-dependent wave function

$$|\Psi(t)\rangle = |\Psi_{\text{el}}(\mathbf{r}_a; \mathbf{R}_A)\rangle |\Psi_{\text{el,nu}}(\mathbf{R}_A; t)\rangle \tag{3.3}$$

is given as a product of the electronic $|\Psi_{\text{el}}\rangle$ and nuclear $|\Psi_{\text{el,nu}}\rangle$ wave functions. It should be recalled that the electronic wave function depends on the electronic coordinates and parametrically on the nuclear coordinates while the nuclear wave function depends on the nuclear coordinates and time. From this point onward the coordinate dependence of the wave functions will be dropped for the sake of simplicity. In order to derive the eqs. of motion for the nuclear wave function, the expression for the nuclear Hamiltonian along with the wave function, eqs. 3.3 and 3.2, are inserted into the TDSE, eq. 3.1, and results in the following,

$$i\hbar \frac{\partial}{\partial t} |\Psi_{\text{el}}\rangle |\Psi_{\text{el,nu}}(t)\rangle = \hat{\mathbf{H}}_{\text{el,nu}} |\Psi_{\text{el}}\rangle |\Psi_{\text{el,nu}}(t)\rangle \tag{3.4}$$

where the nuclear Hamiltonian operator, given in eqs. 2.7 and 3.2, accounts for the electronic Hamiltonian via the electronic energy. Inserting the nuclear Hamiltonian $\hat{\mathbf{H}}_{\text{el,nu}}$ into equation 3.4 results in the following expression,

$$i\hbar \frac{\partial}{\partial t} |\Psi_{\text{el}}\rangle |\Psi_{\text{el,nu}}(t)\rangle = \left(-\sum_A \frac{\hbar^2}{2m_A} \nabla_A^2 + \hat{\mathbf{V}}_{\text{el}}(\mathbf{R}_A) \right) |\Psi_{\text{el}}\rangle |\Psi_{\text{el,nu}}(t)\rangle \tag{3.5}$$

where the potential energy operator $\hat{\mathbf{V}}_{\text{el}}(\mathbf{R}_A)$, see eq. 2.5, contains the adiabatic electronic energy $E_{\text{el}}(\mathbf{R}_A)$ and the nuclear Coulomb energy term. Multiplication from the left with $\langle \Psi_{\text{el}'}|$ results in the following equation,

$$i\hbar \frac{\partial}{\partial t} |\Psi_{\text{el,nu}}(t)\rangle = \langle \Psi_{\text{el}'}| -\sum_A \frac{\hbar^2}{2m_A} \nabla_A^2 |\Psi_{\text{el}}\rangle |\Psi_{\text{el,nu}}(t)\rangle + \hat{\mathbf{V}}_{\text{el}}(\mathbf{R}_A)|\Psi_{\text{el,nu}}(t)\rangle \tag{3.6}$$

where the electronic states are orthogonal to one another. The first term on the left-hand side of this new expression is expanded by applying the product rule twice, which is

rewritten

$$\langle\Psi_{\mathrm{el}'}| - \sum_A \frac{\hbar^2}{2m_A}\nabla_A^2|\Psi_{\mathrm{el}}\rangle|\Psi_{\mathrm{el,nu}}(t)\rangle = \underbrace{\langle\Psi_{\mathrm{el}'}| - \sum_A \frac{\hbar^2}{2m_A}|\Psi_{\mathrm{el}}\rangle\nabla_A^2|\Psi_{\mathrm{el,nu}}(t)\rangle}_{\text{adiabatic term}} +$$

$$\underbrace{\langle\Psi_{\mathrm{el}'}| - \sum_A \frac{\hbar^2}{m_A}\nabla_A|\Psi_{\mathrm{el}}\rangle\nabla_A|\Psi_{\mathrm{el,nu}}(t)\rangle + \langle\Psi_{\mathrm{el}'}| - \sum_A \frac{\hbar^2}{2m_A}\nabla_A^2|\Psi_{\mathrm{el}}\rangle|\Psi_{\mathrm{el,nu}}(t)\rangle}_{\text{nonadiabatic terms}} \quad (3.7)$$

as a sum of adiabatic and nonadiabatic couplings. These nonadiabatic couplings are con-sidered to be small when the surfaces do not cross and will be neglected in this work. However, if there were avoided crossings in the potential energy surfaces then one would need to consider these coupling terms. The final form for the equation of motion for the adiabatic nuclear wave function, excluding the non-adiabatic terms, is

$$\begin{aligned}
i\hbar\frac{\partial}{\partial t}|\Psi_{\mathrm{el,nu}}(t)\rangle &= -\sum_A \frac{\hbar^2}{2m_A}\nabla_A^2\delta_{\mathrm{el}',\mathrm{el}}|\Psi_{\mathrm{el,nu}}(t)\rangle + \hat{\mathbf{V}}_{\mathrm{el}}(\mathbf{R}_A)|\Psi_{\mathrm{el,nu}}(t)\rangle \\
&= \left(\hat{\mathbf{T}}_{\mathrm{nu}}\delta_{\mathrm{el}',\mathrm{el}} + \hat{\mathbf{V}}_{\mathrm{el}}(\mathbf{R}_A)\right)|\Psi_{\mathrm{el,nu}}(t)\rangle, \quad (3.8)
\end{aligned}$$

where the first term on the right describes the kinetic energy of the nuclei and the second term the adiabatic potential energy, which is simply a potential energy surface for each electronic state. In the remainder of the chapter, the indices of "nu" and "el" will be removed for simplicity, and may reappear when necessary for clarity.

3.1.1   Formal Solution - Time Evolution Operator

Wavepacket propagation is accomplished by solving the time-dependent Schrödinger equa-tion. This section will explore the formal solution of the TDSE for a time-independent and a time-dependent Hamiltonian respectively. First, the discussion of the time evolution operator will begin with the field-free or time-independent Hamiltonian. In the following it will be shown how the evolution of the wavepacket can be used to obtain UV absorption spectra. Second, the time evolution operator will be described under the influence of the laser-matter interaction, as is normally the case when considering quantum dynamics.

Time-independent Hamiltonian

Integrating the time-dependent Schrödinger equation, eq. 3.1, leads to

$$|\Psi(t)\rangle = e^{-i/\hbar \hat{\mathbf{H}}(t-t_0)}|\Psi(t_0)\rangle = \hat{\mathbf{U}}(t, t_0)|\Psi(t_0)\rangle, \tag{3.9}$$

where the exponential term has been designated the time evolution operator $\mathbf{U}(t, t_0)$ and carries out the time evolution of the initial wave function. The state function $|\Psi(t)\rangle$ can be expanded in a basis of known stationary eigenfunctions of the Hamiltonian

$$|\Psi(t_0)\rangle = \sum_j |\Psi_j^v\rangle\langle\Psi_j^v|\Psi(t)\rangle. \tag{3.10}$$

The evolution of the wave function can be described in terms of this expansion by inserting eq. 3.10 into eq. 3.9,

$$
\begin{aligned}
|\Psi(t)\rangle &= \sum_j |\Psi_j^v\rangle\langle\Psi_j^v|e^{-i/\hbar \hat{\mathbf{H}}(t-t_0)}|\Psi(t_0)\rangle \\
&= \sum_j |\Psi_j^v\rangle e^{-i/\hbar E_j(t-t_0)}\langle\Psi_j^v|\Psi(t_0)\rangle
\end{aligned} \tag{3.11}
$$

where the last sandwiched term $\langle\Psi_j^v|\Psi(t_0)\rangle$ forms a set of initial expansion coefficients and E_j in eq. 3.11 are the energies for each eigenstate $|\Psi_j^v\rangle$. As can be seen the energy of the eigenstates remains constant over the time in which the evolution operator acts on the wave function. More specifically, the wave function does not lose any energy over the propagation time, and lends itself nicely to the simulation of absorption spectra, as will be seen in section 3.1.2.

The time evolution operator has a few properties which are noteworthy: first, its initial condition, eq. 3.12; second, it is unitary, equation 3.13; and third, it follows the composition property, equation 3.14

$$
\begin{aligned}
\hat{\mathbf{U}}(t_0, t_0) &= \mathbb{1} \tag{3.12} \\
\hat{\mathbf{U}}^\dagger(t, t_0)\hat{\mathbf{U}}(t, t_0) &= \mathbb{1} \tag{3.13} \\
\hat{\mathbf{U}}(t_2, t_0) &= \hat{\mathbf{U}}(t_2, t_1)\hat{\mathbf{U}}(t_1, t_0). \tag{3.14}
\end{aligned}
$$

The initial condition, eq. 3.12, indicates that the time evolution operator at time equal to zero ($t = t_0$), does not influence the wave function, which is simply a matrix multiplication of ones. The second property, eq. 3.13, allows for the mapping of one function onto another, a so-called isomorphism, where the time parameter has changed but the functions,

in this case the wave functions, remain normalized and within the Hilbert space; physically this indicates the conservation of the number of particles. The last property, eq. 3.14, the composition property, allows for the segmentation of the overall time evolution operator into a product of operators that break up the complete time of evolution into time segments.

Time-dependent Hamiltonian and Interaction Picture

In the previous discussion, the formal solution to the time-independent Hamiltonian was reviewed, however, it is often the case that the Hamiltonian of interest is time-dependent. Such a case occurs, as in this work, when one considers the interaction of light on the system, via the electric-dipole approximation, where the time-dependent Hamiltonian takes on the following form

$$\hat{\mathbf{H}}(t) = \hat{\mathbf{H}}_{\mathrm{mol}} + \hat{\mathbf{V}}(t). \tag{3.15}$$

The first term is the molecular Hamiltonian, $\hat{\mathbf{H}}_{\mathrm{mol}}$ previously denoted as $\hat{\mathbf{H}}_{\mathrm{el,nu}}$ as in eq. 3.2, and the second term, $\hat{\mathbf{V}}(t)$, is the perturbation due to the electric field.

The formal solution for the evolution of $\hat{\mathbf{V}}(t)$ is best given in the interaction (I) picture. The wave function then corresponds to the Schrödinger picture in the following way,

$$|\Psi(t)\rangle = e^{-i\hat{\mathbf{H}}_{\mathrm{mol}}(t-t_0)/\hbar}|\Psi^I(t)\rangle = \hat{\mathbf{U}}_0(t,t_0)|\Psi^I(t)\rangle. \tag{3.16}$$

Taking the time derivative results in the following equation,

$$i\hbar\frac{\partial}{\partial t}|\Psi(t)\rangle = \hat{\mathbf{U}}_0(t,t_0)\left(\hat{\mathbf{H}}|\Psi^I(t)\rangle + i\hbar\frac{\partial}{\partial t}|\Psi^I(t)\rangle\right) = \hat{\mathbf{H}}(t)|\Psi(t)\rangle \tag{3.17}$$

and rearranging this expression, the perturbation can be given in terms of the interaction picture

$$i\hbar\frac{\partial}{\partial t}|\Psi^I(t)\rangle = \underbrace{e^{i\hat{\mathbf{H}}_{\mathrm{mol}}(t-t_0)/\hbar}\hat{\mathbf{V}}(t)e^{-i\hat{\mathbf{H}}_{\mathrm{mol}}(t-t_0)/\hbar}}_{\hat{\mathbf{V}}^I(t)}|\Psi^I(t)\rangle. \tag{3.18}$$

The formal solution to the time-dependent Hamiltonian is given by the $\hat{\mathbf{S}}$-operator [73]

$$|\Psi^I(t)\rangle = \hat{\mathbf{S}}(t,t_0)|\Psi^I(t_0)\rangle = \hat{\mathbf{S}}(t,t_0)|\Psi(t_0)\rangle \tag{3.19}$$

where it should be noted that $|\Psi^I(t_0)\rangle = |\Psi(t_0)\rangle$ at the initial time, t_0. Inserting eq. 3.19 into eq. 3.16 one obtains

$$\hat{\mathbf{U}}(t,t_0) = \hat{\mathbf{U}}_0(t,t_0)\hat{\mathbf{S}}(t,t_0) \tag{3.20}$$

for the time evolution operator.

To investigate the form of the $\hat{\mathbf{S}}$-operator, the TDSE is rewritten in terms of the time evolution operator and the time-dependent perturbation operator in the interaction picture.

$$\frac{\partial}{\partial t}\hat{\mathbf{U}}_0(t,t_0)\hat{\mathbf{S}}(t,t_0)|\Psi(t_0)\rangle = -\frac{i}{\hbar}\hat{\mathbf{V}}^I(t)\hat{\mathbf{U}}_0(t,t_0)\hat{\mathbf{S}}(t,t_0)|\Psi(t_0)\rangle. \qquad (3.21)$$

This equation holds for any initial state $|\Psi(t_0)\rangle$ and therefore the operator $\hat{\mathbf{S}}$ must also satisfy the same equation [74].

$$\frac{\partial}{\partial t}\hat{\mathbf{S}}(t,t_0) = -\frac{i}{\hbar}\hat{\mathbf{V}}^I(t)\hat{\mathbf{S}}(t,t_0) \qquad (3.22)$$

Upon integrating eq. 3.22 over time, the time evolution operator can be written as

$$\hat{\mathbf{S}}(t,t_0) = 1 - \frac{i}{\hbar}\int_{t_0}^{t}d\tau_1\hat{\mathbf{V}}^I(\tau_1)\hat{\mathbf{S}}(\tau_1,t_0) \qquad (3.23)$$

where the first term comes from the initial property described in eq. 3.12. Its solution is obtained by an iteration, in which the equation is inserted into itself on the right-hand side of the equation [74]. The first "self" iteration term is

$$\hat{\mathbf{S}}(t,t_0) = 1 - \frac{i}{\hbar}\int_{t_0}^{t}d\tau_1\hat{\mathbf{V}}^I(\tau_1) + \left(-\frac{i}{\hbar}\right)^2\int_{t_0}^{t}d\tau_1\int_{t_0}^{\tau_1}d\tau_2\hat{\mathbf{V}}^I(\tau_1)\hat{\mathbf{V}}^I(\tau_2)\hat{\mathbf{S}}(\tau_2,t_0) \quad (3.24)$$

where subsequent iterations lead to the following time-ordered expansion

$$\hat{\mathbf{S}}(t,t_0) = 1 + \sum_{n=1}^{\infty}\left(-\frac{i}{\hbar}\right)^n\int_{t_0}^{t}d\tau_n\int_{t_0}^{\tau_n}d\tau_{n-1}\ldots\int_{t_0}^{\tau_2}d\tau_1\hat{\mathbf{V}}^I(\tau_n)\hat{\mathbf{V}}^I(\tau_{n-1})\ldots\hat{\mathbf{V}}^I(\tau_1)$$

$$(3.25)$$

which can be compactly written in its final form as

$$\hat{\mathbf{S}}(t,t_0) = 1 + \sum_{n=1}^{\infty}\hat{\mathbf{S}}^n(t,t_0) = e^{-\frac{i}{\hbar}\int_{t_0}^{t}d\tau\hat{\mathbf{V}}^I(\tau)} \qquad (3.26)$$

where $\tau = \tau_1,\tau_2,...\tau_n$. The evolution of a wave function can now be given formally in terms of the time-dependency of the Hamiltonian as

$$|\Psi(t)\rangle = \hat{\mathbf{U}}_0(t,t_0)\hat{\mathbf{S}}(t,t_0)|\Psi(t_0)\rangle. \qquad (3.27)$$

where the evolution operators $\hat{\mathbf{U}}_0(t,t_0)$ and $\hat{\mathbf{S}}(t,t_0)$, evolve the initial wave function $\Psi(t_0)$ over time, and the S-operator is taken as the first-order which describes single photon excitations.

3.1.2   Time-dependent UV Absorption Spectrum

The autocorrelation function maps the evolving wavepacket by calculating the overlap with its initial position

$$S_{tot}(t) = \sum_j S_j(t) = \sum_j \langle \Psi_j(t_0)|\Psi_j(t)\rangle \qquad (3.28)$$

such that the total autocorrelation function is composed of a sum of each autocorrelation function for each electronic state j. Considering for the moment only one electronic state, the autocorrelation function initially begins at unity since the wave function has been normalized. The decay of the autocorrelation function depends on the rate at which the evolving wavepacket moves away from its initial position. In the case that the wavepacket dissociates directly, the autocorrelation function decays to zero. For bound states or metastable states, the wavepacket tends to return partially in a periodic fashion so that small recurrences appear in the overlap function.

According to Heller [75], the absorption spectrum can be theoretically calculated in a time-dependent fashion by Fourier transforming the autocorrelation function [76]. The total cross section is proportional to the autocorrelation function as is given below

$$\sigma_{\text{tot}}(\omega) \propto \int_{-\infty}^{\infty} dt e^{i(\hbar\omega+E_0^0)} S_{tot}(t) \qquad (3.29)$$

where ω is the radiation frequency and E_0^0 is the ground vibrational energy of the ground electronic state. The initial wave function $|\Psi_j(t_0)\rangle$, is a dipole weighted projection of the ground electronic-vibrational wave function $|\Psi_i^0\rangle$ onto the dipole allowed electronic states

$$|\Psi_j(t_0)\rangle = \tilde{\boldsymbol{\mu}}_{ji}|\Psi_i^0\rangle \qquad (3.30)$$

where the normalized transition dipole moments are given as

$$\tilde{\boldsymbol{\mu}}_{ji} = \frac{\sqrt{\boldsymbol{\mu}_{ji,x}^2 + \boldsymbol{\mu}_{ji,y}^2 + \boldsymbol{\mu}_{ji,z}^2}}{\sum_j \boldsymbol{\mu}_{ji}}. \qquad (3.31)$$

The normalized dipole expression, eq. 3.31, is composed of individual transition dipole moments $\boldsymbol{\mu}_{ji}$ for the x, y, and z directions. The time-dependent wavepacket evolves according to

$$|\Psi_j(t)\rangle = \hat{\mathbf{U}}(t,t_0)|\Psi_j(t_0)\rangle. \qquad (3.32)$$

3.1.3   Electric-dipole Approximation

The Hamiltonian's time dependence is apparent when one considers the interaction of matter with light. In the electric-dipole approximation one considers transitions from an initial state to some other state, whether it be a vibrational or an electronic transition, where the time-dependence originates from the electric field. The Hamiltonian in such a case is given as

$$\hat{\mathbf{H}}(t) = \hat{\mathbf{H}}_{\text{mol}} - \hat{\boldsymbol{\mu}}\mathbf{E}(t) \tag{3.33}$$

as was seen in eq. 3.15, where $\hat{\mathbf{V}}(t) = -\hat{\boldsymbol{\mu}}\mathbf{E}(t)$. Equation 3.33 is composed of the molecular Hamiltonian $\hat{\mathbf{H}}_{\text{mol}}$, see eq. 3.2, the dipole moment operator $\hat{\boldsymbol{\mu}}$, and the time-dependent electric field $\mathbf{E}(t)$.

The electric dipole is defined classically as the product of the position vector $\mathbf{r}$ between two electric charges, q^+ and q^- and its moment

$$\boldsymbol{\mu} = q \cdot \mathbf{r} \tag{3.34}$$

is defined as a vector $\boldsymbol{\mu}$ with a magnitude of $q \cdot \mathbf{r}$ [77]. For a molecule with more than two charges, the electric dipole moment can be written as a sum of the individual charges

$$\hat{\boldsymbol{\mu}} = \sum_{i=1}^{N} q_i \cdot \mathbf{r}_i. \tag{3.35}$$

The dipole moment for a quantum mechanical calculation on a molecular system is given now with the operator representation

$$\boldsymbol{\mu}_{\text{el}',\text{el}} = \langle \Psi_{\text{el}'} | - \hat{\boldsymbol{\mu}} | \Psi_{\text{el}} \rangle + \sum_{A} Z_A \mathbf{R}_A e \cdot \delta_{\text{el},\text{el}'} \tag{3.36}$$

where the dipole moment is the sum of the electronic and nuclear dipole moments. The bold character depicts the dipole moment's vector character, and the hat depicts its quantum mechanical description. The first term, a quantum mechanical term, describes the single electron operator acting on the electronic states el and el′ and the second term, which accounts classically for the charge of the nuclei, is added. Specifically, this equation can be written in terms of cartesian coordinates where the following

$$\boldsymbol{\mu}_{\text{el}',\text{el}} = \langle \Psi_{\text{el}'} | - \sum_{i=1}^{N} \mathbf{x}_i | \Psi_{\text{el}} \rangle + \sum_{A} Z_A \mathbf{x}_A e \cdot \delta_{\text{el},\text{el}'} \tag{3.37}$$

depicts the case for the x-coordinate and can also be written for the y or the z components. The permanent dipole is then obtained when $\mathrm{el} = \mathrm{el}'$ and the transition dipole moment when $\mathrm{el} \neq \mathrm{el}'$.

The dipole moment gives the transition probability of transferring population from one state to another, but it is the laser pulse that contains the frequency which carries population from an initial state to some other state. This electric field is given below

$$\mathbf{E}(t) = \mathbf{n}s(t)E_0\cos(\omega t + \eta) \tag{3.38}$$

where the cosine term contains the transition frequency ω and a phase factor η which, for ease, will be considered to be zero. The other terms are the linear polarization unit vector, $\mathbf{n}$, the shape function $s(t)$, and the amplitude of the electric field or the field strength, E_0. The shape function,

$$s(t) = \sin^2\left(\frac{\pi t}{t_p}\right) \qquad \text{for} \qquad t_0 \leq t \leq t_p \tag{3.39}$$

used throughout this work is given as the square of a sine function, where t is time and t_p is the pulse duration.

Re-evaluation of the equations of motion for the nuclear wave function

In view of the electric-dipole approximation, the Hamiltonian acting on the nuclear wave function has changed and so have the equations of motion describing the nuclear wave function. Equation 3.8, which retained the electronic delta function to remind us of the left-multiplication with the electronic wave function, is now modified under the electric-dipole interaction

$$i\hbar\frac{\partial}{\partial t}|\Psi(t)\rangle = \left(\overbrace{\underbrace{\hat{\mathbf{T}}\delta_{\mathrm{el}',\mathrm{el}} + \hat{\mathbf{V}}_{\mathrm{el}}(\mathbf{R}_A)}_{\hat{\mathbf{H}}} - \boldsymbol{\mu}_{\mathrm{el}',\mathrm{el}}\mathbf{E}(t)}^{\hat{\mathbf{H}}(t)} \right)|\Psi(t)\rangle, \tag{3.40}$$

where $\boldsymbol{\mu}_{\mathrm{el}',\mathrm{el}}$ are the matrix elements of the dipole operator and together with the other two operators form the matrix representation of the time-dependent Hamiltonian $\hat{\mathbf{H}}(t)$. For n electronic states the equations of motion described in eq. 3.40, can be written in matrix form

$$i\hbar\frac{\partial}{\partial t}\begin{pmatrix} |\Psi_1(t)\rangle \\ \vdots \\ |\Psi_n(t)\rangle \end{pmatrix} = \begin{pmatrix} \hat{\mathbf{H}}_{11}(t) & \cdots & \hat{\mathbf{H}}_{1n}(t) \\ \vdots & \ddots & \vdots \\ \hat{\mathbf{H}}_{n1}(t) & \cdots & \hat{\mathbf{H}}_{nn}(t) \end{pmatrix}\begin{pmatrix} |\Psi_1(t)\rangle \\ \vdots \\ |\Psi_n(t)\rangle \end{pmatrix}. \tag{3.41}$$

Limiting the number of electronic states to three, which is the maximum number of states used in this work, the equations of motion for the nuclear wave function can be written in the matrix form,

$$
i\hbar\frac{\partial}{\partial t}
\begin{pmatrix}
|\Psi_1(t)\rangle \\
|\Psi_2(t)\rangle \\
|\Psi_3(t)\rangle
\end{pmatrix}
=
\left(\hat{\mathbf{H}}(t)\right)
\begin{pmatrix}
|\Psi_1(t)\rangle \\
|\Psi_2(t)\rangle \\
|\Psi_3(t)\rangle
\end{pmatrix}
\tag{3.42}
$$

where the Hamiltonian matrix elements are given as

$$
\hat{\mathbf{H}}(t) =
\begin{pmatrix}
\hat{\mathbf{H}}_{11} - \boldsymbol{\mu}_{11}\mathbf{E}(t) & -\boldsymbol{\mu}_{12}\mathbf{E}(t) & -\boldsymbol{\mu}_{13}\mathbf{E}(t) \\
-\boldsymbol{\mu}_{21}\mathbf{E}(t) & \hat{\mathbf{H}}_{22} - \boldsymbol{\mu}_{22}\mathbf{E}(t) & -\boldsymbol{\mu}_{23}\mathbf{E}(t) \\
-\boldsymbol{\mu}_{31}\mathbf{E}(t) & -\boldsymbol{\mu}_{32}\mathbf{E}(t) & \hat{\mathbf{H}}_{33} - \mathbf{d}_{33}\mathbf{E}(t)
\end{pmatrix}
\tag{3.43}
$$

The diagonal elements consist of the molecular Hamiltonian $\hat{\mathbf{H}}$ and the permanent dipole moment $\boldsymbol{\mu}_{nm}$ where $n = m$, whereas the off-diagonal elements contain the transition dipole moments $\boldsymbol{\mu}_{nm}$ where $n \neq m$ and the electric-field $\mathbf{E}(t)$ is found throughout the matrix.

The time-dependent electric field in combination with the transition dipole moment allows for electronic transitions. The dynamics that result from the laser-matter interaction are obtained by solving the TDSE, as prescribed by the time evolution operator $\hat{\mathbf{U}}$, eq. 3.27. However, the solution of the nuclear equations of motion is not possible due to the fact that the kinetic and potential operators do not commute, therefore a numerical solution is employed.

3.1.4   Numerical Propagation Methods

There have been several numerical methods developed in order to solve the TDSE. A few of these are the second order differencing scheme developed by McCullough and Wyatt [78], the split-operator method introduced by Feit and Fleck [79], and the Chebyshev polynomial expansion method [80]. In this work, the split-operator method was applied for reasons of its ease and its unitary property, and therefore will be briefly introduced.

Split Operator Technique

The time evolution operator is defined by the molecular Hamiltonian, see eqs. 3.9 and 3.26. The Hamiltonian is a sum of the kinetic and the potential energy terms, which do not commute, i.e. $[\hat{\mathbf{T}}, \hat{\mathbf{V}}] \neq 0$ [81]. In fact the kinetic operator $\hat{\mathbf{T}}$ is local in the momentum representation while the potential operator $\hat{\mathbf{V}}$ is nonlocal. In other words the kinetic operator and the potential operator are diagonal in their respective representations, namely the momentum and coordinate representations. The exponential term can not be split into a product of two exponential terms in which the first term contains the kinetic operator and the second term the potential operator. Instead, an approximation that uses a symmetric splitting of the kinetic energy operator is used and is shown below

$$e^{-\frac{i}{\hbar}\Delta t \hat{\mathbf{H}}} = e^{-\frac{i}{2\hbar}\Delta t \hat{\mathbf{T}}} e^{-\frac{i}{\hbar}\Delta t \hat{\mathbf{V}}} e^{-\frac{i}{2\hbar}\Delta t \hat{\mathbf{T}}} + O(\Delta t^3) \tag{3.44}$$

where the error is of the third order in Δt [79]. With this approximation, it is now possible to propagate the initial wave function $\psi(t_0)$ a step in time $\psi(\tau_1)$. Propagation of the wave function occurs on a discretized time interval and is itemized below:

- The wave function is Fourier transformed to the momentum space where it is multiplied with the first half of the kinetic operator, $e^{-\frac{i}{2\hbar}\Delta t \hat{\mathbf{T}}}$.

- The wave function is Fourier transformed back to coordinate space where it is multiplied by $e^{-\frac{i}{\hbar}\Delta t \hat{\mathbf{V}}}$.

- The wave function is Fourier transformed to the momentum space where it is multiplied with the second half of the kinetic operator, $e^{-\frac{i}{2\hbar}\Delta t \hat{\mathbf{T}}}$.

- The wave function is re-evaluated at the next time step.

The wave function is continually being Fourier transformed from one space to the other to account for the locality of each operator and upon its completion is re-evaluated at the next time step. Implementing this method allows for evaluation of the wave function along each time step in the simulation.

Grid considerations

In the grid representation of quantum dynamics it is important that the wave function does not cross over the grid boundary, which can cause the wave function to wrap around the grid or can cause reflections of the wave function [81]. In such a case, the dynamics which ensue are no longer physical and are rendered moot. One must not only care for the dynamics in position space but also in momentum space, recall section 2.3.1, there it was shown that the density of grid points in position space determines the grid density in momentum space.

Figure 3.1 shows how the density of points in position space affects the density of grid points in momentum space by changing the number of grid points N while holding the grid length ($L = \Delta x N$) constant. The left side of the figure depicts the grid in momentum space and the right side depicts the grid in position space, both in atomic units. The subfigures which are placed side-by-side belong with one another. The top set of subfigures are a scenario where the number of grid points used was a matrix of $N = 64\text{x}64$ points, which, along with the grid length, defines the maximum value of the momentum grid

$$k_{\max} = \pi / \Delta x. \tag{3.45}$$

By doubling the number of points in the position space, the maximum value of the momentum grid increases by two, as can be seen from eq. 2.77.

One problem that can occur in a simulation is that the grid representation for the momentum space is insufficient, i.e. the maximum of the momentum is not large enough to describe the motion of the wave function. This can be seen in fig. 3.1 where the wave function has been plotted on the PESs at a final time t_f. In the first scenario, the wave function did not have enough room to migrate within the momentum space and was forced to wrap around the grid, ending up in another quadrant. This caused the wave function to misbehave by changing either the direction of its motion or by artificially spreading out over the position grid. This figure exemplifies the need to care for the grid boundaries in both the position and momentum space.

The second problem which may occur is that the wave function reaches the grid boundary in position space, due to long-time propagations. This problem can be solved by applying an absorbing boundary function, also known as a "gobbler", to the boarder of the grid. Essentially, the gobbler will absorb the wave function as it enters into this predefined domain, near the edge of the grid.
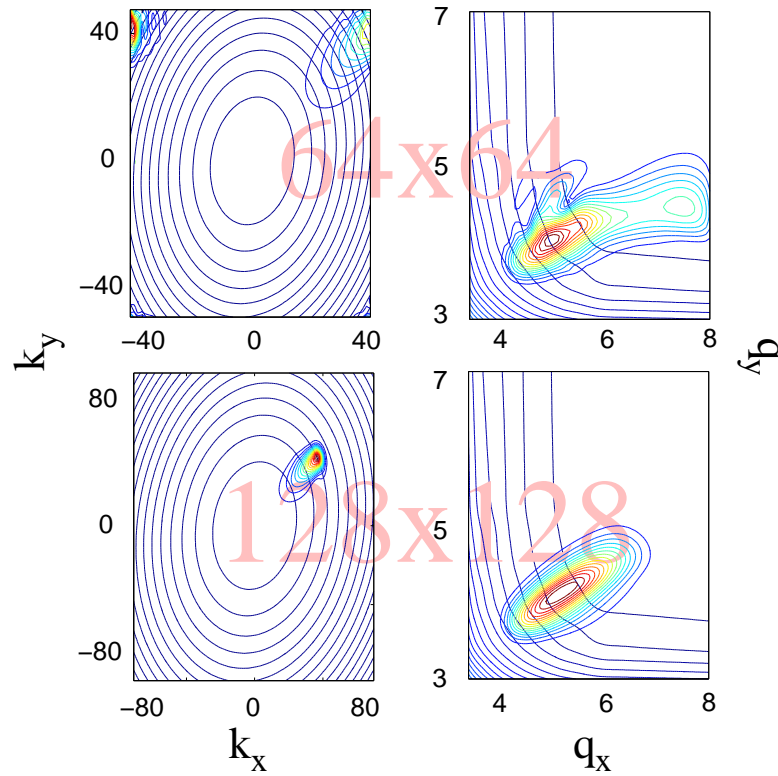
Figure 3.1: This figure compares the position grid and the momentum grid for a constant length $L = \Delta x N$. The number of grid points for the upper two grids is 64x64 where the left subfigures are in momentum space k and the right subfigures are in position space q. The lower two subfigures are on a grid with 128x128 points, exactly double the ones from above. Overlaying these grids is a wave function at a final propagation time t_f, where the above set of subfigures describes a misbehaving wave function, while the second set describes a well behaved one.

The absorbing boundary function, also known as a gobbler, for the case of one-dimension, which is easily cast into multi-dimensions, is given as a Gaussian type function

$$G(x) = \begin{cases} exp^{-d(x-N_x+n_{\text{gobb}})^2} & x > N_x - n_{\text{gobb}} \\ 1 & x < N_x - n_{\text{gobb}} \end{cases} \quad (3.46)$$

where d is a damping function, N the total number of points of the grid x, and n_{gobb} defines the onset of the gobbler [82]. The damping function as implemented in the WavePacket program [83] is defined as $d = -\log(1e^{-4}/n_{\text{gobb}}^2)$. The gobbler then acts on the wave function as follows

$$\Psi(x) = \Psi(x) \cdot G(x), \quad (3.47)$$

where the wave function is multiplied by one unless it is within the defined region of the gobbler where it is then multiplied by the exponential function, this essentially gobbles up the wave function in order to prevent wrapping and reflection.