Numerical simulation of the dynamics of a trapped molecular ion

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Make your choice, adventurous stranger;
Strike the bell and bide the danger;
Or wonder, till it drives you mad;
What would have followed if you had ...

— C. S. Lewis

The Chronicles of Narnia: The magician’s nephew
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Abstract

This thesis explores the dynamics of a heteronuclear diatomic molecular ion, possessing a permanent electric dipole moment, $\mu_0$, which is trapped in a linear Paul trap and can interact with an off-resonance laser field. To build our model we use the rigid-rotor approximation, where the dynamics of the molecular ion are limited to its translational and rotational motions of the center-of-mass. These dynamics are investigated by carrying out suitable numerical calculations.

To introduce our numerical methods, we divide our research topic into two different subjects. First, we ignore the rotational dynamics of the ion by assuming $\mu_0 = 0$. By this assumption, the system resembles an atomic ion, which mainly exhibits translational motion for its center of the mass when exposed to an external trapping field. To study this translational behavior, we implement full-quantum numerical simulations, in which a wave function is attributed to the ion. Finally, we study the quantum dynamics of the mentioned wave packet and we compare our results with those obtained classically.

In the latter case, we keep the permanent dipole moment of the ion and we study the probable effects of the interaction between the dipole moment and the trapping electric field, on both the translational and the rotational dynamics of the trapped molecular ion. In order to study these dynamics, we implement both classical and semi-classical numerical simulations. In the classical method, the rotational and the translational motions of the center of mass of the ion are obtained via classical equations of motion. On the other hand, in the semi-classical method, while the translational motion of the center-of-mass is still obtained classically, the rotation is treated full-quantum mechanically by considering the rotational wave function of the ion. In the semi-classical approach, we mainly study the probable couplings between the rotational states of the molecular ion, due to the interaction of the permanent dipole moment with the trapping electric field. In the end, we also present a semi-classical model, where the trapped molecular ion interacts with an off-resonance laser field.
Publications

I Program for quantum wave-packet dynamics with time-dependent potentials
Dion, C. M., Hashemloo, A., Rahali, G.

II Wave packet dynamics of an atomic ion in a Paul trap: Approximations and stability
Hashemloo, A., Dion, C. M., Rahali, G.

III Rotational dynamics of a diatomic molecular ion in a Paul trap
Hashemloo, A., Dion, C. M.
The Journal of Chemical Physics. 143 (2015) 204308

IV Quantum stability of an atomic ion in a Paul trap revisited
Hashemloo, A., Dion, C. M.
(to be submitted)
Chapter 1

Introduction

Cooling and trapping of atomic and molecular ions have been great tools in studying a wide range of subjects and fields, such as chemical reactions \[1\textsuperscript{-}5\], high-precision spectroscopy \[6\textsuperscript{-}8\], and fast developing fields in quantum information and quantum computation \[9\textsuperscript{-}10\], where the manipulations of the internal states of these ions have become more feasible. One of the most popular forms of trapping a single ion is its confinement in space by a time-dependent, spatially varying electric field which typically is oscillating in the radio-frequency (rf) domain \[17\]. This idea was introduced by Wolfgang Paul \[18\] and such a device providing this confinement, in general, is called a quadrupole ion trap device.

Alongside many existing experimental works with either trapped atomic ions or trapped molecular ions in such devices, atomic ions have also been the subject of many theoretical studies. In some of these studies, the dynamics of trapped atomic ions are explored, considering them as quantum particles. Some of these works are presented in Refs. \[19\textsuperscript{-}25\]. Excluding those, trapped atomic ions are also treated as being classical particles \[26\textsuperscript{-}32\]. When it comes to trapped molecular ions, there have been few attempts to treat them differently than atomic ions when their dynamics is in focus. However, the rotational dynamics of these ions has been considered mostly with respect to a coupling with an external laser field \[33\textsuperscript{-}35\].

In this work, we mainly study the dynamics of a rigid, heteronuclear diatomic molecular ion, which is trapped in a linear Paul trap and eventually can interact with an off-resonance laser field, by carrying out suitable numerical simulations. We are specially interested in investigating the quantum rotational dynamics of this ion with respect to its interaction with the trapping field. This interaction is mostly caused by the coupling between the trapping electric field and the permanent
electric dipole moment of the ion. To complete our investigations on quantum rotational dynamics of the ion, we also present a model for a trapped molecular ion interacting with an off-resonance laser field.

The first part of this thesis is devoted to a brief introduction to linear Paul traps and also to constructing a model for a trapped molecular ion by building the Hamiltonian of the system. In the later part, before studying the dynamics of the aforementioned molecular ion, we firstly introduce and present our numerical methods to study the wave packet dynamics of a trapped atomic ion. In the following section, our classical and semi-classical numerical treatments are introduced and defined which enables us to study the translational and rotational behavior of the trapped molecular ion. Finally, the thesis chapters will be closed by briefly presenting and discussing the obtained results, which can also be found – in more details – in the published papers. These papers are all presented at the end of this thesis and we will refer to them wherever it is needed.
Chapter 2

Linear Paul trap

Quadrupole ion traps exist in many varieties such as cylindrical and linear traps, in which the potential at a point inside such devices – approximately close to the center of the trap – is dependent upon the square of the distance from the origin of the reference [36]. Therefore, the trapping electric potential which consists of two components, time-independent and time-dependent parts, has the general form [17]

\[ \Phi_{\text{Trap}}(x, y, z; t) = U_0 \frac{1}{2}(\alpha x^2 + \beta y^2 + \gamma z^2) + V_0 \cos(\Omega_{rf} t) \frac{1}{2}(\alpha' x^2 + \beta' y^2 + \gamma' z^2), \] (2.1)

where \( U_0 \) and \( V_0 \) are amplitudes of the radio-frequency (with frequency \( \Omega_{rf} \)) and static potentials, respectively. The potential has to fulfill the Laplace equation \( \nabla^2 \Phi_{\text{Trap}} = 0 \) which leads to the restriction of the geometric factors [17]

\[ \alpha + \beta + \gamma = 0, \]
\[ \alpha' + \beta' + \gamma' = 0, \] (2.2)

which result in a dynamical trapping of the ion inside the trap and gives rise to an approximately harmonic and stable motion for the ion in all directions [17].

Now by choosing geometric factors such as \( \alpha = \beta = \gamma = 0 \) and \( \alpha' + \beta' = -\gamma' \) or \( -(\alpha + \beta) = \gamma > 0 \) and \( \alpha' = -\beta' \), we can define confinement by a cylindrical trap or confinement by a linear trap, respectively. In the first kind of the trap (cylindrical), the ion will be trapped in a purely oscillating field, but on the other
hand, the linear trap impose a dynamical confinement of the ion in $xy$-plane and static confinement in the $z$-direction, simultaneously [17].

In this work, our focus will be mainly on linear Paul traps, as they are the most popular form of trapping devices that are used in many experimental works, nowadays. These devices provide a trapping axis rather than just a single point in space, where the trapping of a string of ions will be more feasible and laser cooling of large ion clouds will be possible [37]. This kind of configuration will be greatly advantageous for quantum computing and quantum information processes, where it is necessary to work with a large number of ions and hence it is needed to avoid problems such as the mutual Coulomb repulsion of the ions from the center of the trap [38]. As a consequence, linear Paul traps are the best choice for this purpose, in which the radio-frequency field can vanish along a line (the trapping axis – which is usually directed along the $z$-axis) [38].

Figure 2.1: A linear Paul trap, constructed of four cylindrical and two ring-shaped electrodes. A pair of cylindrical electrodes is attached to a radio-frequency source (shaded with light-grey) and the other pair is grounded (shaded with dark-grey). A static potential is also applied to the ring-shaped electrodes.

Linear Paul traps exist in many different configurations and varieties, but in this work we refer to a linear Paul trap which is constructed of four cylindrical electrodes, each located at the corner of a square and two ring-shaped electrodes, located near the end of the cylindrical electrodes [26, 39, 41]. In this kind of trap, a pair of cylindrical electrodes that are opposing each other diagonally is attached to
a radio-frequency source and the other pair is grounded. Also, in order to confine ions inside the trapping device, a static potential is applied to the ring-shaped electrodes. The schematic configuration of a linear Paul trap is shown in Fig. 2.1.

Now by choosing the appropriate geometric factors for this kind of trap, such as, $\gamma = \frac{2\kappa}{z_0^2}$ and $\alpha = \frac{1}{r_0^2}$, for each component of the potential, we have

$$\Phi_{\text{rf}}(r; t) = \frac{1}{2} \frac{V_0}{r_0^2} \left( x^2 - y^2 \right) \cos \Omega_{\text{rf}} t, \quad (2.3a)$$

$$\Phi_s(r) = \frac{\kappa U_0}{z_0^2} \left[ z^2 - \frac{1}{2} \left( x^2 + y^2 \right) \right], \quad (2.3b)$$

in which $r_0$ and $z_0$ are the minimum distance from the electrodes to the central (trap) axis and half the distance between ring-shaped electrodes, along the trapping axis, respectively. The parameter $\kappa$ is a purely experimental parameter and can be found from the oscillation frequency of an ion in the trap. Finally, we can define the trapping potential of a linear Paul trap as the sum of a radio-frequency, time-dependent potential, and a static potential

$$\Phi_{\text{Trap}}(x, y, z; t) = \frac{1}{2} \frac{V_0}{r_0^2} \left( x^2 - y^2 \right) \cos \Omega_{\text{rf}} t + \frac{1}{2} \frac{\kappa U_0}{z_0^2} \left[ 2z^2 - \left( x^2 + y^2 \right) \right]. \quad (2.4)$$
Chapter 3

Hamiltonian of a rigid diatomic molecular ion trapped in a linear Paul trap

Prior to defining a model for a rigid diatomic molecular ion, trapped in a linear Paul trap, we will introduce the Hamiltonian of a free rigid diatomic molecule using the Born-Oppenheimer approximation, which will be discussed in details in Sec. 3.1.1. Then, we also show how the Hamiltonian will be modified for a rigid diatomic molecular ion exposed to external fields, in general.

3.1 Hamiltonian of a rigid diatomic molecule

3.1.1 Born-Oppenheimer approximation

Considering a free diatomic molecule with its center-of-mass being fixed with respect to a lab-fixed frame, we can write the Hamiltonian of the system as the sum of the kinetic energy of nuclei and electrons and the potential energy

\[
\hat{H} = -\frac{\hbar^2}{2m_1} \frac{\partial^2}{\partial R_1^2} - \frac{\hbar^2}{2m_2} \frac{\partial^2}{\partial R_2^2} - \frac{\hbar^2}{2m_e} \sum_{i=1}^{N} \frac{\partial^2}{\partial r_i^2} + V(R_1, R_2; r_1, r_2, \ldots, r_N),
\]  

(3.1)

in which \(m_1\) and \(m_2\) are masses of nuclei, constituting the diatomic molecule, with coordinates \(R_1\) and \(R_2\) respectively with respect to the origin of the lab-fixed frame (see Fig. 3.1).
Figure 3.1: Representation of a diatomic molecule with respect to the origin of a lab-fixed frame.

On the other hand, electrons are represented by mass \( m_e \) and coordinates \( r_i \). The last term in Eq. (3.1), which for simplicity is shown as \( V(R; r) \), is the potential energy which describes the Coulomb repulsion between nuclei, Coulomb repulsion between electrons and the attraction between electrons and nuclei. We have shown these terms in Eq. (3.2)

\[
V(R; r) = \frac{e^2}{4\pi \varepsilon_0} \left[ \frac{Z_1 Z_2}{R} + \sum_{i \neq i'} \sum_{i'=1}^{N} \frac{1}{r_{i,i'}} - \sum_{k=1}^{2} \sum_{i=1}^{N} \frac{Z_k}{r_{ik}} \right], \tag{3.2}
\]

where

\[
R = |R_1 - R_2|,
\]
\[
r_{i,i'} = |r_i - r_{i'}|,
\]
\[
r_{ik} = |r_i - R_k|,
\]

and \( Z_1 e \) and \( Z_2 e \) are representing charges of constituting nuclei, with \( e \) and \( \varepsilon_0 \) being the elementary charge and the electric constant, respectively.

Since electrons have much smaller mass comparing to nuclei, the cloud of electrons in a molecule follow the changes in nuclear framework somehow instantaneously. Therefore, for each configuration of nuclei, which can be specified by
its nuclear coordinates $\mathbf{R}_1$ and $\mathbf{R}_2$, there is an electron distribution. This distribution of electrons is defined by electronic wave function $\phi_{\text{el}}(R; \mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N) \equiv \phi_{\text{el}}(R; \mathbf{r})$ \cite{22}. The electronic wave function is a function of the coordinates of all electrons $\mathbf{r}_i$ and $R = |\mathbf{R}_1 - \mathbf{R}_2|$ in the electronic wave function is entered as a parameter since $\phi_{\text{el}}$ is calculated for a fixed internuclear distance.

In order to solve the Schrödinger equation corresponding to the Hamiltonian in Eq. (3.1), we can apply the perturbation theory since nuclei has much smaller kinetic energy comparing to electrons (due to its much larger mass). In this way, we assume that the molecule is perturbed by the kinetic energy of the nuclei $\hat{K}_{\text{nuc}}$ \cite{43}. This results in having the Hamiltonian as

$$\hat{H} = \hat{H}_0 + \hat{H}', \quad \hat{H}_0 = \hat{K}_{\text{el}} + V, \quad \hat{H}' = \hat{K}_{\text{nuc}}, \quad (3.4)$$

in which $\hat{K}_{\text{el}}$ is the kinetic energy of electrons.

For the unperturbed Schrödinger equation we have

$$\hat{H}_0 \phi_{n}^{\text{el}}(R; \mathbf{r}) = E_n^{(0)}(R) \phi_{n}^{\text{el}}(R; \mathbf{r}), \quad (3.5)$$

in which wave functions $\phi_{n}^{\text{el}}$ constitute a complete set of orthonormal functions, each representing $n$th electronic state of the molecule corresponding to a configuration $R$ of the nuclei. Therefore, it implies that

$$\int \phi_{n}^{\text{el}*}(R; \mathbf{r}) \phi_{n'}^{\text{el}}(R; \mathbf{r}) d\mathbf{r} = \delta_{n,n'} \quad (3.6)$$

Based on the perturbation theory, now we can expand the solution of the complete Schrödinger equation corresponding to the Hamiltonian mentioned in Eq. (3.1), in the basis of these orthonormal functions $[\phi_{n}^{\text{el}}(R; \mathbf{r})]$ as \cite{44}

$$\Psi(R; \mathbf{r}) = \sum_{n'} \psi_{n'}(R) \phi_{n'}^{\text{el}}(R; \mathbf{r}), \quad (3.7)$$

where $\psi_{n}$ are expansion coefficients, which only depend on the nuclear coordinates $\mathbf{R}$.

In the next step we apply the Hamiltonian $\hat{H}$ shown in Eq. (3.1) or in Eq. (3.4) on the complete wave function $\Psi(R; \mathbf{r})$

$$\hat{H}\Psi(R; \mathbf{r}) = \left(\hat{H}_0 + \hat{H}'\right) \sum_{n'} \psi_{n'}(R) \phi_{n'}^{\text{el}}(R; \mathbf{r})$$

$$= E \sum_{n'} \psi_{n'}(R) \phi_{n'}^{\text{el}}(R; \mathbf{r}), \quad (3.8)$$
and after multiplication by $\phi_n^{el}$ and integration over electronic coordinates $r$ and also using the relation in Eq. (3.6), we have [43]

$$\left[ E_{n}^{(0)}(R) - E \right] \psi_n(R) + \int \left[ \phi_n^{el} \hat{H}' \sum_{n'} \psi_n(R) \phi_n^{el} \right] dr = 0. \quad (3.9)$$

Now considering

$$\hat{H}' = -\frac{\hbar^2}{2} \sum_{k=1}^{2} \frac{1}{m_k} \nabla_k^2,$$  \quad (3.10)

which represents the kinetic energy of the nuclei and also considering that for any two arbitrary functions $f_1$ and $f_2$ we have

$$\nabla^2 (f_1 f_2) \equiv \nabla \cdot (\nabla f_1 f_2) = \nabla^2 f_1 + \nabla^2 f_2 + 2 \nabla f_1 \nabla f_2,$$  \quad (3.11)

the second term in Eq. (3.9) can be written as [43]

$$\int \phi_n^{el} \left( \hat{H}' \sum_{n'} \psi_{n'} \phi_{n'}^{el} \right) dr = \int \left[ \phi_n^{*} \sum_{n'} \left( \hat{H}' \psi_{n'} \right) \phi_{n'} \right] dr - \int \left[ \phi_n^{*} \sum_{n'} \left( \hat{H}' \phi_{n'} \right) \psi_{n'} \right] dr - \hbar^2 \int \phi_n^{*} \sum_{k=1}^{2} \frac{1}{m_k} \sum_{n'} \frac{\partial}{\partial R_k} \phi_{n'} \frac{\partial}{\partial R_k} \psi_{n'} dr. \quad (3.12)$$

The first term in the right-hand side of Eq. (3.12) reduce to $\hat{H}' \psi_n$ since $\hat{H}'$ only depends on coordinates $R$ and the integration, which is over the electronic coordinates $r$ vanishes using the relation in Eq. (3.6). Finally, Eq. (3.9) reduces to

$$\hat{H}' \psi_n(R) + \sum_{n'} [c_{nn'} \psi_{n'}(R)] = [E - E_{n}^{0}(R)] \psi_n,$$  \quad (3.13)

in which

$$c_{nn'} = \int \phi_n^{*} \hat{H}' \phi_{n'} dr - \frac{\hbar^2}{2} \int \phi_n^{*} \sum_{k=1}^{2} \frac{1}{m_k} \frac{\partial}{\partial R_k} \phi_{n'} dr \frac{\partial}{\partial R_k}.$$ \quad (3.14)

The coupling coefficients $c_{nn'}$ in Eq. (3.14) determine how different electronic states are coupled through the motion of the nuclei. Since the electronic distribution moves faster than the nuclei, the variation of the electronic wave function
\( \phi_{\text{el}} \) is small with respect to \( R \), which allows us to neglect \( |\partial \phi_{\text{el}}/\partial R| \) in comparison to \( |\partial \psi/\partial R| \) in Eq. (3.14), which eventually results in having \( c_{nn'} = 0 \). Subsequently, by ignoring the sum term in Eq. (3.13) we have an equation that describes the motion of the nuclei with the kinetic energy \( \hat{H}' \) that moves in the potential \( E_n^0(R) \), which is the solution to Eq. (3.5). Therefore, the Schrödinger equation corresponding to the Hamiltonian in Eq. (3.1) will be separated into two decoupled equations:

\[
\hat{H}_0 \phi_{n}^{\text{el}}(r) = E_n^0 \phi_{n}^{\text{el}}(r), \quad (3.15a)
\]

\[
(\hat{H}' + E_n^0) \psi_{n,m}(R) = E_{n,m} \psi_{n,m}(R), \quad (3.15b)
\]

in which \( \psi_{n,m} \) are considered as nuclear wave functions for the state \( m \) of the nuclear kinetic energy in the electronic state \( n \). Now the total wave function of a molecule, in its \( m \)th nuclear kinetic energy state and \( n \)th electronic state is

\[
\Psi_{n,m}(r; R) = \phi_{n}^{\text{el}}(r) \times \psi_{n,m}(R), \quad (3.16)
\]

which results in having the Eq. (3.7) as a single term.

By neglecting the coupling term in Eq. (3.13), we have approximated our problem using the Born-Oppenheimer approximation, which allows us to separate the motion of atomic nuclei from the motion of electrons in a molecule. Finally, It should also be mentioned that Eq. (3.15b) describes the kinetic energy of the nuclei as vibrations and rotations of the molecule, which moves in the potential \( E_n^0(R) \). Therefore, states \( ms \) are referred as vibrational-rotational states of the molecule in the electronic state \( n \).

### 3.1.2 Coordinate transformation to COM frame

To study the dynamical behavior of a rigid diatomic molecular ion moving with respect to a lab-fixed frame, which eventually will be exposed to external fields, we make a coordinate transformation to the nuclear’s center-of-mass (COM) frame, in order to separate the translational motion of the center of mass of the molecule from its rotational motion (vibrations are ignored since we assumed to have a rigid molecule).

Considering the Hamiltonian in Eq. (3.15b) and redefining the term representing the kinetic energy of the nuclei \( \hat{H}' \) [also see Eq. (3.10)], with respect to the new coordinates (see Fig. 4.3 in Sec. 4.2.1):

\[
R = R_1 - R_2, \quad (3.17a)
\]

\[
R_{\text{cm}} = \frac{m_1 R_1 + m_2 R_2}{m_1 + m_2}, \quad (3.17b)
\]
the Schrödinger equation (3.15b) can be written as

\[
-\frac{\hbar^2}{2m} \nabla^2_{\text{cm}} - \frac{\hbar^2}{2m_{\text{red}}} \nabla^2_{R} + E^0_n(R) \right] \Psi(R_{\text{cm}}; R) = E\Psi(R_{\text{cm}}; R),
\]

(3.18)

in which \( m = m_1 + m_2 \) is the total mass of the molecule and \( m_{\text{red}} = m_1 m_2 / (m_1 + m_2) \) is the reduced mass and \( R_{\text{cm}} \) represents the coordinates of the center of mass of the molecule, with respect to the lab-fixed frame.

The first term in the left-hand side of Eq. (3.18) shows the translational motion of the center-of-mass, hence the derivative is with respect to the coordinate of the center of mass of the molecule. In this regard, we have separated the translational motion of the center of mass of the molecule from its vibrational-rotational dynamics, which is represented by the second term in Eq. (3.18). Consequently, we can also separate the wave function into two parts \( \psi_{\text{cm}}(R_{\text{cm}}) \) and \( \psi_{\text{vib,rot}}(R) \), corresponding to the translational dynamics and the vibrational-rotational dynamics of the molecule, respectively

\[
\Psi(R_{\text{cm}}; R) = \psi_{\text{cm}}(R_{\text{cm}}) \times \psi_{\text{vib,rot}}(R).
\]

(3.19)

On the other hand, due to the fact that potential energy \( E^0_n(R) \) only depends on \( R \) – the distance between nuclei – it is spherically symmetric, hence it allows us to separate \( \psi_{\text{vib,rot}}(R) \) and also the Laplacian \( \nabla^2_{R} \) into spherical coordinates \((R, \theta, \varphi)\). For the Laplacian in spherical coordinates we have

\[
\nabla^2 \equiv \frac{1}{R^2} \frac{\partial}{\partial R} \left( R^2 \frac{\partial}{\partial R} \right) + \frac{1}{R^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{R^2 \sin^2 \theta} \frac{\partial^2}{\partial \varphi^2}.
\]

(3.20)

Now only by considering the Schrödinger equation corresponding to vibrational-rotational motion of the molecule and by substituting the Laplacian shown in Eq. (3.20) into Eq. (3.18) and also by considering that \( \psi_{\text{vib,rot}} \) can be written as

\[
\psi_{\text{vib,rot}}(R) \equiv \psi_{\text{vib,rot}}(R, \theta, \varphi) = R(R) \times Y(\theta, \varphi),
\]

(3.21)

in which \( R(R) \) is the radial part and is corresponding to the vibration of nuclei and \( Y(\theta, \varphi) \) is the angular part of the wave function and is defining the rotation, after some rearrangement we can obtain

\[
\frac{1}{R} \frac{\partial}{\partial R} R^2 \frac{\partial R}{\partial R} + \frac{1}{Y} \left\{ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \varphi^2} \right\}
= \frac{2m_{\text{red}} R^2}{\hbar^2} \left( E_{n}^{(0)} - E_{\text{vib,rot}} \right).
\]

(3.22)
Since we have assumed of having a rigid molecule i.e., \( R = \text{const.} \), the first term in Eq. (3.22), which is representing the vibrational motion of the nuclei, can be neglected. Now by defining the operator \[ \hat{J}^2 = -\hbar^2 \left\{ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right\}, \] (3.23)
with eigenvalues \( \hbar^2 J(J+1) \), in which \( \hat{J} \) and \( J \) are the angular momentum operator and the quantum number of the total angular momentum, respectively, we have

\[ \frac{\hat{J}^2}{2m_{red}R^2} Y(\theta, \varphi) = E_{\text{rot}} Y(\theta, \varphi). \] (3.24)

The equation above [Eq. (3.24)], represents the rotational dynamics of the molecule and functions \( Y(\theta, \varphi) \) are spherical harmonic functions. Now, by introducing the parameter \( B = \hbar^2/(2m_{red}R^2) \), which is called the rotational constant, we can write the Hamiltonian of a rigid diatomic molecule as

\[ \hat{H} = -\frac{\hbar^2}{2m} \nabla_{\text{cm}}^2 + \frac{B\hat{J}^2}{\hbar^2} + E_n^{(0)}. \] (3.25)

Finally, for the total wave function of this rigid molecule (with no vibration), considering a single electronic state, we have

\[ \Psi_{\text{total}} = \psi_{\text{cm}}(R_{\text{cm}}) \times Y(\theta, \varphi). \] (3.26)

### 3.2 Hamiltonian of a rigid diatomic molecular ion in an external electric field

Before introducing a model for a diatomic molecular ion exposed to an external electric field, we consider a system of \( N \) particles with charges \( \delta_i \) each located at \( r_i \) with respect to a lab-fixed frame. If we expose this system of \( N \) charged particles to an external field, each of these charges interacts with the field, individually. Therefore, from a classical point of view, we can define the interaction energy as

\[ V_{\text{int}} = \sum_{i=1}^{N} \delta_i \Phi_{\text{Ext}}(r_i), \] (3.27)
where $\Phi$ is representing the external field. Now, by defining a reference point, $r_{\text{ref}}$ and Taylor expanding the external field around that point, we have

$$
\Phi(r_i) = \Phi(r_{\text{ref}}) + (r_i - r_{\text{ref}})_x \frac{\partial}{\partial x_i} \Phi\bigg|_{r_{\text{ref}}} + (r_i - r_{\text{ref}})_y \frac{\partial}{\partial y_i} \Phi\bigg|_{r_{\text{ref}}}
+ (r_i - r_{\text{ref}})_z \frac{\partial}{\partial z_i} \Phi\bigg|_{r_{\text{ref}}} + \frac{1}{2} (r_i - r_{\text{ref}})_x^2 \frac{\partial^2}{\partial x_i^2} \Phi\bigg|_{r_{\text{ref}}} + \frac{1}{2} (r_i - r_{\text{ref}})_y^2 \frac{\partial^2}{\partial y_i^2} \Phi\bigg|_{r_{\text{ref}}} + \frac{1}{2} (r_i - r_{\text{ref}})_z^2 \frac{\partial^2}{\partial z_i^2} \Phi\bigg|_{r_{\text{ref}}} + \ldots .
$$

(3.28)

and by substituting Eq. (3.28) into Eq. (3.27) we obtain

$$
V_{\text{int}} = \sum_{i=1}^{N} \delta_i \Phi(r_{\text{ref}}) + \sum_{i=1}^{N} \sum_{\xi=x,y,z} \delta_i (r_i - r_{\text{ref}})_\xi \frac{\partial}{\partial \xi_i} \Phi\bigg|_{r_{\text{ref}}}
+ \frac{1}{2} \sum_{i=1}^{N} \sum_{\xi=x,y,z} \delta_i (r_i - r_{\text{ref}})_\xi^2 \frac{\partial^2}{\partial \xi_i^2} \Phi\bigg|_{r_{\text{ref}}} + \ldots .
$$

(3.29)

The dipole moment of the system is defined as

$$
P = \sum_{i=1}^{N} \delta_i (r_i - r_{\text{ref}}),
$$

(3.30)

in which the choice of the reference point is dependent on whether the system of charges has a net-charge or not. Also, since the dipole moment of a system is a property of that systems, we choose a reference point that is attached to the system. For a system with an overall charge neutrality, the dipole moment is generally, independent of the choice of the reference point, but on the other hand, for a non-neutral system – for the convenience – we take this reference point to be the center of mass of the system, $R_{\text{cm}}$. It is also interesting to note that we could also take the reference point to be the center of charge of the system, which would result in $P = 0$.

Now, considering a diatomic molecular ion, which can be represented as a system with two partial charges $\delta_+$ and $\delta_-$, each located at $r_+$ and $r_-$, respectively, with respect to a lab-fixed frame, we can define the permanent electric dipole moment (with $r_{\text{ref}} \equiv R_{\text{cm}}$) of the diatomic molecular ion as

$$
\mu_0 = r'_+ \delta_+ + r'_- \delta_-,
$$

(3.31)
where
\[ r'_\pm = r_\pm - R_{cm}, \]  
which is shown schematically in Fig. 3.2.

![Figure 3.2: A system composed of two partial charges \( \delta_+ \) and \( \delta_- \), each located at \( r_+ \) and \( r_- \), respectively, with respect to a lab-fixed frame (X, Y, Z).](image)

Ignoring the higher terms in Eq. (3.29) and considering the fact that \( \delta_+ + \delta_- = Ze \), in which \( Z \) is the total charge of the ion, we can write the final result for the interaction energy of a diatomic molecular ion in an external electric field as

\[ V_{\text{int}} = Ze \Phi(R_{cm}) + \mu_0 \cdot \nabla \Phi|_{R_{cm}} + \ldots \approx Ze \Phi(R_{cm}) - \mu_0 \cdot \mathcal{E}(R_{cm}), \]  
(3.33)

where \( \mathcal{E}(R_{cm}) = -\nabla \Phi(R_{cm}) \) is the external electric field, which is felt at the center of mass of the ion. We also need to mention that higher-order terms in Eqs. (3.28) and (3.29), correspond to higher-order variations of the field around the center-of-mass, which we assume to be small and negligible. By ignoring the variation of the field around the center of mass of the ion, we literally have approximated the dipole to be a point-like electric dipole moment. The derivation of Eq. (3.33) can be found in more details in Paper III (see Ref. [49]).

In the next step, we can also consider that the external electric field can distort the charge distribution of the molecule or the molecular ion and hence induce an electric dipole moment, if the field is strong enough. The tendency of the molecule to be deformed in response to an external electric field is called electric polarizability of the molecule, which is a property of matter. This polarizability is
the ratio of the induced dipole moment to the electric field \[^{[47]}\]. In the case of the molecule being polarized, we also need to take into account the interaction of the induced dipole moment with the external electric field. In general we can define the dipole moment of a molecule as \[^{[50]}\]

\[
\mu = \mu_0 + \frac{1}{2} \alpha \mathcal{E} + \frac{1}{6} \beta \mathcal{E}^2 + \frac{1}{24} \gamma \mathcal{E}^3 + \ldots,
\]

(3.34)

where \(\mu_0\) represents the zeroth moment, \(\alpha\) is the polarizability tensor, and \(\beta\) and \(\gamma\) are the first and the second hyperpolarizability tensors, respectively.

Now, by using the definition of the total electric dipole moment of a molecular ion in Eq. (3.34) and substituting it into Eq. (3.33) and ignoring the higher terms corresponding to the hyperpolarizability of the molecular ion, the Hamiltonian of a diatomic molecular ion, exposed to an external electric field \(\mathcal{E}\), is

\[
\hat{H} = -\frac{\hbar^2}{2m} \nabla_{R_{\text{cm}}}^2 + \frac{B \mathcal{J}_z^2}{\hbar^2} + Ze\Phi(R_{\text{cm}}) - \mu_0 \cdot \mathcal{E}(R_{\text{cm}}) - \frac{1}{2} \alpha \mathcal{E}^2(R_{\text{cm}}).
\]

(3.35)

3.3 Hamiltonian of a rigid diatomic molecular ion trapped in a linear Paul trap and interacting with an off-resonance laser field

Finally, we consider a rigid diatomic molecular ion, which is trapped in a linear Paul trap and at the same time can interact with an off-resonance laser field. In this case, the external electric field is composed of the trapping electric field and the laser electric field

\[
\mathcal{E}(x, y, z; t) = \mathcal{E}_{\text{Trap}}(x, y, z; t) + \mathcal{E}_{\text{Laser}}(x, y, z; t),
\]

(3.36)
in which the time dependency of both electric fields is explicitly emphasized. We also need to mention that the strength of the trapping electric field is assumed to be small enough to ignore any possibility of the ion being polarized by the trapping electric field. As a result, we only consider the polarizability of the ion by the laser field. Eventually, the Hamiltonian of a rigid diatomic molecular ion, which is trapped in a linear Paul trap and is interacting with a laser field, has the form

\[
\hat{H} = -\frac{\hbar^2}{2m} \nabla_{R_{\text{cm}}}^2 + \frac{B \mathcal{J}_z^2}{\hbar^2} + Ze\Phi_{\text{Trap}}(R_{\text{cm}}; t) - \mu_0 \cdot \mathcal{E}_{\text{Trap}}(R_{\text{cm}}; t) - \mu_0 \cdot \mathcal{E}_{\text{Laser}}(R_{\text{cm}}; t) - \frac{1}{2} \alpha \mathcal{E}_{\text{Laser}}^2(R_{\text{cm}}; t),
\]

(3.37)
where $\mathbf{E}_{\text{Trap}} = -\nabla \Phi_{\text{Trap}}$ [with $\Phi_{\text{Trap}}$ given by Eq. (2.4)], felt at the centre of mass of the ion, is written as

$$
\mathbf{E}_{\text{Trap}}(X,Y,Z;t) = \left[ \frac{\kappa U_0}{z_0^2} - \frac{V_0}{r_0^2} \cos \Omega_{\text{rf}} t \right] X \hat{x} + \left[ \frac{\kappa U_0}{z_0^2} + \frac{V_0}{r_0^2} \cos \Omega_{\text{rf}} t \right] Y \hat{y} - \frac{2\kappa U_0}{z_0^2} Z \hat{z},
$$

(3.38)

in which the unit vectors ($\hat{x}, \hat{y}, \hat{z}$) are those of a lab-fixed frame [see Fig. 4.4 in Sec. 4.2.1].

Concerning the laser electric field, we consider a classical electromagnetic field with a Gaussian profile. The wave length of the laser is assumed to be off-resonance, which means we have eliminated the possibility of any induced transition between the internal states of the ion. The electric field of the laser has the form [51]

$$
\mathbf{E}_{\text{Laser}}(\mathbf{r};t) = \mathbf{E}_{\text{Laser}}(\mathbf{r}) \cos(\mathbf{k} \cdot \mathbf{r} - \Omega_{\text{L}} t),
$$

(3.39)

in which $\Omega_{\text{L}}$ is the frequency of the laser field, $\mathbf{k}$ is the wave vector corresponding to the wave number $k = 2\pi/\lambda$ with $\lambda$ being the wavelength of the laser beam, and $\mathbf{E}_{\text{Laser}}(\mathbf{r})$ is the amplitude of the laser field. Considering the long wavelength approximation, by which we can take $\mathbf{r} = 0$ in $\cos(\mathbf{k} \cdot \mathbf{r} - \Omega_{\text{L}} t)$ [51], the laser field is simplified to $\mathbf{E}_{\text{Laser}}(\mathbf{r};t) = \mathbf{E}_{\text{Laser}}(\mathbf{r}) \cos(\Omega_{\text{L}} t)$.

Figure 3.3: (a) A Gaussian beam propagating along the $z$-axis, with a profile defined as $\exp \left[ -\frac{r^2}{w(z)^2} \right]$, (b) The wave-front of this Gaussian beam with the width $w(z)$ as a function of the distance $z$ along the beam. $w_0$, represents the waist of the beam at $z = 0$. 17
In a Gaussian beam, the amplitude of the electric field is inhomogeneous in space, which is responsible for producing an attractive potential well that can eventually trap particles [52]. Considering this spatial variation of the electric field, it can be shown in its simplest form as [52, 53]

\[ \mathcal{E}_{\text{Laser}}(r) = \mathcal{E}_0 \frac{w_0}{w(z)} \exp \left[ -\frac{(x-x_0)^2 - (y-y_0)^2}{w(z)^2} \right] \hat{\varepsilon}, \]  

(3.40)

which represents a beam propagating along the \( z \)-axis and is focused off-center from the center of the trapping device. For a beam focused at the center of the trap, we have \( x_0 = y_0 = 0 \). The polarization of this beam is indicated by the unit vector \( \hat{\varepsilon} \), which is perpendicular to the direction of the propagation. Also, \( \mathcal{E}_0 \) is defined as [52]

\[ \mathcal{E}_0 = \left( \frac{I}{2\epsilon_0 c} \right)^{\frac{1}{2}}, \]  

(3.41)

with \( I, \epsilon_0 \) and \( c \), being the intensity of the laser, the electric constant, and the speed of light, respectively.

Finally, \( w(z) \) is proportional to the width of the beam and representing the radius, at which the field amplitude and intensity drop to \( 1/e \) and \( 1/e^2 \) of their axial values, respectively [53] and is calculated as

\[ w(z) = w_0 \left[ 1 + \left( \frac{\lambda z}{\pi w_0^2} \right)^2 \right]^{1/2}, \]  

(3.42)

with \( w_0 = w(0) \), known as the waist of the beam [see Fig. 3.3] and \( \lambda \) the wavelength of the laser beam.
Chapter 4

Numerical methods

In this chapter we present a model to study the dynamics of a single diatomic molecular ion, trapped in a linear Paul trap, by solving the Schrödinger equation, corresponding to the Hamiltonian of the system presented in Eqs. (3.35) and (3.37). In order to establish our numerical methods, we have treated the problem using full-classical, full-quantum mechanical and also semi-classical approaches, depending on different conditions imposed on the problem.

We first, by ignoring the rotation of the ion study the translational motion of the center-of-mass inside the linear Paul trap. In a second time, we also consider the rotation of the ion and we study the probable couplings between the rotational and the translational states. In the former case, the problem reduces to the same as having a system composed of an atomic ion inside a linear Paul trap, where we are only interested in translational motion of the center-of-mass. In the latter case, we have a single rigid diatomic molecular ion, which possesses a permanent dipole moment and demonstrates translational and rotational dynamics in the presence of external fields.

4.1 A single atomic ion inside a linear Paul trap

Considering the Hamiltonian in Eq. (3.37) and taking $\mu_0 = 0$ and also by ignoring the presence of the laser field, the Hamiltonian reduces to Eq. (4.1),

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla_{R_{cm}}^2 + Z e \Phi_{\text{Trap}}(R_{cm}; t). \quad (4.1)$$
which represents the Hamiltonian of a single atomic ion, trapped in a linear Paul trap.

As before, the possibility of the atomic ion to become polarized by the external trapping electric field is assumed to be zero as the magnitude of the electric field is not sufficiently large to induce any polarization and hence any induced dipole moment. To find the trajectories of the center of mass of the ion, we have applied both full-classical and full-quantum mechanical approaches. In the classical approach we solve the equations of motion corresponding to the Hamiltonian in Eq. (4.1). On the other hand, to treat the problem quantum mechanically, we consider the wave function to the ion and we solve the corresponding Schrödinger equation, which will be discussed in following sections.

### 4.1.1 Classical approach

The classical Hamiltonian of an atomic ion in a linear Paul trap is written as

\[
H = \frac{p^2}{2m} + Ze\Phi_{\text{Trap}}(\mathbf{R}_{\text{cm}}; t),
\]

which gives the classical equations of motion

\[
m\ddot{\mathbf{R}}_{\text{cm}} + Ze\nabla \Phi_{\text{Trap}}(\mathbf{R}_{\text{cm}}; t) = 0.
\]

Rewriting Eq. (4.3) explicitly in its components (\(X, Y\) and \(Z\) are the coordinates of the ion’s center-of-mass)

\[
m\ddot{X} + Ze \left[ -\frac{kU_0}{z_0^2} + \frac{V_0}{r_0^2} \cos \Omega t \right] X = 0,
\]

\[
m\ddot{Y} + Ze \left[ -\frac{kU_0}{z_0^2} - \frac{V_0}{r_0^2} \cos \Omega t \right] Y = 0,
\]

\[
m\ddot{Z} + Ze \left[ \frac{2kU_0}{z_0^2} \right] Z = 0,
\]

we obtain three differential equations, which obey the Mathieu differential equation

\[
\frac{d^2\mathbf{r}}{d\zeta^2} + (a - 2q \cos 2\zeta) \mathbf{r} = 0,
\]

and considering our equations of motion of an atomic ion trapped in a linear Paul trap [Eqs. (4.4)], we have

\[
\zeta = \frac{\Omega t}{2},
\]
and

\[ a_x = a_y = -\frac{4Ze}{m\Omega^2} \frac{kU_0}{z_0^2}, \quad (4.7a) \]

\[ a_z = \frac{8Ze}{m\Omega^2} \frac{kU_0}{z_0^2}, \quad (4.7b) \]

\[ q_x = -q_y = \frac{2Ze}{m\Omega^2} \frac{V_0}{r_0^2}, \quad (4.7c) \]

\[ q_z = 0, \quad (4.7d) \]

where \( a \) and \( q \) above are the parameters of the Mathieu equation.

The Mathieu equation, in general, is a form of the Hill equation with only one harmonic mode and is useful in studying periodic systems [54] and its parameters \( a \) and \( q \) provide useful information about solutions of the Mathieu equation [54]. The Mathieu equation has either stable or unstable solutions, depending on whether its parameters are located inside or outside of a region in the \( a - q \) plane, called the stability regions. The first three stability regions of the Mathieu equation corresponding to the Eq. (4.5) are shown in Fig. 4.1. In this figure, shaded areas represent regions, where \( r \) remains finite. This figure is produced using Mathematica [55].

![Figure 4.1: First three stability regions of the Mathieu equation, corresponding to Eq. (4.5). These regions are bounded by the characteristic values \( a_0, b_1, a_1, b_2 \) and \( a_2, b_3 \) [54]. All curves are symmetric with respect to \(-q\).](image)

For quadrupole trap devices, in general, parameters of the corresponding Mathieu equation are dependent on the size of the trap, the magnitude of the trapping
potentials and the frequency of the oscillating field and also on the mass and charge of the ion [see Eqs. (4.7)]. As a consequence, upon choosing the right parameters for a trapping system, the corresponding Mathieu equation will have stable solutions, which result in having bounded, periodic trajectories in all directions, for the center-of-mass motion of the ion inside the trap [20, 36, 56]. Otherwise the trajectories are unbounded, and the ion will escape the trapping device.

The bounded trajectories consist of two types of motion, an average and dominant secular motion, on which a high-frequency micromotion is superimposed [20, 36, 56]. The secular motion corresponds to the trajectories of motion, which should be observed in the time average of the trapping electric potential with a time scale bigger than the time scale for the oscillating electric potential. On the other hand, the small-amplitude micromotion, which is driven at the frequency of the oscillation of the electric potential $\Omega_{rf}$, has smaller amplitude [20, 56]. We have shown these two types of motions for a Ca$^+$ ion in Fig. 4.2. For this example, amplitudes of the radio-frequency field ($V_0$) and the static field ($U_0$), are equal to 50 V and 2 V, respectively. As it is shown, the secular motion is purely harmonic, on which a fast oscillating motion is superposed, caused by the time-dependent radio-frequency field.

![Figure 4.2: X-component of the center-of-mass motion of a Ca$^+$ ion, trapped in a linear Paul trap with (U_0, V_0) = (2 V, 50 V). The dotted-black curve represents a purely harmonic motion, named as secular motion, which is caused by a purely harmonic field. On the other hand, the red curve represents a harmonic motion with the fast oscillating micromotion on top of it, which is caused by the time-dependent radio-frequency field.](image-url)
In the case of a linear Paul trap, the oscillation of the center of mass in the $Z$-direction is purely harmonic possessing no micromotion due to the lack of any radio-frequency drive. See the $Z$-component of Eq. (4.4).

To solve the classical equations of motion, we used the Strömer-Verlet scheme, which is a symplectic integrator \[57\]. This method is proven to be a suitable choice among other methods for an ODE of the second order, where the energy conservation the systems is concerned \[57\].

We suppose a second order ODE of the form

$$\ddot{r} = f(r),$$

(4.8)

where $r$ represents the position and $f$ describes forces acting on the particle. In the Strömer-Verlet method, the time discretization of the ODE has the form \[58\]

$$r_{n+1} - 2r_n + r_{n-1} = \Delta t^2 f(r_n),$$

(4.9)

in which $\Delta t$ stands for the step size in time and $n$ represents the number of steps. This relation is a two-step formula and we can change it to a one-step formula by introducing the momentum $p = \dot{r}$ and considering that $\dot{p} = f(r)$, we get discrete approximations of $p$ and $r$ as \[57, 58\]

$$p_n = \frac{r_{n+1} - r_{n-1}}{2\Delta t},$$

$$p_{n-\frac{1}{2}} = \frac{r_n - r_{n-1}}{\Delta t},$$

$$r_{n-\frac{1}{2}} = \frac{r_n + r_{n-1}}{2}. $$

(4.10)

Now by extending the above formulas to a more general form by taking $r$ and $p$ to be generalized coordinates of the system, for which $\dot{r} = H_p(p, r)$ and $\dot{p} = -H_r(p, r)$, they lead to recurrence relations below \[57\]

$$p_{n+\frac{1}{2}} = p_n - \frac{\Delta t}{2} H_r \left[ p_{n+\frac{1}{2}}, r_n \right],$$

$$r_{n+1} = r_n + \frac{\Delta t}{2} \left[ H_p \left( p_{n+\frac{1}{2}}, r_n \right) + H_p \left( p_{n+\frac{1}{2}}, r_{n+1} \right) \right],$$

(4.11)

$$p_{n+1} = p_{n+\frac{1}{2}} - \frac{\Delta t}{2} H_r \left[ p_{n+\frac{1}{2}}, r_{n+1} \right],$$

where $H_p$ and $H_r$ are column vectors of partial derivatives of the Hamiltonian $H(p, r)$ with respect to the generalized coordinates $p$ and $r$, respectively \[57\]. For
our Hamiltonian, this system reduces to
\[ p_{n + \frac{1}{2}} = p_n - \frac{\Delta t}{2} H_{r_n}, \]
\[ r_{n+1} = r_n + \Delta t \frac{p_{n + \frac{1}{2}}}{m}, \] (4.12)
\[ p_{n+1} = p_{n + \frac{1}{2}} - \frac{\Delta t}{2} H_{r_{n+1}}, \]

where the components of \( H_{r_n} \) are given by
\[ H_{X_n} = Z e \left[ -\frac{\kappa U_0}{z_0^2} + \frac{V_0}{r_0^2} \cos(\Omega t_n) \right] X_n, \]
\[ H_{Y_n} = Z e \left[ -\frac{\kappa U_0}{z_0^2} - \frac{V_0}{r_0^2} \cos(\Omega t_n) \right] Y_n, \] (4.13)
\[ H_{Z_n} = 2 \frac{Z e \kappa U_0}{z_0^2} Z_n. \]

Due to the fact that the potential of the system is separable in spatial coordinates, we can also separate the Hamiltonian for each coordinate. We obtain six equations of motion, defining the time variations of coordinates and their corresponding linear momenta
\[ X_{n+1} = \frac{\Delta t}{m} p_n^X + X_n \left\{ 1 - \frac{\Delta t^2}{m} \left[ b_1 \cos (n \Delta t \Omega) - b_2 \right] \right\}, \] (4.14a)
\[ Y_{n+1} = \frac{\Delta t}{m} p_n^Y + Y_n \left\{ 1 + \frac{\Delta t^2}{m} \left[ b_1 \cos (n \Delta t \Omega) + b_2 \right] \right\}, \] (4.14b)
\[ Z_{n+1} = \frac{\Delta t}{m} p_n^Z + Z_n \left\{ 1 - \frac{\Delta t^2}{m} b_2 \right\}, \] (4.14c)
\[ P_{n+1}^X = P_n^X - \Delta t X_n \left\{ b_1 \cos (n \Delta t \Omega) - b_2 \right\} \]
\[ - \Delta t X_{n+1} \left\{ b_1 \cos [(n + 1) \Delta t \Omega] - b_2 \right\}, \] (4.14d)
\[ P_{n+1}^Y = P_n^Y + \Delta t Y_n \left\{ b_1 \cos (n \Delta t \Omega) + b_2 \right\} \]
\[ + \Delta t Y_{n+1} \left\{ b_1 \cos [(n + 1) \Delta t \Omega] + b_2 \right\}, \] (4.14e)
\[ P_{n+1}^Z = P_n^Z - \Delta t Z_n b_2 - \Delta t Z_{n+1} b_2, \] (4.14f)
Finally, the system of equations above can be iterated starting from initial conditions namely $R_{0\text{cm}} \equiv (X_0, Y_0, Z_0)$ and $P_{0\text{cm}} \equiv (P_{0X}^X, P_{0Y}^Y, P_{0Z}^Z)$. We have taken components of the linear momentum equal in all directions ($P_{0X}^X = P_{0Y}^Y = P_{0Z}^Z = P$), corresponding to an initial translational temperature $T_0$ for the ion through the relation

$$P = \sqrt{mk_B T_0},$$

in which $k_B$ is the Boltzmann constant.

At the end, we should mention that the actual motion of the ion in a 3D space is the superposition of the results obtained for each components of the motion.

### 4.1.2 Quantum mechanical approach

As we pointed out earlier, studying the dynamics of the system quantum mechanically is equal to study the time evolution of the wave function of an ion, which is trapped in a linear Paul trap. In order to solve the time-dependent Schrödinger equation numerically, we use *split-operator* method [59–61], for which we need to define grid points in space.

We first consider the time-dependent Schrödinger equation

$$i\hbar \frac{d\Psi(R_{\text{cm}}; t)}{dt} = \hat{H}\Psi(R_{\text{cm}}; t),$$

in which $\Psi(R_{\text{cm}}; t)$ is the wave function for the center-of-mass motion of a trapped atomic ion, with the Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2_{R_{\text{cm}}} + Ze\Phi_{\text{Trap}}(R_{\text{cm}}; t).$$

Solutions to Eq. (4.17) are obtained by using the time-evolution operator $\hat{U}$ [44,46], which evolves the wave function forward in time

$$\Psi(R_{\text{cm}}; t) = \hat{U}(t, t_0)\Psi(R_{\text{cm}}; t_0),$$

with

$$b_1 = \frac{ZeV_0}{2r_0^2},$$  

$$b_2 = \frac{Ze\kappa U_0}{2z_0^2}. $$

(4.15a)

(4.15b)
where $\Psi(R_{cm}; t_0)$ is the initial wave function. The time-evolution operator $\hat{U}$ is also a solution of the time-dependent Schrödinger equation

$$i\hbar \frac{d\hat{U}}{dt} = \hat{H}\hat{U},$$

(4.20)

in which

$$\hat{U}(t + \Delta t, t) = \hat{T}\exp \left[ -\frac{i}{\hbar} \int_t^{t+\Delta t} \hat{H}'(t')dt' \right],$$

(4.21)

where $\hat{T}$ is the Dyson time-ordering operator and in our case

$$\hat{U}(t + \Delta t, t) = \exp \left\{ -\frac{i}{\hbar} \int_t^{t+\Delta t} \left[ \hat{K} + \hat{V}(t') \right] dt' \right\},$$

(4.22)

in which $\hat{K}$ and $\hat{V}(t)$ are operators corresponding to the kinetic and the time-dependent potential energies of the ion in the linear Paul trap, respectively.

Since the time-dependent potential has also a spatial dependence, $\hat{K}$ and $\hat{V}(t)$ do not commute ($e^{\hat{A}+\hat{B}} \neq e^{\hat{A}}e^{\hat{B}}$), the split-operator method provides a good approximation of the evolution operator. Using this method, we can approximate the evolution operator as

$$\hat{U}(t + \Delta t, t) = \exp \left[ -\frac{i\Delta t}{2\hbar} \hat{K} \right] \exp \left[ -\frac{i}{\hbar} \int_t^{t+\Delta t} \hat{V}(t')dt' \right] \exp \left[ -\frac{i\Delta t}{2\hbar} \hat{K} \right] + O(\Delta t^3),$$

(4.23)

where $O(\Delta t^3)$ is the global error.

Since spatial coordinates and momenta are canonical conjugates of each other, we can re-express the spatial wave function in momentum space, using a Fourier transform. This can be implemented as a $O(N\log_2 N)$ order algorithm with the Fast Fourier Transform (FFT), in which $N$ is the number of grid points in our simulation. Finally, using the split-operator method along with the FFT, the time evolution of the wave function will be obtained according to

$$\Psi(R_{cm}; t + \Delta t) = e^{-\frac{i}{\hbar} \Delta t \hat{K}} \mathcal{F}^{-1} e^{-\frac{i}{\hbar} \Delta t \hat{V}} \mathcal{F} e^{-\frac{i}{\hbar} \Delta t \hat{K}} \Psi(R_{cm}; t),$$

(4.24)

where $\mathcal{F}$ and $\mathcal{F}^{-1}$ indicate the direct and inverse Fourier transformation, respectively. The usage and the detailed description of this method is explicitly presented in Paper I (see Ref. [67]).
At this point, we need to select the initial wave function. We note that the time-dependent quadrupole potential of the linear Paul trap gives rise to approximately harmonic secular motion of the ion in all directions \([17]\), specifically near the centre of the trap (trapping axis in the case of a linear Paul trap) \([38]\). Therefore, we can approximate the problem as a harmonic oscillator and take the initial state a Gaussian wave packet \([42]\). This initial wave packet can have any arbitrary size, depending on the spatial grid size \([67]\) we choose for our numerical simulations (split-operator method, mentioned earlier). In this regard, the width of the initial wave packet is desired not to reach beyond the grid boundaries. Therefore, to avoid this situation, we need to increase the grid size, which consequently increases the execution time of the numerical calculations. However, in this work, in order to reduce the numerical operations we have used the effective potential approximation \([20, 38]\) – which will be introduced in the next section – to define our initial wave packet.

Being capable of calculating the time evolution of the ion’s wave function allows us to obtain information about the spatial position of the center of mass of the ion inside the trap, as a function of time. From a quantum-mechanical point of view, the position of the center of mass of the ion, at each time step, corresponds to calculating the expectation values of positions \(X, Y\) and \(Z\)

\[
R_{\text{cm}}(t) \equiv \langle R_{\text{cm}} \rangle_t = \langle \Psi(R_{\text{cm}}; t) | R_{\text{cm}} | \Psi(R_{\text{cm}}; t) \rangle,
\]

(4.25)

and it will be shown later that the time evolution of these expectation values are equal to the time evolution of the classical position of center-of-mass. This is also stated in some previous works such as in the Ref. \([21]\).

It should be mentioned that the wave function in Eq. (4.25) is written as a full wave function in 3D, but as long as our Hamiltonian [see Eq. (4.18)] is separable in coordinates, the wave function is also separable, and consequently the 3D problem will reduce to three 1D problems. In this case the total wave function will be the product of each components of the wave-function

\[
\Psi(R_{\text{cm}}; t) = \Psi(X; t) \times \Psi(Y; t) \times \Psi(Z; t),
\]

(4.26)

however, one needs to be careful when dealing with problems such as the interaction of the trapped ion with the laser field, where the interaction energy of the laser field with the ion contains the laser electric field, which can lead to the Hamiltonian of the system not being separable into spatial coordinates [see Eq. (3.40) in Sec. 3.3].


4.1.3 Effective potential approximation and estimating the initial wave-functions

According to the effective potential approximation, for a sufficiently large trap frequency \(\Omega_{\text{rf}}\), a particle in a time-periodic potential \(V(r)\cos \Omega_{\text{rf}} t\) behaves as if it was subjected to a static potential \([21]\).

If we consider the Schrödinger equation

\[
\frac{i\hbar}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2 \psi(r; t) + U(r)\psi(r; t) + V(r; t)\psi(r; t),
\]

(4.27)

where \(V\) is a time-dependent potential with periodicity \(\tau = 2\pi/\Omega\), we can define a general solution for Eq. (4.27) as \([20]\)

\[
\psi(r; t) = \exp\left[-\frac{i}{\hbar}W(r; t)\right] \Phi(r; t),
\]

(4.28)

where \(\partial W(r; t)/\partial t = V(r; t)\) and \(\langle W \rangle = 0\) \([20]\). Now substituting Eq. (4.28) into the Schrödinger equation, we get

\[
\frac{i\hbar}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2 \phi(r; t) + U(r)\phi(r; t) + S\phi(r; t),
\]

(4.29)

where

\[
S = \frac{i\hbar}{m}(\nabla W)\nabla + \frac{i\hbar}{2m}\nabla^2 W + \frac{1}{2m}(\nabla W)^2,
\]

(4.30)

and the effective potential can be defined as the time average of the expression in Eq. (4.30), which is equivalent to \(V_{\text{eff}}(r) = \langle S \rangle\) \([20]\). Subsequently, the solution to the Schrödinger equation in Eq. (4.27) can be approximated as

\[
\psi_{\text{eff}}(r; t) = \exp\left[-\frac{i}{\hbar}W(r; t)\right] \Phi(r; t),
\]

(4.31)

in which \(\Phi(r; t)\) is the solution to the Schrödinger equation with the time-dependent potential \(V(r; t)\) replaced by the effective potential \(V_{\text{eff}}(r)\). It will be shown later that the validity of this approximation is limited.

To calculate the effective potential energy of a trapped ion in a linear Paul trap, we suppose that the motion of the ion consists of two components, the secular motion and the micromotion, as it is introduced in previous sections. The micromotion, as noted before, is purely caused by the time-dependent part of the potential, giving \([68]\)

\[
m\ddot{r}_{\text{mic}} = -eZ \frac{dV(r; t)}{dr},
\]

(4.32)
in which $\mathbf{r}_{\text{mic}}$ is micro-acceleration and $eZ$ is the charge of the particle. To write the equation of the motion for the ion, we have

$$m\ddot{\mathbf{r}} = F(\mathbf{r}) + f(\mathbf{r}; t), \quad (4.33)$$

where $F(\mathbf{r})$ and $f(\mathbf{r}; t)$ are forces due to static and time-dependent potentials, respectively.

Now by substituting the acceleration with $(\ddot{\mathbf{r}}_{\text{sec}} + \ddot{\mathbf{r}}_{\text{mic}})$ ($\ddot{\mathbf{r}}_{\text{sec}}$ is the secular-acceleration) and expanding Eq. (4.33) around $\ddot{\mathbf{r}}_{\text{mic}}$ to first order, we have

$$m(\ddot{\mathbf{r}}_{\text{sec}} + \ddot{\mathbf{r}}_{\text{mic}}) = F(\mathbf{r}_{\text{sec}}) + f(\mathbf{r}_{\text{mic}}; t) + m\left(\frac{\partial F(\mathbf{r})}{\partial \mathbf{r}} \bigg|_{\mathbf{r}=\mathbf{r}_{\text{sec}}} + \frac{\partial f(\mathbf{r}; t)}{\partial \mathbf{r}} \bigg|_{\mathbf{r}=\mathbf{r}_{\text{mic}}}ight), \quad (4.34)$$

and by averaging Eq. (4.34) over one period of micromotion $2\pi/\Omega_{\text{rf}}$ and using Eq. (4.32), we get the effective potential energy of the form

$$V_{\text{eff}}(\mathbf{r}) = \frac{e^2}{4m\Omega_{\text{rf}}^2} \left(\frac{\partial V(\mathbf{r})}{\partial \mathbf{r}}\right)^2, \quad (4.35)$$

where we have taken $Z = 1$.

Finally, considering the linear Paul trap with the time-dependent and static potentials given in Eqs. (2.3a) and (2.3b), the total effective potential energy is obtained as

$$V_{\text{Total}}(\mathbf{r}) = e\Phi_s + V_{\text{eff}} \equiv \frac{1}{2} \left[ \frac{e\kappa U_0}{z_0^2} (2z^2 - x^2 - y^2) + \frac{e^2}{4m\Omega_{\text{rf}}^2} \left(\frac{\partial \Phi_{\text{rf}}(\mathbf{r})}{\partial \mathbf{r}}\right)^2 \right]. \quad (4.36)$$

Now, referring to the problem of setting the initial wave function for an ion being trapped in a linear Paul trap, we consider a harmonic oscillator that satisfies the Schrödinger equation

$$-\frac{\hbar^2}{2m} \nabla^2_{\mathbf{R}_{\text{cm}}} \Psi(\mathbf{R}_{\text{cm}}) + \frac{1}{2} k\mathbf{R}_{\text{cm}}^2 \Psi(\mathbf{R}_{\text{cm}}) = E \Psi(\mathbf{R}_{\text{cm}}), \quad (4.37)$$

where $k$ is the oscillator constant that in our case it depends on trapping configuration parameters and will be estimated by using the so called effective potential.

On the other hand, eigenfunctions of the Schrödinger equation (4.37) are normalized linear harmonic oscillator eigenfunctions that can be obtained according to

$$\Psi_n(\mathbf{R}_{\text{cm}}) = \left(\frac{1}{\sigma_0 \sqrt{\pi 2^n n!}}\right)^{\frac{1}{2}} \exp \left(-\frac{\mathbf{R}_{\text{cm}}^2}{2\sigma_0^2}\right) H_n \left(\frac{\mathbf{R}_{\text{cm}}}{\sigma_0}\right). \quad (4.38)$$
These eigenfunctions (wave functions) are Gaussian-like wave packets and the parameter \( \sigma_0 = \left( \frac{mk}{\hbar^2} \right)^{1/4} \) represents the initial width of the wave packet, which is also dependent on \( k \). \( H_n \) are the Hermite polynomials and for our initial eigenstate, we take the translational ground state, \( n = 0 \).

We have also assumed that the ion has an initial momentum \( \hbar k_0 \), where \( k_0 \) is the correspondent initial wave number attributed to the ion. This results in an additional complex phase factor for the initial wave packet that is assumed to be initially centered at zero (centre of the trap). Finally, the initial wave function of the ion has the form

\[
\Psi_0(R) = \left( \frac{1}{\pi \sigma_0^2} \right)^{\frac{1}{4}} \exp \left[ -\frac{(R - R_0)^2}{2\sigma_0^2} \right] \exp(ik_0R). \tag{4.39}
\]

Considering \( k_0 \), we assume an initial linear momentum for the ion, which has a magnitude proportional to an initial temperature, as we also pointed out earlier in the classical approach. We can also simply eliminate the phase factor in the initial wave function and give the ion an off-center position in space which eventually works as an initial drive for the ion to start its oscillations, otherwise as the electric field is zero at the center of the trap, the ion will not undergo any oscillations. However, we need to mention that the effect of considering either an initial linear momentum for the ion or assigning an initial spatial position to the ion other than \( \mathbf{R}_c = (0, 0, 0) \), gives the same result qualitatively and do not change the dynamical behavior of the ion.

Now to set the initial width of this initial wave packet, as noted before, we will use the effective potential approximation. This can be done by comparing the effective potential energy in Eq. (4.36) with the harmonic oscillator potential energy, presented in Eq. (4.37), which eventually results in finding \( k \) (oscillator constant) and hence relations below for each components of the initial width of the wave packet

\[
\begin{align*}
\sigma_0^x &= \left[ \frac{e^2 V_0^2}{2\hbar^2 \Omega^2 r_0^4} - \frac{m\kappa U_0}{\hbar^2 z_0^2} \right]^{1/4}, \\
\sigma_0^y &= \left[ \frac{e^2 V_0^2}{2\hbar^2 \Omega^2 r_0^4} - \frac{m\kappa U_0}{\hbar^2 z_0^2} \right]^{1/4}, \\
\sigma_0^z &= \left[ \frac{2m\kappa U_0}{\hbar^2 z_0^2} \right]^{1/4}.
\end{align*}
\tag{4.40}
\]

Finally, the total initial wave function, which is a function of coordinates in
space will be the multiplication of each of its components

\[ \Psi_0(R_{cm}) = \Psi_0(X) \times \Psi_0(Y) \times \Psi_0(Z). \]  \hspace{1cm} (4.41)

4.1.4 Stability region from quantum mechanical point of view

As it was already discussed in Sec. 4.1.1 the classical equations of motion of an ion inside a quadrupole trap obey the Mathieu equation \[20, 56\]. Therefore, for the ion to remain trapped inside the device, or in other words to have bounded trajectories of motion in all directions, parameters of the corresponding equations of motion of the ion, \(a\) and \(q\), must fall into stability regions of the Mathieu equation \[54\]. Choosing certain values of the trapping fields results in stable solutions. Therefore, from the classical point of view, the confinement (stability) of the ion inside the trapping device follows the stability of the Mathieu equation (see the stability regions of the Mathieu equation in Fig. 4.1).

However, to define such conditions for the stability of a quantum particle is more complicated, but it has been claimed in many previous works that classical stability regions apply to a quantum particle as well \[21, 23–25\]. For instance, in Ref. \[21\], Combescure mentions that due to the quadratic character of the interaction of the trapping field with the ion, the time-dependent position and momentum quantum observables (Heisenberg observables) obey the Mathieu equation.

It has also been stated in Refs. \[24, 25\] by Glauber that a Gaussian wave packet attributed to the trapped ion remains confined in size. Its width will pulsate periodically, but have no tendency to spread out. In his works, he has studied the evolution of the wave function of the ion through their Wigner function \[69\]. The Wigner function is a semi-classical and quasi-probability distribution, which is introduced to study quantum corrections to classical statistical mechanics \[69, 70\]. By using this function, it is possible to draw a link between the wave function and the probability distribution in phase space \[69, 70\]. This fact is in exact accordance with his statement that the Gaussian wave packet attributed to the trapped ion follows a classical trajectory in the position-momentum plane (phase space) \[24\].

According to all statements above, we can examine the quantum mechanical validity of the classical stability regions, as well. To do so, we can study the time evolution of the width of the wave packet, which is calculated as

\[ \sigma_\xi = \sqrt{\langle \xi^2 \rangle - \langle \xi \rangle^2}, \]  \hspace{1cm} (4.42)

with \(\xi \in \{X, Y, Z\}\) and the expectation values \(\langle \xi^2 \rangle, \langle \xi \rangle\), are obtained according
to Eq. (4.25). It has been shown in Papers II and IV (see Ref. [71] for Paper II) that the width of the wave packet tends to spread quickly for parameters of the trapping potential even slightly outside the classical stability regions. On the other hand, for parameters inside the classical stability regions, the width of the wave packet will remain bounded.

4.2 A single molecular ion inside a linear Paul trap

In this section, we present a model for the rotational and the translational dynamics of a rigid diatomic molecular ion, trapped in a linear Paul trap, which eventually interacts with an off-resonance laser field. By referring to Eq. (3.35) in Sec. 3.2 and by ignoring the interaction of the ion with the laser field, for the present, we remind that the molecular ion possesses a permeant dipole moment $\mu_0$ which also interacts with the trapping electric field. This interaction affects both the translational and the rotational dynamics of the ion. Therefore, in order to study the probable effects of this interaction, on translational and rotational states of the ion and also to investigate any probable coupling between these states, we carry out both classical and semi-classical simulations.

In the classical approach, we study the dynamics of the center-of-mass of the ion via its classical equations of motion, translationally and rotationally. On the other hand, in the semi-classical approach, while we retain the classical approach for obtaining the coordinates of the molecular ion, the rotation will be treated full-quantum mechanically.

4.2.1 Classical approach

Before introducing a classical model for a molecular ion trapped in a linear Paul trap, we consider a classical free rigid rotor, consisting of two masses, $m_1$ and $m_2$ that are situated in a distance $R$ from each other. This is depicted in Fig. 4.3. Considering the spherical coordinates, this rotor has a rotational energy equivalent to

$$K_{\text{rot}} = \frac{1}{2}m_{\text{red}}R^2 \left[ \dot{\theta}^2 + \dot{\varphi}^2 \sin^2 \theta \right],$$  

(4.43)

in which the terms containing Euler angles represent the angular velocity $\omega$ of the rotor ($\omega^2 \equiv \dot{\theta}^2 + \dot{\varphi}^2 \sin^2 \theta$), precessing around an axis passing through the center-of-mass of the system and perpendicular to $R$. The derivation of Eq. (4.43) is shown in the Paper III (see Ref. [49]), in more details.
Figure 4.3: A classical rigid rotor, constituting of masses $m_1$ and $m_2$, which are situated at a distance $R$ from each other. Angles $\varphi$ and $\theta$ indicate the orientation of this rotor with respect to a lab-fixed frame ($X, Y, Z$).

The Lagrangian of this free rigid rotor $\mathcal{L} = K - V$ (with $V = 0$), gives us general momenta that are canonically conjugate to spherical coordinates $\theta$ and $\varphi$, as

$$P_\theta \equiv \frac{\partial \mathcal{L}}{\partial \dot{\theta}} = m_{\text{red}} R^2 \dot{\varphi}, \quad (4.44a)$$

$$P_\varphi \equiv \frac{\partial \mathcal{L}}{\partial \dot{\varphi}} = m_{\text{red}} R^2 \dot{\varphi} \sin^2 \theta, \quad (4.44b)$$

which result for the rotational Hamiltonian of a free rigid rotor

$$H_{\text{rot}} \equiv \frac{L^2}{2I} = \frac{1}{2m_{\text{red}} R^2} \left[ P_\theta^2 + \frac{P_\varphi^2}{\sin^2 \theta} \right], \quad (4.45)$$

where $L$ and $I = m_{\text{red}} R^2$ are the angular momentum and the moment of inertia of the system, respectively.

Subsequently, by knowing the Hamiltonian of a free rigid rotor [Eq. (4.45)], we can introduce the classical Hamiltonian of a molecular ion trapped in a linear Paul trap

$$H = \frac{P^2}{2m} + \frac{L^2}{2I} + Ze \Phi(R_{\text{cm}}; t) - \mu_0 \cdot E_{\text{Trap}}(R_{\text{cm}}; t). \quad (4.46)$$
Since we know the Hamiltonian of the system, we can derive the equations of motion of the center of mass of the ion, which include both translational and rotational equations of motion. Prior to that, we need to know how the interaction term between the dipole and the electric field appears in equations. In order to redefine this term \(-\mu_0 \cdot E_{\text{Trap}}\), we expand the dipole moment vector that has an arbitrary orientation in space, into its components, with respect to a lab-fixed frame, which is shown in Fig. 4.4.

![Figure 4.4: The orientation of the permanent dipole moment \(\mu_0\) of a diatomic molecule in space with respect to the center-of-mass (COM) frame \((x, y, z)\), which is indicated by angles \(\varphi\) and \(\theta\). The body-fixed frame \((x', y', z')\) shows the principal axes (or symmetry axes) of this molecule. The orientation of the dipole moment is fixed along \(z'\). The COM frame is aligned with the laboratory frame \((X, Y, Z)\), but has its origin at the center of mass of the molecule.](image)

Therefore, the dipole moment vector is obtained as

\[
\mu_0 = \mu_0 [\sin \theta \cos \varphi \hat{x} + \sin \theta \sin \varphi \hat{y} + \cos \theta \hat{z}],
\]  

(4.47)
and using the electric field of Eq. (3.38) in Sec. 3.3 gives

\[ \mathbf{\mu}_0 \cdot \mathbf{E}_{\text{Trap}} = \left[ \frac{\kappa U_0 \mu_0 \sin \theta \cos \varphi}{z_0^2} - \frac{V_0 \mu_0 \sin \theta \cos \varphi}{r_0^2} \cos \Omega_{rt} t \right] X \]

\[ + \left[ \frac{\kappa U_0 \mu_0 \sin \theta \sin \varphi}{z_0^2} + \frac{V_0 \mu_0 \sin \theta \sin \varphi}{r_0^2} \cos \Omega_{rt} t \right] Y \]

\[ - \left[ \frac{2\kappa U_0 \mu_0}{z_0^2} \cos \theta \right] Z. \]

As it is evident, the interaction term in Eq. (4.48) not only has a spatial dependence, but is also dependent on the orientation of the dipole (molecular ion) in space. Therefore, to write the equations of motion of the ion, corresponding to its translational and rotational motion of center-of-mass, we need to consider all its five degrees of freedom (three components of translation and two components of rotation). These equations are derived for generalized coordinates of the system, momentum \( p_r \) and position \( r \), according to

\[ \dot{p}_r = -\frac{\partial H}{\partial r}, \]

\[ \dot{r} = \frac{\partial H}{\partial p_r}, \]

with \( r \in \{X, Y, Z, \theta, \varphi\} \) and \( p_r \in \{P_X, P_Y, P_Z, P_\theta, P_\varphi\} \). However, by considering the rotational Hamiltonian \( (H_{\text{rot}}) \) in Eq. (4.45), these equations of motion present a singularity at \( \theta = 0 \), hence leaving us unable to perform a direct numerical solution.

To avoid this problem, we introduce a method called the body vector method [73], in which the diatomic molecular ion is considered as a di-axes body with a principal inertia tensor of the form

\[ I = \begin{pmatrix} I_{x'} & 0 & 0 \\ 0 & I_{y'} & 0 \\ 0 & 0 & 0 \end{pmatrix}, \]

in which \( I_{x'} = I_{y'} = I \equiv m_{\text{red}} R \) and \( I_{z'} = 0 \) (there is no rotation about the internuclear axis), all expressed in the body-fixed coordinate system \( (x', y', z') \), with unit vectors \( \hat{x}', \hat{y}' \) and \( \hat{z}' \), which are all shown in Fig. 4.4. The body-fixed coordinate system rotates with the ion and its unit vectors have components with respect to the COM-frame (center-of-mass frame of the ion), which always remains parallel to the lab-fixed frame (see Fig. 4.4). Therefore, we can write

\[ \hat{u}' = (u'_x, u'_y, u'_z), \]
where $\hat{u}' \in \{\hat{x}', \hat{y}', \hat{z}'\}$.

In the next step, we set the dipole moment (which is along the internuclear axis) to be always aligned with $z'$. Therefore, the unit vector $\hat{z}'$ simply gives the direction of the dipole moment in space [73]. These unit vectors are similar to variables that are introduced in previous works by Cheung in Refs. [74] and [75] to avoid singularities in equations of motion of diatomic molecules. As a result, we can write the dipole moment vector as

$$\mu_0 = \mu_0 \hat{z}',$$  \hspace{1cm} (4.52)

in which components of $\hat{z}'$ are the trigonometric terms, in Eq. (4.47),

$$z'_x = \sin \theta \cos \varphi,$$
$$z'_y = \sin \theta \sin \varphi,$$
$$z'_z = \cos \theta.$$

Therefore, to find the equations of motion, we can simply substitute the trigonometric functions into Eq. (4.48), by their new definition introduced in Eqs. (4.53). Finally, using Eq. (4.49), we can write the equations of motion for the translation of the center-of-mass of the ion as

\begin{align*}
\dot{X} &= \frac{P_X}{M}, \hspace{1cm} (4.54a) \\
\dot{Y} &= \frac{P_Y}{M}, \hspace{1cm} (4.54b) \\
\dot{Z} &= \frac{P_Z}{M}, \hspace{1cm} (4.54c) \\
\dot{P}_X &= eZ [b'_1 - b'_2 \cos \Omega_{rt} t] X + \mu_0 [b'_1 - b'_2 \cos \Omega_{rt} t] z'_x, \hspace{1cm} (4.54d) \\
\dot{P}_Y &= eZ [b'_1 + b'_2 \cos \Omega_{rt} t] Y + \mu_0 [b'_1 + b'_2 \cos \Omega_{rt} t] z'_y, \hspace{1cm} (4.54e) \\
\dot{P}_Z &= -2Ze b'_1 Z - 2\mu_0 b'_1 z'_z, \hspace{1cm} (4.54f)
\end{align*}

with

$$b'_1 = \frac{\kappa U_0}{z_0^2},$$  \hspace{1cm} (4.55a)
$$b'_2 = \frac{V_0}{r_0^2}.$$  \hspace{1cm} (4.55b)

However, writing the equations of motion of the rotation of the ion is more complicated since we need to perform a coordinate transformation to the body-fixed frame. This transformation is necessary due to the introduction of the new
variables. Therefore, the rotational equations of motion can be found considering the Euler-Lagrange equations \[72, 76\]

\[
\begin{align*}
I_{x'}\dot{\omega}_{x'} &= T_{p_{x'}} + \omega_{y'}\omega_{p_{z'}}(I_{y'} - I_{z'}) \equiv T_{p_{x'}} \\
I_{y'}\dot{\omega}_{y'} &= T_{p_{y'}} + \omega_{z'}\omega_{p_{x'}}(I_{z'} - I_{x'}) \equiv T_{p_{y'}} \\
I_{z'}\dot{\omega}_{z'} &= 0,
\end{align*}
\] (4.56)
in which angular velocities \((\omega_P)\) and torques \((T_P)\) are all calculated in the body-fixed frame, considering the rotation of the ion about its principal rotational axes \((x', y', z')\). As mentioned before, since we have ignored the rotation of the ion around its internuclear axis, we have \(\omega_{p_{z'}} = 0\).

In order to find the \(T_P\), we need to calculate the torque in the lab-fixed frame and transform it to the body-fixed frame. The torque in the lab-fixed frame, which is imposed on the dipole by the trapping electric field, is calculated via \(T_L = \mu_0 \times E_{\text{Trap}}\). Components of this torque, using the relations in Eq. (4.53), give

\[
\begin{align*}
T_{L_x} &= \mu_0 \left[-2b'_1 Z z'_y - (b'_1 + b'_2 \cos \Omega_{rt} t) Y z'_z\right], \\
T_{L_y} &= \mu_0 \left[2b'_1 Z z'_x + (b'_1 - b'_2 \cos \Omega_{rt} t) X z'_z\right], \\
T_{L_z} &= \mu_0 \left[(b'_1 + b'_2 \cos \Omega_{rt} t) Y z'_x - (b'_1 - b'_2 \cos \Omega_{rt} t) X z'_y\right].
\end{align*}
\] (4.57a-b-c)

with \(b'_1\) and \(b'_2\) shown in Eqs. (4.55).

Now, by knowing the torque in the lab-fixed frame, we can calculate the principal torque \(T_P\), which is obtained from the relation \[73\]

\[
T_L = A^T T_P,
\] (4.58)

where \(A^T\) is the transpose of the rotation matrix \[72\], whose columns are the principal axes unit vectors \[73\]

\[
A^T = (\hat{x}', \hat{y}', \hat{z}') \equiv \begin{pmatrix} x'_x & x'_y & x'_z \\ y'_x & y'_y & y'_z \\ z'_x & z'_y & z'_z \end{pmatrix},
\] (4.59)

from which we can obtain the equations of the rotational motion as

\[
\dot{\omega}_P = \frac{1}{I} T_P \equiv \frac{1}{I} (A^T)^{-1} T_L.
\] (4.60)

In the end, we need to emphasize that we also need to calculate the change in the direction of the dipole moment, which is equivalent to the temporal change in the direction of the principal axes according to

\[
\dot{\hat{u}}' = \omega_P \times \hat{u}'.
\] (4.61)
Now to solve the equations of motion for a molecular ion trapped in a linear Paul trap which are given by Eqs. (4.54), (4.60) and (4.61), we assign an initial position \( \mathbf{R}_0 \equiv (X_0, Y_0, Z_0) \) and an initial linear momentum \( \mathbf{P}_0 \equiv (P_{0X}, P_{0Y}, P_{0Z}) \) to the ion, where the latter parameter is estimated by assigning an initial translational temperature to the ion, same as we did for an atomic ion, according to Eq. (4.17).

However, since the equations mentioned also consist in the rotational equations of motion, we need to assign additional initial conditions to the ion, which define the initial state of the system, rotation-wise. To do so, we set an initial angular momentum (or an initial angular velocity), in addition to assigning an initial orientation to the ion (or to the dipole moment) as well.

The initial angular momentum \( \mathbf{L}_0 \equiv (L_{0x}', L_{0y}', L_{0z}') \) corresponds to the rotation of the ion about its principal symmetry axes, for which we take \( L_{0x}' = L_{0y}' = L \) and since there is no rotation about the internuclear axis, we have \( L_{0z}' = 0 \). The magnitude of this initial angular momentum is also calculated corresponding to the same initial temperature we set for the ion, when assigning the initial linear momentum. This angular momentum is calculated as

\[
L = \sqrt{\mu R^2 k_B T_0},
\]

where \( k_B \) and \( T_0 \) are Boltzmann constant and initial temperature, respectively.

When it comes to assigning an initial orientation to the ion (or to the dipole), by this, we mean to assign an initial orientation to the unit vector \( \hat{z}' \) (see Fig. 4.4), with respect to the lab-fixed frame. This is only possible by assigning initial values for the Euler angles \((\theta, \varphi)\). On the other hand, we also need to know orientations of two other principal unit vectors \( \hat{x}' \) and \( \hat{y}' \), in order to start Eq. (4.61). Therefore, we initially set two orthogonal orientation for unit vectors \( \hat{z}' \) and \( \hat{x}' \) and we calculate \( \hat{y}' \) through the relation \( \hat{y}' = \hat{z}' \times \hat{x}' \).

Finally, to solve the equations of motion, we use the 4th-order Runge-Kutta-Fehlberg integrator \([66, 77]\) since all equations are first-order ODEs with respect to their time derivatives. It is also important to note that to run the classical simulations of the trapped molecular ion, care needs to be taken with regards to setting an appropriate time step \( \Delta t \). The time step should be set in such a way that ensures the unit vectors \( \hat{u}' \) remain normalized throughout the numerical simulation.

At the end of this section, it is worth to note that the translational equations of motion of the trapped molecular ion, which are shown in Eq. (4.54), no longer follow the Mathieu equation [see Eq. (1.5)]. Although this fact makes the situation more complicated to define proper conditions on stability of the ion inside the trap,
by taking the term $\nabla \left[ \mu_0 \cdot \mathbf{E}_{\text{Trap}}(\mathbf{R}_{\text{cm}}; t) \right]$ to be only a small perturbation, we still can use the stability criteria of the Mathieu equation as a guideline for the stability of the trapped molecular ion.

### 4.2.2 Semi-classical rotation and equations of motion

As we mentioned earlier, to treat the problem of a trapped molecular ion, semi-classically, we use our classical approach to obtain trajectories of the translational motion of the ion. However, the rotation of the ion is treated full-quantum mechanically by considering the rotational wave function of the ion $\Psi_{\text{rot}}(\theta, \varphi; t)$, which satisfies the Schrödinger equation

$$i\hbar \frac{d}{dt} \Psi_{\text{rot}}(\theta, \varphi; t) = \left[ \frac{B}{\hbar^2} \hat{J}_z - \mu_0 \cdot \mathbf{E}_{\text{Trap}}(\mathbf{R}_{\text{cm}}; t) \right] \Psi_{\text{rot}}(\theta, \varphi; t). \quad (4.63)$$

The rotational wave function $\Psi_{\text{rot}}(\theta, \varphi; t)$ can be expanded on the basis of field-free rotor states (spherical harmonics) $Y_{J,M} \equiv |J,M\rangle$ as

$$\Psi_{\text{rot}}(\theta, \varphi; t) = \sum_{J,M} D_{J,M}(t) Y_{J,M}(\theta, \varphi) \equiv \sum_{J,M} D_{J,M}(t) |J,M\rangle, \quad (4.64)$$

where the expansion coefficients $D_{J,M}$ are time-dependent complex values that determine the rotational states of the ion.

In order to study the time evolution of the rotational states of the ion, affected by the interaction of the dipole with the trapping electric field, which means to study the time evolution of coefficients $D_{J,M}$, we need to solve the time-dependent Schrödinger equation in Eq. (4.63) by substituting the wave function from Eq. (4.64), which gives

$$i\hbar \sum_{J,M} \dot{D}_{J,M}(t) |J,M\rangle = \frac{B}{\hbar^2} \sum_{J,M} D_{J,M}(t) \hat{J}_z |J,M\rangle - \sum_{J,M} D_{J,M}(t) \left[ \mu_0 \cdot \mathbf{E}_{\text{Trap}} \right] |J,M\rangle, \quad (4.65)$$

and by multiplying both sides of the Eq. (4.65) by $\langle J', M' |$ and by interchanging the primed and un-primed variables $J$ and $M$ and considering that

$$\sum_{J,M} \sum_{J',M'} \langle J,M | J', M' \rangle = \sum_{J,M} \delta_{J,M,J',M'}, \quad (4.66)$$

and

$$\hat{J}_z^2 |J,M\rangle = \hbar^2 J(J + 1) |J,M\rangle, \quad (4.67)$$
Eq. (4.65) reads
\[
i\hbar \sum_{J,M} \dot{D}_{J,M}(t) = \sum_{J,M} D_{J,M}(t)BJ(J + 1) - \sum_{J,M} \sum_{J',M'} D_{J',M'}(t)\langle J, M | \mu_0 \cdot \mathcal{E}_{\text{Trap}} | J', M' \rangle,
\] (4.68)
which eventually results in a set of coupled equations for the time evolution of coefficients
\[
\dot{D}_{J,M}(t) = -\frac{i}{\hbar} D_{J,M}(t)BJ(J + 1) + \frac{i}{\hbar} \sum_{J',M'} D_{J',M'}(t)\langle J, M | \mu_0 \cdot \mathcal{E}_{\text{Trap}} | J', M' \rangle.
\] (4.69)

Using Eq. (4.48) for the interaction of the dipole moment with the electric field and substituting trigonometric functions with their equivalent spherical harmonics [78] gives
\[
\mu_0 \cdot \mathcal{E}_{\text{Trap}} = \sqrt{\frac{2}{3}} \mu_0 \left[(\mathcal{E}_x + i\mathcal{E}_y)Y_{1,-1} + \sqrt{2}\mathcal{E}_zY_{1,0} + (-\mathcal{E}_x + i\mathcal{E}_y)Y_{1,1}\right] \] (4.70)
and hence
\[
\langle J, M | \mu_0 \cdot \mathcal{E}_{\text{Trap}} | J', M' \rangle = \sqrt{\frac{2}{3}} \mu_0 \left[(\mathcal{E}_x + i\mathcal{E}_y) \langle J, M | Y_{1,-1} | J', M' \rangle + \sqrt{2}\mathcal{E}_z \langle J, M | Y_{1,0} | J', M' \rangle + (-\mathcal{E}_x + i\mathcal{E}_y) \langle J, M | Y_{1,1} | J', M' \rangle\right].
\] (4.71)

To calculate expressions \( \langle J, M | Y_{1,n} | J', M' \rangle \) in Eq. (4.71), we use Clebsch-Gordan coefficients and their related 3j-symbols according to [78]
\[
\langle J, M | Y_{1,n} | J', M' \rangle = \int_0^\pi \int_0^{2\pi} Y^*_{J,M}(\theta, \varphi)Y_{1,n}(\theta, \varphi)Y_{J',M'}(\theta, \varphi)\sin \theta d\theta d\varphi
\]
\[
= (-1)^n \sqrt{\frac{(2J + 1)(3)(2J' + 1)}{4\pi}} \times
\]
\[
\begin{pmatrix} J & 1 & J' \\ 0 & 0 & 0 \end{pmatrix}
\begin{pmatrix} J & 1 & J' \\ -M & n & M' \end{pmatrix}
\]
\[
= \sqrt{\frac{(2J' + 1)(3)}{4\pi(2J + 1)}} C_{J,01}^{J0} C_{J'M,1n}^{JM},
\] (4.72)
with $n = -1, 0, 1$. The rules for non-zero values of the Clebsch-Gordan coefficients in Eq. (4.72) imply the relations

\begin{align*}
\Delta J &\equiv |J - J'| = 0, \pm 1 \ (J = 0 \not\leftrightarrow 0) \\
\Delta M &\equiv |M - M'| = 0, \pm 1.
\end{align*}  \tag{4.73}

Finally, by substituting Eqs. (4.71) and (4.72) into Eq. (4.69), we obtain equations regarding the time evolutions of the rotational states. However, we need to emphasize that the electric field in Eq. (4.69) is calculated at the center of mass of the ion, which will be updated via the classical equations of motion for the center of mass of the ion.

Now, when it comes to derive the translational equations of motion of the center-of-mass, we still can use the classical equations of motion shown in Eqs. (4.54), however they need to be modified. Since we have treated the rotation quantum mechanically, $\theta$ and $\varphi$ are no longer classical variables. Therefore, to take into account the effect of the rotation, we calculate the orientation of the dipole using

\begin{align*}
z'_x &\equiv \langle \sin \theta \cos \varphi \rangle(t) = \sum_{J,M,J',M'} D^*_{J,M}(t) D_{J',M'}(t) \langle J, M | \sin \theta \cos \varphi | J', M' \rangle, \\
z'_y &\equiv \langle \sin \theta \sin \varphi \rangle(t) = \sum_{J,M,J',M'} D^*_{J,M}(t) D_{J',M'}(t) \langle J, M | \sin \theta \sin \varphi | J', M' \rangle, \tag{4.74a} \\
z'_z &\equiv \langle \cos \theta \rangle(t) = \sum_{J,M,J',M'} D^*_{J,M}(t) D_{J',M'}(t) \langle J, M | \cos \theta | J', M' \rangle. \tag{4.74b}
\end{align*}

where we have indicated that the expectation values are time-dependent variables. Finally, the time evolution of a rigid diatomic molecular ion trapped in a linear Paul trap, in the semi-classical model, will be obtained from the coupled differential
\[
\dot{\mathbf{R}} = \frac{\mathbf{P}}{M}, \quad (4.75a)
\]
\[
\dot{P}_X = eZ [b'_1 - b'_2 \cos \Omega_{rf}t] X + \mu_0 [b'_1 - b'_2 \cos \Omega_{rf}t] \left\langle \sin \theta \cos \varphi \right\rangle(t), \quad (4.75b)
\]
\[
\dot{P}_Y = eZ [b'_1 + b'_2 \cos \Omega_{rf}t] Y + \mu_0 [b'_1 + b'_2 \cos \Omega_{rf}t] \left\langle \sin \theta \sin \varphi \right\rangle(t), \quad (4.75c)
\]
\[
\dot{P}_Z = -2eZ b'_1 Z - 2\mu_0 b'_1 \left\langle \cos \theta \right\rangle(t), \quad (4.75d)
\]
\[
\dot{D}_{J,M} = -\frac{i}{\hbar} D_{J,M}(t)BJ(J + 1) + \frac{i}{\hbar} \sum_{J',M'} D_{J',M'}(t)\langle J, M|\mu_0 \cdot \mathbf{E}_{\text{Trap}}(\mathbf{R}_{\text{cm}}; t)|J', M'\rangle, \quad (4.75e)
\]
with \(b'_1\) and \(b'_2\) defined in Eqs. (4.55).

### 4.2.3 Interaction of the molecular ion with the laser field

The Hamiltonian of a rigid diatomic molecular ion, trapped in a linear Paul trap and interacting with an off-resonance laser field, has been given previously in Sec. 3.3 in Eq. (3.37). For simplicity, we have ignored the interaction of the permanent dipole moment with the laser field, since the time average of this interaction tends to be zero due to the fast oscillation of the laser field \[35, 79\]. Therefore, the Hamiltonian reduces to

\[
\hat{H} = -\frac{\hbar^2}{2m} \nabla_{\mathbf{R}_{\text{cm}}}^2 + \frac{BJ^2}{\hbar^2} + Ze\Phi_{\text{Trap}}(\mathbf{R}_{\text{cm}}; t) - \mu_0 \cdot \mathbf{E}_{\text{Trap}}(\mathbf{R}_{\text{cm}}; t) - \frac{1}{2} \alpha \mathcal{E}_{\text{Laser}}^2(\mathbf{R}_{\text{cm}}; t). \quad (4.76)
\]

We assume that the laser radiation is off-center with respect to the center of the linear Paul trap, which gives

\[
\mathcal{E}_{\text{Laser}}^2(\mathbf{R}_{\text{cm}}; t) = \frac{I}{2\epsilon_0 c} \cos^2(\Omega_{L}t) \exp \left[\frac{-2(X - X_0)^2 - 2(Y - Y_0)^2}{w_0^2}\right], \quad (4.77)
\]
where we have taken \(w(Z)\) constant and equal to \(w_0\). We also assume that the laser field propagates in the \(Z\)-direction, with respect to the lab-fixed frame, which results in a polarization vector located in the \(XY\)-plane. For simplicity, we have taken the polarization vector to be aligned in the \(X\)-direction. We show the position of this vector with respect to the lab-fixed frame and with respect to the dipole moment in Fig. 4.5.
Now considering the components of the polarization tensor, parallel, $\alpha_\parallel$ and perpendicular, $\alpha_\perp$ to the internuclear axis (dipole moment), we can write the term representing the interaction of the molecular ion with the laser field as

$$
-\frac{1}{2} \alpha_\parallel \mathcal{E}_\text{Laser}^2(R_{\text{cm}}; t) = -\frac{1}{2} \mathcal{E}_\text{Laser}^2(R_{\text{cm}}; t) \left[ \alpha_\parallel \cos^2 \Theta + \alpha_\perp \sin^2 \Theta \right],
$$

in which $\Theta$ is the angle between the polarization vector $\hat{\varepsilon}$ of the laser field and the dipole moment (see Fig. 4.5). It is more convenient to define this angle using the predefined Euler angles $\theta$ and $\varphi$, introduced in Sec. 4.2.1. In this way, variables will remain limited to those that we have set before, which means that we can avoid any further complications that may arise in numerical calculation. Now, to define the angle $\Theta$ according to the Euler angles, we use the relation

$$
\mu_0 \cdot \hat{\varepsilon} = |\mu_0| \cos \Theta,
$$

43
in which by using the relation $\mathbf{\mu_0} = \mu_0 \hat{z'}$, mentioned in Eq. (4.52), and considering that the polarization vector is fixed in the X-direction of the lab-fixed frame, we can define

$$\cos \Theta = \hat{z'} \cdot \hat{x}$$

(4.80)

and by using relations mentioned in Eq. (4.53), we get

$$\cos \Theta = z'_x \equiv \sin \theta \cos \phi$$

(4.81)

and finally by introducing the polarizability anisotropy, $\Delta \alpha = \alpha_{||} - \alpha_{\perp}$ and also by using the relation $\sin^2 \Theta = 1 - \cos^2 \Theta$, we can write

$$\alpha \equiv [\Delta \alpha (\sin^2 \theta \cos^2 \phi) + \alpha_{\perp}]$$

(4.82)

Considering the rotational dynamics of the ion, the Schrödinger equation in Eq. (4.63) can be modified as

$$i\hbar \frac{d}{dt} \Psi_{\text{rot}}(\theta, \phi; t) = \left[ \frac{B}{\hbar^2} \hat{J}^2 - \mathbf{\mu}_0 \cdot \mathbf{E}_{\text{Trap}}(R_{\text{cm}}; t) - \frac{1}{2} \alpha \mathbf{E}_{\text{Laser}}^2(R_{\text{cm}}; t) \right] \Psi_{\text{rot}}(\theta, \phi; t),$$

(4.83)

which results in having an additional term in Eq. (4.69) for the time evolution of the coefficients

$$\dot{D}_{J,M}(t) = -\frac{i}{\hbar} D_{J,M}(t) BJ(J + 1) + \frac{i}{\hbar} \sum_{J',M'} D_{J',M'}(t) \langle J, M | \mathbf{\mu}_0 \cdot \mathbf{E}_{\text{Trap}} | J', M' \rangle$$

$$+ \frac{i}{2\hbar} \sum_{J',M'} D_{J',M'}(t) \langle J, M | \alpha \mathbf{E}_{\text{Laser}}^2 | J', M' \rangle,$$

(4.84)

for which the term in brackets, in the last term [Eq. (4.84)], using Eqs. (4.77) and (4.82) and again by substituting the trigonometric functions with their equivalent spherical harmonics, we obtain

$$\langle J, M | \alpha \mathbf{E}_{\text{Laser}}^2 | J', M' \rangle = \left( \frac{\alpha_{\perp}}{3} + \frac{1}{3} \Delta \alpha \right) E^2$$

$$+ \sqrt{\frac{2\pi}{15}} \Delta \alpha \mathbf{E}_{\text{Laser}}^2 \left[ \langle J, M | Y_{2,-2} | J', M' \rangle \right.$$

$$- \sqrt{\frac{2}{3}} \langle J, M | Y_{2,0} | J', M' \rangle$$

$$\langle J, M | Y_{2,2} | J', M' \rangle.$$

(4.85)
Finally, by using Clebsch-Gordan coefficients and their related 3j-symbols, we have

\[ \langle J, M | Y_{2,n'} | J', M' \rangle = \int_0^\pi \int_0^{2\pi} \overline{Y}_{J,M}^*(\theta, \varphi) Y_{2,n'}(\theta, \varphi) Y_{J',M'}(\theta, \varphi) \sin \theta d\theta d\varphi \]

\[ = (-1)^{n'} \sqrt{\frac{(2J+1)(5)(2J'+1)}{4\pi}} \times \]

\[ \left( \begin{array}{ccc} J & 2 & J' \\ 0 & 0 & 0 \end{array} \right) \left( \begin{array}{ccc} J & 2 & J' \\ -M & n' & M' \end{array} \right) \]

\[ = \sqrt{\frac{(2J'+1)(5)}{4\pi(2J+1)}} C_{J,0,20}^J C_{J',M',2n'}^J, \]

with \( n' = 0, \pm 2 \). The rules for non-zero values of the Clebsch-Gordan coefficients in Eq. (4.86) imply the relations

\[ \Delta J \equiv |J - J'| = 0, \pm 2 \quad (J = 0 \not\leftrightarrow 0) \]

\[ \Delta M \equiv |M - M'| = 0, \pm 2. \quad (4.87) \]

Finally, to take into account the effect of the coupling between the ion and the laser field in the translational equations of motion, we calculate the polarizability of the molecular ion, using

\[ \langle \sin^2 \theta \cos^2 \varphi \rangle (t) = \sum_{J,M,J',M'} D_{J,M}^*(t) D_{J',M'}(t) \langle J, M | \sin^2 \theta \cos^2 \varphi | J', M' \rangle, \]

which results in translational equations of motion

\[ \dot{\mathbf{R}} = \frac{\mathbf{P}}{m}, \quad (4.89a) \]

\[ \dot{P}_X = eZ [b'_1 - b'_2 \cos \Omega_\text{tf} t] X + \mu_0 [b'_1 - b'_2 \cos \Omega_\text{tf} t] \langle \sin \theta \cos \varphi \rangle (t) \]

\[ - \frac{b'_3}{w_0^2} \cos^2(\Omega_\text{L} t) (X - X_0) \left[ \Delta \alpha \langle \sin \theta \cos \varphi \rangle^2(t) + \alpha_\perp \right] \exp [...], \quad (4.89b) \]

\[ \dot{P}_Y = eZ [b'_1 + b'_2 \cos \Omega_\text{tf} t] Y + \mu_0 [b'_1 + b'_2 \cos \Omega_\text{tf} t] \langle \sin \theta \sin \varphi \rangle (t) \]

\[ - \frac{b'_3}{w_0^2} \cos^2(\Omega_\text{L} t) (Y - Y_0) \left[ \Delta \alpha \langle \sin \theta \cos \varphi \rangle^2(t) + \alpha_\perp \right] \exp [...], \quad (4.89c) \]

\[ \dot{P}_Z = -2eZ b'_1 z - 2\mu_0 b'_1 \langle \cos \theta \rangle (t), \quad (4.89d) \]
with

\[ b'_{1} = \frac{\kappa U_{0}}{z_{0}} \], \quad (4.90a) \\
\[ b'_{2} = \frac{V_{0}}{r_{0}} \], \quad (4.90b) \\
\[ b'_{3} = \frac{I}{\epsilon_{0} c} \], \quad (4.90c) \\

and

\[ \exp[...] \equiv \exp \left[ -2(X - X_{0})^{2} - 2(X - X_{0})^{2} \right] \frac{w_{0}^{2}}{u_{0}^{2}}. \quad (4.91) \]
Chapter 5

Results and discussions

As mentioned in Chapter 4 in order to study the dynamics of either a trapped molecular ion or a trapped atomic ion – depending on the subject of our study – we have implemented full-classical, full-quantum mechanical, and also semi-classical numerical simulations. All simulation programs are written in the C programming language. The size of the time step ∆\(t\) is chosen based on the frequency of the time-dependent potentials in the Hamiltonian of the system. We have taken the time step to be approximately equal to \(10^{-4}\) up to \(10^{-3}\) of the inverse of the frequency. However, the size of the time step has been estimated to be much smaller – in codes – which implement the 4th-order Runge-Kutta-Fehlberg algorithm. For these codes, we have applied the adaptive step size control from the GNU scientific library [77], which evolves the system from time \(t\) to time \(t+\Delta t\) and adjust the time step by estimating the local errors [77]. As we also mentioned earlier in Sec. 4.2.1 by taking a smaller size for the time step, it is ensured that the unit vectors \(\hat{u}'\) [see Eq. (4.51)] will remain normalized throughout the numerical simulations.

The value of the parameters that describe the configuration of the linear Paul trap, such as \(r_0, z_0, \kappa\) and \(\Omega_{rf}\) [see Eq. (2.4)], are identical for all simulations. The values of these parameters [38], which are based on experimental realization, are all given in Table 5.1.

Furthermore, the magnitude of the trapping potentials \((U_0, V_0)\) are chosen such that the ion remains confined and trapped, with their corresponding Mathieu parameters, \(a\) and \(q\) [see Eq. (4.7)], being located inside either the I or the II stability regions. We have shown these stability regions for a \(\text{Ca}^+\) ion trapped in a linear Paul trap, corresponding to the potential mentioned in Eq. (2.4), in Fig. 5.1. These stability regions are obtained by calculating the characteristic values, \(a_0, b_1,\)
Table 5.1: Trap configuration parameters of a linear Paul trap.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r_0$</td>
<td>$0.769 \times 10^{-3}$ m</td>
</tr>
<tr>
<td>$z_0$</td>
<td>$1.25 \times 10^{-3}$ m</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>0.31</td>
</tr>
<tr>
<td>$\Omega_{rf}$</td>
<td>$2\pi \times 0.8 \times 10^7$ s$^{-1}$</td>
</tr>
</tbody>
</table>

$a_1$, etc. of the Mathieu equation [54] using Mathematica [55]. We should mention that these stability regions hold along both $x$ and $y$ directions, since they depend on $a$ and $|q|$. We should note that the stability of the ion along $z$ is unconditional. An equivalent diagram is found in Paper III (see Ref. [49]), which corresponds to a trapped diatomic molecular ion MgH$^+$. It is important to note that to obtain these stability regions for the molecular ion, we have ignored the presence of the permanent dipole moment ($\mu_0 = 0$).

5.1 Wave packet dynamics of a trapped atomic ion

The main question when it comes to considering a trapped atomic ion, mostly revolves around the extent to which the classical simulations agree with the full-quantum treatment. To investigate this, we have studied the wave packet dynamics of a trapped Ca$^+$ ion and have compared the results to those obtained classically.

To set the initial conditions for both classical and quantum mechanical simulations, we consider the ion to lie initially in the center of the trap. Therefore, we need to assign an initial kinetic energy or in other words an initial momentum to the ion, which essentially works as an initial drive for the ion. Otherwise, the ion will remain stationary at the center of the trap, where the trapping electric field is zero. As we mentioned earlier in Sec. 4.1.1, this initial linear momentum corresponds to an initial temperature $T_0$ in accordance with Eq. (4.16). This initial temperature is chosen to be approximately 5 mK, which is the Doppler temperature achieved by laser cooling of the Ca$^+$ ion [80]. The time step size for both classical and quantum simulations, is taken to be $\Delta t = 10^{-11}$ s.

The spatial grid size in the quantum simulations is chosen to be equal along the $x$- and $y$-directions, confined in the range of $[-1 \mu$m, $1 \mu$m] and it is slightly bigger in $z$-direction, which spans $[-3 \mu$m, $3 \mu$m]. There are also the same number of grid
Figure 5.1: I and II stability regions of the Mathieu equation, corresponding to an atomic Ca$^+$ ion ($m_{\text{Ca}} = 6.6529 \times 10^{-26}$ kg), trapped in a linear Paul trap. Shaded areas correspond to stable trajectories. The borders are designated by the characteristic values of the Mathieu equation $a_0$, $b_1$, $a_1$ and $b_2$ \cite{54}.

5.1.1 Trajectories of the center of mass: quantum vs. classical

We have run numerical simulations for different pairs of $(U_0, V_0)$ and have compared the classical trajectories of the center-of-mass, $R_{\text{cm}}$, with those obtained quantum mechanically, $\langle R \rangle$. We have observed a very good agreement between
the results obtained from both approaches, in all simulations. The results are shown in Paper II (see Ref. [71]). As an example, we show the trajectories of the center of mass of a Ca\(^+\), for each component of the motion, in Fig. 5.2 for \(U_0 = 10\) V and \(V_0 = 140\) V. Trajectories in Figs. 5.2 (a), 5.2 (c) and 5.2 (e) are obtained from quantum mechanical simulations, while on the other hand, trajectories in Figs. 5.2 (b), 5.2 (d) and 5.2 (f) represent the difference between these trajectories and those obtained classically.

By comparing the amplitude of trajectories in Figs. 5.2 (b), 5.2 (d) and 5.2 (f) with the actual amplitudes of the motion, we see that the deviation of trajectories obtained quantum mechanically, from those obtained classically, is indeed very small (~ \(10^{-3}\)) and even smaller than the spacing between the grid points in the quantum simulations. However, it is important to check that this small deviation will not grow with time. To show this, trajectories of the motion are plotted for a longer time in Figs. 5.2 (b), 5.2 (d) and 5.2 (f). We also observe that the Z-component of the motion lacks the rf-driven micromotion since the trapping potential along \(z\) is time-independent.

It is also worth mentioning that we have also run simulations for which the ion was initially located off center. Although by setting an initial off center position for the ion we increase its potential energy, which eventually affects the amplitudes of the motion, the behavior of the ion is the same, qualitatively. This means that if the ion fulfills the condition for being trapped, it will always remain confined. This result is predictable since the condition on stability of the ion only depends on its mass and on the characteristic parameters of the trap [see Sec. (4.1.1)].

5.1.2 Quantum stability and confinement of the wave packet

To examine the quantum stability and the confinement of the wave packet, we have studied the evolution of the width of the wave packet in both the classically stable and the classically unstable regions, as determined for the Ca\(^+\) ion in a linear Paul trap.

We have shown the evolution of components of the width of the wave packet corresponding to \((U_0, V_0) = (10\) V, 140 V), in Fig. 5.3. For this example, the ion was initially set to be in its translational ground state, which corresponds to \(n = 0\) for the initial wave function [see Eqs. (4.38) and (4.39)].

As we see, the width of the wave packet oscillates with time and this oscillation remains bounded in all directions, which confirms the confinement of the ion inside the trapping device, quantum mechanically. To investigate if the boundary between the quantum-stable and quantum-unstable regions, matches with its classical counterpart, we have also studied the evolution of the width of the wave packet.
Figure 5.2: Trajectories of the center-of-mass motion of a Ca\(^{+}\) ion, trapped in a linear Paul trap with \((U_0, V_0) = (10 \text{ V}, 140 \text{ V})\). Panels (a), (c) and (e) show trajectories of motion obtained quantum mechanically. Panels (b), (d) and (f) show the difference between these trajectories and trajectories obtained classically.
Figure 5.3: Time evolution of components of the width of the wave packet of a Ca\(^+\) ion, trapped in a linear Paul trap with \((U_0, V_0) = (10\, \text{V}, 140\, \text{V})\). The initial wave packet is set to be the ground state of the harmonic oscillator \((n = 0)\).
packet in the vicinity of the classical stability borders. For our case of a Ca$^+$ ion, we found that the Mathieu characteristic value $b_1$ (see Fig. 5.1) for $U_0 = 10$ V is at $V_0 = 283.659$ V. Consequently, we ran simulations for points on either side of the border, as close as possible to it. These points are $V_0 = 283.6$ V and $V_0 = 283.66$ V, which are situated in stable and unstable regions, respectively. We observed that the width of the wave packet remained bounded for $V_0 = 283.6$ while in comparison, it grew and expanded even beyond the amplitude of the motion, for $V_0 = 283.66$. The results obtained for this example are all depicted in the Paper II (see the Ref. [71]).

5.1.3 Validity of the effective potential approximation

To end this section, we have also examined the validity of the effective potential approximation by comparing trajectories obtained quantum mechanically, using the actual time-dependent potential, with those, where the effective potential is applied. For completeness, we also calculated the projection of the effective wave function $\psi^{\text{eff}}(R_{\text{cm}}; t)$ [see Eq. (4.31)] on the actual time-dependent wave function $\Psi(R_{\text{cm}}; t)$ [see Eq. (4.26)]

$$P(t) = \left| \langle \Psi(R_{\text{cm}}; t) | \psi^{\text{eff}}(R_{\text{cm}}; t) \rangle \right|^2.$$  \hspace{1cm} (5.1)

We have shown the results obtained for the $X$-component of the motion, in Fig. 5.4. These results are obtained for a Ca$^+$ ion and for three different pairs of $(U_0, V_0)$, namely $(2$ V, $50$ V), $(8$ V, $90$ V) and $(10$ V, $140$ V). As it is apparent in Figs. 5.4 (a), 5.4 (c) and 5.4 (e), the micromotion is not reproduced by the effective potential, and as expected, the effective potential only gives the pure secular motion, which is shown as the dashed, black curve. Also, as we increase the strength of the trapping field, the trajectories appear to have a bigger difference in their oscillation periods. Now if we calculate the corresponding values of $a_x$ and $q_x$ [see Eqs. (4.7)] for all three fields above $(U_0 = 2$ and $V_0 = 50$), $(U_0 = 8$ and $V_0 = 90)$, and $(U_0 = 10$ and $V_0 = 140)$, we get $(a_x \approx -1.5 \times 10^{-3}, q_x \approx 0.16)$, $(a_x \approx -6 \times 10^{-3}, q_x \approx 0.3)$ and $(a_x \approx -7.6 \times 10^{-3}, q_x \approx 0.45)$, respectively. These values agree perfectly with conditions mentioned for the validity of the effective potential approximation, namely $|a|, q^2 \ll 1$, in Ref. [19]. Therefore, as we increase the field, hence increasing the values of $a$ and $q$, the validity of the effective potential approximation decreases dramatically comparing with the results obtained with the actual time-dependent trapping potential. Also, by observing the projection of the effective wave function on the actual wave function in Figs. 5.4 (b), 5.4 (d), 5.4 (f), we realize that the recovery of the exact solutions [when $P(t) = 1$] ceases
as we increase the magnitude of the field, which again confirms a limit on the applicability of the effective potential approximation.

Figure 5.4: Panels (a), (c) and (d) show trajectories of the X-component of the center-of-mass motion of a Ca\(^{+}\) ion, trapped in a linear Paul trap, calculated using the effective potential approximation versus full-quantum dynamics. Panels (b), (d) and (f) show the projection of the effective wave function on the exact wave function. These results are obtained for three different amplitudes of the trapping fields corresponding to \((U_0 = 2, V_0 = 50)\), \((U_0 = 8, V_0 = 90)\) and \((U_0 = 10, V_0 = 140)\).
5.2 Dynamics of a trapped molecular ion

Now when it comes to study the dynamics of a trapped molecular ion in a linear Paul trap, our main goal is to investigate to what extend the coupling of the trapping field with the intrinsic electric dipole moment of the ion affects these dynamics. Carrying out full-quantum simulations to study the dynamics of a trapped molecular ion, is more complex and more demanding numerically, compared to a trapped atomic ion, due to the greater number of degrees of freedom. Therefore, we have implemented classical and semi-classical numerical simulations, where we have chosen MgH$^+$ ion, as an example.

First, we need to assign some initial conditions to run our simulations. We have set an initial position to the ion, along with setting an initial linear momentum. For the classical simulations, we also need to assign an initial angular momentum to the ion, in order to initiate the rotation. These momenta correspond to initial temperatures (initial translational temperature and initial rotational temperature) [see also Eqs. (4.16) and (4.62)]. In this work, we take initial temperatures of the ion based on existing experimental works with MgH$^+$, such as those mentioned in Refs. [81] and [82]. This temperature is taken to be approximately 20 K. We should also mention that depending on whether we are running classical or semi-classical simulations, it is necessary to define some additional initial conditions, which we describe in the following section.

As we mentioned before, (see the beginning of the Chapter 5), we need to adopt a much smaller size for the time step, for both classical and semi-classical simulations, which is taken to be $\Delta t = 10^{-14}$ s. We have also chosen trapping fields $(U_0, V_0)$ in such a way that they result in $a$ and $q$ in the II stability region, in order to magnify the effect of the coupling between the dipole and the trapping electric field.

Finally, the magnitude of the permanent dipole moment, $\mu_0$, the rotational constant, $B$, the mass of each of the constituent atoms, $m_H$ and $m_{Mg}$ and the internuclear distance $R$ of the molecular ion MgH$^+$ are all listed in Table 5.2 [82, 83]. As before, the trap configuration parameters can be found in Table 5.1.

5.2.1 The effect of the classical rotation on the trajectories of the center-of-mass

To run the classical simulations, we also need to set the initial orientation of the dipole moment (or the ion), in the COM frame (see Fig. 4.3). This initial orientation defines the initial orientation of the unit vector $\hat{z}'$, which is along the direction of the dipole moment (along the internuclear axis). We can define this
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$m_H$</td>
<td>$1.6737 \times 10^{-27}$ kg</td>
</tr>
<tr>
<td>$m_{Mg}$</td>
<td>$4.0359 \times 10^{-26}$ kg</td>
</tr>
<tr>
<td>$\mu_0$</td>
<td>3.6 Debye</td>
</tr>
<tr>
<td>$B$</td>
<td>6.4058 cm$^{-1}$</td>
</tr>
<tr>
<td>$R$</td>
<td>1.655 Å</td>
</tr>
</tbody>
</table>

Table 5.2: Parameters for the MgH$^+$ ion.

orientation by setting initial angles $\theta$ and $\varphi$, according to Eq. (4.53). We have chosen three different initial orientations for the dipole: (i) along the z-axis, (ii) in the $xy$-plane and (iii) along a chosen orientation in space, corresponding to $\theta = 0^\circ$, $(\theta = 90^\circ, \varphi = 45^\circ)$, and $(\theta = 45^\circ, \varphi = 30^\circ)$, respectively. As we mentioned before, we also need to set a secondary orientation, either for the unit vector $\hat{x}'$ or the unit vector $\hat{y}'$. This secondary orientation is arbitrary, as long as it fulfills the orthogonality relation.

We have finally run the classical simulations for three different pairs of the trapping fields $(U_0, V_0)$, namely (680 V, 1620 V), (2175 V, 2000 V), and (7080 V, 3000 V). Detailed results can be found in Paper III (see Ref. [49]). They reveal an obvious change in the trajectories due to the coupling between the dipole moment and the trapping field. One of the striking results is that the trajectories still tend to stay bounded, even though there is a term coupling to the rotation [see Eq. (4.54)]. Therefore, the presence of the dipole moment does not appear to affect the stability of the ion in the trap, at least for the parameters considered.

We have shown some of the results obtained for the $X$-component of the motion in Fig. 5.5. For this example, the ion was initially located at the center of the trap. All curves in this figure show the difference between the trajectories when $\mu_0 \neq 0$ and when $\mu_0 = 0$. We have only plotted a part of the entire trajectories, between $[3.5 \mu s, 4 \mu s]$, for more visibility.

It is also apparent that as we increase the field, the amplitude of these trajectories increases. This increase can be either caused by the direct effect of the trapping field on the kinetic energy of the ion, or it can be due to a much stronger coupling between the trapping field and the dipole moment. However, as we have discussed it in Paper III (see Fig. 5 in Ref. [49]), the increase in amplitudes of the motion is more significant when $\mu_0 \neq 0$ than when $\mu_0 = 0$. Also, as we increase the magnitude of the field, hence increasing the energy of the interaction, the deviation of the trajectories for different initial orientations of the dipole becomes more
Figure 5.5: Time evolution of the X-components of the center-of-mass motion of a MgH$^+$ ion, trapped in a linear Paul trap, for different initial orientation of the dipole and for three different trapping fields: (a) $U_0 = 680 \text{ V}, V_0 = 1650 \text{ V}$; (b) $U_0 = 2175 \text{ V}, V_0 = 2000 \text{ V}$ and (c) $U_0 = 7080 \text{ V}, V_0 = 3000 \text{ V}$. All curves present the difference between trajectories of motion when $\mu_0 \neq 0$ and when $\mu_0 = 0$. 
evident. This deviation occurs for the same magnitude of the trapping potential. However, the deviation in the trajectories show the same periodicity and have the same zero crossing.

Finally, we have also examined the effect of setting an off-center initial position for the ion on its translational behavior. What we observed was that assigning an initial off-center position to the ion, does not qualitatively change the outcome. This was also seen and predicted for the case of an atomic ion. However, since this initial off-center position can act as an additional drive, the ion tends to exhibit motion with bigger amplitudes, for some cases. Therefore, upon choosing specific initial conditions for the ion, it can visit some high-field regions, where we still can see a significant effect of the coupling between the dipole moment and the electric field, even for magnitudes of the trapping field smaller than what we presented here.

5.2.2 Quantum rotation of a trapped molecular ion

To study the rotation of a trapped molecular ion, quantum mechanically and to find out to what extent the coupling between the trapping field and the dipole moment affects this rotation, we carry out semi-classical simulations, in which the rotation of the ion is treated quantum mechanically, while on the other hand, the position of the ion is updated, at each time step, according to the classical equations of motion [see Eqs. (4.75)]. Therefore, in addition to the initial conditions set for the ion in the classical simulations, it is necessary to set an initial rotational state to the ion as well. Rotational states of the ion correspond to spherical harmonics \( |J,M⟩ \) and to assign an initial rotational state to the ion, we will take all coefficients \( D_{J,M} \) in Eq. (4.64) equal to zero, at \( t = 0 \), except for the coefficient which represents the initial state, which will have a value equal to 1. We have run the semi-classical simulations using a basis of rotational states up to \( J = 20 \), to take into account all rotational excitation of the molecular ion.

To show the effect of the coupling between the dipole and the trapping field on the rotational states of the ion, we have plotted the time evolution of \( |D_J(t)|^2 \), in a form as

\[
|D_J(t)|^2 \equiv \sum_{M=-J}^{J} |D_{J,M}(t)|^2,
\]

which is the probability of finding the ion in a specific rotational state, corresponding to the quantum number \( J \), in Fig. 5.6 (we have only shown a part of the trajectory between \([1.3 \mu s, 3 \mu s] \)). The trapping fields \((U_0, V_0)\) for this example are chosen to have values equal to \((7080 V, 3000 V)\).
Figure 5.6: Comparison of the time evolution of the quantum rotational ground state $J = 0$ (when the ion is initially in this state), first rotational excited state $J = 1$ (when the ion is initially in the sub-level $J = 1, M = 1$) and the second rotational excited state $J = 2$ (when the ion is initially in the sub-level $J = 2, M = -1$) with each other, for a trapped MgH$^+$ ion. The time evolution of the trapping electric field is also shown with the green curve. The magnitude of the trapping potentials are $U_0 = 7080$ V and $V_0 = 3000$ V.
In this figure (Fig. 5.6), the pink curve represents the temporal change in the rotational ground state \( J = 0 \), while the ion was initially resided in the same state \([D_{0,0}(0) = 1] \). As it is evident, the small perturbation in this state is caused by the local trapping electric field felt by the ion, which is shown by the green curve in Fig. 5.6. Therefore, the trapping field induces a coupling between the rotational ground state and the rotational excited states of the ion, in such a way that the ion revisits its initial rotational state (here, the ground state) as the trapping field goes to zero. However, the effect of the coupling of the trapping field and the dipole moment is much smaller for higher rotational states (rotational excited states), corresponding to \( J \neq 0 \), but the temporal change in these states follows the temporal behavior of the local electric field as well. This is seen in Fig. 5.6, for the rotational excited states corresponding to \( J = 1 \) (purple curve) and \( J = 2 \) (black curve). For these two cases, the ion was initially in the rotational sub-levels \( J = 1, M = 1 \) \([D_{1,1}(0) = 1] \) and \( J = 2, M = -1 \) \([D_{2,-1}(0) = 1] \), respectively. We should note that these curves are obtained according to Eq. (5.2).

To provide more information, we have also plotted the time evolution of the rotational sub-levels \( J = 1, M = -1 \), \( J = 1, M = 0 \) and \( J = 1, M = 1 \) for the case when the ion was initially in the sub-level \( J = 1, M = 1 \), in Fig. 5.7. As it is seen, although none of the sub-levels show the same temporal behavior as the local electric field, they result in a perturbation in the state \( J = 1 \) according to Eq. (5.2) and what is depicted in Fig. 5.6 (purple curve), following the temporal changes in the local electric field. This behavior is seen for all rotational states, as well.

One important thing that we have not discussed yet is that the effect of the quantum rotation on the translational behavior of the ion is so small, compared to what we observed of the effect of the classical rotation on trajectories of the motion. This is shown and discussed in details in Paper III (see Ref. [49]). This is one of the reasons that we have plotted the same local electric field in Fig. 5.6 for all three different situations, when the ion was initially in three different rotational states.

So far, in all semi-classical simulations, we have set the ion to be located initially at the center of the trap. To examine if an initial off-center position for the ion can affect the dynamics of the quantum rotation, we have also run simulations for an initial position equal to \( \mathbf{R}_0 \equiv (X_0 = 10^{-8} \text{ m}, Y_0 = -5 \times 10^{-7} \text{ m}, Z_0 = 3 \times 10^{-6} \text{ m}) \), for the ion. The results obtained are all shown in Fig. 5.8.

In this example, we have compared the time evolution of the local electric field, hence the time evolution of the quantum rotational ground state, for two cases of having different initial position for the ion. For both cases, the ion was initially in \( J = 0 \) (rotational ground state). First, independent of any choice
for the initial condition, the rotational dynamics of the ion always follows the
time evolution of the local electric field. Second, as we see, depending on choosing
different initial position for the ion, the local electric field (felt by the ion) presents
a different temporal behavior, which is a result of an altered trajectory (not shown,
here). Therefore, the ion can visit locations in space where the magnitude of the
local electric field is more significant, which can eventually induce more probable
coupling between the rotational ground state and the rotational excited states.
This is, for instance, obvious by looking at curves between $t = 1 \mu s$ and $t = 1.5 \mu s$
in Fig. 5.8 where the population of other states than the ground state becomes
more probable.

Figure 5.7: Time evolution of the sub-levels of the first quantum rotational excited
state ($J = 0$) of a MgH$^+$, trapped in a linear Paul trap. In this case the ion was
initially in the rotational sub-level $J = 1, M = 1$. The magnitude of the trapping
potentials is $U_0 = 7080$ V and $V_0 = 3000$ V.
Figure 5.8: Comparison of the time evolution of the quantum rotational ground state $J = 0$ (when the ion is initially in this state), for two cases of having a trapped MgH$^+$ ion, located at the center of the trap and located off-center, initially. The time evolution of the trapping electric field is also shown with dashed curves for these two cases. The magnitude of the trapping potentials are $U_0 = 7080$V and $V_0 = 3000$V.
Chapter 6

Conclusion

We have studied the dynamics of a rigid heteronuclear diatomic molecular ion, possessing a permanent dipole moment $\mu_0$, which is trapped in a linear Paul trap. To study these dynamics we have constructed the Hamiltonian of the system and we have solved the corresponding Schrödinger equation, by carrying out suitable numerical calculations.

We have studied these dynamics in two different ways. First, we ignored the rotational dynamics of the molecular ion, by setting $\mu_0 = 0$ in the Hamiltonian of the system and we only investigated the translational behavior of the center of mass of the ion. To achieve this, we studied the quantum dynamic of a wave packet corresponding to the trapped ion, by implanting full-quantum numerical simulations. Next, we compared the quantum-mechanical results with those obtained classically. We observed that the classical trajectories of the center of mass of the ion was reproduced when the ion was treated as a quantum particle. We also showed that the stability criteria of an ion trapped in a quadrupole device applies to a quantum particle as well and the boundaries between the quantum stable and quantum unstable regions for a trapped ion matches the classical boundaries, which are defined by the Mathieu equation. Finally, we showed that the validity of the effective potential approximation is limited to those values of the trapping parameters (here, trapping potential $U_0$ and $V_0$) that result in having small magnitudes for their corresponding Mathieu characteristics $a$ and $q$. The results mentioned so far are all collected and presented in Paper II. We also have to mention that to run our full-quantum numerical simulations, we used the wavepacket program which is designed to solve the time-dependent Schrödinger equation on a one-, two-, or three-dimensional spatial grid using the split-operator method. Designing
this program is the subject of the Paper I.

Subsequently, by considering the presence of the dipole moment, we investigated the effect of the coupling between the dipole and the trapping electric field, on the rotational and the translational dynamics of the ion. We implemented both classical and semi-classical numerical simulations. In the classical method, we mostly studied the influence of the classical rotation on the translational behavior of the center of mass of the ion, by solving the classical equations of motion, consisting of both the translational equations and rotational equations. We showed that the coupling between the dipole and the electric field induces a significant change in the trajectories of the center-of-mass motion, compared to the trajectories obtained from the equations of motion without the dipole moment. Although the translational equations of motion do not obey the Mathieu equation, due to the presence of the coupling term, but the trajectories still stayed bounded. We also observed that the deviations in the classical trajectories were strongly dependent on the initial orientation of the dipole (molecular ion), for the same magnitude of the trapping potential.

We also performed semi-classical numerical simulations, in which we mainly investigated the quantum rotational dynamics in the presence of the coupling between the dipole and the electric field. In this approach we again obtained the trajectories via classical equations. However the rotation of the ion was treated full-quantum mechanically, by considering the rotational wave function of the ion. We observed that the time evolution of the rotational states of the ion follows the time evolution of the local trapping electric field. Therefore, in the presence of the electric field, the initial rotational state will no longer be fully populated and the probability of finding the ion in other rotational states increases. However, as soon as the ion reaches a location in space, where the electric field is zero, the ion tends to revisits its initial rotational state. We also showed that higher rotational states are less affected by the coupling between the dipole and the electric field. We also found that the trajectories are less affected by quantum rotations in comparison to the effect of classical rotation on trajectories of the center-of-mass. All the results mentioned, regarding the dynamics of a trapped molecular ion are presented in Paper III.

Finally, we presented a semi-classical model for a trapped molecular ion, which also interacts with an off-resonance laser field. In this model, we consider the effect of both, the coupling between the permanent dipole moment of the ion and the trapping field, and also the coupling between the laser field and the molecular ion – via its polarizability – on both the translational and the quantum rotational dynamics of the molecular ion.
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Bibliography


