Microcanonical distribution for one-electron triatomic molecules

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We formulate a microcanonical distribution for an arbitrary one-electron triatomic molecule. This distribution can be used to describe the initial state in strongly-driven two-electron triatomic molecules. Namely, in many semiclassical models that describe ionization of two-electron molecules driven by intense infrared laser fields in the tunneling regime initially one electron tunnels while the other electron is bound. The microcanonical distribution presented in this work can be used to describe the initial state of this bound electron.

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The nonlinear response of multi-center molecules to intense laser fields is a fundamental problem. For instance, understanding the break-up dynamics of strongly-driven molecules paves the way for controlling and imaging molecular processes [1]. Semi-classical models are essential in understanding the dynamics during the fragmentation of multi-center molecules driven by intense infrared laser pulses. One reason is that treating the dynamics of electrons and nuclei at the same time poses an immense challenge for fully ab-initio quantum mechanical calculations. Currently quantum mechanical techniques can only address one electron in triatomic molecules in two-dimensions [2]. Semi-classical models have provided significant insights, for example, in double ionization of strongly-driven H2 with “fixed nuclei” [3, 4] and in “frustrated” double ionization during the fragmentation of strongly-driven H2 [5, 6], where one electron eventually stays bound in a highly excited state of the H atom.

The initial state that is commonly employed by semi-classical models for strongly-driven two-electron atoms and molecules, for intensities in the tunneling regime, involves one electron that tunnel-ionizes in the field-lowered Coulomb potential and another electron that remains bound. The electron that tunnel-ionizes emerges from the barrier with a zero velocity along the direction of the laser field, while its velocity perpendicular to the laser field is given by a Gaussian distribution [7]. The tunneling rate can be obtained using semi-classical treatments, for instance see [7] for atoms and [8] for molecules. The electron that is initially bound is commonly described in semi-classical models by a microcanonical distribution.

To our knowledge, in the literature, a microcanonical distribution for any one-electron triatomic molecule which can also describe the initial state of the bound electron in the above described semi-classical models.

I. MICROcanonical DISTRIBUTION

In the following, we formulate a one-electron microcanonical distribution for triatomic molecules. We denote the positions of the nuclei by \( R_a = (0, 0, -R_{ab}/2) \), \( R_b = (0, 0, R_{ab}/2) \) and \( R_c = (x_c, 0, z_c) \) and the inter-nuclear distances by \( R_{ab}, R_{ac} \) and \( R_{bc} \), see Fig. 1 One can show that the coordinates of the nucleus C are expressed in terms of the inter-nuclear distances as follows:

\[
z_c = \frac{R_{ab}^2 - R_{bc}^2}{2R_{ab}}, \quad x_c = \pm \sqrt{R_{ac}^2 - \left( \frac{R_{ac}^2 - R_{bc}^2 + R_{ab}^2}{2R_{ab}} \right)^2}.
\]

(1)

We denote the position vector of the electron by \( \mathbf{r} \) and the distances of the electron from nuclei A, B and C by \( r_a = |\mathbf{r} - \mathbf{R}_a|, \ r_b = |\mathbf{r} - \mathbf{R}_b| \) and \( r_c = |\mathbf{r} - \mathbf{R}_c| \), respectively. We then define the confocal elliptical coordinates \( \lambda \) and \( \mu \) using the nuclei A and B as the foci of the ellipse, that is,

\[
\lambda = \frac{r_a + r_b}{R_{ab}}, \quad \mu = \frac{r_a - r_b}{R_{ab}},
\]

(2)

where \( \lambda \in [1, \infty) \) and \( \mu \in [-1, 1] \). The third coordinate \( \phi \in [0, 2\pi] \) is the angle between the projection of the position vector \( \mathbf{r} \) on the xy plane and the positive x axis; it thus defines the rotation angle around the axis that

FIG. 1. The configuration of the triatomic molecule we use to set-up the microcanonical distribution.
passes through nuclei A and B. The potential of the electron in the presence of the nuclei A, B and C, which have charges \( Z_A, Z_B \) and \( Z_C \), respectively, is given by

\[
W(r_a, r_b, r_c) = -\frac{Z_A}{r_a} - \frac{Z_B}{r_b} - \frac{Z_C}{r_c}. \tag{3}
\]

This potential is expressed in terms of the confocal elliptical coordinates as follows

\[
W(\lambda, \mu, \phi) = -\frac{2}{R_{ab}} \left[ \frac{Z_A}{\lambda + \mu} + \frac{Z_B}{\lambda - \mu} + \frac{4x_c}{R_{ab}} \cos(\phi) \sqrt{(\lambda^2 - 1)(1 - \mu^2)} + \frac{4(x_c^2 + z_c^2)}{R_{ab}^2} \right]^{-\frac{1}{2}}. \tag{4}
\]

The one-electron microcanonical distribution is given by

\[
f(\mathbf{r}, \mathbf{p}) \propto \delta(E - \frac{p^2}{2} - W), \tag{5}
\]

where \( E_i = -I_p \) is the ionization energy of the one-electron triatomic molecule. Note that the energy is given by \( E = p^2/2 + W \). The electron momentum in terms of the confocal elliptical coordinates is expressed as follows

\[
\begin{align*}
p_x &= \sqrt{2(E - W(\lambda, \mu, \phi))} \cos(\phi_p) \sqrt{1 - \nu_p^2}, \\
p_y &= \sqrt{2(E - W(\lambda, \mu, \phi))} \sin(\phi_p) \sqrt{1 - \nu_p^2}, \\
p_z &= \sqrt{2(E - W(\lambda, \mu, \phi))} \nu_p,
\end{align*}
\]

where \( \phi_p \in [0, 2\pi] \) and \( \nu_p \in [-1, 1] \) define the momentum \( \mathbf{p} \) in spherical coordinates. Transforming from \((\mathbf{r}, \mathbf{p}) \rightarrow (\lambda, \mu, \phi, E, \nu_p, \phi_p)\) and integrating over \( E \in (-\infty, 0), \phi_p \) and \( \nu_p \) we find

\[
\rho(\lambda, \mu, \phi) \propto (\lambda^2 - \mu^2)^{\frac{1}{2}} (E_i - W(\lambda, \mu, \phi)). \tag{7}
\]

The \( \rho \) distribution goes to zero and is thus well-behaved when the electron is placed on top of either nucleus A or B. However, when \( \mathbf{r} \rightarrow \mathbf{R}_c \), i.e., the electron is placed on top of nucleus C, \( \rho(\lambda, \mu, \phi) \rightarrow \infty \). We eliminate this singularity by introducing an additional transformation. Setting \( \lambda = \lambda_c = (R_{ac} + R_{bc})/R_{ab}, \phi = 0 \) and expanding \( \rho(\lambda_c, \mu, 0) \) around \( \mu = \mu_c = (R_{ac} - R_{bc})/R_{ab} \) we find

\[
\rho(\lambda_c, \mu, 0) \propto \frac{1}{|\mu - \mu_c|^{1/2}}, \tag{8}
\]

where \( \lambda_c \) and \( \mu_c \) are the values of \( \lambda \) and \( \mu \), respectively, when the electron is placed on top of the nucleus C. To eliminate the singularity in Eq. (8), we introduce a new variable \( t \), such that \( t^\gamma = \mu - \mu_c \). The new distribution takes the form

\[
\tilde{\rho}(\lambda, t, \phi) \propto \begin{cases} 
|t^\gamma|^{-1}|(\lambda^2 - (t^\gamma + \mu_c)^2)\sqrt{P(\lambda, t, \phi)} & \text{for } P(\lambda, t, \phi) \geq 0 \\
0 & \text{for } P(\lambda, t, \phi) < 0
\end{cases}, \tag{9}
\]

where \( P(\lambda, t, \phi) = 2E_i + \frac{4}{R_{ab}} \left[ \frac{Z_A}{\lambda + t^\gamma + \mu_c} + \frac{Z_B}{\lambda - t^\gamma - \mu_c} + \frac{4x_c}{R_{ab}} \cos(\phi) \sqrt{(\lambda^2 - 1)(1 - (t^\gamma + \mu_c)^2)} + \frac{4(x_c^2 + z_c^2)}{R_{ab}^2} \right]^{-\frac{1}{2}} \right].
\]

Since \( \mu \in [-1, 1] \), \( t^\gamma \) and \( t \) take both negative and positive values and therefore, if we choose one \( \gamma \) for all values of \( \mu \), \( \gamma \) must be odd. Moreover, to avoid the singularity when the electron is placed on top of nucleus C, \( \gamma \) must be such that \( t^\gamma / t^\gamma \rightarrow 0, \) i.e., \( \gamma \geq 2 \). Combining the above two conditions, yields \( \gamma = 3, 5, 7, \ldots \). The new distribution \( \tilde{\rho}(\lambda, t, \phi) \) goes to zero when the electron is placed on top of the nucleus C, i.e., when \( \lambda = \lambda_c, t = 0 \) and \( \phi = 0, 2\pi \).
To set up the initial conditions we find $\lambda_{\text{max}}$ so that $\beta^2/2 = E_l - W > 0$ and equivalently $P(\lambda, t, \phi) \geq 0$. We then find the maximum value $\rho_{\text{max}}$ of the distribution $\tilde{\rho}(\lambda, t, \phi)$, for the allowed values of the parameters $\lambda$, $t$ and $\phi$. We next generate the uniform random numbers $\lambda \in [1, \lambda_{\text{max}}]$, $t \in [t_{\text{min}}, t_{\text{max}}]$, and $\phi \in [0, 2\pi]$, with $t_{\text{min}} = -(1 + \mu_e)^{1/3}$ and $t_{\text{max}} = (1 - \mu_e)^{1/3}$. If $\tilde{\rho}(\lambda, t, \phi) > \chi$ then the generated values of $\lambda$, $t$ and $\phi$ are accepted as initial conditions, otherwise, they are rejected and the sampling process starts again.

Following the above described formulation, we obtain the initial conditions of the electron with respect to the origin of the coordinate system. To obtain the initial conditions for the position of the electron with respect to the center of mass of the triatomic molecule, $\mathbf{r}'$, in terms of the ones with respect to the origin, $\mathbf{r}$, we shift the coordinates by $\mathbf{r}' = \mathbf{r} - \mathbf{R}_{\text{cm}}$, where $\mathbf{R}_{\text{cm}}$ is given by $(X_{\text{cm}}, 0, Z_{\text{cm}})$ with

$$X_{\text{cm}} = \frac{m_C x_c}{m_A + m_B + m_C},$$

$$Z_{\text{cm}} = \frac{R_{ab}(m_B - m_A)/2 + m_C z_c}{m_A + m_B + m_C},$$

(10)

with $m_A$, $m_B$ and $m_C$ the masses of the nuclei.

As an example, we next obtain the probability densities of the position and the momentum of the electron that is initially bound in $\text{H}_3^+$ when the molecule is driven by an intense infrared laser field. We assume the other electron tunnel-ionizes in the initial state. We consider the $\text{H}_3^+$ triatomic molecule in its ground state, where the distance of the nuclei in the equilateral triangle arrangement is 1.65 a.u. and the first and second ionization energies are $I_{p_1} = 1.2079$ a.u. and $I_{p_2} = 1.93$ a.u., respectively. We find the ionization potentials and equilibrium distances of the initial state using MOLPRO, which is a quantum chemistry package [10]. For the microcanonical distribution the relevant ionization energy is $I_p = I_{p_2}$, since $I_{p_1}$ is associated with the electron that tunnel-ionizes in the initial state.

In Fig. 2 (b) we plot the probability density of the position of the electron on the x-z plane for $y = 0$ using the above described microcanonical distribution. To compare, in Fig. 2 (a) we plot the quantum mechanical probability density of the position of the electron on the x-z plane. That is, we plot $|\Psi(x, 0, z)|^2$, where $\Psi(x, 0, z)$ is the quantum mechanical wavefunction for the $\text{H}_3^+$ molecule, which we obtain using Molpro. The two plots, Fig. 2 (a) and (b), show that the two probability densities for the electron position compare well. However, the microcanonical probability density underestimates the electron probability density between the nuclei and overestimates the electron probability density around the nuclei.

In addition, in Fig. 3 (b) for all values of the electron momentum component along the y-axis, $p_y$, we plot the probability density of the electron momentum on the $p_x - p_z$ plane using the microcanonical distribution. To compare, in Fig. 3 (a) we plot $\rho_{\text{QM}}(p_x, p_z)$, which we obtain by first computing the quantum mechanical wavefunction in momentum space using the quantum mechanical wavefunction $\Psi(x, 0, z)$ computed from Molpro

$$\Phi(p) = \frac{1}{(2\pi)^3/2} \int \Psi(x, 0, z)e^{-i\mathbf{p}\mathbf{r}}d\mathbf{r},$$

(11)

and then by integrating over $p_y$

$$\rho_{\text{QM}}(p_x, p_z) = \int_{-\infty}^{\infty} |\Phi(p)|^2 dp_y.$$  

(12)

The two plots, Fig. 3 (a) and (b), show that the two probability densities for the electron momentum compare well. However, the microcanonical probability density overestimates the higher values of the electron momentum. This can be seen more clearly in Fig. 3 (c) where we plot the probability density of the electron momentum along the $p_z$ axis both quantum mechanically and using our microcanonical distribution. To obtain the plots in Fig. 3 (c) we project the probability densities of the electron momentum in Fig. 3 (a) and (b) on the $p_z$ axis. Fig. 3 (c) clearly shows that the probability

FIG. 2. The left panel shows the quantum mechanical probability density of the electron position on the x-z plane. The right panel shows the microcanonical probability density of the electron position on the x-z plane.

FIG. 3. The left panel shows the quantum mechanical probability density of the electron on the x-z plane for $y = 0$ using the above described microcanonical distribution.
density of the electron momentum obtained from the microcanonical distribution overestimates the higher values of the momentum component $p_z$. This is consistent with our previous finding that the microcanonical distribution overestimates values of the electron position around the nuclei resulting to higher values of the momentum.

In conclusion, in the current work we have formulated a microcanonical distribution for a general one-electron triatomic molecule. This distribution can be used to describe the initial state of the bound electron in semi-classical models of strongly-driven two-electron triatomic molecules.

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