Scientific Research Publishing

Journal of Applied Mathematics and Physics, 2024, 12, 3655-3678
https://www.scirp.org/journal/jamp
ISSN Online: 2327-4379
ISSN Print: 2327-4352

Path Integral Approach to the Interaction of Two-Electron Atoms with Elliptically Polarized Pulses

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How to cite this paper: Thrapsaniotis, E.G. (2024) Path Integral Approach to the Interaction of Two-Electron Atoms with Elliptically Polarized Pulses. *Journal of Applied Mathematics and Physics*, **12**, 3655-3678.
https://doi.org/10.4236/jamp.2024.1211219

Received: September 30, 2024
Accepted: November 3, 2024
Published: November 6, 2024

Abstract

We study the dynamics of a two-electron atom interacting with a pulsed, elliptically polarized, ultrashort, excited coherent state. We use path integral methods and integrate on the photonic part. We angularly decompose the Coulomb interaction term of the two electrons and the interaction term of the two electrons with the photonic field and solve the sign problem. We give results on the survival probability of the ground state of Helium.

Keywords

Helium, Path Integrals, Angular Decomposition, Sign Solved Propagator, Elliptic Polarization

1. Introduction

The study of the interaction of radiation with matter is an area of major importance in physics. The production of pulses of various durations and central frequencies in laboratories has given a further boost to that study. These pulses can be used in the study of various elementary processes, such as the excitation or photoionization of atoms [1]-[4]. This is possible due to their short time length of the order of a few femtoseconds or of a few hundred attoseconds. Sub-100-as pulses have been generated as well [5]-[8]. Moreover, their photons' energy may belong in the ultraviolet or extreme ultraviolet, and therefore, just one or two photons may be enough to cause excitation or ionization.

In the present paper, we introduce a fully quantum mechanical field theoretical treatment for the interaction of elliptically polarized ultrashort pulses with atoms or molecules. We confront the photonic field from a quantum mechanical—path integral point of view. The atoms or molecules under study can be considered either relativistically or non-relativistically, depending on their structure and the parameters involved. Here, we considered a non-relativistic case. Relativistic systems will be considered elsewhere. More particularly, here we study the Helium atom. So, proceeding, we restrict ourselves to the weak field limit and keep first-order terms in a possible expansion over the field. We consider the transition between an initial excited coherent state and a final coherent one (we have considered other photonic states elsewhere [9] [10]). We integrate over the photonic field and angularly decompose both the Coulomb two-electron interaction and the electrons-photonic field interaction terms. With that technique, we circumvent the use of the spectral representation of the helium atom propagator we would use in a possible perturbative expansion. We use the propagator that appears in its sign solved propagator (SSP) form [11] [12]. As an application, we study the survival probability of the ground state of Helium. After the photonic transition, the atomic system may have a wide range of states. So, the survival probability is smaller than one and decays in an exponential way with possible temporary trappings and changes of channels (for a more extended discussion, see at the end of Section 4).

The present paper proceeds as follows. In Section 2, we describe the present system and integrate over its photonic part. Then, in Section 3, we give the angular decomposition of the propagator in the case of elliptic polarization. In Section 4, we give our results, and in 5, we present our conclusions. In Appendix A, we study the path integral of Helium and give its angular decomposition. In Appendices B and C, we give certain necessary integrals, and in Appendix D, we give a notational list of the variables used.

2. System Hamiltonian and Path Integration

In the present paper, we consider a two-electron atom initially in its ground state under the action of an ultrashort, pulsed, excited coherent state. Therefore, the system Hamiltonian H can be decomposed into a sum of three terms. The two electrons atom one H_{He}, the photonic field one H_f and an interaction term H_I of the photonic field with the two electrons

$$H = H_{He} + H_f + H_I \tag{1}$$

H_{He} has the form

$$H_{He}\left(\boldsymbol{p}_1, \boldsymbol{p}_2, \boldsymbol{r}_1, \boldsymbol{r}_2\right) = \frac{\boldsymbol{p}_1^2}{2} + \frac{\boldsymbol{p}_2^2}{2} - \frac{Z}{|\boldsymbol{r}_1|} - \frac{Z}{|\boldsymbol{r}_2|} + \frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} \tag{2}$$

where Z is the atomic number. $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ are the position vectors of the two electrons with respect to the nucleus. The photonic field has Hamiltonian

$$H_f = \omega a^+ a \tag{3}$$

while the interaction term H_I in the Power-Zienau-Woolley formalism takes the form

$$H_I = -e\boldsymbol{r}_1 \cdot \boldsymbol{E}_f\left(\boldsymbol{r}_1, \tau\right) - e\boldsymbol{r}_2 \cdot \boldsymbol{E}_f\left(\boldsymbol{r}_2, \tau\right) \tag{4}$$

$\boldsymbol{E}_f(\boldsymbol{r},\tau)$ is the field operator of the photonic pulse given by the expression

$$\boldsymbol{E}_f(\boldsymbol{r},\tau)=\frac{1}{\sqrt{V}}il(\omega)\wp(\tau)\left[\hat{\varepsilon}\hat{a}\mathrm{e}^{i\boldsymbol{k}_{ph}\cdot\boldsymbol{r}}-\hat{\varepsilon}^*\hat{a}^+\mathrm{e}^{-i\boldsymbol{k}_{ph}\cdot\boldsymbol{r}}\right] \tag{5}$$

$\wp(\tau)$ is the pulse's envelope function. In expression (5), $l(\omega)=\sqrt{2\pi\omega}$ is a real frequency function, $\hat{\varepsilon}$ is the polarization, ω is the pulse's carrier frequency, $\boldsymbol{k}_{ph}$ is the radiation wave vector and V is a large volume. Then H_I has the form

$$H_I=g(\tau)a+g^*(\tau)a^+ \tag{6}$$

We have set

$$g(\tau)=-\frac{1}{\sqrt{V}}iel(\omega)\wp(\tau)\left(\hat{\varepsilon}\cdot\boldsymbol{r}_1(\tau)\mathrm{e}^{i\boldsymbol{k}_{ph}\cdot\boldsymbol{r}_1(\tau)}+\hat{\varepsilon}\cdot\boldsymbol{r}_2(\tau)\mathrm{e}^{i\boldsymbol{k}_{ph}\cdot\boldsymbol{r}_2(\tau)}\right) \tag{7}$$

The propagator has the following diagonal form after the integration over the photonic field

$$\begin{aligned}&K\left(\alpha^*,\boldsymbol{r}_{1f},\boldsymbol{r}_{2f},t_f;\alpha,\boldsymbol{r}_{1i},\boldsymbol{r}_{2i},t_i\right)\\&=\iint D\boldsymbol{r}_1(\tau)\frac{D\boldsymbol{p}_1(\tau)}{(2\pi)^3}D\boldsymbol{r}_2(\tau)\frac{D\boldsymbol{p}_2(\tau)}{(2\pi)^3}\\&\times\exp\left[i\int_{t_i}^{t_f}\mathrm{d}\tau\left[\boldsymbol{p}_1(\tau)\cdot\dot{\boldsymbol{r}}_1(\tau)+\boldsymbol{p}_2(\tau)\cdot\dot{\boldsymbol{r}}_2(\tau)-H_{He}(\boldsymbol{p}_1,\boldsymbol{p}_2,\boldsymbol{r}_1,\boldsymbol{r}_2)\right]\right.\\&\left.+A(t_f,t_i)-B(t_f-t_i)|\alpha|^2+D_1(t_f,t_i)\alpha+D(t_f,t_i)\alpha^*\right]\end{aligned} \tag{8}$$

The parameters are given as

$$\begin{aligned}A(t_f,t_i)=&-\frac{1}{V}e^2l^2(\omega)\int_{t_i}^{t_f}\mathrm{d}\tau\int_{t_i}^{\tau}\mathrm{d}\rho\,\wp(\tau)\left(\hat{\varepsilon}\cdot\boldsymbol{r}_1(\tau)\mathrm{e}^{i\boldsymbol{k}_{ph}\cdot\boldsymbol{r}_1(\tau)-i\omega\tau}+\hat{\varepsilon}\cdot\boldsymbol{r}_2(\tau)\mathrm{e}^{i\boldsymbol{k}_{ph}\cdot\boldsymbol{r}_2(\tau)-i\omega\tau}\right)\\&\times\wp(\rho)\left(\hat{\varepsilon}^*\cdot\boldsymbol{r}_1(\rho)\mathrm{e}^{-i\boldsymbol{k}_{ph}\cdot\boldsymbol{r}_1(\rho)+i\omega\rho}+\hat{\varepsilon}^*\cdot\boldsymbol{r}_2(\rho)\mathrm{e}^{-i\boldsymbol{k}_{ph}\cdot\boldsymbol{r}_2(\rho)+i\omega\rho}\right)\end{aligned} \tag{9}$$

$$B(t_f-t_i)=1-\mathrm{e}^{-i\omega(t_f-t_i)} \tag{10}$$

$$D(t_f,t_i)=\frac{1}{\sqrt{V}}el(\omega)\int_{t_i}^{t_f}\mathrm{d}\tau\,\wp(\tau)\left(\hat{\varepsilon}^*\cdot\boldsymbol{r}_1(\tau)\mathrm{e}^{-i\boldsymbol{k}_{ph}\cdot\boldsymbol{r}_1(\tau)+i\omega\tau}+\hat{\varepsilon}^*\cdot\boldsymbol{r}_2(\tau)\mathrm{e}^{-i\boldsymbol{k}_{ph}\cdot\boldsymbol{r}_2(\tau)+i\omega\tau}\right)\mathrm{e}^{-i\omega t_f} \tag{11}$$

$$D_1(t_f,t_i)=-\frac{1}{\sqrt{V}}el(\omega)\int_{t_i}^{t_f}\mathrm{d}\tau\,\wp(\tau)\left(\hat{\varepsilon}\cdot\boldsymbol{r}_1(\tau)\mathrm{e}^{i\boldsymbol{k}_{ph}\cdot\boldsymbol{r}_1(\tau)-i\omega\tau}+\hat{\varepsilon}\cdot\boldsymbol{r}_2(\tau)\mathrm{e}^{i\boldsymbol{k}_{ph}\cdot\boldsymbol{r}_2(\tau)-i\omega\tau}\right)\mathrm{e}^{i\omega t_i} \tag{12}$$

In the present paper, we suppose that we have a field transition between an initial photonic state $|\Phi_1\rangle$ and a final one $|\Phi_2\rangle$. Then, the reduced propagator takes the form

$$\tilde{K}\left(\boldsymbol{r}_{1f},\boldsymbol{r}_{2f},t_f;\boldsymbol{r}_{1i},\boldsymbol{r}_{2i},t_i\right)=\int\frac{\mathrm{d}^2\alpha}{\pi}\mathrm{e}^{|\alpha|^2}\langle\Phi_2|\alpha\rangle K\left(\alpha^*,\boldsymbol{r}_{1f},\boldsymbol{r}_{2f},t_f;\alpha,\boldsymbol{r}_{1i},\boldsymbol{r}_{2i},t_i\right)\langle\alpha|\Phi_1\rangle \tag{13}$$

Now we assume that the states $\left|\Phi_{\left\{\begin{smallmatrix}1\\2\end{smallmatrix}\right\}}\right\rangle$ correspond to excited coherent states. Then, they have the following representation

$$\left|\Phi_{\left\{\begin{smallmatrix}1\\2\end{smallmatrix}\right\}}\right\rangle=\sum_p c_{\left\{\begin{smallmatrix}1\\2\end{smallmatrix}\right\}p}\frac{\left(a^+\right)^p}{\sqrt{p!}}\left\{\begin{matrix}|\beta\rangle\\|\gamma\rangle\end{matrix}\right\} \tag{14}$$

To proceed, we define the functions

$$f_{\left\{\begin{smallmatrix}1\\2\end{smallmatrix}\right\}}\left(\alpha^*\right)=\sum_p c_{\left\{\begin{smallmatrix}1\\2\end{smallmatrix}\right\}p}\frac{\left(\alpha^*\right)^p}{\sqrt{p!}} \tag{15}$$

and we integrate over the field variable α. So, after standard manipulations, we obtain the following reduced propagator for the dynamics of the two electrons

$$\begin{aligned}&\tilde{K}\left(\boldsymbol{r}_{1f},\boldsymbol{r}_{2f},t_f;\boldsymbol{r}_{1i},\boldsymbol{r}_{2i},t_i\right)=C\left(t_f-t_i\right)T_{f_1f_2^*}\left(\boldsymbol{r}_{1f},\boldsymbol{r}_{2f},t_f;\boldsymbol{r}_{1i},\boldsymbol{r}_{2i},t_i\right)\\&=C\left(t_f-t_i\right)\iint D\boldsymbol{r}_1(\tau)\frac{D\boldsymbol{p}_1(\tau)}{(2\pi)^3}D\boldsymbol{r}_2(\tau)\frac{D\boldsymbol{p}_2(\tau)}{(2\pi)^3}f_1\left(\frac{1}{B\left(t_f-t_i\right)}\left(\gamma^*+D_1\left(t_f,t_i\right)\right)\right)\\&\times f_2^*\left(\frac{1}{B\left(t_f-t_i\right)}\left(\beta+D\left(t_f,t_i\right)\right)\right)\exp\left\{iS_{tot}\left[\boldsymbol{p}_1,\boldsymbol{p}_2,\boldsymbol{r}_1,\boldsymbol{r}_2,\tau\right]\right\}\end{aligned} \tag{16}$$

where

$$C(t)=\frac{\exp\left(\frac{\beta\gamma^*}{B(t)}-\frac{1}{2}|\beta|^2-\frac{1}{2}|\gamma|^2\right)}{B(t)} \tag{17}$$

Now, we proceed to the study of the contribution of the $C(t)$ factor in Equation (16). At first, we consider the exponential. We expand the function e^{xz}, $x\in(0,1)$ into a Fourier series where $z\neq0$ is a complex number. The result is

$$\frac{\mathrm{e}^{xz}}{\mathrm{e}^{z}-1}=\frac{1}{z}+\sum_{m\neq0}\frac{\mathrm{e}^{2\pi imx}}{z-2\pi im} \tag{18}$$

So, on letting $x\to0^+$ and setting $z=i\omega t$ we get

$$\begin{aligned}\frac{1}{B(t)}&=\frac{1}{1-\mathrm{e}^{-i\omega t}}=1-\frac{1}{1-\mathrm{e}^{i\omega t}}=1-i\left(\frac{1}{\omega t}+\sum_{m=1}^{\infty}\frac{2\omega t}{(\omega t)^2-(2\pi m)^2}\right)\\&=1-\frac{1}{2}i\cot\left(\frac{\omega t}{2}\right)\end{aligned} \tag{19}$$

Then the measure of the exponential in Equation (17) is

$$\left|\exp\left(\frac{\beta\gamma^*}{B(t)}-\frac{1}{2}|\beta|^2-\frac{1}{2}|\gamma|^2\right)\right|^2=\exp\left(-|\beta-\gamma|^2+\operatorname{Im}\left(\beta\gamma^*\right)\cot\left(\frac{\omega t}{2}\right)\right) \tag{20}$$

So, if $\beta=\gamma$ the measure of the exponential becomes one.

Moreover, after a direct and an inverse Fourier transform, we get the identity [9]

$$\frac{A(t)}{B(t)}=A(t)\left[\frac{1}{2}+\frac{\pi}{\omega}\sum_{m=-\infty}^{\infty}\delta\left(\frac{2m\pi}{\omega}-t\right)\right] \tag{21}$$

At the times, $\frac{2m\pi}{\omega}$ the propagator gets zero values. So if $\beta=\gamma$, the $C(t)$ factor in Equation (16) contributes a $\frac{1}{2}$ factor.

The action in Equation (16) is

$$\begin{aligned}
&S_{tot}\left[\boldsymbol{p}_1,\boldsymbol{p}_2,\boldsymbol{r}_1,\boldsymbol{r}_2,\tau\right]\\
&=\int_{t_i}^{t_f}\left[\boldsymbol{p}_1(\tau)\cdot\dot{\boldsymbol{r}}_1(\tau)+\boldsymbol{p}_2(\tau)\cdot\dot{\boldsymbol{r}}_2(\tau)-H_{He}\left(\boldsymbol{p}_1,\boldsymbol{p}_2,\boldsymbol{r}_1,\boldsymbol{r}_2\right)\right]\mathrm{d}\tau\\
&\quad+i\frac{1}{\sqrt{V}}el(\omega)\int_{t_i}^{t_f}\mathrm{d}\tau\Big[\beta\chi(\tau)\Big(\hat{\varepsilon}\cdot\boldsymbol{r}_1(\tau)\mathrm{e}^{i\boldsymbol{k}_{ph}\cdot\boldsymbol{r}_1(\tau)}+\hat{\varepsilon}\cdot\boldsymbol{r}_2(\tau)\mathrm{e}^{i\boldsymbol{k}_{ph}\cdot\boldsymbol{r}_2(\tau)}\Big)\\
&\quad+\gamma^*\chi^*(\tau)\Big(\hat{\varepsilon}^*\cdot\boldsymbol{r}_1(\tau)\mathrm{e}^{-i\boldsymbol{k}_{ph}\cdot\boldsymbol{r}_1(\tau)}+\hat{\varepsilon}^*\cdot\boldsymbol{r}_2(\tau)\mathrm{e}^{-i\boldsymbol{k}_{ph}\cdot\boldsymbol{r}_2(\tau)}\Big)\Big]\\
&\quad+\frac{1}{V}e^2l^2(\omega)\int_{t_i}^{t_f}\mathrm{d}\tau\wp(\tau)\int_{t_i}^{\tau}\mathrm{d}\rho\wp(\rho)\xi(\tau-\rho)\\
&\quad\times\Big(\hat{\varepsilon}^*\cdot\boldsymbol{r}_1(\tau)\mathrm{e}^{-i\boldsymbol{k}_{ph}\cdot\boldsymbol{r}_1(\tau)}+\hat{\varepsilon}^*\cdot\boldsymbol{r}_2(\tau)\mathrm{e}^{-i\boldsymbol{k}_{ph}\cdot\boldsymbol{r}_2(\tau)}\Big)\\
&\quad\times\Big(\hat{\varepsilon}\cdot\boldsymbol{r}_1(\rho)\mathrm{e}^{i\boldsymbol{k}_{ph}\cdot\boldsymbol{r}_1(\rho)}+\hat{\varepsilon}\cdot\boldsymbol{r}_2(\rho)\mathrm{e}^{i\boldsymbol{k}_{ph}\cdot\boldsymbol{r}_2(\rho)}\Big)
\end{aligned}\tag{22}$$

The function $\chi(\tau)$ has the form

$$\chi(\tau)=\wp(\tau)\frac{\mathrm{e}^{-i\omega\tau}}{\mathrm{e}^{-i\omega t_i}-\mathrm{e}^{-i\omega t_f}}\tag{23}$$

And the function $\xi(\tau-\rho)$ is

$$\xi(\tau-\rho)=\frac{\cos\left(\omega(\tau-\rho)-\frac{\omega\left(t_f-t_i\right)}{2}\right)}{\sin\left(\frac{\omega\left(t_f-t_i\right)}{2}\right)}\tag{24}$$

Now we observe that in the absence of the Helium potentials

$$\boldsymbol{r}_i(\rho)=\boldsymbol{r}_i(\tau)+\mathrm{O}\left(\frac{1}{\sqrt{V}}\right)\quad i=1,2\tag{25}$$

When the potentials are present, we have to expand perturbatively over the potentials, apply that approximation and then sum back. Therefore, Equation (22) takes the form

$$\begin{aligned}
&S_{tot}\left[\boldsymbol{p}_1,\boldsymbol{p}_2,\boldsymbol{r}_1,\boldsymbol{r}_2,\tau\right]\\
&=\int_{t_i}^{t_f}\left[\boldsymbol{p}_1(\tau)\cdot\dot{\boldsymbol{r}}_1(\tau)+\boldsymbol{p}_2(\tau)\cdot\dot{\boldsymbol{r}}_2(\tau)-H_{He}\left(\boldsymbol{p}_1,\boldsymbol{p}_2,\boldsymbol{r}_1,\boldsymbol{r}_2\right)\right]\mathrm{d}\tau\\
&\quad+i\frac{1}{\sqrt{V}}el(\omega)\int_{t_i}^{t_f}\mathrm{d}\tau\Big[\beta\chi(\tau)\Big(\hat{\varepsilon}\cdot\boldsymbol{r}_1(\tau)\mathrm{e}^{i\boldsymbol{k}_{ph}\cdot\boldsymbol{r}_1(\tau)}+\hat{\varepsilon}\cdot\boldsymbol{r}_2(\tau)\mathrm{e}^{i\boldsymbol{k}_{ph}\cdot\boldsymbol{r}_2(\tau)}\Big)\\
&\quad+\gamma^*\chi^*(\tau)\Big(\hat{\varepsilon}^*\cdot\boldsymbol{r}_1(\tau)\mathrm{e}^{-i\boldsymbol{k}_{ph}\cdot\boldsymbol{r}_1(\tau)}+\hat{\varepsilon}^*\cdot\boldsymbol{r}_2(\tau)\mathrm{e}^{-i\boldsymbol{k}_{ph}\cdot\boldsymbol{r}_2(\tau)}\Big)\Big]\\
&\quad+\frac{1}{V}e^2l^2(\omega)\int_{t_i}^{t_f}\mathrm{d}\tau\nu(\tau)\left|\hat{\varepsilon}\cdot\boldsymbol{r}_1(\tau)\mathrm{e}^{i\boldsymbol{k}_{ph}\cdot\boldsymbol{r}_1(\tau)}+\hat{\varepsilon}\cdot\boldsymbol{r}_2(\tau)\mathrm{e}^{i\boldsymbol{k}_{ph}\cdot\boldsymbol{r}_2(\tau)}\right|^2
\end{aligned}\tag{26}$$

where

$$\nu(\tau)=\wp(\tau)\int_{t_i}^{\tau}\wp(\rho)\xi(\tau-\rho)\mathrm{d}\rho \tag{27}$$

Eventually we obtain

$$\begin{aligned}&T_{f_1 f_2^*}\left(\boldsymbol{r}_{1f},\boldsymbol{r}_{2f},t_f;\boldsymbol{r}_{1i},\boldsymbol{r}_{2i},t_i\right)\\&=\int\int D\boldsymbol{r}_1(\tau)\frac{D\boldsymbol{p}_1(\tau)}{(2\pi)^3}D\boldsymbol{r}_2(\tau)\frac{D\boldsymbol{p}_2(\tau)}{(2\pi)^3}f_1\left(\frac{1}{B\left(t_f-t_i\right)}\gamma^*+D_0\left(t_f,t_i\right)\right)\\&\times f_2^*\left(\frac{1}{B\left(t_f-t_i\right)}\beta+D_0^*\left(t_f,t_i\right)\right)\exp\left\{iS_{tot}\left[\boldsymbol{p}_1,\boldsymbol{p}_2,\boldsymbol{r}_1,\boldsymbol{r}_2,\tau\right]\right\}\end{aligned} \tag{28}$$

where

$$D_0\left(t_f,t_i\right)=-\frac{1}{\sqrt{V}}el(\omega)\int_{t_i}^{t_f}\mathrm{d}\tau\chi(\tau)\hat{\varepsilon}\cdot\left(\boldsymbol{r}_1(\tau)\mathrm{e}^{i\boldsymbol{k}_{ph}\cdot\boldsymbol{r}_1(\tau)}+\boldsymbol{r}_2(\tau)\mathrm{e}^{i\boldsymbol{k}_{ph}\cdot\boldsymbol{r}_2(\tau)}\right) \tag{29}$$

and the action has the form (26). In the case of more than two electrons, we obtain a similar expression. Finally, in the long wavelength approximation, we can set $\mathrm{e}^{i\boldsymbol{k}_{ph}\cdot\boldsymbol{r}_1}\cong\mathrm{e}^{i\boldsymbol{k}_{ph}\cdot\boldsymbol{r}_2}\cong 1$. Then we get the following expressions

$$\begin{aligned}&S_{tot}\left[\boldsymbol{p}_1,\boldsymbol{p}_2,\boldsymbol{r}_1,\boldsymbol{r}_2,\tau\right]\\&=\int_{t_i}^{t_f}\left[\boldsymbol{p}_1(\tau)\cdot\dot{\boldsymbol{r}}_1(\tau)+\boldsymbol{p}_2(\tau)\cdot\dot{\boldsymbol{r}}_2(\tau)-H_{He}\left(\boldsymbol{p}_1,\boldsymbol{p}_2,\boldsymbol{r}_1,\boldsymbol{r}_2\right)\right]\mathrm{d}\tau\\&+i\frac{1}{\sqrt{V}}el(\omega)\int_{t_i}^{t_f}\mathrm{d}\tau\left[\beta\chi(\tau)\hat{\varepsilon}\cdot\left(\boldsymbol{r}_1(\tau)+\boldsymbol{r}_2(\tau)\right)+\gamma^*\chi^*(\tau)\hat{\varepsilon}^*\cdot\left(\boldsymbol{r}_1(\tau)+\boldsymbol{r}_2(\tau)\right)\right]\\&+\frac{1}{V}e^2l^2(\omega)\int_{t_i}^{t_f}\mathrm{d}\tau\nu(\tau)\left|\hat{\varepsilon}\cdot\left(\boldsymbol{r}_1(\tau)+\boldsymbol{r}_2(\tau)\right)\right|^2\end{aligned} \tag{30}$$

$$D_0\left(t_f,t_i\right)=-\frac{1}{\sqrt{V}}el(\omega)\int_{t_i}^{t_f}\mathrm{d}\tau\chi(\tau)\hat{\varepsilon}\cdot\left(\boldsymbol{r}_1(\tau)+\boldsymbol{r}_2(\tau)\right) \tag{31}$$

As an application in Section 4, we study the survival probability of the ground state of Helium in the case of an initial excited coherent state of the form $\frac{1}{\sqrt{1+|\beta|^2}}a^+|\beta\rangle$ and a final coherent state $|\beta\rangle$.

Now, we proceed to the angular decomposition of the above expressions.

3. Angular Decomposition of the Photonic Part

We intend to perform angular decomposition and evaluate the SSP corresponding to the propagator (28) in the long wavelength approximation.

In the present paper, we consider elliptic polarization so that the polarization vector takes the form

$$\hat{\varepsilon}=\hat{\varepsilon}_x\cos\left(\frac{\xi}{2}\right)\pm i\hat{\varepsilon}_y\sin\left(\frac{\xi}{2}\right) \tag{32}$$

where $\widehat{\varepsilon}_x$ and $\widehat{\varepsilon}_y$ are the unit vectors along the x-axis and y-axis. The upper sign corresponds to left elliptic polarization, while the lower one is to the right one. Here, we consider the right elliptic polarization. Moreover, we direct the wavevector along the z-axis.

The propagator $T^{\xi}_{f_1 f_2^*}\left(\boldsymbol{r}_{1f},\boldsymbol{r}_{2f},t_f;\boldsymbol{r}_{1i},\boldsymbol{r}_{2i},t_i\right)$ of Equation (28) with the above polarization vector has the discrete form

$$
\begin{aligned}
& T^{\xi}_{f_1 f_2^*}\left(\boldsymbol{r}_{1f},\boldsymbol{r}_{2f},t_f;\boldsymbol{r}_{1i},\boldsymbol{r}_{2i},t_i\right) \\
& =\prod_{n=1}^{N}\left[\int_{-\infty}^{\infty}\mathrm{d}\boldsymbol{r}_{1n}\right]\prod_{n=1}^{N+1}\left[\int_{-\infty}^{\infty}\frac{\mathrm{d}\boldsymbol{p}_{1n}}{(2\pi)^3}\right]\prod_{n=1}^{N}\left[\int_{-\infty}^{\infty}\mathrm{d}\boldsymbol{r}_{2n}\right]\prod_{n=1}^{N+1}\left[\int_{-\infty}^{\infty}\frac{\mathrm{d}\boldsymbol{p}_{2n}}{(2\pi)^3}\right] \\
& \times f_1\left(\frac{1}{B\left(t_f-t_i\right)}\gamma^*-\sqrt{\frac{2\pi\omega}{V}}\varepsilon\sum_{n=1}^{N+1}\chi_n\widehat{\varepsilon}\cdot\left(\boldsymbol{r}_{1n}+\boldsymbol{r}_{2n}\right)\right) \\
& \times f_2^*\left(\frac{1}{B\left(t_f-t_i\right)}\beta-\sqrt{\frac{2\pi\omega}{V}}\varepsilon\sum_{n=1}^{N+1}\chi_n^*\widehat{\varepsilon}^*\cdot\left(\boldsymbol{r}_{1n}+\boldsymbol{r}_{2n}\right)\right) \\
& \times\exp\left\{i\sum_{n=1}^{N+1}\left[\boldsymbol{p}_{1n}\cdot\left(\boldsymbol{r}_{1n}-\boldsymbol{r}_{1n-1}\right)+\boldsymbol{p}_{2n}\cdot\left(\boldsymbol{r}_{2n}-\boldsymbol{r}_{2n-1}\right)-\varepsilon H_{He}\right.\right. \\
& +i\sqrt{\frac{2\pi\omega}{V}}\varepsilon\left[\beta\chi_n\widehat{\varepsilon}\cdot\left(\boldsymbol{r}_{1n}+\boldsymbol{r}_{2n}\right)+\gamma^*\chi_n^*\widehat{\varepsilon}^*\cdot\left(\boldsymbol{r}_{1n}+\boldsymbol{r}_{2n}\right)\right] \\
& \left.\left.+\frac{2\pi\omega}{V}\varepsilon v_n\left(\left|\widehat{\varepsilon}\cdot\boldsymbol{r}_{1n}\right|^2+\left|\widehat{\varepsilon}\cdot\boldsymbol{r}_{2n}\right|^2+\left(\widehat{\varepsilon}\cdot\boldsymbol{r}_{1n}\widehat{\varepsilon}^*\cdot\boldsymbol{r}_{2n}+c.c.\right)\right)\right]\right\}
\end{aligned}
\tag{33}
$$

All the functions with index n are evaluated at time $\tau_n=n\varepsilon+t_i$ where $\varepsilon=\dfrac{t_f-t_i}{N+1}$. χ_n and v_n are related to the functions defined in Equations (23), (27) as

$$\chi_n=\chi\left(\tau_n\right) \tag{34}$$

and

$$v_n=v\left(\tau_n\right) \tag{35}$$

Additionally, we notice that we have set $\boldsymbol{r}_0=\boldsymbol{r}_i$ and $\boldsymbol{r}_{N+1}=\boldsymbol{r}_f$.

Now, we insert delta functions in (33) to get

$$
\begin{aligned}
& T^{\xi}_{f_1 f_2^*}\left(\boldsymbol{r}_{1f},\boldsymbol{r}_{2f},t_f;\boldsymbol{r}_{1i},\boldsymbol{r}_{2i},t_i\right) \\
& =\prod_{n=1}^{N}\left[\int_{-\infty}^{\infty}\mathrm{d}\boldsymbol{r}_{1n}\right]\prod_{n=1}^{N+1}\left[\int_{-\infty}^{\infty}\frac{\mathrm{d}\boldsymbol{p}_{1n}}{(2\pi)^3}\right]\prod_{n=1}^{N}\left[\int_{-\infty}^{\infty}\mathrm{d}\boldsymbol{r}_{2n}\right]\prod_{n=1}^{N+1}\left[\int_{-\infty}^{\infty}\frac{\mathrm{d}\boldsymbol{p}_{2n}}{(2\pi)^3}\right]\prod_{n=1}^{N+1}\left[\int_{-\infty}^{\infty}\mathrm{d}^2w_{1n}\right] \\
& \times\prod_{n=1}^{N+1}\left[\delta^{(2)}\left(w_{1n}-\widehat{\varepsilon}\cdot\boldsymbol{r}_{1n}\right)\right]\prod_{n=1}^{N+1}\left[\int_{-\infty}^{\infty}\mathrm{d}^2w_{2n}\right]\prod_{n=1}^{N+1}\left[\delta^{(2)}\left(w_{2n}-\widehat{\varepsilon}\cdot\boldsymbol{r}_{2n}\right)\right] \\
& \times f_1\left(\frac{1}{B\left(t_f-t_i\right)}\gamma^*-\sqrt{\frac{2\pi\omega}{V}}\varepsilon\sum_{n=1}^{N+1}\chi_n\left(w_{1n}+w_{2n}\right)\right) \\
& \times f_2^*\left(\frac{1}{B\left(t_f-t_i\right)}\beta-\sqrt{\frac{2\pi\omega}{V}}\varepsilon\sum_{n=1}^{N+1}\chi_n^*\left(w_{1n}^*+w_{2n}^*\right)\right)
\end{aligned}
$$

$$\begin{aligned}&\times \exp\Bigg\{ i\sum_{n=1}^{N+1}\Big[\boldsymbol{p}_{1n}\cdot\left(\boldsymbol{r}_{1n}-\boldsymbol{r}_{1n-1}\right)+\boldsymbol{p}_{2n}\cdot\left(\boldsymbol{r}_{2n}-\boldsymbol{r}_{2n-1}\right)-\varepsilon H_{He}\\ &+i\sqrt{\frac{2\pi\omega}{V}}\varepsilon\left[\beta\chi_n\left(w_{1n}+w_{2n}\right)+\gamma^*\chi_n^*\left(w_{1n}^*+w_{2n}^*\right)\right]\\ &+\frac{2\pi\omega}{V}\varepsilon\nu_n\left(\left|w_{1n}\right|^2+\left|w_{2n}\right|^2+\left(w_{1n}w_{2n}^*+c.c.\right)\right)\Big]\Bigg\}\end{aligned} \tag{36}$$

We have defined $\delta^{(2)}(z)=\delta(z)\delta(z^*)$. Moreover $w_{jn}=w_{xjn}+iw_{yjn}$. Here and below $j=1,2$.

In Appendix A, we give the angular decomposition of the $\frac{1}{\left|\boldsymbol{r}_{1n}-\boldsymbol{r}_{2n}\right|}$ term appearing in the Helium Hamiltonian. In fact, there, we give the angular decomposition of the path integral of the 3D Helium atom. That approach is an alternative way to introduce the possible correlations in atoms or molecules compared, for instance, with the hyperspherical coordinates methods [13].

The delta functions in Equation (36) have the representation

$$\begin{aligned}&\delta^{(2)}\left(w_{jn}-\hat{\varepsilon}\cdot\boldsymbol{r}_{jn}\right)\\ &=\frac{1}{(2\pi)^2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\mathrm{d}^2\lambda_{jn}\exp\left[i\frac{1}{2}\left(\lambda_{jn}w_{jn}+\lambda_{jn}^*w_{jn}^*\right)-\frac{1}{2}\lambda_{jn}\hat{\varepsilon}\cdot\boldsymbol{r}_{jn}-\frac{1}{2}\lambda_{jn}^*\hat{\varepsilon}^*\cdot\boldsymbol{r}_{jn}\right]\\ &=\frac{1}{(2\pi)^2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\mathrm{d}^2\lambda_{jn}\exp\Big[i\lambda_{xjn}w_{xjn}-i\lambda_{yjn}w_{yjn}-i\lambda_{xjn}\cos\left(\frac{\xi}{2}\right)\hat{\varepsilon}_x\cdot\boldsymbol{r}_{jn}\\ &\quad\pm i\lambda_{yjn}\sin\left(\frac{\xi}{2}\right)\hat{\varepsilon}_y\cdot\boldsymbol{r}_{jn}\Big]\end{aligned} \tag{37}$$

We have set $\lambda_{jn}=\lambda_{xjn}+i\lambda_{yjn}$. Now, we perform the change of variables $\lambda_{xjn}\to\frac{\lambda_{xjn}}{\cos\left(\frac{\xi}{2}\right)}$, $\lambda_{yjn}\to\frac{\lambda_{yjn}}{\sin\left(\frac{\xi}{2}\right)}$, $w_{xjn}\to\cos\left(\frac{\xi}{2}\right)w_{xjn}$, $w_{yjn}\to\sin\left(\frac{\xi}{2}\right)w_{yjn}$. The factor due to the integration over λ_{jn} is canceled with the factor due to the integration on w_{jn}. Further, we expand angularly according to the identity

$$\mathrm{e}^{i\boldsymbol{\kappa}\cdot\boldsymbol{r}}=4\pi\sum_{l=0}^{\infty}\sum_{m=-l}^{l}i^l j_l\left(\left|\boldsymbol{\kappa}\right|r\right)Y_{lm}^*\left(\vartheta_\kappa,\varphi_\kappa\right)Y_{lm}\left(\vartheta,\varphi\right) \tag{38}$$

where j_l are spherical Bessel functions, and Y_{lm} are spherical harmonics. So, for right elliptic polarization, we get

$$\delta^{(2)}\left(w_{jn}-\hat{\varepsilon}\cdot\boldsymbol{r}_{jn}\right)=\sum_{l_{jn}=0}^{\infty}\Gamma_{l_{jn}}\left(w'_{jn},r_{jn},\vartheta_{jn},\varphi_{jn}\right) \tag{39}$$

where

$$\Gamma_{l_{jn}}\left(w'_{jn},r_{jn},\vartheta_{jn},\varphi_{jn}\right)=\sum_{m_{jn}=-l_{jn}}^{l_{jn}}g_{l_{jn}m_{jn}}\left(w'_{jn},r_{jn}\right)\sqrt{4\pi}Y_{l_{jn}m_{jn}}\left(\vartheta_{jn},\varphi_{jn}\right) \tag{40}$$

and

$$g_{l_{jn}m_{jn}}\left(w'_{jn},r_{jn}\right)=\left(-i\right)^{l_{jn}}\frac{O_{l_{jn}m_{jn}}}{\left(2\pi\right)^2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\mathrm{d}^2\lambda_{jn}\exp\left[i\lambda_{xjn}w'_{xjn}-i\lambda_{yjn}w'_{yjn}\right] \times j_{l_{jn}}\left(\left|\lambda_{jn}\right|r_{jn}\right)\exp\left(-im_{jn}\varphi_{\lambda jn}\right) \tag{41}$$

$$\begin{aligned}O_{l_{jn}m_{jn}}&=\sqrt{\left(2l_{jn}+1\right)\frac{\left(l_{jn}-m_{jn}\right)!}{\left(l_{jn}+m_{jn}\right)!}}P_{l_{jn}}^{m_{jn}}\left(0\right)\\&=\sqrt{\left(2l_{jn}+1\right)\frac{\left(l_{jn}-m_{jn}\right)!}{\left(l_{jn}+m_{jn}\right)!}}\frac{\sqrt{\pi}2^{m_{jn}}}{\Gamma\left(\frac{l_{jn}-m_{jn}}{2}+1\right)\Gamma\left(\frac{-l_{jn}-m_{jn}+1}{2}\right)}\end{aligned} \tag{42}$$

We notice that if $l_{jn}+m_{jn}$ is odd then $O_{l_{jn}m_{jn}}$ is zero. Moreover, $\left|\lambda_{jn}\right|$, $\varphi_{\lambda jn}$ are the polar coordinates of λ_{jn} on the x-y plane. We have set

$$w_{xjn}=w'_{xjn}\cos\left(\frac{\xi}{2}\right)=\left|w'_{jn}\right|\cos\left(\varphi_{w'jn}\right)\cos\left(\frac{\xi}{2}\right) \tag{43}$$

$$w_{yjn}=w'_{yjn}\sin\left(\frac{\xi}{2}\right)=\left|w'_{jn}\right|\sin\left(\varphi_{w'jn}\right)\sin\left(\frac{\xi}{2}\right) \tag{44}$$

and

$$w'_{jn}=w'_{xjn}+iw'_{yjn}=\left|w'_{jn}\right|\mathrm{e}^{i\varphi_{w'jn}} \tag{45}$$

On integrating over $\varphi_{\lambda jn}$ we get

$$\begin{aligned}&g_{l_{jn}m_{jn}}\left(w'_{jn},r_{jn}\right)\\&=\left(-i\right)^{l_{jn}}\frac{O_{l_{jn}m_{jn}}}{2\pi}\exp\left(im_{jn}\left(\varphi_{w'jn}+\frac{\pi}{2}\right)\right)\int_0^{\infty}\mathrm{d}\rho_{\lambda_{jn}}\rho_{\lambda_{jn}}j_{l_{jn}}\left(\rho_{\lambda_{jn}}r_{jn}\right)J_{m_{jn}}\left(\rho_{\lambda_{jn}}\left|w'_{jn}\right|\right)\end{aligned} \tag{46}$$

$\rho_{\lambda_{jn}}=\left|\lambda_{jn}\right|$ and $J_{m_{jn}}$ are Bessel functions. In Appendix C, we give results for the expression (46).

Finally, we replace the delta functions in Equation (36) with the above angularly decomposed expressions. As $N\to\infty$ and within the range from $n=0$ to N, we keep first-order angular terms. Only a finite number of terms have non-zero l, otherwise, the angular parts of non-zero order terms would contribute infinities. For a specific transition within the present system, let $l_{\#1n}$ and $l_{\#2n}$ be the leading l_1 and l_2, respectively, with non-zero contribution to the final result. Further, we let those factors correspond to the M_1 values $h_{11},h_{12},\ldots,h_{1M_1}$ of $1n$ and the M_2 values $h_{21},h_{22},\cdots,h_{2M_2}$ of $2n$. Moreover, we set $h_{10}=10$, $h_{20}=20$, and $h_{1M_1+1}=1N+1$, $h_{2M_2+1}=2N+1$.

Finally, the propagator has the expansion

$$\begin{aligned}&T_{f_1f_2^*}^{\xi}\left(\boldsymbol{r}_{1f},\boldsymbol{r}_{2f},t_f;\boldsymbol{r}_{1i},\boldsymbol{r}_{2i},t_i\right)=\frac{\left(4\pi\right)^2}{r_{1f}r_{1i}r_{2f}r_{2i}}\\&\times\sum_{l=0}^{\infty}\sum_{m=-l}^{l}\sum_{l_1=0}^{\infty}\sum_{m_1=-l_1}^{l_1}\sum_{q_{1i}=0}^{\infty}\sum_{p_{1i}=-q_{1i}}^{q_{1i}}\sum_{l_2=0}^{\infty}\sum_{m_2=-l_2}^{l_2}\sum_{q_{2i}=0}^{\infty}\sum_{p_{2i}=-q_{2i}}^{q_{2i}}K_{q_{1i}p_{1i}q_{2i}p_{2i}q_{1f}p_{1f}q_{2f}p_{2f}}^{\xi f_1f_2^*ll_1m_1l_2m_2}\left(r_{1f},r_{2f},t_f;r_{1i},r_{2i},t_i\right)\\&\times i^lY_{l_1m_1}\left(\vartheta_{1f},\varphi_{1f}\right)Y_{lm}\left(\vartheta_{1f},\varphi_{1f}\right)Y_{l_2m_2}\left(\vartheta_{2f},\varphi_{2f}\right)Y_{lm}^*\left(\vartheta_{2f},\varphi_{2f}\right)\\&\times Y_{q_{1f}p_{1f}}\left(\vartheta_{1f},\varphi_{1f}\right)Y_{q_{1i}p_{1i}}^*\left(\vartheta_{1i},\varphi_{1i}\right)Y_{q_{2f}p_{2f}}\left(\vartheta_{2f},\varphi_{2f}\right)Y_{q_{2i}p_{2i}}^*\left(\vartheta_{2i},\varphi_{2i}\right)\end{aligned} \tag{47}$$

On taking into account the transformations below Equation (37), $K^{\xi f_1 f_2^* l l_1 m_1 l_2 m_2}_{q_{1i} p_{1i} q_{2i} p_{2i} q_{1f} p_{1f} q_{2f} p_{2f}}\left(r_{1f}, r_{2f}, t_f; r_{1i}, r_{2i}, t_i\right)$ has the form

$$
\begin{aligned}
&K^{\xi f_1 f_2^* l l_1 m_1 l_2 m_2}_{q_{1i} p_{1i} q_{2i} p_{2i} q_{1f} p_{1f} q_{2f} p_{2f}}\left(r_{1f}, r_{2f}, t_f; r_{1i}, r_{2i}, t_i\right) \\
&= \prod_{j=1}^{2}\left[\int \prod_{\eta=1}^{M_j}\left[\mathrm{d}\Omega_{h_{j\eta}}\right]\right] \prod_{j=1}^{2}\left[Y_{q_{ji} p_{ji}}\left(\vartheta_{jh_{j1}}, \varphi_{jh_{j1}}\right)\right] \\
&\times \prod_{j=1}^{2}\left[\prod_{\eta=2}^{M_j+1}\left[\sum_{q_{jh_{j\eta}}=0}^{\infty} \sum_{p_{jh_{j\eta}}=-q_{jh_{j\eta}}}^{q_{jh_{j\eta}}} Y_{q_{jh_{j\eta}} p_{jh_{j\eta}}}\left(\vartheta_{jh_{j\eta}}, \varphi_{jh_{j\eta}}\right) Y^*_{q_{jh_{j\eta}} p_{jh_{j\eta}}}\left(\vartheta_{jh_{j\eta-1}}, \varphi_{jh_{j\eta-1}}\right)\right]\right] \\
&\times \prod_{n=1}^{N}\left[\int_0^{\infty} \mathrm{d}r_{1n}\right] \prod_{n=1}^{N+1}\left[\int_{-\infty}^{\infty} \frac{\mathrm{d}p_{1n}}{2\pi}\right] \prod_{n=1}^{N}\left[\int_0^{\infty} \mathrm{d}r_{2n}\right] \prod_{n=1}^{N+1}\left[\int_{-\infty}^{\infty} \frac{\mathrm{d}p_{2n}}{2\pi}\right] \prod_{n=1}^{N+1}\left[\int_{-\alpha_n}^{\alpha_n} \mathrm{d}u_n\right] \prod_{n=1}^{N+1}\left[\iint_{\left|w'_{1n}\right|<r_{1n}} \mathrm{d}^2 w'_{1n}\right] \\
&\times \prod_{n=1}^{N+1}\left[\iint_{\left|w'_{2n}\right|<r_{2n}} \mathrm{d}^2 w'_{2n}\right] \prod_{n=1}^{N}\left[f_0^{\alpha_n}\left(u_n\right)\right] f_l^{\alpha_{N+1}}\left(u_{N+1}\right) g_{l_{1N+1} m_{1N+1}}\left(w'_{1N+1}, r_{1N+1}\right) g_{l_{2N+1} m_{2N+1}}\left(w'_{2N+1}, r_{2N+1}\right) \\
&\times \prod_{n=1}^{N}\left[\Gamma_{l_{\#1n}}\left(w'_{1n}, r_{1n}, \vartheta_{1n}, \varphi_{1n}\right)\right] f_1\left(\frac{1}{B\left(t_f - t_i\right)}\gamma^* - \sqrt{\frac{2\pi\omega}{V}}\varepsilon \sum_{n=1}^{N+1} \chi_n\left(w_{1n} + w_{2n}\right)\right) \\
&\times \prod_{n=1}^{N}\left[\Gamma_{l_{\#2n}}\left(\left(w'_{2n}, r_{2n}, \vartheta_{2n}, \varphi_{2n}\right)\right)\right] f_2^*\left(\frac{1}{B\left(t_f - t_i\right)}\beta - \sqrt{\frac{2\pi\omega}{V}}\varepsilon \sum_{n=1}^{N+1} \chi_n^*\left(w_{1n}^* + w_{2n}^*\right)\right) \\
&\times \exp\left\{ i\sum_{n=1}^{N+1}\left[p_{1n}\left(r_{1n} - r_{1n-1}\right) + p_{2n}\left(r_{2n} - r_{2n-1}\right) - \varepsilon\left(H_{1n}^{q_1^*} + H_{2n}^{q_2^*} + \frac{1}{\sqrt{r_{1n}^2 + r_{2n}^2}} \frac{1}{\sqrt{1 - u_n}}\right)\right.\right. \\
&+ i\sqrt{\frac{2\pi\omega}{V}}\varepsilon\left[\beta\chi_n\left(w_{1n} + w_{2n}\right) + \gamma^* \chi_n^*\left(w_{1n}^* + w_{2n}^*\right)\right] \\
&\left.\left.+ \frac{2\pi\omega}{V}\varepsilon v_n\left(\left|w_{1n}\right|^2 + \left|w_{2n}\right|^2 + w_{1n} w_{2n}^* + w_{2n} w_{1n}^*\right)\right]\right\}
\end{aligned}
\tag{48}
$$

Ω is the solid angle and the f_0^{α}, f_l^{α} functions are given by Equations (A9-A11). In Equation (48), after the angular integrations, we drop the factors $Y_{q_{jh_{jM_j+1}} p_{jh_{jM_j+1}}}\left(\vartheta_{jh_{jM_j+1}}, \varphi_{jh_{jM_j+1}}\right)$ $j = 1,2$ that remain there. In fact, those are the final factors $Y_{q_{jf} p_{jf}}\left(\vartheta_{jf}, \varphi_{jf}\right)$ $j = 1,2$ and correspond to the indices $q_{1f} p_{1f} q_{2f} p_{2f}$ in Equations (47), (48).

The Hamiltonians

$$
H_{jn}^{q_j^*} = \frac{p_{jn}^2}{2} + \frac{q_j^*\left(q_j^* + 1\right)}{2r_{jn}^2} - \frac{Z}{r_{jn}} \quad j = 1,2 \tag{49}
$$

correspond to one-electron atoms ones. q_j^* may be n dependent. Due to the Coulomb degeneracy, they do not appear in Equation (48) after the solution of the sign problem. We notice that to evaluate the integrals in Equation (48), we have to take into account the expressions (43-45).

Further, we observe that

$$\begin{aligned}
&\lim_{N\to\infty}\prod_{n=1}^{N}\left[\int_{-\alpha_n}^{\alpha_n}\mathrm{d}u_n\right]\prod_{n=1}^{N}\left[\iint_{|w'_{1n}|<r_{1n}}\mathrm{d}^2w'_{1n}\right]\prod_{n=1}^{N}\left[\iint_{|w'_{2n}|<r_{2n}}\mathrm{d}^2w'_{2n}\right]\prod_{n=1}^{N}\left[f_0^{\alpha_n}\left(u_n\right)\right]\prod_{n=1}^{N}\left[g_{00}\left(w'_{1n},r_{1n}\right)\right]\\
&\times\prod_{n=1}^{N}\left[g_{00}\left(w'_{2n},r_{2n}\right)\right]\exp\left\{i\varepsilon\sum_{n=1}^{N}\left[i\sqrt{\frac{2\pi\omega}{V}}\left[\beta\chi_n\left(w_{1n}+w_{2n}\right)+\gamma^*\chi_n^*\left(w_{1n}^*+w_{2n}^*\right)\right]\right.\right.\\
&\left.\left.+\frac{2\pi\omega}{V}\nu_n\left[\left|w_{1n}\right|^2+\left|w_{2n}\right|^2+w_{1n}w_{2n}^*+w_{2n}w_{1n}^*\right]-\frac{1}{\sqrt{r_{1n}^2+r_{2n}^2}}\frac{1}{\sqrt{1-u_n}}\right]\right\}\\
&=\exp\left\{i\int_{t_i}^{t_f^-}\mathrm{d}\tau\left[\frac{2\pi\omega}{3V}\nu\left(\tau\right)\left(r_1^2\left(\tau\right)+r_2^2\left(\tau\right)\right)-\frac{1}{r_>\left(\tau\right)}\right]\right\}
\end{aligned} \tag{50}$$

In fact, we take as common factors from Equation (48) the integrals on the left-hand side of Equation (50) and let $N\to\infty$. In the remaining expression, the infinitesimal parameter ε is interpreted as a one form, and we integrate it on time.

So, for example, if $f_1 = f_2 = 1$ we obtain the expression

$$\begin{aligned}
&K^{\xi l l_1 m_1 l_2 m_2}_{q_1 p_1 q_2 p_2 q_1 p_1 q_2 p_2}\left(r_{1f},r_{2f},t_f;r_{1i},r_{2i},t_i\right)\\
&=\tilde{F}_{l_1m_1l_2m_2}\left(r_{1f},r_{2f}\right)I_l\left(\frac{t_f-t_i}{\sqrt{r_{1f}^2+r_{2f}^2}},\alpha_f\right)\iiiint Dr_1\left(\tau\right)\frac{Dp_1\left(\tau\right)}{2\pi}\\
&\times Dr_2\left(\tau\right)\frac{Dp_2\left(\tau\right)}{2\pi}\exp\left\{i\int_{t_i}^{t_f}\mathrm{d}\tau\left[p_1\dot{r}_1+p_2\dot{r}_2-H_1^{q_1}\left(\tau\right)-H_2^{q_2}\left(\tau\right)\right]\right.\\
&\left.+i\int_{t_i}^{t_f^-}\mathrm{d}\tau\left[\frac{2\pi\omega}{3V}\nu\left(\tau\right)\left(r_1^2\left(\tau\right)+r_2^2\left(\tau\right)\right)-\frac{1}{r_>\left(\tau\right)}\right]\right\}
\end{aligned} \tag{51}$$

where

$$\begin{aligned}
&\tilde{F}_{l_1m_1l_2m_2}\left(r_{1f},r_{2f}\right)\\
&=\iint_{|w'_{1f}|<r_{1f}}\mathrm{d}^2w'_{1f}\iint_{|w'_{2f}|<r_{2f}}\mathrm{d}^2w'_{2f}\,g_{l_1m_1}\left(w'_{1f},r_{1f}\right)g_{l_2m_2}\left(w'_{2f},r_{2f}\right)\\
&\times\exp\left\{-\sqrt{\frac{2\pi\omega}{V}}\left[\beta\tilde{\chi}\left(t_f\right)\left(w_{1f}+w_{2f}\right)+\gamma^*\tilde{\chi}^*\left(t_f\right)\left(w_{1f}^*+w_{2f}^*\right)\right]\right.\\
&\left.+i\frac{2\pi\omega}{V}\tilde{\nu}\left(t_f\right)\left[\left|w_{1f}\right|^2+\left|w_{2f}\right|^2+w_{1f}w_{2f}^*+w_{2f}w_{1f}^*\right]\right\}
\end{aligned} \tag{52}$$

The I_l functions in Equation (51) are given in Appendix B. For the evaluation of the $\tilde{F}_{l_1m_1l_2m_2}$ functions, we use the expressions in Appendix C. We have set

$$\tilde{\chi}\left(t\right)=\int_{t_i}^{t}\chi\left(\rho\right)\mathrm{d}\rho \tag{53}$$

$$\tilde{\nu}\left(t\right)=\int_{t_i}^{t}\nu\left(\rho\right)\mathrm{d}\rho \tag{54}$$

If $f_1\left(\alpha^*\right)=\frac{1}{\sqrt{1+\left|\beta\right|^2}}\alpha^*$, $f_2\left(\alpha^*\right)=1$, and $\beta=\gamma$ we get

$$
\begin{aligned}
&K^{\xi l l_1 m_1 l_2 m_2}_{q_{1i} p_{1i} q_{2i} p_{2i} q_{1f} p_{1f} q_{2f} p_{2f}}\left(r_{1f}, r_{2f}, t; r_{1i}, r_{2i}, 0\right)\\
&= \frac{1}{\sqrt{1+|\beta|^2}} \tilde{F}_{l_1 m_1 l_2 m_2}\left(r_{1f}, r_{2f}\right) I_l\left(\frac{t}{\sqrt{r_{1f}^2 + r_{2f}^2}}, \alpha_f\right) \iiiint Dr_1(\tau)\frac{Dp_1(\tau)}{2\pi} Dr_2(\tau)\frac{Dp_2(\tau)}{2\pi}\\
&\times \left\{\beta^* \frac{1}{B(t)} \delta_{q_{1f} q_{1i}} \delta_{q_{2f} q_{2i}} \delta_{p_{1f} p_{1i}} \delta_{p_{2f} p_{2i}} - \sqrt{\frac{2\pi\omega}{V}} \left\langle Y_{q_{1f} p_{1f}} \right| \left\langle Y_{q_{2f} p_{2f}} \right| \int_0^t \mathrm{d}\tau \frac{\chi(\tau)}{\tilde{F}_{0000}\left(r_1(\tau), r_2(\tau)\right)}\right.\\
&\left.\times 4\pi\left(\sum_{m_1} L^1_{l_{\#1} m_1 00}\left(r_1(\tau), r_2(\tau)\right) Y_{l_{\#1} m_1} Y_{00} + \sum_{m_2} L^2_{00 l_{\#2} m_2}\left(r_1(\tau), r_2(\tau)\right) Y_{00} Y_{l_{\#2} m_2}\right) \left|Y_{q_{1i} p_{1i}}\right\rangle \left|Y_{q_{2i} p_{2i}}\right\rangle\right\}\\
&\times \exp\left\{i\int_0^t \mathrm{d}\tau\left[p_1\dot{r}_1 + p_2\dot{r}_2 - H_1^{q_1^*}(\tau) - H_2^{q_2^*}(\tau)\right] + i\int_0^{t^-} \mathrm{d}\tau\left[\frac{2\pi\omega}{3V}\nu(\tau)\left(r_1^2(\tau) + r_2^2(\tau)\right) - \frac{1}{r_>(\tau)}\right]\right\}
\end{aligned}
\tag{55}
$$

where

$$
\begin{aligned}
&\tilde{F}_{0000}\left(r_1(\tau), r_2(\tau)\right)\\
&= \iint_{|w_1'|<r_1(\tau)} \mathrm{d}^2 w_1' \iint_{|w_2'|<r_2(\tau)} \mathrm{d}^2 w_2' g_{00}\left(w_1', r_1(\tau)\right) g_{00}\left(w_2', r_2(\tau)\right)\\
&\quad \times \exp\left\{-\sqrt{\frac{2\pi\omega}{V}}\left[\beta\tilde{\chi}(\tau)\left(w_1 + w_2\right) + \beta^*\tilde{\chi}^*(\tau)\left(w_1^* + w_2^*\right)\right]\right.\\
&\quad \left. + i\frac{2\pi\omega}{V}\tilde{\nu}(\tau)\left[|w_1|^2 + |w_2|^2 + w_1 w_2^* + w_2 w_1^*\right]\right\}
\end{aligned}
\tag{56}
$$

and

$$
\begin{aligned}
&L^j_{l_{\#1} m_1 l_{\#2} m_2}\left(r_1(\tau), r_2(\tau)\right)\\
&= \iint_{|w_1'|<r_1(\tau)} \mathrm{d}^2 w_1' \iint_{|w_2'|<r_2(\tau)} \mathrm{d}^2 w_2' g_{l_{\#1} m_1}\left(w_1', r_1(\tau)\right) g_{l_{\#2} m_2}\left(w_2', r_2(\tau)\right) w_j\\
&\quad \times \exp\left\{-\sqrt{\frac{2\pi\omega}{V}}\left[\beta\tilde{\chi}(\tau)\left(w_1 + w_2\right) + \beta^*\tilde{\chi}^*(\tau)\left(w_1^* + w_2^*\right)\right]\right.\\
&\quad \left. + i\frac{2\pi\omega}{V}\tilde{\nu}(\tau)\left[|w_1|^2 + |w_2|^2 + w_1 w_2^* + w_2 w_1^*\right]\right\}
\end{aligned}
\tag{57}
$$

with $j = 1, 2$.

We recall that if σ is the pulse duration then $\chi(\tau)$ has the form (cf. Equation (23))

$$
\chi(\tau) = \wp(\tau)\frac{\mathrm{e}^{-i\omega\tau}}{1 - \mathrm{e}^{-i\omega\sigma}}
\tag{58}
$$

We can expand the above expressions in powers of volume. We give such results in the next section.

4. Application and Results

As an application in the present paper, we study a Helium atom initially prepared in its singlet ground state. According to standard methods [14], it has the following multiconfigurational Hartree-Fock (MCHF) wavefunction

$$
\begin{aligned}
\psi_g\left(\boldsymbol{r}_1, \boldsymbol{r}_2\right) = {} & 0.995965\left(1s^2\right) - 0.06229\left(2s^2\right) - 0.007349\left(3s^2\right)\\
& + 0.010282\left(2p^2\right) + 0.062454\left(3p^2\right) - 0.012099\left(3d^2\right)
\end{aligned}
\tag{59}
$$

$(1s)$, $(2s)$, $(3s)$, $(2p)$, $(3p)$ and $(3d)$ are supposed to be appropriate orbitals with $Z=2$. We derive them variationally and insert them in the various configurations on which we expand to obtain the multiconfigurational wavefunction (59). The energy corresponding to the wavefunction (59) is $E_0=-2.901840$ a.u., while the accurate value of the energy of the state $He\,1s^2\ {}^1\mathrm{S}$ is −2.903724 a.u.

In general, there is a variety of methods and techniques to derive expressions similar to the present one and their corresponding energies. They include hyperspherical coordinates methods [13], variational Monte Carlo methods [15], and density functional theories [16].

The survival amplitude of the state $\psi_g(\boldsymbol{r}_1,\boldsymbol{r}_2)$ is

$$A(t)=\frac{1}{2}\iint\iint \mathrm{d}\boldsymbol{r}_{1f}\mathrm{d}\boldsymbol{r}_{2f}\mathrm{d}\boldsymbol{r}_{1i}\mathrm{d}\boldsymbol{r}_{2i}\left(\psi_g\left(\boldsymbol{r}_{1f},\boldsymbol{r}_{2f}\right)\right)^* T^{\xi}_{f_1f_2^*}\left(\boldsymbol{r}_{1f},\boldsymbol{r}_{2f},t;\boldsymbol{r}_{1i},\boldsymbol{r}_{2i},0\right)\psi_g\left(\boldsymbol{r}_{1i},\boldsymbol{r}_{2i}\right) \quad (60)$$

Here, we have taken into account Equation (16) and the conclusion below Equation (21).

For the photonic part we suppose that we measure a final coherent photonic state so that $|\Phi_2\rangle=|\beta\rangle$, and $f_2(\alpha^*)=1$, and that we prepare it in an excited coherent state of the form $\frac{1}{\sqrt{1+|\beta|^2}}a^+|\beta\rangle$. So $f_1(\alpha^*)=\frac{1}{\sqrt{1+|\beta|^2}}\alpha^*$.

We solve the sign problem and apply the sign solved propagator theorem. Therefore, we replace the Hamiltonians defined in Equation (49) with certain expectation values. Those expectation values do not depend on the q_1 and q_2 parameters due to the Coulomb degeneracy and so the whole phase $\mathrm{e}^{i\langle H_1+H_2\rangle t}$ is canceled in the survival probability $|A(t)|^2$. Therefore, we drop it and the survival amplitude takes the form

$$\begin{aligned}A(t)={}&8\pi^2\frac{1}{\sqrt{1+|\beta|^2}}\\&\times\sum_{l=0}^{\infty}\sum_{m=-l}^{l}\sum_{l_1=0}^{\infty}\sum_{m_1=-l_1}^{l_1}\sum_{q_{1i}=0}^{\infty}\sum_{p_{1i}=-q_{1i}}^{q_{1i}}\sum_{l_2=0}^{\infty}\sum_{m_2=-l_2}^{l_2}\sum_{q_{2i}=0}^{\infty}\sum_{p_{2i}=-q_{2i}}^{q_{2i}}\iint\int\int \mathrm{d}\boldsymbol{r}_{1f}\mathrm{d}\boldsymbol{r}_{2f}\mathrm{d}\boldsymbol{r}_{1i}\mathrm{d}\boldsymbol{r}_{2i}\frac{1}{r_{1f}r_{1i}r_{2f}r_{2i}}\\&\times\left(\psi_g\left(\boldsymbol{r}_{1f},\boldsymbol{r}_{2f}\right)\right)^* K^{\xi ll_1m_1l_2m_2}_{q_{1i}p_{1i}q_{2i}p_{2i}q_{1f}p_{1f}q_{2f}p_{2f}}\left(r_{1f},r_{2f},t;r_{1i},r_{2i},0\right)\\&\times i^lY_{l_1m_1}\left(\vartheta_{1f},\varphi_{1f}\right)Y_{lm}\left(\vartheta_{1f},\varphi_{1f}\right)Y_{l_2m_2}\left(\vartheta_{2f},\varphi_{2f}\right)Y^*_{lm}\left(\vartheta_{2f},\varphi_{2f}\right)\\&\times Y_{q_{1f}p_{1f}}\left(\vartheta_{1f},\varphi_{1f}\right)Y^*_{q_{1i}p_{1i}}\left(\vartheta_{1i},\varphi_{1i}\right)Y_{q_{2f}p_{2f}}\left(\vartheta_{2f},\varphi_{2f}\right)Y^*_{q_{2i}p_{2i}}\left(\vartheta_{2i},\varphi_{2i}\right)\psi_g\left(\boldsymbol{r}_{1i},\boldsymbol{r}_{2i}\right)\end{aligned} \quad (61)$$

$K^{\xi ll_1m_1l_2m_2}_{q_{1i}p_{1i}q_{2i}p_{2i}q_{1f}p_{1f}q_{2f}p_{2f}}\left(r_{1f},r_{2f},t;r_{1i},r_{2i},0\right)$ is given by Equation (55). In its sign solved propagator form [11], it becomes

$$\begin{aligned}&K^{\xi ll_1m_1l_2m_2}_{q_{1i}p_{1i}q_{2i}p_{2i}q_{1f}p_{1f}q_{2f}p_{2f}}\left(r_{1f},r_{2f},t;r_{1i},r_{2i},0\right)\\&=\delta\left(r_{1f}-r_{1i}\right)\delta\left(r_{2f}-r_{2i}\right)\tilde{F}_{l_1m_1l_2m_2}\left(r_{1f},r_{2f}\right)I_l\left(\frac{t}{\sqrt{r_{1f}^2+r_{2f}^2}},\alpha_f\right)\\&\quad\times\left(\beta^*\frac{1}{B(\sigma)}\delta_{q_{1f}q_{1i}}\delta_{q_{2f}q_{2i}}\delta_{p_{1f}p_{1i}}\delta_{p_{2f}p_{2i}}\right.\end{aligned}$$

$$\begin{aligned}&-\sqrt{\frac{2\pi\omega}{V}}\tilde{\chi}(t)\left\langle Y_{q_{1f}p_{1f}}\left|\left\langle Y_{q_{2f}p_{2f}}\left|\hat{\varepsilon}\cdot\left(\vec{r}_{1f}+\vec{r}_{2f}\right)\right|Y_{q_{1i}p_{1i}}\right\rangle\right|Y_{q_{2i}p_{2i}}\right\rangle\Bigg)\\&\times\exp\left\{i\frac{2\pi\omega}{3V}\tilde{\nu}(t)\left(r_{1f}^2+r_{2f}^2\right)-i\frac{t}{r_{>f}}\right\}\end{aligned}\tag{62}$$

We can extract the results

$$\tilde{F}_{0000}\left(r_{1f},r_{2f}\right)=1+\frac{2\pi\omega}{3V}\left(r_{1f}^2+r_{2f}^2\right)\left(i\tilde{\nu}(t)+\left|\beta\tilde{\chi}(t)\right|^2+\cos\xi\,\mathrm{Re}\left[\left(\beta\tilde{\chi}(t)\right)^2\right]\right)\tag{63}$$

$$\tilde{F}_{1100}\left(r_{1f},r_{2f}\right)=\sqrt{\frac{2\pi\omega}{3V}}r_{1f}\left[\cos\left(\frac{\xi}{2}+\frac{\pi}{4}\right)\beta\tilde{\chi}(t)+\sin\left(\frac{\xi}{2}+\frac{\pi}{4}\right)\beta^*\tilde{\chi}^*(t)\right]\tag{64}$$

$$\tilde{F}_{1-100}\left(r_{1f},r_{2f}\right)=-\sqrt{\frac{2\pi\omega}{3V}}r_{1f}\left[\sin\left(\frac{\xi}{2}+\frac{\pi}{4}\right)\beta\tilde{\chi}(t)+\cos\left(\frac{\xi}{2}+\frac{\pi}{4}\right)\beta^*\tilde{\chi}^*(t)\right]\tag{65}$$

$$\tilde{F}_{0011}\left(r_{1f},r_{2f}\right)=\sqrt{\frac{2\pi\omega}{3V}}r_{2f}\left[\cos\left(\frac{\xi}{2}+\frac{\pi}{4}\right)\beta\tilde{\chi}(t)+\sin\left(\frac{\xi}{2}+\frac{\pi}{4}\right)\beta^*\tilde{\chi}^*(t)\right]\tag{66}$$

$$\tilde{F}_{001-1}\left(r_{1f},r_{2f}\right)=-\sqrt{\frac{2\pi\omega}{3V}}r_{2f}\left[\sin\left(\frac{\xi}{2}+\frac{\pi}{4}\right)\beta\tilde{\chi}(t)+\cos\left(\frac{\xi}{2}+\frac{\pi}{4}\right)\beta^*\tilde{\chi}^*(t)\right]\tag{67}$$

$$\tilde{F}_{1111}\left(r_{1f},r_{2f}\right)=\frac{2\pi\omega}{3V}r_{1f}r_{2f}\left(\cos\left(\frac{\xi}{2}+\frac{\pi}{4}\right)\beta\tilde{\chi}(t)+\sin\left(\frac{\xi}{2}+\frac{\pi}{4}\right)\beta^*\tilde{\chi}^*(t)\right)^2\tag{68}$$

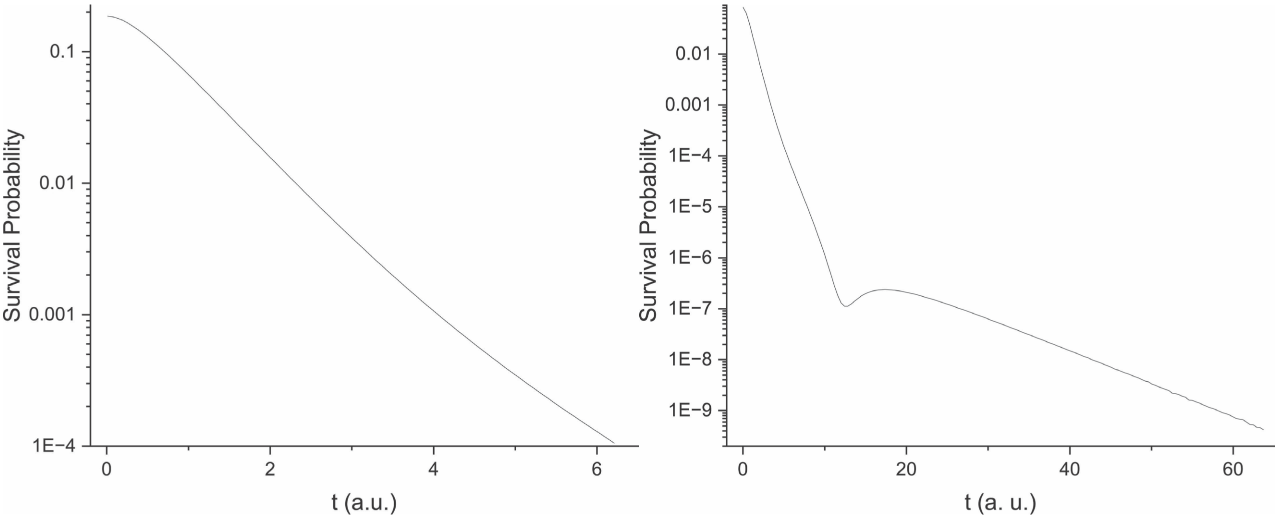
$$\tilde{F}_{1-11-1}\left(r_{1f},r_{2f}\right)=\frac{2\pi\omega}{3V}r_{1f}r_{2f}\left(\sin\left(\frac{\xi}{2}+\frac{\pi}{4}\right)\beta\tilde{\chi}(t)+\cos\left(\frac{\xi}{2}+\frac{\pi}{4}\right)\beta^*\tilde{\chi}^*(t)\right)^2\tag{69}$$

$$\begin{aligned}\tilde{F}_{111-1}\left(r_{1f},r_{2f}\right)&=\tilde{F}_{1-111}\left(r_{1f},r_{2f}\right)\\&=\frac{2\pi\omega}{3V}r_{1f}r_{2f}\left(\cos\left(\frac{\xi}{2}+\frac{\pi}{4}\right)\beta\tilde{\chi}(t)+\sin\left(\frac{\xi}{2}+\frac{\pi}{4}\right)\beta^*\tilde{\chi}^*(t)\right)\\&\times\left(\sin\left(\frac{\xi}{2}+\frac{\pi}{4}\right)\beta\tilde{\chi}(t)+\cos\left(\frac{\xi}{2}+\frac{\pi}{4}\right)\beta^*\tilde{\chi}^*(t)\right)\end{aligned}\tag{70}$$

Here we consider the case of a pulse of duration σ with envelop function of the form

$$\wp(\tau)=\begin{cases}\sin^2\left(\frac{\pi\tau}{\sigma}\right) & 0\le\tau\le\sigma\\ 0 & \text{otherwise}\end{cases}\tag{71}$$

In order to derive $A(t)$, firstly, we evaluate analytically the integrals (53) (54) using Equation (58) and Equations (24) and (27), respectively. Then, we compute the angular parts in Equation (61), taking into account the one-hand expression (59) and, on the other, using the values $l,l_1,l_2=0,1,2$ in the calculations. Finally, due to the delta functions in Equation (62), we obtain a double radial integral, which we evaluate numerically for each time value t. So eventually, we derive and give in **Figure 1** the plot of $\left|A(t)\right|^2$ as a function of t for various values of σ. We observe that the survival probability of the ground state of the atomic system as a function of time is smaller than one and decays. Moreover, we observe that the larger the interaction time before the measurement of the photonic



(a) σ = 150 as (b) σ = 2 fs

Figure 1. Survival probability of the ground state of Helium as a function of the interaction time. We give curves corresponding to pulse durations (a) $\sigma = 150$ as and(b) $\sigma = 2$ fs. We use $\omega = 0.855$ a.u., $\beta = 1.4$, $V = 10^7$ and $Z = 2$.

field state, the larger the probability of transfer of the atom to another state and the smaller the survival probability of the ground state. In fact, according to the results, survival probability decays in an exponential way, and in certain time intervals, we observe temporary trapping or possible change of channels, which cause the modification of the slope of the curve in Figure 1(b).

Further, as we can check from Equations (61)-(70), the zeroth order terms of the survival probability with respect to the volume are independent of the polarization parameter ξ. So, in Figure 2, the survival probability of the ground state of Helium at various times seems to be independent of ξ as, in fact, the perturbative parameter we use in the present approach is the inverse volume. For instance, this may not be the case in studies of possible transitions via scattering theories. We intend to study such points in subsequent papers.

5. Conclusions

In the present paper, we develop path integral methods in the study of the interaction of exited coherent states with two-electron atoms. We integrate over the photonic field and angularly decomposed both the interacting part of the electrons with the field and the propagator of the two-electron atom. We use them in their sign solved propagator representation. Via that approach, we circumvent the introduction and, therefore, the summation over the intermediate atomic eigenstates and eigenenergies appearing in the spectral representation of the Helium propagator, and therefore, we bypass numerical problems relevant to that summation.

We apply the whole method in the evaluation of the survival probability of the ground state of the Helium for a certain photonic transition. In fact, we suppose that we prepare the photonic system in an excited coherent state and measure a final coherent one. Then at the time of the final measurement the atomic system

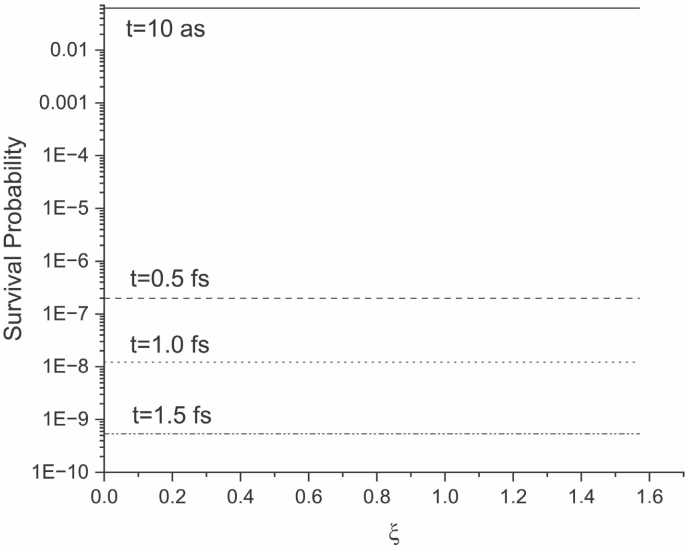


Figure 2. Survival probability of the ground state of Helium as a function of the polarization parameter ξ at several times. We consider the case of pulse duration $\sigma = 2\text{ fs}$. We use $\omega = 0.855\text{ a.u.}$, $\beta = 1.4$, $V = 10^7$ and $Z = 2$.

is expected to be in a range of final states. So, as we should expect, the probability that the atom remains in its initial ground state is smaller than one, and it decays in an exponential way.

To conclude, the present method is a combination of three techniques. The coherent state path integration of photonic systems, the angular decomposition of the path integrals of multidimensional systems, the solution of the sign problem, and the extraction of the relevant sign solved propagator. The whole approach is tractable and can be used in many problems involving the quantum mechanics of two-electron atoms interacting with radiation.

Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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Appendix A: Angular Decomposition of the Helium Path Integral

The Hamiltonian of the 3D Helium atom has the form

$$H_{He}=\frac{\boldsymbol{p}_1^2}{2}+\frac{\boldsymbol{p}_2^2}{2}-\frac{Z}{|\boldsymbol{r}_1|}-\frac{Z}{|\boldsymbol{r}_2|}+\frac{1}{|\boldsymbol{r}_1-\boldsymbol{r}_2|} \tag{A1}$$

where Z is the atomic number. $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ are the position vectors of the two electrons with respect to the nucleus.

The path integral of a Helium atom is given as

$$\begin{aligned}&K_1\left(\boldsymbol{r}_{1f},\boldsymbol{r}_{2f},t_f;\boldsymbol{r}_{1i},\boldsymbol{r}_{2i},t_i\right)\\&=\lim_{N\to\infty}\prod_{n=1}^{N}\int_{-\infty}^{\infty}\mathrm{d}\boldsymbol{r}_{1n}\prod_{n=1}^{N+1}\left[\int_{-\infty}^{\infty}\frac{\mathrm{d}\boldsymbol{p}_{1n}}{(2\pi)^3}\right]\prod_{n=1}^{N}\int_{-\infty}^{\infty}\mathrm{d}\boldsymbol{r}_{2n}\prod_{n=1}^{N+1}\left[\int_{-\infty}^{\infty}\frac{\mathrm{d}\boldsymbol{p}_{2n}}{(2\pi)^3}\right]\\&\times\exp\left\{i\sum_{n=1}^{N+1}\left[\boldsymbol{p}_{1n}\cdot\left(\boldsymbol{r}_{1n}-\boldsymbol{r}_{1n-1}\right)+\boldsymbol{p}_{2n}\cdot\left(\boldsymbol{r}_{2n}-\boldsymbol{r}_{2n-1}\right)\right.\right.\\&\left.\left.-\varepsilon\left(\frac{\boldsymbol{p}_{1n}^2}{2}+\frac{\boldsymbol{p}_{2n}^2}{2}-\frac{Z}{|\boldsymbol{r}_{1n}|}-\frac{Z}{|\boldsymbol{r}_{2n}|}+\frac{1}{|\boldsymbol{r}_{1n}-\boldsymbol{r}_{2n}|}\right)\right]\right\}\end{aligned} \tag{A2}$$

where $\varepsilon=\frac{t_f-t_i}{N+1}$. We have set $\boldsymbol{r}_{10}=\boldsymbol{r}_{1i}$, $\boldsymbol{r}_{20}=\boldsymbol{r}_{2i}$, $\boldsymbol{r}_{1N+1}=\boldsymbol{r}_{1f}$ and $\boldsymbol{r}_{2N+1}=\boldsymbol{r}_{2f}$. Now we observe that we can write

$$\begin{aligned}\frac{1}{|\boldsymbol{r}_{1n}-\boldsymbol{r}_{2n}|}&=\frac{1}{\sqrt{r_{1n}^2+r_{2n}^2-2\boldsymbol{r}_{1n}\cdot\boldsymbol{r}_{2n}}}=\frac{1}{\sqrt{r_{1n}^2+r_{2n}^2-2r_{1n}r_{2n}\cos\vartheta_{12n}}}\\&=\frac{1}{\sqrt{r_{1n}^2+r_{2n}^2}}\frac{1}{\sqrt{1-\frac{2r_{1n}r_{2n}}{r_{1n}^2+r_{2n}^2}\cos\vartheta_{12n}}}\\&=\frac{1}{\sqrt{r_{1n}^2+r_{2n}^2}}\frac{1}{\sqrt{1-\frac{2}{\frac{r_{1n}}{r_{2n}}+\frac{r_{2n}}{r_{1n}}}\cos\vartheta_{12n}}}\\&=\frac{1}{\sqrt{r_{1n}^2+r_{2n}^2}}\frac{1}{\sqrt{1-\alpha\left(r_{1n},r_{2n}\right)\cos\vartheta_{12n}}}\end{aligned} \tag{A3}$$

where

$$\alpha\left(r_{1n},r_{2n}\right)=\frac{2}{\frac{r_{1n}}{r_{2n}}+\frac{r_{2n}}{r_{1n}}}\le 1 \tag{A4}$$

and $r_{1n}=|\boldsymbol{r}_{1n}|$, $r_{2n}=|\boldsymbol{r}_{2n}|$. Therefore, the path integral expression (A2) becomes

$$\begin{aligned}&K_1\left(\boldsymbol{r}_{1f},\boldsymbol{r}_{2f},t_f;\boldsymbol{r}_{1i},\boldsymbol{r}_{2i},t_i\right)\\&=\lim_{N\to\infty}\prod_{n=1}^{N}\int_{-\infty}^{\infty}\mathrm{d}\boldsymbol{r}_{1n}\prod_{n=1}^{N+1}\left[\int_{-\infty}^{\infty}\frac{\mathrm{d}\boldsymbol{p}_{1n}}{(2\pi)^3}\right]\prod_{n=1}^{N}\int_{-\infty}^{\infty}\mathrm{d}\boldsymbol{r}_{2n}\prod_{n=1}^{N+1}\left[\int_{-\infty}^{\infty}\frac{\mathrm{d}\boldsymbol{p}_{2n}}{(2\pi)^3}\right]\end{aligned}$$

$$\times \exp\left\{ i\sum_{n=1}^{N+1}\left[\boldsymbol{p}_{1n}\cdot\left(\boldsymbol{r}_{1n}-\boldsymbol{r}_{1n-1}\right)+\boldsymbol{p}_{2n}\cdot\left(\boldsymbol{r}_{2n}-\boldsymbol{r}_{2n-1}\right) -\varepsilon\left(\frac{\boldsymbol{p}_{1n}^2}{2}+\frac{\boldsymbol{p}_{2n}^2}{2}-\frac{Z}{r_{1n}}-\frac{Z}{r_{2n}}+\frac{1}{\sqrt{r_{1n}^2+r_{2n}^2}}\frac{1}{\sqrt{1-\alpha\left(r_{1n},r_{2n}\right)\cos\vartheta_{12n}}}\right)\right]\right\} \tag{A5}$$

At this point, we insert in Equation (A5) delta functions to get the form

$$\begin{aligned} &K_1\left(\boldsymbol{r}_{1f},\boldsymbol{r}_{2f},t_f;\boldsymbol{r}_{1i},\boldsymbol{r}_{2i},t_i\right) \\ &=\lim_{N\to\infty}\prod_{n=1}^{N}\int_{-\infty}^{\infty}\mathrm{d}\boldsymbol{r}_{1n}\prod_{n=1}^{N+1}\left[\int_{-\infty}^{\infty}\frac{\mathrm{d}\boldsymbol{p}_{1n}}{(2\pi)^3}\right]\prod_{n=1}^{N}\int_{-\infty}^{\infty}\mathrm{d}\boldsymbol{r}_{2n}\prod_{n=1}^{N+1}\left[\int_{-\infty}^{\infty}\frac{\mathrm{d}\boldsymbol{p}_{2n}}{(2\pi)^3}\right] \\ &\times\prod_{n=1}^{N+1}\left[\int_{-\infty}^{\infty}\mathrm{d}u_n\right]\prod_{n=1}^{N+1}\left[\delta\left(u_n-\alpha\left(r_{1n},r_{2n}\right)\cos\vartheta_{12n}\right)\right] \\ &\times\exp\left\{ i\sum_{n=1}^{N+1}\left[\boldsymbol{p}_{1n}\cdot\left(\boldsymbol{r}_{1n}-\boldsymbol{r}_{1n-1}\right)+\boldsymbol{p}_{2n}\cdot\left(\boldsymbol{r}_{2n}-\boldsymbol{r}_{2n-1}\right)\right.\right. \\ &\left.\left.-\varepsilon\left(\frac{\boldsymbol{p}_{1n}^2}{2}+\frac{\boldsymbol{p}_{2n}^2}{2}-\frac{Z}{r_{1n}}-\frac{Z}{r_{2n}}+\frac{1}{\sqrt{r_{1n}^2+r_{2n}^2}}\frac{1}{\sqrt{1-u_n}}\right)\right]\right\} \end{aligned} \tag{A6}$$

Further, the delta functions in Equation (A6) have the representation

$$\begin{aligned} \delta\left(u_n-\alpha_n\cos\vartheta_{12n}\right)&=\frac{1}{2\pi}\int_{-\infty}^{\infty}\mathrm{d}\lambda_n \mathrm{e}^{-i\lambda_n u_n}\mathrm{e}^{i\lambda_n\alpha_n\cos\vartheta_{12n}} \\ &=\frac{1}{2\pi}\sum_{l_n=0}^{\infty}\left(2l_n+1\right)i^{l_n}P_{l_n}\left(\cos\vartheta_{12n}\right)\int_{-\infty}^{\infty}\mathrm{d}\lambda_n\mathrm{e}^{-i\lambda_n u_n}j_{l_n}\left(\alpha_n\lambda_n\right) \end{aligned} \tag{A7}$$

where $\alpha_n=\alpha\left(r_{1n},r_{2n}\right)$. We set the integrals appearing in Equation (A7) as

$$\frac{1}{2\pi}\int_{-\infty}^{\infty}\mathrm{d}\lambda \mathrm{e}^{-i\lambda u}j_l\left(\alpha\lambda\right)=f_l^{\alpha}\left(u\right) \tag{A8}$$

Then, after standard calculations, we obtain the results

$$f_0^{\alpha}\left(u\right)=\begin{cases}\dfrac{1}{2\alpha} & \text{if } |u|<\alpha \\ 0 & \text{otherwise}\end{cases} \tag{A9}$$

and

$$f_1^{\alpha}\left(u\right)=\begin{cases}-\dfrac{iu}{2\alpha^2} & \text{if } |u|<\alpha \\ 0 & \text{otherwise}\end{cases} \tag{A10}$$

Moreover, the following recurrence relation is valid

$$f_{l+1}^{\alpha}\left(u\right)=\frac{l}{l+1}f_{l-1}^{\alpha}\left(u\right)-i\frac{2l+1}{l+1}\frac{u}{\alpha}f_l^{\alpha}\left(u\right) \tag{A11}$$

Therefore, we can perform the integrations in Equation (A7) according to the expressions (A8-A11) and place the results in Equation (A6). Within the range $n=1$ to N, we keep leading terms with respect the l_n as the angular parts of higher order terms contribute infinities as $N\to\infty$. Now expression (A6) becomes

$$
\begin{aligned}
&K_1\left(\boldsymbol{r}_{1f},\boldsymbol{r}_{2f},t_f;\boldsymbol{r}_{1i},\boldsymbol{r}_{2i},t_i\right)\\
&=\lim_{N\to\infty}\prod_{n=1}^{N}\int_{-\infty}^{\infty}\mathrm{d}\boldsymbol{r}_{1n}\prod_{n=1}^{N+1}\left[\int_{-\infty}^{\infty}\frac{\mathrm{d}\boldsymbol{p}_{1n}}{(2\pi)^3}\right]\prod_{n=1}^{N}\int_{-\infty}^{\infty}\mathrm{d}\boldsymbol{r}_{2n}\prod_{n=1}^{N+1}\left[\int_{-\infty}^{\infty}\frac{\mathrm{d}\boldsymbol{p}_{2n}}{(2\pi)^3}\right]\\
&\times\prod_{n=1}^{N+1}\left[\int_{-\alpha_n}^{\alpha_n}\mathrm{d}u_n\right]\prod_{n=1}^{N}\left[f_0^{\alpha}\left(u_n\right)\right]\left(\sum_{l_{N+1}=0}^{\infty}\left(2l_{N+1}+1\right)i^{l_{N+1}}P_{l_{N+1}}\left(\cos\vartheta_{12N+1}\right)f_{l_{N+1}}^{\alpha}\left(u_{N+1}\right)\right)\\
&\times\exp\left\{i\sum_{n=1}^{N+1}\left[\boldsymbol{p}_{1n}\cdot\left(\boldsymbol{r}_{1n}-\boldsymbol{r}_{1n-1}\right)+\boldsymbol{p}_{2n}\cdot\left(\boldsymbol{r}_{2n}-\boldsymbol{r}_{2n-1}\right)\right.\right.\\
&\left.\left.-\varepsilon\left(\frac{\boldsymbol{p}_{1n}^2}{2}+\frac{\boldsymbol{p}_{2n}^2}{2}-\frac{Z}{r_{1n}}-\frac{Z}{r_{2n}}+\frac{1}{\sqrt{r_{1n}^2+r_{2n}^2}}\frac{1}{\sqrt{1-u_n}}\right)\right]\right\}
\end{aligned}
\tag{A12}
$$

We have set the range of integration over u_n in the interval from $-\alpha_n$ to α_n, otherwise, the functions $f_l^{\alpha}(u)$ are zero (see Equations (A8-A11)). Moreover, in Equation (A12), we have kept the full series appearing in Equation (A7) in the case of the $N+1$ factor as it involves the final coordinates.

Now, in Equation (A12), we perform certain standard manipulations [17], including angular decomposition of the path integral and the use of the addition theorem of spherical harmonics for the Legendre polynomial $P_{l_{N+1}}\left(\cos\vartheta_{12N+1}\right)$ to obtain the result

$$
\begin{aligned}
&K_1\left(\boldsymbol{r}_{1f},\boldsymbol{r}_{2f},t_f;\boldsymbol{r}_{1i},\boldsymbol{r}_{2i},t_i\right)\\
&=\frac{4\pi}{r_{1f}r_{1i}r_{2f}r_{2i}}\sum_{l=0}^{\infty}\sum_{m=-l}^{l}\sum_{q_1=0}^{\infty}\sum_{p_1=-q_1}^{q_1}\sum_{q_2=0}^{\infty}\sum_{p_2=-q_2}^{q_2}K_{lq_1q_2}\left(r_{1f},r_{2f},t_f;r_{1i},r_{2i},t_i\right)\\
&\times i^{l}Y_{q_1p_1}\left(\vartheta_{1f},\varphi_{1f}\right)Y_{lm}\left(\vartheta_{1f},\varphi_{1f}\right)Y_{q_2p_2}\left(\vartheta_{2f},\varphi_{2f}\right)Y_{lm}^{*}\left(\vartheta_{2f},\varphi_{2f}\right)\\
&\times Y_{q_1p_1}^{*}\left(\vartheta_{1i},\varphi_{1i}\right)Y_{q_2p_2}^{*}\left(\vartheta_{2i},\varphi_{2i}\right)
\end{aligned}
\tag{A13}
$$

The term $K_{lq_1q_2}\left(r_{1f},r_{2f},t_f;r_{1i},r_{2i},t_i\right)$ corresponds to the path integral

$$
\begin{aligned}
&K_{lq_1q_2}\left(r_{1f},r_{2f},t_f;r_{1i},r_{2i},t_i\right)\\
&=\lim_{N\to\infty}\prod_{n=1}^{N}\int_{0}^{\infty}\mathrm{d}r_{1n}\prod_{n=1}^{N+1}\left[\int_{-\infty}^{\infty}\frac{\mathrm{d}p_{1n}}{2\pi}\right]\prod_{n=1}^{N}\int_{0}^{\infty}\mathrm{d}r_{2n}\prod_{n=1}^{N+1}\left[\int_{-\infty}^{\infty}\frac{\mathrm{d}p_{2n}}{2\pi}\right]\\
&\times\exp\left\{i\sum_{n=1}^{N+1}\left[p_{1n}\left(r_{1n}-r_{1n-1}\right)+p_{2n}\left(r_{2n}-r_{2n-1}\right)-\varepsilon\left(\frac{p_{1n}^2}{2}+\frac{q_1\left(q_1+1\right)}{2r_{1n}^2}\right.\right.\right.\\
&\left.\left.\left.-\frac{Z}{r_{1n}}+\frac{p_{2n}^2}{2}+\frac{q_2\left(q_2+1\right)}{2r_{2n}^2}-\frac{Z}{r_{2n}}\right)\right]\right\}F_l\left(r_{11},r_{12},\cdots,r_{1N+1},r_{21},r_{22},\cdots,r_{2N+1}\right)
\end{aligned}
\tag{A14}
$$

We have set $r_{10}=r_{1i}$, $r_{20}=r_{2i}$, $r_{1N+1}=r_{1f}$ and $r_{2N+1}=r_{2f}$ while the factor $F_l\left(r_{11},r_{12},\cdots,r_{1N+1},r_{21},r_{22},\cdots,r_{2N+1}\right)$ appearing above has the form

$$
\begin{aligned}
&F_l\left(r_{11},r_{12},\cdots,r_{1N+1},r_{21},r_{22},\cdots,r_{2N+1}\right)\\
&=\prod_{n=1}^{N+1}\left[\int_{-\alpha_n}^{\alpha_n}\mathrm{d}u_n\right]\prod_{n=1}^{N}\left[f_0^{\alpha}\left(u_n\right)\right]f_l^{\alpha}\left(u_{N+1}\right)\exp\left\{-i\varepsilon\sum_{n=1}^{N+1}\left[\frac{1}{\sqrt{r_{1n}^2+r_{2n}^2}}\frac{1}{\sqrt{1-u_n}}\right]\right\}
\end{aligned}
\tag{A15}
$$

Some of the integrals in Equation (A15) are given in Appendix B.

So, as $N \to \infty$ the product becomes

$$\lim_{N\to\infty}\prod_{n=1}^{N}\left[\int_{-\alpha_n}^{\alpha_n}\frac{\mathrm{d}u_n}{2\alpha_n}\right]\exp\left\{-i\varepsilon\sum_{n=1}^{N+1}\left[\frac{1}{\sqrt{r_{1n}^2+r_{2n}^2}}\frac{1}{\sqrt{1-u_n}}\right]\right\}=\exp\left[-i\int_{t_i}^{t_f^-}\mathrm{d}\tau\frac{1}{r_>(\tau)}\right] \quad \text{(A16)}$$

where $r_> = \max(r_1, r_2)$ and $r_< = \min(r_1, r_2)$.

Now we combine Equations (A14-A16) to get (see Equation (B5) in Appendix B as well)

$$\begin{aligned}&K_{lq_1q_2}\left(r_{1f},r_{2f},t_f;r_{1i},r_{2i},t_i\right)\\&=I_l\left(\frac{t_f-t_i}{\sqrt{r_{1f}^2+r_{2f}^2}},\alpha_f\right)\int_0^\infty Dr_1\int_{-\infty}^{\infty}\frac{Dp_1}{2\pi}\int_0^\infty Dr_2\int_{-\infty}^{\infty}\frac{Dp_2}{2\pi}\\&\times\exp\left\{i\int_{t_i}^{t_f}\mathrm{d}\tau\left[p_1\dot{r}_1+p_2\dot{r}_2-H_1-H_2\right]-i\int_{t_i}^{t_f^-}\mathrm{d}\tau\frac{1}{r_>}\right\}\end{aligned} \quad \text{(A17)}$$

We have set

$$H_j=\frac{p_j^2}{2}+\frac{q_j\left(q_j+1\right)}{2r_j^2}-\frac{Z}{r_j}\qquad j=1,2 \quad \text{(A18)}$$

The combination of Equations (A13, A17) gives the angular decomposition of the path integral of the 3D Helium atom. Further, the sign solved propagator of expression (A17) has the form

$$\begin{aligned}&K_{lq_1q_2}\left(r_{1f},r_{2f},t_f;r_{1i},r_{2i},t_i\right)\\&=\delta\left(r_{1f}-r_{1i}\right)\delta\left(r_{2f}-r_{2i}\right)\exp\left[-i\left\langle H_1+H_2\right\rangle\left(t_f-t_i\right)\right]\\&\times I_l\left(\frac{t_f-t_i}{\sqrt{r_{1f}^2+r_{2f}^2}},\alpha_f\right)\exp\left(-i\frac{1}{r_{>f}}\left(t_f-t_i\right)\right)\end{aligned} \quad \text{(A19)}$$

The phase in Equation (A19) is calculated with respect to an appropriate sampling function. Then, due to the Coulomb degeneracy of the energy of hydrogen-like atoms, we can conclude that the phase in (A19) is independent of the numbers q_1 and q_2, and the expectation value is constant. So, we can ignore it. Therefore, we obtain the following expression for the SSP of the Helium atom

$$\begin{aligned}&K_1\left(\boldsymbol{r}_{1f},\boldsymbol{r}_{2f},t_f;\boldsymbol{r}_{1i},\boldsymbol{r}_{2i},t_i\right)\\&=\frac{4\pi}{r_{1f}r_{1i}r_{2f}r_{2i}}\delta\left(r_{1f}-r_{1i}\right)\delta\left(r_{2f}-r_{2i}\right)\exp\left(-i\frac{1}{r_{>f}}\left(t_f-t_i\right)\right)\\&\times\sum_{l=0}^{\infty}\sum_{m=-l}^{l}\sum_{q_1=0}^{\infty}\sum_{p_1=-q_1}^{q_1}\sum_{q_2=0}^{\infty}\sum_{p_2=-q_2}^{q_2}I_l\left(\frac{t_f-t_i}{\sqrt{r_{1f}^2+r_{2f}^2}},\alpha_f\right)i^lY_{q_1p_1}\left(\vartheta_{1f},\varphi_{1f}\right)Y_{lm}\left(\vartheta_{1f},\varphi_{1f}\right)\\&\times Y_{q_2p_2}\left(\vartheta_{2f},\varphi_{2f}\right)Y_{lm}^*\left(\vartheta_{2f},\varphi_{2f}\right)Y_{q_1p_1}^*\left(\vartheta_{1i},\varphi_{1i}\right)Y_{q_2p_2}^*\left(\vartheta_{2i},\varphi_{2i}\right)\end{aligned} \quad \text{(A20).}$$

Appendix B: Integrals for the Helium Path Integral

In the equations of Appendix A, there appear integrals of the following form (see

Equations (A8 to A11) for a definition of the $f_l^{\alpha}(u)$)

$$I_l^0(b,u)=\int \mathrm{d}u f_l^{\alpha}(u)\exp\left[-i\frac{b}{\sqrt{1-u}}\right] \tag{B1}$$

After standard calculations, we obtain

$$I_0^0(b,u)=\frac{1}{2\alpha}\left(u-1+ib\sqrt{1-u}\right)\exp\left[-i\frac{b}{\sqrt{1-u}}\right]-\frac{b^2}{2\alpha}Ei\left[-i\frac{b}{\sqrt{1-u}}\right] \tag{B2}$$

$$\begin{aligned} I_1^0(b,u)=&-\frac{1}{24\alpha^2}i\Big(ib^3\sqrt{1-u}+b^2(u-1)+2ib\sqrt{1-u}(u+5)\\ &+6\left(u^2-1\right)\Big)\exp\left[-i\frac{b}{\sqrt{1-u}}\right]+\frac{1}{24\alpha^2}ib^2\left(12+b^2\right)Ei\left[-i\frac{b}{\sqrt{1-u}}\right] \end{aligned} \tag{B3}$$

$$\begin{aligned} I_2^0(b,u)=&\frac{1}{480\alpha^3}\Big(-ib^5\sqrt{1-u}-b^4(u-1)-6b^2(u-1)(u+9)\\ &-2ib^3\sqrt{1-u}(u+29)+120\alpha^2\left(u-1+ib\sqrt{1-u}\right)\\ &-120\left(u^3-1\right)-24ib\sqrt{1-u}\left(u^2+3u+11\right)\Big)\exp\left[-i\frac{b}{\sqrt{1-u}}\right]\\ &+\frac{1}{480\alpha^3}b^2\left(360-120\alpha^2+60b^2+b^4\right)Ei\left[-i\frac{b}{\sqrt{1-u}}\right] \end{aligned} \tag{B4}$$

The functions I_l in Equations (A17, A19, A20) have the form

$$I_l(b,\alpha)=I_l^0(b,\alpha)-I_l^0(b,-\alpha) \tag{B5}$$

Further $\sqrt{1-\alpha}=\frac{|r_1-r_2|}{\sqrt{r_1^2+r_2^2}}$ and $\sqrt{1+\alpha}=\frac{r_1+r_2}{\sqrt{r_1^2+r_2^2}}$.

Appendix C: Integrals

In Equation (46), we have set (here we drop the jn indices)

$$\begin{aligned} g_{lm}(w',r)&=(-i)^l\frac{O_{lm}}{2\pi}\exp\left(im\left(\varphi_{w'}+\frac{\pi}{2}\right)\right)\int_0^{\infty}\mathrm{d}\rho_\lambda\rho_\lambda j_l(\rho_\lambda r)J_m(\rho_\lambda|w'|)\\ &=(-i)^l i^m\frac{O_{lm}}{2\pi}\mathrm{e}^{im\varphi_{w'}}\sqrt{\frac{\pi}{2r}}\int_0^{\infty}\mathrm{d}\rho_\lambda\sqrt{\rho_\lambda}J_{l+\frac{1}{2}}(\rho_\lambda r)J_m(\rho_\lambda|w'|)\\ &=\begin{cases}(-i)^l i^m\frac{O_{lm}}{2\pi}\mathrm{e}^{im\varphi_{w'}}\dfrac{\sqrt{\pi}|w'|^m\Gamma\left(\frac{l+m}{2}+1\right)}{r^{m+2}\Gamma\left(\frac{l-m+1}{2}\right)\Gamma(m+1)}F\left(\frac{l+m}{2}+1,\frac{m-l+1}{2};m+1;\frac{|w'|^2}{r^2}\right), & |w'|<r\\ 0, \ |w'|>r\end{cases}\\ &=\begin{cases}(-i)^l i^m\frac{O_{lm}}{2\pi}\mathrm{e}^{im\varphi_{w'}}\dfrac{2^m\sqrt{\pi}\Gamma\left(\frac{l+m}{2}+1\right)}{r\Gamma\left(\frac{l-m+1}{2}\right)}\dfrac{1}{\sqrt{r^2-|w'|^2}}P_l^{-m}\left(\frac{\sqrt{r^2-|w'|^2}}{r}\right), & |w'|<r\\ 0, \ |w'|>r\end{cases} \end{aligned} \tag{C1}$$

We remind that

$$O_{lm}=\sqrt{(2l+1)\frac{(l-m)!}{(l+m)!}}P_l^m(0)=\sqrt{(2l+1)\frac{(l-m)!}{(l+m)!}}\frac{\sqrt{\pi}2^m}{\Gamma\left(\frac{l-m}{2}+1\right)\Gamma\left(\frac{-l-m+1}{2}\right)} \tag{C2}$$

If $l+m$ is odd then $O_{lm}=0$.

We give the following subcases:

$$g_{00}\left(w',r\right)=\begin{cases}\dfrac{1}{2\pi}\dfrac{1}{r\sqrt{r^2-\left|w'\right|^2}}, & \left|w'\right|<r\\ 0, & \left|w'\right|>r\end{cases} \tag{C3}$$

$$g_{1\pm1}\left(w',r\right)=\begin{cases}\mp\sqrt{\dfrac{3}{2}}\dfrac{\mathrm{e}^{\pm i\varphi_{w'}}}{2\pi}\dfrac{\left|w'\right|}{r^2}\dfrac{1}{\sqrt{r^2-\left|w'\right|^2}}, & \left|w'\right|<r\\ 0, & \left|w'\right|>r\end{cases} \tag{C4}$$

$$g_{20}\left(w',r\right)=\begin{cases}\dfrac{\sqrt{5}}{2}\dfrac{1}{2\pi}\dfrac{2r^2-3\left|w'\right|^2}{r^3\sqrt{r^2-\left|w'\right|^2}}, & \left|w'\right|<r\\ 0, & \left|w'\right|>r\end{cases} \tag{C5}$$

$$g_{2\pm2}\left(w',r\right)=\begin{cases}\dfrac{\sqrt{15}}{2\sqrt{2}}\dfrac{\mathrm{e}^{\pm2i\varphi_{w'}}}{2\pi}\dfrac{\left|w'\right|^2}{r^3}\dfrac{1}{\sqrt{r^2-\left|w'\right|^2}}, & \left|w'\right|<r\\ 0, & \left|w'\right|>r\end{cases} \tag{C6}$$

Appendix D: List of Variables

$\boldsymbol{r}_1,\boldsymbol{r}_2$ = Electron positions

$\boldsymbol{p}_1,\boldsymbol{p}_2$ = Electron momenta

Z = Nuclear charge

H = Total Hamiltonian

H_{He} = Helium Hamiltonian

H_f = Photonic field Hamiltonian

H_I = Interaction Hamiltonian

a^+,a = Creation and annihilation operators

$\wp(\tau)$ = Envelop function

V = Volume

$\boldsymbol{k}_{ph}$ = Radiation wavevector

ϖ = Carrier frequency

$\hat{\varepsilon}$ = Polarization vector

t_i,t_f,t,τ,ρ = Times

$\left|\Phi_1\right\rangle,\left|\Phi_2\right\rangle$ = Photonic states

α^*,α = Field variables

$K,\tilde{K},T^{\xi}_{f_1f_2^*},K_1$ = Propagators

S_{tot} = Action

$A(t)$ = Survival probability

$\dfrac{\xi}{2}$ = Ellipticity angle

ε = Infinitesimal time slice

$\delta^{(2)}$ = Two-dimensional delta function

$r_j, \vartheta_j, \varphi_j$ = Spherical coordinates
$\psi_g(\boldsymbol{r}_1, \boldsymbol{r}_2)$ = Ground state wavefunction
σ = Pulse duration