Chapter 6

Quantum Dynamics of Helium Atom Under Strong Magnetic Fields

6.1 Introduction

The astrophysical discovery of strong magnetic fields on the surface of white dwarfs ($\leq 10^5$ T) and neutron stars ($\approx 10^8$ T) has evoked an enormous interest in the study of behaviour and properties of matter in strong magnetic fields [1,2]. The motivation for studying matter in strong magnetic field arises from the importance of understanding neutron star surface layers which play a key role in many neutron star processes and in the physics of excitons (hydrogen-like bound electron-hole pairs) where laboratory fields are able to dominate the electronic structure of the systems. Also, increasingly stronger fields are becoming accessible in the laboratory. Nondestructive pulsed fields are nowadays available at various facilities up to several hundred tesla and destructive ones are even stronger. The highest static magnetic field currently produced in a terrestrial laboratory is 45 T, far below $B_0$; a stronger transient field of order $10^8$ T can be produced using flux compression techniques, but this is still below $B_0$ (i.e., magnetic field strength, $2m_e^2e^3c/h^3$ and is equal to $4.70108 \times 10^5$ T or 2 a.u.) [3]. There is an extensive literature on the theoretical description of hydrogen atom in strong magnetic fields [1,4-9]; the eigenvalue and quantum mechanical eigenfunctions of the hydrogen atom are, known quite precisely for ground and many excited states. As a consequence, a detailed understanding of properties of the hydrogen atom in strong magnetic fields has been developed and one can now compare the theoretical predictions resulting from ab Initio calculations with the data obtained from astrophysical observations. This had a strong
impact on the physics of magnetic white dwarfs as it could be shown that the absorption features of certain magnetic white dwarfs are caused by atomic transitions of hydrogen embedded in strong fields (see [1] and [9] for review). However, there are several spectral features and structures which cannot be explained by hydrogenic spectra alone such as, for example, in the spectrum of the magnetic white dwarf GD229 [10-12]. This led to the conjecture that there are further components to the atmospheres, i.e. atoms with more than one electron. Recently, detailed spectroscopic calculations were carried out for the helium atom in strong magnetic fields [13]. These investigations have opened the possibility to identify helium-rich spectra of white dwarfs.

Strong magnetic fields are known to have a strong impact on the properties of atoms and molecules. The competition of the diamagnetic and coulomb forces leads to a rich variety of complex properties and phenomena both with respect to the structure as well as dynamics of the particle systems. Many intriguing phenomena in different areas of physics, e.g. the quantum Hall effect in solid state physics or the transition between regularity and chaos in few-body atomic systems [14] are attributed to the combination of the magnetic and coulomb forces. The hydrogen atom in a magnetic field is one of the simplest physical systems that shows both classically as well as quantum mechanically a transition from regularity to chaos [14]. By nature, the spherically symmetric coulomb potential together with the cylindrically symmetric paramagnetic and diamagnetic interaction represents a nonseparable and nonintegrable problem already at the one-particle level. As a result, both the dynamics as well as the electronic structure of atoms or molecules would undergo drastic changes in the presence of strong magnetic fields.

Schmelcher et al have investigated the electronic structure of the helium atom in the magnetic field regime $B = 0-100$ a.u. using a full configuration-interaction approach which is based on a nonlinearly optimized anisotropic Gaussian basis set of one-particle functions [13,15]. However a time-dependent quantum mechanical study of the dynamics of atoms in
strong magnetic fields does not seem to be reported in the literature so far. The purpose of this chapter is to study the quantum dynamics of helium atom in strong magnetic fields and to interpret the possible signatures of quantum chaos.

The chapter is planned as follows: Section 6.2 gives the generalized idea of motion in a magnetic field, section 6.3 gives the numerical method that we employed and section 6.4 presents results and discussion.

### 6.2 Motion in Magnetic Field

In the classical theory, the Hamilton’s function of a charged particle (with charge $e$) in an electromagnetic field is [16]

$$
H = \frac{1}{2m} \left( p - e \frac{\mathbf{A}}{c} \right)^2 + e \Phi
$$

(6.1)

$\Phi$ is the scalar and $\mathbf{A}$ is the vector potential of the field. In quantum mechanics,

$$
\hat{H} = \frac{1}{2m} \left( \hat{p} - e \frac{\mathbf{A}}{c} \right)^2 + e \Phi
$$

(6.2)

Here, $\hat{p}$ does not commute with $\mathbf{A}$ which is a function of coordinates, so

$$
\hat{H} = \frac{\hat{p}^2}{2m} - \frac{e}{2mc} \left( \mathbf{A} \cdot \hat{\mathbf{p}} + \hat{\mathbf{p}} \cdot \mathbf{A} \right) + \frac{e^2 \mathbf{A}^2}{2mc^2} + U
$$

(6.3)

According to the rule of commutation of the momentum operator with any function of the coordinates

$$
\hat{p} \cdot \mathbf{A} - \mathbf{A} \cdot \hat{p} = -i \hbar \text{div} \mathbf{A}
$$

(6.4)

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p and A commute if \( \text{div} \ A = 0 \). This holds for a uniform magnetic field if it is expressed in the form
\[
A = \frac{1}{2} B \times r
\]  
(6.5)

If we consider the charged particle to be an electron (charge \(-e\)) then we have
\[
\hat{H} = \frac{\hat{p}^2}{2m} + \frac{e}{2mc} \left( A \cdot \hat{\pmb{p}} + \hat{\pmb{p}} \cdot A \right) + \frac{e^2 A^2}{2mc^2} + U
\]  
(6.6)

Here, \( U \) is the energy of interaction of electron with the nucleus and other electrons.

\[
\hat{H} = H_0 + \frac{e}{mc} \left( A \cdot \hat{\pmb{p}} \right) + \frac{e^2 A^2}{2mc^2}
\]  
(6.7)

when the field is in \( z \)-direction, then the Hamiltonian \( \hat{H} \) in a.u. is given by
\[
\hat{H} = H_0 + \frac{e}{mc} \left( \frac{1}{2} B \times \pmb{r} \right) \cdot \hat{\pmb{p}} + \frac{e^2}{2mc^2} \left( \frac{1}{2} B \times \pmb{r} \right)^2
\]  
(6.8)

The variable \( L_z \) is the \( z \)-component of the angular momentum defined as
\[
L_z = -i \hbar \frac{\partial}{\partial \phi}
\]
with the magnetic quantum number \( m = 0,1,2,.... \) etc. In terms of the dimensionless unit of magnetic field, \( \beta \) which is defined as \( B/B_0 \), Eq. (6.8) can be rewritten as
\[
\hat{H} = H_0 + \beta L_z + \frac{\beta^2 (x^2 + y^2)}{2}
\]  
(6.9)

While investigating the quantum dynamics of helium atom in a magnetic field, we have considered the external magnetic field term to be time-
dependent. Thus, the external time-dependent magnetic field for the present study is given as

$$E(t) = \frac{\beta(t)^2(x^2 + y^2)}{2}$$

(6.10)

where, $\beta(t) = \beta_0 f(t) \sin(\omega t)$, $f(t)$ is the ramp function and $\omega$ is frequency. Here, we neglect the $\beta L_\alpha$ term as the contribution of $\beta L_\alpha$ term to the Hamiltonian is assumed to be small in comparison to the $\beta^2$ term, for strong magnetic fields (in the present work, $\beta$ is taken as 4.0, i.e. $\beta^2 = 16.0$).

### 6.3 Numerical Method

The Generalized nonlinear Schrödinger equation (GNLSE) (in atomic units; see section 1.6) is

$$-\frac{1}{2} \nabla^2 + V_{\text{eff}}(p; r, t) \psi(r, t) = i \frac{\partial \psi(r, t)}{\partial t}$$

(6.11)

where the effective potential $V_{\text{eff}}(p; r, t)$ contains both classical and quantum terms and is defined as

$$V_{\text{eff}}(p; r, t) = \frac{\delta E_{\text{el-el}}}{\delta \rho} + \frac{\delta E_{\text{mu-el}}}{\delta \rho} + \frac{\delta E_{\text{xc}}}{\delta \rho} + \frac{\delta E_{\text{corr}}}{\delta \rho} + \frac{\delta E_{\text{ext}}}{\delta \rho}$$

(6.12)

$$E_{\text{el-el}} = \frac{1}{2} \int \int \frac{\rho(r, t) \rho(r', t)}{|r - r'|} \, dr \, dr'$$

$$\frac{\delta E_{\text{el-el}}}{\delta \rho} = \int \frac{\rho(r', t)}{|r - r'|} \, dr'$$

(6.13)
Various exchange-correlation functionals are available in the literature but we have employed a local exchange functional \cite{17}

\[
E_{\text{exlda}} = -c x f \rho^{4/3} \left( \frac{1}{r} \right) d\mathbf{r}
\]

\[
\delta E_{\text{ex}-\text{el}} = -\frac{Z}{r}
\]

Correlation effects have been included by using a simple, local parametrized Wigner-type functional \cite{18}

\[
\frac{\delta E_x}{\delta \rho} = \frac{\delta E_x^{\text{LDA}}}{\delta \rho} - C_x \left[ \frac{\int \rho^{1/3}}{1 + r^2 \rho^{2/3}/\alpha_x} \right]^{-1} \left( \frac{3}{2} r^2 \rho^{2/3} \right)
\]

\[
\frac{\delta E_x^{\text{LDA}}}{\delta \rho} = -\frac{4}{3} C_x \rho^{1/3}
\]

\[
E_c = -\int \rho a + b \rho^{-1/3} d\mathbf{r}
\]

\[
\frac{\delta E_c}{\delta \rho} = -\frac{a + c \rho^{-1/3}}{(a + b \rho^{-1/3})^2}
\]

where \(a = 9.81, b = 21.437, c = 28.582667\)
The magnetic field is applied along the $z$ axis. Thus,

$$E_{\text{ext}} = -\int E(\mathbf{r}, \mathbf{z}) \rho(\mathbf{r}, t) \, d\mathbf{r} \tag{6.17}$$

$$\frac{\delta E_{\text{ext}}}{\delta \rho} = -E(\mathbf{t}) \mathbf{z}$$

$$E(t) = \frac{\beta(t)^2 \rho^2}{2}$$

where $\beta(t) = \beta_0 f(t) \sin(\omega t)$ and $\beta_0$ is given as $B/B_0$, where $B_0 = 2$ a.u. Thus, $\beta_0 = B/2$ and in terms of magnetic field strength $B$, $E(t)$ can be written as

$$E(t) = \frac{B^2(f(t)\sin(\omega t))^2 \rho^2}{8} \tag{6.18}$$

The shape function $f(t)$ is given by

$$f(t) = \begin{cases} \frac{t}{t_0}, & t < t_0 \\ 1, & t \geq t_0 \end{cases} \tag{6.19}$$

The solution of TDSE, Eq. (6.11) is

$$\Psi(\mathbf{r}, t+\Delta t) = e^{\Delta t \hat{L}} \Psi(\mathbf{r}, t)$$

or alternatively it can be written as

$$\Psi_{l,m}^{n+1} = e^{\Delta t \hat{L}} \Psi_{l,m}^n \tag{6.20}$$

where

$$\hat{L} = -i \left[ -\frac{1}{2} \nabla^2 + V_{\text{eff}}(\rho; \mathbf{r}, t) \right]$$
We choose the cylindrical coordinate system

\[(\tilde{\rho}, \tilde{z}, \phi; 0 \leq \tilde{\rho} \leq \infty, -\infty \leq \tilde{z} \leq +\infty, 0 \leq \phi \leq 2\pi)\]

Since the electron density in a closed shell atom is cylindrically symmetric (\(\phi\) independent), the \(\frac{\partial^2}{\partial \phi^2}\) term is dropped. Thus the operator \(\hat{L}\) in this coordinate system is given by

\[
\hat{L} = \frac{i}{2} \left[ \frac{\partial^2}{\partial \tilde{\rho}^2} + \frac{1}{\tilde{\rho}} \frac{\partial}{\partial \tilde{\rho}} + \frac{1}{\tilde{\rho}^2} \frac{\partial^2}{\partial \tilde{z}^2} \right] + V_{\text{eff}}(\tilde{\rho}; \tilde{\rho}, \tilde{z}, t) \tag{6.21}
\]

\[
= \frac{i}{8} \frac{\partial^2}{\partial x^2} + \frac{i}{8} \frac{\partial}{\partial x} + \frac{i}{2} \frac{\partial^2}{\partial \tilde{z}^2} - i V_{\text{eff}}(\tilde{\rho}; \tilde{\rho}, \tilde{z}, t)
\]

Now by expressing Eq. (6.20) in a symmetric form we obtain

\[
\exp \left( -\frac{\hat{L} \Delta t}{2} \right) \psi^{n+1}_{l,m} = \exp \left( \frac{\hat{L} \Delta t}{2} \right) \psi^n_{l,m} \tag{6.22}
\]

After putting in the expression for \(\hat{L}\) in cylindrical coordinates and then separating \(x\) and \(z\) variables the following equation is obtained

\[
\exp \left[ -\frac{i \Delta t}{16 x^2} D_1^2 - \frac{i \Delta t}{16 x^3} D_1 + \frac{i \Delta t}{4} V_{\text{eff}} \right] \exp \left[ -\frac{i \Delta t}{4} D_2^2 + \frac{i \Delta t}{4} V_{\text{eff}} \right] \psi^{n+1}_{l,m} = \exp \left[ \frac{i \Delta t}{16 x^2} D_1^2 + \frac{i \Delta t}{16 x^3} D_1 - \frac{i \Delta t}{4} V_{\text{eff}} \right] \exp \left[ \frac{i \Delta t}{4} D_2^2 - \frac{i \Delta t}{4} V_{\text{eff}} \right] \psi^n_{l,m} \tag{6.23}
\]

where \(D_1 = \frac{\partial}{\partial x}\), \(D_1^2 = \frac{\partial^2}{\partial x^2}\), \(D_2^2 = \frac{\partial^2}{\partial \tilde{z}^2}\)
Finally, expanding the exponentials and truncating after the second term, followed by approximation of $D_1$, $D_1^2$ and $D_2^2$ by two- and three-point difference formulas respectively as

\[
D_1^n \Psi_{l,m}^n = \frac{1}{2h} \delta_x \Psi_{l,m}^n = \frac{1}{2h} \left( \Psi_{l+1,m}^n - \Psi_{l-1,m}^n \right)
\]

\[
D_1^2 \Psi_{l,m}^n = \frac{1}{h^2} \delta_x^2 \Psi_{l,m}^n = \frac{1}{h^2} \left( \Psi_{l+1,m}^n - 2 \Psi_{l,m}^n + \Psi_{l-1,m}^n \right)
\]

\[
D_2^2 \Psi_{l,m}^n = \frac{1}{h^2} \delta_z^2 \Psi_{l,m}^n = \frac{1}{h^2} \left( \Psi_{l+1,m}^n - 2 \Psi_{l,m}^n + \Psi_{l-1,m}^n \right)
\]

we obtain

\[
\left( 1 - d \delta_x^2 - e \delta_x - f \right) \Psi_{l,m}^{n+1} = \left( 1 + g \delta_x^2 + e \delta_x + f \right) \Psi_{l,m}^n
\]

(6.24)

Following the Peaceman-Rachford splitting the above Eq. leads to two equations

\[
\left( 1 - d \delta_x^2 - e \delta_x - f \right) \Psi_{l,m}^* = \left( 1 + g \delta_x^2 + e \delta_x + f \right) \Psi_{l,m}^n
\]

(6.25)

\[
\left( 1 - g \delta_z^2 - f \right) \Psi_{l,m}^{n+1} = \left( 1 + d \delta_x^2 + e \delta_x + f \right) \Psi_{l,m}^*
\]

(6.26)

where $\Psi_{l,m}^*$ is a factitious solution which bridges $\Psi_{l,m}^{n+1}$ with $\Psi_{l,m}^n$. The task left now is to solve a tridiagonal matrix twice, as discussed below. Eq. (6.25) can be written as a set of $N_t$ simultaneous equations

\[
\alpha_1 \Psi_{l-1,m}^* + \beta_1 \Psi_{l,m}^* + \gamma_1 \Psi_{l+1,m}^* = \xi_{l,m}^n
\]

(6.27)

where

\[
\alpha_1 = -\frac{i \Delta t}{16 \chi^2 h^2} + \frac{i \Delta t}{32 \chi^3 h}
\]

\[
\beta_1 = 1 + \frac{i \Delta t}{8 \chi^2 h^2} + \frac{i \Delta t}{4} V_{e,f}
\]

\[
\gamma_1 = \frac{i \Delta t}{32 \chi^3 h}
\]
\[
\gamma_i = -\frac{i \Delta t}{4h^2} + \frac{i \Delta t}{16 x^2 h^2}
\]

\[
\xi_{l,m}^n = \Psi_{l,m}^n + \frac{i \Delta t}{4h^2} \left( \Psi_{l,m+1}^n - 2 \Psi_{l,m}^n + \Psi_{l,m-1}^n \right) - \frac{i \Delta t}{4} V_{eff} \Psi_{l,m}^n
\]

Eq. (6.27) can be recast into a tridiagonal matrix equation

\[
\begin{bmatrix}
\beta_1 & \gamma_1 & 0 & 0 & 0 \\
\alpha_2 & \beta_2 & \gamma_2 & 0 & 0 \\
 & \ddots & \ddots & \ddots & 0 \\
 & & \gamma_{N_1-1} & \alpha_{N_1} & \beta_{N_1} \\
0 & & & \alpha_{N_1} & \beta_{N_1}
\end{bmatrix}
\begin{bmatrix}
\Psi_1^n \\
\Psi_2^n \\
\vdots \\
\Psi_{N_1-1}^n \\
\Psi_{N_1}^n
\end{bmatrix} =
\begin{bmatrix}
\xi_1^n \\
\xi_2^n \\
\vdots \\
\xi_{N_1-1}^n \\
\xi_{N_1}^n
\end{bmatrix}
\]

(6.28)

This can be solved for \( R_{l,m}^* \) using the modified Thomas algorithm [19].

Similarly, Eq.(6.26) can be written as a set of \( N_2 \) simultaneous equations

\[
\alpha_1 \Psi_{l,m-1}^{n+1} + \beta_1 \Psi_{l,m}^{n+1} + \gamma_1 \Psi_{l,m+1}^{n+1} = \eta_{l,m}^*
\]

(6.29)

where

\[
\alpha_1 = -\frac{i \Delta t}{4h^2}
\]

\[
\beta_1 = 1 + \frac{i \Delta t}{2h^2} + \frac{i \Delta t}{4} V_{eff}
\]

\[
\gamma_1 = -\frac{i \Delta t}{4h^2}
\]

\[
\eta_{l,m}^* = \Psi_{l,m}^* + \frac{i \Delta t}{16 x^2 h^2} \left( \Psi_{l,m+1}^* - 2 \Psi_{l,m}^* + \Psi_{l,m-1}^* \right)
\]

\[
+ \frac{i \Delta t}{32 x^3 h} \left( \Psi_{l+1,m}^* - \Psi_{l-1,m}^* \right) - \frac{i \Delta t}{4} V_{eff} \Psi_{l,m}^*
\]

Eq. (6.29) has the tridiagonal matrix form,
This can similarly be solved for \( \Psi_{\text{lat}}^{n+1} \) by the modified Thomas algorithm [19].

From the calculated densities at different times, various time-dependent properties have been examined to obtain insights into the dynamics that are discussed in the next section.

### 6.4 Results and Discussion

Various parameters for the present calculations are as follows:

\[ 0 \leq x \leq 10, \quad (\bar{\rho} = x^2), \quad 0 \leq \bar{\rho} \leq 100, \quad -100 \leq \bar{Z} \leq 100, \quad \Delta x = \Delta \bar{Z} = 0.1, \quad dt = 10^{-6}, \quad \beta = 4.0 \]

We first obtained the ground-state energy of helium atom by solving the hydrodynamical equation by using the imaginary-time propagator method (see chapter 1). Various energy values are as reported:

<table>
<thead>
<tr>
<th>Property</th>
<th>Present Value</th>
<th>Literature Value*</th>
</tr>
</thead>
<tbody>
<tr>
<td>( -E )</td>
<td>2.88589632</td>
<td>2.8973</td>
</tr>
<tr>
<td>( -\langle Z/r \rangle )</td>
<td>6.841284</td>
<td>6.7850</td>
</tr>
<tr>
<td>( \langle l/r^2 \rangle )</td>
<td>2.171065</td>
<td>2.0651</td>
</tr>
<tr>
<td>( -E_x )</td>
<td>1.058166</td>
<td>1.0325</td>
</tr>
<tr>
<td>( -E_c )</td>
<td>0.043422</td>
<td>0.0423</td>
</tr>
<tr>
<td>( \langle T \rangle )</td>
<td>2.88589632</td>
<td>2.8974</td>
</tr>
<tr>
<td>( -\langle T \rangle/\langle V \rangle )</td>
<td>2.00000505</td>
<td>1.99996</td>
</tr>
</tbody>
</table>

* Literature values are from Ref. [20]
The ground-state electronic density thus obtained is evolved under the magnetic field. The normalization constant showed rapid fluctuations of ±3% and this was taken care by renormalizing the norm $N(t)$ to the total number of electrons, i.e. 2. Fig. 6.1 shows the plot of $N(t)$ against time before the renormalization is done. It is seen that the initial ±3% fluctuations gradually settle down to about ±1% in course of time.

Fig. 6.1 Plot of normalization constant $N(t)$ against time in a.u.
The behaviour of the autocorrelation function $C(t)$ (see chapter 4) is depicted in Fig. 6.2. It decays sharply to zero and although it is oscillates, it does not return to the starting value. The decay of autocorrelation function indicates a departure of the system from its initial state and can be regarded as a "signature" of quantum chaos. It may be noted here that a similar behaviour was observed in nonlinear oscillators under the laser field of high intensity at which quantum chaos was elucidated in those systems.

Fig. 6.2 Plot of autocorrelation function $C(t)$ against time $t$ in a.u.
The ground-state survival probability, defined as

\[ \text{GSP} = \left| \langle \Psi_0 | \Psi_t \rangle \right|^2 \]  

(6.31)

is plotted against time in Fig. 6.3. It measures how much of the wave packet remains in the vicinity of the initial position. Fig. 6.3 shows that it decays sharply and then oscillates irregularly. Thus, it can be inferred that the density is moving out of the initial positions.

**Fig. 6.3** Ground-state survival probability (GSP) plotted against time t in a.u.
Our earlier work on two-dimensional nonlinearly coupled oscillators (see chapters 4 and 5) demonstrated a greater sensitivity of the quantum dynamical motion to the Hamiltonian than to the initial quantum state. In the present study, we followed our previous approach and studied the sensitivity of the quantum dynamical motion to the Hamiltonian by evolving the ground-state density under the magnetic field of slightly different $\beta$ values, i.e $\beta = 4.0$ and $\beta = 4.001$ and examined the overlap integral $I(t)$ between the time-evolved states.

Fig. 6.4 Overlap integral $I(t)$ obtained for slightly different $\beta$ (4.0 and 4.001) values is plotted versus optical cycle.
Fig. 6.4 shows that, starting from the initial value of 2.0, I(t) decays to 0.9 after 8 optical cycles; after that it oscillates about this value and does not return to the starting value. This clearly indicates that the wavefunctions that are evolved under slightly different β values are growing apart with time. It can be interpreted as a "signature" of quantum chaos as it is analogous to the state sensitivity which is the characteristic feature of classical chaos.

Fig. 6.5 shows the electron density plot over the space grid at time t = 0, as well as after 10 and 20 optical cycles. The ground-state density, i.e. density at time t = 0 has the usual distribution. After the system is evolved in the presence of magnetic field, the density distribution gets altered, as shown in Fig. 6.5 (a) and (b). The gradual contraction of the electron density along both $\bar{z}$- and $\bar{p}$- direction is clearly visible. Additional structure also develops; in particular, the central peak splits into two.

The time-dependent quantities like autocorrelation function, ground-state survival probability and overlap integral studied in the present chapter suggest that quantum chaos marks its presence in the quantum dynamical motion of the helium atom under a strong magnetic field. However, since quantum chaos is a complex phenomenon, one has to be cautious while characterizing it. One needs to examine as many or two diagnostics as possible in order to reach a definite conclusion about quantum chaos. Nevertheless, the present work paves the way for further studies on quantum dynamics of atoms/molecules under strong magnetic fields so that more signatures of quantum chaos are devised in order to reach an unambiguous conclusion. The implications of the neglect of $\beta L_z$ term in Eq. (6.9) also needs to be investigated.
Fig. 6.5 Electronic density plot (a) at time $t=0$, (b) after 10 optical cycles (c) after 20 optical cycles.
References


