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Semiclassical calculation of recurrence spectra of Rydberg He_2^+ molecular ion in a magnetic field*

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Making use of the molecular closed-orbit theory and a new model potential for the Rydberg molecule, we have calculated the recurrence spectra of He_2^+ molecular ion in a magnetic field for different quantum defects. The Fourier transform spectra of He_2^+ molecular ion may be used to perform a direct comparison between peaks in the spectra and the scaled action values of closed orbits of the excited electron in external fields. We find that the spectral modulations can be analysed in terms of the scattering of the excited electron on the molecular core. Unlike the case of the Rydberg atom where the elastic scattering is predominant, modulations produced by inelastic scattering are also vital to the photoabsorption spectrum of the Rydberg molecule. Our results are in good agreement with the quantum results, which suggests that our method is correct.

Keywords: closed orbit theory, recurrence spectra, model potential
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1. Introduction

Over the last 20 years, highly excited Rydberg atoms in external fields have attracted much attention in the field of atomic physics. These atoms are shown to be the real physical examples of the nonintegrable systems to study the quantum manifestations of classical chaos both experimentally and theoretically. Du and Delos' closed-orbit theory (COT) introduced a new way of studying the photoabsorption spectrum of Hamiltonians with chaotic classical dynamic behaviours.[1] The COT relates each oscillation in the absorption spectra to a classical closed-orbit beginning and ending near the nucleus. For hydrogen atoms in strong external fields, the COT has proven itself to be a quantitative and elegant method of calculating and interpreting the recurrence spectra. Experimental and theoretical recurrence spectra for hydrogen atoms in a magnetic field were found to be in good agreement with each other. In addition, the COT was also extended to treating the case of nonhydrogenic Rydberg atoms. The first fully quantum-mechanical calculations for nonhydrogen atoms in a magnetic field at fixed scaled energies showed strong resonance structures in the recurrence spectra, which could not be explained by using the closed orbit of the hydrogen atom.[2] Later studies suggested that the core-scattered effect must be incorporated into the study of the non-hydrogen atoms in external fields.[3] Hupper *et al* put forward a model potential to simulate the core-Rydberg electron interactions.[4] It turns out that an additional core potential classically results in the creation of a huge number of new closed orbits, which appear to be composed of two or more hydrogenic orbits.[5] Their existence can be explained with the scattering of hydrogenic orbits by the core potential.

Compared with atoms which have been extensively studied in experiment and theory, Rydberg molecules in strong external fields have attracted little attention. This is because, in the case of Rydberg molecules, it is anticipated that the multichannel core scattering is more important and its theoretical treatment is very complicated. It is not until recently that the single channel scattering process has been studied in great detail. Whereas for the Rydberg molecules in external fields, there appears a multi-channel quantum scattering phenomenon. During the collision of the Rydberg electron with the molecular core, their

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quantum states will be altered. In Ref.[6], Matzkin and Monteiro proposed a closed-orbit theory of treating the molecules in external fields. Their calculation shows that in addition to elastic scattering, inelastic scattering gives rise to novel spectral modulations. To date, many researchers have studied the recurrence spectra of H_2 molecule theoretically.[7,8] Because hydrogen molecule is the simplest neutral diatomic molecule. An understanding of its high-lying Rydberg states, through a strict comparison between experiment and theory, can provide an important basis for the development of modelling the excited state structure and dynamics of larger molecules. Except for the hydrogen molecule, Matzkin *et al* measured the recurrence spectra of the NO molecule in a magnetic field experimentally,[9] but nobody has given the exact calculation theoretically. As for the other molecules in external fields, few reports can be found. Recently, some researchers have tried to study the characteristics of He_2^+ molecular ions. The helium dimer ion (He_2^+) has been the subject of theoretical and experimental studies because of its importance in diverse fields from quantum chemistry to plasma physics. Bawagan and Davidson have studied the potential energy surface of a He_2^+ molecular ion in order to calculate the femtosecond spectroscopy.[10] Nin *et al* have analysed the impact ionization process of the hydrogen atom and the helium molecular ion.[11] Turbiner and Guevara found that helium molecular ions could exist in a magnetic field.[12] But as to the dynamical character of the He_2^+ molecule ion in external fields, nobody has made any analysis. In this paper, making use of the molecular closed-orbit theory (MCOT) and a region-splitting consistent and iterative method, we study the dynamical behaviour of the Rydberg helium molecular ion in a magnetic field and investigate the recurrence spectra of this system for different quantum defects for the first time. In order to simulate the interaction between the excited electron and molecular core, we put forward a new model potential for the Rydberg helium molecular ion. After considering this model potential, the number of the closed orbits increases greatly, which shows that the core effects are more important for the Rydberg molecules as anticipated. The calculation results indicate that the apparently complex spectrum can be analysed in terms of the elastic and inelastic scatterings of the excited electrons on the molecular core.

2. Theory and quantitative formula

2.1. Model potential for the Rydberg He_2^+ molecular ion

For the Rydberg molecule, in general, the potential acting on the excited electron is the total interaction energy of this electron with all the nuclei and other electrons. The potential acting on the excited electron at position r_1 may be formulated as[8]

$$V(r_1) = V_{\rm nuc} + V_{\rm es} + V_{\rm ex}, \tag{1}$$

where $V_{\rm nuc}$ is the attractive potential of all the nuclei acting on the excited electron

$$V_{\rm nuc} = -\sum_A \frac{z_A}{|\boldsymbol{r}_1 - \boldsymbol{R}_A|}, \tag{2}$$

with z being the charge of the nucleus A, $\boldsymbol{r}_1$ and $\boldsymbol{R}_A$ denoting the electronic and A atomic nucleus coordinates, and the summation with index A referring to running over all atomic nuclei; $V_{\rm es}$ is the Coulomb interaction potential between the excited electron and the remaining electrons

$$V_{\rm es} = \int \frac{\rho(r_2)}{r_{12}} {\rm d}\tau_2, \tag{3}$$

with $\rho(r_2) = \sum\limits_i |\psi_i(r_2)|^2$ being the density function at position r_2, in which $\psi_i(r)$ denotes the i-th molecular orbit and the sum runs over all the different spatial molecular orbit; r_{12} being the distance between electrons 1 and 2. For a Rydberg He_2^+ molecular ion, there are altogether three electrons. Suppose that the two electrons lie in 1s molecular orbit ψ_1 and the third electron is excited to 3s molecular orbit ψ_2.Therefore, according to the molecular orbit theory, the molecular orbit can be written as[13]

$$\psi_1 = \frac{1}{\sqrt{2(1+S)}}[1{\rm s}_A + 1{\rm s}_B], \tag{4}$$

where $S = \iint 1{\rm s}_A 1{\rm s}_B {\rm d}\tau_1 {\rm d}\tau_2$; $1{\rm s}_A$ and $1{\rm s}_B$ are the wavefunctions of the ground-state helium atom. After an electron has absorbed a photon, it is excited from the ground state to the excited 3s state. The excited 3s molecular orbit has a high energy and can be considered to be in a Rydberg state. The molecular orbit of the excited 3s state can be described by

$$\psi_2 = \frac{1}{\sqrt{2(1+S')}}[3{\rm s}_A + 3{\rm s}_B], \tag{5}$$

where $3s_A$ and $3s_B$ are the wavefunctions of the 3s-state helium atom.

Substituting the molecular orbit expressions (4) and (5) into expression (3), using the double centre ellipse coordinate integration,[13] and having performed a lengthy derivation, we obtain

$$\begin{aligned} V_{\rm es} = & -c_1\left(1+\frac{10}{17r_{1A}}\right)\mathrm{e}^{-3.4r_{1A}} - c_1\left(1+\frac{10}{17r_{1B}}\right)\mathrm{e}^{-3.4r_{1B}} \\ & + c_2\left(\frac{1}{r_{1A}}+\frac{1}{r_{1B}}+\frac{9}{25}\right) - c_3\left(\frac{1}{r_{1A}}+\frac{10}{9}+\frac{36}{61}r_{1A}+\frac{24}{61}r_{1A}^2-\frac{5}{61}r_{1A}^3+\frac{1}{17}r_{1A}^4\right)\mathrm{e}^{-\frac{17}{60}r_{1A}} \\ & - c_3\left(\frac{1}{r_{1B}}+\frac{10}{9}+\frac{36}{61}r_{1B}+\frac{24}{61}r_{1B}^2-\frac{5}{61}r_{1B}^3+\frac{1}{17}r_{1B}^4\right)\mathrm{e}^{-\frac{17}{60}r_{1B}}, \end{aligned} \tag{6}$$

where c_1, c_2 and c_3 are coefficients which are related to the distance between the two atomic nuclei, R; at the equilibrium distance of He_2^+, R=2.0431 a.u., $c_1 = 1.3488$, $c_2 = 0.8497$, and $c_3 = 0.0585$; $V_{\rm ex}$ is the exchange potential between this α-spin electron and the rest of the α-spin electrons, expressed as

$$V_{\rm ex} = -\frac{\sum_{i=1}^{2}\sum_{j=1}^{2}\psi_i^*(r_1)\psi_j(r_2)}{\rho(r_1)} \times \int \frac{\psi_j^*(r_2)\psi_i(r_2)}{r_{12}}\mathrm{d}\tau_2. \tag{7}$$

2.2. The molecular closed-orbit theory

The closed-orbit theory can explain the dynamics underlying the photoabsorption spectra of Rydberg atoms or molecules in external fields in terms of closed orbits.[2,6] Following initial photo-excitation, the wavefunction of the excited electron propagates first in a region near the ionic core ('inner region'), in which the external field can be neglected. Beyond the inner region, the wavefunction propagates semiclassically along classical trajectories. Some trajectories return to the inner region, and the semiclassical wavefunction carried by those trajectories is matched with an exact wavefunction in the inner region given by a multichannel quantum-defect theory (MQDT) expansion.[14] The superposition of these returning waves with the initially dipole-excited wavefunction produces sinusoidal modulations in the photoabsorption spectrum, which appear as isolated peaks in the Fourier-transform spectrum (recurrence spectra). Some modulations are caused by the core-scattering process: in a multichannel problem, electrons can exchange their energies and angular momenta with the core, so that after electrons have collided the core, the electron wavefunction propagates outward again, and when it leaves the inner region, the wavefunction will follow classical trajectories once again. If the collision is perfectly elastic, the electron will follow one of the previously followed trajectories; on the other hand, inelastic collisions will result in trajectories pertaining to a different classical regime. For the photoabsorption of molecule in external fields, after photoexcitation, the molecular core can be either rotationally excited or nonexcited. The molecular core then plays a role of an effective two-level scatterer, which combines classical trajectories belonging to two different dynamical regimes (chaotic and near-integrable regimes), thereby producing additional modulations in the photoabsorption spectrum.

We divide the whole space into three characteristic spatial regions: (1) The core region, where the laser field and the core field influences exist while external fields can be neglected. In this region, the dynamics of the electron is coupled with the rotation of the core. (2) The surrounding Coulomb region, where the dynamics of the excited state is predominantly determined by the Coulomb force of the ionic core. (3) The outer region, where the influence of the external field is at least as important as the Coulomb force of the ionic core. In this region, the molecular wavefunction is described in the uncoupled frame. Our approach is to solve the problem quantum- mechanically in the core and Coulomb regions, semiclassically in the Coulomb and outer regions, and then to match these two solutions in the Coulomb region where both are valid.

The dynamics of a molecular Rydberg electron in the field-free situation falls into one of two cases: (1) Near the core, the electron is strongly coupled with the molecular axis and best described in the molecular Born-Oppenheimer basis, with good quantum num-

bers $|\alpha\rangle = |\Lambda_\alpha J_\alpha l_\alpha\rangle$, where Λ is the projection of the electronic angular momentum on the molecular axis, J is the total angular momentum, l is the orbital momentum of the outer electron. (2) Far from the core, in the presence of the external fields, an approximate basis is $|j\rangle = |N_j l_j m_j\rangle$, where m_j is the magnetic quantum number.

2.3. The oscillator strength density

According to the closed –orbit theory, the oscillatory part of the oscillator strength is the overlap of the initially excited waves with the returning waves

$$f^{\rm osc} = \langle\psi_0|D|\psi^{\rm ret}\rangle, \tag{8}$$

where $|\psi_0\rangle$ is a field-free state of the helium molecular ion in the ground state $^2\Sigma_\mu^+$ with the quantum number $\Lambda = 0$. In the molecular frame, the wave function is described in the coupled frame

$$|\psi_0\rangle = |\Lambda = 0 J = 0\rangle|l = 0\lambda = 0\rangle F_{l=0}(r). \tag{9}$$

After photoexcitation, the wavefunction of the excited electron propagates into the ionic core region, where the external field can be neglected. Assuming the laser to be linearly polarized along the z-axis and letting the dipole operator $\boldsymbol{D}$ lie in the space-fixed frame, the resulting outgoing wave is given by $GD|\psi_0\rangle$, where G is the quantum-mechanical outgoing Green's function. For the molecular case, the Green's function G is[7]

$$G(r,r') = -16\pi \sum_j |j\rangle g_{l_j}^+(r') \sum_\alpha {\rm e}^{{\rm i}\pi\mu_\alpha}\langle j|\alpha\rangle \times [f_{l_\alpha}(r)\cos\pi\mu_\alpha + g_{l_\alpha}(r)\sin\pi\mu_\alpha]\langle\alpha|. \tag{10}$$

The outgoing wave is thus obtained as

$$\psi_{\rm out}(r) = -2^{5/2}\pi \sum_j |j\rangle g_{l_j}^+(r') \times \sum_\alpha {\rm e}^{{\rm i}\pi\mu_\alpha}\langle j|\alpha\rangle D_\alpha, \tag{11}$$

in which $D_\alpha = C_\alpha 3^{-1}\int 2^{3/2} r'^3 {\rm d}r'[f_{l_\alpha}(r')\cos\pi\mu_\alpha + g_{l_\alpha}(r')\sin\pi\mu_\alpha]F_{l=0}(r')$ with $C_\alpha = 1$ if $|\Lambda_\alpha J_\alpha l_\alpha\rangle = |011\rangle$,and $C_\alpha = \sqrt{2}$ if $|\Lambda_\alpha J_\alpha l_\alpha\rangle = |111\rangle$, otherwise $C_\alpha = 0$.

As the Rydberg electron leaves the core region , the molecular energy is partitioned between the Rydberg electron and the core; as the core rotation increases, the energy of the Rydberg electron decreases. The energy partition is

$$E = E^{\rm el}_{N_j m_j} + N_j(N_j+1)B_r + m_j\gamma/2, \tag{12}$$

where $E^{\rm el}$ is the energy of the outer electron and $B_{\rm r}$ is the rotational constant of the core. There are two effective dynamical regimes for the outer electron, and each is associated with a different rotational state of the core, N=0 and N=2.

When the outgoing waves enter the outer zone, where the external field cannot be neglected, the wave propagates semiclassically. The molecular wavefunction in the outer zone can be written as

$$\psi(r,\theta) = \sum_{N_j m_j} |N_j m_j\rangle \psi^{N_j m_j}(r,\theta), \tag{13}$$

in which $\psi^{N_j m_j}(r,\theta)$ is the semiclassical wavefunction associated with the core in the state $|N_j m_j\rangle$, and it is expressed as

$$\psi^{N_j m_j}(r,\theta) = \sum_k \psi^{N_j m_j}_{\rm out}(r_i,\theta_{ik})\left|\frac{r_i^2\sin\theta_{ik}}{r^2\sin\theta}\right|^{1/2} \times A_k^{N_j m_j}(r,\theta) \times \exp[{\rm i}(S_k^{N_j m_j}(r,\theta) - \omega_k^{N_j m_j}\pi/2)] \tag{14}$$

with A_k and S_k being the classical amplitude and phase functions for the trajectory k in the two- dimensional axial plane, and ω_k being the associated Maslov index; $\psi^{N_j m_j}_{\rm out}(r_i,\theta_{ik})$ being the wave in the initial surface associated with the core in state $N_j m_j$, expressed as

$$\psi^{N_j m_j}_{\rm out}(r_i,\theta_{ik}) = -{\rm i}2^{3/4}\pi^{1/2} r_i^{-3/4} \sum_{l_j \geq |m_j|} (-1)^{l_j} Y_{l_j m_j}(\theta_{ik}) {\rm e}^{{\rm i}(\sqrt{8r_i} - 3\pi/4)} \times \sum_\alpha {\rm e}^{{\rm i}\pi\mu_\alpha}\langle j|\alpha\rangle D_\alpha. \tag{15}$$

Finally, some trajectories in the outer region return to the inner region where the magnetic field is weak. The returning wave can be written as an MQDT expansion in the uncoupled basis:

$$\psi^1(r) = \sum_j |j\rangle \sum_{j'} c_{j'}[\delta_{jj'} f_{l_j}(r) + T_{jj'} g^+_{l_j}(r)], \tag{16}$$

where the superscript 1 indicates the first return to the inner region. After returning wave $\psi^1(r)$ has been scattered by the molecular core, its outgoing part is split into two different terms: $\psi^1(r) = \psi^1_{\rm Coul}(r) + \psi^1_{\rm core}(r)$, where $\psi^1_{\rm Coul}(r)$ is the Coulomb scattering wave, which is strongly backfocused by the Coulomb field and expressed as

$$\psi^1_{Coul}(r) = \mathrm{e}^{2\mathrm{i}\sqrt{8r_f}}\mathrm{e}^{-\mathrm{i}\pi}\psi^{N_j m_j}(r_f, \theta_f); \qquad (17)$$

$\psi^1_{\rm core}(r)$ represents the core-scattered waves

$$\psi^1_{\rm core}(r,\theta) = \sum_{N_j m_j} |N_j m_j\rangle \sum_{l_j} Y_{l_j m_j}(\theta) g^+_{l_j} \sum_{j'} c_{j'} T_{jj'}. \qquad (18)$$

Each newly outgoing wave leaving the core in the state $|N_j m_j\rangle$ results from the scattering into channel j from waves that previously returned to channel j', i.e. the core reaches a state $|N_{j'} m_{j'}\rangle$. These interchannel mixings are formally represented by the T-matrix elements,

$$T_{jj'} = \sum_{\alpha} \langle j|\alpha\rangle \frac{\mathrm{e}^{2\mathrm{i}\pi\mu_\alpha} - 1}{2i} \langle \alpha|j'\rangle. \qquad (19)$$

Some trajectories q eventually return to the core, and the returning wave is matched with an MQDT expansion

$$\psi^2(r) = \sum_j |j\rangle \sum_{j'} d_{j'} [\delta_{jj'} f_{l_j}(r) + T_{jj'} g^+_{l_j}(r)], \quad (20)$$

where superscript 2 refers to the second return to the inner region. The coefficient d_j is obtained by matching this expansion with the semiclassical returning waves.

The same process takes place. The waves that have returned to the inner region for the second time are scattered by the core, and produce newly outgoing waves given by $\sum_j |j\rangle \sum_{j'} d_{j'} T_{jj'} g^+_{l_j}(r)$. Following the same arguments, we can write the returning waves to the inner region for p times. In each successive step extra terms in the form of $A_q \cdots A_k \mathrm{e}^{\mathrm{i}(s_q + \cdots + s_k)}$ are added to the previous result. Therefore, in successive steps of the iterative process combinations of more and more orbits are included. The overlap of the initially excited waves with all the returning waves makes a contribution to the oscillatory part of the oscillator strength. The imaginary part of expression (8) gives the sinusoidal modulations contributed by each closed orbit of the electron.

2.4. Recurrence spectra

2.4.1. Hamiltonian and scaled variables

The Hamiltonian for the excited electron outside the helium molecular ion core in a magnetic field is (in atomic units)[15]

$$H = \frac{p^2}{2} + \frac{\gamma}{2} l_z + \frac{1}{8}\gamma^2\rho^2 + B_r N^2 + V(r) \qquad (21)$$

where the magnetic field is assumed to be along the z-axis in a cylindrical coordinate system; $\gamma = B/2.35 \times 10^5$($B$ is the magnetic field strength); $B_r = 7.74 \times 10^{-5}$a.u. is the rotational constant of the He_2^+ core; $V(r)$ is the model potential (Eq.(1)). In our computation of closed orbits, we always take into account the effect of this potential. Thus this treatment is more strict and complete.

Although the dynamics associated with the molecular core in states N=0 and 2 cannot be scaled simultaneously, scaling technique may still be applied theoretically by using a magnetic-field-dependent rotational constant.[7] We transform variables according to $\tilde{r} = r\gamma^{2/3}$, $\tilde{p} = p\gamma^{-1/3}$, $\varepsilon = E\gamma^{-2/3}$, $\tilde{t} = t\gamma$ and $\tilde{B}_r = B_r\gamma^{-2/3}$, then the classical motion is governed by the scaled Hamiltonian

$$\tilde{H} = \frac{\tilde{p}^2}{2} + \frac{1}{2}\tilde{l}_z + \frac{1}{8}\tilde{\rho}^2 + \tilde{B}_r N^2 + V(\tilde{r}), \qquad (22)$$

where $\tilde{l}_z = \tilde{x}\tilde{p}_y - \tilde{y}\tilde{p}_x$.

If we omit "$\sim$" and rewrite $\tilde{H}$ as ε, we obtain

$$\varepsilon = \frac{p^2}{2} + \frac{1}{2} l_z + \frac{1}{8}\rho^2 + B_r N^2 + V(r). \qquad (23)$$

From expression (23), we find that the scaled Hamiltonian does not depend on energy E and field strength separately but only on scaled energy ε, thus reducing the value of B.

2.4.2. Closed orbits search

In order to solve numerically the equations of motion generated by Hamiltonian (21), it is convenient to make a regularizing transformation that removes the singularities at points $r_A = 0$ and $r_B = 0$. For the system under consideration, we implement the Thiele–Burrau transformation,[16] which converts the system from the rectangular coordinates (x, y, z) to the new coordinates (u, v, φ) by using the relation $x = -\frac{R}{2}\sin u \sinh v \cos\varphi$, $y = -\frac{R}{2}\sin u \sinh v \sin\varphi$, and $z = \frac{R}{2}\cos u \cosh v$. We integrate the Hamiltonian equations of motion with the help of a high-order

Runge-Kutta algorithm with step width control in order to fulfill the accuracy requirement in the domain of the additional core potential.

We find out the closed orbits of Rydberg helium molecular ion at the scaled energies $\varepsilon = E\gamma^{-2/3} = -0.3$ and $\varepsilon = -0.8$, respectively, in a magnetic field range $\gamma^{-1/3} = 60 - 120$. After the model potential has been employed, the number of the closed orbits is great because of the molecular core scattering. However, we can restrict our attention to a specific time interval and those closed orbits with the scaled actions smaller than 10. For each closed orbit, we evaluate the classical action S and the amplitude A.

2.4.3. Recurrence spectrum

Recurrence spectrum is of the Fourier transform of the photoabsorption spectrum. The rate of production of excited molecule is given by a smooth background term plus oscillatory contributions. At a certain scaled energy, the photoabsorption rate is described as[7]

$$F(\gamma,\varepsilon) = \frac{e}{\pi\hbar_{\rm eff}^{1/2}} \sum_p {\rm Im}[\langle\psi_0|D|\psi^p\rangle], \qquad (24)$$

in which p denotes the number of the excited electrons returning to the core region. For p=2, the oscillatory part of the absorption rate $F(\gamma,\varepsilon)$ reads

$$\begin{aligned} F(\gamma,\varepsilon) =& 2^{19/4}\pi^{3/2} \sum_j \sum_\alpha \sum_{\alpha'} {\rm Im}\Bigg\{ \langle\alpha|j\rangle C_\alpha C_{\alpha'} {\rm e}^{{\rm i}\pi(\mu_\alpha+\mu_{\alpha'})} \times \Bigg[\langle j|\alpha'\rangle \sum_k \tilde{R}_k^j \\ &+ \hbar_{\rm eff}^{1/2} 2^{11/4}\pi^{3/2} \times \sum_{j'} [\langle j'|\alpha'\rangle T_{jj'} \sum_k \tilde{R}_k^{j'} \sum_q \tilde{R}_q^j] \Bigg\}, \end{aligned} \qquad (25)$$

where $\hbar_{\rm eff} = \gamma^{1/3}\hbar$, and $\tilde{R}_k^j$ is now given by terms of the scaled classical variables $\tilde{s}_k^j = \hbar_{\rm eff} s_k^j/2\pi\hbar$ and $\tilde{r}_f A_k^j = |2^{1/2}\cos(\theta_{ik}/2)\cos(\theta_{fk}/2)m_{12}|^{-1/2}$ with m_{12} being the element of the monodromy matrix evaluated in the scaled semiparabolic coordinate system,[17] θ_{ik} and θ_{fk} being the initial and returning angles of the k-th closed orbit.

The Fourier transform recurrence spectrum can be calculated in the interval $[W_1,\ W_2]$. With $W = \gamma^{-1/3}$, $\bar{W} = 1/2(W_1 + W_2)$ and $\Delta W = W_2 - W_1$, we obtain

$$F(\tilde{s}) = \left| \frac{1}{\Delta W} \int_{W_1}^{W_2} F(\gamma,\varepsilon) e^{2\pi i\tilde{s}(W-\bar{W})} {\rm d}W \right|^2. \qquad (26)$$

3. Results and discussion

The recurrence spectra of helium molecular ion in a magnetic field with different quantum defects are shown in Figs.1–3 for M=0 at scaled energies $\varepsilon_{N=0} = -0.3$ and $\varepsilon_{N=2} = -0.8$ with the magnetic field $\gamma^{-1/3} \equiv 60 - 120$. As in Ref.[7], the smooth background term has been subtracted before performing the Fourier transform of the absorption spectra. Each peak corresponds to the classical closed orbit or the combination of those orbits via molecular core scattering. The integers in the figures indicate primary orbits ($1, 2, 3, \cdots$ corresponding to the closed orbits at $\varepsilon_{N=0} = -0.3$ while $1', 2', 3', \cdots$ corresponding to the closed orbits at $\varepsilon_{N=2} = -0.8$). Each pair of integers indicates the combination of two closed orbits, corresponding to a core-scattered peak, while each triple of integers denotes a double-scattering peak due to the combination of three orbits. q^n represents the q-th closed orbit on the nth repetition. Figure 1 shows the recurrence spectra with the quantum defects $\mu_\Sigma = \mu_\pi = 0$. In this case, matrix T vanishes and there exists no molecular core scattering. Each peak corresponds to the primitive orbits and their repetitions of the helium molecular ion in a magnetic field at a single channel N=0 with scaled energy $\varepsilon_{N=0} = -0.3$. The classical closed orbits that make a contribution to the recurrence spectra are plotted in Fig.4. For clarity, we plot and denote only the orbit with the values of scaled action S less than 5. Figure 2 shows the recurrence spectra with the quantum defects $\mu_\Sigma = \mu_\pi = 0.5$. In this situation, no electron associated with an N=2 core is excited by the laser field. Besides, matrix T is diagonal and only the terms with $N_j = N_j' = 0$ remain there. Thus there is no rotational interaction and only elastic core scattering

is expected. A comparison between Fig.2 and Fig.1 shows that some new peaks marked with arrows appear in Fig.2 and they correspond to a combination of the primitive orbits associated with the ground N=0 core state due to elastic molecular core scattering. For example, the arrowed peak (1, 2) located at $\tilde{s} = 2.2475$ corresponds to a combination of orbit 1 at $\tilde{s}_1 = 0.9672$ and orbit 2 at $\tilde{s}_2 = 1.2803$; the arrowed peak (1, 2, 3) at $\tilde{s} = 4.1881$ corresponds to a combination of orbits 1, 2 and 3; the other arrowed peaks can be found in Fig.2. Figure 3 is for the recurrence spectra with the quantum defects $\mu_\Sigma = 0.242$, and $\mu_\pi = -0.019$. These quantum defect values were obtained by Monte Carlo program corresponding to the excited states $^2\Sigma_g^+$ and $^2\pi_\mu$.[10] A greater number of new peaks appear, which result from the elastic and inelastic molecular core scatterings. As the excited electron returns closely to the molecular core, it will recollide with the molecular ion. Owing to the existence of the molecular core, there is core scattering besides the Coulomb scattering. When the returning waves approach to the molecular core, the Coulomb scattering wave is strongly backwardly focused and retraces the orbit, generating repeated traversals of the trajectory. Unlike the Coulomb scattering waves, the molecular core scattering changes the direction of the returning wave from one closed orbit into other closed orbits, thus combined orbits appear. From Fig.3 we find that besides elastic core scattering, inelastic scattering effects of the molecular core on the recurrence are also important. First of all, peaks corresponding to contributions from the orbits associated with an excited core at a scaled energy $\varepsilon_{N=2} = -0.8$ are clearly visible. For example, the peak at $\tilde{s}$ =0.7448 corresponding to orbit $1'$ perpendicular to the z-axis is associated with the $N = 2$, and $m = \pm 1$ submanifold of the rotationally excited state; while the peak at $\tilde{s}$ =0.7863 corresponds to orbit $2'$ parallel to the field axis, and it is associated with the $N = 2$, and $m = 0$ core state. Besides, the repetitions and combination of these orbits are also visible. And the peaks corresponding to orbits associated with the N=0 ground state are still visible, and they each involve both the primitive and core-scattered orbits. Furthermore, there are peaks appearing at a scaled action corresponding to the sum of an $\varepsilon_{N=0} = -0.3$ orbit and $\varepsilon_{N=2} = -0.8$ orbit. For example, the arrowed peak $(1', 5)$ at $\tilde{s} = 3.7741$ arises from the combination of orbit $1'$ at a scaled energy $\varepsilon_{N=2} = -0.8$ with orbit 5 at a scaled energy $\varepsilon_{N=0} = -0.3$. These additional peaks are produced by the inelastic molecular core scatterings: the electron along an orbit k with the core in state j collides with the core, thereby exchanging its energy and leaving the core in state j' along orbit q. Hence, the vast majority of the peaks appearing in the recurrence spectra are explained semiclassically to stem from primitive, elastic and inelastic molecular core-scattered orbits.

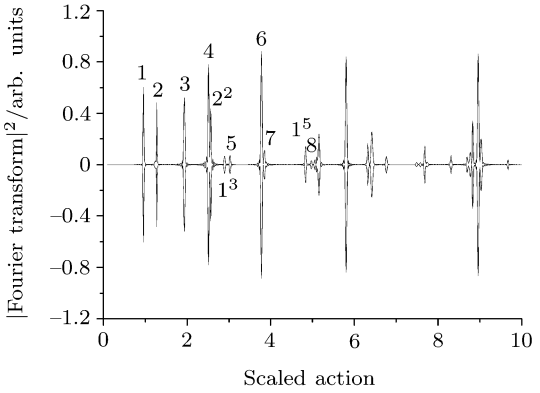


Fig.1. Recurrence spectra of helium molecular ion in a magnetic field at scaled energies $\varepsilon_{N=0} = -0.3$ and $\varepsilon_{N=2} = -0.8$, $\gamma^{-1/3} = 60 - 120$, and the quantum defects $\mu_\Sigma = \mu_\pi = 0$. In this case, only the orbits associated with the core in state N=0 appear in the recurrence spectra, each peak corresponds to primitive closed orbits and their repetitions. The calculations from the semiclassical closed orbit theory are displayed above the zero line while the quantum calculations are below the zero line.

In order to verify our results, we have also calculated the quantum recurrence spectra of He_2^+ in a magnetic field by using the method given in Ref.[18]. In each of Figs.1–3, the part above the zero line is the semiclassical molecular closed orbit result while the part below the zero line is the quantum calculation result. They are in good agreement with each other, which suggests that our calculation is correct.

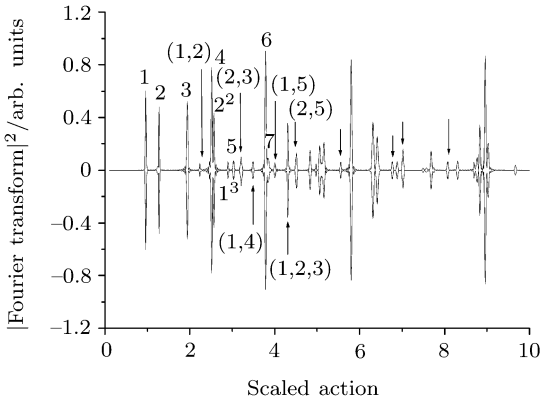


Fig.2. The same as Fig.1 except the quantum defects being $\mu_\Sigma = \mu_\pi = 0.5$. New peaks appear which result from the elastic molecular core scattering of N=0 state.

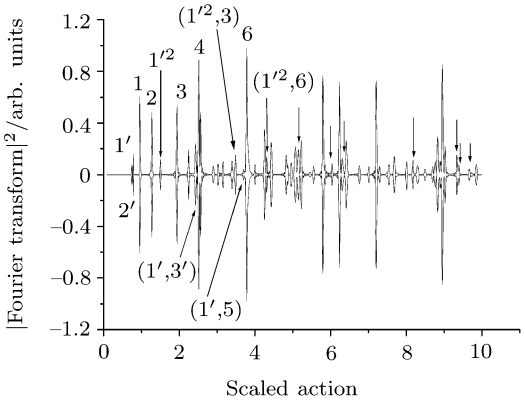


Fig.3. The same as Fig.1 except the quantum defects being $\mu_\Sigma = 0.242$, and $\mu_\pi = -0.019$. Additional peaks appear, which stem from the elastic core scattering of N=2 state and inelastic core scattering between N=0 and N=2 states.

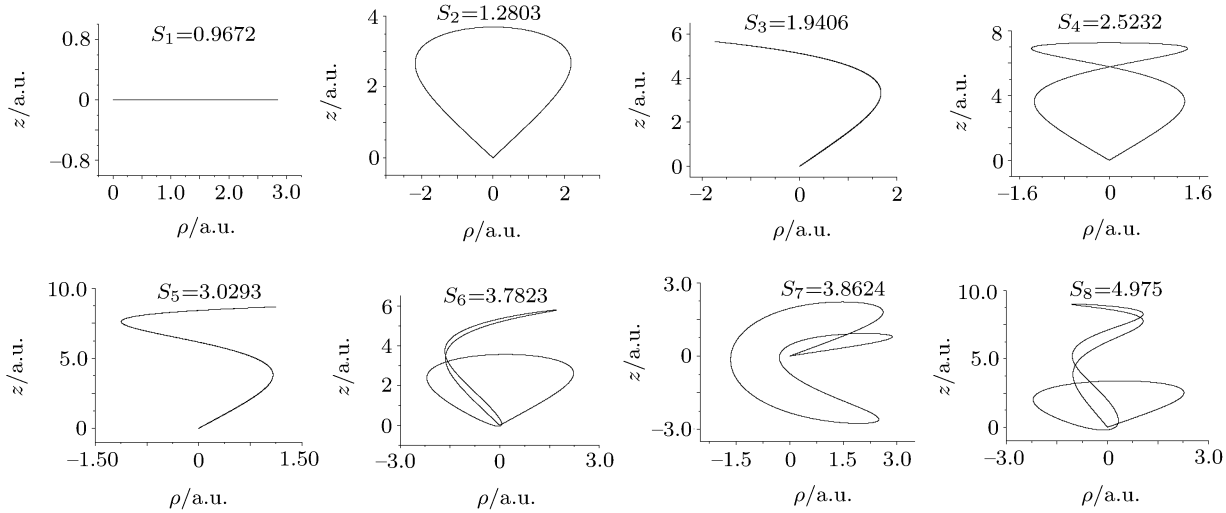


Fig.4. Some closed orbits corresponding to Fig.1 for the Rydberg helium molecular ion in a magnetic field at a scaled energy $\varepsilon_{N=0} = -0.3$. S is the scaled action. The geometries of the closed orbits are shown in (ρ, z) coordinates.

4. Conclusions

Making use of the molecular closed-orbit theory and a new model potential, we have calculated the recurrence spectra of helium molecular ion in a magnetic field for different quantum defects. The results show that for the Rydberg molecule in external fields, in addition to the elastic molecular core scattering, the inelastic scattering is also essential to an account for the photoabsorption spectrum. The model potential we put forward is quite universal and suitable to all diatomic molecules. In the future, we will use this model potential to calculate the recurrence spectra of NO molecules in external fields theoretically. In this paper, we consider only the influence of molecular core scattering on the recurrence spectra. As to the recollision probability between electron and molecular ion, we will discuss it by using the time-dependent-wave-packet method as given in Refs.[19, 20] in our another work. Presently no experiments on the recurrence spectra of helium molecular ion in external fields can be found. Therefore, no experimental results can be used to be compared directly with our results, for the rotational constant in this model is a function of magnetic field. In the future, we will consider calculations that can be compared directly with experimental results. We hope that our results may guide the future study.

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