Two-electron systems: Stability analysis of the Wannier ridge

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We examine the stability of classical two-electron systems with an electron moving along elliptic orbits on the Wannier ridge. Lyapunov exponents are evaluated analytically for circular orbits within the first-order perturbation theory. In the case of the helium atom, these results compare favorably with numerical values obtained by means of the monodromy matrix method.

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Since Wannier's seminal work [1] it has become clear that electronic correlations play a crucial role in the structure of two-electron systems [2]. For the past two decades extensive efforts in the classification of double excited states of two-electron systems have been made [3]. These studies suggest that collective quantization of two-electron systems is more valid than quantizing the individual angular momenta of each electron, as emphasized in Berry's paper [4]. Leopold and Percival [5] recognized that the failure of the old quantum theory was not due to the semiclassical approximation itself but rather due to its incomplete implementation. Modern semiclassical quantization introduced through invariant tori and Maslov indices is known as Einstein-Brillouin-Keller (EBK) quantization [6]. The EBK quantization formalism is applicable to the case of integrable systems, more generally, to systems whose motion is confined to an invariant torus. The Kolmogorov-Arnold-Moser theorem says that if a system is not too far from integrable (so-called quasi-integrable systems), most tori survive. The helium atom is a notorious nonintegrable system and a rigorous torus quantization is possible only for a stable island around periodic orbits. Gutzwiller [7] has shown how the spectra for nonintegrable systems can be obtained through the analysis of periodic orbits. It is this feature that underlies the importance of finding stable periodic orbits.

The stability of orbits is measured by the Lyapunov exponents, which for periodic orbits can be defined as logarithms of eigenvalues μ_i of a monodromy matrix $\lambda_i=\ln\mu_i/T$, where T is the period. The monodromy (stability) matrix $\mathcal{M}$ connects arbitrary infinitesimal variations in the initial conditions, with the corresponding changes of the orbits after one period. Since $\mathcal{M}$ is symplectic [8], all eigenvalues of $\mathcal{M}$ occur in pairs of inverses [9]. This leads to two possible cases. In one case, the eigenvalues have unit modules and are complex conjugates ($e^{\pm i\alpha}$), so the Lyapunov exponents are zero or imaginary. This is the stable case. In the other case, the eigenvalues are real and the Lyapunov exponents are larger than zero. This is the unstable case. Alternatively one considers trace $\mathrm{Tr}\mathcal{M}$ and finds that two-particle planar orbits (eight-dimensional phase space) are unstable if $\mathrm{Tr}\mathcal{M}<-4$ or $\mathrm{Tr}\mathcal{M}>8$.

The fundamental role of electronic correlations is revealed through the inherent instabilities which various semiclassical helium models imply. In this paper, we report the study on the stability of two-electron configurations with electrons moving symmetrically along elliptic orbits in a common plane. If $\mathbf{r}_{12}$ and $\mathbf{r}_{13}$ are electron radius vectors relative to the nucleus, we define an angle ϑ between these two vectors and a "mock" angle $\alpha=\arctan(r_{13}/r_{12})$. In this case we have motion on the Wannier ridge ($\alpha=\pi/4$) with $\vartheta=\pi$, so two-electron excitations with this configuration are often called "Wannier ridge states." In independent-particle models we have stable motion for arbitrary configurations. For example, excluding the interaction between electrons for this configuration, we obtain $\mathrm{Tr}\mathcal{M}=8$ (all $\mu_i=1$). After including the interaction this becomes $\mathrm{Tr}\mathcal{M}>8$, with this value and Lyapunov exponents depending on eccentricities of ellipses ε (i.e., angular momenta $l_2=l_3$ of each electron).

In the case of circular orbits ($\varepsilon=0$), Lyapunov exponents can be obtained analytically, calculating small variations around the solution on the Wannier ridge, as shown for the case of gravitational interaction [10]. (A similar method has been used before to calculate threshold exponents for three-body fragmentation processes [11].)

Newton equations for a Coulombic three-particle system with identical particles 2 and 3 ($m_1=M$, $m_2=m_3=m$, $q_1=Zq$, and $q_2=q_3=-q$) in the center-of-mass reference frame read

$$\frac{m(M+m)}{M+2m}\ddot{\mathbf{r}}_{12}-\frac{m^2}{M+2m}\ddot{\mathbf{r}}_{13}=-\frac{Zq^2}{r_{12}^3}\mathbf{r}_{12}+\frac{q^2}{|\mathbf{r}_{12}-\mathbf{r}_{13}|^3}(\mathbf{r}_{12}-\mathbf{r}_{13}) , \quad (1a)$$

$$-\frac{m^2}{M+2m}\ddot{\mathbf{r}}_{12}+\frac{m(M+m)}{M+2m}\ddot{\mathbf{r}}_{13}=-\frac{Zq^2}{r_{13}^3}\mathbf{r}_{13}-\frac{q^2}{|\mathbf{r}_{12}-\mathbf{r}_{13}|^3}(\mathbf{r}_{12}-\mathbf{r}_{13}) , \quad (1b)$$

where $\mathbf{r}_{1i}=\mathbf{r}_1-\mathbf{r}_i$ ($i=2,3$) are radius vectors of identical particles relative to the particle 1. The rigid-rotator solution is

$$\mathbf{r}_{12}=-\mathbf{r}_{13}=\mathbf{r} , \quad r=\text{const} , \quad (2)$$

which upon substituting into (1a) and (1b) gives, in polar coordinates,

$$r^3=\frac{q^2}{m}\frac{Z-\frac{1}{4}}{\Omega^2}\ ,\quad \Omega\equiv\dot{\varphi}=\text{const.} \tag{3}$$

One introduces now small variations around the circular solutions

$$\mathbf{r}_{12}=\mathbf{r}+\boldsymbol{\delta}_1+\boldsymbol{\delta}_2\ , \tag{4a}$$

$$\mathbf{r}_{13}=-\mathbf{r}+\boldsymbol{\delta}_1+\boldsymbol{\delta}_2\ , \tag{4b}$$

$$\boldsymbol{\delta}_1\|\mathbf{r},\quad \boldsymbol{\delta}_1\perp\boldsymbol{\delta}_2\quad(\delta_{1,2}\ll r)\ . \tag{4c}$$

Inserting (4a) and (4b) into (1a) and (1b) we get

$$\ddot{\delta}_1-2\Omega\dot{\delta}_2=\Lambda_1\delta_1\ , \tag{5a}$$

$$\ddot{\delta}_2+2\Omega\dot{\delta}_1=\Lambda_2\delta_2\ , \tag{5b}$$

where

$$\Lambda_1=\frac{12Z-1+16Zm/M}{4Z-1}\Omega^2\ , \tag{6a}$$

$$\Lambda_2=-\frac{1+8Zm/M}{4Z-1}\Omega^2\ . \tag{6b}$$

Equations (5a) and (5b) are equivalent to

$$\delta_{1,2}^{(iv)}+(4\Omega^2-\Lambda_1-\Lambda_2)\ddot{\delta}_{1,2}+\Lambda_1\Lambda_2\delta_{1,2}=0\ , \tag{7}$$

with the general solution

$$\delta_{1,2}=\sum_{i=1}^{4}c_i^{(1,2)}e^{\lambda_i t}\ , \tag{8}$$

where Lyapunov exponents are the roots of characteristic equation

$$\lambda^4+(4\Omega^2-\Lambda_1-\Lambda_2)\lambda^2+\Lambda_1\Lambda_2=0 \tag{9}$$

which read

$$\lambda_{1-4}^2=\frac{\Lambda_1+\Lambda_2-4\Omega^2}{2}\pm\tfrac{1}{2}\sqrt{(4\Omega^2-\Lambda_1-\Lambda_2)^2-4\Lambda_1\Lambda_2}\ . \tag{10}$$

It should be noted that the c_i in (8) are not arbitrary, but are constrained by

$$\frac{c_1^{(2)}}{c_i^{(1)}}=\frac{2\Omega\lambda_i}{\Lambda_2-\lambda_i^2}\ . \tag{11}$$

From (6a) and (6b) one has

$$\frac{\lambda^2}{\Omega^2}=\frac{1-2Z+4Zm/M}{4Z-1}\pm\frac{2}{4Z-1}\sqrt{(1+2m/M)(Z^2+2Z+18Z^2m/M)} \tag{12}$$

and

$$\frac{c_i^{(2)}}{c_i^{(1)}}=-\frac{2(4Z-1)\lambda_i/\Omega}{1+8Zm/M+(4Z-1)\lambda_i^2/\Omega^2}\ . \tag{13}$$

The eigenvalues of the monodromy matrix are $\mu_i=e^{\lambda_i T}$. Using (12) we get μ_i $(i=1,2,3,4)$. The remaining four eigenvalues are units ($\lambda_{5,6}=0$ and $\lambda_{7,8}=\pm\Omega i$) and correspond to the case when variations of the electrons are of the opposite sign: $\delta_i^{(1)}=-\delta_i^{(2)}$. Then the trace of the monodromy matrix is

$$\mathrm{Tr}\mathcal{M}=\sum_{i=1}^{8}\mu_i=\sum_{i=1}^{4}e^{2\pi\lambda_i/\Omega}+4\ . \tag{14}$$

Note that $\mathrm{Tr}\mathcal{M}$ is not a function of Ω because all λ_i are directly proportional to Ω.

In Fig. 1(a) we plot λ_i^2/Ω^2 against the mass ratio m/M for a few values of Z. It can be seen that the systems with smaller m/M are less unstable. In the case of helium and heliumlike ions the results obtained by taking the exact value of the nucleus mass ($m/M\sim10^{-4}$) are slight-

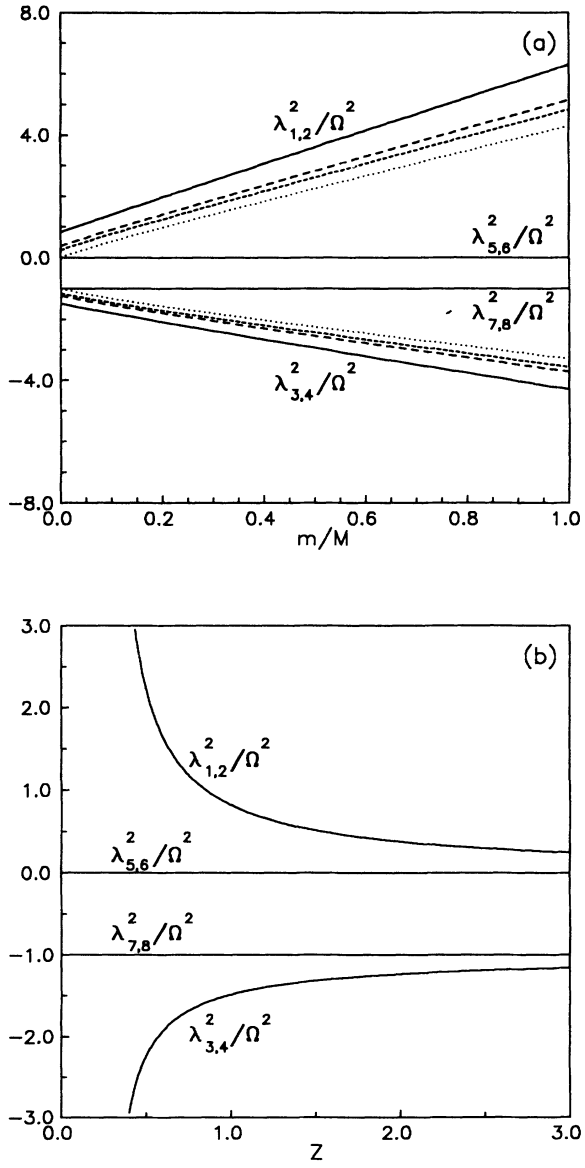

FIG. 1. (a) λ_i^2/Ω^2 $(i=1,\ldots,8)$ against the mass ratio m/M for circular orbits with various Z values: $Z=1,2,3,100$ (from above for $\lambda_{1,2}^2/\Omega^2$ and from below for $\lambda_{3,4}^2/\Omega^2$). (b) λ_i^2/Ω^2 against Z for circular orbits in the limit $M\to\infty$.

ly different from those in the approximation of infinitely heavy nucleus ($m/M=0$). In Fig. 1(b) λ_i^2/Ω^2 against Z is shown in this approximation. As can be seen from (12) only $Z>\frac{1}{4}$ are allowed. This is a characteristic feature of all configurations on the Wannier ridge, for both bound and continuous states. Analogous analytical results [Eq. (12) in the limit $M\to\infty$] have been obtained by Poirier [12] by analyzing linearized equations of motion in the rotating frame of reference.

Let us first consider one unusual case of two-electron systems that cannot be treated in the approximation of an infinitely heavy nucleus: $e^-e^+e^-$ system ($Z=1$ and $m/M=1$). In this case (12) reduces to

$$\frac{\lambda^2}{\Omega^2}=1\pm2\sqrt{7}\ , \tag{15}$$

giving $\lambda_{1,2}/\Omega=\pm2.508\,287$, $\lambda_{3,4}/\Omega=\pm2.071\,594i$, and $\mathrm{Tr}\mathcal{M}=6.990\,29\times10^6$, so it is clear that the configuration considered for this system is highly unstable.

We consider now the most interesting case of helium ($Z=2$ and $M\to\infty$) in more detail. It follows that

$$\frac{\lambda^2}{\Omega^2}=\frac{-3\pm4\sqrt{2}}{7}\ . \tag{16}$$

Thus $\lambda_{1,2}/\Omega=\pm0.616\,077$, $\lambda_{3,4}/\Omega=\pm1.112\,067i$, and $\mathrm{Tr}\mathcal{M}=53.531\,912$. (Exact values for the helium atom by taking $m/M=1.371\times10^{-4}$ are $\lambda_{1,2}/\Omega=\pm0.616\,698$, $\lambda_{3,4}/\Omega=\pm1.112\,271i$, and $\mathrm{Tr}\mathcal{M}=53.717\,876$.)

From (13) we have

$$\frac{c_i^{(2)}}{c_i^{(1)}}=\mp\frac{\sqrt{-21\pm28\sqrt{2}}}{-1\pm2\sqrt{2}}=\begin{cases}\mp2.358\,605\\ \pm2.033\,334i\ .\end{cases} \tag{17}$$

The general solution (8) now takes the explicit form

$$\delta_1(t)=c_1e^{\lambda_1 t}+c_2e^{-\lambda_1 t}+c_3e^{\lambda_3 t}+c_4e^{-\lambda_3 t}\ , \tag{18a}$$

$$\delta_2(t)=-2.358\,605(c_1e^{\lambda_1 t}-c_2e^{-\lambda_1 t})+2.033\,334i(c_3e^{\lambda_3 t}-c_4e^{-\lambda_3 t})\ . \tag{18b}$$

Radial and transversal variations of the electron impulses are

$$\delta p_r=\dot\delta_1-\Omega\delta_2\ ,\quad \delta p_\varphi=\dot\delta_2+\Omega\delta_1\ . \tag{19}$$

According to (4a) and (4b), variations for both electrons are the same. Introducing vectors of small variations in the two-electron phase space

$$Z(t)=[\delta_1^{(1)}(t),\delta_2^{(1)}(t),\delta p_r^{(1)}(t),\delta p_\varphi^{(1)}(t),\delta_1^{(2)}(t),\delta_2^{(2)}(t),\delta p_r^{(2)}(t),\delta p_\varphi^{(2)}(t)]\ , \tag{20}$$

and by taking successively single nonzero c_i one obtains eigenvectors $Z_i\equiv Z_i(0)$ of the monodromy matrix for the corresponding eigenvalues μ_i ($i=1,2,3,4$).

For a circular orbit with the ground-state energy ($E=-3.0625$ a.u.), the angular frequency is $\Omega=\frac{49}{16}$ a.u., which yields

$$\lambda_{1,2}=\pm1.886\,735,\quad \lambda_{3,4}=\pm3.405\,706i \tag{21}$$

with the corresponding eigenvectors

$$Z_{1,2}=\begin{bmatrix}1.0\\ \mp2.358\,605\\ \pm9.109\,963\\ -1.387\,563\\ 1.0\\ \mp2.358\,605\\ \pm9.109\,963\\ -1.387\,563\end{bmatrix},\qquad Z_{3,4}=\begin{bmatrix}1.0\\ \pm2.033\,334i\\ \mp2.821\,379i\\ -3.862\,438\\ 1.0\\ \pm2.033\,334i\\ \mp2.821\,379i\\ -3.862\,438\end{bmatrix}. \tag{22}$$

These analytical results appear in remarkably good agreement with the numerical results shown in the first row in Table I. Using the so-called monodromy method [13] (originally developed for the case of a single particle), extended for the case of two particles [14], we have evaluated two-electron orbits with $\varepsilon\geq0$ and their monodromy matrices. One starts with an approximate discretized periodic orbit and finds an exact (also discretized) orbit of a given period T using an iterative procedure which is a variant of the Newton-Raphson method. Discretization consists in dividing each orbit into N segments with a constant step $\Delta t=T/N$. The eigenvalues and trace of the monodromy matrix, and the Lyapunov exponent λ_1, the single one, which corresponds to unstable degrees of freedom (others are zero or imaginary), are shown in Table I for these orbits with different eccentricities ε and the same energy ($E=-3.0625$ a.u.) and nuclear charge ($Z=2$). Orbits are calculated with $N=1500$ segments, which gives in that case sufficient numerical accuracy up to $\varepsilon=0.9$ (a convenient test for this can be the check of the accuracy of the four eigenvalues equal to 1). Extrapolating the function $\lambda_1(\varepsilon)$ to $\varepsilon>0.9$, it is clear that λ_1 diverges for $\varepsilon=1$.

The eccentricity $\varepsilon=\sqrt{3}/2$ corresponds to the orbit with individual angular momenta of each electron $l_2=l_3=\frac{1}{2}$ (implying zero orbital quantum numbers of each electon, within the quantization procedure of individual angular momenta). Eigenvectors of the monodromy matrix are also calculated numerically and are in good agreement with those given by (22). The agreement between analytical and numerical calculations for the case $\varepsilon=0$ confirms that the monodromy matrix method is useful for such calculations. On the other hand, it is shown

TABLE I. Stability parameters for elliptic two-electron orbits with $Z=2$ and ground-state energy $E=-3.0625$ a.u. (period $T=2.051\,65$ a.u.) as functions of eccentricities ε.

ε	$\mu_1(\mu_2^{-1})$	$\mu_{3,4}$	$\mu_5(\mu_6^{-1})$	$\mu_7(\mu_8^{-1})$	TrM	λ_1
0.0	47.987	$0.7622\pm0.6474i$	1.0001	1.0000	53.5319	1.8867
0.1	49.286	$0.7610\pm0.6487i$	1.0061	1.0001	54.8288	1.8998
0.2	53.492	$0.7575\pm0.6529i$	1.0001	1.0000	59.0254	1.9397
0.3	61.682	$0.7511\pm0.6602i$	1.0002	1.0000	67.2005	2.0091
0.4	76.356	$0.7411\pm0.6714i$	1.0047	1.0002	81.8513	2.1131
0.5	103.31	$0.7259\pm0.6878i$	1.0034	1.0000	108.771	2.2605
0.6	157.68	$0.7025\pm0.7117i$	1.0064	1.0001	163.094	2.4666
0.7	288.43	$0.6647\pm0.7472i$	1.0156	1.0001	293.768	2.7602
0.8	725.22	$0.5963\pm0.8027i$	1.0438	1.0005	730.415	3.2103
$\sqrt{3}/2$	1890.8	$0.5110\pm0.8596i$	1.1849	1.0001	1895.86	3.6774
0.9	3868.9	$0.4361\pm0.8999i$	5.3000	$1.0000\pm0.0018i$	3877.31	4.0264

that the first-order perturbation theory is sufficient to obtain analytically exact values (as is expected due to the infinitesimal variations).

As for the physical meanings of these results, note that all orbits are unstable, but the orbit with $\varepsilon=0$ (circular) appears less so. For $\varepsilon\rightarrow1$, ellipses degenerate to straight lines, so in that case we have a collinear symmetric two-electron configuration (so-called "symmetric-stretching mode"), which is extremely unstable. As a consequence, this implies that this kind of two-electron configuration cannot be associated with resonant structures in quantum spectra. This conclusion is in agreement with inferences due to Richter and Wintgen [15]. Recent studies indicate that intrashell resonances of heliumlike systems should be associated with the "asymmetric-stretching mode" rather than the symmetric one [16]. This suggestion could be extended to the corresponding planar configurations. The results of these investigations will be presented elsewhere.

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