Possible rigid rotations in two-electron atoms

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The path-integral formulation of quantum mechanics has promoted the study of classical periodic trajectories. In this spirit, the three-body Coulomb problem with a nucleus of infinite mass is considered in the special case of a rigid rotation. Using only Newton's fundamental law for a classical atomic system, one can show that both electrons must be equidistant from the nucleus, and one obtains the solutions previously derived by Klar [Phys. Rev. Lett. **57**, 66 (1986); Z. Phys. D **3**, 353 (1986); J. Opt. Soc. Am. B **4**, 788 (1987)]. Nevertheless, if one allows the charge at rest to be arbitrary, one finds that for Z less than unity unsymmetrical solutions may exist. The stability of each of these configurations is considered. In each case an exponentially increasing solution is present, but the unstable character is less marked in the unsymmetrical configuration. Possible consequences for atomic systems are discussed.

I. INTRODUCTION

The remarkable successes of quantum mechanics in modern physics have established it as the only valuable tool in the interpretation of microscopic phenomena. However, considerations from classical mechanics may be really useful in various cases, especially concerning states with some "classical character" such as the Rydberg levels.[1] Besides, it came to the physicist's attention a few decades ago that some intrinsically quantal values could be extracted from a classical-mechanics analysis through the correspondence principle.[2] Though its applicability range is *a priori* restricted, it has been shown that a suitable choice of the classical trajectory parameters gives correct values for a wide variety of matrix elements.[3] Furthermore, the exact quantal computation of certain matrix elements may be cumbersome, while their corresponding semiclassical expression remains tractable.[4] In addition, some years ago it was pointed out by several authors[5,6] that, using a path-integral formulation of quantum mechanics, the spectrum for nonintegrable systems can be derived through the analysis of periodic orbits. Moreover, classical mechanics came back to the foreground of modern physics quite recently in connection with the domain of chaos.[7,8] This revival of classical-mechanics studies suggests their application to atomic spectroscopy and more explicitly to doubly excited states, which are now under active investigation.[9,10] It should be remembered that the pioneering work by Wannier[11] on multiple ionization was based on a classical analysis. In the same spirit, Klar[12] has recently demonstrated that rigid configurations exist in two-electron atoms. Several justifications can be found to this approach. One then has the ability to describe atomic systems with *strongly correlated electrons.* While the three-body problem is not separable in classical mechanics and thus cannot lead to quantization via Bohr's correspondence principle, the search for stable periodic orbits may allow quantization using the approach of Gutzwiller.[5,8] This description relates the doubly excited atom spectroscopy to the more familiar molecular spectroscopy. Finally the well-known Wannier configuration[11] appears as a special case of such rigid configurations. Klar uses a top description of the "solid" formed by the two electrons and the nucleus, and the equations of motion are derived through a six-variable Lagrangian formalism. In this paper we would like to show that such a motion may be studied in an alternative and perhaps simpler way using the fundamental law of point dynamics. For atomic systems, our derivation explicitly establishes that the distance of both electrons to the nucleus is equal. This symmetry property arises from the explicit expression of the Coulomb force, and from the fact that the nucleus charge Z is at least equal to 1. We then show here that removing this constraint leads to unsymmetrical solutions; a partially screened nucleus charge could give a physical image of this situation. Furthermore, a stability analysis of such solutions provides pieces of information about the spectrum of doubly excited states as well as a classical picture for autoionization, which has been developed in an alternate way by other authors.[13]

II. BASIC FORMALISM

Rotating rigid solutions for the classical N-body problem have been recently investigated by Gerver[14] in the case of N particles with equal masses and charges of equal absolute values, with N ranging from 3 to 5. Our present aim is to search for solutions to the three-body problem in classical mechanics where the distances $|\mathbf{r}_1|$ and $|\mathbf{r}_2|$ from each electron to the nucleus and their mutual distance $|\mathbf{r}_{12}|$ are time independent. In this work, the nucleus is assumed to be at rest at the origin of the coordinates. If the attractive force acting on electron n is written $-\varphi_n \mathbf{r}_n$, and if the repulsive force on electron 1 (2) is $-\phi(r_{12})\mathbf{r}_{12}$ $[+\phi(r_{12})\mathbf{r}_{12}]$, the classical equations of motion are

$$\frac{d^2\mathbf{r}_1}{dt^2} = -(\varphi_1-\phi)\mathbf{r}_1 - \phi\mathbf{r}_2 \ , \tag{1a}$$

$$\frac{d^2\mathbf{r}_2}{dt^2}=-\phi\mathbf{r}_1-(\varphi_2-\phi)\mathbf{r}_2 \ . \tag{1b}$$

For the Coulomb interaction one has

$$\varphi_n=\frac{Z}{r_n^3} \ , \tag{2a}$$

$$\phi=\frac{1}{r_{12}^3} \ . \tag{2b}$$

Atomic units are used throughout. Since all distances are kept fixed, the basic differential system (1) is linear with time-independent coefficients. Its general solution is a linear combination of exponentials. The nature of system (1) ensures that scalar variables are coupled pair by pair ($\hat{\mathbf{u}}$ being any of the three fixed rectangular axes, $\mathbf{r}_1\cdot\hat{\mathbf{u}}$ is only coupled to $\mathbf{r}_2\cdot\hat{\mathbf{u}}$). This system is simpler than true solid-motion equations, where the various angular motions are coupled.

Since (1) is a second-order system, the general solution is a combination of four exponentials. Due to time-reversal invariance, if $e^{i\Omega t}$ is a solution, $e^{-i\Omega t}$ is a solution too. Writing

$$\mathbf{r}_n(t)=\mathbf{r}_n(\Omega)e^{i\Omega t} \quad (n=1,2) \ , \tag{3}$$

where $\mathbf{r}_n(\Omega)$ is taken as a *time-independent, possibly complex* value, system (1) transforms into

$$(\Omega^2-\varphi_1+\phi)\mathbf{r}_1(\Omega)-\phi\mathbf{r}_2(\Omega)=0 \ , \tag{4a}$$

$$-\phi\mathbf{r}_1(\Omega)+(\Omega^2-\varphi_2+\phi)\mathbf{r}_2(\Omega)=0 \ . \tag{4b}$$

The secular equation is even with respect to Ω and is written as

$$(S-\Omega^2)(S-2\phi-\Omega^2)-D^2=0 \ , \tag{5}$$

where

$$S=\tfrac{1}{2}(\varphi_1+\varphi_2) \ , \tag{6a}$$

$$D=\tfrac{1}{2}(\varphi_2-\varphi_1) \ . \tag{6b}$$

Its solutions are

$$\Omega^2=S-\phi\pm(D^2+\phi^2)^{1/2}=\begin{cases}\Omega'^2\\ \Omega''^2.\end{cases} \tag{7}$$

Since ϕ never cancels [see definition (2b)], Ω' and Ω'' are always distinct. The only possible "degeneracy" occurs when one of the roots cancels. This case is explicitly studied below.

III. SOLUTION IN THE NONDEGENERATE CASE

Assuming *nondegeneracy,* the general solution of (1) may be written as

$$\mathbf{r}_1(t)=\mathbf{C}'\cos\Omega' t+\mathbf{S}'\sin\Omega' t+\mathbf{C}''\cos\Omega'' t+\mathbf{S}''\sin\Omega'' t \ , \tag{8}$$

where the constant vectors $\mathbf{C}'$, $\mathbf{C}''$, $\mathbf{S}'$, and $\mathbf{S}''$ are real. We now express the condition that $|\mathbf{r}_1(t)|^2$ must be *time independent.* Expanding the square of expression (8) and cancelling each coefficient at nonzero frequency, one easily verifies that

$$\mathbf{C}'\cdot\mathbf{S}'=\mathbf{C}''\cdot\mathbf{S}''=\mathbf{C}'\cdot\mathbf{C}''=\mathbf{S}'\cdot\mathbf{S}''=\mathbf{C}'\cdot\mathbf{S}''=\mathbf{S}'\cdot\mathbf{C}''=0 \ , \tag{9a}$$

$$\mathbf{C}'^2-\mathbf{S}'^2=\mathbf{C}''^2-\mathbf{S}''^2=0 \ . \tag{9b}$$

The four vectors $\mathbf{C}'$, $\mathbf{C}''$, $\mathbf{S}'$, and $\mathbf{S}''$ are orthogonal. In the three-dimensional space, one of them must be of null length, and because of (9b), only one frequency is present:

$$\mathbf{r}_1(t)=\mathbf{r}_1'(t)\equiv\mathbf{C}'\cos\Omega' t+\mathbf{S}'\sin\Omega' t \ , \tag{10}$$

with $|\mathbf{C}'|=|\mathbf{S}'|$ and $\mathbf{C}'\cdot\mathbf{S}'=0$; an alternate expression holds when changing primes to double primes. Using Eq. (4a) one gets

$$\mathbf{r}_2(t)=\mathbf{r}_2'(t)=\frac{(\Omega')^2-\varphi_1+\phi}{\phi}\mathbf{r}_1'(t)$$
$$=\frac{(\Omega')^2-\varphi_1+\phi}{\phi}(\mathbf{C}'\cos\Omega' t+\mathbf{S}'\sin\Omega' t) \ , \tag{11}$$

and a similar expression for $\mathbf{r}_2''(t)$. Inspection of formulas (10) and (11) immediately shows that $\mathbf{r}_1(t)$ and $\mathbf{r}_2(t)$ follow a *uniform circular motion* at the same frequency and are *colinear.* Then, one demonstrates very simply that these vectors must be opposite. Clearly, both electrons cannot be on the same side of the nucleus because they repel each other and because $\varphi(r)$ is a decreasing function. Alternatively, if the electrons are on both sides of the nucleus, writing the equilibrium equation for each electron gives

$$-r_{12}\phi=-r_1\varphi_1+\Omega^2 r_1=-r_2\varphi_2+\Omega^2 r_2 \ . \tag{12}$$

Assuming here that $r\varphi(r)$ is a *decreasing* function [the Coulomb force (2a) fulfills this condition], the quantity $-r\varphi(r)+\Omega^2 r$ is thus monotonically increasing and Eq. (12) implies

$$r_1=r_2 \ . \tag{13}$$

In the "nondegenerate" case, the position vectors of both electrons $\mathbf{r}_1$ and $\mathbf{r}_2$ are opposite and undergo a uniform circular motion. This is the rotor (or Wannier) configuration.

IV. SOLUTION IN THE DEGENERATE CASE

Let us now consider the "degenerate" case where *the frequency Ω'' cancels* [Ω'^2 never cancels since from (7) this quantity is always greater than $(\varphi_1+\varphi_2)/2$]. From Eq. (7) and definition (6) one derives the degeneracy condition

$$\frac{1}{\phi}=\frac{1}{\varphi_1}+\frac{1}{\varphi_2} \ . \tag{14}$$

An analysis completely similar to the one for the "nondegenerate" case shows that

$$\mathbf{r}_1(t)=\mathcal{R}+\mathcal{T} \ . \tag{15a}$$

In (15a), $\mathcal{R}$ is a rotating vector at frequency Ω'

$$\mathcal{R}=\mathbf{C}'\cos\Omega' t+\mathbf{S}'\sin\Omega' t \tag{15b}$$

and $\mathcal{J}$ is a time-independent vector. The invariance of $|\mathbf{r}_1(t)|^2$ ensures that

$$\mathbf{C}'\cdot\mathbf{S}'=0\ , \tag{15c}$$

$$\mathbf{C}'^2-\mathbf{S}'^2=0\ , \tag{15d}$$

$$\mathcal{R}\cdot\mathcal{J}=0\ . \tag{15e}$$

Relation (4a) allows us to derive the components $\mathbf{r}_2(\Omega')$ and $\mathbf{r}_2(\Omega''=0)$. Using the degeneracy condition (14), one readily obtains

$$\mathbf{r}_2(t)=\frac{\varphi_2}{\varphi_1}\mathcal{R}-\frac{\varphi_1}{\varphi_2}\mathcal{J}\ . \tag{16}$$

The relative position $\mathbf{r}_{12}$ is thus

$$\mathbf{r}_{12}\equiv\mathbf{r}_2-\mathbf{r}_1=\left[\frac{\varphi_2}{\varphi_1}-1\right]\mathcal{R}-\left[1+\frac{\varphi_1}{\varphi_2}\right]\mathcal{J}\ . \tag{17}$$

Using relations (15a), (15e), (16), and (17) one can express $\mathbf{r}_1^2$, $\mathbf{r}_2^2$, and $\mathbf{r}_{12}^2$ as functions of $\mathcal{R}^2$ and $\mathcal{J}^2$:

$$\mathbf{r}_1^2=\left[\frac{Z}{\varphi_1}\right]^{2/3}=\mathcal{R}^2+\mathcal{J}^2\ , \tag{18a}$$

$$\mathbf{r}_2^2=\left[\frac{Z}{\varphi_2}\right]^{2/3}=\left[\frac{\varphi_2}{\varphi_1}\right]^2\mathcal{R}^2+\left[\frac{\varphi_1}{\varphi_2}\right]^2\mathcal{J}^2\ , \tag{18b}$$

$$\mathbf{r}_{12}^2=\phi^{-2/3}=\left[\frac{\varphi_2-\varphi_1}{\varphi_1}\right]^2\mathcal{R}^2+\left[\frac{\varphi_1+\varphi_2}{\varphi_2}\right]^2\mathcal{J}^2\ . \tag{18c}$$

Two cases must be distinguished here. If the attractive forces are such that

$$\varphi_1=\varphi_2\ , \tag{19}$$

one deduces from (16)

$$\mathbf{r}_2(t)=\mathcal{R}-\mathcal{J}\ , \tag{20a}$$

and from (14) and (18c),

$$\mathcal{J}^2=\frac{r_1^2}{(4Z)^{2/3}}\ , \tag{20b}$$

$$\mathcal{R}^2=\left[1-\frac{1}{(4Z)^{2/3}}\right]r_1^2\ . \tag{20c}$$

This is Klar's solution.[12] The positions $\mathbf{r}_1$ and $\mathbf{r}_2$ are symmetrical with respect to a plane perpendicular to the rotation axis $\mathcal{J}$.

A second case needs further consideration. If the quantities φ_1 and φ_2 are no longer equal, one can solve the system (18a), (18b) with respect to $\mathcal{R}^2$ and $\mathcal{J}^2$ and obtain

$$\mathcal{R}^2=Z^{2/3}\varphi_1^2\frac{\varphi_2^{4/3}-\varphi_1^{4/3}}{\varphi_2^4-\varphi_1^4}\ , \tag{21a}$$

$$\mathcal{J}^2=\left[\frac{Z}{\varphi_1\varphi_2}\right]^{2/3}\varphi_2^2\frac{\varphi_2^{8/3}-\varphi_1^{8/3}}{\varphi_2^4-\varphi_1^4}\ . \tag{21b}$$

Introducing the values (21) in (18c) we get

$$\begin{aligned}\phi^{-2/3}&=\left[\frac{\varphi_1+\varphi_2}{\varphi_1\varphi_2}\right]^{2/3}\\&=\left[\frac{Z}{\varphi_1\varphi_2}\right]^{2/3}\frac{\varphi_2^{4/3}-\varphi_1^{4/3}}{\varphi_2^4-\varphi_1^4}\\&\quad\times[(\varphi_1\varphi_2)^{2/3}(\varphi_2-\varphi_1)^2\\&\quad+(\varphi_1^{4/3}+\varphi_2^{4/3})(\varphi_1+\varphi_2)^2]\ .\end{aligned} \tag{22}$$

If we define the ratio

$$r\equiv\frac{r_1}{r_2}=\left[\frac{\varphi_2}{\varphi_1}\right]^{1/3}\ , \tag{23}$$

after some elementary algebra, Eq. (22) transforms into

$$(1+r^3)^{2/3}=Z^{2/3}\left[1+r^2+\frac{2r^3}{1+r^2+r^4}\right]\ . \tag{24}$$

Since r is essentially positive, one clearly has from (24)

$$(1+r^3)^{2/3}>Z^{2/3}(1+r^2)>Z^{2/3}(1+r^3)^{2/3}\ . \tag{25}$$

Inequalities (25) cannot be satisfied for atomic systems in which Z is at least equal to 1. Thus for $Z\geq 1$, relation (13) holds and Klar's solutions are the only ones possible. Nevertheless, it is worth noting that (24) may be fulfilled for r different from 1 in systems such that Z is *less than unity*. This remark applies for classical charged systems with moving particles of charge $+Z_1$ and a fixed particle of charge $-Z_2$ with Z_2 less than Z_1. It could possibly apply to atomic systems with a nucleus partially screened by inner electrons.

The relation between Z and r as stated by (24) is plotted in Fig. 1. It proves that when

$$1>Z>\tfrac{1}{4}(\tfrac{3}{2})^{3/2}\simeq 0.459\ , \tag{26}$$

Eq. (25) for r admits a real solution between 0 and 1. An example of such an unsymmetrical configuration is illustrated by Fig. 2, in the case $Z=\frac{1}{2}$. When Z tends to the minimum value stated in (26), the ratio r tends to unity; $\mathbf{r}_1(t)$ and $\mathbf{r}_2(t)$ are then symmetrical with respect to the

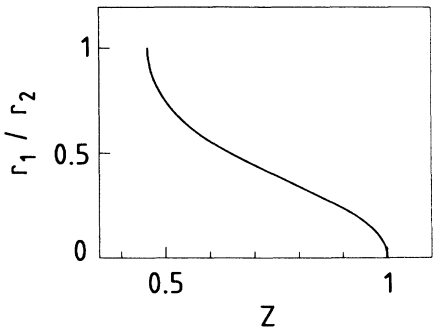

FIG. 1. Ratio of the electronic distances from the nucleus as a function of the fixed charge Z in the unsymmetrical configuration.

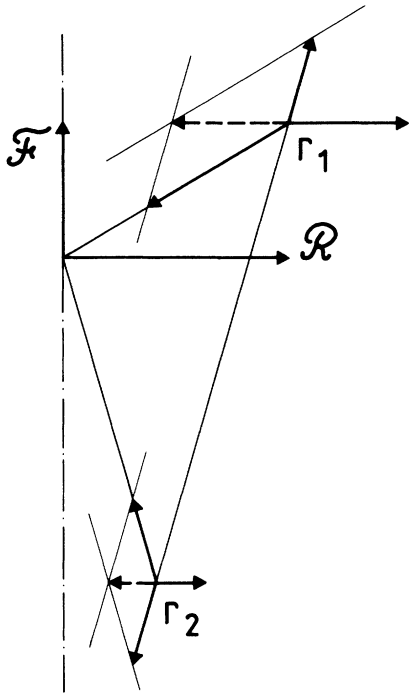

FIG. 2. Example of an unsymmetrical configuration in the case $Z=\frac{1}{2}$. The ratio r_1/r_2 is here equal to $(2^{1/2}-1)^{1/3}\simeq 0.745$, and the squared rotation frequency is $\Omega^2=(2^{1/2}-1)/r_1^3=1/r_2^3$. The rotation axis is parallel to $\mathcal{F}$. Coulombic and centrifugal forces are indicated for each electron.

plane containing the nucleus and orthogonal to $\mathcal{F}$. Then if Z increases, the dissymmetry gets higher and higher. In the limit of Z close to unity, the ratio r tends to zero; one electron then moves in a plane almost containing the nucleus, while the other describes a small circle around the angular momentum axis (the $\mathcal{F}$ direction) far from the nucleus. We then have a picture of an atom with weakly correlated electrons. Of course when (26) is fulfilled, the symmetrical geometry characterized by (13) and (20) is also possible. When varying r from 0 to 1, one therefore has classical solutions varying continuously from unsymmetrical to symmetrical motion, or in other words from a situation of independent electrons to a situation of strongly correlated electrons. Besides, the presence of several equilibrium states may increase the stability of the system, as is discussed below.

V. STABILITY ANALYSIS

A. General

Once the classical rotation motions have been characterized, one has to analyze their stability properties. Using traditional methods of classical mechanics,[15] we consider small perturbations around the derived solutions, linearize the equations of motion, and look at the characteristic frequencies. For Hamiltonian systems, this method is equivalent to the analysis of Liapunov's characteristic exponents.[16]

The linearized equation of motion for particle 1 in the rotating frame is

$$\delta\ddot{\mathbf{r}}_1=Z\frac{3\hat{\mathbf{r}}_1^0(\delta\mathbf{r}_1\cdot\hat{\mathbf{r}}_1^0)-\delta\mathbf{r}_1}{|\mathbf{r}_1^0|^3}-\frac{3\hat{\mathbf{r}}_{12}^0(\delta\mathbf{r}_{12}\cdot\hat{\mathbf{r}}_{12}^0)-\delta\mathbf{r}_{12}}{|\mathbf{r}_{12}^0|^3}$$
$$-2\boldsymbol{\Omega}\times\delta\dot{\mathbf{r}}_1-\boldsymbol{\Omega}\times(\boldsymbol{\Omega}\times\delta\mathbf{r}_1)\ , \tag{27}$$

where $\mathbf{r}_1^0$ is the unperturbed position for particle 1, as determined above, and $\mathbf{r}_{12}^0$ is the difference $\mathbf{r}_2^0-\mathbf{r}_1^0$; $\hat{\mathbf{r}}_1^0$ and $\hat{\mathbf{r}}_{12}^0$ are the unit vectors in these directions. The linear equation (27) together with the corresponding equation for $\delta\mathbf{r}_2$ can be projected on three axes in the rotating frame. Let $\hat{\mathbf{i}}$ and $\hat{\mathbf{k}}$ be the unit vectors parallel to the rotating direction $\mathcal{R}$ and to the fixed direction $\mathcal{F}$, respectively, and let $\hat{\mathbf{j}}$ be $\hat{\mathbf{k}}\times\hat{\mathbf{i}}$. One writes for each electron and for their relative position their unperturbed coordinates in this rotating frame:

$$\hat{\mathbf{r}}_n^0=\cos\theta_n\hat{\mathbf{i}}+\sin\theta_n\hat{\mathbf{k}}\quad(n=1,2)\ , \tag{28a}$$

$$\hat{\mathbf{r}}_{12}^0=\cos\Theta\hat{\mathbf{i}}+\sin\Theta\hat{\mathbf{k}}\ . \tag{28b}$$

In the case considered by Klar, θ_n is $\pm$ arcsin $[(4Z)^{-1/3}]$ [see (20b)] and Θ is $-\pi/2$. In the Wannier configuration, the above formulas apply with $\theta_1=0$, $\theta_2=\Theta=\pi$. If we are looking at harmonic oscillations, $\delta\mathbf{r}_1$ and $\delta\mathbf{r}_2$ vary as

$$\delta\mathbf{r}_n(t)=\delta\mathbf{r}_n(\omega)e^{i\omega t}\ , \tag{29a}$$

with

$$\delta\mathbf{r}_n(\omega)=x_n\hat{\mathbf{i}}+y_n\hat{\mathbf{j}}+z_n\hat{\mathbf{k}}\ . \tag{29b}$$

The amplitudes $\delta\mathbf{r}_n(\omega)$ of this displacement obey the matrix equation

$$\mathcal{M}\begin{bmatrix}\delta\mathbf{r}_1(\omega)+\delta\mathbf{r}_2(\omega)\\ \delta\mathbf{r}_2(\omega)-\delta\mathbf{r}_1(\omega)\end{bmatrix}=0\ . \tag{30}$$

The 6×6 matrix $\mathcal{M}$ is expressed in Table I versus the above-defined angles θ_n and Θ and versus the quantities φ_n and ϕ. In Eq. (30) a six-component vector is built with the sum and the difference $\delta\mathbf{r}_1(\omega)\pm\delta\mathbf{r}_2(\omega)$ to benefit from the symmetry in the exchange of the electrons. One has to search for the ω values cancelling the determinant of $\mathcal{M}$ and to analyze the corresponding motions; generally speaking, this determinant is a polynomial of sixth degree in ω^2. We will now study separately each of the above-distinguished cases: the Wannier configuration, and the Klar solution in the symmetrical and unsymmetrical cases.

B. Stability of the Wannier configuration

In the Wannier case, the characteristic frequencies can be found easily. Expressing the squared frequencies in units of Ω^2 (Ω is the angular frequency of rotation), one obtains the six solutions

$$\omega_1^2=0\ , \tag{31a}$$

$$\omega_2^2=\omega_3^2=1\ , \tag{31b}$$

TABLE I. Matrix elements of $\mathcal{M}$, involved in the stability analysis of rotating rigid configurations. X_n ($n=1,2$) being a quantity relative to electron n, one defines $\langle X\rangle \equiv (X_1+X_2)/2$, $\Delta X \equiv (X_2-X_1)/2$.

$$\mathcal{M}=\begin{bmatrix} M & P \\ P & M+N \end{bmatrix}, \quad M=\begin{bmatrix} \omega^2+a & 2ib\omega & d \\ -2ib\omega & \omega^2+c & 0 \\ d & 0 & \omega^2+e \end{bmatrix}, \quad P=\begin{bmatrix} f & 0 & g \\ 0 & h & 0 \\ g & 0 & j \end{bmatrix}, \quad N=\begin{bmatrix} A & 0 & D \\ 0 & C & 0 \\ D & 0 & E \end{bmatrix}$$

$a=\Omega^2-\langle\varphi(1-3\cos^2\theta)\rangle$	$f=-\Delta[\varphi(1-3\cos^2\theta)]$	$A=2\phi(1-3\cos^2\Theta)$
$b=\Omega$		
$c=\Omega^2-\langle\varphi\rangle$	$h=-\Delta\varphi$	$C=2\phi$
$d=3\langle\varphi\sin\theta\cos\theta\rangle$	$g=3\Delta(\varphi\sin\theta\cos\theta)$	$D=-6\phi\sin\Theta\cos\Theta$
$e=-\langle\varphi(1-3\sin^2\theta)\rangle$	$j=-\Delta[\varphi(1-3\sin^2\theta)]$	$E=2\phi(1-3\sin^2\Theta)$

$$\omega_4^2=\zeta\ , \tag{31c}$$

$$\omega_5^2=1-\frac{\zeta}{2}+\frac{1}{2}(9\zeta^2-8\zeta)^{1/2}\ , \tag{31d}$$

$$\omega_6^2=1-\frac{\zeta}{2}-\frac{1}{2}(9\zeta^2-8\zeta)^{1/2}\ , \tag{31e}$$

where

$$\zeta=\frac{Z}{Z-\frac{1}{4}}\ . \tag{31f}$$

These squared frequencies are plotted in Fig. 3 versus the parameter Z (which is the only variable in the present formalism).

The first three frequencies can be easily interpreted in terms of Keplerian motion. The zero frequency corresponds to a symmetrical motion in the $z_n=0$ plane. One obtains explicitly

$$x_1=-x_2=a\ , \tag{32a}$$

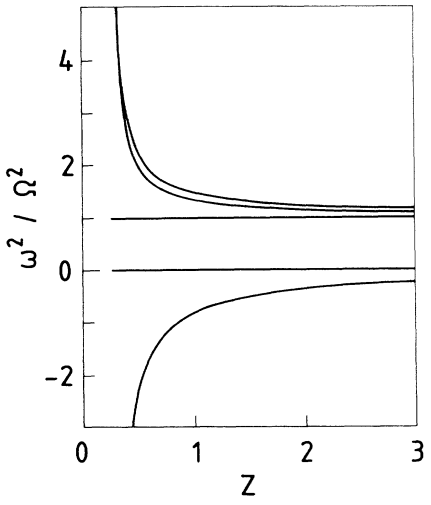

FIG. 3. Plot of the squared frequencies ω^2 in the Wannier configuration as a function of the nuclear charge Z (in units of the squared rotation frequency Ω^2). Frequency $\omega=1$ is degenerated. One of the eigenvalues is negative, corresponding to an exponential solution $\exp(\pm|\omega|t)$.

$$y_1=-y_2=-\tfrac{3}{2}a\Omega t+b\ , \tag{32b}$$

$$z_1=z_2=0\ , \tag{32c}$$

where a and b are constants. This solution is obtained through a *spatial dilatation*. If all distances are multiplied by $(1+a/|\mathbf{r}_1^0|)$, according to the third Kepler law, the rotation frequency experiences a relative variation $\delta\Omega/\Omega$ equal to $-3a/2|\mathbf{r}_1^0|$, and in the rotating frame the particles acquire a tangential backward linear velocity equal to $3a\Omega/2$.

The frequency $\omega^2=1$ is degenerated. Analyzing the sytem (30) in this case, one first finds a motion along the rotation axis:

$$x_1=y_1=x_2=y_2=0\ , \tag{33a}$$

$$z_1=-z_2\ . \tag{33b}$$

This motion is simply obtained from the unperturbed one by tilting the angular momentum (or the plane of motion) by a small angle. The presence of the frequency equal to 1 only refers to the *space isotropy*.

The second possible motion at frequency $\omega=1$ develops in the $z_n=0$ plane and preserves the condition

$$\mathbf{r}_1(t)+\mathbf{r}_2(t)=0\ . \tag{34}$$

One finds explicitly,

$$y_1=2ix_1=-y_2=-2ix_2\ . \tag{35}$$

Going back to the laboratory frame, the electrons move on weakly eccentric elliptical orbits. As stated by (34), these ellipses are symmetrical with respect to the nucleus.[17]

Up to now, we have analyzed motions obeying condition (34) and which are pure duplications of single-electron motions. The second group of frequency is far different. The frequency ω_4 stands for an oscillation of both electrons in the angular momentum direction. This symmetric bending of the "molecule" ($z_1=z_2$ in this mode) corresponds to the smaller of the two frequencies greater than unity in Fig. 3. The presence of such an oscillation is related to the stability of Wannier states versus *angular* deformations.

The last two modes ω_5^2 and ω_6^2 correspond to *unsymmetrical* motions in the $z_n=0$ plane:

$$x_1 = x_2 \ , \tag{36a}$$

$$y_1 = y_2 \tag{36b}$$

(one has to remember that the Wannier equilibrium configuration is $\mathbf{r}_1^0 = -\mathbf{r}_2^0$). Frequency ω_5 is the largest in the list (31) and corresponds to an unsymmetrical vibration, combining bending and stretching coupled by the Coriolis force. In the rotating frame, $\delta\mathbf{r}_n(t)$ moves on a small elliptic trajectory.

Finally, one can easily check that the last quantity ω_6^2 is negative whatever the nuclear charge. This means that one can achieve an exponentially increasing (or decreasing) motion. For example, in the helium atom ($Z=2$), one obtains the relation $y_1 \simeq -2.36x_1$. For positive x_1 electron 1 escapes from the nucleus, and its angular frequency is smaller than Ω. Conversely, electron 2 comes closer to the nucleus with increasing angular velocity. The atom then autoionizes. As was already known, we verify that the Wannier solution is unstable versus radial deformations. In this decay mode, relations (36) prove that the interelectronic distance $|\mathbf{r}_{12}|$ is conserved, as far as the small-deformation equation (30) holds. The adiabatic behavior of $|\mathbf{r}_{12}|$ is the basis of the molecular descriptions of two-electron atoms, e.g., as developed by Feagin and Briggs.[18]

C. Stability of the Klar configuration

The Klar solution may be studied in the same framework. Cancelling the determinant of matrix $\mathcal{M}$ leads to the following set of squared frequencies:

$$\omega_1^2 = 0 \ , \tag{37a}$$

$$\omega_2^2, \omega_3^2 = 2 \pm (4 - 3\cos^2\theta)^{1/2} \ , \tag{37b}$$

$$\omega_4^2 = 1 \ , \tag{37c}$$

$$\omega_5^2, \omega_6^2 = -\frac{1}{2} \pm \frac{i}{2}(24\cos^2\theta - 9)^{1/2} \ , \tag{37d}$$

where the angle θ is the half aperture between electrons; according to (20b) and (28a), it is determined by

$$\theta = \arcsin[(4Z)^{-1/3}] \ . \tag{37e}$$

For small values of $\cos\theta$, the frequencies $\omega_{5,6}^2$ become both real

$$\omega_5^2, \omega_6^2 = -\tfrac{1}{2} \pm \tfrac{1}{2}(9 - 24\cos^2\theta)^{1/2} \quad \text{if } Z \le 2(\tfrac{2}{5})^{3/2} \simeq 0.506 \ . \tag{37f}$$

This set of squared frequencies is plotted versus Z in Fig. 4.

One equally checks here that 0 and 1 are eigenfrequencies, corresponding respectively to the transformation property of Klar's solution versus space dilatation and rotation. The first group of three frequencies of (37) corresponds to *motions symmetric with respect to the $z=0$ plane.* Frequencies ω_2 and ω_3 depict two vibration modes. The last three frequencies in the set (37) are associated with motions such that

$$x_1 = -x_2 \ , \tag{38a}$$

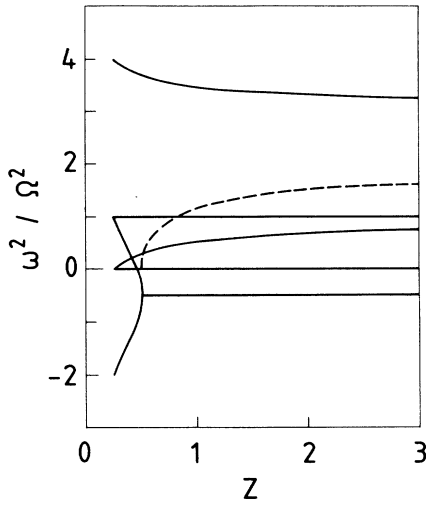

FIG. 4. Squared eigenfrequencies ω^2/Ω^2 in the symmetrical Klar configuration, as a function of Z. For Z larger than $2(\frac{2}{5})^{3/2}$, ω_5^2 and ω_6^2 are complex and conjugated. Their real part ($-\frac{1}{2}$) is plotted in the solid line, and the absolute value of their imaginary part is plotted in the dashed line.

$$y_1 = -y_2 \ , \tag{38b}$$

$$z_1 = z_2 \ . \tag{38c}$$

Putting aside the frequency ω_4 associated with the rotational invariance, one verifies in Fig. 4 that at least one of the squared frequencies ω_5^2, ω_6^2 is negative or complex; the corresponding motion is unbounded (exponential or oscillating with exponentially increasing amplitude). As the Wannier solution, this second solution is unstable. In a similar way, the decay mode preserves the $|\mathbf{r}_{12}|$ value up to first order in the displacement $\delta\mathbf{r}$, confirming the adiabatic character of the interelectronic distance.[18]

D. Stability of the unsymmetrical configuration

Finally, the squared characteristic frequencies associated with Klar's unsymmetrical configuration are plotted in Fig. 5 versus Z in their range of existence. In this case, a numerical computation of the determinant given in Table I is necessary. Several conclusions arise from this graph. On the one hand, one checks that for Z equal to its minimal value given by (26), the solution branches to the one obtained in the symmetrical case (37). On the other hand, if Z tends to unity, one electron is far away from the nucleus and the eigenfrequencies tend to 0 and 1 (twofold and fourfold degenerate), which characterize the *single-electron atom.* Since this unsymmetrical configuration has invariance properties under spatial dilatation and rotation, the eigenfrequencies 0 and 1 (nondegenerate) are still present for each value of Z. In Fig. 5, one verifies that whatever Z is, one squared frequency is negative and two other ones are complex. Therefore, one

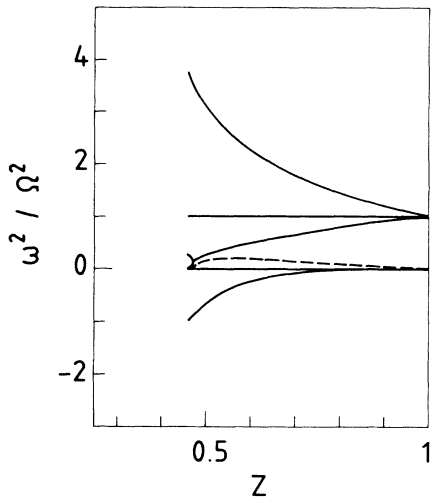

FIG. 5. Squared eigenfrequencies ω^2/Ω^2 in the unsymmetrical Klar configuration, as a function of Z. For Z larger than $Z_{\min} \simeq 0.469\,78$, two roots are complex conjugated. As in Fig. 4, the solid line is their real part and the dashed line the absolute value of their imaginary part.

can find exponentially increasing motions with or without oscillations. In this sense, this unsymmetrical solution is not that different from Klar's symmetrical solution. Nevertheless, for Z close to unity, the negative squared frequency is very small (varying as $-r^5$), and the imaginary part of the complex roots is small too (varying as r^2). Thus the instability character is less marked for unsymmetrical solutions than for symmetrical ones. This tends to prove that weakly correlated systems are less unstable.

VI. CONCLUSION

The existence of rigid rotating configurations in classical mechanics may be established within a very tractable formalism. It can be generalized to a higher number of electrons.[14] For the three-body problem, we have obtained the two known solutions and predicted a new one if the nuclear charge is arbitrarily allowed to be less than unity. One can easily apply the present formalism to a screened potential intermediate between $-1/r$ and 0 and one will certainly obtain unsymmetrical solutions, as those described here. If more than two electrons are present, one will probably find a series of other unsymmetrical configurations. It has been shown that all of these two-electron rigid configurations are unstable from the point of view of classical mechanics. Quantities equivalent to the Liapunov characteristic exponents have been expressed analytically except in the unsymmetrical case; in the latter case, invariance properties allow a direct determination of two characteristic frequencies (0 and 1) and the other frequencies have been numerically computed. For Z close to unity, it has been shown that the unsymmetrical configuration is almost stable. The present analysis is not sufficient to obtain a complete spectrum of doubly excited atoms, since consideration of *all* periodic orbits would be necessary[5]: this has been done in some cases considered in the literature.[8] Nevertheless, it would be interesting to seek in the doubly-excited-atom spectra for Bohr frequencies corresponding to the vibration modes analyzed here. As demonstrated by recent results on atomic magnetism,[7,8] the contribution of classical mechanics to the quantum spectrum analysis may be quite significant.

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[1]R. F. Stebbings and F. B. Dunning, *Rydberg States of Atoms and Molecules* (Cambridge University Press, Cambridge, England, 1983) and especially the paper by M. R. Flannery, p. 393.
[2]I. C. Percival and D. Richards, J. Phys. B **3**, 1035 (1970).
[3]P. F. Naccache, J. Phys. B **5**, 1308 (1972).
[4]R. V. Jensen, J. G. Leopold, and D. Richards, J. Phys. B **21**, L527 (1988).
[5]M. C. Gutzwiller, J. Math. Phys. (N.Y.) **8**, 1979 (1967); Phys. Rev. Lett. **45**, 150 (1980); Physica **5D**, 183 (1982).
[6]M. V. Berry and K. E. Mount, Rep. Prog. Phys. **35**, 315 (1972); M. V. Berry and M. Tabor, Proc. R. Soc. London, Ser. A **349**, 101 (1976); J. Phys. A **10**, 371 (1977).
[7]D. Delande and J. C. Gay, Phys. Rev. Lett. **57**, 2006 (1986); in *Atomic Physics 11*, edited by S. Haroche, J. C. Gay, and G. Grynberg (World Scientific, Singapore, 1989), p. 281.
[8]D. Wintgen, Phys. Rev. Lett. **61**, 1803 (1988); U. Eichmann, K. Richter, D. Wintgen, and W. Sandner, *ibid.* **61**, 2438 (1988).
[9]I. C. Percival, Proc. R. Soc. London, Ser. A **353**, 289 (1977).
[10]U. Fano, Rep. Prog. Phys. **46**, 97 (1983).
[11]G. H. Wannier, Phys. Rev. **90**, 817 (1953).
[12]H. Klar, Phys. Rev. Lett. **57**, 66 (1986); Z. Phys. D **3**, 353 (1986); J. Opt. Soc. Am. B **4**, 788 (1987).
[13]A. L. Belov and V. P. Krainov, Zh. Eksp. Teor. Fiz. **92**, 456 (1987) [Sov. Phys.—JETP **654**, 257 (1987)].
[14]J. L. Gerver, Phys. Lett. **109A**, 257 (1985).
[15]L. A. Pars, *A Treatise on Analytical Dynamics* (Heinemann, London, 1965).
[16]A. J. Lichtenberg and M. A. Liberman, *Regular and Stochastic Motion* (Springer-Verlag, New York, 1983).
[17]J. Macek and S. Watanabe, Comments At. Mol. Phys. **19**, 313 (1987).
[18]J. M. Feagin and J. S. Briggs, Phys. Rev. Lett. **57**, 984 (1986); Phys. Rev. A **37**, 4599 (1988); J. M. Rost and J. S. Briggs, J. Phys. B **21**, L233 (1988).