

Nonspreading Wave Packets for Rydberg Electrons in Rotating Molecules with Electric Dipole Moments

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Nonspreading wave packets for Rydberg electrons are predicted in rotating molecules with electric dipole moments. We have named them the Trojan wave packets since their stability is due to the same mechanism that governs the motion of the Trojan asteroids in the Sun-Jupiter system. Unlike all previously predicted Trojan wave packets in atoms, molecular Trojan states do not require external fields for their existence. [S0031-9007(96)01683-3]

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Following an earlier indication based on a semiclassical analysis by Klar [1], we have recently shown analytically and numerically [2,3] that in the presence of a circularly polarized electromagnetic wave impinging on hydrogenic atoms there exist new quantum states of highly excited electrons. The analytic results were further refined in [4], and extensive numerical calculations [5,6] fully confirmed the existence of these states and their very long lifetimes. In the rotating frame, these states are almost stationary and, therefore, in the laboratory frame they represent nonspreading electronic wave packets moving on circular orbits around the nucleus with the frequency of the wave. The Trojan wave packets are centered around the classical equilibrium points produced by the external field of the polarized wave that are close analogs of the stable Lagrange equilibrium points in celestial mechanics [7] around which the Trojan asteroids move. The electric field of the applied wave provides the same stabilizing force as does the gravitational pull of Jupiter in the case of the asteroids. The stability of Trojan wave packets in circularly polarized wave fields may be further increased, as proposed in [8,9,10], by applying an additional homogeneous magnetic field.

In this Letter, we show that the Trojan wave packets of Rydberg electrons also exist in molecules even *in the absence* of any external field. The conditions for the existence of such stable wave packets circulating on large orbits around the molecular core are a sufficiently large electric dipole moment ea and a rotation of the molecular core. The quantum dynamics of Trojan states in polar molecules is governed essentially by the same Schrödinger equation as for Trojan states in atoms placed in a circularly polarized electromagnetic wave. The electron wave functions for these two problems are related by a sequence of two simple transformations: a shift in the coordinate space and a shift in the momentum space. Because of the mathematical equivalence of the two problems, one may use all the results obtained before for strongly driven Rydberg electrons in hydrogenic atoms.

The only difference is that the force $-e\mathcal{E}$ due to the electric field of the wave is replaced now by the inertial force $ma\Omega^2$. Although the three categories of systems, planetary, atomic, and molecular, that exhibit the existence of Trojan states are subjected to different forces, their mathematical description reveals striking similarities, owing to the crucial importance of the Coriolis force in all these systems. The molecular Trojan states differ, however, in an essential way from atomic Trojan states. The atomic Trojan states can be modified continuously by changing the amplitude of the applied field, while the molecular Trojan states are controlled by the rotational frequency Ω which is quantized. Also, the breaking of rotational symmetry is not due to an applied microwave field but it occurs spontaneously (the complete molecular Hamiltonian is fully invariant under rotations).

We are interested in a motion of a molecular Rydberg electron whose wave function is localized on a large circular orbit. Since such an electron is always far from the rest of the molecule, it does not interact with individual particles but only feels a certain charge distribution of the remaining core. The action of this core on the electron may be represented by a Coulomb field whose center is, in general, shifted by a vector \mathbf{a} with respect to the center of mass of the molecule. The dipole moment of the core, measured with respect to the center of mass, is in this case equal to $e\mathbf{a}$. In order to realize the conditions for the existence of the Trojan wave packets, we will consider the situation when the core is rotating. For a charge distribution rotating with the angular frequency Ω around the z axis that passes through the center of mass, the components of the displacement vector \mathbf{a} depend on time through the formulas

$$a_x(t) = a_x \cos(\Omega t) - a_y \sin(\Omega t), \quad (1)$$

$$a_y(t) = a_x \sin(\Omega t) + a_y \cos(\Omega t), \quad (2)$$

$$a_z(t) = a_z. \quad (3)$$

Under these assumptions, we can describe the dynamics of the Rydberg electron by the following simplified model Hamiltonian

$$H_L = \frac{\mathbf{p}^2}{2} - \frac{1}{|\mathbf{r} + \mathbf{a}(t)|}, \quad (4)$$

where we used the atomic units ($\hbar = 1$, $e = 1$, $m = 1$). The same model Hamiltonian has been used previously [11,12] to study the autoionization of molecular Rydberg states in the classical regime. The laboratory-frame Hamiltonian H_L is time dependent, but we can get rid of this dependence by transforming the Schrödinger wave equation to the rotating frame. The wave function in the rotating frame $\psi_R(\mathbf{r}, t)$ is obtained from the wave function in the laboratory frame $\psi_L(\mathbf{r}, t)$ by applying the rotation operator with the angular frequency Ω ,

$$\psi_R(\mathbf{r}, t) = e^{i\Omega M_z t} \psi_L(\mathbf{r}, t), \quad (5)$$

where M_z is the z component of the angular momentum operator. Because of the transformation properties of the components of the position vector under rotation

$$e^{i\Omega M_z t} x e^{-i\Omega M_z t} = x \cos(\Omega t) - y \sin(\Omega t), \quad (6)$$

$$e^{i\Omega M_z t} y e^{-i\Omega M_z t} = x \sin(\Omega t) + y \cos(\Omega t), \quad (7)$$

$$e^{i\Omega M_z t} z e^{-i\Omega M_z t} = z, \quad (8)$$

the wave function $\psi_R(\mathbf{r}, t)$ fulfills the Schrödinger equation with the time-independent Hamiltonian H_R ,

$$H_R = \frac{\mathbf{p}^2}{2} - \frac{1}{|\mathbf{r} + \mathbf{a}|} - \Omega M_z. \quad (9)$$

The Hamiltonian H_R contains an additional term $-\Omega M_z$ that accounts for the inertial forces (centrifugal and Coriolis) acting in the rotating frame. The Schrödinger equation in the rotating frame

$$i \partial_t \psi_R(\mathbf{r}, t) = \left(\frac{\mathbf{p}^2}{2} - \frac{1}{|\mathbf{r} + \mathbf{a}|} - \Omega M_z \right) \psi_R(\mathbf{r}, t) \quad (10)$$

can be transformed to the form known from our previous work [2] by successive shifts of the coordinate and the momentum. In order to obtain the most favorable conditions for the existence of the Trojan states, we shall assume that the dipole is perpendicular to the axis of rotation and we align the x axis along the dipole moment ($a_x = a$). Upon expressing $\psi_R(\mathbf{r}, t)$ in terms of a new function $\psi(\mathbf{r}, t)$,

$$\psi_R(\mathbf{r}, t) = e^{a\partial_x} e^{-ia\Omega y} \psi(\mathbf{r}, t), \quad (11)$$

and with the use of the relations

$$e^{-a\partial_x} x e^{a\partial_x} = x - a, \quad (12)$$

$$e^{ia\Omega y} p_y e^{-ia\Omega y} = p_y - a\Omega \quad (13)$$

we obtain the Schrödinger equation for the wave function $\psi(\mathbf{r}, t)$ with the "shifted" Hamiltonian H ,

$$H = \frac{\mathbf{p}^2}{2} - \frac{1}{|\mathbf{r}|} + a\Omega^2 x - \Omega M_z - a^2 \Omega^2 / 2. \quad (14)$$

This Hamiltonian has the same form (except for the trivial constant term $a^2 \Omega^2 / 2$) as the one that governs the time evolution in the rotating frame of the electron in the driven hydrogen atom [2] with the term $a\Omega^2$ playing now the role of the electric field of the circularly polarized wave. Therefore we may use all the results obtained in Refs. [2–6] for the Trojan wave packets of driven electrons. In particular, it has been shown that the Hamiltonian H possesses an approximate eigenstate in the form of a Gaussian wave packet

$$\psi(\mathbf{r}, t) = N e^{-\Omega[A(x-x_0)^2 + By^2 - 2iC(x-x_0)y]/2} \times e^{i\Omega x_0 y} e^{-\Omega Dz^2/2} e^{-iEt}, \quad (15)$$

where N is the normalization constant. The center of the wave packet (15) is obtained from the Hamilton equations of the corresponding classical problem

$$\dot{x} = p_x + \Omega y, \quad \dot{y} = p_y - \Omega x, \quad \dot{z} = p_z, \quad (16)$$

$$\dot{p}_x = -\frac{x}{|\mathbf{r}|^3} - a\Omega^2 + \Omega p_y, \quad (17)$$

$$\dot{p}_y = -\frac{y}{|\mathbf{r}|^3} - \Omega p_x, \quad \dot{p}_z = -\frac{z}{|\mathbf{r}|^3}. \quad (18)$$

The static solution of these equations

$$\mathbf{r} = (x_0, 0, 0), \quad \mathbf{p} = (0, \Omega x_0, 0) \quad (19)$$

determines a stable Lagrange equilibrium point. The distance x_0 is determined by the equilibrium condition

$$\frac{1}{x_0^2} + a\Omega^2 = x_0 \Omega^2, \quad (20)$$

which expresses the balance between the Coulomb force, the dipole force, and the centrifugal force. It is convenient to introduce a dimensionless parameter q that determines the ratio of the Coulomb force to the centrifugal force,

$$q = \frac{1}{\Omega^2 x_0^3}. \quad (21)$$

The equilibrium condition (20) expressed in terms of q has the form

$$q + \frac{a}{x_0} = 1. \quad (22)$$

Now we shall expand the Hamiltonian H around the equilibrium values (19) of the positions and momenta and retain only the quadratic terms.

$$H_Q = \frac{p_x^2 + (p_y - \Omega x_0)^2}{2} - q\Omega^2(x - x_0)^2 + q\Omega^2 \frac{y^2}{2} - \Omega(x - x_0)(p_y - \Omega x_0) + \Omega y p_x + \frac{p_z^2}{2} + q\Omega^2 \frac{z^2}{2} - \frac{1}{x_0} \left(1 + \frac{q}{2} \right). \quad (23)$$

We have used here the equilibrium condition (20) to cancel the linear terms. The motion in the z direction decouples in this approximation from the motion in the xy plane, but in this plane the motion is truly two dimensional. For simplicity, we have applied the quadratic approximation in the Cartesian coordinates, because we are interested in proving merely the existence of the Trojan states in molecules. Our analysis can be extended easily to cylindrical coordinates which were shown in [3,4] to be much more suitable for describing the “banana-shaped” long living wave packets. We expect that our predictions based on the simplified model will be fully confirmed by *ab initio* numerical calculations.

The Trojan state of the Rydberg electron given by the Gaussian wave function (15) is an eigenstate of the Hamiltonian H_Q and, therefore, it will be an approximate eigenstate of the exact shifted Hamiltonian in Eq. (14) when the neglected higher order terms are small, i.e., when x_0 is sufficiently large. In the rotating frame, this state is stationary and it is localized around the classical equilibrium point. The extension of the Trojan wave packet in the directions x, y , and z are determined by the coefficients A, B , and D , respectively. All the coefficients characterizing this wave packet can be determined from the eigenvalue equation $H_Q\psi = E\psi$,

$$A = \sqrt{(1+2q)(4f(q) - 9q^2)}/3q, \quad (24)$$

$$B = \sqrt{(1-q)[4f(q) - 9q^2]}/3q, \quad (25)$$

$$C = f(q)/3q, \quad (26)$$

$$D = \sqrt{q}, \quad (27)$$

$$E = \Omega(A + B + D)/2 - (1 + q/2)/x_0, \quad (28)$$

where

$$f(q) = 2 + q - 2\sqrt{(1-q)(1+2q)}. \quad (29)$$

The original wave function ψ_R in the rotating frame obtained from the formula (11) has the form

$$\begin{aligned} \psi_R(\mathbf{r}, t) = & N e^{-\Omega[A(x-x_0+a)^2 + By^2 - 2iC(x-x_0+a)y]/2} \\ & \times e^{i\Omega(x_0-a)y} e^{-\Omega Dz^2/2} e^{-iEt}. \end{aligned} \quad (30)$$

In the laboratory frame, the Trojan state is *nonstationary*. The wave packet circles around the center of mass of the molecule keeping in phase with the rotation of the molecular dipole.

The Hamiltonian (23) can be brought to the canonical form [2,4]

$$H_Q = \omega_+ a_+^\dagger a_+ - \omega_- a_-^\dagger a_- + \omega_z a_z^\dagger a_z + E, \quad (31)$$

where the characteristic frequencies ω_\pm and ω_z have the values

$$\omega_\pm = \Omega \sqrt{\frac{2 - q \pm \sqrt{9q^2 - 8q}}{2}}, \quad \omega_z = \Omega \sqrt{q}. \quad (32)$$

The same frequencies characterize, of course, the classical oscillations described by the Hamiltonian (23). The region of classical stability of these oscillations, where all the frequencies are real, extends from $q = 8/9$ to $q = 1$. In the same region all the coefficients A, B, C , and D that characterize the shape of the quantum mechanical wave packet are real which suggests also the quantum mechanical stability. The quantum stability of wave packets in this region has, indeed, been fully confirmed. Exact numerical solutions [3,5,6] of the Schrödinger equation with the Hamiltonian H restricted to the xy plane that correspond to the approximate Gaussian wave function (15) live up to this expectation. The lifetimes of these exact solutions for high Rydberg states are of the order of millions of Kepler periods [5].

Our analysis leading to a prediction of Trojan states of electrons in polar molecules is based on the assumption that the radius x_0 of the circular Rydberg orbit is large as compared to the dimension of the core. Thus the ratio a/x_0 represents a small parameter in this analysis since a is always limited by the linear dimensions of the core. The smallness of a/x_0 is in correspondence with the requirement of stability. Indeed, the equilibrium condition (20) means that a/x_0 must be smaller than $1/9$ if q is to fall between $8/9$ and 1 . We shall show below that, in realistic cases, the value of q is very close to 1 .

The essential requirement for the existence of the Trojan states is the rotation of the molecular core. The frequency of this rotation Ω can be expressed in terms of x_0 and a with the use of Eq. (20)

$$\Omega = \frac{1}{x_0 \sqrt{x_0 - a}} \approx \frac{1}{x_0^{3/2}}. \quad (33)$$

On the other hand, the value of Ω is determined by the rotational quantum number J and the moment of inertia I of the molecule, $\Omega = J/I$. Hence, for a given molecule, the value of x_0 depends only on the value of J . For small a/x_0 , this relation has the form

$$x_0 \approx \left(\frac{I}{J}\right)^{2/3}. \quad (34)$$

Even for the smallest molecules (cf. the discussion below), when the moment of inertia is of the order of 5000 (in atomic units), x_0 is of the order of 300 for the lowest rotational state. Such a large value of x_0 guarantees that the electron probability density $\rho(\mathbf{r})$,

$$\rho(\mathbf{r}) = N^2 e^{-\Omega A(x-x_0+a)^2 - \Omega B y^2 - \Omega D z^2}, \quad (35)$$

is well localized far from the core; the ratio of the density at the center to the density at the equilibrium point is equal to $\exp(-\Omega A x_0^2) \approx \exp(-\sqrt{x_0})$ since $A \approx 1$. The localization in the azimuthal direction is not as good as in the radial direction because the coefficient $B \approx \sqrt{a}/3x_0$ is much smaller than A .

In order to demonstrate that the Trojan states of Rydberg electrons in molecules are not highly exotic, we shall show

now that even in the simplest case of the hydrogen molecule there exist favorable conditions for their existence. Obviously, the Trojan states cannot exist in homonuclear molecules, since by symmetry such molecules do not have dipole moments. However, when one hydrogen atom is replaced by its isotope, by deuterium, or even better by tritium, the center of mass is shifted with respect to the center of charge and a dipole moment is created in the corresponding molecular ion. In particular, in the hydrogen-tritium molecule the center of mass is shifted by $1/4$ of the distance R between the nuclei. Taking the standard value $R = 2$ a.u. for the hydrogen molecular ion [13], we obtain $a = 0.5$. The moment of inertia of the core is equal in this case to a product of the reduced mass of the nuclei ($3/4$ of the proton mass) by the square of the distance R . This gives for the lowest rotational state $x_0 \approx 312$. Such a value of the mean distance from the center for standard Rydberg states in hydrogenic atoms would correspond to the principal quantum number n equal to about 18. One should keep in mind, however, that the Trojan states are nonstationary and are made of many hydrogenic eigenstates, so that the effective value of n is to be used only to get a better intuitive picture. The effective value of n for higher rotational states with J equal to 2, 3, and 4 decreases successively to about 14, 12, and 11. On the other hand, when we move to heavier molecules, the effective value of n increases. Since the moment of inertia may easily increase by 2 orders of magnitude as compared to the hydrogenic value [14], we may reach the value $n = 60$ that has been used in [2] as a characteristic value for the Trojan states in atoms. Thus the Trojan states in polar molecules are not only described by the same mathematical model as the Trojan states in hydrogenic atoms placed in microwave fields but they also may have similar geometric dimensions. This makes us confident that the characteristic parameters of the Trojan states of electrons in polar molecules are not only correctly predicted on the basis of the quadratic approximation but also that the corresponding solutions of the exact Schrödinger equation will exhibit the same high degree of stability and very long lifetimes as has been found for the Trojan states in atoms. Our confidence is further strengthened by earlier theoretical predictions [12] of stable periodic Rydberg orbits near the ionization threshold that were based on classical theory. The stability of Trojan states in molecules may be further enhanced by applying the external magnetic fields as has been suggested for atomic states in Refs. [8–10,15].

Despite all the formal similarities, the molecular Trojan states are different from the atomic Trojan states since there is no microwave field that can be diabatically switched on, as proposed in [5], to assemble these states on the orbit. The dipole moment of the molecule is fixed. The rotational frequency Ω cannot be turned on gradually

because it is quantized. Therefore we have to invent different methods to produce the molecular Rydberg states. One possible production mechanism is the capture of a passing-by free electron into a Trojan state by a rotating molecular ion. Of course, a third body or an external field is needed in this case to carry away the energy surplus. Another production mechanism might employ the recently developed subpicosecond broad-band, half-cycle field pulses [16–18] to excite one of the electrons in the molecule to its Trojan state. Such pulses might be capable of creating electron wave packets made of many stationary states.

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