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SERIES REPORT

(Laser, Atomic and Molecular Physics)

SEMICLASSICAL HYPERSPHERICAL MATRIX ELEMENTS FOR HELIUM DOUBLY EXCITED STATES

J. Mahecha Gómez

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ABSTRACT

A classical description of the two-electron atom, analogous to the quantum adiabatic hyperspherical channel approach, is presented. The classical problems, analogue to the quantum eigenvalue problem for the great angular momentum operator, and the separated dynamical systems defined by each of the other constants of the motion of the non-interacting system, are solved, using the Hamilton-Jacobi method. Some matrix elements of the Coulomb interaction terms of the Hamiltonian for doubly excited helium atom using the Heisenberg correspondence principle are calculated.

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Preface

The ICTP-LAMP reports consist of manuscripts relevant to seminars and discussions held at ICTP in the field of Laser, Atomic and Molecular Physics (LAMP).

These reports aim at informing LAMP researchers on the activity carried out at ICTP in their field of interest, with the specific purpose of stimulating scientific contacts and collaboration of physicists from Third World Countries.

If you are interested in receiving additional information on the Laser and Optical Fibre activities at ICTP, kindly contact Professor Gallieno Denardo, ICTP.

I. INTRODUCTION

The theoretical and experimental study of atomic doubly excited states is a topic of current interest. Experiments start with spectroscopic measurements in doubly excited states of helium using synchrotron radiation [1], and in doubly excited states of H^- ion using UV tunable lasers [2], and continue with recent experiments like the preparation of two electrons of Ba atoms in states known as "frozen planet orbits" [3,4]. From this experiments it has been concluded that atomic doubly excited states have the characteristic that is not possible an approximate description of the electronic states as a whole in terms of its constituents parts. As many of those states are highly excited, and located in the region of validity of the correspondence principle, then classical models are expected to be valid [5].

Moreover, some full quantum-mechanical calculations about doubly excited states shown [6] that the conventional CI methods are very slowly convergent. The adiabatic channel treatment in hyperspherical coordinates for helium atom [7,8], as other three-body systems with Coulomb interactions [9], proves useful, even is not free of convergence problems; it separates the coordinates in a set which gives the the shape and orientation of the system, and a coordinate responsible of the overall size.

Even does not pretends to compete with the quantum adiabatic hyperspherical methods, nor with highly accurate *ab initio* calculations [10] in a quantitative agreement, the present paper shows that some relevant results of the adiabatic hyperspherical approach in highly excited states can be easily obtained using a simple semiclassical method.

Section II presents the Hamilton-Jacobi solution of the dynamical systems associated with the great angular momentum of two particles, and the orbital angular momentum of a particle. Section III presents the classical problem in the Hamilton-Jacobi formalism analogous to the adiabatic hyperspherical channel description of the two-electron atom developed by Macek, Fano, and Lin [6–8]. In section IV a semiclassical calculation of matrix elements is presented.

We assume that the system consists of two particles with equal masses of value m, and the nuclear mass is infinity. In the numerical calculations, atomic units were used.

II. THE HYPERSPHERICAL HAMILTONIAN

The hyperradius and the mock angle are defined respectively by

$$R = (r_1^2 + r_2^2)^{1/2}, \text{ and } \tan\alpha = \frac{r_1}{r_2} = u. \tag{1}$$

Fano [6] uses the following hyperspherical coordinate set to describe the two-particle system,

$$\{R, \alpha, \theta_1, \phi_1, \theta_2, \phi_2\} \equiv \{R, w\}, \tag{2}$$

instead of the independent particle coordinate set,

$$\{\vec{r}_1, \vec{r}_2\} = \{r_1, \theta_1, \phi_1, r_2, \theta_2, \phi_2\}, \tag{3}$$

in which the Hamiltonian can be expressed in terms of one-free-particle Hamiltonians and the Coulomb interaction potential energy, in the form

$$H = \frac{p_{r_1}^2}{2m} + \frac{p_{r_2}^2}{2m} + \frac{\vec{l}_1^2}{2mr_1^2} + \frac{\vec{l}_2^2}{2mr_2^2} - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{r_{12}}. \tag{4}$$

From Eqns. 1 can be derived the following expression for Eq. 4,

$$H = \frac{1}{2m}\left(p_R^2 + \frac{p_\alpha^2}{R^2}\right) + \frac{1}{2mR^2}\left(\frac{l_1^2}{\cos^2\alpha} + \frac{l_2^2}{\sin^2\alpha}\right) + V(R, \alpha, \theta_{12}), \tag{5}$$

in which V is the Coulomb potential energy,

$$V(R, \alpha, \theta_{12}) = \frac{e^2}{R}\left[-\frac{Z}{\cos\alpha} - \frac{Z}{\sin\alpha} + \frac{1}{(1 + \sin 2\alpha \cos\theta_{12})^{1/2}}\right]. \tag{6}$$

Eq. 5 for H can be expressed in the form $H = H_0 + V$ where

$$H_0 = \frac{1}{2m}\left(p_R^2 + \frac{\Lambda^2}{R^2}\right), \text{ and } \Lambda^2 = p_\alpha^2 + \frac{l_1^2}{\cos^2\alpha} + \frac{l_2^2}{\sin^2\alpha}. \tag{7}$$

We see that H_0 depends on R, p_R and Λ, and Λ depends on p_α, α and the coordinates from which depend the squares of the angular momenta,

$$l_i^2 = p_{\theta_i}^2 + \frac{p_{\phi_i}^2}{\sin^2\theta_i}. \tag{8}$$

Λ is a constant of the motion for the non-interacting system, as the energy, and the magnitudes of the angular momenta of the individual particles.

Λ^2 can be identified [11] with the square of the magnitude of a 6×6 tensor, called great angular momentum, or generalized angular momentum, with components of the form $\Lambda_{mn}^{xy} = x_m p_{yn} - y_n p_{xm}$, where $m, n = 1, 2$ are labels for the particles, with similar relations for the xz and yz components. The diagonal components respect to m, n are the usual angular momentum components. A condition for a close (or not exact) 3-body collision is that Λ^2 be small. Λ has a minimum when the velocities v_i of the particles have the same relation as their impact parameters b_i. The "maximum symmetry" is obtained in the case in which not only Λ is minimum, but also $v_1 = v_2$ and $b_1 = b_2$. Λ is related with the "correlation degree" between the motions of the particles through a cross term $(v_1 b_2 - v_2 b_1)^2$. In the non-interacting case, l_1, l_2, Λ and E are functions of v_1, v_2, b_1 and b_2.

A. Hamilton-Jacobi equation for H_0

As ϕ_i do not appear in H_0, it follows that the p_{ϕ_i} are constants of the motion. Also are constants l_i and Λ. In consequence, the coordinates R and α can be separated, $S = S_{\Lambda E} + S_{\Lambda l_1 l_2}$, and the corresponding Hamilton-Jacobi equations are:

$$\left(\frac{dS_{\Lambda E}}{dR}\right)^2 + \frac{\Lambda^2}{R^2} = 2mE,$$
$$\left(\frac{dS_{\Lambda l_1 l_2}}{d\alpha}\right)^2 + \frac{l_1^2}{\cos^2\alpha} + \frac{l_2^2}{\sin^2\alpha} = \Lambda^2. \tag{9}$$

As Λ is a constant, H_0 describes the hyperradial motion; Λ measures the strength of a "centrifugal" field that keeps a pair of particles from approaching a force centre simultaneously. It can be defined an effective potential for the hyperradial motion having a minimum at certain large R_a, in order to consider the motion as periodic; at the end, R_a goes to infinity; compare with Eq. 42.

The solution for the hyperradial motion depends on Λ, R_a and $R_0 = (b_1^2 + b_2)^{1/2}$,

$$\pm S_{\Lambda E} = \begin{cases} \Lambda\left[(R/R_0)^2 - 1\right]^{1/2} - \cos^{-1}(R_0/R)\right] \text{ if } R < R_a \\ \Lambda\left[(2R_a - R)^2/R_0^2 - 1\right]^{1/2} - \cos^{-1}[R_0/(2R_a - R)]\right] \text{ if } R > R_a \end{cases} \tag{10}$$

The action variable for the R motion is given by

$$I_R = \frac{1}{2\pi}\oint p_R\, dR, \tag{11}$$

where it follows that

$$E = \frac{\pi^2}{8}\frac{(I_R + \Lambda)^2}{mR_a^2}. \tag{12}$$

The "frequency" of the R motion is

$$\omega_R = \frac{\partial E}{\partial I_R} = \frac{\pi\Lambda}{2mR_aR_0}, \tag{13}$$

The angular variable θ_R is

$$\theta_R = \frac{\partial S_{\Lambda E}}{\partial I_R}, \tag{14}$$

from where is obtained the following expression for R in terms of θ_R or t is:

$$R = R_0\left[1 + \left(1 + \frac{I_R}{\Lambda}\right)^2\theta_R^2\right]^{1/2} = R_0\left[1 + \left(\frac{\Lambda}{mR_0^2}\right)^2(t + t_0)^2\right]^{1/2}. \tag{15}$$

In the quantum case, the **Schrödinger** equation, corresponding to the first of Eqns. 9, can be solved by a Bessel function of integer order depending on the kinetic energy through the product kR, as it represents an unbound motion.

B. Motion on the sub-manifold Λ = constant

Λ is a constant of the motion in the absence of a force field, such as $-C/R$, which depends on the angular variables. Several values of l_1 and l_2 can be associated with each Λ, so the Λ eigenvalues are highly degenerated; that degeneracy is removed by $-C/R$.

Second of Eqns. 9 describes a dynamical system whose "Hamiltonian" is Λ^2. The "potential" well is

$$V_{l_1 l_2} = \frac{l_1^2}{\cos^2\alpha} + \frac{l_2^2}{\sin^2\alpha}. \tag{16}$$

If l_1 and l_2 are different from zero, it occurs an oscillatory "motion" around the minimum of $V_{l_1 l_2}$, located at

$$\tan\alpha_e = \left(\frac{l_2}{l_1}\right)^{1/2}, \tag{17}$$

and the value of $V_{l_1 l_2}$ at equilibrium is $V^e_{l_1 l_2} = (l_1 + l_2)^2$.

The turning points of the motion are such that $\alpha = \alpha_+$ or $\alpha = \alpha_-$, which can be expressed by means of Δ, defined at Eq. 20,

$$\cos^2\alpha_\pm = \frac{1}{\Lambda^2}(l_1^2 - l_2^2 \pm \Delta^{1/2}). \tag{18}$$

For given values of l_1 and l_2, Λ must to be larger than $l_1 + l_2$, and when Λ attains its minimum, then α = constant = α_e.

The solution to the second of the Hamilton-Jacobi equations in Eqns. 9 is

$$\pm S_{\Lambda l_1 l_2} = \frac{l_1}{2}\sin^{-1}\left(\frac{2au^2 + b}{\Delta^{1/2}}\right) - \frac{l_2}{2}\sin^{-1}\left(\frac{bu^2 + 2c}{u^2\Delta^{1/2}}\right) + \frac{\Lambda}{2}\sin^{-1}\left(\frac{b'(1+u^2) + 2c'}{[(1+u^2)\Delta]^{1/2}}\right), \tag{19}$$

where

$$\begin{array}{lll} a = -l_1^2, & b = \Lambda^2 - l_1^2 - l_2^2, & c = -l_2^2, \\ a' = a, & b' = \Lambda^2 + l_1^2 - l_2^2, & c' = -\Lambda^2 \\ b'' = \Lambda^2 - l_1^2 + l_2^2, & \Delta = (l_2 + l_1 - \Lambda)(l_2 - l_1 + \Lambda)(l_2 - l_1 - \Lambda)(l_2 + l_1 + \Lambda). & \end{array} \tag{20}$$

It is convenient to define a function X, with $x = u^2$ and $y = 1 + u^2$, by

$$X = a\,x^2 + b\,x + c = a'\,y^2 + b'\,y + c'. \tag{21}$$

The action variable I_α is defined analogously as I_R in Eq. 11, from which results

$$\Lambda = 2I_\alpha + l_1 + l_2. \tag{22}$$

The "frequency" is $\omega_\alpha = \partial\Lambda^2/\partial I_\alpha = 4\Lambda$. The angular variable θ_α is defined in analogous way to θ_R in Eq. 14. Now, using the expression for $S_{\Lambda l_1 l_2}$, an expression for θ_α as function of u is obtained, which when is inverted gives u as a function of "time" through θ_α:

$$u = \Big(\frac{b'' + \Delta^{1/2}\sin\theta_\alpha}{b' - \Delta^{1/2}\sin\theta_\alpha}\Big)^{1/2}. \tag{23}$$

The phase curves for different values of Λ, with fixed l_1 and l_2, show periodicities and the absence of separatrices. Also, the variations of u are very fast when Λ growths, the same as the excursions of $\dot{u}$. From this behaviour can be concluded that the radial correlations have an important kinematic component.

The Schrödinger equation corresponding to this problem has as solutions the called hyperspherical harmonics [6, 7].

The semiclassical wave functions, WKB approximation, have the form [5]:

$$\psi(q, I) = A\Big[det\Big(\frac{\partial^2 S(q, I)}{\partial q_i \partial I_j}\Big)\Big]^{1/2}\exp[iS(q, I)/\hbar]. \tag{24}$$

Then, from $S_{\Lambda l_1 l_2}$ can be easily calculated the WKB function which approximates the "Jacobi polynomial" part of the hyperspherical harmonics [12].

The density, or distribution function in the configuration space respect to u is

$$\rho(u) = \frac{d\theta_\alpha}{du} = \frac{\Lambda}{\pi}\frac{u}{(1+u^2)X^{1/2}}, \tag{25}$$

as $X = 0$ at the turning points of u, in that points the density is infinite. The function $\rho(u)$ satisfies the normalization relation:

$$2\int_{u_{min}}^{u_{max}} \rho(u)\, du = 1, \tag{26}$$

where u_{min}, u_{max} are easily obtained from Eq. 23. The density function will be useful to calculate classical average values, like $< C(\alpha, \theta_{12}) >$.

C. Motion on the sub-manifolds l_i = constant

Eq. 8 defines a dynamical system with "Hamiltonian" l^2. Next we will drop the indexes, to represent any particle described by spherical coordinates (θ, ϕ).

p_ϕ is a constant of the motion, equals to m, which determines a "potential" $V_m = m^2/\sin^2\theta$. The turning points of the θ motion are determined by $\sin^2\theta = m^2/l^2$; $l \geq m$ and at equilibrium $l = m$.

The maximum and minimum values of p_θ occurs when $\theta = \pi/2$; and $\theta_{max,min}$ are symmetrical around that value. When θ varies from $\pi/2$ to θ_{min}, then p_θ is negative.

The Hamilton-Jacobi equation which is derived from Eq. 8 has as solution [13, 14]

$$S_{lm} = m\phi - l\tan^{-1}\frac{x}{l} + m\tan^{-1}\frac{x}{m} + \frac{\pi}{2}(l - m), \tag{27}$$

where

$$x = \frac{1}{\cos\theta}(-m^2 + l^2\sin^2\theta)^{1/2}. \tag{28}$$

It is deduced the following expression for l and m in terms of the action variables:

$$l = I_\theta + I_\phi, \quad m = I_\phi. \tag{29}$$

The "frequency" of this motion is $\omega = 2l$.

From S_{lm}, the following expression for θ and p_θ in terms of the action-angle variables $(I_\theta, \theta_\theta)$ is deduced,

$$\cos\theta = \gamma\sin\theta_\theta, \text{ and } p_\theta = -\frac{l\gamma\cos\theta_\theta}{(1 - \gamma^2\sin^2\theta_\theta)^{1/2}}, \text{ where } \gamma^2 = 1 - m^2/l^2. \tag{30}$$

For the motion along the ϕ coordinate it follows that

$$\tan\phi = \frac{(1-\gamma^2)^{1/2}\sin\theta_\theta\cos\theta_\phi + \sin\theta_\phi\cos\theta_\theta}{-(1-\gamma^2)^{1/2}\sin\theta_\theta\sin\theta_\phi + \cos\theta_\phi\cos\theta_\theta}, \; p_\phi = m. \tag{31}$$

The evolution parameter associated with this "Hamiltonian" is not a time. In this case it is a parameter describing all the possible realizations of θ_θ (perihelion line argument) and θ_ϕ (node line argument). In the α motion, whose Hamiltonian is Λ^2, the evolution parameter determine all the realizations of θ_α, or the radial correlation variable u.

From $S_{l,m}$, can be calculated the WKB wave function corresponding to the $\Omega_i = \{\theta_i, \phi_i\}$ dependence [15] in the hyperspherical harmonics, after a coupling by superposing their products multiplied by Clebsch-Gordan coefficients in the classical limit [16, 17].

III. HAMILTON-JACOBI EQUATION FOR THE TWO-ELECTRON ATOM

In this section we will develop the adiabatic hyperspherical channel approximation, within the Hamilton-Jacobi formalism, on a parallel way with the quantum formulation presented in by Fano [6]. A semiclassical treatment of this problem was given before by Peterkop [18], in a plane situation in which $L = 0$, when the only relevant coordinates are α, R and θ_{12}, using an expansion near the Wannier saddle point on the coulomb potential.

The Hamiltonian in Eq. 5 can be written as

$$H = \frac{1}{2m}\Big(p_R^2 + \frac{\Lambda^2}{R^2}\Big) + \frac{e^2 C(\alpha, \theta_{12})}{R} = H_R + \frac{p_R^2}{2m} \tag{32}$$

where it is defined H_R by the relation

$$2mR^2H_R = \Lambda^2 + 2me^2\,R\,C(\alpha,\theta_{12}). \tag{33}$$

Then the Hamilton-Jacobi equation for H_R, with R fixed, which involves only the angular coordinates, is

$$H_R = U_\mu(R). \tag{34}$$

The presence of C, which depends on θ_1, θ_2, and $\phi_1 - \phi_2$, makes than l_1 and l_2 are not longer constants of the motion. As also C depends on α, it is concluded that Λ is not a constant of the motion. Here the index μ denotes three quantities which replace the constants of the motion (Λ, l_1, l_2), and tends to them when the Coulomb interaction effects are small, that is, when $R \to 0$ (limit in which is dominant the centrifugal potential energy over the Coulomb potential energy) [19].

A characteristic function Σ_μ generates a canonical transformation to the action-angle variables of H_R, with fixed R,

$$\{\alpha, p_\alpha, \theta_1, p_{\theta_1}, \phi_1, p_{\phi_1}, \theta_2, p_{\theta_2}, \phi_2, p_{\phi_2}\} \to \{I_\alpha, \theta_\alpha, I_{\theta_1}, \theta_{\theta_1}, I_{\theta_2}, \theta_{\theta_2}, I_{\phi_1}, \theta_{\phi_1}, I_{\phi_2}, \theta_{\phi_2}\}, \tag{35}$$

and is a solution to Eq. 34, which explicitly has the form,

$$\frac{1}{2mR^2}\Big[\Big(\frac{\partial\Sigma_\mu}{\partial\alpha}\Big)^2 + \frac{1}{\cos^2\alpha}\Big(\frac{\partial\Sigma_\mu}{\partial\theta_1}\Big)^2 + \frac{1}{\cos^2\alpha\sin^2\theta_1}\Big(\frac{\partial\Sigma_\mu}{\partial\phi_1}\Big)^2 + \frac{1}{\sin^2\alpha}\Big(\frac{\partial\Sigma_\mu}{\partial\theta_2}\Big)^2 + \frac{1}{\sin^2\alpha\sin^2\theta_2}\Big(\frac{\partial\Sigma_\mu}{\partial\phi_2}\Big)^2\Big] - \frac{Ze^2}{R\cos\alpha} - \frac{Ze^2}{R\sin\alpha} + \frac{e^2}{R}\{1 - \sin 2\alpha[\cos\theta_1\cos\theta_2 + \sin\theta_1\sin\theta_2\cos(\phi_1 - \phi_2)]\}^{-1/2} = U_\mu(R). \tag{36}$$

This equation determines Σ_μ up to an R dependent constant like in Eq. 27; when R makes a complete cycle, that constant can has a change which is not an integer multiple of 2π, so the WKB wave function acquires a "geometric phase", which could has effects on the semiclassical spectrum of adiabatic curves.

The behaviour of the adiabatic channel potential curves $U_\mu(R)$ is such that

$$\text{For } R \to \infty,\ U_\mu(R) \to \frac{e^2C}{R} \text{ and for } R \to 0,\ U_\mu(R) \to \frac{\Lambda^2}{2mR^2}. \tag{37}$$

A. Adiabatic approximation

The Hamilton-Jacobi equation for H is

$$\frac{1}{2m}\Big(\frac{\partial\Sigma}{\partial R}\Big)^2 + H_R\Big(\frac{\partial\Sigma}{\partial\alpha}, \frac{\partial\Sigma}{\partial\theta_1}, \frac{\partial\Sigma}{\partial\theta_2}, \frac{\partial\Sigma}{\partial\phi_1}, \frac{\partial\Sigma}{\partial\phi_2},\ \alpha, \theta_1, \theta_2, \phi_1, \phi_2; R\Big) = E. \tag{38}$$

If we call $w = \{\alpha, \theta_1, \theta_2, \phi_1, \phi_2\}$, and assume that, in Born-Oppenheimer approximation, Σ is approximated by

$$\Sigma(R; w) = F_\mu(R) + \Sigma_\mu(R; w), \tag{39}$$

then Eq. 38 obtains the form

$$\frac{1}{2m}\Big(\frac{dF_\mu}{dR} + \frac{\partial\Sigma_\mu}{\partial R}\Big)^2 + H_R\Big(\frac{\partial\Sigma_\mu}{\partial w}; w; R\Big) = E. \tag{40}$$

The adiabatic approximation consists in taking

$$\frac{dF_\mu}{dR} \gg \frac{\partial\Sigma_\mu}{\partial R}, \tag{41}$$

with which Eq. 40 reduces to

$$\frac{1}{2m}\Big(\frac{dF_\mu}{dR}\Big)^2 + U_\mu(R) = E, \tag{42}$$

whose solution is $F_\mu = \pm\int\{2[E - U_\mu(R)]\}^{1/2}\,dR$.

To know the adiabatic channel potential curves U_μ is necessary to solve the angular motion at fixed values of R, that is to find the action-angle variables (I_μ, ϕ_μ), according to Eq. 36. The potential energy curves $U_\mu(R)$ will be the eigenvalues of the matrix corresponding to H_R according to the equation Eq. 34. On the adiabatic potential energy curves depend the hyperradial motion and the values of the total energy, according to Eq. 42.

IV. MATRIX OF COULOMB INTERACTIONS

A set of action-angle variables for the two-electron system is given by Eq. 35. This set can be completed with (I_R, θ_R), associated to the hyperradial motion. In Eq. 35, when $R \to 0$, the quantities $\{I_\alpha, I_{\theta_1}, I_{\theta_2}, I_{\phi_1}, I_{\phi_2}, \theta_\alpha, \theta_{\theta_1}, \theta_{\theta_2}, \theta_{\phi_1}, \theta_{\phi_2}\}$ replace the set $\{I_\mu, \phi_\mu\}$. This set corresponds to the uncoupled states $|n_r l_1 m_1 l_2 m_2>$ in the quantum description. When the angular momenta of the particles are coupled to give a total angular momentum state, like the quantum $|n_r l_1 l_2 L M>$, the set of action-angle variables is $\{I_\alpha, I_{\theta_1}, I_{\theta_2}, I_\theta, I_\phi, \theta_\alpha, \theta_{\theta_1}, \theta_{\theta_2}, \theta_\theta, \theta_\phi\}$, where θ_θ describes the rotation of the plane $\vec{l}_1 - \vec{l}_2$ around $\vec{L}$, and θ_ϕ is the conjugate to L_z, [20].

Action variables can be replaced by the five constants of the motion in which is expressed the hyperspherical basis in the quantum case, so in principle the function $C(\alpha, \theta_{12})$ has a dependence on all the quantities in Eq. 35, which we will write as,

$$C = C(\Lambda, l_1, l_2, m_1, m_2; \theta_\Lambda, \theta_{l_1}, \theta_{l_2}, \theta_{m_1}, \theta_{m_2}). \tag{43}$$

There are two ways to handle the w or angular part. One is to solve the Hamilton-Jacobi equation, Eq. 36, that is, to find an expression U_μ for H_R as a function of the action variables I_μ. The other is to diagonalize the semiclassical matrix associated with H_R, whose non trivial part according to Eq. 33 is given by the matrix of C. According to the Heisenberg's procedure to associate a matrix to a classical dynamical variable [20–22], C must be expressed in a Fourier series as:

$$C = \sum_{n_\Lambda}\sum_{n_{l_1}}\sum_{n_{l_2}}\sum_{n_{m_1}}\sum_{n_{m_2}} C_{n_\Lambda n_{l_1} n_{l_2} n_{m_1} n_{m_2}}(\Lambda, l_1, l_2, m_1, m_2)$$
$$\exp i(n_\Lambda\,\theta_\Lambda + n_{l_1}\,\theta_{l_1} + n_{l_2}\,\theta_{l_2} + n_{m_1}\,\theta_{m_1} + n_{m_2}\,\theta_{m_2}), \tag{44}$$

and the Fourier coefficients have the expression:

$$C_{n_\Lambda, n_{l_1} n_{l_2} n_{m_1} n_{m_2}}(\Lambda, l_1, l_2, m_1, m_2) = \frac{1}{(2\pi)^5}\oint d\theta_\Lambda \oint d\theta_{l_1} \oint d\theta_{l_2} \oint d\theta_{m_1} \oint d\theta_{m_2}$$
$$C(\Lambda, l_1, l_2, m_1, m_2; \theta_\Lambda, \theta_{l_1}, \theta_{l_2}, \theta_{m_1}, \theta_{m_2})$$
$$\exp i(-n_\Lambda\,\theta_\Lambda - n_{l_1}\,\theta_{l_1} - n_{l_2}\,\theta_{l_2} - n_{m_1}\,\theta_{m_1} - n_{m_2}\,\theta_{m_2}). \tag{45}$$

The integrals over the angular variables can be changed by integrals over u, θ_i and ϕ_i with help of the Jacobian

$$d\theta_\Lambda\, d\theta_{l_1}\, d\theta_{l_2}\, d\theta_{m_1}\, d\theta_{m_2} = J\Big(\frac{\theta_\Lambda\,\theta_{l_1}\,\theta_{l_2}\,\theta_{m_1}\,\theta_{m_2}}{u, \theta_1, \theta_2, \phi_1, \phi_2}\Big)\, du\, d\theta_1\, d\theta_2\, d\phi_1\, d\phi_2. \tag{46}$$

That Jacobian, according to before mentioned formulas, Eq. 23, Eq. 30, and Eq. 31, is given by

$$J = \frac{2\Lambda u}{(1+u^2)X^{1/2}}\,\frac{\sin\theta_1}{(\gamma_1^2 - \cos^2\theta_1)^{1/2}}\,\frac{\sin\theta_2}{(\gamma_2^2 - \cos^2\theta_2)^{1/2}}, \tag{47}$$

where X was defined in Eq. 21, and γ_i in Eq. 30.

J corresponds to the square of the quantum wave function, $G^{\Lambda}_{l_1 l_2}(\alpha) Y_{l_1 m_1}(\Omega_1)$ $Y_{l_2 m_2}(\Omega_2)$, in the uncoupled representation [7].

The final expression for the Fourier coefficients of C is

$$C_{n_\Lambda n_{l_1} n_{l_2} n_{m_1} n_{m_2}}(\Lambda, l_1, l_2, m_1, m_2) = \frac{1}{(2\pi)^5}\oint du \oint d\theta_1 \oint d\theta_2 \oint d\phi_1 \oint d\phi_2$$
$$\frac{2\Lambda u}{(1+u^2)X^{1/2}}\,\frac{\sin\theta_1}{(\gamma_1^2 - \cos^2\theta_1)^{1/2}}\,\frac{\sin\theta_2}{(\gamma_2^2 - \cos^2\theta_2)^{1/2}}$$
$$\Big\{-Z(1+u^2)^{1/2}\Big(1+\frac{1}{u}\Big) + \Big[1 - \frac{2u}{1+u^2}(\cos\theta_1\cos\theta_2 + \sin\theta_1\sin\theta_2\cos(\phi_1 - \phi_2))\Big]^{-1/2}\Big\}$$
$$\exp i(-n_\Lambda\,\theta_\Lambda - n_{l_1}\,\theta_{l_1} - n_{l_2}\,\theta_{l_2} - n_{m_1}\,\theta_{m_1} - n_{m_2}\,\theta_{m_2}), \tag{48}$$

where

$$\theta_\Lambda = \sin^{-1}\frac{b'(1+u^2) + 2c'}{(-\Delta)^{1/2}(1+u^2)},\quad \theta_{li} = \cos^{-1}\frac{\cos\theta_i}{\gamma_i}, \tag{49}$$

and

$$\theta_{m_i} = \phi_i + \cos^{-1}\frac{\cos\theta_i}{\gamma_i} - \tan^{-1}\Big[\frac{l_i}{m_i}\frac{(\gamma_i^2 - \cos^2\theta_i)^{1/2}}{\cos\theta_i}\Big]. \tag{50}$$

A quantization process leads to (with $\hbar = 1$, and the Langer correction [23])

$$I_\alpha = n_{rc} + \frac{1}{2},\ l_i \to l_i + \frac{1}{2},\ m_i \to m_i, \tag{51}$$

with which

$$\Lambda^2 = (2n_{rc} + 1 + l_1 + l_2 + 1)^2 = (\lambda + 2)^2. \tag{52}$$

This expression for Λ in terms of the quantum numbers agrees in the semiclassical limit with the known expression $\Lambda = (\lambda+2)^2 - 1/4$, Ref [6]. It was included the Langer correction 1/2, which accounts some zero point field effects.

With these Fourier coefficients can be constructed the C matrix in the semiclassical limit [17, 21, 22]. For that is required to express the harmonics of the Fourier series as a difference between quantum numbers:

$$\begin{aligned} n_\Lambda &= n_{rc} - n'_{rc} \\ n_{l_1} &= l_1 - l'_1 - m_1 + m'_1 \\ n_{l_2} &= l_2 - l'_2 - m_2 + m'_2 \\ n_{m_1} &= m_1 - m'_1 \\ n_{m_2} &= m_2 - m'_2. \end{aligned} \tag{53}$$

The relation between the matrix and the Fourier coefficients then has the form

$$C_{n_{rc}, l_1 - m_1, l_2 - m_2, m_1\ m_2; n'_{rc}, l'_1 - m'_1, l'_2 - m'_2, m'_1, m'_2} \equiv$$
$$C_{n_\Lambda, n_{l_1}, n_{l_2}, n_{m_1}, n_{m_2}}(2n_{rc} + l_1 + l_2 + 2, l_1 + 1/2, l_2 + 1/2, m_1, m_2). \tag{54}$$

It is convenient to perform a canonical transformation in order to give to the C matrix an identical form to the one in the quantum treatment, like $C_{n_{rc}, l_1, l_2, m_1, m_2; n'_{rc}, l'_1, l'_2, m'_1, m'_2}$. Note that must to be satisfied the relation $m_1 + m_2 = m'_1 + m'_2$.

The before found matrix elements are evaluated between uncoupled states. In the full quantum mechanical calculation the following formula was found for the general matrix element [6], when the angular momenta of electrons are coupled to form the total angular momentum:

$$< n_{rc} l_1 l_2 LM|C|n'_{rc} l'_1 l'_2 L'M' >= \delta_{LL'}\delta_{MM'}\Big[- < n_{rc}|\Big(\frac{z}{\cos\alpha} + \frac{z}{\sin\alpha}\Big)|n'_{rc} > \delta_{l_1 l'_1}\delta_{l_2 l'_2}$$
$$+ \sum_{k=0}^{\infty} < n_{rc}|\frac{\sin^k\alpha}{\cos^{k+1}\alpha}\theta\Big(\frac{\pi}{4} - \alpha\Big) + \frac{\cos^k\alpha}{\sin^{k+1}\alpha}\theta\Big(\alpha - \frac{\pi}{4}\Big)|n'_{rc} >$$
$$< l_1 l_2 LM|P_k(\cos\theta_{12})|l'_1 l'_2 LM >\Big], \tag{55}$$

where $\theta(x)$ is a unit step function, and the coupled angular states $|l_1 l_2 LM>$ are obtained from the on e-particle angular states, given by the spherical harmonics functions, with help of the Clebsch-Gordan coefficients.

The diagonal elements have a classical counterpart which can be easily obtained with help of the classical probability density for the u motion, and the following formula to evaluate the average value of $P_k(\cos\theta_{12})$ in the coupled states obtained by Leopold *et al* [20]:

$$f_k^{cl} =< P_k(\cos\theta_{12}) >_{\theta_{l_1}\theta_{l_2}\theta_L\theta_M} = [P_k(0)]^2 P_k(\cos\chi), \tag{56}$$

where χ is the angle between the individual angular momentum vectors, given by:

$$\cos\chi = \frac{(l_1+\frac{1}{2})^2 + (l_2+\frac{1}{2})^2 - (L+\frac{1}{2})^2}{2(l_1+\frac{1}{2})(l_2+\frac{1}{2})}. \tag{57}$$

This expression guarantees that are valid the inequalities $|l_1 - l_2| \le L \le l_1 + l_2$. The expression $< P >_{\theta_{l_1}}$ denotes an average of P over the angular variable θ_{l_1}.

Then the following expression for the matrix elements, diagonal respect to the quantum numbers l_1, l_2, L, M, and diagonal or not respect to the n_{rc} quantum numbers, is obtained:

$$\begin{aligned} &< n_{rc} l_1 l_2 LM|C|n'_{rc} l_1 l_2 LM >= -Z < (1+u^2)^{1/2}\Big(1+\frac{1}{u}\Big) >_{n_{rc}n'_{rc}} \\ &+\sum_{k=0}^{\infty} < \Big(u^k\theta(1-u) + u^{-k-1}\theta(u-1)\Big)(1+u^2)^{1/2}\Big(1+\frac{1}{u}\Big) >_{n_{rc}n'_{rc}} \\ &[P_k(0)]^2 P_k(\cos\chi). \end{aligned} \tag{58}$$

Here $< ... >_{n_{rc}n'_{rc}}$ denotes an average respect to u using the "probability density"

$$\rho(u)\,\cos[(n_{rc} - n'_{rc})\theta_\Lambda], \tag{59}$$

where $\rho(u)$ is given by Eq. 25, taking into its dependence of Λ on n_{rc} an average between n_{rc} and n'_{rc}. The relation between u and the angular variable θ_Λ is given by Eq. 23.

Tables show some of the numerical results. In order to obtain a sign agreement with the quantum mechanical values, it was necessary in Eq. 19 to add the constant $I_\alpha\pi/2$, like in Eq 27. That give up a phase shift in the semiclassical wave function, which contributes with an overall phase factor of $\exp[i(n_{rc} - n'_{rc})\pi/2]$ into the matrix element defined by Eq. 48.

A more general expression, valid for non diagonal matrix elements respect to (l_i, l'_i), is obtained from an adequate classical limit for the Percival-Seaton factor, $f_k(l'_1 l'_2, l_1 l_2; L)$, given in Ref. [24] by,

$$\begin{aligned} &< l_1 l_2 LM|P_k(\cos\theta_{12})|l'_1 l'_2 LM >= \\ &(-1)^{l_1+l'_1+L} < l'_1||C^{(k)}||l_1 >< l'_2||C^{(k)}||l_2 > \begin{Bmatrix} L & l'_2 & l'_1 \\ k & l_1 & l_2 \end{Bmatrix}, \end{aligned} \tag{60}$$

which depends on the reduced matrix elements of Racah's tensor operators $C^{(k)}$ and on the Wigner symbol $6-j$.

Dickinson and Richards [25] obtained a simple expression for the classical limit of the Percival-Seaton factors, Ref. [26]:

$$f_k(l'_1 l'_2, l_1 l_2; L) \approx (-1)^s P_k^s(0) P_k^t(0) d^{(k)}_{-t,s}(\chi); \tag{61}$$

$d^{(k)}_{q,q'}(\beta)$ is a matrix element associated with a finite rotation, $s = l_1 - l'_1$, $t = l_2 - l'_2$, and χ is given by Ref. [25].

V. CONCLUSION

The dynamical system defined by Λ = constant is a zeroth approximation to the real system at constant R, if are neglected the interactions. That is the reason why the C matrix, in the hyperspherical representation, has larger elements on the diagonal, fact detected by Lin [19]. The potential $V_{l_1 l_2}$ is shallow, and infinite at $\alpha = 0$ and $\alpha = \pi/2$; the u motion presents hard bumps at the turning points; that behaviour is conserved in the real situation in which R is an adiabatic coordinate. It was found a formula for the WKB approximation to the hyperspherical harmonics, and an analytic expression for the semiclassical matrix elements of C; that formula would be optimized by choosing adequate intermediate values for n_{rc} between the two involved states. Table I shows a sign discrepancy on one of the matrix elements, which can be attributed to that the weight of the quantum effects on small matrix elements is comparable with the classical value; this behaviour occurs in almost all the elements which are small, most of them located far from the diagonal. This formulation also can be useful in order to identify the dominant classical effects, and the strength of the quantum effects which can be important in some states. A classical description based on adiabatic hyperspheric channels can give satisfactory results in highly doubly excited states of helium and other two-electron systems.

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[1] R. P. Madden, and K. Codling, *Astrophys. J.* **141**, 364-375 (1965); *Phy. Rev. Lett.* **10**, 516-518 (1963).

[2] H. C. Bryant *et al*, *Phy. Rev. Lett.* **38**, 228-230 (1977).

[3] U. Eichman, V. Lange, and W. Sandner, *Phy. Rev. Lett.* **64**, 274-277 (1990).

[4] K. Richter, and D. Wintgen, *Phys. Rev. Lett.* **65**, 1965-1965 (1990).

[5] I. C. Percival, *Adv. Chem. Phys.* **36**, 1-61 (1977).

[6] U. Fano, *Rep. Prog. Phys.* **46**, 97-165 (1983).

[7] J. H. Macek, *Phys. Rev.* **146**, 50-53 (1966); **160**, 170-174 (1967).

[8] C. D. Lin, *Adv. At. Mol. Phys.* **22**, 77-142 (1986).

[9] J. Botero, *Phys. Rev. A* **35**, 36-50 (1987).

[10] D. Wintgen, and D. Delande, *J. Phys. B* **26**, L399-L405 (1993).

[11] F. T. Smith, *Phys. Rev.* **120**, 1058-1069 (1960).

[12] D. L. Knirk, *Phys. Rev. Lett.* **32**, 651-654 (1974).

[13] M. Born, *The Mechanics of the Atom* (Bell, and Sons ltd., London, 1927), page 137.

[14] J. Mahecha, (unpublished), (1979).

[15] R. M. More, *Ann. Phys.* **207**, 282-342 (1991), and references cited herein.

[16] P. J. Brussaard, and H. A. Tolhoek, *Physica* **XXIII**, 955-971 (1957).

[17] S. C. McFarlane, *J. Phys. B* **25**, 4045-4057 (1992); **26**, 1871-1884 (1993).

[18] R. Peterkop, *J. Phys. B* **4**, 513-521 (1971).

[19] C. D. Lin, *Phys. Rev. A* **10**. 1986-2001 (1974).

[20] J. G. Leopold, I. C. Percival, and A. S. Tworkowski, *J. Phys. B* **13**, 1025-1036 (1980); J. G. Leopold, and I. C. Percival, *ibid.* **13**, 1037-1047 (1980).

[21] L. D. Landau, and E. M. Lifshitz, *Quantum Mechanics (non relativistic theory)* (Pergamon, London, 1958), page 166.

[22] A. B. Migdal, *Qualitative Methods in Quantum Theory* (Benjamin, New York, 1977), page 166.

[23] R. Langer, *Phys. Rev.* **51**, 669-676 (1937).

[24] A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University Press, Princeton, 2nd. ed. 1974), page 111.

[25] A. S. Dickinson, and D. Richards, *J. Phys. B* **14**, 1916-1936 (1974); Dickinson A S, and Liu W K *J. Phys. Chem.* **90**, 3612-3619 (1986).

[26] I. C. Percival, and M. J. Seaton, *Proc. Camb. Phil. Soc.* **53**, 654-659 (1957).

TABLE I. Matrix elements of the Coulomb interaction terms of the hyperspherical Hamiltonian for helium S states. QM, exact quantal results; SC, semiclassical approximation. * Given by [19].

	$< n_{rc} l_1\, l_2 0M \vert C(\alpha,\theta_{12}) \vert n'_{rc} l_1 l_2 0M >$							
(l_1, l_2)	(0,0)		(1,1)		(2,2)		(3,3)	
(n_{rc}, n'_{rc})	SC	QM	SC	QM	SC	QM	SC	QM
(0,0)	12.09	11.18*	9.85	9.39*	9.18	8.79*	8.82	8.47*
(0,2)	4.63	3.69*	2.12	2.12*	1.46	1.60*	1.16	1.35
(0,4)	3.31	1.98*	0.82	0.50*	0.28	0.10	0.07	-0.07
(0,6)	2.89	1.49*	0.64	0.47	0.26	0.29	0.14	0.24
(2,2)	17.38	16.86*	13.24	13.06*	11.78	11.65*	10.99	10.89
(2,4)	7.71	7.18*	4.02	4.05*	2.81	2.91	2.20	2.32
(2,6)	5.35	4.59*	1.87	1.70	0.89	0.81	0.47	0.41
(4,4)	19.85	19.47*	15.21	15.10*	13.41	13.35	12.40	12.35
(4,6)	9.58	9.23*	5.43	5.51	3.91	4.03	3.09	3.21
(6,6)	21.46	21.19*	16.61	16.55	14.64	14.60	13.48	13.46

TABLE II. The same as Table I, but for P states.

	$< n_{rc} l_1\, l_2 1M \vert C(\alpha,\theta_{12}) \vert n'_{rc} l_1 l_2 1M >$							
(l_1, l_2)	(0,1)		(1,1)		(1,2)		(2,2)	
(n_{rc}, n'_{rc})	SC	QM	SC	QM	SC	QM	SC	QM
(0,0)	11.77	15.98	10.17	10.22	9.92	15.16	9.48	9.51
(0,2)	3.50	2.68	1.98	1.74	1.75	1.18	1.32	1.23
(0,4)	2.26	1.65	0.88	0.68	0.65	0.66	0.35	0.31
(0,6)	1.88	1.07	0.61	0.38	0.45	0.24	0.21	0.16
(2,2)	15.58	19.78	13.46	13.55	12.71	17.54	11.97	12.04
(2,4)	5.87	5.29	3.88	3.7.	3.36	2.88	2.68	2.64
(2,6)	3.74	3.40	1.93	1.84	1.48	1.56	0.96	0.97
(4,4)	17.73	21.99	15.41	15.54	14.47	19.26	13.58	13.68
(4,6)	7.48	7.01	5.29	5.22	4.60	4.17	3.78	3.78
(6,6)	19.22	23.54	16.81	16.97	15.77	20.56	14.80	1 .92

TABLE III. The same as Table I, but for D states.

$< n_{rc} l_1 l_2 2M \vert C(\alpha, \theta_{12}) \vert n'_{rc} l_1 l_2 2M >$								
(l_1, l_2)	(0,2)		(1,1)		(1,2)		(1,3)	
(n_{rc}, n'_{rc})	SC	QM	SC	QM	SC	QM	SC	QM
(0,0)	12.44	11.91	10.19	9.89	10.15	14.61	10.20	10.04
(0,2)	3.45	3.02	1.97	1.89	1.67	1.40	1.66	1.61
(0,4)	2.24	1.66	0.88	0.61	0.67	0.57	0.64	0.51
(0,6)	1.86	1.22	0.61	0.42	0.44	0.29	0.44	0.33
(2,2)	15.16	14.85	13.48	13.35	12.87	17.22	12.52	12.47
(2,4)	5.42	5.18	3.87	3.87	3.28	3.08	3.11	3.13
(2,6)	3.44	3.08	1.94	1.78	1.50	1.48	1.36	1.29
(4,4)	17.00	16.76	15.43	15.36	14.61	18.97	14.09	14.07
(4,6)	6.81	6.65	5.28	5.34	4.52	4.36	4.23	4.29
(6,6)	18.35	18.16	16.83	16.80	15.90	20.28	15.28	15.29

TABLE IV. The same as Table I, but for F states.

$< n_{rc} l_1 l_2 3M \vert C(\alpha, \theta_{12}) \vert n'_{rc} l_1 l_2 3M >$								
(l_1, l_2)	(0,3)		(1,2)		(1,3)		(2,2)	
(n_{rc}, n'_{rc})	SC	QM	SC	QM	SC	QM	SC	QM
(0,0)	13.27	17.39	10.10	14.96	10.40	10.50	9.73	9.79
(0,2)	3.58	3.03	1.68	1.26	1.60	1.47	1.24	1.15
(0,4)	2.37	1.86	0.67	0.63	0.66	0.56	0.37	0.33
(0,6)	1.97	1.35	0.44	0.26	0.43	0.31	0.20	0.15
(2,2)	15.12	19.38	12.84	17.43	12.66	12.75	12.13	12.21
(2,4)	5.31	4.81	3.29	2.95	3.05	2.98	2.59	2.56
(2,6)	3.42	3.16	1.50	1.53	1.38	1.35	0.99	0.99
(4,4)	16.69	20.98	14.58	19.16	14.22	14.33	13.73	13.84
(4,6)	6.53	6.08	4.53	4.24	4.16	4.13	3.69	3.69
(6,6)	17.90	22.22	15.88	20.46	15.41	15.54	14.94	15.07