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CLASSICAL-LIMIT GREEN'S FUNCTION (FIXED-ENERGY PROPAGATOR)
AND CLASSICAL QUANTIZATION OF NON-SEPARABLE SYSTEMS*

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ABSTRACT

On the basis of a classical-limit approximation for the Green's function a classical quantum condition for general, non-separable dynamical systems is obtained. Bound-state eigenvalues are seen to be associated with stable periodic trajectories, and quasi-bound (or metastable) states are related to unstable periodic trajectories. Application is made to ns^2 states of the two-electron atom, and quite reasonable results are obtained for the energies of the $1s^2$ and $2s^2$ states of He and H^- . An accurate value is also obtained for the lowest eigenvalue of three identical Bosons (e.g. helium atoms) interacting through pair Morse potentials.

I. Introduction

Recent work¹⁻² has shown how exact solutions of the classical equations of motion (i.e., numerically computed trajectories) for a complex, non-separable dynamical system (such as an atom plus diatomic molecule) can be used to construct the classical limit of quantum mechanical scattering amplitudes, or S-matrix elements. Applications³ have shown that this exact classical-limit theory is capable of accurately describing quantum interference (and to some extent tunneling) effects in molecular collisions; it also effectively circumvents the two primary road blocks⁴ that hinder purely quantum treatments of molecular collision phenomena, namely the large number of channels (i.e., rotational-vibrational states) one is forced to deal with in a quantum treatment and the complexity that arises when chemical reaction occurs due to scrambling of the coordinate systems.

This paper considers the classical limit of the corresponding bound-state (eigenvalue) problem for non-separable dynamical systems; i.e., one seeks the proper generalization of the Bohr-Sommerfeld quantization condition⁵ for systems with one degree of freedom. Although we do not envision that classical quantization will be nearly so useful in practice as the classical-limit description of scattering, it may be quite useful in gaining insight regarding the general applicability of classical-limit theories to complex dynamical systems, be they bound-state or scattering situations.

Our approach follows closely the recent important work of Gutzwiller^{6a}, although there are some extensions and modifications of his results, including a modification of his quantum condition. Section

II obtains the classical limit of the fixed-energy Green's function from the classical limit of the propagator in time, and Section III develops the classical quantum condition for bound and quasi-bound, or metastable states. Bound states are seen to be associated with stable periodic trajectories, whereas quasi-bound states are connected with unstable periodic trajectories. Section IV presents two applications of the classical quantum condition, and it is seen that quite reasonable results are obtained.

II. Classical-Limit Green's Function

The Green's function for energy E is given in terms of the propagator by⁷

$$G(E) = (i\hbar)^{-1} \int_0^{\infty} dt \, e^{iEt/\hbar} e^{-iHt/\hbar}, \quad (1)$$

or in terms of their matrix elements

$$G(q_2, q_1; E) = (i\hbar)^{-1} \int_0^{\infty} dt \, e^{iEt/\hbar} K(q_2, q_1; t), \quad (2)$$

where

$$G(q_2, q_1; E) \equiv \langle q_2 | G(E) | q_1 \rangle$$

$$K(q_2, q_1; t) \equiv \langle q_2 | e^{-iHt/\hbar} | q_1 \rangle,$$

and q denotes all the coordinates of the system collectively.

In the classical limit^{8,6a} the propagator is

$$K(q_2, q_1; t) = \left[-\frac{\partial^2 \phi(q_2, q_1; t)}{\partial q_2 \partial q_1} / 2\pi i \hbar \right]^{\frac{1}{2}} e^{i\phi(q_2, q_1; t)/\hbar}, \quad (3)$$

where

$$\phi(q_2, q_1; t) = \int_0^t dt' p(t') \dot{q}(t') - H(p, q), \quad (4)$$

and $q(t')$, $p(t')$ is the classical trajectory determined by the classical equations of motion with boundary conditions $q(0) = q_1$, $q(t) = q_2$, for the fixed time interval $(0, t)$. [If there is more than one such classical trajectory, then Equation (4) is a sum of similar terms over them all.]

Since

$$\frac{\partial \phi(q_2, q_1; t)}{\partial q_1} = -p_1,$$

Equation (3) is given equivalently by

$$K(q_2, q_1; t) = \left[2\pi i \hbar \left(\frac{\partial q_2}{\partial p_1} \right)_{q_1} \right]^{-\frac{1}{2}} \exp \left[i\phi(q_2, q_1; t)/\hbar - i\pi\ell/2 \right], \quad (5)$$

where the phase $\exp(-i\pi\ell/2)$ is the correct branch of the square root of the Jacobian⁹ $(\partial q_2/\partial p_1)_{q_1}$; i.e., ℓ is the number of zeros of $[\partial q(t')/\partial p_1]_{q_1}$ in the interval $0 \leq t' \leq t$.^{6a}

Evaluating the time integral in Equation (2) by stationary phase (consistent with the classical limit) thus gives

$$G(q_2, q_1; E) = \sum (i\hbar)^{-1} \left[\frac{\partial t(q_2, q_1; E)}{\partial E} / \left(\frac{\partial q_2}{\partial p_1} \right)_{q_1, t} \right]^{\frac{1}{2}} \exp \left[i\Phi(q_2, q_1; E)/\hbar - i\pi\ell/2 \right], \quad (6)$$

where

$$\Phi(q_2, q_1; E) = Et + \phi(q_2, q_1; t) = \int_0^t dt' p(t') \dot{q}(t'), \quad (7)$$

and the summation in Equation (6) indicates a sum over all values of $t \equiv t(q_2, q_1; E)$ which satisfy the stationary phase relation

$$E = \frac{\partial \phi(q_2, q_1; t)}{\partial t} \quad (8)$$

Since it is well-known¹⁰ that $\partial \phi(q_2, q_1; t)/\partial t$ is the constant value of the energy along the classical trajectory determined by q_2, q_1 , and t , Equations (2) and (6) stand in the usual quantum-classical relation to one another: all values of time contribute quantum mechanically to the fixed-energy propagator, but classically only those particular times contribute (à la stationary phase) which are related classically to the particular value of the energy.

Although not in its most symmetrical form, Equation (6) is actually the form of $G(E)$ most useful for our purposes. To show that it is equivalent to the symmetrical expression used by Gutzwiller,⁶ the relations

$$t(q_2, q_1; E) = \partial \Phi(q_2, q_1; E) / \partial E$$

$$p_1 = - \partial \Phi(q_2, q_1; E) / \partial q_1$$

$$\left(\frac{\partial p_1}{\partial q_2} \right)_{q_1, t} = - \frac{\partial^2 \Phi(q_2, q_1; E)}{\partial q_2 \partial q_1} - \frac{\partial^2 \Phi(q_2, q_1; E)}{\partial q_1 \partial E} \left(\frac{\partial E}{\partial q_2} \right)_{q_1, t}$$

$$\left(\frac{\partial E}{\partial q_2}\right)_{q_1, t} = - \frac{\frac{\partial^2 \Phi(q_2, q_1; E)}{\partial E \partial q_2}}{\frac{\partial^2 \Phi(q_2, q_1; E)}{\partial E^2}}$$

can be used to show that the pre-exponential factor in Equation (6) is equivalently given by

$$\frac{1}{h} \left[\frac{\frac{\partial^2 \Phi}{\partial q_2 \partial q_1}}{\frac{\partial^2 \Phi}{\partial E^2}} - \frac{\frac{\partial^2 \Phi}{\partial q_2 \partial E}}{\frac{\partial^2 \Phi}{\partial q_1 \partial E}} \right]^{\frac{1}{2}} \quad (9)$$

The reason the form of the pre-exponential factor in Equation (6) is more useful than the one in Equation (9) is because in any non-trivial application one will ordinarily integrate the classical equations of motion in time with specified initial conditions (q_1, p_1) ; the Jacobian $(\partial q_2 / \partial p_1)_{q_1, t}$ is therefore quite readily determined in practice, and (as seen in the next Section) its general properties can be easily established. Jacobians at fixed energy are cumbersome (unless the system is sufficiently simple that one has an analytic solution) because q_1 and p_1 are not independent variables if E is fixed - for $E = H(p_1, q_1)$ is required.

III. Classical Quantum Condition

Following Gutzwiller^{6d}, we consider the "response function" $g(E)$, defined by

$$g(E) \equiv \text{trace}[G(E)] \quad (10)$$

$$= \int dq \, G(q, q; E) \quad (11)$$

The quantum expression for $g(E)$ is

$$g(E) = \sum_n (E - E_n)^{-1} , \quad (12)$$

indicating that $g(E)$ is singular when E is equal to one of the discrete eigenvalues. This fact is used to determine the classical quantum condition: the classical-limit approximation in Equation (6) is used for $G(q, q; E)$, the resulting approximation for $g(E)$ is computed via Equation (11), and the requirement that $g(E)$ be singular is the condition that E be an eigenvalue.

a. Periodic Trajectories

One needs the matrix elements $G(q_2, q_1; E)$, therefore, only in the special case $q_2 = q_1 \equiv q$, i.e., one seeks trajectories that begin at q at $t = 0$ and return to the same q after time t . There may be many such trajectories; but, as Gutzwiller^{6d} has argued, since

$$\begin{aligned} \frac{\partial \Phi(q, q; E)}{\partial q} &= \left[\frac{\partial \Phi(q_2, q_1; E)}{\partial q_2} + \frac{\partial \Phi(q_2, q_1; E)}{\partial q_1} \right]_{q_2 = q_1 = q} \\ &= p_2 - p_1 = p(t) - p(0) , \end{aligned} \quad (13)$$

the phase $\Phi(q, q; E)$ oscillates with q so that most such trajectories contribute negligibly to the integral over q in Equation (11). The only exception to this are the periodic trajectories for which, by definition, $p(t) = p(0)$; i.e., Equation (13) shows that $\Phi(q, q; E)$ is independent of q for a periodic trajectory, and the integrand of Equation (11) is thus not oscillatory.

Consider the contribution to $G(q, q; E)$ of a particular periodic

trajectory $Q(t)$ with period τ and initial value q ; i.e., $Q(t + \tau) = Q(t)$, $\dot{Q}(t + \tau) = \dot{Q}(t)$ for all t . The trajectory has a definite energy E and definite values of all other constants of the motion (such as total angular momentum J). The stationary phase relation in Equation (8) is satisfied for $t = \tau, 2\tau, 3\tau, \dots, n\tau, \dots$, corresponding to one, two, etc., passages over the same trajectory. Since the contribution to $G(q, q; E)$ is a sum over all times which satisfy Equation (8), one has

$$G(q, q; E) = \sum_{n=1}^{\infty} (i\hbar)^{-1} \left[\frac{\partial t_n}{\partial E} \left/ \left| \frac{\partial q(t_n)}{\partial p(o)} \right| \right]^{\frac{1}{2}} \times \exp(i\Phi_n/\hbar - i\pi\ell_n/2) , \quad (14)$$

where $t_n = n\tau$. It is clear, however, that

$$\Phi_n \equiv \int_0^{n\tau} dt P(t) \dot{Q}(t) = n\Phi \quad (15a)$$

$$\ell_n = n\ell , \quad (15b)$$

where Φ is the phase and ℓ the number of zeros of $[\partial q(t)/\partial p(o)]$ which correspond to one passage over the trajectory; $\Phi = \Phi(E, J, \dots)$ is a function only of all the conserved quantities associated with the periodic trajectory. Thus, Equation (14) becomes

$$G(q, q; E) = \sum_{n=1}^{\infty} (i\hbar)^{-1} \left[n \frac{\partial \tau}{\partial E} \left/ \left| \frac{\partial q(n\tau)}{\partial p(o)} \right| \right]^{\frac{1}{2}} \times e^{in(\Phi/\hbar - \pi\ell/2)} \quad (16)$$

Before proceeding further, it is necessary to explore in some detail the structure of the Jacobian $[\partial \dot{q}(n\tau)/\partial p(o)]$.

b. Stability Considerations

The Jacobian $[\partial \dot{q}(n\tau)/\partial p(o)]$ is intimately related to the stability of the periodic trajectory. Stability of periodic trajectories, however, is a subject that has received extensive study in the classical literature¹¹. Although our discussion of stability will employ second-order differential equations and thus appear different from Whittaker's¹¹, it is actually equivalent; use of the Newtonian equations of motion, however, helps to eliminate some redundancies in the usual treatment and gives a clearer picture of the physical meaning of the characteristic exponents.

Since the trace of $G(E)$ in Equation (10) is independent of the particular representation in which it is carried out, we can without restriction take the coordinates q to be the Cartesian coordinates of the system; the equations of motion are then

$$m_i \ddot{q}_i(t) + \frac{\partial V}{\partial q_i} = 0, \quad (17)$$

for $i = 1, \dots, N$, where we are now expanding the notation to indicate explicitly the N degrees of freedom of the system; $V = V(q_1, q_2, \dots, q_N)$ is the total potential energy.

The coordinates $q_i(t)$ are functions of all the initial values $[q_i(o), \dot{q}_i(o)]$, $i = 1, \dots, N$, as well as the time t ; i.e., $q_i(t) = q_i[t; q_1(o), q_2(o), \dots, q_N(o); \dot{q}_1(o), \dot{q}_2(o), \dots, \dot{q}_N(o)]$. Differentiating Equation (17) with respect to a particular initial velocity $\dot{q}_j(o)$, holding all other initial values and the time t fixed, gives

$$m_i \frac{d^2}{dt^2} \frac{\partial q_i(t)}{\partial \dot{q}_j(o)} + \sum_k \frac{\partial^2 V}{\partial q_i \partial q_k} \frac{\partial q_k(t)}{\partial \dot{q}_j(o)} = 0 \quad (18)$$

Replacing $\dot{q}_k(o)$ by $p_k(o)/m_k$, defining

$$u_{i,j}(t) \equiv m_i^{-\frac{1}{2}} \partial q_i(t) / \partial p_j(o) \quad , \quad (19)$$

and taking the trajectory $\{q_i(t)\}$ to be the periodic trajectory $\{Q_i(t)\}$,

Equation (18) becomes (in matrix notation)

$$\frac{d^2}{dt^2} \vec{u}(t) + \vec{K}(t) \cdot \vec{u}(t) = 0 \quad , \quad (20)$$

where

$$K_{i,j}(t) = (m_i m_j)^{-\frac{1}{2}} \frac{\partial^2 V(q_1, \dots, q_N)}{\partial q_i \partial q_j} \quad . \quad (21)$$

The initial values for $\vec{u}(t)$ are obviously

$$u_{i,j}(o) = 0 \quad (22a)$$

$$\dot{u}_{i,j}(o) = m_i^{-\frac{1}{2}} \delta_{i,j} \quad . \quad (22b)$$

Solution of the coupled linear second order equations of Equation (20)

with the initial conditions in Equation (22) determines $\vec{u}(t)$; the

Jacobian in Equation (16) is then given by

$$\det \left[\partial q_i(n\tau) / \partial p_j(o) \right] = \det \left[u_{i,j}(n\tau) \right] \times \left(\prod_{i=1}^N m_i^{-\frac{1}{2}} \right) \quad , \quad (23)$$

and l is the number of zeros of $\det[u_{i,j}(t)]$ in the time interval $(0, \tau)$.

The physical meaning of Equation (20) is the following: $u_{i,j}(t)$ is the displacement in coordinate i away from $Q_i(t)$ (its value on the periodic trajectory) resulting from an infinitesimal change of initial momentum j . It is seen that the equations of motion for these displacements are those of coupled harmonic oscillators with time-dependent force constants. The displacements, therefore, describe oscillations about the periodic trajectory $\{Q_i(t)\}$.

Since $\{Q_i(t)\}$ is periodic, the force constant matrix $\vec{K}(t)$ in Equation (21) is also periodic with period τ : $\vec{K}(t + \tau) = \vec{K}(t)$ for all t . The Floquet-Poincare Theorem¹² of ordinary differential equations thus implies that the solution for $\vec{u}(t)$ is of the form

$$\vec{u}(t) = \vec{A}(t) \cdot \cos(\vec{\omega}t) + \vec{B}(t) \cdot \vec{\omega}^{-1} \cdot \sin(\vec{\omega}t),$$

where the matrixes $\vec{A}(t)$ and $\vec{B}(t)$ are periodic functions of t with period τ , and $\vec{\omega}$ is a constant diagonal matrix, the elements ω_i being characteristic of the system. If $\vec{K}(t)$ were time-independent and diagonal, for example, $\vec{A}(t)$ and $\vec{B}(t)$ would also be time-independent.

$$\begin{aligned} \vec{A}(t) &= \vec{u}(0) \\ \vec{B}(t) &= \vec{u}(0), \end{aligned}$$

and

$$\omega_i = K_{i,i}^{\frac{1}{2}}.$$

In general, therefore, the frequencies ω_i may be thought of as "normal modes" of the system; normal modes exist for a system with time-varying force constants only because the force constants vary periodically with

time. If all of the frequencies are real, then the displacements about the periodic trajectory are oscillatory, and the periodic trajectory is stable. If any of the frequencies have a non-zero imaginary part, then there is some configuration of displacements whose amplitude increases exponentially in time, meaning that the periodic trajectory is unstable.

After n periods, therefore,

$$\begin{aligned}\vec{u}(n\tau) &= \vec{A}(n\tau) \cdot \cos(\vec{\omega}n\tau) + \vec{B}(n\tau) \cdot \vec{\omega}^{-1} \cdot \sin(\vec{\omega}n\tau) \\ &= \vec{A}(0) \cdot \cos(\vec{\omega}n\tau) + \vec{B}(0) \cdot \vec{\omega}^{-1} \cdot \sin(\vec{\omega}n\tau) .\end{aligned}$$

The initial condition Equation (22a) implies that $\vec{A}(0) = 0$, so that this becomes

$$\vec{u}(n\tau) = \vec{B}(0) \cdot \vec{\omega}^{-1} \cdot \sin(\vec{\omega}n\tau) , \quad (24)$$

and thus

$$\det[\vec{u}(n\tau)] = \det[\vec{B}(0)] \cdot \prod_{i=1}^N \frac{\sin(\omega_i n\tau)}{\omega_i} . \quad (25)$$

Equation (24) also shows that once Equation (20) has been solved, the normal frequencies can be easily identified, for example, by using the relation

$$\vec{u}(\tau)^{-1} \cdot \vec{u}(2\tau) = 2 \cos(\vec{\omega}\tau) .$$

It is generally true¹³, however, that for every integral constant of the motion (e.g., E , J , ...) one of the frequencies ω_i is zero. [They may not appear physically to be zero, but rather an integral multiple of $2\pi/\tau$; since $\sin(2\pi nt/\tau)$ has period τ , however, this factor is by convention absorbed into $\vec{B}(t)$.] Equation (25) thus becomes

$$\det \left[\vec{u}(n\tau) \right] = \det \left[\vec{B}(0) \right] (n\tau)^M \prod_i' \frac{\sin(\omega_i n\tau)}{\omega_i}, \quad (26)$$

where M is the number of conserved quantities, and the prime indicates omission of the zero frequencies.

c. WKB Solution for the Normal Frequencies

Before proceeding, we note that if the force constant matrix is a slowly varying function of time, then Equation (20) may be solved in a WKB-like approximation.

Let $\vec{U}(t)$ be the unitary matrix that diagonalized the real symmetric matrix $\vec{K}(t)$:

$$\vec{K}(t) = \vec{U}^\dagger(t) \cdot \vec{k}(t) \cdot \vec{U}(t),$$

where $\vec{k}(t)$ is diagonal, $k_i(t) \equiv \omega_i(t)^2$; $\omega_i(t)$, the instantaneous normal frequencies, are real or pure imaginary. The WKB-like solution for $\vec{u}(t)$ is

$$\begin{aligned} \vec{u}(t) = & \vec{U}(t)^\dagger \cdot \cos \left[\int_0^t dt' \vec{\omega}(t') \right] \vec{\omega}(t)^{-\frac{1}{2}} \vec{\omega}(0)^{\frac{1}{2}} \cdot \vec{U}(0) \cdot \vec{u}(0) \\ & + \vec{U}^\dagger(t) \cdot \sin \left[\int_0^t dt' \vec{\omega}(t') \right] \vec{\omega}(t)^{-\frac{1}{2}} \vec{\omega}(0)^{-\frac{1}{2}} \cdot \vec{U}(0) \cdot \dot{\vec{u}}(0), \end{aligned}$$

from which one can easily identify the (constant) normal frequencies ω_i :

$$\omega_i = \frac{1}{\tau} \int_0^\tau dt \omega_i(t);$$

i.e., the normal frequencies in this approximation are the time average

of the instantaneous normal frequencies. It is clear that ω_i will be complex if $\omega_i(t)$ is imaginary (i.e., the trajectory is unstable) for any finite interval of time.

d. Singularities

With the Jacobian given by Equation (26), the Green's function in Equation (16) thus becomes

$$G(q, q; E) = f(q) \sum_{n=1}^{\infty} \left[\prod_i' |\sin(\omega_i n \tau)|^{-\frac{1}{2}} \right] n^{-(M-1)/2} e^{i n (\Phi/\hbar - \pi \ell/2)}, \quad (27)$$

where $f(q)$ takes into account various constants and the fact that $\det \left[\vec{B}(0) \right]$ may depend on q ; the response function is thus given by

$$g(E) = (\text{constant}) \sum_{n=1}^{\infty} \left[\prod_i' |\sin(\omega_i n \tau)| \right]^{-\frac{1}{2}} n^{-(M-1)/2} e^{i n (\Phi/\hbar - \pi \ell/2)}. \quad (28)$$

If

$$\Phi/\hbar - \pi \ell/2 = 2\pi \times (\text{integer}) \quad (29)$$

and if all the frequencies ω_i are real, then

$$g(E) = (\text{constant}) \sum_{n=1}^{\infty} n^{-(M-1)/2} \left[\prod_i' |\sin(\omega_i n \tau)| \right]^{-\frac{1}{2}}, \quad (30)$$

which is clearly infinite since the limit of the positive definite summand as $n \rightarrow \infty$ is not zero — regardless of the value of M . The value of E for which Equation (29) is true must therefore be an

eigenvalue. If equation (29) is not true, then the summand oscillates infinitely rapidly as $n \rightarrow \infty$, so that no singularity results.

If some of the frequencies have imaginary parts, then for large n

$$|\sin(\omega_i n \tau)| = \frac{1}{2} e^{n \tau |\operatorname{Im} \omega_i|},$$

so that the summand of Equation (28) is

$$\left[\prod_i'' |\sin(\omega_i n \tau)| \right]^{-\frac{1}{2}} n^{-(M-1)/2} \exp \left[i n \Phi / \hbar - i n \pi \ell / 2 - \frac{1}{2} n \tau \sum_i |\operatorname{Im} \omega_i| \right],$$

where the double prime means that only the real frequencies are included in the product. As above, the sum will be infinite if, and only if,

$$\Phi / \hbar - \pi \ell / 2 + i \frac{\tau}{2} \sum_i |\operatorname{Im} \omega_i| = 2\pi \times (\text{integer}). \quad (31)$$

It is clear that Equation (31) cannot be satisfied for any real value of E , for Φ and ℓ are then real. If, however, E is allowed to have a small negative imaginary part,

$$E = E_r - i\Gamma/2,$$

where E_r and Γ are real, then if $\Gamma \ll E_r$,

$$\begin{aligned} \Phi(E) &= \Phi(E_r - i \frac{\Gamma}{2}) \\ &= \Phi(E_r) - i \frac{\Gamma}{2} \frac{\partial \Phi}{\partial E} \\ &= \Phi(E_r) - i \Gamma \tau / 2. \end{aligned}$$

Equation (31) thus becomes

$$\Phi(E_r)/\hbar - i\frac{\Gamma\tau}{2\hbar} - \frac{\pi l}{2} + i\frac{\tau}{2} \sum_i |\text{Im } \omega_i| = 2\pi \times (\text{integer}), \quad (32)$$

so that the "quasi-quantum condition" is exactly the same as Equation (29) for the real part of the pole of $G(E)$, and Γ (the "width" of the state) is given by

$$\Gamma = \sum_i |\text{Im } (\hbar\omega_i)|. \quad (33)$$

Equation (29) is the quantum condition obtained much earlier by Keller¹⁴ by a completely different approach, although it is not clear that his prescription for determining the integer l is equivalent to that above. Gutzwiller^{6d}, on the otherhand, uses a different argument than ours to identify the singularities of $g(E)$ and obtains a somewhat different quantum condition. Our conclusion is that the quantum condition obtained by Keller [Equation (29)] is correct, but that the stability considerations employed by Gutzwiller (and above) give a more precise definition of the integer l .

e. Summary and Uniqueness

In summary, therefore, one must first find the periodic trajectory $[Q_i(t)]$ (in practice this is probably the most difficult step); all the integral constants of the motion have definite values along this (or any) classical trajectory. One may ask whether or not there might be more than one periodic trajectory corresponding to the same value of $E, J, \dots$. On the basis of Whittaker's discussion¹⁵ of "ordinary" and "singular" periodic trajectories one concludes the following: for

specified values of all the integral constants of the motion there is no other periodic trajectory adjacent to (i.e., infinitesimally close to) the given one; i.e., a periodic trajectory is a member of a family of ∞^M (M = number of conserved quantities) periodic trajectories which vary continuously with the M quantities $E, J, \dots$. This statement does not preclude, however, the possibility that there might be another periodic trajectory with the same $E, J, \dots$ which is not adjacent to the original one; i.e., there might be several disjoint families of ∞^M periodic trajectories, members of each family being parameterized by continuously variable values of $E, J, \dots$. We conjecture that such disjointed families, if they exist, are characterized by some discrete symmetry of the system (e.g., a finite rotation axis, exchange symmetry, etc.). The statement would then be that the periodic trajectory is unique, if one specified the particular discrete symmetry as well as values for all M integral constants of the motion.

The quantum condition is then given by

$$\Phi_{\sigma}(E, J, \dots) \equiv \int_0^{\tau} dt \sum_{i=1}^N P_i(t) \dot{Q}_i(t) = 2\pi n(n + \ell/4) \quad , \quad (34)$$

for $n = 0, 1, \dots$, where $\{Q_i(t)\}$ is that (unique) periodic trajectory determined by $E, J, \dots$ and the discrete symmetry index σ ; ℓ must be determined by solving Equation (20) and observing how many zeros $\det[\vec{u}(t)]$ has in the interval $(0, \tau)$. Equation (34) defines the eigenvalue $E_n(\sigma, J, \dots)$ implicitly. Consistent with quantum mechanics, therefore, eigenvalues are classified by the discrete symmetries of the system, all the constants of the motion (other than energy), and lastly the "ordering

quantum number" n which simply counts the eigenvalues of each sub-space. For one-dimensional systems one has $\ell = 2$ and $\phi = 2\pi \int_{x_<}^{x_>} dx k(x)$, so that Equation (34) reproduces the Bohr-Sommerfeld relation⁵ for this case.

The width Γ associated with the eigenvalue is given by Equation (33). If all the normal frequencies are real, then $\Gamma = 0$ and the state is a truly stationary state. Otherwise it is a quasi-bound, or metastable state which decays with a characteristic lifetime $\hbar/\Gamma$. It should be clear that these are Feshbach-type metastable states since they can decay classically¹⁶; states which decay by tunneling ("single particle" resonances) cannot decay classically.

IV. Examples.

a. The Two-Electron Atom

As the first example, consider the S ($J = 0$) states of the two electron atom of nuclear charge Z . Searching for periodic trajectories of lowest energy, consider the "symmetric stretch": the two electrons on opposite sides of the nucleus, each with zero orbital angular momentum, moving symmetrically to and away from the nucleus; the motion obviously takes place in a line.

The Hamiltonian (in atomic units) is

$$H = (1/2)p_1^2 + (1/2)p_2^2 - Z/r_1 - Z/r_2 + 1/r_{12},$$

and by the symmetry of this trajectory one has

$$r_1 = r_2 \equiv r$$

$$p_1^2 = p_2^2 \equiv p^2$$

$$r_{12} = r_1 + r_2 = 2r ,$$

so that

$$\begin{aligned} H = \text{constant} \equiv E &= p^2 - 2Z/r + \frac{1}{2}r , \\ \text{or } E/2 &= \frac{1}{2} p^2 - (Z - \frac{1}{4})/r . \end{aligned} \quad (35)$$

Equation (35) is the one-particle hydrogenic Hamiltonian, however, so that the classical (or quantum) eigenvalues for it are

$$E/2 = - (Z - \frac{1}{4})^2 / 2n^2 ,$$

and the total energy is thus

$$E_n = - (Z - \frac{1}{4})^2 / n^2 , \quad (36)$$

for $n = 1, 2, \dots$

Since both electrons are compelled to "vibrate" symmetrically in these periodic trajectories, it is clear that the eigenvalues in Equation (36) correspond to the ns^2 states of the atom. Table I shows the comparison of Equation (36) with the quantum eigenvalues for the $1s^2$ and $2s^2$ states of He and H^- . The agreement is surprisingly good.

Even better agreement for the $1s^2$ states would presumably be obtained by invoking the standard semiclassical trick of using $J = 1/2, 3/2, \dots$, rather than $J = 0, 1, \dots$, in making the correspondence with S, P, ... states. Increasing J would certainly raise the energies and thus bring the $1s^2$ eigenvalues into better agreement. With non-zero J, however, the periodic trajectory will be much more complicated, and one would need to search for it numerically.

b. Three Identical Particles

Consider the system of three identical (spinless) particles with a potential energy which is the sum of the three two-body interactions; i.e., the classical Hamiltonian is

$$H = T_1 + T_2 + T_3 + v(r_{12}) + v(r_{13}) + v(r_{23}) ,$$

where T_i is the kinetic energy of particle i , $v(r)$ is the two-body potential, and r_{ij} is the distance between particles i and j . We consider only the case that the total angular momentum $J = 0$.

As discussed in Section IIIe, the periodic trajectories are characterized by the discrete symmetries of the system, in this case, the symmetry of three identical particles. The "symmetric stretch" periodic trajectories - an equilateral triangle configuration with all three particles moving symmetrically inward and outward - are obviously associated with eigenvalues of A symmetry. The "antisymmetric stretch" periodic trajectories lead to the doubly degenerate eigenvalues of E symmetry. The ground state is totally symmetric and thus of A symmetry; for the remainder of this section, therefore, we consider only the symmetric stretch periodic trajectories.

Because of the symmetry of these periodic trajectories one has

$$T_1 = T_2 = T_3$$

$$r_{12} = r_{13} = r_{23} ,$$

so that

$$H = E = 3[T_1 + v(r_{12})] ,$$

or

$$E/3 = T_1 + v(r_{12}) \quad (37)$$

To express the kinetic energy of particle 1 it is necessary to refer its position to a space-fixed coordinate system. The center of the equilateral triangle of particles is a convenient space-fixed point to choose as origin. If the distance from this origin to particle 1 is x , then from simple geometry one finds that

$$r_{12} = 3^{\frac{1}{2}}x ,$$

so that Equation (37) becomes

$$E/3 = \frac{1}{2}m \dot{x}(t)^2 + v(3^{\frac{1}{2}}x) . \quad (38)$$

The semiclassical quantum condition is

$$\begin{aligned} 2\pi n(n + \frac{1}{2}) &= \int_0^{\tau} dt \, 2(T_1 + T_2 + T_3) \\ &= 3 \int_0^{\tau} dt \, m \dot{x}^2 . \end{aligned}$$

From Equation (38) one has

$$\dot{x} = \pm \{ 2[E/3 - v(3^{\frac{1}{2}}x)] / m \}^{\frac{1}{2}} ,$$

so that the quantum condition becomes

$$2\pi n(n + \frac{1}{2}) = 6 \int dx \, m \{ 2[E/3 - v(3^{\frac{1}{2}}x)] / m \}^{\frac{1}{2}} . \quad (39)$$

Changing variables of integration from x to $r = 3^{\frac{1}{2}}x$, Equation (39) becomes

$$(n + \frac{1}{2})\pi = \int dr \left\{ 2m[E - 3v(r)]/\hbar^2 \right\}^{\frac{1}{2}} .$$

A more explicit form for the three-body eigenvalues can be obtained by writing Equation (40) as

$$(n + \frac{1}{2})\pi 6^{-\frac{1}{2}} = \int dr \left\{ m[E/3 - v(r)]/\hbar^2 \right\}^{\frac{1}{2}} \equiv [N(E/3) + \frac{1}{2}]\pi , \quad (41)$$

where $N(\epsilon)$ is the inverse function of the two-body eigenvalue function $\epsilon(N)$. (The factor m appears in the radicand in the definition of $N(\epsilon)$, rather than $2m$, because the reduced mass of the two-body system is $m/2$.) Solving for N gives

$$N(E/3) = 6^{-\frac{1}{2}}(n + \frac{1}{2}) - \frac{1}{2} ,$$

and inverting this equation gives the final result

$$E_n = 3 \epsilon [6^{-\frac{1}{2}}(n + \frac{1}{2}) - \frac{1}{2}] \quad (42)$$

Equation (42) gives the three-body eigenvalues explicitly in terms of the two-body eigenvalue function $\epsilon(N)$ where $N = 6^{-\frac{1}{2}}(n + \frac{1}{2}) - \frac{1}{2}$.

If, for example, $v(r)$ is a Morse potential

$$v(r) = D \left\{ \exp[-2a(r - r_0)] - 2 \exp[-a(r - r_0)] \right\} ,$$

then the two-body eigenvalue function (classically or quantum mechanically) is

$$\epsilon(n) = -D [1 - (2n + 1)/k]^2 \quad (43a)$$

where

$$k = (2/a)(mD/\hbar^2)^{\frac{1}{2}} . \quad (43b)$$

According to Equation (42), the three-body eigenvalues of A symmetry are obtained by replacing n in Equation (43a) by $6^{-\frac{1}{2}}(n + \frac{1}{2}) - \frac{1}{2}$ and multiplying by 3; this gives

$$E_n = - 3D[1 - (2n + 1) 6^{-\frac{1}{2}}/k]^2 . \quad (44)$$

Recently a quantum mechanical calculation for the ground state of this Morse system has been reported¹⁷ in which the parameter k of Equation (43b) was chosen to make ϵ_0 (the lowest eigenvalue of the two-body system) exactly 0; from Equation (43a) this is seen to be $k = 1$. Equation (44) then gives E_0 , the ground state eigenvalue of the three-body system, as

$$E_0 = - 3D[1 - 6^{-\frac{1}{2}}]^2 = -1.050 D \quad (45)$$

and this is the only bound state of the three-body system of this symmetry. With $D = 10.2^\circ \text{ K}$ (the approximate well-depth of the helium-helium pair potential) one obtains

$$E_0 = - 10.7^\circ \text{ K} ;$$

the (approximate) quantum calculation¹⁷ gave a value of -6° K .

c. Four Identical Particles

Finally, consider the system of four identical (spinless) particles interacting through pair potentials, the classical Hamiltonian being

analogous to that of the previous section

$$H = \sum_{i=1}^4 T_i + \sum_{i < j=1}^4 v(r_{ij}) .$$

We again consider the periodic trajectories (with $J = 0$) of highest symmetry, which in this case is the symmetric stretch of a regular tetrahedron formed by the four particles. [Searching for periodic trajectories is, of course, similar to searching for the "normal modes" of the system, except that one does not wish to make any harmonic approximation to the potential.] For these periodic trajectories all six interparticle distances are equal, and the kinetic energy of each particle is the same, so that

$$H = E = 4T_1 + 6 v(r) , \quad (46)$$

r being the common interparticle distance. With the space-fixed origin chosen as the center of the tetrahedron, one has

$$T_1 = \frac{1}{2} m \dot{x}^2 ,$$

where x is the distance from the origin to particle 1; simple geometry gives

$$r = 2 (2/3)^{\frac{1}{2}} x ,$$

so that Equation (46) becomes

$$E/4 = \frac{1}{2} m \dot{x}^2 + \frac{3}{2} v[2(2/3)^{\frac{1}{2}} x] . \quad (47)$$

The quantum condition is

$$\begin{aligned}
 2\pi n (n + \frac{1}{2}) &= \int dt \, 2 (T_1 + T_2 + T_3 + T_4) \\
 &= 4 \int dt \, m \dot{x}^2 \\
 &= 8 \int dx \, m \dot{x} \quad .
 \end{aligned} \tag{48}$$

Proceeding just as in the previous section, one solves Equation (47) for $\dot{x}$ in terms of x and substitutes this in the integrand of Equation (48); changing variables of integration from x to $r = 2(2/3)^{\frac{1}{2}}x$ then gives

$$\begin{aligned}
 (n + \frac{1}{2})\pi \, 3^{-1} \, 2^{-\frac{1}{2}} &= \int dr \, \left\{ m[E/6 - v(r)]/n^2 \right\}^{\frac{1}{2}} \quad , \\
 &\equiv [N(E/6) + \frac{1}{2}] \pi \quad ,
 \end{aligned} \tag{49}$$

where, as before, $N(\epsilon)$ is the inverse function of the two-body eigenvalue function $\epsilon(N)$. Thus

$$N(E/6) = (n + \frac{1}{2}) \, 3^{-1} \, 2^{-\frac{1}{2}} - \frac{1}{2} \quad ,$$

and inverting this equation gives the final result for the four-body eigenvalues of the totally symmetric representation explicitly in terms of the two-body eigenvalue function:

$$E_n = 6 \, \epsilon \left[(n + \frac{1}{2}) \, 3^{-1} \, 2^{-\frac{1}{2}} - \frac{1}{2} \right] \quad . \tag{50}$$

For the example of the Morse potential of the previous section, Equation (50) becomes

$$E_n = -6D \left[1 - (2n + 1) \, 3^{-1} \, 2^{-\frac{1}{2}}/k \right]^2 \quad . \tag{51}$$

If $k = 1$ so that the lowest two-body eigenvalue is exactly zero, then Equation (50) gives

$$E_0 = -D[6^{\frac{1}{2}} - 3^{-\frac{1}{2}}]^2 = -3.505 D$$

$$E_1 = -D[6^{\frac{1}{2}} - 3^{\frac{1}{2}}]^2 = -0.515 D ,$$

and all higher states of this symmetry are unbound.

The four-body system, therefore, has considerably more binding than the corresponding three-body system, evidenced by a much lower ground state energy (-3.505 D compared to -1.050 D) as well as the existence of a bound excited state. It is not possible for more than four particles to arrange themselves so that all interparticle distances are equal.

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Table I
Classical-Limit Eigenvalues for ns^2 States
of the Two-Electron Atom^a

State ^b	<u>Classical-Limit Eigenvalue^c</u>	<u>Exact Quantum Eigenvalue</u>
He	$1s^2$	-3.062
	$2s^2$	-2.904
	$2s^2$	-0.777
H^-	$1s^2$	-0.563
	$2s^2$	-0.528
	$2s^2$	-0.149

^a Energies are in hartree atomic units (1 hartree = 27.21 eV).

^b The $2s^2$ state is, of course, a quasi-bound (auto-ionizing) state.

^c The classical-limit eigenvalue formula is $E_n = - (Z - \frac{1}{4})^2 / n^2$,
Z being the nuclear charge.

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