

다차원 비분리계의 균일준고전적 해법*

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Multidimensional Uniform Semiclassical (WKB) Solutions for Nonseparable Problems*

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요약. 본 논문에서는 비분리계의 균일준고전(WKB)해를 close coupling formalism 을 쓰지 않고 구하였으며, 여러가지 물리적으로 흥미있고 현실적인 경우들에, 구해진 해들이 잘 알려져 있는 해석 함수들로서 주어졌다. 전환점이나 전환면이 구해진 해들의 특이점이 되지 않으며, 그들의 점근형을 취했을 때, 그 해들은 보통의 WKB 해들로 복귀된다. 그러한 균일해들을 얻기 위해서는 비분리계의 Schroedinger 방정식들을 변형하여 풀 수 있는 형으로 적절히 "재규격화" 하였다. Ehrenfest의 단열 원리가 그러한 "재규격화"된 균일해들을 도출하는데 중요한 역할을 한다. 적절한 고전적 궤적들이 얻어지면 Hamiltonian의 고유치들은 확장된 Bohr-Sommerfeld 양자화 규칙으로 계산된다. 다전자계에 대한 응용이 시사되었고, 현 방법의 유용성을 보여주기 위한 가장 간단한 예의 하나로써 helium 원자의 바닥상태의 파동함수를 근사적으로 계산하였다.

ABSTRACT. Uniform semiclassical (WKB) solutions are obtained for nonseparable systems without using a close coupling formalism and are given explicitly in terms of well known analytic functions for various physically interesting and realistic cases. They do not become singular at turning points or surfaces and when taken in their asymptotic forms, they reduce to the usual WKB solutions that could be obtained if the Stokes phenomenon was properly taken care of for solutions. In obtaining such uniform solutions, the Schroedinger equations for nonseparable systems are suitably "renormalized" to solvable "normal" forms through certain transformations. Ehrenfest's adiabatic principle plays an important guiding role for obtaining such "renormalized" uniform solutions for nonseparable systems. The eigenvalues of the Hamiltonian can be calculated from the extended Bohr-Sommerfeld quantization rules when appropriate classical trajectories are obtained. An application is made to many-electron systems and for one of the simplest examples to show the utility of the method the approximate wavefunction is calculated of the ground state helium atom.

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1. INTRODUCTION

The most important feature in the semiclassical (WKB) theory of solution for Schroedinger equations is that quantum mechanical wavefunctions can be given in terms of solutions of the corresponding classical equations of motion. For example, the semiclassical wavefunctions in one-dimensional or separable problems are given in terms of momenta and simple phase integrals which are the solutions of the one-dimensional Hamilton-Jacobi equations. The basic WKB solutions in multidimensional nonseparable problems still resemble the one-dimensional solutions, but the phase integrals are no longer simple quadratures and can be calculated only if the classical trajectories are computed by solving the nonseparable Hamilton-Jacobi equations. Such formal WKB solutions were first obtained for arbitrary multidimensional problems by Van Vleck¹ and later by many authors²⁻⁷.

The WKB solutions are basically asymptotic solutions to second order partial differential equations and as such they are not uniformly valid in the entire domain of the variables, since they become singular at some points in the domain. This nonuniformity ultimately originates from the well-known Stokes phenomenon⁸ and calls for connection formulae for the solutions in different domains separated by the singular points (or surfaces). This problem is fully solved for one-dimensional cases⁹.

In a multidimensional nonseparable problem¹⁰ the general semiclassical solution is a linear combination of the basic WKB solutions whose phases are the solutions of the Hamilton-Jacobi equation. When traced in the complex plane of the variables from one domain of variables to another separated by a turning surface, the expansion coefficients change discontinuously in

order for the solution to emerge as a correct physically acceptable solution in the domain of interest. This aspect was discussed to some degree by Keller¹¹ and Marcus^{12,13}, but its complete solution is still not available mainly due to the complexity of the problem. However, in order to construct the correct S -matrix, it is essential to obtain correct wavefunctions that have correct phases and satisfy the proper boundary conditions.

There are ways to avoid entirely the use of the connection formulas within the framework of the WKB theory in one-dimensional problems. In these methods the so-called uniform semiclassical solutions are obtained, which do not break down at the classical turning points. Indeed, when such uniform semiclassical (WKB) solutions, which were developed by Langer¹⁴, Erdélyi¹⁵, and others¹⁶, are used¹⁷ for scattering problems, the numerical results¹⁸ are remarkably accurate for the S -matrix elements of the processes examined so far. This uniform WKB theory is, however, based on a close coupling formalism. It would be interesting and useful for a deeper understanding of such a semiclassical theory, if a similar theory is formulated without a close coupling approximation.

The motivation of the present paper lies in our desire to formulate a uniform semiclassical theory for nonseparable systems by extending the ideas of Langer, Erdélyi and Miller and Good¹⁹ in a way that it disposes of a close coupling formalism. The method used in this paper is different from what Ludwig²⁰ and his coworkers²¹ used in their studies of nonseparable problems. The solutions obtained enable us to derive (1) connection formulas for nonseparable problems when their asymptotic formulas are employed - if we desire to obtain them - (2) extension of the Bohr-Sommerfeld quantization rules and (3) the S -matrix elements. The Bohr-

Sommerfeld quantization rules agree with the recent by Marcus and his coworkers¹² who considered a particular case of a two-dimensional problem, and also used by Percival and Pomphrey¹³.

In obtaining uniform semiclassical solutions, one invariably faces the important question of which form is physically the most realistic uniform semiclassical solution and which should be taken for a given problem. This question is easily answered for one-dimensional problems by inspecting the differential equations and the nature of the problems involved. However, for multidimensional nonseparable problems the question is not easy to answer and the precise answer differs from system to system. Nevertheless, it is possible to have a fairly general guiding principle. We wish to elaborate on this, since it is important.

The system of interest becomes separable, if the intricate interactions are removed between the various degrees of freedom of the system. If the system is divided on a certain physical ground into parts made up by a smaller number of particles and if the interactions are removed between the groups of particles, the system becomes partially separable. Let us call such a state and the corresponding Schroedinger equation "normal". For example, one can imagine a state of an atom ionized into an ion and an electron at infinite separation, or the initial or final state of a collision process of aggregates of particles. Then, if a system is brought adiabatically to such a "normal" state from a fully interacting state, the quantum state (number) of the system remains unchanged according to Ehrenfest's adiabatic principle²²⁻²⁴. The same would hold even if the process is reversed. The "normal" Schroedinger equations are more often solvable or at least more easily amenable to solution (we assume that this would always

be the case). Then, Ehrenfest's adiabatic principle points the direction to take. That is, we introduce certain transformations to the variables and the wavefunctions such that the resulting new Schroedinger equations are "normal" at least in the classical limit. In other words, we "renormalize" the Schroedinger equations of nonseparable systems into the "normal" Schroedinger equations in the classical limit $\hbar \rightarrow 0$. This is basically what is achieved in the subsequent sections and the transformations introduced there permit us to have such renormalizations. However, one must recognize that the dynamical problems are not fully solved, until the classical trajectories are obtained.

The concept outlined above is carried through for various cases of physical interest and in a sufficient generality in the subsequent sections.

2. THE CASE OF AN OPEN TURNING SURFACE

In this section we study cases of systems whose classically allowed region is open. That is, the turning surface (caustic) defined by $E = V(x_1, \dots, x_n)$ is open so that the systems do not undergo periodic or quasiperiodic motions. Here, as an example, we shall consider a two-dimensional problem. (There is no difficulty in generalizing it to an n dimension). In this case, if we assume that V is positive everywhere and $E > 0$ then the caustic at an E is the line of equipotential energy. The classically allowed region is the exterior of the domain defined by the line.

The Schroedinger equation is

$$\sum_{i=1}^2 \frac{\partial^2 \psi}{\partial q_i^2} + \lambda^2 [E - V(q_1, q_2)] \psi(q_1, q_2) = 0, \quad (2.1)$$

where $\lambda = \hbar^{-1}$ and $q_i = \sqrt{2\mu_i} x_i$, μ_i being the mass and x_i the cartesian coordinates. Here the potential is not separable.

We now introduce a coordinate transformation

$$\{x_i\} \rightarrow \{\xi_i\}$$

such that the new coordinates are related to the old one by the relations

$$\sum_j f_j(\xi_j) \left(\frac{\partial \xi_j}{\partial q_i} \right)^2 = \left(\frac{\partial W}{\partial q_i} \right)^2, \quad (2.2)$$

where W is the characteristic function of Hamilton, which satisfies the Hamilton-Jacobi equation,

$$\sum_i \left(\frac{\partial W}{\partial q_i} \right)^2 + V(q_1, q_2) = E, \quad (2.3)$$

We have not specified $f_j(\xi_j)$ as yet except that $f_i(\xi_i)$ is a function of ξ_i only. Now the wavefunction is written in the form,

$$\psi(q_1, q_2) = \Phi^{-1} Y. \quad (2.4)$$

With a further impositions of the conditions²⁰

$$\sum_i \frac{\partial \xi_\alpha}{\partial q_i} \frac{\partial \xi_\beta}{\partial q_i} = 0, \quad (\alpha \neq \beta), \quad (2.5)$$

and

$$\sum_i \left[\frac{\partial^2 \xi_\alpha}{\partial q_i^2} - 2\Phi^{-1} \frac{\partial \Phi}{\partial q_i} \frac{\partial \xi_\alpha}{\partial q_i} \right] = 0, \quad (\alpha=1, 2), \quad (2.6)$$

we now obtain the equation for Y ,

$$\begin{aligned} & \sum_i \left[\left(\sum_j \left(\frac{\partial \xi_j}{\partial q_i} \right)^2 \right) \frac{\partial^2 Y}{\partial \xi_i^2} + \lambda^2 \left(\frac{\partial W}{\partial q_i} \right)^2 Y \right] \\ & = \sum_i \left(\Phi^{-1} \frac{\partial^2 \Phi}{\partial q_i^2} + 2 \frac{\partial \Phi}{\partial q_i} \frac{\partial \Phi^{-1}}{\partial q_i} \right) Y. \end{aligned} \quad (2.7)$$

The rhs is $O(1)$ while the second term on the lhs is $O(\lambda^2)$ which becomes dominant in the classical limit $\lambda \rightarrow \infty$. In this limit we define a function $Y^{(0)}$ by the equation

$$\sum_i \left[\sum_j \left(\frac{\partial \xi_j}{\partial q_i} \right)^2 \frac{\partial^2 Y^{(0)}}{\partial \xi_i^2} + \lambda^2 \left(\frac{\partial W}{\partial q_i} \right)^2 Y^{(0)} \right] = 0. \quad (2.8)$$

Let us define functions $Y_i^{(0)}(\xi_i)$ by the equations,

$$\frac{\partial^2 Y_i^{(0)}}{\partial \xi_i^2} + \lambda^2 f_i(\xi_i) Y_i^{(0)}(\xi_i) = 0, \quad (2.9)$$

subject to the appropriate boundary conditions. then it is easily seen that (2.8) is solved by

$$Y^{(0)}(\xi_1, \xi_2) = \prod_{i=1}^2 Y_i^{(0)}(\xi_i). \quad (2.10)$$

Before proceeding further, it is useful to examine the conditions imposed. By multiplying (2.5) with $(f_i, f_j)^{1/2}$ and summing the result over i and j , we obtain after combining it with (2.2) the equation,

$$\begin{aligned} \sum_j f_j^{1/2}(\xi_j) \cdot f_j^{1/2}(\xi_j) & = E - V \\ & = \sum_j \left(\frac{\partial W}{\partial q_j} \right)^2. \end{aligned} \quad (2.11)$$

This condition together with (2.6) determines Φ . We return to the determination of Φ later.

The functions $f_j(\xi_j)$ are not determined by any dynamical means, and their choice is based entirely on the physical nature of the problem and our perception of the nature of the system. We choose them such that (2.9) is solvable in terms of known functions. Their choice was considered before in the cases of one-dimensional problems.^{14-16,25} In the present case we choose $f_i(\xi_i)$ as a linear function of ξ_i , i.e.,

$$f_i(\xi_i) = \xi_i \quad (2.12)$$

The the physically acceptable solution for (2.9) is the Airy function,

$$Y_i^{(0)}(\xi_i) = A_i(-\lambda^{2/3} \xi_i). \quad (2.13)$$

Its linearly independent solution is then $B_i(-\lambda^{2/3} \xi_i)$. We now show why (2.13) is physically acceptable.

If (2.12) is substituted into (2.11) we obtain

$$\sum_j \left[-\frac{\partial}{\partial q_j} \left(\sum_i \frac{2}{3} \xi_i^{3/2} \right) \right]^2 = \sum_j \left(\frac{\partial W}{\partial q_j} \right)^2 \quad (2.14)$$

That is, within a constant factor the solution is

$$W = \pm \sum_i \frac{2}{3} \xi_i^{3/2}. \quad (2.15)$$

If $E < V$, then the inequality must hold,

$$\sum_j \left(\frac{\partial W}{\partial q_j} \right)^2 < 0,$$

which means that

$$\frac{\partial W}{\partial q_j} = \text{imaginary}.$$

This implies that in the domain where $E < V$, ξ_j becomes negative for every j and the solution takes the form,

$$Y_j^{(c)}(\xi_j) = A_i(\lambda^{2/3}\xi_j). \quad (2.16)$$

Hence it is clear that $A_i(-X)$ is the physically acceptable solution.

Eq. (2.15) does not fully determine ξ_i . For the purpose of relating the new variables ξ_i to more physically transparent quantities, let us examine the Hamilton-Jacobi equation (2.3). In the small neighborhood of the caustic where $E = V(x_1^0, x_2^0)$, we may expand $E - V$ into a series of $(x_i - x_i^0)$ retaining the linear terms only:

$$E - V = \sum_i \left(\frac{\partial V}{\partial q_i^0} \right) (q_i - q_i^0). \quad (2.16)$$

Then we see that (2.3) becomes separable in the small neighborhood and we find

$$W = \sum_i W_i(q_i) = \sum_i \frac{2}{3} \left(\frac{\partial V}{\partial q_i^0} \right)^{1/2} (q_i - q_i^0)^{3/2}. \quad (2.17)$$

Since (2.15) must hold also in the same neighborhood, we see that in the neighborhood

$$\xi_i^{1/2} d\xi_i = \left(\frac{\partial V}{\partial q_i^0} \right)^{1/2} (q_i - q_i^0)^{1/2} dq_i = p_i dx_i \quad (2.18a)$$

along the trajectory emanating from the caustic. This relation is local at the moment, but the second equality, by the reason of continuity, should hold globally. Thus, we make the following correspondence in the global sense:

$$\xi_j^{1/2} d\xi_j = p_j dx_j \quad (2.18b)$$

and the integration over x_i is to be done along the classical trajectory. In the classically forbidden domain the relation

$$(-\xi_j)^{1/2} d\xi_j = i p_j dx_j, \quad (i = \sqrt{-1}), \quad (2.18c)$$

must hold. On integration, these lead to the relations,

$$\frac{2}{3} \xi_j^{3/2} = \int_C p_j dx_j, \quad (2.19a)$$

and

$$\frac{2}{3} (-\xi_j)^{3/2} = - \int_C i p_j dx_j. \quad (2.19b)$$

Therefore, the variables ξ_j are completely determined by solution of Hamilton-Jacobi equation and consequently by the classical trajectories. The variables ξ_i , thus determined, would enable us to calculate the well-behaved functions $Y_j^{(c)}(\xi_j)$ in terms of the Airy functions, $A_i(-\lambda^{2/3}\xi_j)$.

Now we turn to (2.6) in order to complete the present scheme of approximate solution of (2.1). Let us define

$$A = \log \Phi^2. \quad (2.20)$$

Then (2.6) may be written as

$$\sum_i \frac{\partial \xi_i}{\partial q_i} \frac{\partial A}{\partial q_i} = \sum_i \frac{\partial^2 \xi_i}{\partial q_i^2} \equiv B_i. \quad (2.6a)$$

Since the Jacobian Δ_2 of transformation

$$\Delta_2 = \frac{\partial(\xi_1, \xi_2)}{\partial(q_1, q_2)}, \quad (2.21)$$

is not equal to zero for the transformation (2.18), Eq. (2.6a) is easily solved for $\frac{\partial A}{\partial q_i}$:

$$\frac{\partial A}{\partial q_i} = \Delta_2^{-1} \sum_{j=1}^2 B_j D_{ji}, \quad (2.22)$$

where D_{ji} is the (ji) cofactor of Δ_2 . We emphasize that Δ_2 is not zero everywhere since we deliberately choose ξ_i such that it is not equal to zero. This nonzero Δ_2 is essential for the present uniform WKB theory of solution.

It is not difficult to see that this condition is met by the the transformations (2.18a) and (2.18b) and the transformations introduced later.

By summing (2.22) over i and making use of the properties of determinants, we obtain from (2.22) the equation

$$\sum_i \frac{\partial A}{\partial q_i} = \sum_i \frac{\partial}{\partial q_i} \log \Delta_2. \quad (2.23)$$

This implies that

$$A = \log \Delta_2$$

or

$$\Phi = \Delta_2^{1/2} \quad (2.24)$$

up to a constant. This result can be easily generalized to the case of arbitrary number of dimensions, n . In general, we have

$$\Phi(q_1, \dots, q_n) = \left[\frac{\partial(\xi_1, \dots, \xi_n)}{\partial(q_1, \dots, q_n)} \right]^{1/2} \equiv \Delta_n^{1/2}. \quad (2.24a)$$

We remark that (2.24a) is valid for all transformations and not just for (2.18).

By combining these results, we finally obtain the approximate semiclassical, but uniform, solution to (2.1);

$$\psi(x_1, x_2) = \mathcal{N} \Delta_2^{1/2} A_i(-\lambda^{2/3} \xi_1) A_j(-\lambda^{2/3} \xi_2). \quad (2.25)$$

Since (2.18a) holds in the neighborhood of the caustic and ξ_i , in that neighborhood, depends only on q_i , it is easy to see that Δ_2 is finite along the caustic. Thus the wavefunction is also finite along it— $A_i(-x)$ is finite at $x=0$. The wavefunction as given by (2.25) is also semiclassical, since it is the leading term for the asymptotic expansion of ψ as $\lambda \rightarrow \infty$. If we take the asymptotic formula for $A_i(-x)$, then we indeed recover the WKB solution in the classically allowed domain,

$$\psi(x_1, x_2) \sim \mathcal{N} \prod_{i=1}^2 p_i^{-1/2} \sin(\lambda \int_C p_i dx_i + \pi/4). \quad (2.26)$$

This result agrees with that by Marcus¹², although he was concerned with bound state problems, which should have the same form for the primitive WKB solutions as for the present scattering state problem.

Since the present result is trivially generalizable, we simply write down the result for completeness,

$$\psi(x_1, \dots, x_n) = \mathcal{N} \Delta_n^{-1/2} \prod_{j=1}^n A_j(-\lambda^{2/3} \xi_j). \quad (2.27)$$

Note that q_i is the mass normalized cartesian coordinate: $q_i = \sqrt{2\mu_i} x_i$.

3. THE CASE OF A CLOSED TURNING SURFACE

In this section we shall consider the case when the classically allowed states are confined in a closed domain. A simplest example is two anharmonic oscillators weakly coupled so that the motion of the system is at least quasiperiodic. Although the weak coupling assumption is made here, it is not absolutely necessary as long as the system of two oscillators does not break apart into, say, one (bound) oscillator and another in a continuum state. This situation is avoided if we assume the caustic (turning surface) is closed.

We shall consider, again for simplicity, a two-dimensional case (two oscillators): Its generalization is straightforward. The procedure remains basically the same as in Sec. 2, the only difference being in the different for $f_i(\xi_i)$ from that is Sec. 2. In the present case we take for $f_i(\xi_i)$ the following:

$$f_i(\xi_i) = C_i^2 - \xi_i^2, \quad (3.1)$$

where the constant C_i is to be determined later. We then obtain (2.11) in the form

$$\sum_i \left[\frac{\partial}{\partial q_i} \sum_{j=-C_i}^{\xi_j} dS(C_j^2 - S^2)^{1/2} \right]^2 = \sum_i \left(\frac{\partial W}{\partial q_i} \right)^2, \quad (3.2)$$

and thus

$$\begin{aligned} W &= \sum_i \int_{-C_i}^{\xi_i} dS (C_i^2 - S^2)^{1/2} \\ &= \sum_i \int_C \dot{p}_i dx_i, \end{aligned} \quad (3.3)$$

where the integration over x_i is along the trajectory. The integration over "a period" gives the relation,

$$\pi \sum_i C_i^2 = \sum_i \oint_C \dot{p}_i dx_i. \quad (3.4)$$

One can also show that the equivalents of (2.18c) hold:

$$\int_{-C_j}^{\xi_j} (C_j^2 - S^2)^{1/2} dS = \int_C \dot{p}_j dx_j \quad \text{for } |\xi_j| \leq C_j, \quad (3.5a)$$

or

$$\int_{\xi_j}^{-C_j} (S^2 - C_j^2)^{1/2} dS = - \int_C \dot{p}_j dx_j \quad \text{for } |\xi_j| \geq C_j. \quad (3.5b)$$

Then under the transformation

$$\phi(x_1, x_2) = \Phi^{-1} Y \quad (3.5)$$

and with the same set of conditions on ξ_i as (2.2), (2.5) and (2.6), and with the definition of $Y_i^{(\circ)}$ by the differential equation

$$\frac{d^2 Y_i^{(\circ)}}{d\xi_i^2} + \lambda^2 (C_i^2 - \xi_i^2) Y_i^{(\circ)}(\xi_i) = 0, \quad (i=1, 2), \quad (3.6)$$

we obtain physically acceptable solutions for $Y^{(\circ)}$:

$$Y^{(\circ)}(\xi_1, \xi_2) = \prod_{i=1}^2 \exp\left(-\frac{1}{2} \lambda \xi_i^2\right) H_{n_i}(\lambda^{1/2} \xi_i), \quad (3.7)$$

provided that λC_i^2 is equal to an integer:

$$\lambda C_i^2 = 2n_i + 1, \quad (n_i = 0, 1, 2, \dots). \quad (3.8)$$

Here n_i will turn out to be the vibrational quantum number of the i th mode and $H_{n_i}(Z)$ are the Hermite polynomial of order n_i . It is important to notice that the argument ξ_i is a function of the coordinates $\{x_i\}$.

Since the transformation $\{x_i\} \rightarrow \{\xi_i\}$ depends on the state of the oscillators, it is convenient to introduce reduced variables z_i such that

$$\lambda^{1/2} \xi_i = \lambda^{1/2} C_i z_i \equiv N_i z_i. \quad (3.9)$$

Then the Jacobian of transformation Δ_2 may be written as

$$\Delta_2 \equiv \lambda^{-1} N_1 N_2 D_2 \equiv \lambda^{-1} \Delta_1 N_2 \frac{\partial(z_1, z_2)}{\partial(q_1, q_2)}, \quad (3.10)$$

and the approximate uniform WKB solution to the Schroedinger equation is

$$\begin{aligned} \phi(x_1, x_2) &= \mathcal{N}_{n_1 n_2} D_2^{1/2} \prod_{i=1}^2 \exp\left(-\frac{1}{2} N_i^2 z_i^2\right) \\ &H_{n_i}(N_i z_i). \end{aligned} \quad (3.11)$$

Here $\mathcal{N}_{n_1 n_2}$ is the normalization constant;

$$\begin{aligned} \mathcal{N}_{n_1 n_2}^{-2} &= \iint dx_1 dx_2 D_2^{-1} \left[\prod_{i=1}^2 \exp\left(-\frac{1}{2} N_i^2 z_i^2\right) \right. \\ &\left. H_{n_i}(N_i z_i) \right]^2. \end{aligned} \quad (3.12)$$

On substitution of (3.8) into (3.4), we obtain the Bohr-Sommerfeld quantization conditions for the nonseparable system

$$\begin{aligned} h \sum_i \left(n_i + \frac{1}{2}\right) &= \sum_i \oint_C \dot{p}_i dx_i \\ &= 2 \sum_i \int_C \dot{p}_i dx_i, \end{aligned} \quad (3.13)$$

where the integration is to be carried along the projection of the trajectory onto x_i and from one turning surface to the other.²⁶ This agrees with the result of Marcus^{12a} by a different method. However, it differs from the result by Gutzwiller²⁷ and Miller²⁸ who obtained it indirectly by calculating the density matrix and Green's function. They used the primitive semiclassical wavefunctions for which the Stokes phenomenon was not at all taken into consideration. As Miller noticed, his result appears to be correct only when the $(n-1)$ degrees of freedom among n behave like harmonic oscillators.

Again, the result given here is easily ge-

neralized to systems with n degrees of freedom, viz.

$$\int_C \prod_{i=1}^n p_i dx_i = h \sum_i \left(\nu_i + \frac{1}{2} \right), \quad (\nu_i = 0, 1, 2, \dots), \quad (3.14)$$

and

$$\psi(x_1, \dots, x_n) = \mathcal{N}_{\nu_1 \dots \nu_n} D_n^{-1/2} \prod_{i=1}^n \exp\left(-\frac{1}{2} N_i^2 z_i^2\right) H_{\nu_i}(N_i z_i), \quad (3.15)$$

where

$$C_i^2 \int_{-1}^{z_i} dt (1-t^2)^{1/2} = \int_C p_i dx_i, \quad (i=1, 2, \dots, n; |z_i| \leq 1), \quad (3.16a)$$

and

$$\pm C_i^2 \int_{z_i}^{\pm 1} dt (t^2-1)^{1/2} = \sqrt{-1} \int_C p_i dx_i, \quad (|z_i| > 1) \quad (3.16b)$$

The (+) sign must be taken for $z_i > 1$ and the (-) sign for $z_i < -1$. Since D_n is finite everywhere, $\psi(x_1, \dots, x_n)$ is also uniformly finite. Thus it is the uniform semiclassical (WKB) solution, since (3.11) and (3.15) are approximate solutions valid within $O(\hbar^2)$ in the classical limit $\hbar \rightarrow 0$. By using the asymptotic formula for hermite polynomials as $\nu_i \rightarrow \infty$, it is easy to see that (3.11) and (3.15) can be given in terms of phase integrals, *i. e.*,

$$\psi \sim \prod_{i=1}^n p_i^{-1/2} \cos\left(\lambda \int_C p_i dx_i - \pi/4\right)$$

(see, Sec. 7 below).

It is important to note that despite its appearance (3.15) is not to be mistaken for a wavefunction for separable systems, since the z_i are functions of the original coordinates x_i . It reduces to the wavefunction of separable systems only if the couplings between various degrees of freedom disappear. That is, if we write the potential energy in the form,

$$V(x_1, \dots, x_n) = \sum_i V_i(x_i) + \sum_i V_i(x_1, \dots, x_n),$$

(3.15) becomes a product of truly independent oscillator wavefunctions when $V_i(x_1, \dots, x_n) = 0$. The outstanding feature of (3.15) then is that as $V_i(x_1, \dots, x_n)$ are gradually increased in their magnitude, the form of the wavefunction, apart from the factor $D_n^{-1/2}$, stays unchanged except that the arguments go through the transformations $\{x_i\} \rightarrow \{\xi_i\}$. Therefore, the nodes of the wavefunction are preserved even though the couplings are increased,²⁹ since the quantum numbers remain invariant under the transformations. This is in conformation with Ehrenfest's adiabatic principle. This feature is repeatedly seen in the subsequent sections.

4. THE MIXED CASE

Here we consider the case when some degrees of freedom are periodic while the rest are not. A typical example would be the one-dimensional vibrational-translational energy transfer process in which a one-dimensional oscillator undergoes a collision with an atom moving along the line of the center of mass and the axis of the oscillator. Since its generalization is trivial, we consider such a case as an example below:

The procedure is the same as before. Here we choose

$$f_1(\xi_1) = \xi_1 \equiv C_1 z_1, \quad (4.1)$$

and

$$f_2(\xi_2) = C_2^2 - \xi_2^2 = C_2^2(1 - z_2^2), \quad (4.2)$$

where the meaning of C_2 is the same as those in Sec. 3. The constant C_1 may be chosen such that

$$C_1 = (2\mu_1 E_1)^{2/3}$$

with μ_1 being the reduced mass and E_1 defined by the relative kinetic energy at large distance where the coupling is absent between the

oscillator and the atom. Then, when the procedures in Secs. 2 and 3 are combined, the physically acceptable solution for the present case has the form,

$$\phi(x_1, x_2) = \mathcal{N}_n D_2^{-1/2} A_i(-\lambda^{2/3} C_1 x_1) \exp\left(-\frac{1}{2} N_2^2 x_2^2\right) H_n(N_2 x_2), \quad (4.3)$$

where \mathcal{N}_n is the normalization constant. The new variables ξ_1 and ξ_2 or z_1 and z_2 are connected to the old variables x_1 and x_2 through (2.19) and (3.16). We do not write the connecting equations here to avoid a repetition. It is now convenient to express the x_1 -part of motion in Hankel functions so that the wave functions take the form,

$$\phi^{(\pm)}(x_1, x_2) = \mathcal{N}_n' (iz_1/D_2^{3/2})^{1/3} \mathcal{H}_n^{(\pm)}\left(\frac{2}{3}\lambda C_1^{3/2} z_1^{3/2}\right) \exp\left(-\frac{1}{2} N_2^2 x_2^2\right) H_n(N_2 x_2), \quad (4.4)$$

where

$$\mathcal{H}_n^{(\pm)}(z) = H_{n+1/2}^{(2)}(z) \quad (4.5)$$

and

$$\mathcal{H}_n^{(-)}(z) = H_{n+1/2}^{(2)}(z)$$

are the Hankel functions of the first and second kind of order $1/3$, respectively. By using the asymptotic formulas³⁰ for the Hankel functions as $z \rightarrow \infty$, it is easy to see that (4.4) satisfies the scattering boundary conditions:

$$\mathcal{H}_n^{(\pm)}\left(\frac{2}{3}\lambda C_1^{3/2} z_1^{3/2}\right) \sim \exp\left(\pm i\lambda \int_C p_1 dx_1 \mp i\frac{\pi}{4}\right) \sim \exp(\pm i k_1 x_1)$$

with

$$k_1 = (2\mu_1 E_1)^{1/2}/\hbar.$$

The asymptotic formula for the x_2 -part of motion takes the form indicated in Sec. 3 (see also Sec. 7).

The S -matrix element can be obtained from (4.4):

$$\begin{aligned} S_{nm} &= \langle \phi_n^{(-)} | \phi_m^{(+)} \rangle \\ &= \mathcal{N}_n' \mathcal{N}_m \iint dx_1 dx_2 \mathcal{H}_n^{(-)*}(t_1) \phi_n^*(z_2) \\ &\quad (z_1/D_2^{3/2})_n^{1/3} (z_1/D_2^{3/2})_m^{1/3} \mathcal{H}_m^{(+)}(t_1) \phi_m(z_2) \end{aligned} \quad (4.6)$$

where

$$t_1 = \frac{2}{3} \lambda C_1^{3/2} z_1^{3/2},$$

$$\phi_n(z_i) = \exp\left(-\frac{1}{2} N_i^2 z_i^2\right) H_n(N_i z_i), \quad (4.7)$$

and the subscript to $(z_1/D_2^{3/2})$ indicates that the quantity in the parenthesis refers to state n . This follows since the transformation $\{x_i\} \rightarrow \{z_i\}$ depends in general on the state of the system: an important point to remember in actual computation of the wavefunctions. We may write (4.6) in a more symbolic form,

$$S_{nm} = \langle h^{(-)} \phi_n | (D_2)_n^{-1/2} (D_2)_m^{-1/2} | h^{(+)} \phi_m \rangle \quad (4.8)$$

where

$$h_i^{(\pm)} = (iz_1)^{1/3} \mathcal{H}_i^{(\pm)}. \quad (4.9)$$

It is interesting to note that (4.8) has the appearance of a Born approximation matrix element of $(D_2)_n^{-1/2} (D_2)_m^{-1/2}$. Eq. (4.8) is a semiclassical approximation to S_{nm} . This formula can be evaluated by taking the asymptotic formulas for the wave functions as indicated above and then employing the stationary phase method in the neighborhood of the classical path. This procedure leads to the usual semiclassical formulas for S_{nm} when the interference terms are dropped. The application of (4.8) will be considered in the future.

5. SPHERICAL COORDINATE SYSTEMS

It is sometimes convenient to use spherical coordinates instead of cartesian coordinates. This usually is the case, when the system undergoes a collision process. When the relative motion of colliding molecules is described in spherical

coordinates, the Schroedinger equation is given in the form,

$$-\frac{\hbar^2}{2\mu_1} \left[\frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{1}{r^2 \sin^2 \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right] \psi(r, x_4, \dots, x_n) - \sum_{i=4}^n \frac{\hbar^2}{2\mu_i} \frac{\partial^2 \psi}{\partial x_i^2} + [V(r, x_4, \dots, x_n) - E] \psi(r, x_4, \dots, x_n) = 0. \quad (5.1)$$

Since it is sufficient for our purpose to consider the relative motion alone, we shall ignore the internal part for now and consider only the equation

$$-\frac{\hbar^2}{2\mu_1} \left[\frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{1}{r^2 \sin^2 \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right] \psi + [V(r, \theta, \varphi) - E] \psi(r, \theta, \varphi) = 0. \quad (5.2)$$

In order to proceed further, it is necessary to introduce the transformation

$$\psi = u(r, \theta, \varphi) / r (\sin \theta)^{1/2}. \quad (5.3)$$

Then we obtain equation for u ,

$$\frac{\partial^2 u}{\partial r^2} + \frac{1}{r^2} \left(\frac{\partial^2}{\partial \theta^2} + \frac{1}{4} \right) u + \frac{1}{r^2 \sin^2 \theta} \left(\frac{\partial^2}{\partial \varphi^2} + \frac{1}{4} \right) u + \lambda^2 (E - V) u = 0,$$

where

$$\lambda = \sqrt{2\mu_1} / \hbar.$$

In the same spirit as before, we introduce transformations

$$(r, \theta, \varphi) \rightarrow (\xi_1, \xi_2, \xi_3): \begin{aligned} \xi_1 &= \phi_1(r, \theta, \varphi) \\ \xi_2 &= \phi_2(r, \theta, \varphi) \\ \xi_3 &= \phi_3(r, \theta, \varphi). \end{aligned} \quad (5.5)$$

Functions ϕ_i are not specified yet, but it is sufficient to assume that they exist and are well-behaved. We also define a new function Y such that

$$u(r, \theta, \varphi) = \Phi^{-1}(r, \theta, \varphi) Y(r, \theta, \varphi). \quad (5.6)$$

Let us introduce operators \mathcal{D}_α such that

$$\begin{aligned} \mathcal{D}_1 &\equiv \mathcal{D}_r = \frac{\partial}{\partial r} \\ \mathcal{D}_2 &\equiv \mathcal{D}_\theta = \frac{1}{r} \frac{\partial}{\partial \theta} \\ \mathcal{D}_3 &\equiv \mathcal{D}_\varphi = \frac{1}{r \sin \theta} \frac{\partial}{\partial \varphi} \end{aligned} \quad (5.7)$$

Then imposing the following conditions on possible ξ_i and Φ ,

$$\sum_{\alpha=1}^3 \mathcal{D}_\alpha \xi_i \mathcal{D}_\alpha \xi_j = 0 \quad \text{for } i \neq j \quad (5.8)$$

and

$$\sum_{\alpha=1}^3 \mathcal{D}_\alpha^2 \xi_i - 2\Phi \sum_{\alpha=1}^3 \mathcal{D}_\alpha \Phi^{-1} \mathcal{D}_\alpha \xi_i = 0, \quad (i=1, 2, 3), \quad (5.9)$$

we obtain an equation for Y ,

$$\sum_{i=1}^3 (\mathcal{D} \xi_i)^2 \frac{\partial^2 Y}{\partial \xi_i^2} + \lambda^2 (E - V) Y = -\Phi \left[\mathcal{D}^2 \Phi^{-1} + \left(\frac{1}{4r^2} + \frac{1}{4r^2 \sin^2 \theta} \right) \Phi^{-1} \right] Y, \quad (5.10)$$

where

$$(\mathcal{D} \xi_i)^2 = \sum (\mathcal{D}_\alpha \xi_i)^2$$

and

$$\mathcal{D}^2 \Phi^{-1} = \sum \mathcal{D}_\alpha^2 \Phi^{-1}.$$

The conditions (5.8) and (5.9) are equivalent to the conditions (2.5) and (2.6). The rhs of (5.10) is $O(\lambda^0)$, while the second term on the lhs is $O(\lambda^2)$. Therefore, the former may be dropped in comparison with the latter which is much larger than the classical limit $\lambda \rightarrow \infty$. We define the approximate solution $Y^{(0)}$ by the equation

$$\sum_{i=1}^3 (\mathcal{D} \xi_i)^2 \frac{\partial^2 Y^{(0)}}{\partial \xi_i^2} + \lambda^2 (E - V) Y^{(0)} = 0. \quad (5.11)$$

We also define functions $Y_i^{(0)}(\xi_i)$ by the equations

$$\frac{d^2 Y_i^{(0)}}{d\xi_i^2} + \lambda^2 f_i(\xi_i) Y_i^{(0)}(\xi_i) = 0, \quad (i=1, 2, 3). \quad (5.12)$$

Then provided that

$$\sum_{i=1}^3 f_i(\xi_i) (\mathcal{D}\xi_i)^2 = E - V, \quad (5.13)$$

(5.11) is solved by

$$Y^{(0)}(\xi_1, \xi_2, \xi_3) = \prod_{i=1}^3 Y_i^{(0)}(\xi_i). \quad (5.14)$$

We thus choose f_i such that (5.12) is solvable, and in particular such that the differential equations for $Y_i^{(0)}$ resemble those of separable problems in spherical coordinates. In this spirit we choose f_i as follows:

$$\begin{aligned} f_1(\xi_1) &= 1 - C_2^2/\xi_1^2, \\ f_2(\xi_2) &= C_2^2 - C_3^2/\sin^2\xi_2 + \frac{1}{4}\lambda^{-2}, \\ f_3(\xi_3) &= C_3^2. \end{aligned} \quad (5.15)$$

Here we have added a small term of $O(\lambda^{-2})$ to the rhs of equation for f_2 . It is also permissible to add small terms of $O(\lambda^0)$ on the rhs of (5.12) follows:

$$\begin{aligned} S_1(\xi_1) &= 1/4\xi_1^2 \\ S_2(\xi_2) &= -1/4\sin^2\xi_2 \\ S_3(\xi_3) &= 0. \end{aligned} \quad (5.16)$$

We then have the equations for $Y_i^{(0)}$ in the following form:

$$\frac{d^2 Y_i^{(0)}}{d\xi_i^2} + \lambda^2 f_i(\xi_i) Y_i^{(0)}(\xi_i) = S_i(\xi_i) Y_i^{(0)}(\xi_i), \quad (5.17)$$

This procedure of adding $S_i(\xi_i)$ and any terms of $O(\lambda^0)$ is equivalent to changing the quantum numbers, *e.g.*, the angular momentum quantum number, into half integers and the error incurred to the solution by doing this is only $O(\lambda^{-2})$ in the classical limit $\lambda \rightarrow \infty$. There is no mathematical inconsistency involved with adding such small terms.

We choose the range of variables follows:

$$0 \leq \xi_1 < \infty, \quad 0 \leq \xi_2 \leq \pi, \quad 0 \leq \xi_3 \leq 2\pi. \quad (5.18)$$

Following a similar argument used in Sec. 2 for making connections between f_i and the old variables, we have for $\xi_i > \xi_i^\circ$

$$\int_{\xi_i^\circ}^{\xi_i} f_i^{1/2}(\xi_i) d\xi_i = \int_C p_i dx_i \quad (5.19a)$$

and for $|\xi_i| < |\xi_i^\circ|$

$$\int_{\xi_i}^{\xi_i^\circ} f_i^{1/2}(\xi_i) d\xi_i = -\int_C \sqrt{-1} p_i dx_i \quad (5.19b)$$

where ξ_i° are such that $f_i(\xi_i^\circ) = 0$. This point also corresponds to the points x_i° where $p_i(x_i^\circ, \dots, x_n^\circ) = 0$ for every i , *i.e.*, the turning surface.

The physically acceptable solutions are easily obtained in terms of known analytic functions, if the following conditions on C_2 and C_3 are for $Y_2^{(0)}$ and $Y_3^{(0)}$:

$$\lambda^2 C_2^2 = l(l+1), \quad (l=0, 1, 2, \dots) \quad (5.20)$$

$$\lambda^2 C_3^2 = m^2, \quad (m=0, \pm 1, \pm 2, \dots) \quad (5.21)$$

That is, the solutions are

$$Y_3^{(0)}(\xi_3) = \exp(\pm im\xi_3), \quad (5.22)$$

$$Y_2^{(0)}(\xi_2) = (\sin\xi_2)^{1/2} P_l^m(\cos\xi_2), \quad (5.23)$$

and

$$Y_1^{(0)}(\xi_1) = (\pi\xi_1/2)^{1/2} J_{l+1/2}(\lambda\xi_1), \quad (5.24)$$

where P_l^m and $J_{l+1/2}$ are the associate Legendre polynomial of order (l, m) and the cylindrical Bessel function of order $l+1/2$ respectively. Eqs. (5.19a) and (5.21) imply that

$$\oint p_3 dx_3 = mh. \quad (5.25)$$

(5.19a) and (5.20) imply that

$$\oint_C p_2 dx_2 = \left(l - m + \frac{1}{2}\right)h. \quad (5.26)$$

The integrations in (5.25) and (5.26) are to be carried along the classical trajectory. The fact we have the solution $Y_2^{(0)}(\xi_2)$ in terms of associated Legendre polynomial leads to a bound

for $m: -l \leq m \leq l$. Since the x_1 -part of motion is not quantized, we do not have an analogous condition for (5.25) or (5.26).

it is easy to show that Φ is again given in terms of the Jacobian of transformation,

$$\Delta_3(r, \theta, \varphi) = \frac{\partial(\xi_1, \xi_2, \xi_3)}{\partial(r, \theta, \varphi)}. \quad (5.27)$$

That is,

$$\Phi = \Delta_3^{-1/2}. \quad (5.28)$$

Now collecting the results obtained up to now, we have the approximate solution to (5.2) in the form,

$$\begin{aligned} \phi(r, \theta, \varphi) = & \mathcal{N} \left(\frac{\xi_1}{r} \right) \left(\frac{\sin \xi_2}{\sin \theta} \right)^{1/2} \Delta_3^{-1/2} \\ & j_l(\lambda \xi_1) P_l^m(\cos \xi_2) \exp(im \xi_3), \end{aligned} \quad (5.29)$$

which, except for the factor

$$\mathcal{F} \equiv \left(\frac{\xi_1}{r} \right) \left(\frac{\sin \xi_2}{\sin \theta} \right)^{1/2} \Delta_3^{-1/2}, \quad (5.30)$$

looks exactly like a free particle wavefunction in spherical coordinates, which we call "a normal solution".

Then one can look at (5.29) as "a renormalized solution" under the renormalization transformation

$$\{x_i\} \rightarrow \{\xi_i\}$$

subject to the conditions imposed on ξ_i . This point of view is interesting and will be applied to electronic problems later.

It is also useful to express ϕ in the following form in order to satisfy the scattering boundary conditions:

$$\phi^{(\pm)}(r, \theta, \varphi) = \mathcal{N} \mathcal{F} h_l^{(\pm)}(\lambda \xi_1) P_l^m(\cos \xi_2) \exp(im \xi_3) \quad (5.31)$$

where

$$h_l^{(\pm)} \equiv j_l \pm iy_l \quad (5.32)$$

y_l being the spherical Bessel function of the

third kind. Eq. (5.31) may be used for calculation of the S -matrix elements:

$$S_{ij} = \langle \psi_i^{(-)} | \psi_j^{(+)} \rangle.$$

It is now easy to construct $\Phi(r, \theta, \varphi, x_4, \dots, x_n)$ in terms of (5.31) and suitable uniform semiclassical solutions for the rest of degrees of freedom just by following the procedures described in the previous sections. In this case the new variables ξ_i of course would be obtained when the classical trajectories are calculated for the entire system.

6. ELECTRONIC WAVEFUNCTIONS OF ATOMS

The method discussed so far can be applied to calculation of wavefunctions of electrons bound in atoms. Since calculation of bound state electronic wavefunctions is a difficult task, especially for many-electron systems, the present semiclassical approximation to such problems might be useful for some practical purposes, although we may not be able to obtain sufficiently accurate energies. As will be shown by an example considered below, a calculation of this kind can be quick and sometimes even analytic. In any case it appears that there are some potentially useful aspects in this kind of approach. The subsequent discussion will show these.

We briefly sketch what is done below:

Our basic approach is the same as before. We "renormalize" the Schroedinger equation for a correlated system into that for an apparently uncorrelated system in the classical limit $\hbar \rightarrow 0$ by means of transformations. By such transformations the wavefunctions, apart from the Jacobian of transformation, are cast into a product of the well-known single electron wavefunctions, but whose arguments are new variables, but not the original ones. The new variables are obtained explicitly, if

the Hamilton-Jacobi equation of the corresponding classical problem is solved and the energies are quantized by the old quantum theory quantization rules.

We can easily see that our aim can be achieved by taking suitable forms for $f_i(\xi_i)$. Here, we shall consider a two-electron system which displays the essential features of calculation necessary for generalization of the result. For the moment we shall ignore the question of the symmetry of wavefunctions.

The Schrodinger equation for a two-electron system is

$$\left(-\frac{\hbar^2}{2\mu}\nabla^2-\frac{\hbar^2}{2\mu}A^2-\frac{Ze^2}{r_1}-\frac{Ze^2}{r_2}+\frac{e^2}{r_{12}}\right)\psi(r_1, r_2)=E\psi(r_1, r_2), \quad (6.1)$$

where Z is the charge number of the nucleus. This equation may be cast in the form as (5.4), if we define u such that

$$u(r_1, \theta_1, \varphi_1; r_2, \theta_2, \varphi_2) = r_1 r_2 (\sin\theta_1 \sin\theta_2)^{1/2} \psi(r_1, r_2). \quad (6.2)$$

We then obtain the Schrodinger equation in the form,

$$\begin{aligned} & \left[\frac{\partial^2}{\partial r_1^2} + \frac{\partial^2}{\partial r_2^2} + \frac{1}{r_1^2} \left(\frac{\partial^2}{\partial \theta_1^2} + \frac{1}{4} \right) \right. \\ & \left. + \frac{1}{r_2^2} \left(\frac{\partial^2}{\partial \theta_2^2} + \frac{1}{4} \right) + \frac{1}{r_1^2 \sin^2 \theta_1} \left(\frac{\partial^2}{\partial \varphi_1^2} + \frac{1}{4} \right) \right. \\ & \left. + \frac{1}{r_2^2 \sin^2 \theta_2} \left(\frac{\partial^2}{\partial \varphi_2^2} + \frac{1}{4} \right) \right] u(r_1, \dots, r_2, \dots) \\ & + \lambda^2 \left(E + \frac{Ze^2}{r_1} + \frac{Ze^2}{r_2} - \frac{e^2}{r_{1,2}} \right) u(r_1, \dots; r_2, \dots) \\ & = 0, \quad (6.3) \end{aligned}$$

where $\lambda = \sqrt{2m}/\hbar$. From now on we shall denote $r_1, \theta_1, \varphi_1, r_2, \theta_2, \varphi_2$ by q_1, q_2, \dots, q_6 , respectively, for notational simplicity.

Then, if $f_i(\xi_i)$ are chosen such that

$$f_i(\xi_i) = 2C_i - C_{i+1}^2/\xi_i^2 + 2/\xi_i, \quad (i=1, 4) \quad (6.4a)$$

$$f_j(\xi_j) = C_j^2 - C_{j+1}^2/\sin^2 \xi_j + \frac{1}{4}\lambda^{-2}, \quad (j=2, 5) \quad (6.4b)$$

$$f_k(\xi_k) = C_k^2, \quad (k=3, 6), \quad (6.4c)$$

where C_i are constants yet to be determined, and S_i are such that

$$\begin{aligned} S_i(\xi_i) &= 1/4\xi_i^2, \quad (i=1, 4) \\ S_j(\xi_j) &= -1/4\sin^2 \xi_j, \quad (j=2, 5) \\ S_k(\xi_k) &= 0, \quad (k=3, 6), \end{aligned} \quad (6.5)$$

we obtain a set of differential equations for $Y_i^{(\alpha)}$, analogous to (5.17). These equations can be solved by well known analytic functions. Indeed, provided that the constants C_i obey the conditions,

$$\lambda^2 C_k^2 = m_\alpha, \quad (m_\alpha = 0, \pm 1, \pm 2, \dots; k=3, 6), \quad (6.6)$$

$$\lambda^2 C_j^2 = l_\alpha(l_\alpha + 1), \quad (l_\alpha = 0, 1, 2, \dots; j=2, 5), \quad (6.7)$$

$$2\lambda^2 C_i = -n_\alpha^{-2}, \quad (n_\alpha = 0, 1, 2, \dots; i=1, 4), \quad (6.8)$$

and

$$n_\alpha \geq l_\alpha + 1; \quad -l_\alpha \leq m_\alpha \leq l_\alpha, \quad (6.9)$$

the physically acceptable solutions to such equations are

$$Y_k^{(\alpha)}(\xi_k) = \exp(\pm im_\alpha \xi_k), \quad (k=3, 6) \quad (6.10)$$

$$Y_j^{(\alpha)}(\xi_j) = (\sin \xi_j)^{1/2} P_{l_\alpha}^{m_\alpha}(\cos \xi_j), \quad (j=2, 5) \quad (6.11)$$

$$Y_i^{(\alpha)}(\xi_i) = \xi_i^{n_\alpha+1} \exp(-N_\alpha \xi_i) L_{n_\alpha}^{2N_\alpha+1} (2N_\alpha \xi_i), \quad (i=1, 4). \quad (6.12)$$

Here α stands for the electrons of the system and L_β^γ are the associated Laguerre polynomials with $N_\alpha \xi_i$ for their argument. We emphasize that despite its appearance, $Y_i^{(\alpha)}(\xi_i)$ as given by (6.12) is not a one-electron radial wavefunction, since the new variable ξ_i is in general a function of the coordinates of the two electrons. The same remark applies to other solutions in (6.10) and (6.11). The constant N_α is defined by

$$N_\alpha = \sqrt{2C_i}, \quad (i=1, 4),$$

and the ranges of the variables ξ_i are as follows:

$$0 \leq \xi_1, \quad \xi_4 < \infty; \quad 0 \leq \xi_2, \quad \xi_5 \leq \pi; \quad 0 \leq \xi_3, \quad \xi_6 \leq 2\pi. \quad (6.13)$$

The conditions on the constants, (6.6)~(6.8) are needed on the one hand to obtain the physically acceptable solutions finite everywhere, and are on the other hand connected with the phase integrals by the relations (5.19), leading to the quantization conditions. The following quantizations conditions are obtained from (5.19), (6.6), (6.7) and (6.8):

$$\oint_C p_k dq_k = m_\alpha h, \quad (k=3, 6), \quad (6.14)$$

$$\oint_C p_j dq_j = \left(l_\alpha - m_\alpha + \frac{1}{2}\right)h, \quad (j=2, 5), \quad (6.15)$$

$$\oint_C p_i dq_i = \left(n_r + \frac{1}{2}\right)h, \quad (i=1, 4) \quad (6.16)$$

where

$$n_r = n - l_\alpha - 1 \geq 0,$$

is the radial quantum number. The phase integrals must be carried over the trajectory from a turning surface to another. More precisely put, the phase integral must be carried over a period of the projection of the classical trajectory onto the i th coordinate.

In choosing (6.4) for $f_i(\xi_i)$ above, we have relied on Ehrenfest's adiabatic principle. This seems reasonable, since the basic electronic structure of the two-electron system should not be completely and qualitatively altered by the electronic correlation r_{12}^{-1} (this does not of course mean that the energy does not change as a result of such a correlation). This follows from the fact that n_α , l_α and m_α are quantum numbers as is obvious from (6.14)~(6.16), and they must remain unaltered. Indeed if (6.14)~(6.16) are added side by side, we obtain

$$\sum_i \oint_C p_i dq_i = \sum_i \iint d p_i dq_i = \left(n' + \frac{1}{2}\right)h, \quad (6.17)$$

$$(n' = 0, 1, 2, \dots),$$

which is simply Ehrenfest's adiabatic hypothesis²² which states that the phase integral of (6.17) is an adiabatic invariant. That is, the

quantum numbers are adiabatic invariants. This view has been essential for our calculation here and consequently the results obtained for the wavefunctions imply that even if there exist interactions that make the problem nonseparable, the actual forms for the wavefunctions do stay essentially the same as in the case of the separable noninteracting "normal" system. The first equality of (6.17) is a consequence of the properties of integral invariants³¹ of Hamilton systems.

By collecting the results above, we obtain the wavefunction in the form,

$$\psi(r_1, r_2) = \mathcal{N} \Delta_6^{-1/2} \prod_{\alpha=1}^2 \left(\frac{\sin \xi_{3\alpha-1}}{\sin \theta_\alpha} \right)^{1/2} \left(\frac{\xi_{3\alpha-2}}{r_\alpha} \right) \exp(-N_\alpha \xi_{3\alpha-2}) L_{n_r+l_\alpha}^{2l_\alpha+1/2}(2N_\alpha \xi_{3\alpha-2}) P_{l_\alpha}^{m_\alpha}(\cos \xi_{3\alpha-1}) \exp(im_\alpha \xi_{3\alpha}),$$

where

$$\int f_i^{1/2}(\xi_i) d\xi_i = \int_C p_i dq_i. \quad (6.18b)$$

Our discussion so far implicitly assumes that the wavefunctions are not altered of their signs by an interchange of identical particles. Therefore the approximate uniform semiclassical wavefunction obtained must be for the states of even symmetry, since it is symmetric with respect to an interchange of particle indices. The case of odd symmetry demands a fresh inquiry in the present semiclassical scheme, since the semiclassical method utilizes the Hamilton-Jacobi equation, *i. e.*, the classical equations of motion, which has no such quantum mechanical exchange symmetry attached to it: particle exchange symmetry is a quantum mechanical concept without a classical analog. We consider it here.

Let us denote the wavefunction by $\phi(r_1, r_2)$. Since it must be either symmetric or antisymmetric in the space coordinates, we have

$$\phi(r_1, r_2) = \pm \phi(r_2, r_1). \quad (6.19)$$

This must hold even in the classical limit where the wavefunction may be taken for the moment to be the primitive WKB solution,

$$\psi^0(r_1, r_2) = A_0 \exp[i\hbar^{-1}W(r_1, r_2)], \quad (6.20)$$

where W is the characteristic function of Hamilton and A_0 is given by

$$A_0 = \left[\frac{\partial(\dot{p}_1, \dot{p}_2, \dots, \dot{p}_6)}{\partial(\alpha_1, \alpha_2, \dots, \alpha_6)} \right]^{1/2} \quad (6.21)$$

with

$$\dot{p}_i = \frac{\partial W}{\partial x_i}$$

$\alpha_i = \text{new momenta.}$

Since (6.20) must satisfy (6.19) under a permutation of particle indices and the Jacobian in (6.21) must be taken positive in any case, we see that Hamilton's characteristic function must satisfy the relation under a particle permutation,

$$W(r_2, r_1) = W(r_1, r_2) + \gamma\hbar, \quad (6.22)$$

where

$$\gamma = \begin{cases} 0 & \text{for a symmetric case} \\ \pm\pi & \text{for an antisymmetric case} \end{cases} \quad (6.23)$$

More generally, we must take $\gamma = \pm(2\alpha+1)\pi$, α being an integer, for an antisymmetric case. In other words, for antisymmetric states Hamilton's characteristic function $W(r_1, r_2)$ acquires an additive factor proportional to \hbar . Therefore, although $W(r_1, r_2)$ and $W(r_2, r_1)$ satisfy the same Hamilton-Jacobi equation which is invariant to a particle permutation, the associated quantization rules differ by a factor $\gamma\hbar$ for symmetric and antisymmetric states. Eq. (6.22) implies that we must have

$$\sum_i \oint_C \dot{p}_i dq_i = \sum_i \gamma_i \hbar + \gamma \hbar \quad (6.24)$$

for antisymmetric states and

$$\sum_i \oint_C \dot{p}_i dq_i = \sum_i \gamma_i \hbar \quad (6.25)$$

for symmetric states, where γ_i are either an integer or half-integer.

The additional phase factor γ has a sign ambiguity. It is not possible to settle this ambiguity in the present formalism. However, we may proceed in the following manner. If the spatial part of the wavefunction is antisymmetric, the spin part must be symmetric. This means that in the present case it is a triplet. Since triplet states are lower in energy according to Hund's rule³² than the corresponding singlet states, the negative sign should be chosen. This argument is admittedly not definitive and at best empirical. We believe that further investigation should be necessary to have this aspect of the symmetry property of semiclassical wavefunctions more fully clarified.

It is not difficult, however, to construct antisymmetric wavefunctions. One simply takes an antisymmetric combination of (6.18), which now must be subject to the quantization conditions (6.24).

The wavefunction given in (6.18) can be easily generalized to a system of many electrons. The procedure is exactly parallel to that for (6.18).

Before closing this section, we shall consider one of the simplest particular situations where we can carry out calculations analytically. We believe this example of calculation shows an aspect of uniform semiclassical method as a powerful tool for some theoretical investigations.

Let us consider a helium atom in the ground electronic state. We wish to calculate the energy and the wavefunction. Since the wavefunction is independent of angle coordinates, the characteristic function is also independent of them and we have the Hamilton-Jacobi equation

in the form,

$$\frac{1}{2}\left(\frac{\partial W}{\partial r_1}\right)^2 + \frac{1}{2}\left(\frac{\partial W}{\partial r_2}\right)^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} = E, \quad (6.27)$$

where all the quantities are in atomic units and Z is the atomic number of helium. This equation is in general nonseparable and must be solved by either a numerical method or a perturbation theory. In the following we consider a special case of orbits for the two electrons which stay on a plane. In this case, if the orbits are to be steady, they must satisfy the condition³³

$$r_1 = r_2. \quad (6.28)$$

Then, one can easily obtain for the energy eigenvalue³³

$$E_{n_1 n_2} = -\frac{\left(Z - \frac{1}{4}\right)^2}{2n_1^2} - \frac{\left(Z - \frac{1}{4}\right)^2}{2n_2^2} \quad (6.29)$$

in atomic units. For $n_1 = n_2 = 1$, $E_{11} = -3.062$ hartree, while the best result³⁴ by a variational method is $E_{11} = -2.9037225$ hartree. We can calculate the corresponding wavefunction quite easily. For this purpose we first calculate ξ_1 and ξ_2 in terms of r_1 and r_2 by using the relation,

$$\lambda \int^{\xi_i} \left(2C_i + \frac{2}{\xi_i}\right)^{1/2} d\xi_i = \lambda \int_C p_i dr_i, \quad (i=1, 2) \quad (6.30)$$

Owing to the restriction (6.28), the phase integral on the rhs of (6.30) is simply

$$\int p_i dr_i = \int dr_i \left[2E_i + 2\left(Z - \frac{1}{4}\right)/r_i\right]^{1/2} \quad (6.31)$$

Eqs. (6.13), (6.30) and (6.31) lead to the solution ξ_i in the form,

$$\lambda(2C_i)^{1/2} \xi_i = \left(Z - \frac{1}{4}\right) r_i \quad (6.32)$$

in atomic units of r_i . Then, we have

$$\frac{\partial(\xi_1, \xi_2)}{\partial(r_1, r_2)} = \left[\left(Z - \frac{1}{4}\right)/\lambda\right]^2,$$

and finally for the wavefunction

$$\phi_{11}(r_1, r_2) = \mathcal{N}_{12} \exp\left(-\frac{1}{2} k S\right), \quad (6.33)$$

where $k = \left(2Z - \frac{1}{2}\right)$, $S = r_1 + r_2$ and \mathcal{N}_{12} is the normalization constant. Chandrasekhar, Elbert and Herzberg³⁴ used 10- and 18-parameter variational wavefunctions whose exponents of the exponential factors are respectively $k = 3.5100255$, and 3.8499613 , and obtained the values of energy equal to -2.9036027 and -2.9037063 hartree, respectively. We note that we have a similar exponential factor with its exponent k equal to 3.5 . Unfortunately, due to the restriction (6.28) we have lost the r_{12} dependence of $\phi_{11}(r_1, r_2)$. Nevertheless, it is remarkable to see that the present uniform semiclassical theory can produce such a smooth wavefunction without any numerical effort at all and without a variational method. This example appears to indicate that the uniform semiclassical theory might be useful for more complex systems.

7. DISCUSSION

The approximate wavefunctions $Y^{(0)}$ obtained in the previous sections are semiclassical in the following sense: in Eq. (2.7), and the equivalent equations, the terms on the rhs of 0 (λ^0) are neglected in the classical limit $\lambda \rightarrow \infty$; when taken in their asymptotic forms, they lead to linear combinations of the primitive WKB solutions; the eigenvalues are determined by the Bohr-Sommerfeld quantization rules. They are uniformly finite throughout the domain of the variables and with them we can avoid the difficult but important question of the connection formulas for proper use of the primitive WKB solutions of multidimensional nonseparable systems.

One may be able to estimate the contribution of the rhs of (2.7) to the solution Y , *i. e.*, the

correction to $Y^{(0)}$, by converting (2.7) into an integral equation with the rhs as an inhomogeneous term. Although the correction term would be $O(\lambda^0)$ at most, it is not easy to calculate its precise magnitude for a multidimensional problem. If experience^{19,35} with one-dimensional problems is an indication to base hope on, the uniform semiclassical solutions $Y^{(0)}$ should be sufficiently accurate for all practical purposes.

When applied to scattering problems, the uniform semiclassical solutions supply us with the S -matrices, which may be calculated by the formula as given by (4.8). Such an expression for the S -matrix does not resemble the classical S -matrix formula⁴⁻⁷, but may be put into a form given in terms of action integrals, if we use the asymptotic formulas for the uniform semiclassical wavefunctions and the method of stationary phase for evaluation of the integrals for S_{if} . Since the systems may permit many stationary phase points (lines or surfaces), the resulting approximate S -matrix formulas would acquire richer structures than the usual classical S -matrix formulas. Since detailed structures would depend on the nature of the system in hand, a general formula in such an approximation is not feasible to obtain with an assurance of wide validity. One needs at least a careful case-by-case study of the prototypes of systems in order to obtain such approximate formulas, unless one uses the formulas like (4.8) for the S -matrices.

In order to help the reader see that the uniform semiclassical solutions would lead to linear combinations of the primitive WKB solutions, we present some asymptotic formulas for the previous sections.

The asymptotic formulas for $A_i(-z)$ are well known³⁰:

$$A_i(z) \sim \frac{1}{2} \pi^{-1/2} z^{-1/4} e^{-\zeta}, \quad (-\pi < \arg z < \pi), \quad (7.1)$$

$$A_i(-z) \sim \pi^{-1/2} z^{-1/4} \cos(\zeta - \pi/4), \quad (z > 0, z \rightarrow \infty), \quad (7.2)$$

where

$$\zeta = \frac{2}{3} z^{3/2},$$

If $z = \xi_i$, then ξ is one of the phase integrals given by, for example, Eq. (2.19).

The uniform semiclassical solutions for vibrational motions have the asymptotic formulas,

$$\exp\left(-\frac{1}{2} N^2 z_i^2\right) H_n(Nz_i) \sim z_i^N \exp\left(-\frac{1}{2} N^2 z_i^2\right), \quad |z_i| \rightarrow \infty, \quad (7.3)$$

$$\exp\left(-\frac{1}{2} N^2 z_i^2\right) H_n(Nz_i) \sim \sqrt{2} N^{n+4/3} e^{-1/4N} p_i^{-1/2} \cos\left(\lambda \int_C dx_i p_i - \pi/4\right), \quad (N \rightarrow \infty, -1 < z_i < 1), \quad (7.4)$$

where N was defined before [see Eq. (3.9)].

The Laguerre polynomials appearing in (6.9a) with the variables ξ_i defined by Eq. (6.9b) have the following asymptotic behaviors:

$$\xi_i^{(\beta+1)/2} e^{-N\xi_i} L_n^\beta(2N\xi_i) \sim \frac{(-2N)^n}{n!} \xi_i^N e^{-N\xi_i}, \quad \text{as } \xi_i \rightarrow \infty, \\ \xi_i^{(\beta+1)/2} e^{-N\xi_i} L_n^\beta(2N\xi_i) \sim \frac{(-)^n}{n!} 2^{-a+1/2} N^{n+2/3} p_i^{-1/2} \cos\left(\lambda \int dx_i p_i - \frac{\pi}{4}\right), \quad |N\xi_i| \rightarrow \infty, \quad (7.6)$$

where the notations are the same as before.

The asymptotic formulas (7.3)~(7.6) can be easily deduced from the formulas obtained by Erdelyi.¹⁵ The asymptotic formulas (7.2), (7.4) and (7.6) have the forms for the one-dimensional WKB solutions in the classically allowed region.

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