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Publication Date

1972-07-01

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July 1972

AEC Contract. No. W-7405-eng-48



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CLASSICAL-LIMIT QUANTIZATION OF NON-SEPARABLE SYSTEMS:

MULTI-DIMENSIONAL WKB PERTURBATION THEORY*

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ABSTRACT

A general dynamical system of N degrees of freedom is considered as a zeroth-order separable part plus a non-separable perturbation, and explicit formulas are derived for the classical-limit approximation to the eigenvalues through second order in the non-separable interaction. As a numerical example, the first and second order perturbation energies of the helium atom are calculated semiclassically, and agreement with the exact quantum mechanical values is quite reasonable.

I. INTRODUCTION

Paralleling recent developments of semiclassical scattering theory¹⁻³ is the development of related techniques for bound state problems. Aside from historical interest in the problem there is the desire for some way to facilitate analysis of the eigenvalue spectrum of multi-dimensional systems. The long-range goal of this direction of study is the establishment of "inversion relations" analogous to the one-dimensional RKR formulas⁴ whereby one could use the experimentally observed spectrum of a triatomic molecule, for example, to construct its multidimensional potential energy surface.

Recent work by Gutzwiller⁵ and Miller⁶ has established the generalization of the Bohr-Sommerfeld quantization rule to general, non-separable systems. By examining the singularities of the semiclassical approximation to the Green's function it was shown that the multidimensional quantization condition again involves an action integral, the paths of integration being along the periodic orbits of the system; earlier work by Keller⁷ led to a quantization condition of the same form.

While these periodic orbits are trivial for systems of one degree of freedom, their multidimensional counterparts are in general quite difficult to establish. Moreover, even if the periodic trajectories could be conveniently determined, a more serious shortcoming of this periodic orbit theory is the difficulty it has with "almost separable" systems: since separable and non-separable degrees of freedom enter this theory in an intrinsically different manner⁶, systems with weak coupling between various degrees of freedom are inaccurately described. This is a serious defect in practice, for systems of interest are often of this

"almost separable" variety; for example, a good zeroth order description of the vibrational states of a polyatomic molecule is the normal mode approximation. Thus although periodic orbit theory appears to be a formally correct solution of the classical-limit eigenvalue problem, it is not a particularly useful solution in its present form.

One thus seeks alternant formulations of the problem that avoid these difficulties of periodic orbit theory. In this paper we develop such an approach, a multidimensional WKB perturbation theory for the eigenvalues of non-separable systems. Since the unperturbed system is separable and only the perturbation non-separable, it is clear that this theory will apply best to "almost separable" systems and thus complement periodic orbit theory.

Similar in spirit to this perturbative approach is the generalized Miller-Good theory developed by Pechukas⁸, in which one attempts to map a non-separable potential onto a related separable one by a suitable transformation. Since both approaches relate the original non-separable system to a simpler separable one, the eigenvalues for the non-separable system are characterized by the full set of quantum numbers of the underlying separable reference system; this is in contrast to periodic orbit theory in which there is no reference to the "bad quantum numbers", but only the single "ordering quantum number"⁶.

Section II first carries out a perturbation expansion of the one-dimensional WKB quantum condition, obtaining explicit expressions for the first and second order perturbation energies. Since this procedure is possible only for systems of one degree of freedom, it is also shown in Section II how these same expressions can be derived in a manner that is directly

extendable to the general N-dimensional case; namely, we begin with the known quantum mechanical expressions for the perturbation energies and evaluate them semiclassically. (In the course of this approach it is necessary to develop a semiclassical expression for the projector onto the unperturbed sub-space.) In Section III the desired multi-dimensional expressions are obtained, and Section IV concludes by showing that these general expressions give quite reasonable results for the first and second order perturbation energies of the ground state two electron atom.

II. ONE-DIMENSIONAL SYSTEMS

A. Direct Expansion of the WKB Quantum Condition.

For one dimensional systems the semiclassical quantum condition is the well-known WKB, or Bohr-Sommerfeld relation⁹

$$(n + \frac{1}{2})2\pi\hbar(2m)^{-\frac{1}{2}} = \oint dx [E - V(x)]^{\frac{1}{2}}, \quad (\text{II.1})$$

$n = 0, 1, \dots$, where the contour integral in the complex x-plane encloses the two classical turning points x_1 and x_2 . (One usually writes the contour integral as a real integral

$$\oint dx = 2 \int_{x_1}^{x_2} dx, \quad ,$$

but Equation (II.1) is more convenient at present.) If the potential energy $V(x)$ is an unperturbed part plus a perturbation,

$$V(x) = V_0(x) + \lambda V_1(x), \quad ,$$

and if the eigenvalue E is similarly expanded,

$$E = E_0 + \lambda E_1 + \lambda^2 E_2 + \dots, \quad ,$$

then expansion of the RHS of Equation (II.1) in powers of λ gives

$$\begin{aligned}
 (n + \frac{1}{2})2\pi\hbar(2m)^{-\frac{1}{2}} &= \oint dx [E_0 - V_0(x)]^{\frac{1}{2}} \\
 &+ \lambda \oint dx [E_0 - V_0(x)]^{-\frac{1}{2}} \frac{1}{2}[E_1 - V_1(x)] \\
 &+ \lambda^2 \oint dx [E_0 - V_0(x)]^{-\frac{1}{2}} \left\{ \frac{1}{2}E_2 - \frac{1}{8}[E_1 - V_1(x)]^2 \right. \\
 &\times [E_0 - V_0(x)]^{-1} \left. \right\} + O(\lambda^3) \quad . \quad (II.2)
 \end{aligned}$$

Equating corresponding powers of λ gives the expected quantum condition for E_0 and the following expressions for the first and second order perturbation energies:

$$E_1 = \oint dx V_1(x) [E_0 - V_0(x)]^{-\frac{1}{2}} / \oint dx [E_0 - V_0(x)]^{-\frac{1}{2}} \quad (II.3a)$$

$$E_2 = \frac{1}{4} \oint dx \bar{V}_1(x)^2 [E_0 - V_0(x)]^{-\frac{3}{2}} / \oint dx [E_0 - V_0(x)]^{-\frac{1}{2}} \quad , \quad (II.3b)$$

where

$$\bar{V}_1(x) \equiv V_1(x) - E_1 \quad .$$

The contour integrals in Equation (II.3a) can be immediately reduced to real ones, so that

$$E_1 = D^{-1} \int_{x_1}^{x_2} dx V_1(x) [E_0 - V_0(x)]^{-\frac{1}{2}} \quad , \quad (II.4)$$

where

$$D = \int_{x_1}^{x_2} dx [E_0 - V_0(x)]^{-\frac{1}{2}} \quad ; \quad (II.5)$$

this is the standard expression⁹ for the time average of the perturbation in the unperturbed potential. To express the numerator of Equation (II.3b)

as a real integral one first uses the relation

$$\oint dx \bar{V}_1(x)^2 [E_0 - V_0(x)]^{-\frac{3}{2}} = -2 \frac{d}{dE_0} \oint dx \bar{V}_1(x)^2 [E_0 - V_0(x)]^{-\frac{1}{2}}, \quad (\text{II.6})$$

so that the second order expression can be written as

$$E_2 = -(2D)^{-1} \frac{d}{dE_0} \int_{x_1}^{x_2} \bar{V}_1(x)^2 [E_0 - V_0(x)]^{-\frac{1}{2}}. \quad (\text{II.7})$$

(It is necessary to make the replacement in Equation (II.6) because the real integral with integrand $[E_0 - V_0(x)]^{-\frac{3}{2}}$ is divergent.) Higher order terms can be similarly derived.

Equations (II.4), (II.5) and (II.7) are the desired one-dimensional expressions. As a simple application, consider the quartic perturbation of a harmonic oscillator; i.e.,

$$V_0(x) = \frac{1}{2} m \omega^2 x^2$$

$$V_1(x) = x^4.$$

Thus

$$E_0(n) = (n + \frac{1}{2}) \hbar \omega,$$

and Equations (II.4) and (II.7) give

$$E_1(n) = \frac{3}{2} (n + \frac{1}{2})^2 \hbar \omega$$

$$E_2(n) = -\frac{17}{4} (n + \frac{1}{2})^3 \hbar \omega,$$

compared to the exact quantum mechanical results

$$E_1(n) = [\frac{3}{2} (n + \frac{1}{2})^2 + \frac{3}{8}] \hbar \omega$$

$$E_2(n) = \left[-\frac{17}{4}(n + \frac{1}{2})^3 - \frac{67}{16}(n + \frac{1}{2}) \right] \hbar\omega$$

The semiclassical perturbation energies are accurate, therefore, for quantum numbers not too small.

Although the above derivation of Equations (II.4) and (II.7) is quite adequate for the one dimensional case, it offers little clue as to how one should proceed for the general case of N dimensions. The remainder of Section II, therefore, will be devoted to a re-derivation of Equations (II.4) and (II.7) by a procedure that can be extended to multidimensional systems.'

The quantum mechanical expressions¹⁰ for the perturbation energies are

$$E_1 = \langle \phi | V_1 | \phi \rangle \quad (II.8a)$$

$$E_2 = \langle \phi | \bar{V}_1 (E_0 - H_0)^{-1} \bar{V}_1 | \phi \rangle, \quad (II.8b)$$

where ϕ is the unperturbed eigenfunction for the potential $V_0(x)$ and the singular operator $(E_0 - H_0)^{-1}$ is interpreted in a principal value sense. It is actually more suggestive to write Equation (II.8) in the form

$$E_1 = \text{tr}[PV_1] \quad (II.9a)$$

$$E_2 = \text{tr}[\bar{P}\bar{V}_1(E_0 - H_0)^{-1}\bar{V}_1] \quad (II.9b)$$

where $P \equiv |\phi\rangle\langle\phi|$ is the projector onto the unperturbed state and $\text{tr}[\quad]$ means a quantum mechanical trace,

$$\text{tr}[A] \equiv \sum_n \langle n | A | n \rangle,$$

A being any operator and $\{|n\rangle\}$ a complete set of states.

To obtain the classical limit of Equation (II.9) one simply replaces the quantum mechanical trace by a classical trace; i.e., if A_{op} is a quantum mechanical operator expressed in terms of the coordinate and momentum operators,

$$A_{op} = A(x_{op}, p_{op}) ,$$

then its trace is given in the classical limit by a phase space integral

$$\text{tr}[A_{op}] \approx h^{-1} \int dx \int dp A(x,p) , \quad (\text{II.10})$$

where $A(x,p)$ is the same algebraic function of the classical variables x and p that A_{op} is of x_{op} and p_{op} . Applying Equation (II.10) to Equation (II.9) thus gives the following classical limit approximations to the perturbation energies:

$$E_1 = h^{-1} \int dx \int dp V_1(x) P(x,p) \quad (\text{II.11a})$$

$$E_2 = h^{-1} \int dx \int dp \bar{V}_1(x)^2 [E_0 - V_0(x) - p^2/2m]^{-1} P(x,p) \quad (\text{II.11b})$$

where $P(x,p)$ is the classical phase space distribution corresponding to the projection operator P . The determination of $P(x,p)$ and its properties are the subject of the next section.

B. Semiclassical Projection Operator

The projector P is an integral operator defined by

$$Pf(x) = \phi(x) \int dx' \phi(x')^* f(x') . \quad (\text{II.12})$$

We wish to express P in terms of the multiplicative and differential operators x and p , so that Equation (II.12) will have the form

$$Pf(x) = P(x, p_{op}) f(x) ,$$

where

$$p_{op} = -i\hbar \frac{d}{dx} .$$

To accomplish this, $f(x')$ in the integral of Equation (II.12) is expanded in a Taylor series about x

$$f(x') = f(x) + f'(x)(x' - x) + \dots$$

$$= \exp\left[\frac{i}{\hbar}(x' - x)p_{op}\right] f(x) ,$$

so that Equation (II.12) becomes

$$Pf(x) = \phi(x) \exp\left[-\frac{i}{\hbar} x p_{op}\right] \int dx' \phi(x')^* \exp\left[\frac{i}{\hbar} x' p_{op}\right] f(x) ,$$

and one therefore deduces the desired classical function $P(x, p)$ to be

$$P(x, p) = \phi(x) \exp\left(-\frac{i}{\hbar} xp\right) \int dx' \phi(x')^* \exp\left(\frac{i}{\hbar} x' p\right) . \quad (II.13)$$

It is easy to see that $P(x, p)$ in Equation (II.13) gives the correct coordinate and momentum distributions when it is separately integrated over the conjugate variable, i.e.,

$$\hbar^{-1} \int dp P(x, p) = |\phi(x)|^2 \quad (II.14a)$$

$$\hbar^{-1} \int dx P(x, p) = |\phi(p)|^2 , \quad (II.14b)$$

where $\phi(p)$ is the normalized momentum wavefunction

$$\phi(p) = (2\pi\hbar)^{-\frac{1}{2}} \int dx \phi(x) \exp\left(-\frac{i}{\hbar} xp\right) . \quad (II.15)$$

From both Equation (II.14a) and (II.14b) it is seen that $P(x,p)$ is correctly normalized

$$\hbar^{-1} \int dx \int dp P(x,p) = 1.$$

Equation (II.13), having the form of a "half Fourier transform", is quite reminiscent of the Wigner distribution function¹¹ of statistical mechanics, and indeed Hahn and Watson¹² have shown that this result can be derived by that approach.

To proceed further semiclassically the integral over x' in Equation (II.13) is evaluated by stationary phase. Thus the WKB approximation for $\phi(x)$ is introduced

$$\phi(x) = C^{\frac{1}{2}} p(x)^{-\frac{1}{2}} \sin\left[\frac{\pi}{4} + \hbar^{-1} \int_{x_1}^x dx' p(x')\right] \quad (\text{II.16})$$

where

$$p(x) = \{2m[E_0 - V_0(x)]\}^{\frac{1}{2}} \quad (\text{II.17})$$

$$C = E_0'(n) \quad 2m/(\pi\hbar) \quad ,$$

$E_0(n)$ being the zeroth order quantum number function. The stationary phase integration in Equation (II.13) then proceeds as usual, and one obtains

$$P(x,p) = E_0'(n) \left(\frac{2m}{4\pi\hbar}\right)^{\frac{1}{2}} [p(x)V_0(x(p))]^{-\frac{1}{2}} \exp\left[\frac{i\pi}{4} + \frac{i}{\hbar} \left\{ \int_{x(p)}^x dx' p(x') - p[x-x(p)] \right\} \right] \quad , \quad (\text{II.18})$$

where $x(p)$ is that value of x determined by the classical relation

$$E_0 = p^2/2m + V_0(x) \quad ; \quad (\text{II.19})$$

i.e., $x(p)$ is the inverse of the function $p(x)$ defined by Equation (II.17). (There are actually two values of x that satisfy Equation (II.19) — i.e., $x(p)$ is a multi-valued function — so that Equation (II.18) is actually the sum of two such terms. The notation is simpler, however, if we do not indicate this explicitly, and it shall not be necessary for our purposes to deal with this feature,)

The usefulness of Equation (II.18) is that it shows $P(x,p)$ to be an oscillatory function of its arguments. Thus an integral of the form

$$\int dx P(x,p) f(x) ,$$

where $f(x)$ is a smooth (i.e., non-oscillatory) function, must be evaluated by stationary phase. The value of x that is the point of stationary phase is determined by the condition

$$0 = \frac{\partial}{\partial x} \left\{ \int_{x(p)}^x dx' p(x') - [x - x(p)]p \right\} ,$$

$$= p(x) - p ,$$

or $x = x(p)$ is the point of stationary phase; i.e., the stationary phase relation is the same as the classical relation between x and p in Equation (II.19). Within the stationary phase approximation the above integral thus becomes

$$\int dx P(x,p) f(x) \approx f(x(p)) \int dx P(x,p) . \quad (II.20)$$

Similarly, an integral over momentum such as

$$\int dp P(x,p) f(p) ,$$

where $f(p)$ is a non-oscillatory function of p , is to be evaluated by

stationary phase. In this case the stationary phase condition is

$$0 = \frac{\partial}{\partial p} \left\{ \int_{x(p)}^x dx' p(x') - [x - x(p)] p \right\} = -px'(p) + x'(p) - [x - x(p)]$$

$$= x(p) - x, \quad ,$$

or $p = p(x)$ is the point of stationary phase; i.e., the same relation between p and x is recovered. The above momentum integral thus becomes

$$\int dp P(x,p) f(p) \simeq f(p(x)) \int dp P(x,p). \quad (\text{II.21})$$

It is important to note in Equations (II.20) and (II.21) that once the integral of $P(x,p)$ over x or p is carried out, the resulting function of p or x is not oscillatory; this is true because the phase

$$\int_{x(p)}^x dx' p(x') - [x - x(p)] p$$

evaluated at $x = x(p)$ or $p = p(x)$ is identically zero. In particular, it is not difficult to show that these integrals are

$$\int dx P(x,p) = E_0'(n) [1/|V_0'(x_1(p))| + 1/|V_0'(x_2(p))|] \quad (\text{II.22a})$$

and

$$\int dp P(x,p) = E_0'(n) 2m/p(x), \quad (\text{II.22b})$$

where $x_1(p)$ and $x_2(p)$ are the two branches of $x(p)$.

C. Semiclassical Evaluation of Quantum Expressions.

With the semiclassical limit of the projector established it is now rather straight forward to evaluate the phase space integrals in Equation (II.11). For the first order perturbation energy [Equation

(II.11a)] the momentum integral can be carried out according to Equation (II.21), so that one obtains

$$E_1 = E_0'(n) 2m \hbar^{-1} \int_{x_1}^{x_2} dx V_1(x)/p(x) , \quad (II.23)$$

and since

$$E_0'(n) = \hbar(2m)^{-1/2} \int_{x_1}^{x_2} dx [E_0 - V_0(x)]^{-1/2} , \quad (II.24)$$

it is seen that Equation (II.4) is reproduced.

In carrying out the momentum integral for E_2 in Equation (II.11b) one must proceed more carefully, for the value of p which is the point of stationary phase is also a singularity of the integrand. Thus the integral over p in Equation (II.11b) is of the generic form

$$I = \int dp (\bar{p}^2 - p^2)^{-1} \exp[i\alpha(p - \bar{p})^2] , \quad (II.25)$$

where $\bar{p} = p(x)$, and where we are considering only the positive stationary phase value of p ; there is an identical contribution from the negative of this value. Letting $z = p - \bar{p}$, Equation (II.25) becomes

$$I = - \int dz z^{-1} (z + 2\bar{p})^{-1} \exp(i\alpha z^2) ;$$

since the dominant contribution to the integral is from the region about $z \approx 0$ (because this is the stationary phase point and also a singularity of the integrand), one expands the non-singular factor about $z = 0$

$$(z + 2\bar{p})^{-1} = (2\bar{p})^{-1} - (2\bar{p})^{-2} z + O(z^2) ,$$

so that the integral becomes

$$I = - \int dz z^{-1} \exp(i\alpha z^2) + (2\bar{p})^{-2} \int dz \exp(i\alpha z^2) + \dots$$

The first term is zero because the integrand is an odd function of z , so that the desired approximation for the integral in Equation (II.25) is

$$\int dp (\bar{p}^2 - p^2)^{-1} \exp[i\alpha(p - \bar{p})^2] \approx (2\bar{p})^{-2} \int dp \exp[i\alpha(p - \bar{p})^2] \quad (\text{II.26})$$

Using the integral approximation in Equation (II.26) to evaluate the momentum integral for E_2 in Equation (II.11b) gives

$$E_2 = h^{-1} \int dx \bar{V}_1(x)^2 \frac{1}{4} [E_0 - V_0(x)]^{-1} \int dp P(x,p),$$

and with Equations (II.22b) and (II.24) this becomes

$$E_2 = (4D)^{-1} \int dx \bar{V}_1(x)^2 [E_0 - V_0(x)]^{-\frac{3}{2}}, \quad (\text{II.27})$$

D being the normalization constant of Equations (II.5). As was noted in Section IIA, however, the real integral with the above integrand is divergent, so that it must be replaced by the derivative expression in Equation (II.6); with this replacement the previous expression for E_2 [Equation (II.7)] is recovered.

Having thus verified that the semiclassical perturbation energies obtained directly from the WKB quantum condition also result from a semiclassical evaluation of the quantum mechanical perturbation formulas, we are now ready to proceed to the multi-dimensional case.

III. MULTI-DIMENSIONAL SYSTEMS

The quantum mechanical expressions in Equations (II.8) and (II.9) apply, of course, to systems of any numbers of degrees of freedom, and the classical-limit approximation for the traces in Equation (II.9) is the

following generalization of Equation (III.11):

$$E_1 = h^{-N} \int d\tilde{x} \int d\tilde{p} V_1(\tilde{x}) P(\tilde{x}, \tilde{p}) \quad (\text{III.1a})$$

$$E_2 = h^{-N} \int d\tilde{x} \int d\tilde{p} \bar{V}_1(\tilde{x})^2 [E_0 - H_0(\tilde{x}, \tilde{p})]^{-1} P(\tilde{x}, \tilde{p}) \quad , \quad (\text{III.1b})$$

where $\tilde{x} \equiv (x_1, x_2, \dots, x_N)$ and $\tilde{p} \equiv (p_1, p_2, \dots, p_N)$,

$$H_0(\tilde{x}, \tilde{p}) = \sum_{i=1}^N p_i^2 / 2m_i + V_0(\tilde{x}) \quad , \quad (\text{III.2})$$

and $P(\tilde{x}, \tilde{p})$ is the unperturbed phase space density. Progress can only be made if the unperturbed potential is separable,

$$V_0(\tilde{x}) = \sum_{i=1}^N v_i(x_i) \quad , \quad (\text{III.3})$$

for in this case $P(\tilde{x}, \tilde{p})$ is correspondingly separable into a product of N factors, one for each degree of freedom

$$P(\tilde{x}, \tilde{p}) = P_1(x_1, p_1) P_2(x_2, p_2) \dots P_N(x_N, p_N) \quad .$$

Each one dimensional phase space density $P_i(x_i, p_i)$ is of the form discussed in Section IIB. The unperturbed energy is

$$E_0 = \sum_{i=1}^N \epsilon_i \quad , \quad (\text{III.4})$$

ϵ_i being the WKB eigenvalue for the one dimensional potential $v_i(x_i)$.

The perturbation is in general not separable, of course, or else the complete problem would be separable and therefore exactly solvable without recourse to perturbation theory.

The task is to carry out the integrations over momenta in Equation (III.1). For the first order perturbation energy this is quite simple,

for the only dependence of the integrand on momenta is that in $P(\underline{x}, \underline{p})$; and since

$$\int d\underline{p} P(\underline{x}, \underline{p}) = [\int dp_1 P_1(x_1, p_1)] [\int dp_2 P_2(x_2, p_2)] \dots [\int dp_N P_N(x_N, p_N)] ,$$

Equation (II.21) of the previous section can be used and it is then easy to show that Equation (III.1a) becomes

$$E_1 = D^{-1} \int d\underline{x} V_1(\underline{x}) [\epsilon_1 - v_1(x_1)]^{-\frac{1}{2}} [\epsilon_2 - v_2(x_2)]^{-\frac{1}{2}} \dots [\epsilon_N - v_N(x_N)]^{-\frac{1}{2}} \quad (III.5)$$

where the normalization constant D is

$$D = \int d\underline{x} [\epsilon_1 - v_1(x_1)]^{-\frac{1}{2}} [\epsilon_2 - v_2(x_2)]^{-\frac{1}{2}} \dots [\epsilon_N - v_N(x_N)]^{-\frac{1}{2}} \quad (III.6)$$

It is considerably trickier to carry out the momentum integrations in Equation (III.1b) for the second order perturbation energy. For the case $N = 2$, for example, the momentum integral is a generalization of the generic form in Equation (II.25), namely

$$I = \int dp_1 \int dp_2 (\bar{p}_1^2 + \bar{p}_2^2 - p_1^2 - p_2^2)^{-1} \exp[i\alpha_1(p_1 - \bar{p}_1)^2 + i\alpha_2(p_2 - \bar{p}_2)^2] \quad (III.7)$$

where we are again considering only the contribution from the positive stationary phase points. With the aid of integral tables¹³ the integral over p_2 , say, can be carried out explicitly

$$\begin{aligned} & \int dp_2 (\bar{p}_1^2 + \bar{p}_2^2 - p_1^2 - p_2^2)^{-1} \exp[i\alpha_2(p_2 - \bar{p}_2)^2] \\ &= (2\bar{p}_2)^{-2} [(i\pi/\alpha_2)^{\frac{1}{2}} - i\pi^{\frac{1}{2}} 2\bar{p}_2 z \Gamma(\frac{1}{2}, z)] \quad (III.8) \end{aligned}$$

where

$$z = i\alpha_2 (2\bar{p}_2)^{-2} (p_1^2 - \bar{p}_1^2) ,$$

and $\Gamma(\frac{1}{2}, z)$ is the incomplete gamma function¹⁴. Since we seek the asymptotic value of the integral for large α_1 and α_2 , the large z limit of the gamma function¹⁴ is invoked, whereby the RHS of Equation (III.8) becomes

$$(i\pi/\alpha_2)^{\frac{1}{2}} [(2\bar{p}_2)^{-2} + (\bar{p}_1^2 - p_1^2)^{-1}] .$$

The remaining integration over p_1 can now be performed just as for the one dimensional case in Section IIC, giving

$$I \approx (i\pi/\alpha_1)^{\frac{1}{2}} (i\pi/\alpha_2)^{\frac{1}{2}} [(2\bar{p}_1)^{-2} + (2\bar{p}_2)^{-2}] ;$$

thus the following asymptotic approximation is established as the generalization of Equation (II.26):

$$\begin{aligned} & \int dp_1 \int dp_2 (\bar{p}_1^2 + \bar{p}_2^2 - p_1^2 - p_2^2)^{-1} \exp[i\alpha_1 (p_1 - \bar{p}_1)^2 + i\alpha_2 (p_2 - \bar{p}_2)^2] \\ & \approx [(2\bar{p}_1)^{-2} + (2\bar{p}_2)^{-2}] \int dp_1 \int dp_2 \exp[i\alpha_1 (p_1 - \bar{p}_1)^2 + i\alpha_2 (p_2 - \bar{p}_2)^2] . \end{aligned} \quad (III.9)$$

Applying the relation in Equation (III.9), generalized in the obvious fashion to N dimensions, to the momentum integrations in Equation (III.1b) thus gives

$$\begin{aligned} E_2 &= (4D)^{-1} \int d\tilde{x} \bar{V}_1(\tilde{x})^2 [\epsilon_1 - v_1(x_1)]^{-\frac{1}{2}} [\epsilon_2 - v_2(x_2)]^{-\frac{1}{2}} \dots \\ & \quad [\epsilon_N - v_N(x_N)]^{-\frac{1}{2}} \{ [\epsilon_1 - v_1(x_1)]^{-1} + [\epsilon_2 - v_2(x_2)]^{-1} + \dots \\ & \quad + [\epsilon_N - v_N(x_N)]^{-1} \} . \end{aligned} \quad (III.10)$$

Just as for the one dimensional case in Section IIC, however, integrals involving the factor $[\epsilon_i - v_i(x_i)]^{-\frac{3}{2}}$ in the integrand are to be replaced using the following relation

$$\int dx_i [\epsilon_i - v_i(x_i)]^{-\frac{3}{2}} = -2 \frac{\partial}{\partial \epsilon_i} \int dx_i [\epsilon_i - v_i(x_i)]^{-\frac{1}{2}} ;$$

using this transcription the final expression for the second order perturbation energy is the following generalization of the one-dimensional result:

$$E_2 = -(2D)^{-1} \left[\frac{\partial}{\partial \epsilon_1} + \frac{\partial}{\partial \epsilon_2} + \dots + \frac{\partial}{\partial \epsilon_N} \right] \int dx \bar{V}_1(x)^2 \times [\epsilon_1 - v_1(x_1)]^{-\frac{1}{2}} [\epsilon_2 - v_2(x_2)]^{-\frac{1}{2}} \dots [\epsilon_N - v_N(x_N)]^{-\frac{1}{2}} , \quad (\text{III.11})$$

D being the normalization constant in Equation (III.6).

Equations (III.5), (III.6), and (III.11) are the desired expressions for the classical limit of the first and second order perturbation energies and are the primary result of this paper.

In concluding this section it is illustrative to note the limiting form taken by these expressions in the special case that $V_1(x)$ is separable,

$$V_1(x) = \sum_{i=1}^N v_i^{(1)}(x_i) . \quad (\text{III.12})$$

In such a case the perturbation energy should simply be the sum of individual contributions from each degree of freedom:

$$E_1 = \sum_{i=1}^N \epsilon_i^{(1)} \quad (\text{III.13a})$$

$$E_2 = \sum_{i=1}^N \epsilon_i^{(2)} . \quad (\text{III.13b})$$

It is easy to show that Equation (III.13a) does result from Equation (III.5) when the perturbation is of the form in Equation (III.12), but the second order perturbation energy has the following term in addition to the sum of individual terms in Equation (III.13b):

$$\sum_{i,j=1}^N \langle \frac{1}{v_i} \rangle^{(1)2} > n_j''(\epsilon_j)/n_j'(\epsilon_j) \quad , \quad (III.14)$$

$i \neq j$

where

$$\langle \frac{1}{v_i} \rangle^{(1)2} > = \int dx_i [v_i^{(1)}(x_i) - \epsilon_i^{(1)}]^2 [\epsilon_i - v_i(x_i)]^{-\frac{1}{2}} \\ \div \int dx_i [\epsilon_i - v_i(x_i)]^{-\frac{1}{2}} \quad ,$$

and $n_j(\epsilon_j)$ is the zeroth order quantum number for the j th degree of freedom; i.e., the desired relation in Equation (III.13b) is true only if the expression in Equation (III.14) is zero. If the unperturbed potentials are harmonic, then $n_j''(\epsilon_j) = 0$ and the term in Equation (III.14) is indeed zero. In general, however, this will not be true, although the additional term in Equation (III.14) is expected to be small compared to those in Equation (III.13b). The fact that it is identically zero for harmonic systems is another example of the special role of the harmonic potential in semiclassical theory.

IV. EXAMPLE: THE GROUND STATE HELIUM ATOM

An interesting application of the formulas developed in the previous section is to the ground state of the two electron atom, taking the interelectronic repulsion as the perturbation. This problem received considerable attention in the days of the "old quantum theory"¹⁵, and indeed the inability of the theory to deal effectively with it was then

considered an omen of its eventual downfall.

Scaling length by the nuclear charge Z gives the usual Z^{-1} expansion for the energy

$$E = Z^2(E_0 + Z^{-1}E_1 + Z^{-2}E_2 + \dots) \quad , \quad (IV.1)$$

and by introducing the known angular functions (i.e., spherical harmonics) one can reduce the problem to one involving only internal coordinates¹⁶. Equations (III.4), (III.5), and (III.11) then give

$$E_0 = \epsilon_1 + \epsilon_2 \quad (IV.2)$$

$$E_1 = \frac{1}{2\pi^2} \int dr_1 \int dr_2 \, d\gamma \sin\gamma [k_1(r_1)k_2(r_2)]^{-1} r_{12}^{-1} \quad (IV.3)$$

$$E_2 = \frac{1}{2\pi^2} \left(-\frac{1}{2}\right) \left(\frac{\partial}{\partial \epsilon_1} + \frac{\partial}{\partial \epsilon_2}\right) \int dr_1 \int dr_2 \, d\gamma \sin\gamma [k_1(r_1)k_2(r_2)]^{-1} \times (E_1 - r_{12}^{-1})^2 \quad (IV.4)$$

where

$$k_1(r) = \left(2\epsilon_1 + \frac{2}{r} - \frac{1}{4r^2}\right)^{1/2} \quad (IV.5)$$

$$r_{12}^2 = (r_1^2 + r_2^2 - 2r_1r_2 \cos\gamma)^{1/2} \quad (IV.6)$$

$$\epsilon_1 = \epsilon_2 = -\frac{1}{2} \quad . \quad (IV.7)$$

The $(4r^2)^{-1}$ term in $k(r)$ arises from the usual semiclassical replacement of $\ell(\ell+1)$ by $(\ell + \frac{1}{2})^2$ in the centrifugal potential.

One thus obtains

$$E_0 = -1 \quad , \quad (IV.8)$$

and direct evaluation of the integral in Equation (IV.3) gives

$$E_1 = 1 - 2\sqrt{3}/\pi^2 \approx 0.649 \quad ;$$

the exact quantum mechanical result is the same for E_0 , and for E_1 it is

$$E_1^{\text{exact}} = 0.625 \quad .$$

For the second order energy some of the integrations and differentiations must be carried out numerically, and one obtains

$$E_2 = - 0.181 \quad ,$$

compared to the exact quantum mechanical value¹⁶

$$E_2^{\text{exact}} = - 0.158.$$

It is seen, therefore, that the semiclassical expressions give quite reasonable approximations to the exact quantum perturbation energies even though the zeroth order potential, $-\frac{1}{r} + \frac{1}{8r^2}$, is far from pure harmonic.

In conclusion it is expected that the semiclassical perturbation formulas [Equations (III.5), (III.6), (III.11)] should be a useful approximation for the eigenvalues of non-separable systems. In particular, they should apply quite well to the description of vibrational states of polyatomic molecules for which the coupling between normal modes is not so strong as to invalidate perturbation theory.

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