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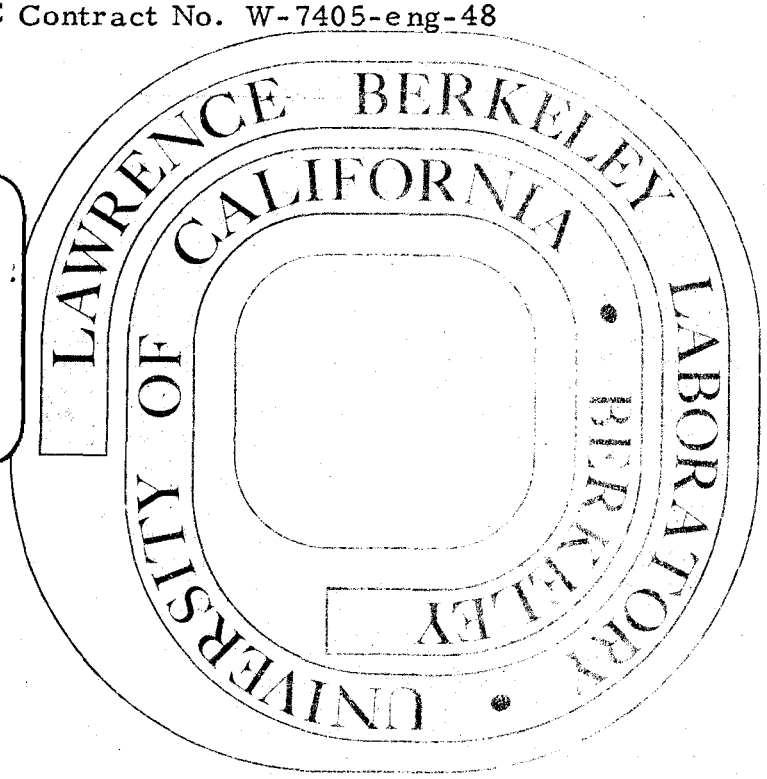

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Classical Limit of Fredholm Theory for Elastic and Inelastic Scattering; Inability of Phase Space Integrals to Describe Inelastic Transitions

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Abstract

Using a classical phase space integral to approximate certain quantum mechanical operations, the classical limit of the Fredholm determinant for a general multichannel scattering system is derived. This statistical form of the classical limit of scattering is found to give exactly the same "classical S-matrix" for the case of potential scattering as does a dynamical treatment of the classical limit. For inelastic scattering, however, the classical S-matrix which results from this Fredholm determinant is only an approximation to that obtained by exact classical dynamics. Reasons for this failure of the statistical version of the classical limit for inelastic scattering are discussed.

I. INTRODUCTION

In two recent papers[1,2] we have dealt with the classical-limit eigenvalue relation for general non-separable dynamical systems. A particularly interesting feature of this study of the bound-state problem is the correspondence between a dynamical form of the quantum condition and a statistical form. The dynamical version involves an action integral along a particular classical trajectory (the periodic trajectory of the system corresponding to a given energy E), whereas the statistical version is expressed in terms of a phase space integral (the volume of phase space with energy less than or equal to the given value E). The practical importance of this correspondence between statistical and dynamical approaches lies in the fact that statistical methods are generally much easier to apply than dynamics.

Analogous to these treatments of bound-state problems we explore in this present paper the relation between dynamical and statistical approaches to the classical limit of scattering for a general non-separable system. Thus it has previously been shown[3] how one can use exact classical trajectories for a general collision system to construct the classical-limit of the quantum mechanical S-matrix (the "classical S-matrix") for the scattering processes. Corresponding to this dynamical prescription for obtaining the classical S-matrix, therefore, we wish to find the statistical procedure (i.e., one based on phase space integrals) which is related to it.

In order to use a formalism developed for bound-state problems, one can always convert a scattering problem into a bound-state one by some variation of "box normalization".[4] The statistical version of the classical limit of scattering can then be obtained by invoking the statistical eigenvalue relation established previously.[2] As a particularly simple example of how scattering is related to the box-normalized eigenvalue problem, consider s-wave potential scattering; the WKB (i.e., classical limit) phase shift can be written as

$$\eta(E) = \int_{r_o}^{R} dr\, k(r) - \int_{0}^{R} dr\, k, \tag{1}$$

where $k(r) = \{2\mu[E-V(r)]/\hbar^2\}^{\frac{1}{2}}$, $k = (2\mu E/\hbar^2)^{\frac{1}{2}}$, $V(r)$ is the scattering potential, E the collision energy, μ the reduced mass, r_o the classical turning point (i.e., $V(r_o) = E$), and R is some indefinitely large value. Eq.(1) may be interpreted in terms of classical-limit eigenvalues: Thus $n(E)$,

$$[n(E) + \tfrac{1}{2}]\pi \equiv \int_{r_o}^{R} dr\, k(r), \tag{2}$$

is the classical-limit quantum number function [the inverse function of the eigenvalue function $E(n)$] for the "potential well" formed by the actual potential $V(r)$ with an impenetrable barrier imposed at $r=R$; Eq.(2) is the well-known Bohr-Sommerfeld quantum condition for this box-normalized potential. Similarly, $n_o(E)$, the quantum number function for the potential well with $V(r)$ replaced by 0, is defined by the relation in Eq.(2) with $k(r)$ replaced by k. Eq.(1) for the phase shift is thus written in terms of these quantum number functions as

$$\eta(E) = \pi[n(E) - n_o(E)]. \qquad (3)$$

Scattering results are obtained, therefore, in terms of the eigenvalues of the box-normalized system and those of its unperturbed ($V \equiv 0$) counterpart.

For more general collision systems (i.e., ones with internal degrees of freedom) it is also possible to extract the S-matrix from a consideration of the box-normalized eigenvalue problem; the theoretical machinery for doing this is Fredholm theory.[5] [Although present day discussions of Fredholm theory do not resemble this box normalization approach, it originated from such considerations.[6]] Rather than follow the box normalization procedure directly, therefore, we develop the classical phase space approximation for the Fredholm determinant and then appeal to the general results of Fredholm theory to construct the S-matrix. Section II discusses the classical limit of Fredholm theory as it applies to potential scattering, and Section III carries this out for the more general case of inelastic scattering.

This statistical version of the classical limit of Fredholm theory is seem to reproduce the usual classical S-matrix for the case of potential scattering, but it is unfortunately not able to provide the correct description of inelastic scattering. Reasons for this failure are discussed in Section IV.

II. POTENTIAL SCATTERING

For a general discussion of Fredholm theory (as it applies to scattering) the reader is referred to the text by Newton[5]; a clear summary of the basic results is also contained in the

recent work by Reinhardt and co-workers[7] who have shown that the Fredholm approach can also be a useful tool for quantum mechanical computations. In what follows we shall simply extract the results of the general theory which are required for our purposes.

The S-matrix for potential scattering (a one-dimensional matrix in this case) is given in terms of the Fredholm determinant $\Delta(k)$ by

$$S = \Delta(-k)/\Delta(k), \tag{4}$$

where $k = (2\mu E/\hbar^2)^{\frac{1}{2}}$, E being the collision energy; since

$$\Delta(-k) = \Delta(k)^*, \tag{5}$$

one sees that S is a complex number of unit modulus. The Fredholm determinant is in turn given by formal expression

$$\Delta(k) = \det[(E-H)(E-H_o)^{-1}], \tag{6}$$

where $H = H_o+V$ is the Hamiltonian operator for the system, and V is the scattering interaction. By the determinant of an operator A one means the determinant of its matrix representation in some complete set of states:

$$\det[A] = \det|\langle i|A|j\rangle|. \tag{7}$$

To evaluate the determinant of an operator, it is convenient to employ the identity

$$\det[A] = \exp[\mathrm{tr}(\ell nA)], \tag{8}$$

where tr(ℓnA) means the trace of the operator ℓn A; i.e.,

$$\mathrm{tr}(\ell nA) = \sum_i \langle i|\ell nA|i\rangle, \tag{9}$$

where the sum is over some complete set of states. Combining Eqs.(6) and (8), one has

$$\ell n\, \Delta(k) = tr\{\ell n[(E-H)(E-H_o)^{-1}]\}. \tag{10}$$

All of the above equations of this Section are exact quantum mechanical relations; the statistical version of the classical limit approximation for the Fredholm determinant is obtained by using a phase space integral to evaluate the trace in Eq.(10). Thus if B_{op} is some operator which is expressed in terms of the coordinate and momentum operators r_{op} and p_{op} as $B(r_{op},p_{op})$, then the phase space approximation for its trace is

$$tr(B_{op}) \simeq h^{-1}\int dr \int dp\; B(r,p), \tag{11}$$

where $B(r,p)$ is the same function of the classical variables r and p that B_{op} is of r_{op} and p_{op}; $h = 2\pi\hbar$ is Planck's constant. Since all the operators of interest for our purposes are Hamiltonians, there is no ambiguity about the appropriate correspondence with the classical functions.

With the phase space approximation of Eq.(11), Eq.(10) becomes

$$\ell n\, \Delta(k) = h^{-1}\int_0^\infty dr \int_{-\infty}^{\infty} dp\; \{\ell n[E-H(p,r)] - \ell n[E-H_o(p,r)]\}, \tag{12}$$

and the classical Hamiltonian functions are

$$H(p,r) = p^2/2\mu + V(r) \tag{13a}$$

$$H_o(p,r) = p^2/2\mu\ ; \tag{13b}$$

the domain of integration is, as indicated, all of phase space. The integral over momentum can be carried out by elementary

methods, and one obtains

$$\int_{-\infty}^{\infty} dp \; \ell n(E-H) - \ell n(E-H_o) = 2\pi i\hbar[k - k(r)], \tag{14}$$

where $k = (2\mu E/\hbar^2)^{\frac{1}{2}}$ and $k(r) = \{2\mu[E-V(r)]/\hbar^2\}^{\frac{1}{2}}$; if $E - V(r) < 0$, then $k(r) = i|k(r)|$. Eq.(12) thus becomes

$$\ell n\, \Delta(k) = -i\int_0^{\infty} dr\; k(r) - k, \tag{15}$$

or

$$\Delta(k) = \exp(\theta - i\eta) \tag{16}$$

where

$$\theta = \int_0^{r_o} dr\; |k(r)|$$

$$\eta = \lim_{R\to\infty} \int_{r_o}^{R} dr\; k(r) - \int_0^{R} dr\; k,$$

r_o being the classical turning point; i.e., θ is real, and η is the WKB phase shift.

With the Fredholm determinant given by Eq.(16), Eq.(14) then gives the S-matrix as

$$S = \exp(2i\eta^{WKB}). \tag{17}$$

This is the usual result which is also obtained by a strictly dynamical approach.

Before concluding this discussion of potential scattering, it is useful to note a few details of the replacement of k by -k in applying Eq.(4) to the phase integral in Eqs.(15) and (16). In classically allowed regions ($r>r_o$) one has

$$k(r) \to -k(r)$$

when k is replaced by -k; in classically forbidden regions ($r<r_o$), however, one has

$$-ik(r) \equiv |k(r)| \to |k(r)| \equiv -ik(r).$$

With regard to $k \to -k$, therefore, the real (imaginary) part of k(r) is considered to be an odd (even) function of k. For this reason the contribution to the coordinate integral in Eq.(15) from classically forbidden regions cancels out in the ratio in Eq.(4).

III. INELASTIC SCATTERING

Now suppose there are internal degrees of freedom in addition to the scattering (translational) degree of freedom. The internal degrees of freedom are quantized in the initial and final asymptotic regions, and the S-matrix is the matrix of transition probability amplitudes from initial internal states (or channels) to final internal states (or channels); the dimension of the S-matrix is the number of energetically accessible internal states (the number of open channels).

The Fredholm determinant is still given formally by Eq.(6), but one must now consider it to be an independent function (sign-wise at least) of all the channel momenta; i.e.,

$$\Delta(\underset{\sim}{k}) \equiv \Delta(k_1,k_2,\ldots) = \exp\left\{\mathrm{tr}[\ell n(E-H)(E-H_o)^{-1}]\right\}, \qquad (18)$$

where the asymptotic momentum (in units of $\hbar$) for channel i is

$$k_i = [2\mu(E-\varepsilon_i)/\hbar^2]^{\frac{1}{2}},$$

E being the (fixed) total energy and ε_i the internal energy of internal state i. The channel momenta $\{k_i\}$ are all related to one another through their definition in Eq.(19), and the only sense in which they are considered independent in Eq.(18) is that one needs to change the sign of some of them and not to change the sign of others.

The S-matrix is given in terms of the Fredholm determinant of Eq.(18) by

$$S_{i,i} = \Delta_i(\underset{\sim}{k})/\Delta(\underset{\sim}{k}) \tag{20a}$$

$$S_{i,j} = [S_{i,i}S_{j,j} - \Delta_{i,j}(\underset{\sim}{k})/\Delta(\underset{\sim}{k})]^{\frac{1}{2}}, \tag{20b}$$

where $i \neq j$, and

$$\Delta_i(\underset{\sim}{k}) = \Delta(k_1, k_2, \ldots, -k_i, \ldots) \tag{21a}$$

$$\Delta_{i,j}(\underset{\sim}{k}) = \Delta(k_1, k_2, \ldots -k_i, \ldots, -k_j, \ldots). \tag{21b}$$

As in the preceeding Section we use a classical phase space integral to calculate $\Delta(\underset{\sim}{k})$ and then construct the S-matrix by using Eqs.(20) and (21).

For notational convenience we assume there to be just one internal degree of freedom; the treatment is identical for any number of internal degrees of freedom. With the phase space integral approximation to the trace in Eq.(18), one has

$$\ell n\, \Delta(\underset{\sim}{k}) = h^{-2} \int_0^{2\pi} dq \int_0^{\infty} dn\, \hbar \int_0^{\infty} dr \int_{-\infty}^{\infty} dp\, [\ell n(E-H) - \ell n(E-H_o)], \tag{22}$$

where the normalization factor is h^{-2} since there are two degrees of freedom. Since an integral over all phase space is

```
  312 CONTINUE
    2 FORMAT (21X, *INTENSITY AS A FUNCTION OF WAVELENGTH WITH FILM THIC
     XKNESS AS A PARAMETER ON A *, A10, * ELECTRODE*,////)
    5 FORMAT (10X, *WAVELENGTH*, 4X, 9I11,///)
    6 FORMAT (10X, *PHASE CHANGE*,/, 10X, *METAL*, 9X, 9F11.2,/)
    7 FORMAT (10X, *FILM THICKNESS*,45X, *INTENSITY*,//)
   11 FORMAT (13X, I4, 7X, 9F11.4)
   13 FORMAT (10X, *TOTAL*, 9X, 9F11.2, ///)
      STOP
      END
C
      FUNCTION RIC(WAVLTH)
C     THIS FUNCTION GIVES REFRACTIVE INDEX OF THE SOLUTION AT A SPECIFIED
C       WAVELENGTH USING A POLYNOMIAL OF 6 TERMS.
C
      COMMON /RICOM/ B,NO
      DIMENSION B(20,8)
      REAL A
      A=WAVLTH
      C=0.0
      A=A/4000
      DO 601 K=1,NO
      C=C+(B(K)*(A**(K-1)))
  601 CONTINUE
      RIC=C
      RETURN
      END
      FUNCTION REFRXC (SCALE, LAMBDA)
C     THIS FUNCTION GIVES REFRACTIVE INDEX OF THE SOLUTION FROM THE SCALE
C       READINGS OF THE REFRACTOMETER.
C       FOR THE NEW PRISM (749-1)
C
      REAL NPRIS, PC(8), LAMB
      LAMB=LAMBDA/4000
      APRIS=0.0174533*68.0
      PC(1)=2.1098525761
      PC(2)=-1.8465725697
      PC(3)=2.4203415165
      PC(4)= -1.6347815115
      PC(5)=0.5602598970
      PC(6)=-0.0773841103
      NPRIS=0.
      DO 701 J=1,6
      NPRIS=NPRIS+PC(J)*(LAMB**(J-1))
  701 CONTINUE
      AMEAS=24.0-(2.0*SCALE)/3.0
      AMEAS=AMEAS*0.0174533
      ACALC=ASIN(SIN(AMEAS)/NPRIS)
      APRIM=APRIS-ACALC
      REFRXC=SIN(APRIM)*NPRIS
      RETURN
      END
```

MAXIMA AND MINIMA OF INTENSITY AS A FUNCTION OF WAVELENGTH ON A PLATINUM ELECTRODE

S POLARIZATION

WAVELENGTH		FILM THICKNESS	INTENSITY
380 NM			
	MAXIMA AT	30 NM	.8563
		217	
		405	
		592	
		779	
		966	
		1154	
		1341	
	MINIMA AT	120 NM	.1699
		307	
		495	
		682	
		869	
		1056	
		1244	
		1431	
385 NM			
	MAXIMA AT	30 NM	.8567
		220	
		409	
		599	
		789	
		979	
		1168	
		1358	
	MINIMA AT	120 NM	.1720
		310	
		499	
		689	
		879	
		1069	
		1258	
		1448	
390 NM			
	MAXIMA AT	30 NM	.8571
		222	
		414	
		607	
		799	
		991	
		1183	
		1375	
	MINIMA AT	120 NM	.1774
		312	
		504	
		697	
		889	
		1081	
		1273	
		1465	
395 NM			
	MAXIMA AT	30 NM	.8574
		225	

		252					929	
		474					1185	
		695					1441	
		917					1698	
		1139					1954	
		1361			525 NM			
		1582				MAXIMA AT	30 NM	.8617
	MINIMA AT	140 NM	.1852				299	
		362					547	
		584					806	
		805					1065	
		1027					1324	
		1249					1582	
		1471					1841	
		1692				MINIMA AT	160 NM	.1905
455 NM							419	
	MAXIMA AT	30 NM	.8606				677	
		254					936	
		478					1195	
		703					1454	
		927					1712	
		1151					1971	
		1375			530 NM			
		1600				MAXIMA AT	30 NM	.8617
	MINIMA AT	140 NM	.1818				291	
		364					552	
		588					814	
		813					1075	
		1037					1336	
		1261					1597	
		1485					1858	
		1710				MINIMA AT	160 NM	.1861
460 NM							421	
	MAXIMA AT	30 NM	.8608				682	
		257					944	
		483					1205	
		710					1466	
		937					1727	
		1163					1988	
		1390			535 NM			
		1617				MAXIMA AT	30 NM	.8616
	MINIMA AT	140 NM	.1810				294	
		367					557	
		593					821	
		820					1085	
		1047					1348	
		1273					1612	
		1500					1876	
		1727				MINIMA AT	160 NM	.1836
465 NM							424	
	MAXIMA AT	30 NM	.8609				687	
		259					951	
		488					1215	
		717					1478	
		947					1742	
		1176					2006	
		1405			540 NM			
		1634				MAXIMA AT	30 NM	.8616
	MINIMA AT	140 NM	.1826				296	
		369					562	
		598					828	
		827					1094	

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independent of the particular canonical variables one uses to carry out the integral, in Eq.(22) we have chosen the usual translational coordinate and momentum (r,p) for the translational degree of freedom, but have used the action-angle variables (hn,q) for the internal degree of freedom. The factor $\hbar$ has been included explicitly in the definition of the action variable, so that the quantity n is dimensionless and is the classical equivalent of the quantum number of the internal degree of freedom. In terms of these canonical variables the Hamiltonian functions are

$$H = p^2/2\mu + \varepsilon(n) + V(r,q,n)$$

$$H_o = p^2/2\mu + \varepsilon(n),$$

where $\varepsilon(n)$ is the eigenvalue function for the isolated internal degree of freedom, and V is the scattering interaction.

Just as in the case of potential scattering, the integral over the translational momentum can be carried out by elementary means, and upon doing this Eq.(22) becomes

$$\ell n\, \Delta(\underset{\sim}{k}) = -i \int_0^\infty dn\, (2\pi)^{-1} \int_0^{2\pi} dq \int_0^\infty dr\, k(r,q,n) - k(n), \quad (23)$$

where the momenta are defined as

$$k(n) = \{2\mu[E - \varepsilon(n)]/\hbar^2\}^{\frac{1}{2}}$$

$$k(r,q,n) = \{2\mu[E - \varepsilon(n) - V(r,q,n)]/\hbar^2\}^{\frac{1}{2}}.$$

Classically, of course, n is a continuous variable, whereas quantum mechanically it is quantized. To make the appropriate identification with the discrete internal states, therefore, we

make the replacement

$$\int_0^\infty dn \to \sum_n , \tag{24}$$

where the sum is over all integer values of n. Eq.(23) thus becomes

$$\ell n\, \Delta(\underset{\sim}{k}) = -i \sum_n (2\pi)^{-1} \int_0^{2\pi} dq \int_0^\infty dr\, k(r,q,n) - k(n). \tag{25}$$

One may further simply matters by noting that, just as in the previous section, the energetically forbidden regions of phase space in the integrals in Eq.(25) will cancel when one constructs the ratios of Fredholm determinants in Eq.(20). This follows from the discussion at the end of Section II. This means that Eq.(25) is of the form

$$\ell n\, \Delta(\underset{\sim}{k}) = E(\underset{\sim}{k}) - i \sum_n \eta(k_n), \tag{26}$$

where $E(\underset{\sim}{k})$ is real and an even function of all the channel momenta, and

$$\eta(k_n) = (2\pi)^{-1} \int_0^{2\pi} dq \lim_{R\to\infty} \left[\int_{r_o}^R dr\, k(r,q,n) - \int_0^R dr\, k(n) \right]; \tag{27}$$

$\eta(k_n)$ is an odd function of k_n and is seen to be the WKB phase shift for the frozen internal degree of freedom (i.e., fixed n and q), which is then averaged over the angle variable q.

From Eq.(26) for the Fredholm determinant, it is easy to see that the determinants in Eq.(21) are given by

$$\Delta_i(\underset{\sim}{k}) = \Delta(k) \exp[2i\eta(k_i)] \tag{28a}$$

$$\Delta_{i,j}(\underset{\sim}{k}) = \Delta(\underset{\sim}{k}) \exp[2i\eta(k_i) + 2i\eta(k_j)], \tag{28b}$$

so that the S-matrix elements of Eq.(20) are

$$S_{i,i} = \exp[2i\eta(k_i)] \tag{29a}$$

$$S_{i,j} = 0, \quad i \neq j. \tag{29b}$$

There are no inelastic transitions in this approach, therefore, and the elastic scattering is only an approximation to the exact classical dynamics. Eq.(29a) is, in fact, a classical-limit version of the sudden approximation for the elastic scattering in channel i.

IV. DISCUSSION

The short-comings of this statistical version of the classical-limit of inelastic scattering are probably most directly related to the asymptotic degeneracy that is inherent in a multi-channel scattering system. Thus in establishing the correspondence between statistical and dynamical quantum conditions[2] it was essential that there was only one periodic trajectory of the system for a given energy. If other periodic trajectories existed, they had to be related to some constant of the motion (such as total angular momentum) or a discrete symmetry of the system and explicitly removed; the eigenvalue problem could then be considered separately for each value of the conserved quantity or discrete symmetry, there then being only one periodic trajectory of the system at the given energy for that particular subspace.

For a multi-channel scattering system, however, there are N (N ≡ number of open channels) degenerate quantum states of the system, corresponding to the N different internal states

which can be the initial state. When the system is enclosed in a finite box, these N degenerate states are split--only in the limit of an infinite box does the degeneracy appear. Furthermore, this degeneracy is not related to any constant of motion or discrete symmetry--rather it is associated with constants of the motion of the unperturbed Hamiltonian to and from which the system evolves asymptotically.

Corresponding to this quantum degeneracy, there is thus more than one "periodic" classical trajectory for the system at a given energy. [Periodicity comes about here only artificially by reflection from the walls of the large "box"; the appropriate trajectories are actually the aperiodic scattering trajectories.] Similarly, these several "periodic" trajectories cannot be classified according to any discrete or continuous symmetry of the system; i.e., there is no way to decompose (or factor) the dynamical problem so that there is only one "periodic" trajectory per energy per subspace. As noted above, this difficulty is directly related to the asymptotic degeneracy that is an intrinsic feature of scattering systems with internal degrees of freedom; for in a bound state situation degeneracies can always be related to some symmetry of the system and thus explicitly removed (i.e., there are no accidental degeneracies).

One might imagine classifying the various "periodic" classical trajectories of the scattering system by the "constants of the motion" which are simply the initial conditions of the individual trajectories. Initial conditions, however, although they are constants of integration of the equations of motion, are not integral constants of the motion in the usual sense

(i.e., functions of the coordinates and momenta--but not involving the time explicitly--which remain constant in time). Such an approach, too, introduces dynamics *per se* and clearly foils the attempt to develop a theory based solely on phase space integrals.

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