Calculation of semiclassical eigenvalues with one arbitrary trajectory

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A method is described for determining semiclassical eigenvalues for systems with many degrees of freedom that requires the calculation of only one trajectory per eigenvalue. Furthermore, this trajectory is "arbitrary", i.e., one must not carry out an iterative root-search procedure to find it. The method is a derivative of earlier approaches developed by Sorbie and Handy and by De Leon and Heller. It is also shown that within the local linearization approximation used by De Leon and Heller, the Sorbie–Handy method is exact (semiclassically).

I. INTRODUCTION

There has been considerable activity in recent years in the development of methods for computing semiclassical (EBK) eigenvalues for systems of more than 1 degree of freedom.\(^1\) In addition to its inherent theoretical interest, this has gained practical importance because of the enormous experimental progress in the spectroscopy of highly vibrationally excited states of polyatomic molecules.

Most of the methods that have been developed for computing semiclassical eigenvalues, however, suffer the serious shortcomings of being impractical for systems with more than 2 or 3 degrees of freedom. The method of Sorbie and Handy\(^6\) is a possible exception to this, but it involves an approximation in addition to the semiclassical approximation itself. De Leon and Heller\(^7\) have recently suggested another approach which also has potential for being able to treat many degrees of freedom and which claims to avoid the approximation inherent in the Sorbie–Handy method; this method, however, involves another approximation (a local linearization of the eigenvalue function).

The purpose of this paper is to describe a hybrid semiclassical quantization method which combines features of both the Sorbie–Handy and the De Leon–Heller schemes. The important practical feature of the approach is that it requires only one classical trajectory per eigenvalue, and the trajectory is essentially arbitrary, i.e., there is no iteration or root-search involved. The approach thus has considerable potential for application to systems with many degrees of freedom. Finally, it also shown that within the linearization approximation used by De Leon and Heller, the Sorbie–Handy quantization method is actually exact.

II. SEMICLASSICAL EIGENVALUES WITH ONE TRAJECTORY

\(\langle n|q\rangle\) is the classical Hamiltonian of the system in terms of some zeroth order action-angle variables \(\{q_i,\phi_i\}, \ i = 1,\ldots, F\). The goal is to find the "good" action-angle variables \(\{N_i,Q_i\}=\{N_i,Q_i\}, \ i = 1,\ldots, F\), in terms of which the Hamiltonian is a function only of the action variables \(N\). Eigenvalues are obtained by then setting the good action variables to integer values. (Units such that \(\hbar = 1\) are assumed, and the "1/2" is included in the definition of the zeroth order action variables \(n\). The notation follows that of Ref. 3 most closely.)

The relation between the zeroth order action-angle variables \(\{n,q\}\) and the good ones \(\{N,Q\}\) is specified by a generating function\(^8\) \(F(q,N)\) which can be represented as\(^9\)

\[
F(q,N) = q - N + \sum_k B_k(N)e^{i\omega_k},
\]

where \(k = (k_1,\ldots, k_F)\) are all integer values. The equations which define the transformation \(\{n,q\} \rightarrow \{N,Q\}\) are

\[
n = \frac{\partial F(q,N)}{\partial q} = N + \sum_k B_k(N)e^{i\omega_k},
\]

\[
Q = \frac{\partial F(q,N)}{\partial N} = q + \sum_k \frac{\partial B_k(N)}{\partial N}e^{i\omega_k}.
\]

Along a classical trajectory \(N\) is constant, so that one has the following relations between the variables along a trajectory:

\[
n(t) = N + \sum_k B_k(N)e^{i\omega_k(t)},
\]

\[
Q(t) = q(t) + \sum_k \frac{\partial B_k(N)}{\partial N}e^{i\omega_k(t)},
\]

and furthermore,

\[
\omega(N) = \frac{\partial H(N)}{\partial N}.
\]

The key idea, due to Sorbie and Handy,\(^6\) is to begin a trajectory with some initial values of the zeroth order variables

\[
n(0) = n_0,
\]

\[
q(0) = q_0,
\]

and to run it (i.e., solve Hamilton’s equations numerically) until the time \(T\) at which

\[
q(T) = q_0 + 2\pi M,
\]

where \(M = (M_i), i = 1,\ldots, F\) is some set of (positive) integers. It is easy to see that Eq. (2.6) with Eq. (2.3a), also guarantees that \(n(T) = n_0\). Eq. (2.6) is thus the condition that the trajectory has closed on itself. A way in practice to determine the time \(T\) is simply to monitor the function \(F(t)\):

\[
F(t) = \sum_{i=1}^F \left| e^{i\phi_i(t)} - e^{i\phi_i(0)} \right| = \sum_{i=1}^F \left| \sin \left( \frac{1}{2} [q_i(t) - q_i(0)] \right) \right|,
\]

\(\)
along the trajectory, and to stop at the the time \( t = T \) for which \( F(T) \) is below some small value. Because the dynamics is quasiperiodic (by assumption—otherwise EBK eigenvalues do not exist) this is guaranteed to occur to within arbitrary accuracy.

With Eq. (2.6) it is easy to show from Eq. (2.3b) that

\[
Q(T) = Q(0) + 2rM,
\]

and comparing this to Eq. (2.4a) leads to the first important result

\[
\omega(N) = \frac{2\pi}{T} M;
\]

i.e., one can immediately identify the frequencies without approximation.

Next, consider the classical action integral along the trajectory

\[
\phi(n_0, q_0) = \int_0^T dt \dot{q}(t) \cdot \mathbf{n}(t);
\]

using Eq. (2.3a), one has

\[
\phi = \int_0^T dt \dot{q}(t) \left[ N + \sum_k B_k(N) \mathbf{k} e^{i\omega_k t} \right]
= \left[ \dot{q}(T) - \dot{q}(0) \right] \cdot \mathbf{N} + \sum_k B_k(N) \left[ \mathbf{k} e^{i\omega_k T} \right],
\]

and with Eqs. (2.6) and (2.8), this gives the second important result

\[
\phi(n_0, q_0)/T = \omega(N) \cdot \mathbf{N}.
\]

What one needs to be able to determine, though, are the good action variables \( N \equiv N(n_0, q_0) \) that correspond to the initial values \( (n_0, q_0) \) of the zeroth order action-angle variables (so that one can require them to be integers). However this is not easy to do, so the linearization approximation suggested by De Leon and Heller is used. Thus let \( N_{\text{int}} \) be a set of integers that is close to (in general nonintegral) values of \( N \equiv N(n_0, q_0) \); then the semiclassical eigenvalue \( E(N_{\text{int}}) \) is given approximately by linearizing \( H(N) \) about \( N_{\text{int}} \):

\[
E(N_{\text{int}}) \approx H(N_{\text{int}}) \sim H(N) + \frac{\partial H(N)}{\partial N} (N_{\text{int}} - N)
= H(n_0, q_0) + \omega(N) \cdot N_{\text{int}} - \omega(N) \cdot \mathbf{N}.
\]

The last term in the above equation is given by Eq. (2.10), so that the final important result is

\[
E(N_{\text{int}}) = H(n_0, q_0) + \omega(N) \cdot N_{\text{int}} - \phi(n_0, q_0)/T.
\]

Equation (2.11) has the most important feature that one does not need to know the precise values of the action variables \( N \equiv N(n_0, q_0) \); the first term in Eq. (2.11) is simply the energy corresponding to the initial phase point for the trajectory (and which, of course, is conserved along it); the second term is calculable because the frequencies \( \omega(N) \) are given by Eq. (2.8); and the third term, the action integral, is also directly calculable from the trajectory. The only thing one needs to know about the values of the good action variables \( N \equiv N(n_0, q_0) \) is some approximation to them that is good enough so that one can identify the integers \( N_{\text{int}} \) that are close to them. Also, one notes that Eq. (2.11) requires the calculation of only the one classical trajectory with initial conditions \( (n_0, q_0) \).

To complete the picture, one needs to specify a prescription for identifying the integers \( N_{\text{int}} \). The simplest approach is to choose the initial values for the trajectory to be

\[
n_0 = N_{\text{int}},
q_0 = \text{anything},
\]

and then to assume that the values of the good action variables \( N(n_0, q_0) \) are not so strongly perturbed from the zeroth order values \( n_0 = N_{\text{int}} \) that the linearization approximation is inaccurate. (For most of the calculations of semiclassical eigenvalues reported in the literature to date, the perturbation is sufficiently weak that this would indeed be true.) The linearization approximation will be best if \( N_{\text{int}} \) are the integers closest to the good action variables \( N(n_0, q_0) \), and the procedure suggested here should usually make this true. As De Leon and Heller point out, though, even if this is not the case, the linearization approximation is still applicable, it will simply be less accurate.

Finally, it is interesting to note the relation of the present scheme to the original Sorbie–Handy approach. These authors suggest the following approximation\(^{10} \) for \( N(n_0, q_0) \):

\[
N_i(n_0, q_0) \approx N_i^{\text{S}}(n_0, q_0) \equiv \frac{1}{2\pi M_i} \int_0^T dt \dot{q}_i(t) n_i(t),
\]

and then proceed to iterate on the initial conditions so that

\[
N_i^{\text{S}}(n_0, q_0) = N_{\text{int}};
\]

i.e., if \( q_0 \) is held fixed, one varies \( n_0 \) until Eq. (2.14) is satisfied. Though \( N_i^{\text{S}}(n_0, q_0) \) is only an approximation\(^{10} \) to \( N_i(n_0, q_0) \), Eqs. (2.8) with Eq. (2.13) shows that

\[
\sum_i \omega_i(N) N_i^{\text{S}} = \frac{1}{T} \sum_i \int_0^T dt \dot{q}_i(t) n_i(t),
\]

i.e.,

\[
\omega(N) \cdot N_i^{\text{S}} = \frac{1}{T} \int_0^T dt \dot{q}_i(t) n_i(t) \equiv \phi(n_0, q_0)/T,
\]

and with Eq. (2.10) this shows the important result

\[
\omega(N) \cdot N_i^{\text{S}} = \omega(N) \cdot N;
\]

i.e., even though the approximate Sorbie–Handy action variables \( N_i^{\text{S}}(n_0, q_0) \) are not the exact ones \( N_i(n_0, q_0) \), their dot product with the frequency vector is the same as that of the exact ones. With the additional aspect that one iterates the trajectory until Eq. (2.14) is satisfied, Eq. (2.15) shows that

\[
\omega(N) \cdot N_i = \omega(N) \cdot \mathbf{N} = \mathbf{\phi}(n_0, q_0)/T,
\]

so that the linearized eigenvalue equation [Eq. (2.11)] gives

\[
E(N_{\text{int}}) = H(n_0, q_0),
\]

which is the Sorbie–Handy result. The conclusion, therefore, is that within the linearization approximation suggested by De Leon and Heller, the Sorbie–Handy scheme is exact.

It is also possible to use the Sorbie–Handy approximation to the good actions to make a better choice for \( N_{\text{int}} \) than the simple one suggested in the paragraph containing Eq. (2.12). Thus having chosen some initial conditions \( (n_0, q_0) \), one calculates \( N_i^{\text{S}}(n_0, q_0) \) via Eq. (2.13) and then chooses
II. CONCLUDING REMARKS

To conclude it is useful to summarize the one-trajectory scheme which has been suggested. With initial conditions

\[ n(0) = n_0 = N_{int}, \]
\[ q(0) = q_0 = \text{anything}, \]

one integrates the trajectory until the time \( T \) for which \( F(T) \) [Eq. (2.7)] is less than some prescribed small value. The integers \( M \) are defined by

\[ M_i = \frac{q_i(T) - q_i(0)}{2\pi}. \]

The semiclassical eigenvalue with quantum numbers \( N_{int} \) is then given, within the linearization approximation, by Eq. (2.11). By using Eqs. (2.8), (3.2), and (3.1), and the fact that

\[ q_i(T) - q_i(0) = \int_0^T dt \dot{q}_i(t), \]

Eq. (2.11) can be written in the following more convenient form:

\[ E[N_{int}] = H(n_0, q_0) + \frac{1}{T} \int_0^T dt \dot{q}(t) \cdot [n_0 - n(t)]; \]

or, integrating the last term in the above equation by parts, it can be written in still another equivalent form

\[ E[N_{int}] = H(n_0, q_0) + \frac{1}{T} \int_0^T dt q(t) \cdot \dot{n}(t). \]

Because the approach involves the calculation of only one classical trajectory per eigenvalue, it is clear that it has considerable potential for application to systems of many degrees of freedom. The primary prerequisite for its success would appear to be that coupling between the modes not be so strong that the zeroth order actions \( n_0 \) be grossly different from the good actions \( N \). (Since \( n_0 \) is chosen to be \( N_{int} \), this means that \( N \) will not be too far from \( N_{int} \).) If there is the possibility of resonance effects between modes, therefore, it would be necessary to choose zeroth order action-angle variables to take cognizance of this, e.g., by defining new zeroth order action angle variables that are linear combinations of the original degenerate ones.

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6(a) K. S. Sorbie, Mol. Phys. 32, 1577 (1976); (b) K. S. Sorbie and N. C. Handy, ibid. 32, 1327 (1976); (c) 33, 1319 (1977).
10If one actually had the function \( n(q, N) \), then it is easy to show from Eq. (2.2a) that

\[ \frac{1}{\pi M_i} \int_0^T dt \dot{q}_i(t) \cdot \{ q_{i+1}, \ldots, q_{i+k} \} \]

where all the angle variables other than \( q_i(t) \) are held fixed. In Eq. (2.13), though, \( n_i(t) = n_i \{ q_i(t) \dot{q}_i(t), \ldots, q_F(t) \} \).