Regularized semiclassical radial propagator for the Coulomb potential

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(Received 11 March 1994)

We derive a regularized semiclassical radial propagator for the Coulomb potential, a case for which standard approaches run into well-known difficulties associated with a non-Cartesian radial coordinate and a potential singularity. Following Kleinert [*Path Integrals in Quantum Mechanics, Statistics and Polymer Physics* (World Scientific, Singapore, 1990)], we first perform a quantum-mechanical regularization of the propagator. The semiclassical limit is then obtained by stationary phase approximation of the resulting integrals. The semiclassical propagator so derived has the standard Van Vleck–Gutzwiller form for the radial Coulomb problem with a potential correction (Langer modification) term included. The regularized semiclassical propagator is applied to compute the autocorrelation function for a Gaussian Rydberg wave packet.

PACS number(s): 03.65.Sq, 03.65.Ge, 32.30.−r

I. INTRODUCTION

Recent advances in the semiclassical theory of non-integrable systems [1–3], most notably the Gutzwiller trace formula for the density of states [1], have led to renewed interest in the semiclassical mechanics of few-body Coulomb systems. Single-particle Coulomb problems that have been the focus of semiclassical methods include the anisotropic Kepler problem [4], the Rydberg electron in a magnetic field [5], microwave ionization of Rydberg electrons [6,7], and the excitation of Rydberg wave packets [8]. These efforts have prompted a reexamination of the classical-quantum correspondence for two-electron atoms [9,10], and much has been learned concerning the connection between correlated classical motions (periodic orbits) of the electron pair and the properties of doubly-excited resonant states [11–14].

Most of the aforementioned work has employed time-independent (energy-dependent Green's function) methods. There is however a growing interest in the investigation and application of time-dependent semiclassical methods [15–18], in which the quantum-mechanical propagator is replaced with its semiclassical (Van Vleck–Gutzwiller) approximation [19,20] or generalizations thereof [18]. Heller and co-workers have found that the semiclassical approach yields wave packet autocorrelation functions that are accurate for surprisingly long propagation times, considerably longer than naive wave packet spreading arguments would suggest [15,16]. This long-time accuracy of the semiclassical propagator is possibly an important clue to understanding the remarkable ability of periodic orbit quantization procedures to provide reasonable approximations to the quantum spectrum in several applications [2,3].

The application of time-dependent semiclassical methods of the kind introduced by Tomsovic and Heller [16] to Coulomb systems is a natural development of the above lines of research, especially in light of recent experiments that probe the time evolution of electronic wave packets [21]. There are, however, certain technical difficulties that arise due to the singular nature of the Coulomb potential, and the appearance of non-Cartesian (radial) coordinates [22].

One route to the semiclassical propagator proceeds via stationary phase approximation of the integrals appearing in a discretized version of the path integral form for the quantum propagator [23]. For central field problems, it is natural to use polar coordinates, in which case it is necessary to face the problem of defining path integral representations of the propagator in non-Cartesian coordinates (for a full discussion of this problem, see [22]). A second difficulty arises when attempting to pass to the semiclassical limit of the radial propagator; since the radial coordinate x goes from 0 to ∞, rather than from $-\infty$ to ∞, there are difficulties when trajectories pass through the origin (e.g., for s states in an attractive Coulomb potential). It has long been known that straightforward application of WKB quantization to radial Coulomb motion yields an incorrect (l-dependent) energy spectrum [24], and that the WKB approximation itself breaks down for s states as $x \to 0$ [25]. In the time-independent case, these difficulties are removed using the coordinate transformation $x = e^q$ introduced by Langer [25]. Langer's transformation simultaneously moves the potential singularity at $x = 0$ to $q = -\infty$, and introduces a correction to the potential of the form $\Delta V = \hbar^2/8mx^2$. The WKB approximation is valid in the new coordinate system.

In the present paper we define a *regularized* semiclassical radial propagator for the one-dimensional (1D) Coulomb potential. Our approach exploits the natural mapping of the Coulomb potential onto the Morse oscillator [22,25], and may be viewed as an implementation of the Langer transformation in the time domain. The regularized propagator is then used to compute the auto-

correlation function of a Gaussian Rydberg wave packet.

We note that Suarez-Barnes *et al.* (henceforth SBNNT) have recently tackled the same problem using a rather different approach [26]. We comment on the relation between the two theories in detail below. Mallalieu and Stroud have also used a semiclassical propagator to compute the time evolution of a Rydberg wave packet [27].

II. PATH INTEGRALS

A. Standard theory

The path integral approach to quantum mechanics provides great insight into the concepts and computational procedures of the standard formulation of the theory [22,28,29]. Path integral expressions for transition amplitudes provide moreover a direct route to the semiclassical limit [23,29].

The quantum-mechanical propagator

$$K(\mathbf{x}_b,\mathbf{x}_a,t)\equiv\langle\mathbf{x}_b|\hat{U}(t)|\mathbf{x}_a\rangle=\langle\mathbf{x}_b|e^{-i\hat{H}t/\hbar}|\mathbf{x}_a\rangle \tag{1}$$

can be expressed as a path integral following the standard procedure in which the evolution operator $\hat{U}(t)$ is "time-sliced [22]" into N pieces:

$$\langle\mathbf{x}_b|e^{-i\hat{H}t/\hbar}|\mathbf{x}_a\rangle=\langle\mathbf{x}_b|\left[e^{-i\hat{H}t/N\hbar}\right]^N|\mathbf{x}_a\rangle, \tag{2}$$

and $N-1$ complete sets $\int|\mathbf{x}_i\rangle d\mathbf{x}_i\langle\mathbf{x}_i|$ are inserted over intermediate positions. For Hamiltonians of the form

$$\hat{H}=\frac{\hat{\mathbf{p}}^2}{2m}+V(\hat{\mathbf{x}}),\ \mathbf{x}\in\mathbb{R}^n, \tag{3}$$

complete sets of momentum eigenstates can be inserted and the matrix elements of the short-time (large-N) propagator approximated as

$$\begin{aligned}\langle\mathbf{x}_i|e^{-i\hat{H}t/N\hbar}|\mathbf{x}_{i+1}\rangle&\sim\left(\frac{mN}{2\pi i\hbar t}\right)^{\frac{1}{2}}\exp\left[\frac{iNm(\mathbf{x}_i-\mathbf{x}_{i+1})^2}{2t\hbar}\right]\\&\quad\times\exp\left[\frac{-iV(\mathbf{x}_i)t}{N\hbar}\right].\end{aligned} \tag{4}$$

As $N\to\infty$, the propagator is written as the path integral

$$K(\mathbf{x}_b,\mathbf{x}_a,t)=\int\mathcal{D}[\mathbf{x}(t)]\exp\left\{\frac{i}{\hbar}\int L[\mathbf{x}(\tau)]d\tau\right\}. \tag{5}$$

The symbol $\int\mathcal{D}[\mathbf{x}(t)]$ denotes integration over all continuous paths connecting $\mathbf{x}_a$ to $\mathbf{x}_b$ in time t, where the measure in the space of paths is defined by the limiting process outlined above [28]. A key aspect of the path integral form of the propagator is the appearance of the classical Lagrangian $L=T-V$ in the exponent of the integrand.

Since the path integral expression is equivalent to the Schrödinger equation formulation of quantum mechanics, for most systems it is not possible to compute the path integral exactly, just as it is not possible to find an exact solution to the Schrödinger equation. Nevertheless, the path integral formulation provides a convenient setting for *approximate* computations, particularly in the semiclassical limit $\hbar\to 0$ [23,29,30]. The procedure for passing to the semiclassical limit is well known [23], and involves evaluating the integrals in the discretized version of the path integral [Eq. (2)] by the stationary phase approximation in path space. The stationary paths turn out to be the *classical* trajectories from $\mathbf{x}_a$ to $\mathbf{x}_b$ in time t, and each such trajectory contributes with a weight determined entirely by the classical mechanics of that trajectory:

$$\begin{aligned}&K_{sc}(\mathbf{x}_b,\mathbf{x}_a,t)\\&\quad=(2\pi i\hbar)^{-\frac{n}{2}}\sum_\nu\left|\frac{\partial^2R_\nu}{\partial x_{bi}\partial x_{aj}}\right|^{\frac{1}{2}}\exp\left(\frac{iR_\nu}{\hbar}-\frac{iM_\nu\pi}{2}\right).\end{aligned} \tag{6}$$

$R_\nu(\mathbf{x}_b,\mathbf{x}_a,t)$ is Hamilton's principal function (the stationary value, from among all paths $\mathbf{x}(\tau)$, of the term $\int L[\mathbf{x}(\tau)]d\tau$), n is the number of degrees of freedom, the vertical bars represent the absolute value of an n-by-n determinant, and M_ν is the number of conjugate points along the trajectory (see [1] for details). This sum-over-classical-trajectories form for the semiclassical propagator is known as the Van Vleck–Gutzwiller propagator [1,20].

B. Difficulties with non-Cartesian coordinates

The standard procedure described above for semiclassical evaluation of K runs into difficulty when faced with non-Cartesian coordinates, i.e., when $\mathbf{x}$ is restricted to some domain other than $\mathbb{R}^n$. For example, consider the partial wave expansion of the propagator [22]:

$$\begin{aligned}&K(\mathbf{x}_b,\mathbf{x}_a,t)\\&\quad=\frac{1}{(x_bx_a)^{\frac{n-1}{2}}}\sum_{k,l}S_l^{k*}(\hat{\Omega}_b)S_l^k(\hat{\Omega}_a)K_l(x_b,x_a,t)\ ,\end{aligned} \tag{7}$$

which reduces the n-dimensional propagator K to a set of one-dimensional radial propagators K_l. The difficulties involved in obtaining a path integral representation for the K_l are fully discussed in [22,31]. The key point is that, although K_l can be written in the suggestive form [22]:

$$\begin{aligned}K_l(x_b,x_a,t)&=\int\mathcal{D}[x(t)]\mu_l[x(t)]\\&\quad\times\exp\left\{\frac{i}{\hbar}\int L[x(\tau)]d\tau\right\},\end{aligned} \tag{8}$$

the path-weight $\mu_l[x(t)]$ *cannot* simply be reexpressed as a centrifugal contribution to the Lagrangian in the exponent. It is essential to note that the Lagrangian appearing in the exponent in Eq. (8) is that for the s-wave ($l=0$) radial problem [22]. The presence of the path weight factor $\mu_l[x(t)]$ prohibits a straightforward stationary phase evaluation of the path integral, which is the

essential step in deriving a Van Vleck–Gutzwiller sum-over-classical-trajectories formula for the radial propagator K_l. Previous incorrect efforts to transform the path-weight $\mu_l[x(t)]$ into a centrifugal potential correction term in $L[x(\tau)]$ are discussed in [22,31].

C. Example: One-dimensional Coulomb system

The system to be treated in the present paper is a one-dimensional Coulomb system corresponding to the 3D radial Coulomb problem restricted to the $l = 0$ subspace, with the Hamiltonian (cf. [26]):

$$\hat{H} = -\frac{1}{2}\frac{d^2}{dx^2} - \frac{Z}{x}, \qquad x \geq 0. \tag{9}$$

Atomic units are used throughout. The wave function inner product is $\langle\phi|\psi\rangle \equiv \int_0^\infty dx\, \phi^*(x)\psi(x)$.

By the discussion above, we can see that an attempt to obtain a semiclassical propagator by the standard treatment will encounter difficulties, as x is restricted to the domain $x \geq 0$. Moreover, computation of the Van Vleck–Gutzwiller semiclassical propagator requires classical trajectories to be continued past the collision with the singularity at $x = 0$; correct determination of the conjugate point count for these continued trajectories is not straightforward. In the energy domain, Langer [25] noted long ago that the conditions for applicability of the WKB approximation were violated in the $l = 0$ radial Coulomb problem as $x \to 0$.

To eliminate the difficulties indicated above, we adopt the strategy of regularizing the propagator *before* taking the semiclassical limit in the path integral calculation. The quantum-mechanical regularization of the propagator is due to Kleinert [22], and is closely analogous to standard regularization techniques in classical mechanics. These regularization techniques are briefly reviewed in the following sections.

III. CLASSICAL REGULARIZATION

Classical regularization procedures enable trajectory integration to be continued through gravitational or Coulomb singularities [32–34]. In this section we outline the classical regularization of the one-dimensional Coulomb system introduced above. The classical limit of the Hamiltonian of Eq. (9) is

$$H = \frac{p_x^2}{2} - \frac{Z}{x} \qquad (x \geq 0). \tag{10}$$

The Hamiltonian equations of motion are clearly singular at $x = 0$ due to the presence of the Coulomb potential. To regularize the equations of motion, we first introduce an extended phase space $(x, p_x, t, -E)$ [32], with the Hamiltonian:

$$\mathcal{H} = H - E. \tag{11}$$

If we restrict attention to the invariant subspace $\mathcal{H} = 0$, so that $H = E$, then the dynamics of system Eq. (11) with timelike parameter τ, where $dt/d\tau = 1$, is equivalent to that of the original system.

In the extended phase space setting we now introduce an x-dependent scaling of the time variable by changing the Hamiltonian to

$$\mathcal{H}' = f(x)(H - E). \tag{12}$$

On the subspace $\mathcal{H}' = 0$, the Hamiltonian equations of motion with Hamiltonian $\mathcal{H}'$ are equivalent to the original equations of motion with the time parameter transformed from τ to σ by $d\tau = f(x)d\sigma$. The function $f(x)$ can now be chosen to remove the singularities in the Hamiltonian. For example, in the one-dimensional Coulomb problem, the function $f(x) = x^2$ gives a new Hamiltonian:

$$\mathcal{H}' = x^2(H - E) = \frac{p_x^2 x^2}{2} - Zx - Ex^2. \tag{13}$$

However, the resulting Hamiltonian $\mathcal{H}'$ no longer has the standard form $p_x^2/2 + V(x)$, and the variable x is still restricted to be non-negative. Both issues can be resolved if we next make a point transformation to variables (q, p_q) originally introduced by Langer [25]:

$$x = e^q, \qquad p_x = p_q/e^q, \tag{14}$$

where the variable q can take any value from $-\infty$ to ∞. The Hamiltonian (13) becomes

$$\mathcal{H}' = \frac{p_q^2}{2} - Ze^q - Ee^{2q}. \tag{15}$$

That is, the one-dimensional Coulomb potential is transformed into a Morse potential [35]:

$$\mathcal{V}_E(q) \equiv -Ee^{2q} - Ze^q, \tag{16}$$

parametrized by the physical energy E. Motion in the physical Coulomb potential at energy E is mapped onto the $\epsilon = 0$ "pseudo-energy" level of the Morse potential $\mathcal{V}_E(q)$, so that the particle will approach $q = -\infty$ (corresponding to $x = 0$) asymptotically. The singularity at $x = 0$ has been removed to $q = -\infty$, and the time-scaling ensures that the x origin is reached only in infinite time. [The proposed time scaling $f(x) = x^2$ is, therefore, of little practical use for integration of classical trajectories; the scaling function $f(x) = x$ followed by the change of variables $x \equiv \xi^2$ is used in actual computations [32–34].]

IV. QUANTUM REGULARIZATION

The quantum analogue of the classical regularization discussed above is the so-called Duru-Kleinert mapping of the path integral for one problem onto another [36]. The key aspect of the Duru-Kleinert mapping is a transformation of both space and time coordinates in the path integral. Full details are given by Kleinert [22]; in the present section we apply the space-time transformation

of the previous section to the 1D Coulomb Hamiltonian $\hat{H}$ of Eq. (9).

Consider the propagator:

$$K(x_b,x_a,t)=\langle x_b|e^{-i\hat{H}t/\hbar}|x_a\rangle = \lim_{\eta\to 0+}\int_{-\infty}^{\infty}\frac{dE}{2\pi\hbar}e^{-\frac{iEt}{\hbar}}\left\langle x_b\left|\frac{i\hbar}{E-\hat{H}+i\eta}\right|x_a\right\rangle. \tag{17}$$

The key to quantum regularization is the identity [22]:

$$\frac{1}{E-\hat{H}+i\eta}=g(\hat{x})\left[\frac{1}{g(\hat{x})(E-\hat{H}+i\eta)g(\hat{x})}\right]g(\hat{x}) \equiv -g(\hat{x})\hat{\mathcal{H}}^{-1}g(\hat{x}), \tag{18}$$

where the last line defines a new (regularized and E-dependent) Hamiltonian $\hat{\mathcal{H}}$, analogous to the classical regularized Hamiltonian $\mathcal{H}$. The identity (18) turns the propagator into

$$\begin{aligned}K(x_b,x_a,t) &= \frac{-i}{2\pi}\lim_{\eta\to 0+}\int_{-\infty}^{\infty}dE\,e^{-iEt/\hbar}\langle x_b|g(\hat{x})\hat{\mathcal{H}}^{-1}g(\hat{x})|x_a\rangle \\ &= \frac{-ig(x_b)g(x_a)}{2\pi}\lim_{\eta\to 0+}\int_{-\infty}^{\infty} \times dE\,e^{-iEt/\hbar}\langle x_b|\hat{\mathcal{H}}^{-1}|x_a\rangle,\end{aligned} \tag{19}$$

which can be written as a double integral:

$$K(x_b,x_a,t) = \frac{g(x_b)g(x_a)}{2\pi\hbar}\int_{-\infty}^{\infty}dE\,e^{-iEt/\hbar}\int_0^{\infty}ds\,\mathcal{K}(x_b,x_a,s,E)\ , \tag{20}$$

where the integrand $\mathcal{K}(x_b,x_a,s,E)$ is the scaled-time propagator $\langle x_b|e^{-is\hat{\mathcal{H}}/\hbar}|x_a\rangle$ for the regularized Hamiltonian $\hat{\mathcal{H}}$ (which is E dependent).

At this point, we would like to write the propagator $\mathcal{K}$ as a path integral and then pass to the semiclassical limit. This is not possible, however, because the incorporation of the regularizing function g changes the kinetic energy in $\hat{\mathcal{H}}$ to a nonstandard form (exactly as in the classical regularization). Instead, we make a coordinate transformation $x=h(q)$, with $h'\equiv dh(q)/dq=g(h(q))$, which transforms the Hamiltonian

$$\hat{\mathcal{H}}=g(\hat{x})\left[-\frac{1}{2}\frac{d^2}{dx^2}+V(\hat{x})-E\right]g(\hat{x}) \tag{21}$$

to

$$\hat{\mathcal{H}}'=-\frac{1}{2}\frac{d^2}{dq^2}+g(h(\hat{q}))\{V(h(\hat{q}))-E\}g(h(\hat{q}))+\Delta\mathcal{V}(\hat{q}) \tag{22}$$

with the potential correction term $\Delta\mathcal{V}$ [22]:

$$\Delta\mathcal{V}=-\frac{\hbar^2}{m}\left[\frac{1}{4}\frac{h'''}{h'}-\frac{3}{8}\left(\frac{h''}{h'}\right)^2\right]. \tag{23}$$

Details of the derivation of the potential correction term $\Delta\mathcal{V}$ by explicit transformation of the path integral are given in [22]. The correction term can also be obtained by direct transformation of the Schrödinger equation.

The final result for the transformed propagator is [22]

$$K(x_b,x_a,t)=\frac{[g(x_b)g(x_a)]^{1/2}}{2\pi\hbar}\int_{-\infty}^{\infty}dE\,e^{-iEt/\hbar} \times\int_0^{\infty}ds\,\mathcal{K}'(h^{-1}(x_b),h^{-1}(x_a),s,E), \tag{24}$$

where $\mathcal{K}'$ is a new propagator defined by $\mathcal{K}'(q_b,q_a,s,E)=\langle q_b|e^{-is\hat{\mathcal{H}}'/\hbar}|q_a\rangle$, with $|q\rangle\equiv|x(q)\rangle e^{q/2}$.

For the one-dimensional Coulomb problem, we use the regularizing function $g(\hat{x})=\hat{x}$, in analogy with the classical regularization procedure, and use the Langer transformation $x=h(q)=e^q$. The regularized quantum Hamiltonian is then

$$\hat{\mathcal{H}}'=-\frac{1}{2}\frac{d^2}{dq^2}-Ze^q-Ee^{2q}+\frac{\hbar^2}{8m}, \tag{25}$$

which describes a Morse oscillator with shifted potential $\mathcal{V}_E(q)+\Delta\mathcal{V}(q)$.

V. THE SEMICLASSICAL LIMIT

The quantum propagator $\mathcal{K}'(q_b,q_a,s,E)$ determines the time evolution in a system with a Cartesian-like coordinate q and a well-behaved potential $\mathcal{V}_E(q)+\Delta\mathcal{V}(q)$. To determine the semiclassical limit of the original propagator $K(x_b,x_a,t)$, we therefore replace $\mathcal{K}'(q_b,q_a,s,E)$ by its semiclassical limit, in the standard Van Vleck–Gutzwiller sum-over-classical-trajectories form:

$$K_{sc}(x_b,x_a,t)=\frac{[g(x_b)g(x_a)]^{1/2}}{2\pi\hbar}\int_{-\infty}^{\infty}dE\,e^{-iEt/\hbar} \times\int_0^{\infty}ds\sum_{\substack{q_a\to q_b\\ \text{in time } s}}(2\pi i\hbar)^{-\frac{1}{2}}\left|\frac{\partial^2\mathcal{R}'}{\partial q_b\partial q_a}\right|^{\frac{1}{2}} \times\exp\left(\frac{i\mathcal{R}'}{\hbar}-\frac{i\pi M_1}{2}\right). \tag{26}$$

Expression (26) is difficult to evaluate, since we must determine the q-space trajectories that connect q_a to q_b in scaled time s for *all* values of the physical energy E (which appears in $\hat{\mathcal{H}}'$ as a parameter), and then integrate over s and E. In the spirit of general semiclassical theory [30], we shall do both integrals by stationary phase, and thereby find considerable simplification.

First, we evaluate the s integral using the stationary phase approximation. We must determine trajectories that satisfy $\frac{\partial\mathcal{R}'(q_b,q_a,s,E)}{\partial s}=0$; the quantity $\frac{\partial\mathcal{R}'(q_b,q_a,s,E)}{\partial s}$ is however just the negative of the trajectory pseudo-energy $\epsilon=\hat{\mathcal{H}}'$ [1]. (The physical energy E is considered fixed at this point.) The stationary points s^* are therefore all scaled times taken by trajectories that go from q_a to q_b at $\epsilon=0$. These scaled times depend on E, since the underlying Lagrangian does, so we write them as $s^*(E)$.

Evaluating the contributions to the integral from each

stationary point we have [1]

$$K_{sc}(x_b,x_a,t)=\frac{[g(x_b)g(x_a)]^{1/2}}{2\pi\hbar}\int_{-\infty}^{\infty}dE\,e^{-iEt/\hbar}\times\sum_{\substack{q_a\to q_b\\ \text{at }\epsilon(E)=0}}\left|\frac{\partial^2\mathcal{R}'}{\partial q_b\partial q_a}\right|^{\frac{1}{2}}\left|\frac{\partial^2\mathcal{R}'}{\partial s^2}\right|^{-\frac{1}{2}}\times\exp\left[\frac{i}{\hbar}\mathcal{R}'-\frac{i\pi(M_1+M_2)}{2}\right],\tag{27}$$

where

$$M_2=\begin{cases}1 & \text{if } \partial^2\mathcal{R}'/\partial s^2<0\\ 0 & \text{if } \partial^2\mathcal{R}'/\partial s^2>0\,.\end{cases}\tag{28}$$

$\mathcal{R}'$ and its derivatives are evaluated at $(q_b,q_a,s^*(E),E)$. Next, we do the E integral by stationary phase; the stationarity condition is $\frac{d}{dE}\big(\mathcal{R}'(q_b,q_a,s^*(E),E)\big)-t=0$. This derivative is shown in Appendix A to equal $t^*(E)$, the physical time taken by the trajectory. The stationary points E^* are therefore those values of the physical energy E which make $t^*(E)=t$, i.e., when there is a q trajectory with $\epsilon(E^*)=0$ that takes physical time t to get from q_a to q_b. Evaluating the contribution from each such trajectory, the semiclassical propagator becomes

$$K_{sc}(x_b,x_a,t)=\sqrt{\frac{i}{2\pi\hbar}}[g(x_b)g(x_a)]^{1/2}\times\sum_{\substack{\text{traj. } q_a\to q_b\\ \text{at }\epsilon(E^*)=0\text{ in time }t}}e^{-iE^*t/\hbar}\left|\frac{\partial^2\mathcal{R}'}{\partial q_b\partial q_a}\right|^{\frac{1}{2}}\left|\frac{\partial^2\mathcal{R}'}{\partial s^2}\right|^{-\frac{1}{2}}\left|\frac{dt^*}{dE}\right|^{-1/2}\exp\left[\frac{i}{\hbar}\mathcal{R}'-\frac{i\pi(M_1+M_2+M_3)}{2}\right].\tag{29}$$

The term $\mathcal{R}'$ and its derivatives are now evaluated at $(q_b,q_a,s^*(E^*),E^*)$, and

$$M_3=\begin{cases}1 & \text{if } dt^*/dE<0\\ 0 & \text{if } dt^*/dE>0\,.\end{cases}\tag{30}$$

Remarkable simplification of the semiclassical propagator of Eq. (29) occurs if we express the right-hand side in terms of the classical mechanics of the original system in x variables *with a corresponding potential correction term* $\frac{1}{g(x)}\Delta\mathcal{V}(h^{-1}(x))\frac{1}{g(x)}$ *included.* For the one-dimensional Coulomb case, the potential correction is just the usual Langer modification $\frac{\hbar^2}{8mx^2}$ [25]. As discussed in detail in Appendix B, a q-space trajectory from q_a to q_b at pseudoenergy $\epsilon(E^*)=0$ of real time duration t matches up with a trajectory in real space from $x_a=h(q_a)$ to $x_b=h(q_b)$ in real time t. In addition, if we denote by $R'(x_b,x_a,t)$ Hamilton's principal function for the original system *with* the potential correction, and by M' the number of conjugate points, then, as shown in Appendix B:

$$\mathcal{R}'(q_b,q_a,s^*(E^*),E^*)-E^*t=R'(x_b,x_a,t),\tag{31a}$$

$$g(x_b)g(x_a)\left|\frac{\partial^2\mathcal{R}'}{\partial q_b\partial q_a}\left[\frac{\partial^2\mathcal{R}'}{\partial s^2}\frac{dt^*}{dE}\right]^{-1}\right|=\left|\frac{\partial^2R'}{\partial x_b\partial x_a}\right|,\tag{31b}$$

$$\sqrt{i}\exp\left[-\frac{i\pi}{2}(M_1+M_2+M_3)\right]=\frac{1}{\sqrt{i}}\exp\left[-\frac{i\pi}{2}M'\right].\tag{31c}$$

Using these expressions in Eq. (29), we obtain our final result:

$$K_{sc}(x_b,x_a,t)=\frac{1}{\sqrt{2\pi i\hbar}}\sum_{\substack{x_a\to x_b\\ \text{in time }t}}\left|\frac{\partial^2R'}{\partial x_b\partial x_a}\right|^{\frac{1}{2}}\exp\left(\frac{iR'}{\hbar}-\frac{iM'\pi}{2}\right).\tag{32}$$

This form for the semiclassical propagator is, remarkably, precisely the Van Vleck–Gutzwiller expression obtained for the original problem including the Langer correction to the potential. Our approach via the regularized quantum propagator therefore justifies inclusion of the Langer modification in the time-dependent semiclassical propagator. A similar result was obtained by Gerry and Inomata [37]. See also Ref. [1], Sec. 13.5.

VI. SEMICLASSICAL AUTOCORRELATION FUNCTION FOR 1D COULOMB PROBLEM

In this section we use the regularized semiclassical propagator derived above to compute a wave packet autocorrelation function (survival amplitude) for the one-dimensional Coulomb problem Eq. (9). For this case the regularization qualitatively changes the underlying classical mechanics, since all trajectories in the unmodified potential reach the singularity at $x=0$, and semiclassical continuation (including a conjugate point analysis) through the Coulomb singularity is not straightforward.

We shall compute the autocorrelation function $C(t)$ for a wave packet $\psi(x)=\langle x|\psi(0)\rangle$ evolving under the Hamiltonian (9):

$$\begin{aligned}C(t)&=\langle\psi(0)|\psi(t)\rangle\\&=\langle\psi(0)|\hat{U}(t)|\psi(0)\rangle\\&=\int dx_a\int dx_b\,\psi^*(x_b)\,\psi(x_a)\,K(x_b,x_a,t).\end{aligned}\tag{33}$$

The semiclassical approximation for $C(t)$ is obtained by replacing the quantum propagator K with its regularized semiclassical approximation and computing the double integral over x_a and x_b numerically [15]. Following Heller [15], we use an "initial value representation," which converts the integration over initial and final position to one over initial position and initial momentum:

$$C(t) = \int dx_a \int dx_b\, \psi^*(x_b)\, \psi(x_a) \left(\frac{1}{2\pi i\hbar}\right)^{1/2} \times \int dp_a \left| \left(\frac{\partial x_t}{\partial p_a}\right)_{x_a}^{1/2} \delta(x_b - x_t) \right| \times \exp\left[\frac{iR(x_t, x_a)}{\hbar} - \frac{i\nu\pi}{2}\right], \quad (34)$$

where $x_t(x_a, p_a)$ is the final position after time t of the trajectory with initial position x_a and momentum p_a. Integrating over x_b we have

$$C(t) = \int dx_a \int dp_a\, \psi^*(x_t)\, \psi(x_a) \left(\frac{1}{2\pi i\hbar}\right)^{1/2} \times \left| \frac{\partial^2 R}{\partial x_b \partial x_a}(x_t, x_a) \right|^{-\frac{1}{2}} \exp\left[\frac{iR(x_t, x_a)}{\hbar} - \frac{i\nu\pi}{2}\right]. \quad (35)$$

We consider initial states $\psi(x)$ that are minimum uncertainty Gaussian wave packets localized in both position and momentum, so both integrations can effectively be restricted to finite ranges of x_a and p_a, and thus computed by a simple discretization. In a general application of the initial value representation, one would use numerical integration to determine the final values of x_t, R, and $\partial^2 R/\partial x_b \partial x_a$. However, the classical equations of motion for the Coulomb-plus-Langer potential are explicitly soluble, so that, for given (x_a, p_a, t), the final position x_t can be obtained by a straightforward Newton search, and all quantities in (35) easily computed [38].

We have applied the above procedure to compute the semiclassical $C(t)$ for a Gaussian Rydberg wave packet of the form

$$\psi(x, t = 0) = \frac{1}{(\pi\sigma^2)^{\frac{1}{4}}} \exp\left[i\langle p\rangle(x - \langle x\rangle) - \frac{(x - \langle x\rangle)^2}{2\sigma^2}\right], \quad (36)$$

with $(\langle x\rangle, \langle p\rangle) = (7200, 0)$ (corresponding to the outer turning point of the trajectory at the energy of the $n = 60$ level) and width $\sigma = 600$. These parameters were chosen to match those used by SBNNT [26]. The exact survival amplitude was determined by expanding the wave packet (36) as a linear combination of bound hydrogenic s-state eigenfunctions $\psi(x) = \sum_n c_n \phi_n(x)$ (the contribution from the continuum is negligible), where $\phi_n(x) = \frac{2}{n^{5/2}} x e^{-x/n} L_{n-1}^1(2x/n)$ (the radial hydrogen wave function including an extra factor of x to account for the x^2 in the three-dimensional volume element). We have $C(t) = \langle\psi|e^{-i\hat{H}t/\hbar}|\psi\rangle = \sum_n |c_n|^2 e^{-iE_n t/\hbar}$, with the expansion coefficients $c_n = \int dx\, \psi(x)\phi_n^*(x)$ obtained by numerical quadrature.

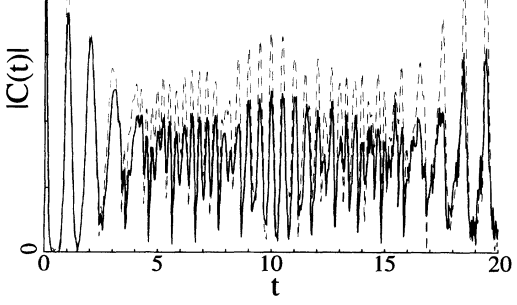

FIG. 1. Semiclassical (solid line) and exact quantum (dashed line) autocorrelation functions $|C(t)|$ for the Rydberg wave packet, Eq. (36).

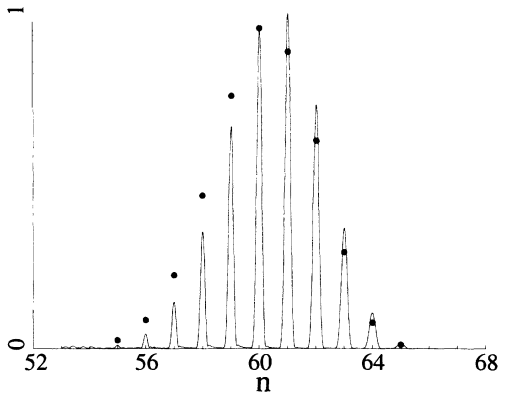

FIG. 2. Semiclassical (solid line) and exact quantum (filled circles) eigenstate overlap spectra for the Rydberg wave packet Eq. (36); intensities are plotted as a function of the quantum number $n(E) = (-2E)^{-1/2}$. The semiclassical spectrum is obtained by Fourier transforming the semiclassical autocorrelation function $C(t)$. The exact quantum and semiclassical spectra are scaled to have the same value at $n = 60$.

The semiclassical and exact autocorrelation functions $C(t)$ for initial state (36) are shown in Fig. 1 for times up to 20 periods of the central ($n = 60$) orbit. The periodicities of the oscillations of $C(t)$ are well reproduced by the regularized semiclassical propagator; the amplitudes of the oscillations in our semiclassical approximation appear to be less accurate than those obtained by SBNNT [26]. Fourier transformation of $C(t)$ gives a semiclassical approximation to the hydrogenic spectrum [15]. The semiclassical and exact overlap spectra for $\psi(0)$ are shown in Fig. 2. Here, our semiclassical results are very accurate and of the same quality as those obtained by SBNNT [26].

VII. DISCUSSION AND CONCLUSIONS

In this paper, we have derived a regularized semiclassical radial propagator for the Coulomb problem. The derivation of a semiclassical propagator in this case is not straightforward due to the Coulomb singularity and the non-Cartesian nature of the radial coordinate. In our approach, we first regularize the quantum propagator following Kleinert [22]; the regularized quantum propagator thus obtained is then replaced by its semiclassical limit, which has the standard Van Vleck–Gutzwiller form. The

propagator of interest is now a double integral over energy and (scaled) time. Performing both integrals by stationary phase yields the result, Eq. (29). A detailed analysis then shows this expression to simplify, remarkably, to the form (32), which is simply the Van Vleck–Gutzwiller semiclassical propagator for the Coulomb potential plus Langer correction $\hbar^2/8mx^2$ [25].

The regularized semiclassical propagator is applied to compute the autocorrelation function (survival amplitude) $C(t)$ for a Rydberg wave packet centered at the $n = 60$ level. Although our semiclassical method does not reproduce the oscillation amplitudes in $C(t)$ quite as accurately as the approach of Suarez-Barnes, Nauenberg, Nockleby, and Tomsovic [26], the Fourier transform of the semiclassical $C(t)$ yields a wave packet eigenstate spectrum of accuracy comparable to that of Ref. [26].

Several points remain to be discussed. First, it is necessary to clarify the relation between the semiclassical propagation method of SBNNT [26] and the approach developed here. At each time t, there is a set of periodic orbits with initial condition $(x_{0j}, p = 0)$ and period t/j. Following Heller [39], SBNNT employ a Gaussian ansatz for the time-dependent wave packet in the vicinity of *each* reference trajectory, and use a quadratic expansion of the potential about the trajectory to determine the time-evolved Gaussians [26]. The autocorrelation function $C(t)$ then consists of a sum of terms, one term for every reference orbit. The reference trajectories change as the propagation time t changes. As SBNNT have noted, the quadratic expansion of the potential fails in the vicinity of the origin. Although SBNNT claim that "this causes no problems once the trajectory remerges from the origin," there is in their approach no well defined continuation of the dynamics through the potential singularity. In particular, the relative phases of the branches of the wave packet are not determined. SBNNT simply set the relative phases equal to unity [26].

In Appendix C, we show that the SBNNT expression for the wave packet autocorrelation function is obtained by replacing the quantum propagator with the (unregularized) Van Vleck–Gutzwiller form in the usual way, and performing the double integral over radial coordinates x and x' by stationary phase, after expanding Hamilton's principal function to second order in displacements about the reference point (x_{0j}, x_{0j}). In this approach, the relative phases of the wave function branches are also indeterminate, due to the breakdown of the conditions for validity of semiclassical mechanics at the potential singularity; this breakdown is, of course, the motivation for introduction of a regularized semiclassical propagator.

A second point concerns the relation of our results to previous work on the Coulomb propagator.

The exact quantum Green's function for the Coulomb potential has been known for some time [40], but a "closed form" expression for the Coulomb propagator was only obtained recently by Blinder [41]. Blinder's result is complicated, and its semiclassical limit is not easily found (see also [42]). Our numerical results (cf. Fig. 1) indicate that our regularized semiclassical propagator (32), which is defined in (transformed) configuration space, is not exact. On the other hand, in several instances semiclassical approximations for the Coulomb problem yield *exact* results. In the pioneering work of Gutzwiller, a semiclassical approximation to the momentum space Green's function was found to give the exact spectrum and exact wave functions for the H atom [43]. The general question of "correspondence identities" has been discussed by Norcliffe [44]. Rost and Heller have recently shown that the semiclassical propagator in the momentum representation gives the exact quantum result for the Coulomb scattering differential cross section [45]; even interference effects due to exchange symmetry of identical particles are reproduced exactly.

These results illustrate the representation dependence of the quality of semiclassical approximations, and raise the interesting question of the determination of an optimal representation for a given problem.

Finally, we note that the regularized propagator discussed here has potential applications beyond the propagation of one-electron Rydberg wave packets. As noted in the Introduction, there has been much recent interest in the semiclassical mechanics of two-electron systems [9,10]. One model system that has received much attention is a "collinear" model of He with two (radial) degrees of freedom (x_1, x_2) [10,11,33,34]; this model can be thought of as two s-state ($l = 0$) one-electron systems coupled together by an interaction potential $1/(x_1 + x_2)$ that depends only on the radial variables. Study of the collinear model has provided much insight into the nature of "near-collinear" doubly-excited states in the full three-dimensional He atom [9,12]. Previous work on the semiclassical mechanics of collinear Helium has however implicitly used the unregularized propagator, and has extensively exploited the homogeneity properties of the unmodified Coulomb potential. Regularization of the collinear Helium problem would modify the potential by addition of a term

$$\Delta V(x_1, x_2) = \frac{1}{8x_1^2} + \frac{1}{8x_2^2}. \tag{37}$$

Addition of this term would have two consequences. First, the effective potential would no longer be homogeneous of degree -1, and the classical phase space structure would then be energy dependent. Second, the "symmetric stretch" or Wannier mode, which for $E < 0$ is infinitely unstable [33], would have a finite (albeit large) instability exponent. The effects of regularization on this and other few-particle systems remain to be explored.

ACKNOWLEDGMENTS

This work was supported by NSF Grant No. CHE-9101357. Computations reported here were performed in part on the Cornell National Supercomputing Facility, supported by NSF and IBM Corporation.

APPENDIX A: STATIONARY PHASE CONDITION FOR THE E INTEGRAL

The stationary phase evaluation of the s integral in Eq. (26) leads to the appearance of $s^*(E)$, the scaled time

required to go from q_a to q_b at pseudo-energy $\mathcal{H}' = 0$. (Note that $\mathcal{H}'$, $\mathcal{L}'$, and $\mathcal{R}'$ denote the q-space Hamiltonian, Lagrangian and Hamilton's principal function, respectively, all of which depend on E parametrically.) For the second stationary phase integration over E, we need to know $\frac{d}{dE}[\mathcal{R}'(q_b, q_a, s^*(E), E)]$. In this appendix we show that it is simply $t^*(E)$, the physical time taken by the corresponding trajectory in x space.

For a given physical energy E, there is a q-space trajectory $q_0(\sigma)$ which takes scaled time $s^*(E)$ to get from q_a to q_b at $\mathcal{H}' = 0$. To be precise (it is essential to not miss any dependences), we write $[q_0(\sigma)](q_b, q_a, s^*(E), E)$; the four slots $(q_f, q_i, \sigma_{\rm tot}, E)$ indicate that for each choice of final point q_f, initial point q_i, total time $\sigma_{\rm tot}$, and E (which determines the underlying Lagrangian and Hamiltonian), we have a trajectory parametrized by σ (from 0 to $\sigma_{\rm tot}$). Thus, the function we are differentiating is

$$\mathcal{R}'(q_b, q_a, s^*(E), E) = \int_0^{s^*(E)} d\sigma\ \mathcal{L}'[[\dot{q}_0(\sigma)], [q_0(\sigma)], E], \tag{A1}$$

where $[q_0(\sigma)] = [q_0(\sigma)](q_b, q_a, s^*(E), E)$ and $[\dot{q}_0(\sigma)] = [\dot{q}_0(\sigma)](q_b, q_a, s^*(E), E)$. Notice that $\mathcal{L}'$ depends explicitly on E, as well as implicitly through the trajectory q_0. Taking the derivative gives

$$\begin{aligned}\frac{d}{dE}\big(\mathcal{R}'(q_b, q_a, s^*(E), E)\big) &= \mathcal{L}'[[\dot{q}_0(s^*(E))], [q_0(s^*(E))], E]\frac{ds^*}{dE} + \int_0^{s^*(E)} d\sigma \\ &\times\left[\frac{\partial\mathcal{L}'}{\partial\dot{q}}[[\dot{q}_0(\sigma)], [q_0(\sigma)], E]\left(\frac{\partial[\dot{q}_0(\sigma)]}{\partial\sigma_{\rm tot}}\frac{ds^*}{dE} + \frac{\partial[\dot{q}_0(\sigma)]}{\partial E}\right)\right. \\ &\left. + \frac{\partial\mathcal{L}'}{\partial q}[[\dot{q}_0(\sigma)], [q_0(\sigma)], E]\left(\frac{\partial[q_0(\sigma)]}{\partial\sigma_{\rm tot}}\frac{ds^*}{dE} + \frac{\partial[q_0(\sigma)]}{\partial E}\right) + \frac{\partial\mathcal{L}'}{\partial E}[[\dot{q}_0(\sigma)], [q_0(\sigma)], E]\right].\end{aligned} \tag{A2}$$

Here, $[q_0(s^*(E))]$, $[\dot{q}_0(s^*(E))]$, $[q_0(\sigma)]$, $[\dot{q}_0(\sigma)]$ and their derivatives are evaluated at $(q_b, q_a, s^*(E), E)$. There are various simplifications. First, we have

$$[q_0(s^*(E))](q_b, q_a, s^*(E), E) = q_b \tag{A3}$$

(by definition, the position at the final time is the final position). In addition, the Euler-Lagrange equations tell us that $\frac{\partial\mathcal{L}'}{\partial q} = \frac{d}{d\sigma}\frac{\partial\mathcal{L}'}{\partial\dot{q}}$. Finally, we have $\frac{\partial\mathcal{L}'}{\partial E} = [g(h(q))]^2$, since

$$\mathcal{L}' = \frac{m(\dot{q})^2}{2} - [g(h(q))]^2[\mathcal{V}(q) - E] - \Delta\mathcal{V}(q). \tag{A4}$$

Together, we have the simplification

$$\begin{aligned}\frac{d}{dE}\big(\mathcal{R}'(q_b, q_a, s^*(E), E)\big) &= \mathcal{L}'[[\dot{q}_0(s^*(E))], q_b, E]\frac{ds^*}{dE} + \int_0^{s^*(E)}\Big[g(h(q_0(\sigma)))\Big]^2 d\sigma + \int_0^{s^*(E)} d\sigma \\ &\times\left[\frac{\partial\mathcal{L}'}{\partial\dot{q}}[\text{as above}]\Big(\frac{\partial[\dot{q}_0(\sigma)]}{\partial\sigma_{\rm tot}}\frac{ds^*}{dE} + \frac{\partial[\dot{q}_0(\sigma)]}{\partial E}\Big)\right. \\ &\left. + \frac{d}{d\sigma}\frac{\partial\mathcal{L}'}{\partial\dot{q}}[\text{as above}]\Big(\frac{\partial[q_0(\sigma)]}{\partial\sigma_{\rm tot}}\frac{ds^*}{dE} + \frac{\partial[q_0(\sigma)]}{\partial E}\Big)\right].\end{aligned} \tag{A5}$$

Next, we integrate the last line by parts, with

$$\begin{aligned} dv &= \frac{d}{d\sigma}\frac{\partial\mathcal{L}'}{\partial\dot{q}}[[\dot{q}_0(\sigma)], [q_0(\sigma)], E]\ , \\ u &= \frac{\partial[q_0(\sigma)]}{\partial\sigma_{\rm tot}}\frac{ds^*}{dE} + \frac{\partial[q_0(\sigma)]}{\partial E}\ , \\ v &= \frac{\partial\mathcal{L}'}{\partial\dot{q}}[[\dot{q}_0(\sigma)], [q_0(\sigma)], E]\ , \\ du &= \frac{\partial[\dot{q}_0(\sigma)]}{\partial\sigma_{\rm tot}}\frac{ds^*}{dE} + \frac{\partial[\dot{q}_0(\sigma)]}{\partial E}\ . \end{aligned} \tag{A6}$$

Clearly, the $-v\,du$ term will cancel the rest of the integral, leaving only the boundary terms at $\sigma = s^*(E)$ and $\sigma = 0$. The values of u on the boundary give the greatest simplification.

First, $q_0(0)$ is not affected by a change in $\sigma_{\rm tot}$ or E, since it is always equal to q_a. Thus, $u = 0$ at the lower endpoint $\sigma = 0$. Similarly, $[q_0(s^*(E))](q_b, q_a, s^*(E), \Box) = q_b$ for any value of $\Box$, so the $\frac{\partial}{\partial E}$ term in u at the upper limit is also zero. [The fact that it is $\frac{\partial}{\partial E}$ and not $\frac{d}{dE}$ means exactly that we vary the fourth slot *without* affecting the E inside $s^*(E)$.] The remaining term is a bit tricky. From the definition of the derivative $[A = s^*(E)]$,

$$\frac{\partial[q_0(A)]}{\partial\sigma_{\rm tot}}(q_b, q_a, A, E) = \lim_{h\to 0+} \frac{[q_0(A)](q_b, q_a, A+h, E) - [q_0(A)](q_b, q_a, A, E)}{h}$$
$$= \lim_{h\to 0+} \frac{[q_0(A)](q_b, q_a, A+h, E) - q_b}{h}. \tag{A7}$$

By expanding $[q_0(\sigma = A)](q_b, q_a, A+h, E)$ about $\sigma = A+h$ and inserting it into (A7), we find that

$$\frac{\partial[q_0(A)]}{\partial\sigma_{\rm tot}}(q_b, q_a, A, E) = -[\dot q_0(A)](q_b, q_a, A, E). \tag{A8}$$

The result of the integration by parts is therefore

$$\frac{d}{dE}\left(\mathcal{R}'(q_b, q_a, s^*(E), E)\right)$$
$$= \int_0^{s^*(E)} \left[g\big(h(q_0(\sigma))\big)\right]^2 d\sigma$$
$$+\mathcal{L}'[[\dot q_0(s^*(E))], q_b, E]\frac{ds^*}{dE}$$
$$-[\dot q_0(s^*(E))]\frac{ds^*}{dE}\frac{\partial\mathcal{L}'}{\partial\dot q}[[\dot q_0(s^*(E))], q_b, E]. \tag{A9}$$

The scaled time σ is related to the real time τ by $g[h(q)]^2 d\sigma = d\tau$ [22], so that integrating g^2 over σ from $\sigma = 0$ to $\sigma = s^*(E)$ gives $t^*(E)$, the physical time taken by the trajectory. Moreover, we note the appearance of $\mathcal{H}' = \dot q\frac{\partial\mathcal{L}'}{\partial\dot q} - \mathcal{L}'$. Since $\mathcal{H}' = 0$ on the path q_0, we have

$$\frac{d}{dE}\left(\mathcal{R}'(q_b, q_a, s^*(E), E)\right)$$
$$= -\mathcal{H}'[[\dot q_0(s^*(E))], q_b, E]\frac{ds^*}{dE} + t^*(E) = t^*(E). \tag{A10}$$

APPENDIX B: RELATING REGULARIZED q-SPACE DYNAMICS TO THE LANGER MODIFIED x-SPACE SYSTEM

We start with the basic relations for the Kleinert regularization: $x = h(q)$, $h'(q) = g(h(q))$, $p_x = p_q/g(h(q))$, $d\tau = g\{h[q(\sigma)]\}^2 d\sigma$, and

$$\Delta\mathcal{V}(q) = -\frac{\hbar^2}{m}\left[\frac{1}{4}\frac{h'''(q)}{h'(q)} - \frac{3}{8}\left(\frac{h''(q)}{h'(q)}\right)^2\right]. \tag{B1}$$

It is easy to check that the following two Hamiltonian systems are equivalent, in the sense that any solution $x(\tau)$ of the first equation will, when transformed by the above rules to $q(\sigma)$, also satisfy the second, and vice versa:

$$\frac{1}{2}p_x^2 + V(x) + \frac{\Delta\mathcal{V}(h^{-1}(x))}{[g(x)]^2} = E, \tag{B2a}$$

$$\frac{1}{2}p_q^2 + [g(h(q))]^2\{V(h(q)) - E\} + \Delta\mathcal{V}(q) = 0. \tag{B2b}$$

Thus, we can relate $[q_0(\sigma)](q_b, q_a, s, E^*(q_b, q_a, s))$ and $[x_0(\tau)](x_b, x_a, t)$, where the former is the q-space path (time parametrized by σ) from q_a to q_b in time s at the special value of the parameter $E = E^*$ which makes the pseudo-energy equal to zero, and the latter is the x-space path (time parametrized by τ) from x_a to x_b in time t:

$$[q_0(\sigma)](q_b, q_a, s, E^*) = h^{-1}\big([x_0(\tau)](x_b, x_a, t)\big)\,, \tag{B3}$$

where

$$\tau = \int_0^\sigma [g(h(q_0(\sigma')))]^2\, d\sigma', \tag{B4a}$$

$$x_b = h(q_b), \quad x_a = h(q_a), \tag{B4b}$$

$$t = \int_0^s [g(h(q_0(\sigma')))]^2\, d\sigma'. \tag{B4c}$$

Thus we have related the x-space Hamiltonians and trajectories to their partners in q space. We next relate the corresponding Lagrangians:

$$\mathcal{L}' = \frac{1}{2}\left(\frac{dq}{d\sigma}\right)^2 - [g(h(q))]^2\{V(h(q)) - E\} - \Delta\mathcal{V}(q)\,, \tag{B5a}$$

$$L = \frac{1}{2}\left(\frac{dx}{d\tau}\right)^2 - V(x) - \frac{\Delta\mathcal{V}(h^{-1}(x))}{[g(x)]^2}\,. \tag{B5b}$$

From (B3), we find the following relation:

$$\frac{d[q_0(\sigma)](q_b, q_a, s; E^*)}{d\sigma} = \frac{1}{h'(q_0(\sigma))}\left[\frac{dx_0}{d\tau}(\tau)\right]\frac{\partial\tau}{\partial\sigma}$$
$$= \frac{1}{g(h(q_0(\sigma)))}\left[\frac{dx_0}{d\tau}(\tau)\right][g(h(q_0(\sigma)))]^2$$
$$= g(h(q_0(\sigma)))\left[\frac{dx_0}{d\tau}(\tau)\right]. \tag{B6}$$

Inserting this into (B5a), one can see

$$\mathcal{L}'\left[\left[\frac{dq_0}{d\sigma}(\sigma)\right](q_b,q_a,s,E^*),[q_0(\sigma)](q_b,q_a,s,E^*),E^*\right]$$

$$=[g(h(q_0(\sigma)))]^2\left(L\left(\left[\frac{dx_0}{d\tau}(\tau)\right](x_b,x_a,t),[x_0(\tau)](x_b,x_a,t)\right)+E^*\right), \quad \text{(B7)}$$

subject to the relations (B4). Integrating $\mathcal{L}'$ over σ from 0 to s to get $\mathcal{R}'$, and using the relation $[g(h(q))]^2 d\sigma = d\tau$, leads easily to

$$\mathcal{R}'(q_b,q_a,s,E^*)=R'(x_b,x_a,t)+E^*t. \quad \text{(B8)}$$

Equation (B8) is one of the key relations that enable us to transform the expression (29) into the Langer modified Van Vleck propagator (32). Another important relation involves the densities (the second derivatives of R' and $\mathcal{R}'$) [1]:

$$g(x_b)g(x_a)\left|\frac{\partial^2\mathcal{R}'(q_b,q_a,s,E^*)}{\partial q_b\partial q_a}\left(\frac{\partial^2\mathcal{R}'(q_b,q_a,s,E^*)}{\partial s^2}\right)^{-1}\right|=\left|\frac{\partial^2R'(x_b,x_a,t)}{\partial x_b\partial x_a}\frac{\partial t(x_b,x_a,E^*)}{\partial E}\right|. \quad \text{(B9)}$$

To prove this relation we first note that

$$\frac{\partial^2\mathcal{R}'(q_b,q_a,s,E^*)}{\partial s^2}=-\frac{\partial\epsilon(q_b,q_a,s,E^*)}{\partial s}$$
$$=-\left(\frac{\partial s(q_b,q_a,\epsilon,E^*)}{\partial\epsilon}\right)^{-1}. \quad \text{(B10)}$$

Hence, we must prove that

$$g(x_b)g(x_a)\left|\frac{\partial^2\mathcal{R}'(q_b,q_a,s,E^*)}{\partial q_b\partial q_a}\frac{\partial s(q_b,q_a,\epsilon,E^*)}{\partial\epsilon}\right|$$
$$=\left|\frac{\partial^2R'(x_b,x_a,t)}{\partial x_b\partial x_a}\frac{\partial t(x_b,x_a,E^*)}{\partial E}\right|. \quad \text{(B11)}$$

It is useful to relate the second derivatives of R' (a time-domain "action") to second derivatives of S' (an energy-domain "action") as follows [1]:

$$\left|\frac{\partial^2R'}{\partial x_b\partial x_a}\frac{\partial t}{\partial E}\right|=\left|\frac{\partial^2S'}{\partial x_a\partial E}\frac{\partial^2S'}{\partial x_b\partial E}\right|, \quad \text{(B12)}$$

and likewise in q space, replacing x by q, t by s, and E by ϵ. Hence, we must show that

$$g(x_b)g(x_a)\left|\frac{\partial^2\mathcal{S}'(q_b,q_a,\epsilon,E^*)}{\partial q_b\partial\epsilon}\frac{\partial^2\mathcal{S}'(q_b,q_a,\epsilon,E^*)}{\partial q_a\partial\epsilon}\right|$$
$$=\left|\frac{\partial^2S'(x_b,x_a,E^*)}{\partial x_b\partial E}\frac{\partial^2S'(x_b,x_a,E^*)}{\partial x_a\partial E}\right|. \quad \text{(B13)}$$

Since $\frac{\partial S'}{\partial x_b}=p_b$ and $\frac{\partial S'}{\partial x_a}=-p_a$, (B13) becomes

$$g(x_b)g(x_a)\left|\left|\frac{\partial p_b'(q_b,q_a,\epsilon,E^*)}{\partial\epsilon}\right|\left|\frac{\partial p_a'(q_b,q_a,\epsilon,E^*)}{\partial\epsilon}\right|\right|_{\epsilon=0}=\left|\frac{\partial p_b(x_b,x_a,E^*)}{\partial E}\frac{\partial p_a(x_b,x_a,E^*)}{\partial E}\right|. \quad \text{(B14)}$$

Next, we use the relations for p in each system

$$p'=\pm\sqrt{2\epsilon-2g[h(q')]^2\{V(h(q'))-E^*\}}\,,$$
$$p=\pm\sqrt{2E^*-2V(x)}\,, \quad \text{(B15)}$$

to compute the derivatives

$$\frac{\partial p'}{\partial\epsilon}(\epsilon=0)=\pm1/\sqrt{-2g[h(q')]^2\{V(h(q'))-E^*\}},$$
$$\frac{\partial p}{\partial E}=\pm1/\sqrt{2E^*-2V(x)}. \quad \text{(B16)}$$

The desired result (B9) follows immediately.

Finally, we consider the relation between conjugate points. We seek to show that

$$\sqrt{i}\exp\left[-\frac{i\pi}{2}(M_1+M_2+M_3)\right]=\frac{1}{\sqrt{i}}\exp\left[-\frac{i\pi}{2}M'\right], \quad \text{(B17)}$$

where M' is the number of conjugate points in x space (including the Langer correction to the potential), M_1 is the number of conjugate points in q space, M_2 is 1 if $\frac{d^2\mathcal{R}'}{ds^2}$ is negative (and 0 otherwise), and M_3 is 1 if $\frac{dt}{dE}$ is negative (and 0 otherwise). In other words, we need to show that

$$\exp\left[-\frac{i\pi}{2}(M_1+M_2)\right]=\frac{1}{i}\exp\left[-\frac{i\pi}{2}(M'-M_3)\right]$$
$$=\exp\left[-\frac{i\pi}{2}(M'-M_3+1)\right]. \quad \text{(B18)}$$

Note that $M_1 + M_2$ is just the number of energy-shell conjugate points in the q space (cf. the argument on p. 188 of [1]), given by the number of times $\frac{\partial^2 \mathcal{R}'}{\partial q_b \partial q_a} / \frac{\partial^2 \mathcal{R}'}{\partial s^2}$ blows up along the trajectory. If we convert $\frac{\partial t}{\partial E}$ in (B9) to $-\left(\frac{\partial^2 R'}{\partial t^2}\right)^{-1}$, we see that $\frac{\partial^2 \mathcal{R}'}{\partial q_b \partial q_a} / \frac{\partial^2 \mathcal{R}'}{\partial s^2}$ is just a constant $\left(\frac{\pm 1}{g(x_b) g(x_a)}\right)$ multiple of the analogous density ratio $\frac{\partial^2 R'}{\partial x_b \partial x_a} / \frac{\partial R'}{\partial t^2}$ in the (Langer-corrected) x space. The two ratios will therefore blow up at the same points, so that the energy-shell conjugate points are the same in the transformed and the original systems. Hence, we just need to show that $M' - M_3 + 1$ is the number of energy-shell conjugate points in the Langer corrected original system. Again, using the fact that $\frac{\partial t}{\partial E} = -\left(\frac{\partial^2 R'}{\partial t^2}\right)^{-1}$,

$$M_3 = \begin{cases} 1 & \text{if } \partial t/\partial E < 0 \\ 0 & \text{if } \partial t/\partial E > 0, \end{cases}$$

$$M_3 = \begin{cases} 1 & \text{if } \partial^2 R'/\partial t^2 > 0 \\ 0 & \text{if } \partial^2 R'/\partial t^2 < 0, \end{cases}$$

$$1 - M_3 = \begin{cases} 0 & \text{if } \partial^2 R'/\partial t^2 > 0 \\ 1 & \text{if } \partial^2 R'/\partial t^2 < 0\ . \end{cases} \tag{B19}$$

Hence (again, cf. p. 188 of [1]), $1 - M_3$ is exactly the correct term to add to the number of conjugate points M' to get the number of energy-shell conjugate points, as required.

APPENDIX C: ON THE APPROACH OF SUAREZ-BARNES, NAUENBERG, NOCKLEBY, AND TOMSOVIC [26]

A semiclassical method has recently been proposed by Suarez-Barnes, Nauenberg, Nockleby, and Tomsovic (henceforth SBNNT) to propagate a Rydberg wave packet for the 1D Coulomb potential [26]. The approach of Ref. [26] differs from that taken in the present paper, and in this appendix we explore the connection between the two methods further. SBNNT do not provide a full derivation of their working equations [Eqs. (7) and (8) of Ref. [26]] in [26], so in this appendix we derive their results bringing out the essential approximations and connection with the standard Van Vleck–Gutzwiller approach.

We start with an initial wave packet $\psi(x) = \langle x|\psi(0)\rangle$, and propagate to time t in the standard way

$$\psi(x,t) = \int_0^\infty dx' K(x,x',t)\psi(x',0). \tag{C1}$$

The autocorrelation function $C(t)$ is defined as

$$C(t) = \int dx\, \psi^*(x,0)\psi(x,t)$$
$$= \int dx \int dx' \psi^*(x,0) K(x,x',t)\psi(x',0). \tag{C2}$$

The quantum propagator K in (C1) is now replaced by its semiclassical approximation, which is *assumed* to have the standard Van Vleck form for the unmodified Coulomb potential $V(x) = -Z/x$:

$$\psi(x,t) = (2\pi i\hbar)^{-1/2} \int dx' \sum \left| \frac{\partial^2 R}{\partial x_a \partial x_b}(x,x',t) \right|^{1/2} \times \exp\left[\frac{iR(x,x',t)}{\hbar} - \frac{i\phi}{2} \right] \psi(x',0). \tag{C3}$$

As we have emphasized throughout the present paper, however, it is not valid to assume the validity of the Van Vleck form without including the Langer modification in the potential.

The wave packets considered by SBNNT are of the form

$$\psi(x, t=0) = \frac{1}{(\pi\sigma^2)^{\frac{1}{4}}} \exp\left[i\langle p\rangle (x - \langle x\rangle) - \frac{(x - \langle x\rangle)^2}{2\sigma^2} \right], \tag{C4}$$

that is, the product of a real Gaussian centered at $x = \langle x\rangle$ and a plane wave of momentum $p = \langle p\rangle$. We now imagine doing the integrals over x' and x in Eq. (C2) by stationary phase, with attention focused only on the imaginary part of the exponent. For real Gaussians with zero average momentum $\langle p\rangle = 0$, the dominant contributions to the double integral will come from the vicinity of points where $\frac{\partial R}{\partial x'} = \frac{\partial R}{\partial x} = 0$, or $p_a = p_b = 0$. Hence, the most important coordinate pairs (x, x') are those which are close to some (x_{0j}, x_{0j}), where there is a classical trajectory which starts at x_{0j} with zero momentum and returns to x_{0j} in time t. For each value of the time t, there is a discrete set of such trajectories, distinguished by the Kepler period t/j. (Note that we assume continuation of the classical trajectory by elastic reflection from the singularity at the origin $x = 0$.)

Motivated by the above discussion, we now expand Hamilton's principal function R in a Taylor series in its two variables about the central point $x = x' = x_0$ (for convenience, we drop the index j, though in the end we will have to sum over all the x_{0j}). The first derivatives are zero at (x_0, x_0) since both momenta are zero. There is then a zeroth-order term and three second derivatives:

$$\frac{iR(x,x',t)}{\hbar} \approx \frac{iR(x_0,x_0,t)}{\hbar} + \frac{i}{2\hbar}\frac{\partial^2 R}{\partial x_a^2}(x_0,x_0,t)(x' - x_0)^2 + \frac{i}{\hbar}\frac{\partial^2 R}{\partial x_a \partial x_b}(x_0,x_0,t)(x' - x_0)(x - x_0) + \frac{i}{2\hbar}\frac{\partial^2 R}{\partial x_b^2}(x_0,x_0,t)(x - x_0)^2. \tag{C5}$$

Next, we do the integral over x' by stationary phase. The stationarity condition is

$$\frac{\partial^2 R}{\partial x_a^2}(x_0,x_0,t)(x' - x_0) + \frac{\partial^2 R}{\partial x_a \partial x_b}(x_0,x_0,t)(x - x_0) = 0,$$

$$(x' - x_0) = -\frac{\frac{\partial^2 R}{\partial x_a \partial x_b}(x_0,x_0,t)}{\frac{\partial^2 R}{\partial x_a^2}(x_0,x_0,t)}(x - x_0). \tag{C6}$$

The classical mechanics for the one-dimensional Coulomb problem with elastic reflection from the origin is explicitly soluble, and the exact expressions for the second derivatives of R give

$$-\frac{\partial^2 R}{\partial x_a \partial x_b}(x_0,x_0,t)\Big/\frac{\partial^2 R}{\partial x_a^2}(x_0,x_0,t)=\frac{2E}{3tp_ap_b+2x_ap_b-2x_bp_a}\frac{-x_a^2(3tp_ap_b+2x_ap_b-2x_bp_a)}{-3tZp_b+2Zx_b-x_a^2p_ap_b}$$
$$=\frac{-2Ex_a^2}{-3tZp_b+2Zx_b-x_a^2p_ap_b}(x_0,x_0,t)$$
$$=\frac{-2Ex_0^2}{-3tZ(0)+2Zx_0-x_0^2(0)(0)}=\frac{-Ex_0}{Z}=1\ . \tag{C7}$$

Hence, by (C6), $x'_{\rm stat}=x$, so the stationary value of the exponent is

$$\frac{iR(x_0,x_0,t)}{\hbar}+\frac{i(x-x_0)^2}{2\hbar}\left[\frac{\partial^2 R}{\partial x_a^2}(x_0,x_0,t)+\frac{\partial^2 R}{\partial x_b^2}(x_0,x_0,t)+2\frac{\partial^2 R}{\partial x_a\partial x_b}(x_0,x_0,t)\right]. \tag{C8}$$

Again, we can insert exact expressions for the second derivatives of R to compute the bracketed term

$$\frac{\partial^2 R}{\partial x_a^2}(x_0,x_0,t)+\frac{\partial^2 R}{\partial x_b^2}(x_0,x_0,t)+2\frac{\partial^2 R}{\partial x_a\partial x_b}(x_0,x_0,t)=\frac{-\frac{3tZp_a}{x_b^2}-\frac{2Zx_a}{x_b^2}+p_ap_b+\frac{3tZp_b}{x_a^2}-\frac{2Zx_b}{x_a^2}+p_ap_b-4E}{3tp_ap_b+2x_ap_b-2x_bp_a}. \tag{C9}$$

We require the limiting behavior of the ratio (C9) as $p_a,p_b\to 0$. Let $x_a=-\frac{Z}{E}-\epsilon_a$ and $x_b=-\frac{Z}{E}-\epsilon_b$. Then,

$$p_a=\frac{\gamma_a}{x_0}\sqrt{2Z\epsilon_a}+O(\epsilon_a)\ ,$$
$$p_b=-\frac{\gamma_b}{x_0}\sqrt{2Z\epsilon_b}+O(\epsilon_b)\ . \tag{C10}$$

If we now compute the numerator and denominator of (C9) to order $\sqrt{\epsilon}$ we have

$$\frac{\partial^2 R}{\partial x_a^2}(x,x_0,t)+\frac{\partial^2 R}{\partial x_b^2}(x,x_0,t)+2\frac{\partial^2 R}{\partial x_a\partial x_b}(x,x_0,t)=\frac{-\frac{3tZ\gamma_a\sqrt{2Z\epsilon_a}}{x_0^3}-\frac{2Z}{x_0}-\frac{3tZ\gamma_b\sqrt{2Z\epsilon_b}}{x_0^3}-\frac{2Z}{x_0}-4E+O(\epsilon)}{-2\gamma_b\sqrt{2Z\epsilon_b}-2\gamma_a\sqrt{2Z\epsilon_a}+O(\epsilon)}$$
$$=\frac{-3tZ\gamma_a\sqrt{2Z\epsilon_a}/x_0^3-3tZ\gamma_b\sqrt{2Z\epsilon_b}/x_0^3+O(\epsilon)}{-2\gamma_b\sqrt{2Z\epsilon_b}-2\gamma_a\sqrt{2Z\epsilon_a}+O(\epsilon)}$$
$$=\frac{-3tZ/x_0^3}{-2}+O(\sqrt{\epsilon})=\frac{3tZ}{2x_0^3}+O(\sqrt{\epsilon}). \tag{C11}$$

Hence, the stationary value of the exponent becomes

$$\frac{iR(x_0,x_0,t)}{\hbar}+\frac{3itZ(x-x_0)^2}{4\hbar x_0^3}. \tag{C12}$$

Since $R(x_0,x_0,t)=-3Et=\frac{3Zt}{x_0}$, this is just

$$\frac{3itZ}{\hbar x_0}+\frac{3itZ(x-x_0)^2}{4\hbar x_0^3}. \tag{C13}$$

In addition to the stationary value of the exponent, we must compute the amplitude contributed by the stationary phase integration:

$$(2\pi i\hbar)^{1/2}\left|\frac{\partial^2 R}{\partial x_a^2}\right|^{-1/2}\exp[-i\chi/2]. \tag{C14}$$

In conjunction with the original prefactor, assumed slowly varying, the final amplitude is

$$\left|\frac{\frac{\partial^2 R}{\partial x_a\partial x_b}(x_0,x_0,t)}{\frac{\partial^2 R}{\partial x_a^2}(x_0,x_0,t)}\right|^{1/2}\exp[-i(\chi+\phi)/2]\psi(x'_{\rm stat},0). \tag{C15}$$

We have already shown that this ratio of densities is -1, and that $x'_{\rm stat}=x$, so the amplitude is just $\exp[-i(\chi+\phi)/2]\psi(x,0)$.

Hence, with the above approximations we have

$$\psi(x,t)=\sum_j\exp\left[-\frac{i(\chi_j+\phi_j)}{2}+\frac{3itZ}{\hbar x_{0j}}+\frac{3itZ(x-x_{0j})^2}{4\hbar x_{0j}^3}\right]\psi(x,0). \tag{C16}$$

At this point we note that the value of the phase factor $\exp[-i(\chi_j+\phi_j)/2]$ has not been specified. Determination of the phase ϕ_j in the semiclassical propagator, Eq. (C4), presents some difficulty for, although the classical trajectories are easily continued through collisions with the singularity at the origin, the usual semiclassical analysis breaks down there [25]. Indeed, one of the points of the present paper is that one should regularize the quantum dynamics *before* passing to the semiclassical limit. SBNNT however claim without proof that the phase drops out, so the reference trajectories add with "relative phase equal to unity [26]." If we accept this assumption concerning the relative phases of the root trajectories, then inserting the wave packet $\psi(x,0)$ of Eq. (C4) and performing the Gaussian integration over x explicitly recovers the expression for $C(t)$ given by SBNNT [Eq. (7) of [26]].

Equation (C16) expresses the time evolved wave packet $\psi(x,t)$ at time t as a superposition of terms, each of which consists of the original (unspread) wave packet multiplied by a phase factor $\exp\left[\frac{3itZ}{\hbar x_{0j}} + \frac{3itZ(x-x_{0j})^2}{4\hbar x_{0j}^3}\right]$. This form for $\psi(x,t)$ arises by approximating the semiclassical time-evolved state (C1) in the vicinity of those points in phase space where it overlaps the initial wave packet (cf. Fig. 1 of [26]) by quadratic expansion of Hamilton's principal function and stationary phase evaluation of the integral over x'. Of course, this procedure is well suited for computation of an autocorrelation function, as the regions of overlap are the only points of interest.

[1] M.C. Gutzwiller, *Chaos in Classical and Quantum Mechanics* (Springer-Verlag, Berlin, 1990).

[2] *Chaos and Quantum Physics*, edited by M.-J. Giannoni, A. Voros, and J. Zinn-Justin (Elsevier, New York, 1991).

[3] *Quantum Chaos*, Proceedings of the International School of Physics, "Enrico Fermi," Course CXIX, Varenna, 1991, edited by G. Casati, I. Guarneri, and U. Smilansky (North-Holland, Amsterdam, 1993).

[4] M.C. Gutzwiller, J. Math. Phys. **12**, 343 (1971).

[5] H. Friedrich and D. Wintgen, Phys. Rep. **183**, 37 (1989).

[6] R.V. Jensen, S.M. Susskind, and M.M. Saunders, Phys. Rep. **201**, 1 (1991).

[7] G. Casati, B.V. Chirikov, D.L. Shepelyansky, and I. Guarneri, Phys. Rep. **154**, 77 (1987).

[8] G. Alber and P. Zoller, Phys. Rep. **199**, 232 (1991).

[9] D. Wintgen, K. Richter, and G. Tanner, Chaos **2**, 19 (1992).

[10] R. Blumel and W.P. Reinhardt, in *Directions in Chaos*, edited by B.L. Hao *et al.* (World Scientific, Singapore, 1991), Vol. 4.

[11] J.H. Kim and G.S. Ezra, in *Proceedings of the Adriatico Conference on Quantum Chaos*, edited by H.A. Cerdiera *et al.* (World Scientific, Singapore, 1991).

[12] G.S. Ezra, K. Richter, G. Tanner, and D. Wintgen, J. Phys. B **24**, L413 (1991).

[13] J. Muller, J. Burgdorfer, and D. Noid, Phys. Rev. A **45**, 1471 (1992); J. Muller and J. Burgdorfer, Phys. Rev. Lett. **70**, 2375 (1993).

[14] G. Handke, M. Draeger, and H. Friedrich, Physica A **197**, 113 (1993); G. Handke, M. Draeger, W. Ihra, and H. Friedrich, Phys. Rev. A **48**, 3699 (1993).

[15] E.J. Heller, J. Chem. Phys. **94**, 2723 (1991); P.W. O'Connor, S. Tomsovic, and E.J. Heller, J. Stat. Phys. **68**, 131 (1992); Physica D **55**, 340 (1992); M.A. Sepulveda, S. Tomsovic, and E.J. Heller, Phys. Rev. Lett. **69**, 402 (1992).

[16] S. Tomsovic and E.J. Heller, Phys. Rev. Lett. **67**, 664 (1991); Phys. Rev. E **47**, 282 (1993); Phys. Rev. Lett. **70**, 1405 (1993).

[17] A.G. Basile and C.G. Gray, J. Comput. Phys. **101**, 80 (1992).

[18] K. Kay, J. Chem. Phys. **100**, 4377 (1994); **100**, 4433 (1994).

[19] J.H. Van Vleck, Proc. Natl. Acad. Sci. **14**, 178 (1928).

[20] R.G. Littlejohn, J. Stat. Phys. **68**, 7 (1992).

[21] J.A. Yeazell, M. Mallalieu, and C.R. Stroud, Phys. Rev. Lett. **64**, 2007 (1990); J.A. Yeazell and C.R. Stroud, Phys. Rev. A **43**, 5153 (1991).

[22] H. Kleinert, *Path Integrals in Quantum Mechanics, Statistics and Polymer Physics* (World Scientific, Singapore, 1990).

[23] M.V. Berry and K.E. Mount, Rep. Prog. Phys. **35**, 315 (1972).

[24] L.A. Young and G.E. Uhlenbeck, Phys. Rev. **36**, 1154 (1930).

[25] R.E. Langer, Phys. Rev. **51**, 669 (1937).

[26] I.M. Suarez-Barnes, M. Nauenberg, M. Nockleby, and S. Tomsovic, Phys. Rev. Lett. **71**, 1961 (1993).

[27] M. Mallalieu and C.R. Stroud, Phys. Rev. A **49**, 2329 (1994). See also J.A. Yeazell, M. Mallalieu, M. Parker, and C.R. Stroud, *ibid.* **40**, 5040 (1989); Z.D. Gaeta and C.R. Stroud, *ibid.* **42**, 6308 (1990).

[28] R.P. Feynmann and A.R. Hibbs, *Quantum Mechanics and Path Integrals* (McGraw-Hill, New York, 1965).

[29] L.S. Schulman, *Techniques and Applications of Path Integration* (Wiley, New York, 1981).

[30] W.H. Miller, Adv. Chem. Phys. **25**, 69 (1974); **30**, 77 (1976).

[31] F. Steiner, in *Path Integrals from meV to MeV*, edited by M.C. Gutzwiller (World Scientific, Singapore, 1986); C. Grosche and F. Steiner, Z. Phys. C **36**, 699 (1987).

[32] V. Szebehely, *Theory of Orbits* (Academic, New York, 1967).

[33] K. Richter and D. Wintgen, J. Phys. B **23**, L197 (1990); K. Richter, G. Tanner, and D. Wintgen, Phys. Rev. A **48**, 4182 (1993).

[34] J.-H. Kim, Ph.D. thesis, Cornell University, 1992.

[35] P.M. Morse, Phys. Rev. **34**, 57 (1929).

[36] I.H. Duru and H. Kleinert, Phys. Lett. B **84**, 185 (1979); N.K. Pak and I. Sokmen, Phys. Lett. A **100**, 327 (1984).

[37] C. Gerry and A. Inomata, J. Math. Phys. **23**, 2402 (1983).

[38] R. Manning, Ph.D. thesis, Cornell University, 1994.

[39] E.J. Heller, J. Chem. Phys. **62**, 1544 (1975).

[40] L. Hostler, J. Math. Phys. **5**, 591 (1964).

[41] S.M. Blinder, Phys. Rev. A **43**, 13 (1991).

[42] S.M. Blinder, Phys. Rev. Lett. **52**, 1771 (1984); Chem. Phys. Lett. **134**, 288 (1987).

[43] M.C. Gutzwiller, J. Math. Phys. **8**, 1979 (1967); **10**, 1004 (1969); **11**, 1791 (1970).

[44] A. Norcliffe, Case Stud. At. Phys. **4**, 1 (1973).

[45] J.M. Rost and E.J. Heller, J. Phys. B **27**, 1387 (1994).