# Exact wave functions from classical orbits: The isotropic harmonic oscillator and semiclassical applications

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The wave function for a state of definite angular momentum of the three-dimensional isotropic harmonic oscillator is expressed exactly in terms of the corresponding classical trajectories. In particular, the three-dimensional wave function as well as the radial wave function and the spherical harmonics are obtained as integrals over quantities determined entirely by the classical motion. The expression for the harmonic-oscillator radial wave function is shown also to yield the exact radial wave function for the free particle. The expressions are cast in forms suitable for use as uniform semiclassical approximations for wave functions of other systems. Numerical examples confirm that such wave functions obey boundary conditions appropriate for spherical coordinates and that they are free of caustic singularities. The wave functions obtained by this technique can be quite accurate even for low-energy states where semiclassical approximations are expected to be poor.

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## I. INTRODUCTION

In this paper and subsequent work we show that quantum-mechanical wave functions for a number of systems can be expressed exactly, analytically, and simply in terms of the corresponding classical trajectories. In addition to being exact for specific reference systems, these classical wave-function expressions become uniformly accurate in the classical limit for other systems obeying similar boundary conditions. Such expressions thus serve as uniform semiclassical approximations for the wave functions of a more general class of systems. Apart from their application as semiclassical approximations, the exact classical descriptions of quantum wave functions should lead to a clearer understanding of the quantum-classical relationship.

The new expressions are generalizations of an existing semiclassical approximation [1,2] for time-independent wave functions. To understand the motivation for the present paper and the context in which it arises, it is necessary to review that treatment. References [1] and [2] establish that the energy eigenstates for an integrable system with $f$ degrees of freedom can be approximated semiclassically as

$$\psi(\mathbf{x}')=\mathcal{N}\int C\, e^{i(\Phi+W)/\hbar} d\boldsymbol{\alpha}. \tag{1.1}$$

The integral is over the $f$-dimensional Lagrangian manifold [3,4] corresponding semiclassically to the state of interest and $\boldsymbol{\alpha}$ are variables parametrizing this manifold. For example, in the case of a bound state with quantum numbers $\mathbf{n}=(n_1,\ldots,n_f)$, the manifold is the quantized torus defined by the Einstein-Brillouin-Keller (EBK) condition $\mathbf{J}=(\mathbf{n}+\boldsymbol{\delta})\hbar$, [5] where the $\mathbf{J}$ and $\boldsymbol{\delta}$ are vectors containing the actions and Maslov indices for the degrees of freedom. In such a case, the $\boldsymbol{\alpha}$ can be taken as the angle variables conjugate to the $\mathbf{J}$. The quantity $W$ appearing in Eq. (1.1) is Hamilton's characteristic function, satisfying the time-independent Hamilton-Jacobi equation

$$H(\nabla W,\mathbf{x})=E, \tag{1.2}$$

where $H(\mathbf{p},\mathbf{x})$ is the Hamiltonian for the system with momenta $\mathbf{p}$ and coordinates $\mathbf{x}$. $E$ is the semiclassical energy for the state and is determined by EBK quantization if the state is bound. The solution of Eq. (1.2) can be expressed as

$$W=\int^{\mathbf{x}(\boldsymbol{\alpha})}\mathbf{p}\cdot d\mathbf{x}, \tag{1.3}$$

where the integration is performed over a path on the Lagrangian manifold. The lower integration limit is arbitrary (it only affects the overall phase of the wave function), while the upper limit is the coordinate $\mathbf{x}(\boldsymbol{\alpha})$ that depends on the integration parameters $\boldsymbol{\alpha}$. The function $\Phi$ in Eq. (1.1) is defined by

$$\Phi=\mathbf{p}\cdot(\mathbf{x}'-\mathbf{x})+i(\mathbf{x}'-\mathbf{x})\cdot\boldsymbol{\Gamma}\cdot(\mathbf{x}'-\mathbf{x}), \tag{1.4}$$

where $\mathbf{x}=\mathbf{x}(\boldsymbol{\alpha})$, $\mathbf{p}=\mathbf{p}(\boldsymbol{\alpha})$, and $\boldsymbol{\Gamma}=\boldsymbol{\Gamma}(\boldsymbol{\alpha})$ is an $f\times f$ complex symmetric matrix function of $\boldsymbol{\alpha}$. This matrix can be chosen almost arbitrarily, but the real parts of all of its eigenvalues are required to be positive (apart from certain special cases where they may be zero) and, for bound states, its elements must be a $2\pi$-periodic functions of the angles $\boldsymbol{\alpha}$. The preexponential factor $C$ in Eq. (1.1) is given by

$$C=[\det(\mathbf{P}-2i\boldsymbol{\Gamma}\mathbf{X})]^{1/2}, \tag{1.5}$$

where

$$(\mathbf{P})_{ij}=\frac{\partial p_i}{\partial\alpha_j},\quad (\mathbf{X})_{ij}=\frac{\partial x_i}{\partial\alpha_j},\quad i,j=1,\ldots,f. \tag{1.6}$$

Finally, $\mathcal{N}$ is a normalization constant.

Although expressed solely in terms of classical variables, Eq. (1.1) turns out to be an exact expression for the quantum-mechanical wave functions of the multidimensional harmonic oscillator, with potential-energy function

$$V(\mathbf{x})=\frac{1}{2}\sum_{i=1}^{f}\mu_i\omega_i^2x_i^2,$$

 

provided that the matrix $\mathbf{\Gamma}$ is chosen so that $(\mathbf{\Gamma})_{ij} = (\frac{1}{2}\mu_i\omega_i)\delta_{ij}$. In addition, Eq. (1.1) can be shown to yield exact wave functions for free motion and (with $\mathbf{\Gamma}=0$) for motion in a linear potential.

Equation (1.1) suggests an attractive classical picture of the wave-function's formation. As the classical particle moves over the Lagrangian manifold associated with the quantum state, it produces contributions to the wave function at points $\mathbf{x}'$. The Gaussian factor

$$G(\mathbf{x}',\mathbf{x}) = e^{-(\mathbf{x}'-\mathbf{x})\cdot\mathbf{\Gamma}\cdot(\mathbf{x}'-\mathbf{x})/\hbar} \tag{1.7}$$

in the integrand localizes these contributions to values $\mathbf{x}'$ near the particle's position $\mathbf{x}$, while the complex factor $C\exp i[\mathbf{p}\cdot(\mathbf{x}'-\mathbf{x})+W]/\hbar$ further weights these contributions and provides a phase so that their coherent superposition produces $\psi(\mathbf{x}')$.

When applied to the harmonic oscillator, linear potential and free particle cases, Eq. (1.1) becomes identical to an expression proposed earlier by Heller [6]. More generally, however, Heller's expression, differs from the present one in the form of the preexponential factor $C$. Heller showed that his expression yields approximate wave functions for more general anharmonic systems when the dynamical quantities $\mathbf{x},\mathbf{p},W$, etc., are replaced by those for the systems of interest [7]. This approximation (known as the frozen Gaussian approximation) is, however, not semiclassical—it does not generally become exact in the classical limit.

In contrast, the present form for the pre-exponential factor makes Eq. (1.1) a true semiclassical approximation. One way of establishing this property is to note that, if the integral over $\boldsymbol{\alpha}$ is evaluated by the lowest-order stationary phase method, the expression for the wave function becomes identical to that obtained by the primitive semiclassical Wentzel-Kramers-Brillouin (WKB) treatment [1,2]. Since both the stationary phase and the WKB treatments become exact in the classical limit for all values of $\mathbf{x}'$ except those along caustics, where the WKB expression is singular, the semiclassical nature of Eq. (1.1) is also established except, perhaps, at caustics. However, it is possible to prove a stronger result: unlike the WKB expression, the approximation given in Eq. (1.1) is free of caustic singularities and approaches the exact wave function uniformly for all $\mathbf{x}'$ as $\hbar\rightarrow 0$ [1,2]. Thus Eq. (1.1) is not only a semiclassical approximation, but a uniform semiclassical approximation. Calculations indeed confirm that this approximation is capable of high accuracy and describes the phase and oscillations of the wave function more faithfully than does the frozen Gaussian approximation [1,2].

One problem, however, with the semiclassical wave functions obtained from this treatment is that they obey specific boundary conditions only at $x_i\rightarrow\pm\infty$. Although such conditions are appropriate for wave functions that are expressed as functions of Cartesian coordinates, they are not appropriate for wave functions described in terms of more general choices of coordinates, which must obey boundary conditions at finite points in space. Thus, for example, wave functions obtained from Eq. (1.1) can satisfy neither periodic boundary conditions, as required for angular variables, nor regular boundary conditions at the origin, as needed for radial spherical variables. Some of the consequences that arise when related semiclassical treatments fail to obey the correct boundary conditions are illustrated in Ref. [8].

The boundary condition restrictions limit the treatment of Eq. (1.1) to systems described in terms of Cartesian coordinates. This is unfortunate since introduction of more general coordinates allows one to exploit constants of motion and often greatly simplifies quantum, classical, as well as certain semiclassical treatments. Thus, the inapplicability of the present approach to wave functions described in terms of such variables is a serious limitation that can complicate both the resulting theoretical analysis and computations. Ultimately, this restriction also complicates application of the treatment to determine quantities (such as scattering and spectroscopic transition probabilities) that are semiclassically expressed most naturally in terms of more general classical canonical variables (e.g., action-angle coordinates). The applicability of other, more familiar, semiclassical methods [5,9] to such variables is responsible for much of their power.

These considerations motivate an attempt to generalize the semiclassical theory of Refs. [1] and [2] to wave functions obeying arbitrary boundary conditions. To understand how this may be accomplished, we note that the feature determining the boundary behavior of $\psi$ in this approximation is the specific structure of the integrand. In particular, it is the Gaussian form $G(\mathbf{x}',\mathbf{x})$ [see Eq. (1.7)], obtained from $\exp(i\Phi/\hbar)$ in Eq. (1.4), that builds in the boundary conditions that are appropriate for Cartesian coordinates. However, the integrand need not be chosen in this specific way. In order that the expression be a uniform semiclassical approximation for $\psi$, it is sufficient that it have the more general form [2]

$$\psi(\mathbf{x}') = \mathcal{N}\int F\, e^{iW/\hbar} d\boldsymbol{\alpha}, \tag{1.8}$$

where $F$ is a function obeying

$$\lim_{\hbar\rightarrow 0} F = C\, e^{i\Phi/\hbar} + D. \tag{1.9}$$

In this expression, $\Phi$ is redefined to obey the condition

$$\Phi \sim \mathbf{p}\cdot(\mathbf{x}'-\mathbf{x}) + O(|\mathbf{x}'-\mathbf{x}|^2), \tag{1.10}$$

that is far less restrictive than the one presented in Eq. (1.4), and $D$ is a possible additional term that does not contribute to a lowest-order stationary phase treatment of the integral. $C$ is still defined as in Eq. (1.5), but the matrix $\mathbf{\Gamma}$ needed for its construction is now determined by

$$\Gamma_{ij} = \frac{1}{2i}\left(\frac{\partial^2\Phi}{\partial x_i'\,\partial x_j'}\right)_{\mathbf{x}'=\mathbf{x}}. \tag{1.11}$$

This matrix must obey the same conditions as described in connection with Eq. (1.4).

The continued validity of Eq. (1.8) as a *uniform* semiclassical approximation may be verified by examining the effect of its substitution in the Schrödinger equation [2]. However,

its validity as a (perhaps nonuniform) semiclassical approximation is much easier to establish since, by construction, a lowest-order stationary phase treatment does not distinguish between Eqs. (1.1) and (1.8). Thus, the revised expression for $\psi$ still gives the correct primitive (WKB) semiclassical result as $\hbar \to 0$.

Equation (1.8) means that the integrand in the expression for $\psi$ needs to have the form prescribed by Eq. (1.1) only in the classical limit (if we neglect $D$) and that, even in this limit, the function $\Phi$ is required to have the form given by Eq. (1.4) only to order $|\mathbf{x}'-\mathbf{x}|^2$. The actual form of the integrand of Eq. (1.8) for nonvanishing $\hbar$ and arbitrary $|\mathbf{x}'-\mathbf{x}|$ need not be Gaussian at all. These considerations provide the freedom to choose the integrand so that the resulting semiclassical wave functions obey desired boundary conditions.

But the allowable form for the integrand is now so general that one suspects that the revised expression for $\psi$ may be capable of describing exact wave functions for systems beyond those for which Eq. (1.1) is exact. In other words, it might be possible to obtain expressions for wave functions, described entirely in terms of the corresponding classical motion, that are exact for certain *new* ''reference'' systems. In analogy to the treatment of Ref. [1], these could serve as uniform semiclassical expressions when applied to ''target'' systems for which they are not exact. If the wave functions of the reference systems obeyed boundary conditions appropriate for non-Cartesian coordinates, the semiclassical wave functions of the target systems would likewise obey these conditions, and the desired extension of the semiclassical treatment of Ref. [1] to more general coordinate systems would thus be accomplished.

Though not strictly necessary for the semiclassical applications, the property of being exact for particular reference systems could have important advantages. We note that, due to its exactness for the harmonic oscillator, Eq. (1.1) yields accurate wave functions for typical anharmonic bound systems even at low energies [1,2] where semiclassical treatments are usually inaccurate, but the motion is effectively harmonic. We should expect the new expressions to have corresponding advantages of being especially accurate when the target and reference systems are similar.

The direction of the present paper is exemplified by a recent paper [10] that describes exact expressions for the wave functions of the Coulomb system in terms of the corresponding classical orbits. Here and in subsequent publications [11] we rederive this result in detail and show how Eq. (1.1) can be further generalized to obtain exact classical expressions for wave functions of several additional systems.

Our approach to deriving analytical, classical exact (CE) wave functions for a variety of systems is first to generalize Eq. (1.1) to obtain CE wave functions for the three-dimensional isotropic harmonic oscillator (IHO) in terms of spherical variables. This already serves as a reference system, allowing determination of semiclassical wave functions in spherical coordinates for general single-particle systems. A mapping procedure [11] can then be applied to derive wave functions for several other systems (including the Coulomb problem [10]) from the radial and angular functions of the IHO. The present paper is devoted to the treatment of the IHO and some immediate consequences; the extension to additional systems will be described elsewhere [11]. A related semiclassical treatment of quantum amplitudes $\langle x_2|x_1\rangle$, involving general classical variables $x_2$ and $x_1$ [9], is also presented in a separate work [12] and an application of that treatment to scattering is likewise described elsewhere [13].

The remainder of this paper is organized as follows: In Sec. II we derive the CE expression for the IHO. In Sec. III we present minor extensions of this result to obtain an alternative CE expression for the three-dimensional IHO wave function and a CE expression for the free particle radial wave function. In Sec. IV we present forms that are suitable as semiclassical approximations for the treatment of the rotational, orbital, and radial motion of more general systems. In Sec. V we present some numerical examples that apply these semiclassical approximations. Finally, in Sec. VI we summarize and discuss our results.

## II. THE ISOTROPIC HARMONIC OSCILLATOR

### A. Classical expression for the wave function

In this section we derive a CE expression for the simultaneous energy and angular momentum eigenstates of the three-dimensional IHO. The system of interest is characterized by the classical Hamiltonian

$$H=\frac{1}{2\mu}(p_x^2+p_y^2+p_z^2)+V(r), \tag{2.1}$$

where

$$V(r)=\tfrac{1}{2}\mu\omega^2 r^2, \tag{2.2}$$

$r^2=x^2+y^2+z^2$, and $\mu$ and $\omega$ are, respectively, the mass and frequency of the oscillator.

In the quantum treatment of this system it is well known that a separation of variables is possible both in Cartesian and in spherical coordinates [14]. Thus, the energy eigenstates can be labeled by either the set of quantum numbers $(n_1,n_2,n_3)$ or the set $(n,l,m)$. Wave functions $\psi_{n_1n_2n_3}(x,y,z)$ are products of three one-dimensional harmonic-oscillator wave functions in the individual Cartesian coordinates $x$, $y$, and $z$, with quantum numbers $n_1$, $n_2$, and $n_3$, respectively. These satisfy

$$n_1,n_2,n_3=0,1,2,\ldots,$$

and specify the energy in each degree of freedom, so that the energy eigenvalue associated with $\psi_{n_1n_2n_3}(x,y,z)$ is

$$E=(n_1+n_2+n_3+\tfrac{3}{2})\hbar\omega.$$

The functions $\psi_{nlm}(r,\theta,\phi)$, on the other hand, are angular momentum eigenstates and are products of radial and angular wave functions in the spherical coordinates $r$, $\theta$, and $\phi$. The angular momentum quantum numbers $l$ and $m$ satisfy the familiar conditions

$$l=0,1,2,\ldots, \quad m=-l,-l+1,\ldots,l, \tag{2.3}$$

while the principle quantum number $n$ is constrained by

$$n = l, l+2, l+4, \ldots, \tag{2.4}$$

and determines the energy of the state via

$$E = (n + \tfrac{3}{2})\hbar\omega. \tag{2.5}$$

Clearly, wave functions $\psi_{nlm}$ and $\psi_{n_1 n_2 n_3}$ with the same energy $E$ are related by

$$\psi_{nlm} = \sum_{n_1+n_2+n_3=n} A_{n_1 n_2 n_3} \psi_{n_1 n_2 n_3}, \tag{2.6}$$

where the $A$ are certain coefficients.

Since Eq. (1.1) yields CE wave functions for the $\psi_{n_1 n_2 n_3}$, we can use Eq. (2.6) to obtain a CE expression for $\psi_{nlm}$ as a finite linear combination of functions of Cartesian coordinates. However, since it is known that $\psi_{nlm}$ can be expressed directly and compactly as a function of the spherical coordinates, we expect that it should also be possible to derive a more compact CE expression for $\psi_{nlm}$ in terms of the spherical variables. Part of the structure of such an expression can be guessed from Eq. (2.6). In view of the isotropic nature of the system, we would expect that the matrix $\mathbf{\Gamma}$ of Eq. (1.4) should be replaced by a certain scalar $\gamma$ (with $\Re\gamma > 0$) that is common to each term in Eq.(2.6). In that case, the CE expression for each such term would contain a factor $\exp(i\Phi/\hbar)$ of the same form, where

$$\Phi = \mathbf{p}\cdot(\mathbf{r}' - \mathbf{r}) + i\gamma|\mathbf{r}' - \mathbf{r}|^2, \tag{2.7}$$

so that a similar factor should also appear in the CE expression for $\psi_{nlm}$ in spherical coordinates. In the following, we seek to verify this hypothesis.

Thus, by analogy to Eq. (1.1), we consider the expression

$$\psi_{nlm}(r', \theta', \phi') = \mathcal{N}\int C\, e^{i(\Phi + W)/\hbar} d\boldsymbol{\alpha}, \tag{2.8}$$

where the integration is now over the Lagrangian manifold for the state with quantum numbers $(n,l,m)$ [which is different from that for the state with quantum numbers $(n_1,n_2,n_3)$] and $\boldsymbol{\alpha}$ denotes the three angle variables parametrizing this manifold. $W$ is again Hamilton's characteristic function, and $\Phi$ is given by Eq. (2.7). The preexponential factor $C$ is determined from

$$r^2 \sin\theta\, C^2 = \det(\mathbf{P} - 2i\mathbf{\Gamma}\mathbf{X}), \tag{2.9}$$

where $\mathbf{P}$, $\mathbf{X}$, and $\mathbf{\Gamma}$ are $3\times 3$ matrices defined as in Eqs. (1.6) and (1.11), with the understanding that $p_i$ and $x_i$ now refer to the spherical components of momentum $\mathbf{p}$ and coordinate $\mathbf{r}$, and that $x_i'$ and $x_j'$ refer to the spherical components of $\mathbf{r}'$.

Note that the form of $C$ in Eq. (2.9) differs from that given in Eq. (1.5) by the factor $r^{-1}\sin\theta^{-1/2}$. We choose the present form because, in order to establish the semiclassical nature of Eq. (2.8) for $\psi_{nlm}$, we require it to reduce to an appropriate WKB expression when the integral is evaluated by the stationary phase method [as in the case of Eq. (1.1)]. However, the WKB formula is strictly derived only for wave functions obeying a ''normal'' Schrödinger equation having no first-derivative terms [5]. Since the Schrödinger equation in spherical coordinates contains first derivatives with respect to $r'$ and $\theta'$, the WKB treatment should not be applied directly to the wave function $\psi_{nlm}(r', \theta', \phi')$. Multiplying $\psi_{nlm}$ by the factor $(r'^2 \sin\theta')^{1/2}$, however, effectively removes these terms from the Schrödinger equation and produces a function that can be properly treated by the WKB method [5]. Our choice of $C$ is designed so that the integral in Eq. (2.8) reduces, upon stationary phase evaluation, to the WKB expression for the function $(r'^2 \sin\theta')^{1/2}\psi_{nlm}$ divided by the factor $(r'^2 \sin\theta')^{1/2}$, to yield an approximation for $\psi_{nlm}$.

### B. Transformation to spherical coordinates

Upon transformation from Cartesian to spherical variables, the function $\Phi$ of Eq. (2.7) can be conveniently expressed as

$$\Phi = p_r(r' - r) + i\gamma(r' - r)^2 + (r'/r)(f + \delta g), \tag{2.10}$$

where

$$\begin{aligned} f = &-iL\{[\cos(\theta' - \theta) - 1] + \sin\theta' \sin\theta[\cos(\phi' - \phi) - 1]\} \\ &+ p_\theta\{\sin(\theta' - \theta) + \sin\theta'\cos\theta[\cos(\phi' - \phi) - 1]\} \\ &+ p_\phi(\sin\theta'/\sin\theta)\sin(\phi' - \phi), \end{aligned} \tag{2.11}$$

$$g = [\cos(\theta' - \theta) - 1] + \sin\theta' \sin\theta[\cos(\phi' - \phi) - 1], \tag{2.12}$$

and

$$\delta = p_r r - 2i\gamma r^2 + iL. \tag{2.13}$$

In these expressions, $(r,\theta,\phi)$, $(r',\theta',\phi')$, and $(p_r, p_\theta, p_\phi)$ are the spherical components of $\mathbf{r}$, $\mathbf{r}'$, and $\mathbf{p}$, respectively, and $L$ is the magnitude of the angular momentum,

$$L = [p_\theta^2 + p_\phi^2/\sin^2\theta]^{1/2}. \tag{2.14}$$

Equation (2.10) allows us to apply the definition of $\mathbf{\Gamma}$ in Eq. (1.11) to obtain

$$2i\mathbf{\Gamma} = \begin{pmatrix} 2i\gamma & p_\theta/r & p_\phi/r \\ p_\theta/r & iL - \delta & p_\phi\cot\theta \\ p_\phi/r & p_\phi\cot\theta & [(iL - \delta)\sin\theta - p_\theta\cos\theta]\sin\theta \end{pmatrix}. \tag{2.15}$$

It can be shown that the real parts of the eigenvalues of $\mathbf{\Gamma}$ are indeed positive, as required, provided that $\Re\gamma > 0$.

### C. Transformation to action-angle variables

To perform the integrations in Eq. (2.8), we need to express the integrand in terms of the action-angle variables for the IHO. The transformation from spherical coordinates and momenta to action-angle variables and the explicit expression for $W$ are reviewed in Appendix A.

It is convenient to focus here on transformations of quantities that depend on the angular coordinates and momenta, leaving the transformations of $r$ and $p_r$ until later. Thus, we substitute Eqs. (A36)–(A39) into Eqs. (2.11) and (2.12), yielding

$$f = iL + e^{-i(\alpha_L+\xi)}\{-i(L^2-M^2)^{1/2}\cos\theta' + [L\sin(\alpha_M-\phi') + iM\cos(\alpha_M-\phi')]\sin\theta'\} \tag{2.16}$$

and

$$g = \cos(\alpha_L+\xi)[(1-M^2/L^2)^{1/2} \times \cos\theta' - (M/L)\sin\theta'\cos(\alpha_M-\phi')] + \sin(\alpha_L+\xi) \times \sin\theta'\sin(\alpha_M-\phi') - 1, \tag{2.17}$$

where $M = p_\phi$ is the $z$ component of the angular momentum. In presenting this result, both $L$ and $M$ are recognized as action variables. Since the integration in Eq. (2.8) is taken over the manifold corresponding to the state $(n,l,m)$, these actions have the quantized values $L=(l+1/2)\hbar$ and $M=m\hbar$, according to Eqs. (A21) and (A22). The quantities $\alpha_L$ and $\alpha_M$ appearing above are the angle variables conjugate to $L$ and $M$, while $\xi$ is defined in Eq. (A32).

To evaluate the pre-exponential factor $C$, we substitute Eqs. (A42)–(A48) into Eqs. (2.9) and (2.15). The result is

$$r^2\sin\theta\, C^2 = \left(\frac{1}{\mu\omega}\right)\begin{vmatrix} p_r(\partial p_r/\partial r - 2i\gamma) - L^2/r^3 & -L/r & -M/r \\ -2i\gamma p_\theta & (\delta/L-i)p_\theta & -M\cot\theta \\ -2i\gamma M & (\delta/L-i)M & -2i\Gamma_{\phi\phi} \end{vmatrix}, \tag{2.18}$$

where

$$2i\Gamma_{\phi\phi} = [(iL-\delta)\sin\theta - p_\theta\cos\theta]\sin\theta. \tag{2.19}$$

To obtain Eq. (2.18), we have eliminated derivatives with respect to the third angle variable $\alpha_N$, defined in Appendix A, using the expressions

$$\partial r/\partial\alpha_N = p_r/\mu\omega \tag{2.20}$$

and

$$\partial p_r/\partial\alpha_N = (p_r/\mu\omega)(\partial p_r/\partial r) \tag{2.21}$$

that follow from the relationship [5] $\alpha_N = \text{const.} + \omega t$ between the angle $\alpha_N$ and time $t$ [also see Eqs. (A35), (A40), and (A41)]. The determinant in Eq. (2.18) may now be expanded, yielding

$$C^2 = -(L^2-M^2)^{1/2}\frac{Lp_r}{\mu\omega r^2}\left[\frac{L}{r^2} + \left(i-\frac{\delta}{L}\right)\left(\frac{\partial p_r}{\partial r} - 2i\gamma\right)\right] \times [e^{-i(\alpha_L+\xi)} + (\delta/L)\sin(\alpha_L+\xi)]. \tag{2.22}$$

These expressions, together with Eq. (A53) for $W$, can now be substituted into Eq. (2.8) for $\psi$ and the integrations over $\alpha_L$ and $\alpha_M$ can be attempted. Unfortunately, this does not generally yield an expression for the wave function in the form of a product of independent radial and angular factors, characteristic of the exact result. We find that, to obtain this desired form, we must choose the as-yet unspecified quantity $\gamma$ to obey the particular condition

$$\gamma = \frac{L}{2r^2} - i\frac{p_r}{2r} \tag{2.23}$$

that causes $\delta$ to vanish [see Eq. (2.13)]. Our expressions then simplify to

$$\Phi = p_r(r'-r) + i\gamma(r'-r)^2 + (r'/r)f = p_r(r'-r) + \left(i\frac{L}{2r^2} + \frac{p_r}{2r}\right)(r'-r)^2 + (r'/r)f \tag{2.24}$$

and

$$C = C_r C_\theta, \tag{2.25}$$

where

$$C_r = \left\{\frac{p_r}{\mu\omega r^2}\left[\frac{2L}{r^2} + i\left(\frac{\partial p_r}{\partial r} - \frac{p_r}{r}\right)\right]\right\}^{1/2}, \tag{2.26}$$

$$C_\theta = i(L^2-M^2)^{1/4}L^{1/2}e^{-i(\alpha_L+\xi)/2}. \tag{2.27}$$

Substitution of these results into Eq. (2.8) and use of Eq. (A6) to decompose $W$ into the sum of one-dimensional integrals $W_r$, $W_\theta$, and $W_\phi$ [defined in Eqs. (A7)–(A9)] casts our expression for the IHO wave function in the form

$$\psi_{nlm}(r',\theta',\phi') = \mathcal{N}\int_0^{2\pi} d\alpha_N\, C_r \times \exp\{i[p_r(r'-r) + i\gamma(r'-r)^2 + W_r]/\hbar\} \times T(\theta',\phi',r'/r), \tag{2.28}$$

where

$$T(\theta',\phi',\rho)=\int_0^{2\pi} d\alpha_L \int_0^{2\pi} d\alpha_M\, C_\theta\, e^{i(\rho f+W_\theta+W_\phi)/\hbar}. \tag{2.29}$$

### D. Angular integrations

We now turn our attention to the evaluation of $T$ defined in Eq. (2.29). Applying Eqs. (A50) and (A49), which establish that

$$W_\theta+W_\phi=L(\alpha_L+\xi)+M\alpha_M, \tag{2.30}$$

along with Eq. (2.16) for $f$, we obtain

$$\begin{aligned} T(\theta',\phi',\rho)=e^{im\phi'}e^{-L\rho/\hbar}\int_0^{2\pi} d\sigma\, C_\theta \\ \times\exp(\rho\sqrt{L^2-M^2}\cos\theta' e^{-i\sigma}/\hbar+iL\sigma/\hbar) \\ \times\int_0^{2\pi} d\tau\, e^{im\tau}\exp\{\rho e^{-i\sigma}\sin\theta' \\ \times[(L-M)e^{i\tau}-(L+M)e^{-i\tau}]/2\hbar\}, \end{aligned} \tag{2.31}$$

where $\sigma=\alpha_L+\xi$, $\tau=\alpha_M-\phi'$, and we have used the periodicity of the integrands to adjust the integration limits. If the second exponential in the integral over $\tau$ is expanded in a power series and the factor $[(L-M)e^{i\tau}-(L+M)e^{-i\tau}]^j$ is further expanded in powers of $\exp(i\tau)$, the integration over $\tau$ is easily performed yielding a Kronecker delta. This reduces the double sum to a single sum that can be immediately related to the power-series expansion for the Bessel function of the first kind $J_m$ [15]. As a consequence, we obtain

$$\begin{aligned} T(\theta',\phi',\rho)=2\pi(-1)^m\left(\frac{L+M}{L-M}\right)^{m/2} e^{im\phi'}e^{-L\rho/\hbar} \\ \times\int_0^{2\pi} d\sigma\, C_\theta\, e^{z\cos\theta'+iL\sigma/\hbar}J_m(z\sin\theta'), \end{aligned} \tag{2.32}$$

where

$$z=\rho\sqrt{L^2-M^2}e^{-i\sigma}/\hbar. \tag{2.33}$$

Applying Eq. (2.27) for $C_\theta$ and the quantization condition for $L=(l+1/2)\hbar$, this result can be expressed as

$$\begin{aligned} T(\theta',\phi',\rho)=2\pi i(-1)^m\left(\frac{L+M}{L-M}\right)^{m/2} \\ \times(L^2-M^2)^{1/4}L^{1/2}e^{im\phi'}e^{-L\rho/\hbar} \\ \times\int_0^{2\pi} d\sigma\, e^{il\sigma}e^{z\cos\theta'}J_m(z\sin\theta'). \end{aligned} \tag{2.34}$$

Expanding the above integrand in terms of Legendre functions via [16–18]

$$e^{z\cos\theta'}J_m(z\sin\theta')=\sum_{j=0}^{\infty}\frac{z^{j+m}}{j!}P_{j+m}^{-m}(\cos\theta'), \tag{2.35}$$

and integrating over $\sigma$ yields a contribution proportional to $\delta_{j,l-m}$ from each term. Thus,

$$\begin{aligned} T(\theta',\phi',\rho)=a_m 4\pi^2 i(-1)^m(\rho/\hbar)^l e^{-L\rho/\hbar}L^{1/2} \\ \times\frac{(L+M)^{l/2+m/2+1/4}(L-M)^{l/2-m/2+1/4}}{(l+|m|)!} \\ \times e^{im\phi'}P_l^{|m|}(\cos\theta'), \end{aligned} \tag{2.36}$$

where the factor $a_m$, defined as 1 if $m<0$ and as $(-1)^m$ if $m>0$, arises from the relation between $P_l^{-m}(x)$ and $P_l^{+m}(x)$ for $-1<x<1$ [18,19]. Finally, applying a standard definition of the spherical harmonics $Y_l^m$ [14], we can express our result for $T$ as

$$T(\theta',\phi',\rho)=\mathcal{M}_{lm}\,\rho^l e^{-L(\rho-1)/\hbar}Y_l^m(\theta',\phi'), \tag{2.37}$$

where

$$\begin{aligned} \mathcal{M}_{lm}=(-1)^m(2\pi)^{5/2}i\hbar \\ \times\left[\frac{(l+m+\frac{1}{2})^{(l+m+1/2)}(l-m+\frac{1}{2})^{(l-m+1/2)}}{(l+m)!(l-m)!}\right]^{1/2} e^{-L/\hbar}. \end{aligned} \tag{2.38}$$

### E. The radial factor

Returning to the three-dimensional wave function $\psi_{nlm}$, we substitute Eq. (2.37) into Eq. (2.28), to find that this function is now in the expected separable form

$$\psi_{nlm}(r',\theta',\phi')=R_{nl}(r')Y_l^m(\theta',\phi'), \tag{2.39}$$

where the radial function $R_{nl}$ is given by

$$R_{nl}(r')=\mathcal{N}_{nl}\int_0^{2\pi} d\alpha_N\, C_r\exp[i(\Phi_r+W_r)/\hbar], \tag{2.40}$$

with $\mathcal{N}_{nl}=\mathcal{N}\mathcal{M}_{lm}$ and

$$\Phi_r=-i\hbar l\ln(r'/r)+iL(r'/r-1)+p_r(r'-r)+i\gamma(r'-r)^2 \tag{2.41}$$

$$=-i\hbar l\ln(r'/r)+\frac{1}{2}(p_r r+iL)\left(\frac{r'^2}{r^2}-1\right). \tag{2.42}$$

The integral in Eq. (2.40) is over the angle variable $\alpha_N$ that determines the radial coordinate $r$ [see Eq. (A34)] along an orbit for which the action variable $N$, conjugate to $\alpha_N$, has the quantized value $(n+3/2)\hbar$ [see Eq. (A25)] or, equivalently, the energy $E$ has the value $(n+3/2)\hbar\omega$ [see Eq. (A20)].

To evaluate the radial function we need an explicit expression for $C_r$ in terms of $\alpha_N$. Applying

$$\frac{\partial p_r}{\partial r}=\left(\frac{\partial p_r}{\partial \alpha_N}\right)\left(\frac{\partial r}{\partial \alpha_N}\right)^{-1} \tag{2.43}$$

as well as Eqs. (A34), (A35), (A40), (A41), and (A30) to Eq. (2.26) yields

$$C_r=\frac{\mu^{3/4}\omega E_0^{1/2}e^{i\pi/4}}{(E-E_0\cos 2\alpha_N)^{5/4}}[(E+L\omega)^{1/2}e^{-i\alpha_N} -(E-L\omega)^{1/2}e^{i\alpha_N}], \tag{2.44}$$

where $E_0$ is given in Eq. (A30). If we define

$$a_\pm=e^{-i\pi/4}[(E+L\omega)^{1/2}e^{i\alpha_N}\mp(E-L\omega)^{1/2}e^{-i\alpha_N}], \tag{2.45}$$

we find that

$$E-E_0\cos 2\alpha_N=\tfrac{1}{2}a_+a_+^*, \tag{2.46}$$

so that we can write

$$C_r=2^{5/4}\mu^{3/4}\omega E_0^{1/2}/(a_+^*a_+^5)^{1/4}. \tag{2.47}$$

The definition in Eq. (2.45) also allows us to express other quantities appearing in $R_{nl}(r')$ in a compact way. The term $\xi$ in Eq. (A52) for $W_r$ can be written as

$$\xi=-\frac{i}{2}\ln\left(\frac{ia_+}{a_+^*}\right), \tag{2.48}$$

and, applying Eq. (2.46) to Eq. (A34), $r$ can be expressed as

$$r=\left(\frac{a_+a_+^*}{2\mu\omega^2}\right)^{1/2}. \tag{2.49}$$

In addition, from Eqs. (A34) and (A35) we have

$$p_r r=(E_0/\omega)\sin 2\alpha_N=i(a_+^*a_-/2\omega-L). \tag{2.50}$$

Substituting these results into Eq. (2.42) and Eq. (A52) for $W_r$, and Eq. (2.40), yields the relatively simple expression

$$R_{nl}(r')=B_1\int_0^{2\pi}d\alpha_N\ \frac{1}{a_+^{l+3/2}} \times\exp\left[-\frac{\mu\omega r'^2}{2\hbar}\left(\frac{a_-}{a_+}\right)\right]\exp iE\alpha_N/\hbar\omega, \tag{2.51}$$

where

$$B_1=\mathcal{N}_{nl}2^{5/4}\mu^{3/4}\omega E_0^{1/2}e^{L/2\hbar}e^{-i\pi L/4\hbar}(2\mu\omega r'^2)^{l/2}. \tag{2.52}$$

To cast this integral in a standard form, we define

$$y=\mu\omega r'^2/\hbar, \tag{2.53}$$

$$\beta=\left(\frac{E+L\omega}{E-L\omega}\right)^{1/2}, \tag{2.54}$$

$$z=-y\beta/(e^{-2i\alpha_N}-\beta), \tag{2.55}$$

which allows us to establish that

$$a_-/a_+=2z/y-1, \tag{2.56}$$

$$a_+=\left[\frac{(E-L\omega)e^{-i\pi/2}\beta y^2}{z(z-y)}\right]^{1/2}, \tag{2.57}$$

$$d\alpha_N=-y\,dz/[2iz(z-y)]. \tag{2.58}$$

Substituting these relations into Eq. (2.51) then yields

$$R_{nl}(r')=B_2\int_C\frac{dz\,e^{-z}z^{k+l+1/2}}{(z-y)^{k+1}}, \tag{2.59}$$

where

$$B_2=B_1\frac{ie^{i\pi L/4\hbar}e^{y/2}}{2y^{l+1/2}\beta^{l+k+3/2}(E-L\omega)^{l/2+3/4}} \tag{2.60}$$

and

$$k=\tfrac{1}{2}(E/\hbar\omega-l-3/2)=\tfrac{1}{2}(n-l)=0,1,2,\ldots \tag{2.61}$$

[see Eqs. (A19) and (A20)]. The contour $\mathcal{C}$ twice encircles $z=y$ in the negative sense as $\alpha_N$ varies from 0 to $2\pi$ and excludes the point $z=0$. However, apart from the sense of motion and the number of circuits, the integral in Eq. (2.59) is a representation of the Laguerre function, [20] so that we can write

$$R_{nl}(r')=-4\pi iB_2e^{-y}y^{l+1/2}L_k^{(l+1/2)}(y) \tag{2.62}$$

$$=\mathcal{N}_{nl}4\pi\hbar^{-(1/4)}(\mu\omega)^{3/4}\left[\frac{[(n-l+1)/2]^{n-l+1}}{[(n+l+2)/2]^{n+l+2}}\right]^{1/4} \times e^{l/2+1/4}e^{i\pi/4}y^{l/2}e^{-(y/2)}L_{(n-l)/2}^{(l+1/2)}(y). \tag{2.63}$$

When we compare this result with the normalized solution of the radial Schrödinger equation for the IHO [21], i.e.,

$$R_{nl}^{qm}(r')=\left(\frac{\mu\omega}{\hbar}\right)^{3/4}\left[\frac{2\,\Gamma[(n-l+2)/2]}{\Gamma[(n+l+3)/2]}\right]^{1/2} \times y^{l/2}e^{-(y/2)}L_{(n-l)/2}^{(l+1/2)}(y), \tag{2.64}$$

we see that the two differ only by normalization. Thus, we can make our expression for $R_{nl}(r')$ identical to the exact result simply by choosing the constant $\mathcal{N}_{nl}$ to have the value:

$$\mathcal{N}_{nl}=\frac{e^{-i\pi/4}}{4\pi\hbar^{1/2}}\left[2\,e^{-l-1/2} \times\frac{\Gamma[(n-l+2)/2]}{\Gamma[(n+l+3)/2]}\frac{[(n+l+2)/2]^{(n+l+2)/2}}{[(n-l+1)/2]^{(n-l+1)/2}}\right]^{1/2}. \tag{2.65}$$

This completes the proof that our classical expression for the IHO wave function, Eq. (2.8), is exact. Additionally, the normalization constant $\mathcal{N}$ appearing there is determined to be

$$\mathcal{N}=\mathcal{N}_{nl}\mathcal{N}_{lm}, \tag{2.66}$$

where

$$\mathcal{N}_{lm}=1/\mathcal{M}_{lm} \tag{2.67}$$

and $\mathcal{M}_{lm}$ is given in Eq. (2.38).

## III. SOME EXTENSIONS

### A. Spherical harmonics and an alternate CE expression

In view of Eqs. (2.29), (2.37), and (2.67), we can express the spherical harmonics in the CE form

$$Y_l^m(\theta',\phi')=\mathcal{N}_{lm}T(\theta',\phi',1) \tag{3.1}$$

$$=\mathcal{N}_{lm}\int_0^{2\pi}d\alpha_L\int_0^{2\pi}d\alpha_M\,C_\theta \times\exp[i(f+W_\theta+W_\phi)/\hbar]. \tag{3.2}$$

Since the three-dimensional wave function is a product of a spherical harmonic and a radial factor [see Eq. (2.39)], we may write $\psi$ as a product of the above expression for $Y_l^m$ and Eq. (2.40) for $R_{nl}$. Thus, applying Eqs. (2.25), (2.66), and (A6) we obtain

$$\psi_{nlm}(r',\theta',\phi')=\mathcal{N}\int C\exp[i(\Phi_r+f+W)/\hbar]d\boldsymbol{\alpha}. \tag{3.3}$$

This expression is clearly a CE formula for the IHO wave function but it is not identical to our original expression, Eq. (2.8), since $\Phi$ is not equal to $\Phi_r+f$ [compare with Eqs. (2.24) and (2.42)]. This illustrates that CE expressions for the IHO wave function are not unique. In fact, Eqs. (2.8) and (3.3) are but two examples of a more general class of IHO CE formulas that can be obtained from Eq. (2.37) with different choices for the quantity $\rho$. Nonuniqueness is a general property of CE expressions.

We can cast Eq. (3.2) in an interesting form if we note, from Eq. (2.24), that $f$ is identical to $\Phi$ when $r'=r$. Since Eq. (2.11) shows that $f$ does not depend on these radial coordinates, we may choose them to have the value of unity. Thus, we obtain

$$Y_l^m(\theta',\phi')=\mathcal{N}_{lm}\int C_\theta\exp[i(\Phi^{(2)}+W^{(2)})/\hbar]d\boldsymbol{\alpha}^{(2)}, \tag{3.4}$$

where the two-dimensional integration is over $(\alpha_L,\alpha_M)$,

$$W^{(2)}=W_\theta+W_\phi, \tag{3.5}$$

$$\Phi^{(2)}=i\gamma|\hat{\mathbf{r}}'-\hat{\mathbf{r}}|^2+\mathbf{p}\cdot(\hat{\mathbf{r}}'-\hat{\mathbf{r}}), \tag{3.6}$$

and $\hat{\mathbf{r}}$ and $\hat{\mathbf{r}}'$ are unit vectors along $\mathbf{r}$ and $\mathbf{r}'$, respectively. Since $f$ is independent of $p_r$, the radial component of the momentum can be chosen to be zero in Eq. (3.4), in which case Eq. (2.23) shows that we must choose

$$\gamma=L/2 \tag{3.7}$$

in Eq. (3.6). This form effectively shows how the radial variables can be eliminated from Eq. (2.8) for the three-dimensional IHO wave function to obtain a CE expression for the spherical harmonics.

### B. Radial wave function for the free particle

We recall that the original expression for the wave function in Cartesian coordinates, Eq. (1.1), is a CE formula not only for the harmonic oscillator but for the free particle too. Here we show that the same is true of our new expression, Eq. (2.8), for the three-dimensional wave function in spherical coordinates. In particular, we demonstrate that, with expected adjustments, our expression for the radial function $R(r')$ is a CE formula for the free particle as well as for the IHO.

As a first step in this direction, we consider transforming the harmonic-oscillator system into that of a free particle by letting the frequency $\omega$ tend to zero while $n$ becomes infinite so that the energy remains constant, i.e., we treat the case

$$\omega\to 0,\ \ E\approx n\hbar\omega\to\hbar\kappa^2/2\mu=\text{const.},\ \ l=\text{const.}, \tag{3.8}$$

where $\kappa$ is a constant wave number. In this limit, it can be shown that the unnormalized IHO radial functions indeed tend to the corresponding free particle functions [22]

$$y^{l/2}e^{-y/2}L_{(n-l)/2}^{l+1/2}(y)\to(4/\pi)^{1/2}(n/2)^{(l+1)/2}j_l(\kappa r'), \tag{3.9}$$

where $y$ is defined as in Eq. (2.53) and $j_l$ are spherical Bessel functions. We can now examine how the function $R_{nl}$ of Eq. (2.63) behaves in this limit. Using $(1+a/n)^n\to e^a$ to simplify the coefficient, we obtain

$$R_{nl}(r')\to\mathcal{N}_{nl}\frac{4}{\hbar}\left(\frac{\pi}{n}\right)^{1/2}(\hbar\kappa)^{3/2}e^{i\pi/4}j_l(\kappa r'), \tag{3.10}$$

so that Eq. (2.40) implies that

$$j_l(\kappa r')=\frac{\hbar e^{-i\pi/4}}{4\pi^{1/2}(\hbar\kappa)^{3/2}}\lim_{n\to\infty}n^{1/2}\int_0^{2\pi}d\alpha_N\,C_r \times\exp[i(\Phi_r+W_r)/\hbar]. \tag{3.11}$$

Since the integrand in Eq. (3.11) is periodic, we can shift the integration limits from $(0,2\pi)$ to $(-\pi/2,3\pi/2)$. Then, since Eqs. (A34) and (A35) show that the IHO undergoes two cycles of radial motion over this interval of $\alpha_N$, we can replace the integral in Eq. (3.11) by twice the integral over the range $(-\pi/2,\pi/2)$. We identify the time $t$ for motion along the classical trajectory by means of the relation

$$\alpha_N=\omega t\to\frac{\hbar\kappa^2}{2\mu\ \ n}t, \tag{3.12}$$

where we have used Eq. (3.8) to express $\omega$ in terms of $n$. In terms of this variable, the integration limits $(-\pi/2<\alpha<\pi/2)$ correspond to $(-\infty<t<\infty)$. Defining an $n$-independent preexponential factor $C_r^{(0)}$ via

$$C_r^{(0)}=\left\{\frac{p_r}{\mu r^2}\left[\frac{2L}{r^2}+i\left(\frac{\partial p_r}{\partial r}-\frac{p_r}{r}\right)\right]\right\}^{1/2} \tag{3.13}$$

$$=\omega^{1/2}C_r=\left(\frac{\hbar\kappa^2}{2\mu\ \ n}\right)^{1/2}C_r, \tag{3.14}$$

Eq. (3.11) becomes

$$j_l(\kappa r')=\frac{e^{-i\pi/4}}{(8\pi\mu\kappa)^{1/2}}\int_{-\infty}^{\infty}C_r^{(0)}\exp[i(\Phi_r+W_r)/\hbar]dt. \tag{3.15}$$

Equation (3.15), which may be verified by explicit evaluation of the integral, expresses the exact radial wave function for the free particle in terms of the radial motion of a classical free particle with energy $E=\hbar^2\kappa^2/2\mu$. The form of this result is identical to that of Eq. (2.40) for the IHO except for the use of the time $t$ instead of the angle $\alpha_N$ as the integration variable. Angle variables are, of course, undefined for unbounded motion, and the time variable is the proper way to parametrize the Lagrangian manifold in such cases. Equations (2.8) and (3.3) are thus shown to be CE expressions for both the IHO and the free particle.

## IV. SEMICLASSICAL FORMS

We have pointed out that the CE expressions for the IHO can serve as semiclassical approximations for various target systems with wave functions obeying boundary conditions appropriate for spherical coordinates. However, for this purpose, the expressions must be cast in forms that do not rely on properties of the action-angle variables that are specific to the IHO. Nevertheless, these expressions must still obey the conditions of Eqs. (1.8)–(1.11), ensuring that the wave function becomes uniformly exact in the classical limit. Thus, before our results can be used as semiclassical approximations for other systems, they must be generalized appropriately. This is accomplished in the present section.

### A. Three-dimensional motion

Equation (2.8) for the wave function $\psi(r',\theta',\phi')$ of the IHO is already expressed in sufficiently general terms to serve as a semiclassical approximation for other regular, three-dimensional systems expressed in terms of spherical coordinates. For such an application we just need to replace the dynamical quantities in Eq. (2.8) with those of the target system. This means that $W$ should be evaluated using

$$W=\int^{\mathbf{r}(\boldsymbol{\alpha})}\mathbf{p}\cdot d\mathbf{r}, \tag{4.1}$$

while $\Phi$ [with $\gamma$ not necessarily constrained by Eq. (2.23)] and $C$ should be calculated using Eqs. (2.7) and (2.9), respectively, at each point $\boldsymbol{\alpha}$ on the three-dimensional Lagrangian manifold corresponding to the state of interest. Finally, the integration over this manifold must be carried out. Practical methods for determining the Lagrangian manifold associated with a quantized state of a multidimensional system, and for performing the necessary integrations, are addressed in Ref. [2].

It is worth noting that, although the factor $|\exp(i\Phi/\hbar)|$ appearing in the integrand of Eq. (2.8) is a Gaussian when expressed as a function of the Cartesian coordinates [see Eq. (2.7)], it is clearly no longer a Gaussian in terms of the individual spherical coordinates [see Eqs. (2.10)–(2.12)]. The validity of Eq. (2.8) as a uniform semiclassical approximation for target systems is due to the satisfaction of the conditions discussed in connection with Eqs. (1.8)–(1.10). Thus, the present case illustrates how non-Gaussian integral expressions can serve as semiclassical approximations.

### B. Anisotropic rigid rotor

We now recast Eq. (3.4) for the spherical harmonics in a form suitable for a semiclassical treatment of regular, anisotropic, rigid rotational motion. This should allow the approximate calculation of wave functions $\chi(\theta',\phi')$ obeying boundary conditions appropriate for angular variables $\theta'$ and $\phi'$.

The classical Hamiltonian for the target system is assumed to be

$$H=\frac{p_\theta^2}{2I}+\frac{p_\phi^2}{2I\sin^2\theta}+V(\theta,\phi), \tag{4.2}$$

where $I$ is the moment of inertia. Basing our treatment upon the free rigid rotor $(V=0)$ as a reference system, we generalize Eq. (3.4) to express the semiclassical wave function as

$$\chi(\theta',\phi')=\mathcal{N}\int C_\theta\exp[i(\Phi^{(2)}+W^{(2)})/\hbar]d\boldsymbol{\alpha}^{(2)}, \tag{4.3}$$

where the integral is over the two-dimensional Lagrangian manifold corresponding to the rotational state of interest:

$$W^{(2)}=\int^{\hat{\mathbf{r}}(\boldsymbol{\alpha}^{(2)})}\hat{\mathbf{p}}\cdot d\hat{\mathbf{r}}, \tag{4.4}$$

where $\hat{\mathbf{r}}$ and $\hat{\mathbf{p}}$ are, respectively, the two-dimensional vectors $(\theta,\phi)$ and $(p_\theta,p_\phi)$;

$$\Phi^{(2)}=i\gamma|\hat{\mathbf{r}}'-\hat{\mathbf{r}}|^2+\hat{\mathbf{p}}\cdot(\hat{\mathbf{r}}'-\hat{\mathbf{r}})=-2i\gamma\{[\cos(\theta'-\theta)-1]+\sin\theta'\sin\theta[\cos(\phi'-\phi)-1]\}+p_\theta\{\sin(\theta'-\theta)+\sin\theta'\cos\theta[\cos(\phi'-\phi)-1]\} \tag{4.5}$$

$$+p_\phi(\sin\theta'/\sin\theta)\sin(\phi'-\phi), \tag{4.6}$$

with $\gamma$ not necessarily restricted by Eq. (3.7);

$$\sin\theta\, C_\theta^2=\det(\mathbf{P}-2i\boldsymbol{\Gamma}\mathbf{X})_{2\times2}, \tag{4.7}$$

where $\mathbf{P}$ and $\mathbf{X}$ are $2\times 2$ matrices as defined in Eqs. (1.6) but applied for variables $\hat{\mathbf{r}},\hat{\mathbf{p}}$ and $\boldsymbol{\alpha}^{(2)}$, and

$$2i\boldsymbol{\Gamma}=\begin{pmatrix} 2i\gamma & p_\phi\cot\theta \\ p_\phi\cot\theta & (2i\gamma\sin\theta - p_\theta\cos\theta)\sin\theta \end{pmatrix}. \quad (4.8)$$

It is easy to verify that the above equations revert to the CE expression for the spherical harmonics, Eq. (3.4), when $V=0$.

### C. Orbital motion

We specialize the result obtained in the previous section to the case where the potential $V=V(\theta)$ is axially symmetric so that the $\phi$ dependence of the wave function can be separated out. We will see how our CE expressions yield a semiclassical treatment for the remaining orbital motion in $\theta$ so that the wave functions obey the appropriate boundary conditions at angles 0 and $\pi$.

Applying the results presented in Appendix B, Eq. (4.3) for the wave function of the present system can be expressed as

$$\chi_{jm}(\theta',\phi')=\mathcal{N}_{jm}\int_0^{2\pi}d\alpha_J\int_0^{2\pi}d\alpha_M\,C_\theta \times\exp[i(\Phi^{(2)}+W_\theta+W_\phi)/\hbar], \quad (4.9)$$

where $J=(j+1/2)\hbar$ and $M=m\hbar$ are the two quantized actions and $\alpha_J$ and $\alpha_M$ are the corresponding angle variables for the system; $W_\theta$ and $W_\phi$ are defined in Eqs. (B6) and (B7); and $\Phi^{(2)}$ may be expressed as in Eq. (4.6) with $p_\phi=M$.

To simplify Eq. (4.7) for the preexponential factor, we apply Eqs. (B21)–(B23) for the elements of $\mathbf{P}$ and $\mathbf{X}$ to obtain

$$C_\theta=\left[\left(\frac{\partial p_\theta}{\partial\alpha_J}-2i\gamma\frac{\partial\theta}{\partial\alpha_J}\right)(p_\theta\cos\theta-2i\gamma\sin\theta) - \frac{M^2\cos^2\theta}{\sin^3\theta}\frac{\partial\theta}{\partial\alpha_J}\right]^{1/2}. \quad (4.10)$$

Using Eqs. (A45), (A46), (A36), and (A37), it is not hard to show that, apart from a phase factor, this result reduces to Eq. (2.27) when $V=0$ and $\gamma=L/2$.

Substituting Eq. (B10) for $W_\phi$ and Eq. (4.6) into Eq.(4.9), we obtain

$$\begin{aligned}\chi_{jm}(\theta',\phi')=\mathcal{N}_{jm}(-1)^m e^{im\phi'}e^{-2\gamma/\hbar} &\times\int_0^{2\pi}d\alpha_J\,C_\theta\exp\{i[p_\theta\sin(\theta'-\theta) \\ &-2i\gamma\cos(\theta'-\theta)+W_\theta]/\hbar\} \\ &\times\exp[-i\sin\theta'(p_\theta\cos\theta-2i\gamma\sin\theta)/\hbar] \\ &\times\int_0^{2\pi}d\tau\,e^{im\tau}\exp\{i\sin\theta'[(p_\theta\cos\theta \\ &-2i\gamma\sin\theta)\cos\tau - M\sin\tau/\sin\theta]/\hbar\},\end{aligned} \quad (4.11)$$

where we have applied Eq. (B22) to express $d\alpha_M=d\phi$, changed variables to $\tau=\phi-\phi'$, and used the periodicity of the integrand to adjust the $\tau$-integration limits. The integral over $\tau$ can be easily recast into a form similar to that in Eq. (2.31) and, repeating the treatment presented there, the result can be expressed in terms of the Bessel function $J_m$. Specifically, we find

$$\chi_{jm}(\theta',\phi')=2\pi(-i)^m e^{-2\gamma/\hbar}e^{im\phi'}S_{jm}(\theta'), \quad (4.12)$$

where

$$\begin{aligned}S_{jm}(\theta')=\mathcal{N}_{jm}\int_0^{2\pi}d\alpha_J\,C_\theta &\times\exp\{i[W_\theta-\cos\theta'(p_\theta\sin\theta+2i\gamma\cos\theta)]/\hbar\} \\ &\times e^{im\tan^{-1}(b/a)}J_m(\sqrt{a^2+b^2}),\end{aligned} \quad (4.13)$$

and we have defined

$$a=(p_\theta\cos\theta-2i\gamma\sin\theta)\sin\theta'/\hbar, \quad (4.14)$$

$$b=-M\sin\theta'/\hbar\sin\theta. \quad (4.15)$$

Once again, in the isotropic case ($V=0$) when $\gamma$ is chosen as $L/2$, it is not hard to show that the above results reduce to the expressions obtained in Sec. II D, namely, Eq. (4.12) becomes equivalent to Eq. (2.34) and $S_{jm}(\theta')$ becomes proportional to the Legendre function $P_l^{|m|}(\cos\theta')$. Thus, Eq. (4.13) is a CE expression when applied to free orbital motion.

However, it is more relevant here to examine the suitability of this expression as a semiclassical approximation for other systems. When $\hbar\to 0$, the argument of the Bessel function in Eq. (4.13) becomes large (except when $\theta'$ is near 0 or $\pi$). Application of an asymptotic expression for the Bessel function [23], casts the integrand as a sum of forms $C_\theta^{(\nu)}\exp(i\Phi_\theta^{(\nu)}/\hbar)$, $\nu=1,2$, where $\Phi_\theta^{(\nu)}$ obeys the condition of Eq. (1.10) and the quantities $\boldsymbol{\Gamma}$ appearing in $C_\theta^{(\nu)}$ are consistent with Eq. (1.11). This ensures that, despite its evident nonGaussian form, Eq. (4.13) can indeed be applied as a semiclassical approximation for more general systems. Fur-

thermore, by substituting the expansion for $J_m$ with small argument [15], it is easy to confirm that

$$S_{jm}(\theta') \sim \text{const.} \times \sin^{|m|}\theta' \tag{4.16}$$

as $\theta' \to 0, \pi$. These are the correct boundary conditions for general orbital motion wave functions, as can be shown by noting that such functions can be expanded in terms of the Legendre functions $P_l^{|m|}(\cos\theta')$, all of which behave as described by Eq. (4.16). Thus, Eq. (4.13) serves as a semiclassical approximation and yields wave functions obeying the proper boundary conditions for orbital motion at $\theta' = 0$ and $\pi$.

### D. Radial motion

Equation (2.40) for $R(r')$ is already in a sufficiently general form to serve as a semiclassical approximation for the radial wave functions of bound states for systems other than the IHO, provided that the quantities $W_r$, $\Phi_r$, and $C_r$ are evaluated for the target systems using Eqs. (A7), (2.41), and (2.26), respectively. In fact, the treatment presented in Sec. III B suggests that Eq. (2.40) can also be used for unbound states if the integration variable is taken as time and the integration limits are replaced by $\pm\infty$. As is apparent from Eqs. (2.41) and (2.42), the resulting approximate wave functions obey the proper boundary conditions for states that are regular at the origin, namely,

$$R_{nl}(r') \sim \text{const.} \times r'^{l}, \tag{4.17}$$

as $r' \to 0$.

It is, nevertheless, worthwhile to further generalize our approximation for $R_{nl}(r')$ a bit. We observe that the quantity $\gamma$, which was chosen to obey Eq. (2.23) in order to make the three-dimensional wave function separate into angular and radial parts, need no longer be restricted in this manner. Even if $\gamma$ is chosen to be an arbitrary function of $\alpha_N$ having a positive real part, a stationary phase evaluation of the integral will still give the correct primitive semiclassical result, and the integral expression for $R(r')$ given in Eq. (2.40) will remain a uniform semiclassical approximation, provided that $C_r$ is suitably redefined.

In a manner similar to Eqs. (1.5) and (2.9), the correct generalized definition of $C_r$ requires that

$$r^2 C_r^2 = i\left(\frac{\partial p_r}{\partial \alpha_N} - 2i\Delta\frac{\partial r}{\partial \alpha_N}\right), \tag{4.18}$$

where the factor $i$ has been introduced for compatibility with Eq. (2.26), and

$$2i\Delta = \left(\frac{\partial^2 \Phi_r}{\partial r'^2}\right)_{r'=r}, \tag{4.19}$$

in analogy with Eq. (1.11). Substituting Eq. (2.41) in Eq. (4.19) yields

$$\Delta = L/2r^2 + \gamma. \tag{4.20}$$

Finally, use of Eqs. (2.20) and (2.21) produces the desired generalization

$$C_r = \left[\frac{p_r}{\mu\omega r^2}\left(\frac{L}{r^2} + 2\gamma + i\frac{\partial p_r}{\partial r}\right)\right]^{1/2}, \tag{4.21}$$

which reduces to Eq. (2.26) when $\gamma$ obeys Eq. (2.23). The treatment given above assumes that the state of interest is bound. For an unbound state, the factor $\omega^{-1/2}$ in Eq. (4.21) should be eliminated.

## V. NUMERICAL EXAMPLES

We now present two examples that illustrate how the expressions presented in Sec. IV can be used as semiclassical approximations.

### A. Perturbed orbital motion

We consider a one-dimensional system characterized by

$$H = \frac{L^2}{2I} + V(\theta) = \frac{p_\theta^2}{2I} + U_m(\theta), \tag{5.1}$$

where

$$U_m(\theta) = \frac{m^2\hbar^2}{2I\sin^2\theta} + V_0\cos\theta. \tag{5.2}$$

The classical Hamiltonian of Eq. (5.1) determines the motion along angle $\theta$ in the cylindrically symmetrical potential $V(\theta) = V_0\cos\theta$, under the condition that the $z$ component of the angular momentum is fixed at $M = m\hbar$. We choose the parameters in $H$ to have the values $\hbar = I = V_0 = 1$.

Semiclassical calculations of the wave functions $S_{jm}(\theta')$ for states with quantum numbers $(j,m)$ are performed using Eq. (4.13) so that our treatment is based on free orbital motion as a reference system. The parameter $\gamma$ in the calculations is rather arbitrarily chosen as $\frac{1}{2}J = \frac{1}{2}(j+\frac{1}{2})\hbar$, in analogy to Eq. (3.7), and no attempt is made to optimize it. The semiclassical wave functions are numerically normalized to satisfy

$$\int_0^\pi |S_{jm}(\theta')|^2 \sin\theta' d\theta' = 1. \tag{5.3}$$

In Fig. 1 we present the semiclassical wave functions for states with $j = 0,1,2$ and compare them with accurate quantum wave functions obtained by diagonalizing the Hamiltonian in a converged basis of Legendre functions. These numerical results confirm that the semiclassical wave functions have no caustic singularities at the classical turning points where $U_m(\theta') = E$, as do the WKB wave functions. Furthermore, the semiclassical wave functions evidently obey the proper boundary conditions at $\theta' = 0$ and $\pi$ described by Eq. (4.16), which imply that

$$S_{jm}(\theta') \sim \text{const.} \times \theta'^{m} \tag{5.4}$$

as $\theta' \to 0$,

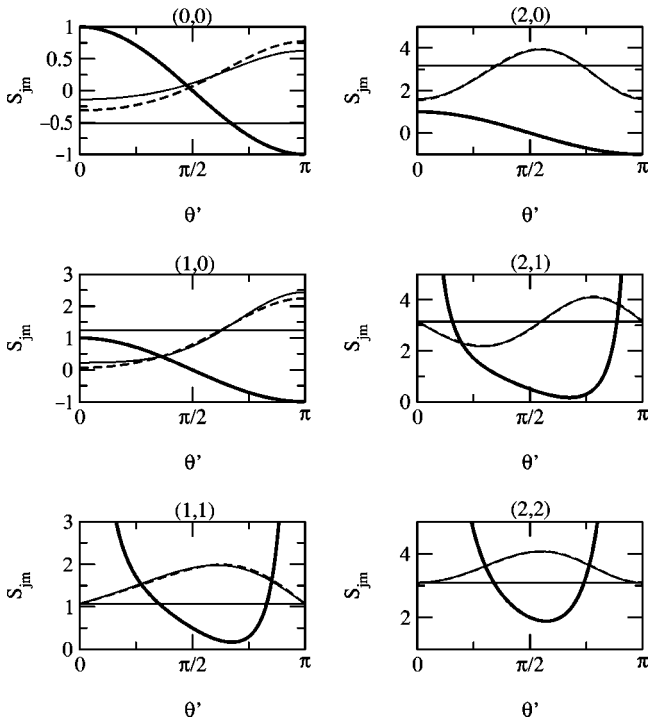


FIG. 1. Wave functions $S_{jm}(\theta')$ with $j=0,1,2$ for perturbed orbital motion. In each subfigure the horizontal line gives the energy of the state, the heavy curve is the effective potential-energy function $U_m(\theta')$ [see Eq. (5.2)], the lighter, solid curve is the semiclassical wave function, and the dashed curve is the quantum-mechanical wave function. The wave-function curves are unscaled but have been shifted vertically so that the value zero coincides with the horizontal energy line. On the scale shown, it is difficult to distinguish between the semiclassical and quantum curves except for states (0,0) and (1,0).

$$S_{jm}(\theta') \sim \text{const.} \times (\theta' - \pi)^m \tag{5.5}$$

as $\theta' \to \pi$ and, in particular,

$$\lim_{\theta' \to 0,\pi} \frac{dS_{jm}(\theta')}{d\theta'} = 0 \tag{5.6}$$

for $m=0$. As discussed above, this behavior is a consequence of the specific form of the integrand in Eq. (4.13). Semiclassical wave functions obeying the correct boundary conditions for this system cannot be obtained using an integral expression containing a single Gaussian function, such as Eq. (1.1).

We note that the semiclassical results are very accurate, even in classically forbidden regions [where $U_m(\theta') > E$], except for states (0,0) and (1,0). These, of course, are very highly quantum-mechanical cases. Indeed, for state (0,0), the classical motion is forbidden for most values of $\theta'$.

Since we are dealing with states that are far from the classical limit, where semiclassical approximations are appropriate, it is likely that the accuracy obtained here is, to some extent, due to the similarity of the target and reference systems. Yet, even for state (0,0), the semiclassical result is closer to the quantum wave function for the perturbed system than to the wave function for the unperturbed system (which would appear as a horizontal line in Fig. 1). In addition, the ''perturbation'' $V_0 \cos\theta'$ is not ''weak'' in the usual sense and the orbital motion of the target system is rather far from free, especially for low $j$. This can be seen in the curves for the potential-energy function $U_m(\theta')$, which would be symmetric about $\pi/2$ for free motion (and identically zero for $m=0$), and in the wave functions, which would be either even or odd with respect to reflection about $\pi/2$ for free motion. Evidently, the target and reference systems need not be very similar for the present semiclassical approximation to achieve good accuracy, even for states that are far from the classical limit.

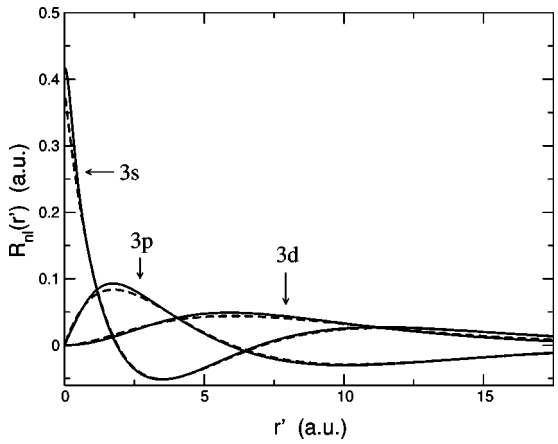


FIG. 2. Radial wave functions $R_{nl}(r)$ for the hydrogen atom with $n=3$. Semiclassical functions (solid curves) and exact functions (broken curves) are shown for $l=0,1,2$.

### B. The hydrogen atom

We next apply our approach to calculate semiclassical radial wave functions $R_{nl}(r')$ of the hydrogen atom. Our calculations are performed using the semiclassical expression, Eq. (2.40), so that we effectively use the IHO as a reference system in our treatment of hydrogen. The semiclassical functions are numerically normalized by requiring

$$\int_0^\infty |R_{nl}(r')|^2 \, r'^2 \, dr' = 1. \tag{5.7}$$

Figure 2 presents the semiclassical radial wave functions for states with principle quantum number $n=3$ and compares them to the exact quantum functions. Once again, the semiclassical results do not display caustic singularities at classical turning points. Furthermore, it is evident that these functions obey the proper boundary conditions for regular wave functions at $r'=0$, as described by Eq. (4.17). This behavior is not to be taken for granted. If, instead of Eq. (2.42), $R_{nl}$ were calculated using a Gaussian form (e.g., based on a second-order expansion of $\Phi_r$ about $r'=r$), the semiclassical radial wave functions would diverge at $r'=0$. The behavior at the origin obtained here is a direct consequence of the specific, non-Gaussian, form of the integrand in Eq. (2.40).

We emphasize that no attempt was made to optimize the parameter $\gamma$ in these calculations. This quantity was defined as in Eq. (2.23) so that the expression for $R_{nl}$ would yield the exact result for the IHO system. However, if we had adjusted $\gamma$ as suggested in Sec. IV D, not only could we have made our semiclassical treatment of the hydrogen atom more accurate, we could have made it *exact*. This conclusion (which can be verified numerically) follows from the property [10] that the CE radial wave functions for the IHO presented here become CE wave functions for the Coulomb problem when $\gamma$ is chosen to be 0. Further discussion of the relationship between the IHO and hydrogenic wave functions will be presented elsewhere [11].

## VI. DISCUSSION

In this paper, we have obtained an expression that describes the exact wave functions of the three-dimensional isotropic harmonic oscillator in terms of the corresponding classical motion. In the process of this derivation, we have also obtained CE formulas for the radial and angular components of this wave function, the latter being the spherical harmonics. By examining a limiting case of the radial factor, we have also derived a CE expression for the radial wave function for the free particle. Furthermore, by simplifying the classical expression for the spherical harmonics (free rigid rotor wave functions) we have effectively obtained a one-dimensional CE formula for the Legendre functions [free orbital motion wave functions—see Eq. (4.13)].

The above CE expressions have also been presented in forms suitable for use as uniform semiclassical approximations for the calculation of wave functions of various target systems, when these are expressed in terms of spherical coordinates. Such semiclassical forms include: Eq. (2.8) for 3D wave functions, Eq. (4.3) for anisotropic rigid rotor wave functions, Eq. (4.13) for orbital motion wave functions, and Eq. (2.40) for wave functions corresponding to either bounded or unbounded radial motion. Unlike Eq. (1.1), the new formulas involve integrands that are not Gaussians in the coordinates $(r',\theta',\phi')$. However, it is precisely this property that allows the resulting wave functions to obey the boundary conditions appropriate for spherical coordinates. Since, despite their non-Gaussian forms, these expressions obey the conditions of Eqs. (1.8)–(1.11), they remain applicable as semiclassical approximations.

We have illustrated the semiclassical applications of our expressions with two numerical examples. An additional example is presented in Ref. [12]. These demonstrate that the resulting wave functions indeed obey the correct boundary conditions, are not affected by caustic singularities at turning points, and are capable of rather good accuracy, even for states with low energies where semiclassical approximations are not expected to be optimal. Although this accuracy is enhanced when the target system is similar to the reference IHO system, it can still be high even when the two systems are rather different.

The expressions obtained here serve as the starting point for the derivation of analytical CE expressions for additional systems. These include the Coulomb system [10], the Morse oscillator, Rosen-Morse oscillator, and the Eckart barrier. Derivations of such results will be presented in a subsequent paper [11].

There is little doubt that the treatment presented here can be applied to obtain analytical CE expressions for higher-dimensional IHO's. Such an extension of this paper would be very worthwhile since it would be expected to provide reference systems for the treatment of wave functions of multiparticle systems that are expressed in terms of hyperspherical coordinates. More importantly, such an extension could yield CE expressions for angular momentum vector coupling coefficients [5,9] and show how to generalize the semiclassical method described here to multiparticle systems characterized by fixed total angular momentum and its $z$ projection.

The present treatment for the IHO and that of Ref. [10] for the Coulomb problem rely on the separability of the respective three-dimensional Hamiltonians in spherical coordinates and (implicitly) the exact solvability of the resulting one-dimensional Schrödinger equations. However, since the Laplace operator in three dimensions is separable in at least 11 coordinate systems [24], the separability and solvability conditions are clearly obeyed for a rather wide variety of additional choices of coordinates and potential-energy functions. In principle, it should be possible to generalize our treatments to such systems to derive nontrivial examples of three-dimensional CE wave functions that are not eigenstates of the angular momentum operator $\hat{L}^2$. Among other benefits, such studies could yield useful reference CE expressions for semiclassical treatments of atoms in external fields, electronic states of diatomic molecules, and other interesting problems.

To place our paper in a somewhat broader context, we recall that wave functions for bound, integrable systems can be expressed semiclassically [9] as $\psi_{\mathbf{n}}(\mathbf{q})=\langle \mathbf{q}|\mathbf{J}\rangle$, where $\mathbf{J}$ are the action variables associated with the quantized state $\mathbf{n}$. It is, therefore, possible to regard the expressions derived here for wave functions as particular examples of semiclassical integral expressions for more general ''inner products'' $\langle \mathbf{x}_2|\mathbf{x}_1\rangle$, where the $\mathbf{x}_i$ denote classical generalized coordinate or momentum variables. Such inner products include propagators in various representations and differential scattering cross sections. When both $\mathbf{x}_1$ and $\mathbf{x}_2$ are action variables, they also include autocorrelation functions, matrix elements, amplitudes for collisional transitions, and amplitudes for spectroscopic transitions between energy eigenstates [9]. The problems addressed in this paper, concerning the correct form of the wave-function expressions for non-Cartesian variables, also arise in these more general cases. We show elsewhere that the non-Gaussian integrands derived here can be used to obtain semiclassical approximations for such more general quantities $\langle \mathbf{x}_2|\mathbf{x}_1\rangle$ in several important instances [12]. Calculations demonstrate that the resulting approximations are of practical value since they are capable of high accuracy and numerical efficiency [12,13].

## ACKNOWLEDGMENTS

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## APPENDIX A: ACTION-ANGLE VARIABLES FOR THE ISOTROPIC HARMONIC OSCILLATOR

Here we review the transformation from spherical coordinates and momenta to action-angle variables for the three-dimensional IHO and present some relations needed for our derivation. Some of these results are similar to those found in Refs. [5] and [25] for the cases of the hydrogen atom and the two-dimensional IHO.

The generating function for the canonical transformation between the variables of interest is Hamilton's characteristic function $W$, considered as a function of the spherical coordinates and the action variables. This function can be obtained by solving the Hamilton-Jacobi equation, Eq. (1.2), in spherical coordinates. Since the classical Hamiltonian for the IHO is given by

$$H=\frac{1}{2\mu}\left(p_r^2+\frac{p_\theta^2}{r^2}+\frac{p_\phi^2}{r^2\sin^2\theta}\right)+\frac{1}{2}\mu\omega^2r^2, \tag{A1}$$

the Hamilton-Jacobi equation has the form

$$\frac{1}{2\mu}\left[\left(\frac{\partial W}{\partial r}\right)^2+\frac{1}{r^2}\left(\frac{\partial W}{\partial\theta}\right)^2+\frac{1}{r^2\sin^2\theta}\left(\frac{\partial W}{\partial\phi}\right)^2\right]+\frac{1}{2}\mu\omega^2r^2=E. \tag{A2}$$

This may be solved by separation of variables. Thus, introducing separation constants $M$ and $L$, we can replace Eq. (A2) by the three equations:

$$p_\phi=\partial W/\partial\phi=M, \tag{A3}$$

$$p_\theta^2+M^2/\sin^2\theta=(\partial W/\partial\theta)^2+M^2/\sin^2\theta=L^2, \tag{A4}$$

and

$$\frac{1}{2\mu}\left(p_r^2+\frac{L^2}{r^2}\right)+\frac{1}{2}\mu\omega^2r^2=\frac{1}{2\mu}\left[\left(\frac{\partial W}{\partial r}\right)^2+\frac{L^2}{r^2}\right]+\frac{1}{2}\mu\omega^2r^2=E. \tag{A5}$$

It is clear that a solution to these equations can be written as

$$W=W_r+W_\theta+W_\phi, \tag{A6}$$

where

$$W_r=\int_{r_-}^{r}p_r\,dr, \tag{A7}$$

$$W_\theta=\int_{\theta_-}^{\theta}p_\theta\,d\theta, \tag{A8}$$

$$W_\phi=\int_{-\pi}^{\phi}p_\phi\,d\phi, \tag{A9}$$

and

$$p_\phi=M, \tag{A10}$$

$$p_\theta(\theta)=\pm(L^2-M^2/\sin^2\theta)^{1/2}, \tag{A11}$$

$$p_r(r)=\pm[2\mu E-(L/r)^2-(\mu\omega r)^2]^{1/2}. \tag{A12}$$

The quantities $\theta_-$ and $r_-$ in Eqs. (A7) and (A8) are, respectively, the lower turning points for motion in the $\theta$ and $r$ coordinates. These choices for lower integration limits are arbitrary but convenient.

We now define the three action variables

$$I_\phi=\frac{1}{2\pi}\oint p_\phi\,d\phi,$$

$$I_\theta=\frac{1}{2\pi}\oint p_\theta\,d\theta,$$

$$I_r=\frac{1}{2\pi}\oint p_r\,dr. \tag{A13}$$

Substituting Eqs. (A10)–(A12), these integrals may be evaluated [5] to obtain

$$I_\phi=M,$$

$$I_\theta=L-|M|,$$

$$I_r=E/2\omega-L/2. \tag{A14}$$

However, applying the appropriate quantization conditions [5] to the actions also gives

$$I_\phi=m\hbar,$$

$$I_\theta=(v+1/2)\hbar,$$

$$I_r=(k+1/2)\hbar, \tag{A15}$$

where the quantum numbers can have the values $m=\pm1, \pm2,\ldots$ and $v,k=0,1,2,\ldots$. Thus, comparison of Eqs. (A14) and (A15) implies that

$$M=m\hbar, \tag{A16}$$

$$L=(v+|m|+1/2)\hbar, \tag{A17}$$

$$E=(v+|m|+2k+3/2)\hbar\omega. \tag{A18}$$

We now introduce new quantum numbers defined by

$$l=v+|m|,$$

$$n=l+2k, \tag{A19}$$

so that we can express Eqs. (A16)–(A18) as

$$E=(n+3/2)\hbar\omega, \tag{A20}$$

$$L=(l+1/2)\hbar, \tag{A21}$$

$$M=m\hbar, \tag{A22}$$

where $l=0,1,2,\ldots,$ $n=l,l+2,l+4,\ldots,$ and $m=-l,-l+1,\ldots,l$.

At this point we define

$$N=2I_r+L, \tag{A23}$$

so that

$$E=N\omega \tag{A24}$$

and

$$N=(n+3/2)\hbar, \tag{A25}$$

and consider $N$, $L$, and $M$ as new action variables. Accordingly, we regard Hamilton's characteristic function as having the functional dependence $W=W(r,\theta,\phi;N,L,M)$. This allows us to determine the angle variables $(\alpha_N,\alpha_L,\alpha_M)$, conjugate to the new actions, by differentiating $W$ with respect to the $(N,L,M)$. Thus, applying Eqs. (A6)–(A12), we obtain

$$\begin{aligned}\alpha_N&=\frac{\partial W}{\partial N},\\ &=\int_{r_-}^{r}\frac{\partial p_r}{\partial N}dr,\\ &=\mu\omega\int_{r_-}^{r}\frac{dr}{p_r},\end{aligned} \tag{A26}$$

$$\begin{aligned}\alpha_L&=\frac{\partial W}{\partial L},\\ &=\int_{r_-}^{r}\frac{\partial p_r}{\partial L}dr+\int_{\theta_-}^{\theta}\frac{\partial p_\theta}{\partial L}d\theta,\\ &=-L\int_{r_-}^{r}\frac{dr}{r^2p_r}dr+L\int_{\theta_-}^{\theta}\frac{d\theta}{(L^2-M^2/\sin^2\theta)^{1/2}},\end{aligned} \tag{A27}$$

$$\begin{aligned}\alpha_M&=\frac{\partial W}{\partial M},\\ &=\int_{\theta_-}^{\theta}\frac{\partial p_\theta}{\partial M}d\theta+\int_{-\pi}^{\phi}\frac{\partial p_\phi}{\partial M}d\phi,\\ &=-M\int_{\theta_-}^{\theta}\frac{d\theta}{(\sin^2\theta)(L^2-M^2/\sin^2\theta)^{1/2}}+\phi+\pi.\end{aligned} \tag{A28}$$

These integrals can be evaluated [5] to yield

$$\alpha_N=\frac{1}{2}\cos^{-1}\left(\frac{E-\mu\omega^2r^2}{E_0}\right), \tag{A29}$$

with

$$\begin{aligned}E_0&=(E^2-L^2\omega^2)^{1/2},\\ &=(N^2-L^2)^{1/2}\omega;\end{aligned} \tag{A30}$$

as well as

$$\alpha_L=\cos^{-1}\left(\frac{L\cos\theta}{\sqrt{L^2-M^2}}\right)-\xi(N,L), \tag{A31}$$

with [5,26]

$$\begin{aligned}\xi(N,L)&=L\int_{r_-}^{r}\frac{dr}{r^2p_r}dr,\\ &=\frac{1}{2}\cos^{-1}\left(\frac{L^2-\mu Er^2}{\mu E_0r^2}\right)\end{aligned} \tag{A32}$$

and

$$\alpha_M=\phi+\pi-M\tan^{-1}\left(\sqrt{\frac{L^2}{M^2}-\frac{1}{\sin^2\theta}}\tan\theta\right). \tag{A33}$$

Inverting these equations and applying Eqs. (A10)–(A12), we have

$$r=\left(\frac{1}{\mu\omega^2}\right)^{1/2}(E-E_0\cos 2\alpha_N)^{1/2}, \tag{A34}$$

$$p_r=\frac{\mu^{1/2}E_0\sin 2\alpha_N}{(E-E_0\cos 2\alpha_N)^{1/2}}, \tag{A35}$$

$$\theta=\cos^{-1}[(1-M^2/L^2)^{1/2}\cos(\alpha_L+\xi)], \tag{A36}$$

$$p_\theta=\frac{L(L^2-M^2)^{1/2}\sin(\alpha_L+\xi)}{[L^2\sin^2(\alpha_L+\xi)+M^2\cos^2(\alpha_L+\xi)]^{1/2}}, \tag{A37}$$

$$\phi=\alpha_M-\pi+\tan^{-1}[(L/M)\tan(\alpha_L+\xi)], \tag{A38}$$

$$p_\phi=M. \tag{A39}$$

These results allow us to evaluate the following derivatives needed for the calculation of **P**, **X**, and $C$:

$$\frac{\partial r}{\partial\alpha_N}=\frac{E_0\sin 2\alpha_N}{\mu^{1/2}\omega(E-E_0\cos 2\alpha_N)^{1/2}}, \tag{A40}$$

$$\frac{\partial p_r}{\partial\alpha_N}=-\mu^{1/2}E_0\frac{E_0(1+\cos^2 2\alpha_N)-2E\cos 2\alpha_N}{(E-E_0\cos 2\alpha_N)^{3/2}}, \tag{A41}$$

$$\frac{\partial\theta}{\partial\alpha_N}=\frac{p_\theta}{\mu\omega r^2}, \tag{A42}$$

$$\frac{\partial p_\theta}{\partial\alpha_N}=\frac{M^2\cos\theta}{\mu\omega r^2\sin^3\theta}, \tag{A43}$$

$$\frac{\partial \phi}{\partial \alpha_N} = \frac{M}{\mu \omega r^2 \sin^2 \theta}, \tag{A44}$$

$$\frac{\partial \theta}{\partial \alpha_L} = p_\theta / L, \tag{A45}$$

$$\frac{\partial p_\theta}{\partial \alpha_L} = \frac{M^2 \cos \theta}{L \sin^3 \theta}, \tag{A46}$$

$$\frac{\partial \phi}{\partial \alpha_L} = \frac{M}{L \sin^2 \theta}, \tag{A47}$$

$$\frac{\partial \phi}{\partial \alpha_M} = 1. \tag{A48}$$

The remaining derivatives of momenta and coordinates with respect to the angle variables are zero.

Finally, explicit expressions for $W$ are needed as a functions of the angle variables. Substituting Eq. (A10) for $p_\phi$ into Eq. (A9) and using Eq. (A38) we immediately obtain

$$W_\phi = M(\phi + \pi),$$

$$= M\{\alpha_M + \tan^{-1}[(L/M)\tan(\alpha_L + \xi)]\}. \tag{A49}$$

Substituting Eqs. (A11) and (A45) into Eq. (A8), we obtain

$$W_\theta = L(L^2 - M^2)^{1/2} \int_{\alpha_L(\theta_-)}^{\alpha_L} \times \frac{\sin^2(\alpha_L + \xi)}{L^2 \sin^2(\alpha_L + \xi) + M^2 \cos^2(\alpha_L + \xi)} d\alpha_L,$$

$$= L(\alpha_L + \xi) - M \tan^{-1}[(L/M)\tan(\alpha_L + \xi)], \tag{A50}$$

where we have used the tabulated expression for the integral in the first line [27] and recognized that $\cos\theta_- = (1 - M^2/L^2)^{1/2}$ [5]. The quantity $W_r$ is most easily evaluated by substituting Eq. (A12) into Eq. (A7) and transforming to the variable $z = r^2$. This integral is again tabulated [28] and, using $r_- = [(E - E_0)/\mu\omega^2]^{1/2}$ together with Eqs. (A34) and (A35), yields

$$W_r = \frac{E}{\omega}\alpha_N + \frac{E_0}{2\omega}\sin 2\alpha_N - \frac{L}{2}\cos^{-1}\left(\frac{E\cos 2\alpha_N - E_0}{E - E_0 \cos 2\alpha_N}\right). \tag{A51}$$

In view of Eqs. (A32), (A30), and (A34), this result can be expressed more compactly as

$$W_r = \frac{E}{\omega}\alpha_N + \frac{E_0}{2\omega}\sin 2\alpha_N - L\xi. \tag{A52}$$

Thus, combining Eqs. (A6), (A23), (A49), and (A50), we see that

$$W = N\alpha_N + L\alpha_L + M\alpha_M + \tfrac{1}{2}(N^2 - L^2)^{1/2}\sin 2\alpha_N. \tag{A53}$$

## APPENDIX B: ACTION-ANGLE VARIABLES FOR ROTATION IN AN AXIALLY SYMMETRIC POTENTIAL

As in the previous case, the transformation from spherical to action-angle variables is again here generated by Hamilton's characteristic function $W$, which may be obtained by solving the Hamilton-Jacobi equation in spherical coordinates. Since the classical Hamiltonian for the present system is given by

$$H = \frac{p_\theta^2}{2I} + \frac{p_\phi^2}{2I \sin^2 \theta} + V(\theta), \tag{B1}$$

where $I$ is the moment of inertia, the Hamilton-Jacobi equation is

$$\left(\frac{\partial W}{\partial \theta}\right)^2 + \frac{1}{\sin^2\theta}\left(\frac{\partial W}{\partial \phi}\right)^2 + 2I[V(\theta) - E] = 0. \tag{B2}$$

Introducing the separation constant $M$, we can replace this equation by two independent equations:

$$p_\phi = \partial W/\partial\phi = M \tag{B3}$$

and

$$\left(\frac{\partial W}{\partial \theta}\right)^2 = 2I[E - V(\theta)] - \frac{M^2}{\sin^2\theta}. \tag{B4}$$

A solution can be found in the form

$$W = W_\theta + W_\phi, \tag{B5}$$

where

$$W_\theta = \int_{\theta_-}^{\theta} p_\theta \, d\theta, \tag{B6}$$

$$W_\phi = \int_{-\pi}^{\phi} p_\phi \, d\phi, \tag{B7}$$

and

$$p_\phi = M, \tag{B8}$$

$$p_\theta(\theta) = \pm[2I(E - V) - M^2/\sin^2\theta]^{1/2}. \tag{B9}$$

Clearly,

$$W_\phi = M(\phi + \pi). \tag{B10}$$

The action variables may be chosen to be

$$\frac{1}{2\pi}\oint p_\phi \, d\phi = M, \tag{B11}$$

$$\frac{1}{2\pi}\oint p_\theta \, d\theta + |M| = J, \tag{B12}$$

and the usual semiclassical quantization rules yield [5]

$$M = m\hbar, \tag{B13}$$

$$J=(j+\tfrac{1}{2})\hbar, \tag{B14}$$

where $j=0,1,2,\ldots$ and $m=0,\pm 1,\pm 2,\ldots,\pm j$.

Treating the functional dependence of $W$ to be $W(J,M;\theta,\phi)$, the angle variables are obtained as

$$\begin{aligned}\alpha_J&=\frac{\partial W}{\partial J},\\ &=\int_{\theta_-}^{\theta}\frac{\partial p_\theta}{\partial J}d\theta,\\ &=\int_{\theta_-}^{\theta}\frac{\partial p_\theta}{\partial E}\Omega\, d\theta,\\ &=I\Omega\int_{\theta_-}^{\theta} d_\theta/p_\theta \end{aligned}\tag{B15}$$

and

$$\begin{aligned}\alpha_M&=\frac{\partial W}{\partial M},\\ &=\phi+\pi+\int_{\theta_-}^{\theta}\frac{\partial p_\theta}{\partial M}d\theta,\\ &=\phi+\pi-M\int_{\theta_-}^{\theta} d\theta/p_\theta\sin^2\theta, \end{aligned}\tag{B16}$$

where

$$\Omega(J)=\partial E(J)/\partial J. \tag{B17}$$

These equations may be inverted to show that

$$\theta=\theta(\alpha_J), \tag{B18}$$

$$\phi=\alpha_M+\zeta(\alpha_J), \tag{B19}$$

where

$$\zeta(\alpha_J)=M\int_{\theta_-}^{\theta} d\theta/p_\theta\sin^2\theta-\pi. \tag{B20}$$

These allow us to establish the following relations that are needed to evaluate the preexponential factor $C_\theta$:

$$\frac{\partial\phi}{\partial\alpha_J}=\frac{M}{p_\theta\sin^2\theta}\frac{\partial\theta}{\partial\alpha_J}, \tag{B21}$$

$$\frac{\partial\phi}{\partial\alpha_M}=1, \tag{B22}$$

and

$$\frac{\partial\theta}{\partial\alpha_M}=\frac{\partial p_\theta}{\partial\alpha_M}=\frac{\partial p_\phi}{\partial\alpha_J}=\frac{\partial p_\phi}{\partial\alpha_M}=0. \tag{B23}$$


[1] D. Zor and K. G. Kay, Phys. Rev. Lett. **76**, 1990 (1996).
[2] M. Madhusoodanan and K. G. Kay, J. Chem. Phys. **109**, 2644 (1998).
[3] V. P. Maslov and M. V. Fedoriouk, *Semi-Classical Approximation in Quantum Mechanics* (Reidel, Boston, 1981).
[4] J. B. Delos, Adv. Chem. Phys. **65**, 161 (1986).
[5] M. S. Child, *Semiclassical Mechanics with Molecular Applications* (Clarendon, Oxford, 1991).
[6] E. J. Heller, J. Chem. Phys. **62**, 1544 (1975); **65**, 4794 (1976).
[7] E. J. Heller, J. Chem. Phys. **75**, 2923 (1981); M. J. Davis and E. J. Heller, *ibid.* **75**, 3916 (1981); N. DeLeon and E. J. Heller, *ibid.* **78**, 4005 (1983); **81**, 5957 (1984).
[8] G. van de Sand and J. M. Rost, Phys. Rev. A **59**, R1723 (1999).
[9] W. H. Miller, Adv. Chem. Phys. **25**, 69 (1974).
[10] K. G. Kay, Phys. Rev. Lett. **83**, 5190 (1999).
[11] K. G. Kay (unpublished).
[12] K. G. Kay, J. Phys. Chem. (to be published).
[13] Y. Elran and K. G. Kay, J. Chem. Phys. (to be published).
[14] A. Messiah, *Quantum Mechanics* (Wiley, New York, 1966).
[15] *Handbook of Mathematical Functions*, edited by M. Abramowitz and I. A. Stegun (National Bureau of Standards, Washington, DC, 1996), Eq. (9.1.10).
[16] Reference [15], Eq. (22.9.5).
[17] A. Erdelyi, W. Magnus, F. Oberhettinger, and F. G. Tricomi, *Higher Transcendental Functions* (McGraw-Hill, New York, 1953), Vol. 1, p. 175, Eq. (4).
[18] Reference [17], p. 143, Eq. (5).
[19] Reference [17], p. 140, Eq. (5).
[20] Reference [15], Eq. (22.10.7).
[21] See, e.g., A. S. Davydov, *Quantum Mechanics* (NEO, Ann Arbor, 1966), p. 135.
[22] Reference [15], Eqs. (22.15.2) and (10.1.1).
[23] Reference [15], Eq. (9.2.1).
[24] P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill, New York, 1953), Part I, pp. 655–665.
[25] M. Born, *The Mechanics of the Atom* (Ungar, New York, 1960).
[26] I. S. Gradshteyn and I. M. Ryzhik, *Table of Integrals Series and Products* (Academic, New York, 1965), Eq. (2.266).
[27] Reference [26], Eq. (2.559.3).
[28] Reference [26], Eq. (2.267.1).