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QUASICLASSICAL SELECTION OF INITIAL COORDINATES AND MOMENTA FOR A ROTATING MORSE OSCILLATOR

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Quasiclassical selection of initial coordinates and momenta for a rotating Morse oscillator

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The classical orbits of a rotating Morse oscillator are calculated by means of Hamilton–Jacoby theory after truncating the Hamiltonian to permit analytical solution. Except at very high J, the approximate analytic orbit for the radial coordinate is in good agreement with that obtained by numerical integration of the exact equations of motion. Bohr quantization gives an expression for the rotation–vibration energy correct through quadratic terms in $(v+\frac{1}{2})$ and $J(J+1)$, where v and J are the vibrational and rotational quantum numbers, respectively. The principal result is an analytic prescription for obtaining values of the coordinates and momenta, given v, J, and a set of random numbers, that facilitates properly weighted quasiclassical selection of initial states of diatomic molecules in trajectory calculations.

I. INTRODUCTION

The use of classical trajectory calculations as a theoretical tool for studying the molecular dynamics of diatomic molecules[1] has revived an interest in the classical mechanics of the Morse oscillator.[2] Slater[3] has given an expression for the classical orbit of a nonrotating Morse oscillator from which the probability density for the displacement can be easily obtained. Rankin and Miller[4] have solved the nonrotating Morse oscillator problem by means of action-angle variables. In this paper, we derive several useful classical formulas for a rotating Morse oscillator whose Hamiltonian has been truncated to allow analytic solution of the dynamical problem. The accuracy of the orbit calculated from the truncated Hamiltonian is assessed by comparison with the results of a numerical integration of the exact equations of motion. We apply the rules of Bohr quantization to obtain quasiclassical formulas, namely classical expressions for a Morse oscillator with a quantum-mechanically allowed internal energy and rotational angular momentum. Finally, we give an easily programmed prescription for randomly selecting the initial coordinates and momenta of a rotating diatomic molecule in a quasiclassical trajectory calculation.[5]

II. EXPANSION OF THE CLASSICAL HAMILTONIAN

The classical Hamiltonian for a rotating Morse oscillator with angular momentum L and reduced mass μ is[2]

$$H = \frac{p_r^2}{2\mu} + \frac{L^2}{2\mu r^2} + D(1 - e^{-\alpha(r-r_e)})^2 , \qquad (1)$$

where D, α, and r_e are the usual Morse parameters.[2] A natural variable is

$$\xi = e^{-\alpha(r-r_e)} . \qquad (2)$$

Expanding $1/r^2$ about $r = r_e$ is equivalent to expanding about $\xi = 1$:

$$\frac{1}{r^2} = \frac{1}{r_e^2} + \frac{2}{\alpha r_e^3}(\xi - 1) - \frac{1}{\alpha r_e^3}\left(1 - \frac{3}{\alpha r_e}\right)(\xi - 1)^2 + \cdots . \qquad (3)$$

Neglecting powers of $\xi - 1$ greater than the second, we have for the Hamiltonian

$$H = \frac{p_r^2}{2\mu} + \frac{L^2}{2\mu r_e^2} + \frac{L^2}{\alpha\mu r_e^3}(\xi - 1) + \left[D - \frac{L^2}{2\alpha\mu r_e^3}\left(1 - \frac{3}{\alpha r_e}\right)\right] \times (\xi - 1)^2 . \qquad (4)$$

Solving for p_r at a fixed energy E gives

$$p_r = \mu\dot{r} = \pm(2\mu)^{1/2}(a + b\xi + c\xi^2)^{1/2} , \qquad (5)$$

where

$$a = E - D - AL^2,$$
$$b = 2D - BL^2,$$
$$c = -D + CL^2,$$
$$A = \frac{1}{2\mu r_e^2}\left[1 - \frac{3}{\alpha r_e}\left(1 - \frac{1}{\alpha r_e}\right)\right] , \qquad (6)$$
$$B = \frac{2}{\mu\alpha r_e^3}\left(1 - \frac{3}{2\alpha r_e}\right) ,$$
$$C = \frac{1}{2\mu\alpha r_e^3}\left(1 - \frac{3}{\alpha r_e}\right) .$$

III. TRANSFORMATION TO ACTION-ANGLE VARIABLES AND SOLUTION OF THE EQUATIONS OF MOTION

To solve the dynamical problem, we transform to a system of conjugate variables (Q_j, P_j) in which the momenta P_j are constants of the motion. Since H is independent of time, the generator of such a transformation is Hamilton's characteristic function,[6,7] namely

$$W(r, \theta, \phi; P_1, P_2, P_3) = W_r + W_\theta + W_\phi , \qquad (7)$$

where

$$W_r = \int p_r \, dr = -\frac{(2\mu)^{1/2}}{\alpha} \int (a + b\xi + c\xi^2)^{1/2} \frac{d\xi}{\xi} , \quad (8a)$$

$$W_\theta = \int p_\theta \, d\theta = \int \left(L^2 - \frac{M^2}{\sin^2\theta} \right)^{1/2} d\theta , \quad (8b)$$

$$W_\phi = \int p_\phi \, d\phi = M\phi . \quad (8c)$$

The new coordinates are given by

$$Q_i = \frac{\partial W}{\partial P_i} . \quad (9)$$

We therefore need the derivatives

$$\frac{\partial W_r}{\partial a} = -\left(\frac{\mu}{2}\right)^{1/2} \frac{1}{\alpha} \frac{1}{\sqrt{-a}} \arcsin\left(\frac{b\xi + 2a}{\xi\sqrt{b^2 - 4ac}}\right) , \quad (10a)$$

$$\frac{\partial W_r}{\partial b} = \left(\frac{\mu}{2}\right)^{1/2} \frac{1}{\alpha} \frac{1}{\sqrt{-c}} \arcsin\left(\frac{2c\xi + b}{\sqrt{b^2 - 4ac}}\right) , \quad (10b)$$

$$\frac{\partial W_r}{\partial c} = \left(\frac{\mu}{2}\right)^{1/2} \frac{1}{\alpha} \frac{b}{2(-c)^{3/2}} \arcsin\left(\frac{2c\xi + b}{\sqrt{b^2 - 4ac}}\right) - \frac{1}{2c\alpha} |p_r| , \quad (10c)$$

$$\frac{\partial W_\theta}{\partial L} \equiv q_L = \arccos\left(\frac{\cos\theta}{\sqrt{1 - \lambda^2}}\right) , \quad (11a)$$

$$\frac{\partial W_\theta}{\partial M} = -\arccos\left(\frac{\lambda \cot\theta}{\sqrt{1 - \lambda^2}}\right) , \quad (11b)$$

$$\frac{\partial W_\phi}{\partial M} = \phi , \quad (12)$$

where

$$\lambda \equiv M/L . \quad (13)$$

We take as the conserved momenta three quantities that are proportional to the action variables,

$$P_1 \equiv N = \frac{1}{2\pi} \oint p_r \, dr = \frac{1}{\pi} \frac{(2\mu)^{1/2}}{\alpha} \int_{\xi_<}^{\xi_>} (a + b\xi + c\xi^2)^{1/2} \frac{d\xi}{\xi}$$
$$= \frac{(2\mu)^{1/2}}{\alpha} \left(\frac{b}{2\sqrt{-c}} - \sqrt{-a} \right) , \quad (14)$$

$$P_2 \equiv L = \left(p_\theta^2 + \frac{p_\phi^2}{\sin^2\theta} \right)^{1/2} , \quad (15)$$

$$P_3 \equiv M = p_\phi , \quad (16)$$

where $\xi_>$, $\xi_<$ are the roots of $p_r = 0$,

$$\xi_> = (2c)^{-1} (-b - \sqrt{b^2 - 4ac}) , \quad (17a)$$

and

$$\xi_< = (2c)^{-1} (-b + \sqrt{b - 4ac}) . \quad (17b)$$

From Eqs. (9)–(17) we obtain the equations of transformation to the new variables,

$$Q_N = \left(\frac{\partial W}{\partial N}\right)_{L,M} = \left(\frac{\partial W_r}{\partial a}\right)_{b,c} \Big/ \left(\frac{\partial N}{\partial a}\right)_{b,c} = -\arcsin\left(\frac{b\xi + 2a}{\xi\sqrt{b^2 - 4ac}}\right) , \quad (18)$$

$$Q_L = \left(\frac{\partial W}{\partial L}\right)_{N,M} = -\left(\frac{\partial W_r}{\partial a}\right)_{b,c} \left[\left(\frac{\partial N}{\partial b}\right)_{a,c} \frac{db}{dL} + \left(\frac{\partial N}{\partial c}\right)_{a,b} \frac{dc}{dL}\right] \Big/ \left(\frac{\partial N}{\partial a}\right)_{b,c}$$
$$+ \left(\frac{\partial W_r}{\partial b}\right)_{a,c} \frac{db}{dL} + \left(\frac{\partial W_r}{\partial c}\right)_{a,b} \frac{dc}{dL} + \left(\frac{\partial W_\theta}{\partial L}\right)_M$$

$$= q_L - L\left\{\left(\frac{\mu}{2}\right)^{1/2} \frac{1}{\alpha} \frac{1}{\sqrt{-c}} \left(\frac{bC}{c} + 2B\right) \left[\arcsin\left(\frac{b\xi + 2a}{\xi\sqrt{b^2 - 4ac}}\right)\right.\right.$$
$$\left.\left. + \arcsin\left(\frac{2c\xi + b}{\sqrt{b^2 - 4ac}}\right)\right] + \frac{C}{c\alpha} |p_r|\right\} , \quad (19)$$

$$Q_M = \left(\frac{\partial W}{\partial M}\right)_{N,L} = \left(\frac{\partial W_\theta}{\partial M}\right)_L + \frac{\partial W_\phi}{\partial M} = \phi - \arccos\left(\frac{\lambda \cot\theta}{\sqrt{1 - \lambda^2}}\right) . \quad (20)$$

In Eqs. (18)–(20), the old coordinates ξ, θ, ϕ are held constant in all the differentiations. The time derivatives of the new coordinates are given by Hamiltonian's equation,

$$\dot{Q}_i = \frac{\partial H}{\partial P_i} . \quad (21)$$

Thus we find that Q_M is constant and that Q_N and Q_L are proportional to the time:

$$\dot{Q}_N = \left(\frac{\partial E}{\partial N}\right)_{L,M} = \alpha\left(\frac{2}{\mu}\right)^{1/2} \sqrt{-a} \equiv \omega_N , \quad (22a)$$

$$\dot{Q}_L = \left(\frac{\partial E}{\partial L}\right)_{N,M} = 2L\left[A + \left(\frac{a}{c}\right)^{1/2}\left(B + \frac{b}{2c} C\right)\right] \equiv \omega_L , \quad (22b)$$

$$\dot{Q}_M = \left(\frac{\partial E}{\partial M}\right)_{N,L} \equiv \omega_M = 0 . \quad (22c)$$

Solution of the equation of motion thus takes the simple form

$$Q_N(t) = \delta_N + \omega_N t , \quad (23a)$$

$$Q_L(t) = \delta_L + \omega_L t , \quad (23b)$$

$$Q_M(t) = \delta_M . \quad (23c)$$

The radial orbit is easily obtained from Eqs. (18) and (23a):

$$r(t) = r_e - \frac{1}{\alpha} \ln\{(-2a)[b + \sqrt{b^2 - 4ac} \sin(\omega_N t + \delta_N)]^{-1}\} . \quad (24)$$

The orbit for θ is obtained from Eqs. (11a), (19), and (23b):

$$\theta(t) = \arccos[\sqrt{1 - \lambda^2} \cos(\omega_L t + \delta_L + L\Delta_L)] , \quad (25)$$

where

$$\Delta_L \equiv \left(\frac{\mu}{2}\right)^{1/2} \frac{1}{\alpha} \frac{1}{\sqrt{-c}} \left(\frac{bC}{c} + 2B\right) \left[\arcsin\left(\frac{b\xi + 2a}{\xi\sqrt{b^2 - 4ac}}\right)\right.$$
$$\left. + \arcsin\left(\frac{2c\xi + b}{\sqrt{b^2 - 4ac}}\right)\right] + \frac{C}{c\alpha} (2\mu)^{1/2} (a + b\xi + c\xi^2)^{1/2} , \quad (26)$$

and

$$\xi = (-2a)[b + \sqrt{b^2 - 4ac} \sin(\omega_N t + \delta_N)]^{-1} . \quad (27)$$

Finally, from Eqs. (20) and (23c) we obtain for the orbit of ϕ

$$\phi(t) = \delta_N + \arccos\left(\frac{\lambda \cot[\theta(t)]}{\sqrt{1 - \lambda^2}}\right) . \quad (28)$$

The Cartesian components of the linear momentum can be expressed in terms of the variables Q_N, Q_L, and Q_M [and thus through Eqs. (23) as functions of t] and of the constant angular momenta. Transformation to the polar coordinates

$$x = r \sin\theta \cos\phi, \tag{29a}$$

$$y = r \sin\theta \sin\phi, \tag{29b}$$

$$z = r \cos\theta \tag{29c}$$

gives for the conjugate momenta

$$p_r = \mu\dot{r} = p_x \sin\theta \cos\phi + p_y \sin\theta \sin\phi + p_z \cos\theta, \tag{30a}$$

$$p_\theta = \mu\dot{\theta} r^2 = p_x r \cos\theta \cos\phi + p_y r \cos\theta \sin\phi + p_z r \cos\theta, \tag{30b}$$

$$p_\phi = \mu\dot{\phi} r^2 \sin^2\theta = -p_x r \sin\theta \sin\phi + p_y r \sin\theta \cos\phi. \tag{30c}$$

In matrix form, the inverse transformation is

$$\begin{pmatrix} p_x \\ p_y \\ p_z \end{pmatrix} = \begin{pmatrix} \sin\theta \cos\phi & \cos\theta \cos\phi & -\sin\phi \\ \sin\theta \sin\phi & \cos\theta \sin\phi & \cos\phi \\ \cos\theta & -\sin\theta & 0 \end{pmatrix} \begin{pmatrix} p_r \\ p_\theta/r \\ p_\phi/r\sin\theta \end{pmatrix}. \tag{31}$$

From Eqs. (11a) and (20), we find that

$$\sin\theta = (\sin^2 q_L + \lambda^2 \cos^2 q_L)^{1/2}, \tag{32a}$$

$$\cos\theta = \sqrt{1-\lambda^2} \cos q_L, \tag{32b}$$

$$\sin\phi = \frac{\sin q_L \cos Q_M + \lambda \cos q_L \sin Q_M}{(\sin^2 q_L + \lambda^2 \cos^2 q_L)^{1/2}}, \tag{32c}$$

$$\cos\phi = -\frac{\sin q_L \sin Q_M - \lambda \cos q_L \cos Q_M}{(\sin^2 q_L + \lambda^2 \cos^2 q_L)^{1/2}}. \tag{32d}$$

Substitution of Eqs. (32) into Eq. (31) gives after some algebraic simplification

$$\begin{pmatrix} p_x \\ p_y \\ p_z \end{pmatrix} = p_r \begin{pmatrix} -\sin q_L \sin Q_M + \lambda \cos q_L \cos Q_M \\ \sin q_L \cos Q_M + \lambda \cos q_L \sin Q_M \\ \sqrt{1-\lambda^2} \cos q_L \end{pmatrix}$$

$$+ L/r \begin{pmatrix} -\cos q_L \sin Q_M - \lambda \sin q_L \cos Q_M \\ \cos q_L \cos Q_M - \lambda \sin q_L \sin Q_M \\ -\sqrt{1-\lambda^2} \sin q_L \end{pmatrix}. \tag{33}$$

In Eq. (33), the "intermediate" variable q_L is given by

$$q_L = Q_L + L\Delta_L, \tag{34}$$

p_r is given by Eq. (5), r is given by

$$r = r_e - \frac{1}{\alpha} \ln\xi, \tag{35}$$

Δ_L is given by Eq. (26), and ξ by

$$\xi = (-2a)[b + \sqrt{b^2 - 4ac} \sin Q_N]^{-1}. \tag{36}$$

From Eqs. (29) and (32), the components of r are found to be given by

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} = r \begin{pmatrix} -\sin q_L \sin Q_M + \lambda \cos q_L \cos Q_M \\ \sin q_L \cos Q_M + \lambda \cos q_L \sin Q_M \\ \sqrt{1-\lambda^2} \cos q_L \end{pmatrix}. \tag{37}$$

IV. CLASSICAL RADIAL DISTRIBUTION

The radial density function is obtained in the usual way from the radial period τ_r,

$$P(r)dr = \frac{2dt}{\tau_r} = \frac{2|\dot{r}|^{-1}dr}{\tau_r}; \tag{38}$$

since $p_r = \mu\dot{r}$ and since $\tau_r = 2\pi/\omega_N$, we have

$$P(r) = \frac{\alpha}{\pi}(-2a\mu)^{1/2}|p_r|^{-1}. \tag{39}$$

The (cumulative) radial distribution function is

$$D(r) = \int_{r_<}^{r} P(r')dr' = \frac{1}{\pi}(-2a\mu)^{1/2}\int_{r_<}^{r} p_r^{-1}dr'. \tag{40}$$

From Eqs. (5) and (40) we obtain

$$D(r) = \frac{\sqrt{-a}}{\pi}\int_{\xi}^{\xi_>}(a + b\xi' + c\xi'^2)^{-1/2}\frac{d\xi'}{\xi'}$$

$$= \frac{1}{2} - \frac{1}{\pi}\arcsin\left(\frac{b\xi + 2a}{\xi\sqrt{b^2 - 4ac}}\right), \tag{41}$$

where a, b, c are given by Eqs. (6) and ξ by Eq. (2).

The derivation of $D(r)$ directly from the results of Sec. III is trivial. Inspection of Eqs. (2), (17), and (18) shows that r goes from $r_<$ to $r_>$ as Q_N goes from $-\pi/2$ to $\pi/2$. Thus, with boundary condition $D(r_<) = 0$, it follows that

$$D(r) = \frac{1}{\pi}[Q_N(r) - Q_N(r_<)], \tag{42}$$

which is the same result as Eq. (41). The radial density is therefore

$$P(r) = \frac{1}{\pi}\frac{dQ_N}{dr} = -\frac{\alpha\xi}{\pi}\frac{dQ_N}{d\xi} = \frac{\alpha\sqrt{-a}}{\pi}(a + b\xi + c\xi^2)^{1/2}, \tag{43}$$

which is equivalent to Eq. (39).

V. BOHR–SOMMERFELD QUANTIZATION

The Bohr–Sommerfeld quantization rule is[8]

$$N = (v + \tfrac{1}{2})\hbar, \tag{44}$$

where v is the vibrational quantum number, and N is given by Eq. (14). To compare with the quantum-mechanical eigenvalues for a rotating Morse oscillator, we use Eq. (6) to expand $b/2\sqrt{-c}$ in powers of L^2:

$$\frac{b}{2\sqrt{-c}} = D^{1/2} - FL^2 - GL^4 + \cdots, \tag{45}$$

where

$$F = \frac{3}{4\mu\alpha r_e^3 D^{1/2}}\left(1 - \frac{1}{\alpha r_e}\right),$$

$$G = \frac{1}{32\mu^2\alpha^2 r_e^6 D^{3/2}}\left(5 - \frac{3}{\alpha r_e}\right)\left(1 - \frac{3}{\alpha r_e}\right). \tag{46}$$

Solving Eq. (14) for a, substituting the definition of a from Eq. (6), and using Eq. (44) for N, we obtain for E

$$E = D + AL^2 - \left[(v + \tfrac{1}{2})\frac{\hbar\alpha}{(2\mu)^{1/2}} - D^{1/2} + FL^2 + GL^4\right]^2. \tag{47}$$

Writing out Eq. (47) to the fourth power of L, substituting the definitions for all constants, and setting $L^2 = J(J+1)\hbar^2$ gives

$$E_{vJ} = \frac{\hbar^2}{2\mu r_e^2} J(J+1) + \hbar\omega_0(v+\tfrac{1}{2}) - \frac{\hbar^2\omega_0^2}{4D}(v+\tfrac{1}{2})^2 - \frac{\hbar^4}{4\mu^2\alpha^2 r_e^6 D}\left[(J(J+1))^2 - \frac{3[1-(1/\alpha r_e)]}{4\mu\alpha r_e^3 D}\hbar^3\omega_0(v+\tfrac{1}{2})J(J+1)\right], \tag{48}$$

in agreement with the quantum-mechanical results.[9] Thus, the value of v found from a classical trajectory for a diatomic molecule by the prescription

$$v = -\tfrac{1}{2} + \frac{2}{\hbar}\int_{r_<}^{r_>} p_r dr \tag{49}$$

is unambiguously the vibrational "quantum number" even when separation of vibration and rotation is a poor assumption, since insertion of v from Eq. (49) and J from the expression[10]

$$J = -\tfrac{1}{2} + \tfrac{1}{2}(1+4L^2/\hbar^2)^{1/2} \tag{50}$$

into Eq. (48) [or better, Eq. (14) and solution of the resulting equation for E] correctly gives the (unseparable) rotation–vibration energy.

Here, our chief interest in Bohr–Sommerfeld quantization of N and L is to facilitate quasiclassical selection of initial coordinates and momenta (see Sec. VII) by means of the results of Sec. III. Before proceeding, however, we turn to the question of errors introduced by truncating the Hamiltonian.

VI. NUMERICAL ACCURACY OF THE RADIAL ORBIT AND THE RADIAL DISTRIBUTION

Since Eqs. (24)–(28) give solutions of the classical equations of motion for a Hamiltonian truncated to the terms quadratic in $(\xi-1)$ [Eq. (4)], the errors induced by the truncation need to be examined. Comparison of Eq. (48) with Ref. 9 testifies to the accuracy of the energy quantization through quadratic terms in the quantum numbers. In this section we numerically test the accuracy of the radial orbit and the radial distribution.

Table I compares values of the radial coordinate as given by the analytic expression Eq. (24) with values for the same times obtained by numerical integration of the exact equations of motion. The numerical integration is accurate to at least eight significant figures, as can be seen by comparing values of $r(t)$ with those calculated from Eq. (24) for $J=0$, since the analytic expression is exact for a nonrotating molecule. For $J\neq 0$, the agreement of the numerical and approximate analytic results for $r(t)$ are excellent when the rotational energy is not too large a fraction of the total internal energy. The error after one complete period is about 1% for $v=10$, $J=10$ where the rotational energy is about 0.03 of the total internal energy; the error after a complete period increases to 19.5% for $v=10$, $J=30$ where the rotational energy is about 0.2 of the total internal energy.

The approximate analytic expression for the radial probability density is much more accurate, however. Figure 1 compares $P(r)$ calculated from Eqs. (43) and (2) with the radial density calculated from the numerically exact trajectory for $v=10$, $J=30$. From the figure one sees that even for this case in which the analytical expression for $r(t)$ is in error by almost 20% after one period, the analytic expression for the radial density is

entirely acceptable. The greatest error in the density is near the turning points. The analytic expressions can

TABLE I. Orbit of a rotating Morse oscillator.[a]

v	J	E(eV)	t[b]	Numerical integration r(a.u.)	Eq. (21) r(a.u.)
0	0[c]	0.1835	0	2.4100000	2.4100000
			0.530	2.2306325	2.2306325
			1.055	2.4894230	2.4894230
			1.585	2.6315951	2.6315951
			2.100	2.4183750	2.4183750
0	4	0.2093	0	2.4100000	2.4100000
			0.530	2.2340684	2.2340620
			1.060	2.4957977	2.4957830
			1.590	2.6336871	2.6336794
			2.115	2.4119575	2.4119421
0	10	0.3248	0	2.4100000	2.4100000
			0.535	2.2474418	2.2474084
			1.070	2.5172910	2.5172216
			1.605	2.6436397	2.6435846
			2.135	2.4122819	2.4121631
2	0[c]	0.8801	0	2.4100000	2.4100000
			0.575	2.1187399	2.1187399
			1.150	2.7995140	2.7995140
			1.725	2.9599080	2.9599080
			2.300	2.4131772	2.4131772
2	4	0.9044	0	2.4100000	2.4100000
			0.575	2.1215817	2.1215405
			1.155	2.8065219	2.8064771
			1.730	2.9620295	2.9619462
			2.310	2.4071156	2.4069132
2	10	1.0130	0	2.4100000	2.4100000
			0.580	2.1388586	2.1386400
			1.165	2.8265814	2.8263466
			1.745	2.9745255	2.9740138
			2.330	2.4137778	2.4125441
10	4	3.0894	0	2.4100000	2.4100000
			0.900	2.8838100	2.8836702
			1.800	4.0423125	4.0418722
			2.700	3.9116854	3.9095214
			3.600	2.4007287	2.3947490
10	10	3.1704	0	2.4100000	2.4100000
			0.915	2.9225111	2.9217751
			1.830	4.0744397	4.0718377
			2.745	3.9419554	3.9292280
			3.665	2.4153917	2.3801441
10	30	3.8655	0	2.4100000	2.4100000
			1.135	3.3978372	3.3929283
			2.270	4.4459384	4.3926178
			3.405	4.2025554	3.9593128
			4.540	2.4115216	1.9431636

[a]The Morse parameters are those for the HCl molecule: $r_e = 2.410$ a.u., $\alpha = 4.61534$ a.u., $D = 4.61534$ eV.

[b]The unit of time is 0.5387×10^{-14} sec.

[c]Equation (21) is exact for $J=0$; inclusion of these entries provides a check of the accuracy of the numerical integration of the exact equations of motion.
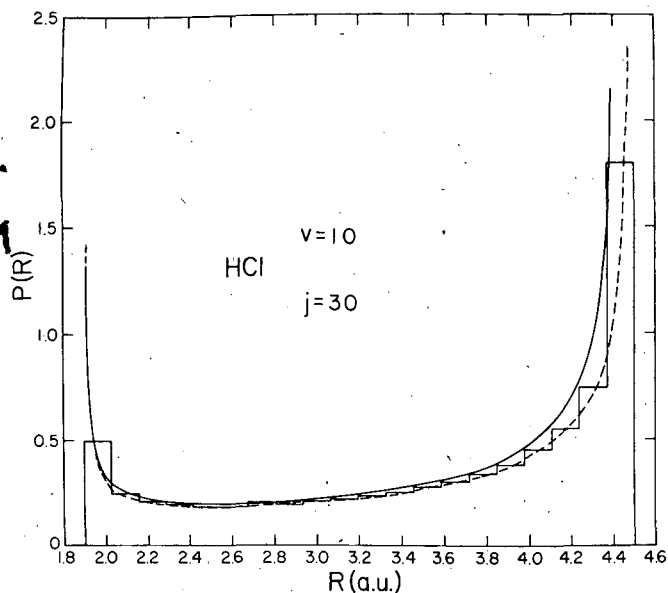
Fig. 1. The classical radial probability density for a rotating Morse oscillator. Parameters are chosen to represent the HCl molecule (see footnote a, Table I) in a quasiclassical state $v = 10$, $J = 30$. Approximate analytic expression: solid curve (—); exact density from numerical trajectory: dashed curve (---). The figure also shows a histogram for the density determined by assigning trajectory results for $r(t)$ to 20 equal time intervals spanning the period.

be made more exact in these regions by modifying them to give the correct turning points[11] if these are known. It should also be obvious that numerical integration of Eq. (8a) and subsequent numerical extraction of the radial distribution can be accomplished without expanding the rotational term, if greater accuracy than that provided by the approximate analytic formula is required when rotational energy is a significant fraction of the total energy.

VII. QUASICLASSICAL SELECTION OF INITIAL COORDINATES AND MOMENTA

There are several equivalent methods by which the radial coordinate r can be selected at random. The radial distribution function $D(r)$ given in Eq. (41) can be set equal to a number R chosen randomly from the closed interval (0, 1) with uniform density, and the result solved for r with the assistance of Eq. (2). Alternatively, one can set $\delta_N = 0$ and $\omega_N t / 2\pi = R$ in Eq. (24). Both of these methods lead to[12]

$$r = r_e - \frac{1}{\alpha} \ln\{(-2a)[b + \sqrt{b^2 - 4ac}\, \sin(2\pi R)]^{-1}\}. \tag{51}$$

While these methods are adequate for r, they are not so easy to apply in the case of θ, ϕ, and the components of **p**.

Since the independent angle variables Q_N, Q_L, and Q_M [see Eqs. (23)] all range from 0 to 2π and are at most linear in t, it is clear that one need merely to set

$$Q_N = 2\pi R_1,$$
$$Q_L = 2\pi R_2, \tag{52}$$
$$Q_M = 2\pi R_3,$$

where the R_i are mutually random numbers with flat distributions in the closed interval (0, 1). The components of **r** and **p** calculated from Eqs. (33)–(37) then have the properly weighted distributions for a rotating Morse oscillator. The quasiclassical selection is implemented by the use of Eq. (44) and

$$L^2 = J(J+1)\hbar^2 \tag{53}$$

in the evaluation of the constants a, b, and c by means of Eq. (6).

This prescription is analogous to the situation in quantum mechanics when the values of the momenta (here the action variables) are sharp and the values of their conjugate coordinates (here the angle variables) are therefore completely random.

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[1] See, for example, D. L. Bunker, Methods Comput. Phys. **10**, 287 (1971); J. C. Polanyi and J. L. Schreiber, in *Physical Chemistry*, Vol. VI A *Kinetics of Gas Reactions* (Academic, New York, 1974), p. 383; R. N. Porter, Ann. Rev. Phys. Chem. **25**, 317 (1974).

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[10] Although the semiclassical quantization of angular momentum is $L = (J + \frac{1}{2})\hbar$, we use the quantum-mechanical result $L^2 = J(J+1)\hbar^2$ here for consistency with previous quasiclassical calculations (see Ref. 5).

[11] J. L. Schreiber (private communication).

[12] The first method actually gives πR as the argument of the sin function in Eq. (51), but the equivalence of these two results for r is obvious.