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The Morse oscillator in position space, momentum space, and phase space

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We present a unified description of the position-space wave functions, the momentum-space wave functions, and the phase-space Wigner functions for the bound states of a Morse oscillator. By comparing with the functions for the harmonic oscillator the effects of anharmonicity are visualized. Analytical expressions for the wave functions and the phase space functions are given, and it is demonstrated how a numerical problem arising from the summation of an alternating series in evaluating Laguerre functions can be circumvented. The method is applicable also for other problems where Laguerre functions are to be calculated. The wave and phase space functions are displayed in a series of curves and contour diagrams. An Appendix discusses the calculation of the modified Bessel functions of real, positive argument and complex order, which is required for calculating the phase space functions for the Morse oscillator.

I. INTRODUCTION

The celebrated Morse potential has the form

$$V(x) = D(1 - e^{-\alpha x})^2, \quad -\infty < x < \infty. \tag{1}$$

It was constructed by Morse[1] from restrictions on its behavior for large values of $|x|$, and from the requirement that it should lead to a quantum mechanical energy level spectrum of the form

$$\mathscr{E}_n = [(n + 1/2) - \chi(n + 1/2)^2]\hbar\omega_0,$$

$$n = 0,1, \ldots, n_{max}. \tag{2}$$

Qualitatively, this is the characteristic energy level spectrum of a vibrating, nonrotating diatomic molecule. An energy level spectrum does admittedly not determine the potential uniquely,[2,3] but the analytic expression (1) does in general give a good fit to the potential curves of diatomic molecules. The energy levels and wave functions of the Morse oscillator are, accordingly, good approximations to those of actual molecules.

In a diatomic molecule x stands for $r - r_e$, where r is the internuclear distance and r_e its "equilibrium" value. Thus, the true domain of x is from $-r_e$ to ∞, but the physical effects of substituting $-\infty$ for $-r_e$, as in Eq. (1), have been found to be entirely negligible.[1,4]

The Schrödinger equation for the Morse oscillator is, in the coordinate representation,

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi = \mathscr{E}\psi. \tag{3}$$

For a diatomic molecule m is the reduced mass and $\psi(x)$ represents the nuclear vibration. But, although we take Eq. (3) to be the Schrödinger equation for a nonrotating molecule, it is important to note that the rotational influence on the vibration can be taken into account to a fair approximation by simply changing the parameters r_e, α, and D in the potential. This was shown by Morse[1] and Pekeris,[5] and has

more recently been discussed by, e.g., Rundgren[6] and Elsum and Gordon.[7]

Today, the Morse potential plays a dominant role in model calculations in molecular spectroscopy, even for polyatomic molecules. But it is also being extensively used in several other branches of chemical physics, including collision theory, the theory of intra- and intermolecular energy transfer, the theory of photodissociation, etc. The Morse oscillator has accordingly been the subject matter of many detailed studies. These studies have almost exclusively been carried out in the position space representation, but recently there has also been an increasing interest in the use of the phase space representation, especially in connection with time dependent problems. The phase space representation works with Wigner functions instead of wave functions, but a general analysis of these functions is still lacking for the Morse oscillator.

The present paper remedies this situation by presenting a self-contained treatment of the Morse oscillator in the phase space representation. This representation combines the position-space and momentum-space characteristics in a single picture. We have previously discussed the phase-space description of stationary states for some other one-dimensional systems like the harmonic oscillator,[8,9] a particle in a linear potential,[9] and a free particle.[9] In addition, we have presented detailed phase-space pictures of the hydrogen atom,[10] the LiH molecule,[11] and a series of closed-shell atoms.[12] The present phase-space analysis of the Morse oscillator is also a natural and instructive extension of these studies.

In order to put our results in perspective, we begin (Sec. II) by recalling the form of the wave functions and the Wigner functions for the harmonic oscillator. We present these functions in such a way that the harmonicity of the potential is reflected as a complete symmetry between the wave functions in position space and the wave functions in momentum space. Correspondingly, the contours of the

Wigner functions become circles centered on the origin of phase space.

Section III discusses the form of the Morse wave functions in position space, and introduces a position variable Q which has a close resemblance to the harmonic oscillator coordinate introduced in Sec. II. This leads to an especially clear exposure of the anharmonicity effects. In Sec. III, we also draw attention to the fact that the analytic expression for the Morse wave functions is computationally unstable, in the sense that a direct use of this expression leads to a serious loss of significant figures for higher excited states. We present a recurrence relation which allows us to circumvent this problem.

In Sec. IV we derive and display the form of the Morse wave functions in momentum space. These have not previously been discussed in the literature. We also show that the Schrödinger equation in momentum space is a linear difference equation rather than a differential equation. A momentum space approach should, for instance, be of relevance in collision studies. But, in addition, our analysis adds to the general understanding of momentum wave functions for simple systems.

Section V contains our detailed description of the Wigner functions for the Morse oscillator. We discuss how the functions may be calculated and display their form in a particular case, as one moves from the ground state to the highest excited states. Again, the phase space coordinates are chosen in such a way that the anharmonicity effects are easily visualized. The results obtained in this section extend and surpass those by previous workers and should be of considerable use in future discussions of, for instance, excited states dynamics.

Section VI contains our concluding remarks. In the Appendix we discuss the calculation of the modified Bessel functions which occur in the expression for the Wigner functions.

II. THE HARMONIC OSCILLATOR

In this section we review the position, momentum, and phase-space descriptions of the harmonic oscillator, for later comparison with the Morse oscillator.

The Hamiltonian for a harmonic oscillator with mass m and angular frequency ω_0 is[13]

$$\hat{\mathscr{H}} = \frac{\hat{p}^2}{2m} + \frac{1}{2} m\omega_0^2 \hat{x}^2, \tag{4}$$

where $\hat{x}$ and $\hat{p}$ are the position and momentum operators, respectively. They satisfy the usual commutation relation

$$[\hat{x}, \hat{p}] = i\hbar. \tag{5}$$

The stationary states of the oscillator are determined by the eigenvalue equation

$$\hat{\mathscr{H}} |\psi\rangle = \mathscr{E} |\psi\rangle, \tag{6}$$

with $\mathscr{E}$ being the energy.

By dividing both sides of Eq. (6) with $\hbar\omega_0$ we get instead

$$\hat{H} |\psi\rangle = E |\psi\rangle, \tag{7}$$

with

$$\hat{H} = \tfrac{1}{2}\hat{P}^2 + \tfrac{1}{2}\hat{Q}^2 \tag{8}$$

and

$$E = \mathscr{E}/(\hbar\omega_0). \tag{9}$$

E is the dimensionless energy, and $\hat{Q}$ and $\hat{P}$ are the dimensionless coordinate and momentum operators

$$\hat{Q} = (m\omega_0/\hbar)^{1/2}\hat{x}, \tag{10}$$

$$\hat{P} = (m\omega_0\hbar)^{-1/2}\hat{p}. \tag{11}$$

They satisfy the commutation relation

$$[\hat{Q}, \hat{P}] = i. \tag{12}$$

The substitutions (9)–(11) make all harmonic oscillators mathematically equivalent. The Hamiltonian (8) may, accordingly, be said to define the standard harmonic oscillator.

Let us now introduce the coordinate representation in which

$$\hat{Q} = Q, \quad \hat{P} = -i\frac{d}{dQ}, \tag{13}$$

and $|\psi\rangle$ is represented by the wave function

$$\psi(Q) = \langle Q|\psi\rangle. \tag{14}$$

Then Eq. (7) becomes the Schrödinger equation

$$-\frac{1}{2}\frac{d^2\psi}{dQ^2} + \frac{1}{2}Q^2\psi = E\psi. \tag{15}$$

It has the well-known solutions[8]

$$E_n = n + 1/2, \quad n = 0,1,2, \ldots, \tag{16}$$

$$\psi_n(Q) = (\pi^{1/2}2^n n!)^{-1/2} H_n(Q)\exp(-\tfrac{1}{2}Q^2), \tag{17}$$

where $H_n(Q)$ is the nth Hermite polynomial, and $\psi_n(Q)$ is normalized such that

$$\int_{-\infty}^{\infty} \psi_n(Q)^2 \, dQ = 1. \tag{18}$$

For later comparisons, Fig. 1 shows the potential energy function

$$V(Q) = \tfrac{1}{2}Q^2 \tag{19}$$

that appears in the Schrödinger equation (15). It also shows the four lowest energy levels [Eq. (16)]. Figure 2 shows the wave functions (17) for the same levels.

Let us now also introduce the momentum representation, in which

$$\hat{Q} = i\frac{d}{dP}, \quad \hat{P} = P. \tag{20}$$

$|\psi\rangle$ is then represented by the momentum wave function

$$\phi(P) = \langle P|\psi\rangle, \tag{21}$$

which is the Fourier transform of $\psi(Q)$,

$$\phi(P) = (2\pi)^{-1/2}\int_{-\infty}^{\infty} \psi(Q)e^{-iPQ} \, dQ. \tag{22}$$

Evaluating the integral gives

HARMONIC OSCILLATOR

$$\phi_n(P) = (-i)^n(\pi^{1/2}2^n n!)^{-1/2}H_n(P)\exp(-\tfrac{1}{2}P^2). \tag{23}$$

Thus, $\psi_n(Q)$ and $\phi_n(P)$ have the same analytical form, apart from the physically unimportant phase factor $(-i)^n$. This is in accordance with the fact that the momentum representation of Eq. (7) is

$$-\frac{1}{2}\frac{d^2\phi}{dP^2} + \frac{1}{2}P^2\phi = E\phi, \tag{24}$$

which is similar to Eq. (15).

The wave functions in Fig. 2 may, accordingly, also be taken to represent the momentum wave functions, with the phase factor $(-i)^n$ neglected, and the axis labels being changed from (Q,ψ) to (P,ϕ).

Finally, let us introduce the phase-space representation in which a state $|\psi\rangle$ is represented by a Wigner function[14] $f(Q,P)$, defined by the following equivalent expressions:

$$f(Q,P) = \frac{1}{\pi}\int_{-\infty}^{\infty} dQ'\psi(Q-Q')^*$$
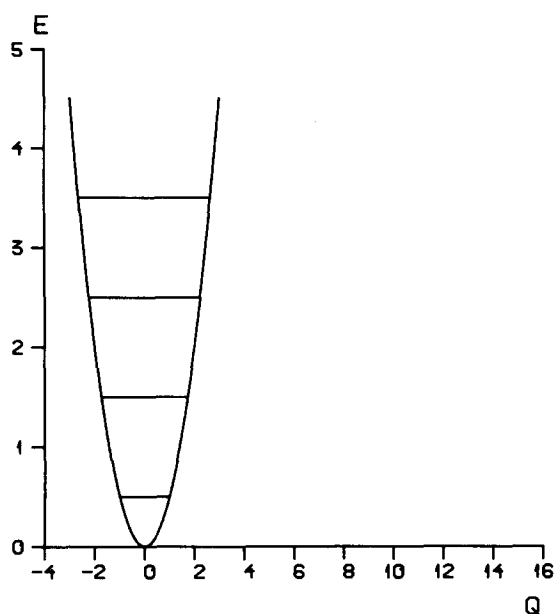$$\times \psi(Q+Q')\exp(-2iQ'P) \tag{25}$$

and

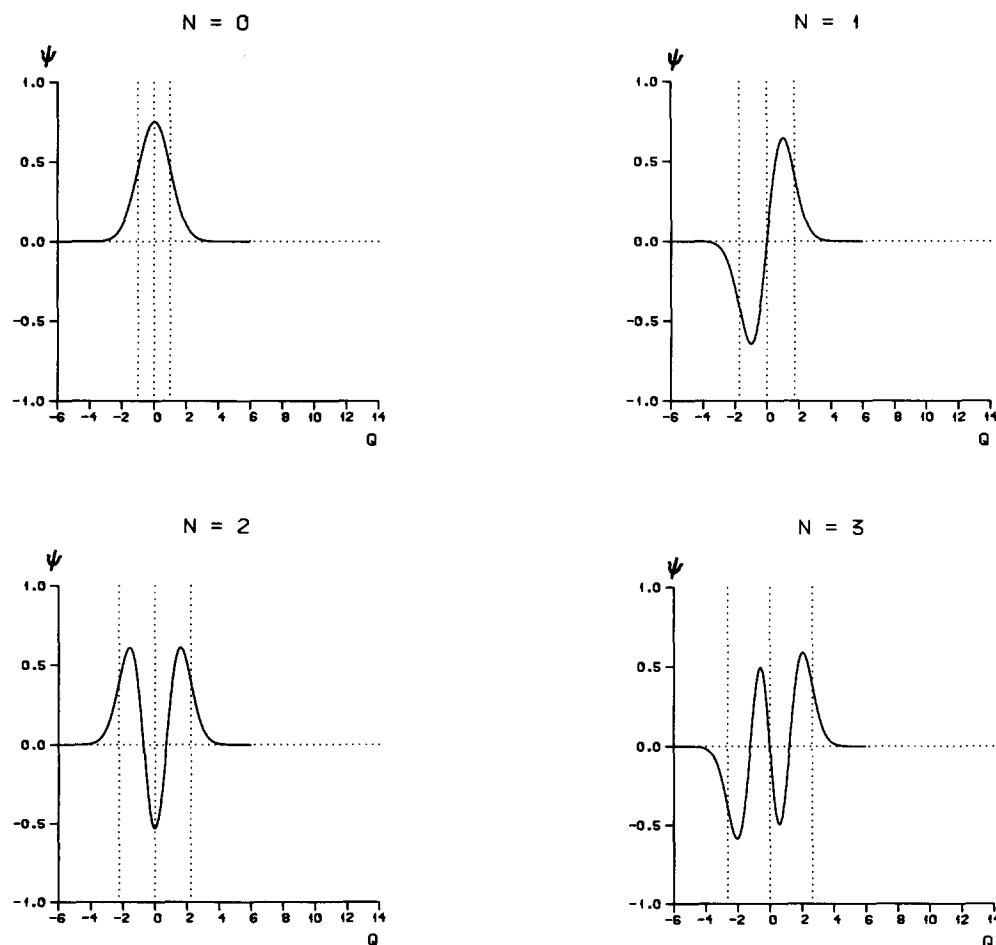FIG. 1. Harmonic oscillator potential and energies.

FIG. 2. Harmonic oscillator wave functions. The dotted reference lines mark the $Q = 0$ and $\psi = 0$ axes, and the turning points for a classical vibrator with the same energy.

$$f(Q,P) = \frac{1}{\pi} \int_{-\infty}^{\infty} dP' \phi(P - P')^*$$

$$\times \phi(P + P') \exp(2iQP'). \qquad (26)$$

A Wigner function satisfies the normalization condition

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dQ \, dP f(Q,P) = 1, \qquad (27)$$

and plays the role of a phase-space probability density, in an operational sense.[14]

Substitution of Eq. (17), or Eq. (23), gives

$$f_n(Q,P) = (-1)^n \frac{1}{\pi} \exp(-R^2) L_n^{(0)}(2R^2), \qquad (28)$$

where

$$R^2 = Q^2 + P^2, \qquad (29)$$

and $L_n^{(0)}(2R^2)$ is a Laguerre polynomial. The general (associated) Laguerre polynomial is here given by the definition[15]

$$L_n^{(\alpha)}(\xi) = \frac{\Gamma(n + \alpha + 1)}{n! \Gamma(\alpha + 1)} \, _1F_1(-n, \alpha + 1; \xi), \qquad (30)$$

where $_1F_1$ is a confluent hypergeometric function (Kummer's function).[15]

Expression (27) was first derived by Groenewold,[16] and independently by Bartlett and Moyal,[17] and Takabayasi,[18] as well as later authors. Two independent derivations have also been presented by one of the present authors.[8,9]

Equation (28) shows that the contours of $f_n(Q,P)$ are circles centered on the origin of phase space. For the four lowest states of the harmonic oscillator, Fig. 3 shows the variation of $f_n(Q,P)$ along a line extending from the origin. We note that the value at the origin is $(-1)^n/\pi$. This reflects the fact that the wave functions (17) have a definite parity.[8,19–21] We also note the following relation which holds for any Wigner function[20,22]:
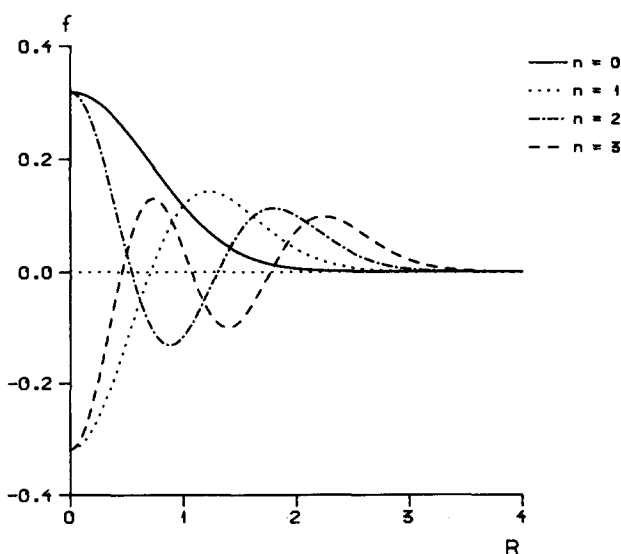

FIG. 3. Wigner functions for the four lowest states of the harmonic oscillator, along a line extending from the origin of phase space.

$$|f(Q,P)| \leqslant 1/\pi \qquad (31)$$

and for all (Q,P), provided the operators $\hat{Q}$ and $\hat{P}$ are chosen to satisfy Eq. (12).

III. THE MORSE OSCILLATOR IN POSITION SPACE

Let us now focus on the Morse potential (1) and the associated Schrödinger Equation (3), i.e.,

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + D(1 - e^{-\alpha x})^2 \psi = \mathscr{E} \psi. \qquad (32)$$

We introduce the dimensionless variable

$$y = \alpha x, \quad -\infty < y < \infty, \qquad (33)$$

and get the equation

$$\frac{d^2\psi}{dy^2} + \lambda^2 [\epsilon - (1 - e^{-y})^2] \psi = 0, \qquad (34)$$

where

$$\epsilon = \mathscr{E}/D \qquad (35)$$

and λ is a dimensionless parameter,

$$\lambda = \frac{\sqrt{2mD}}{\alpha \hbar}. \qquad (36)$$

We shall only consider bound states and assume these to be normalized such that

$$\int_{-\infty}^{\infty} \psi(y)^2 \, dy = 1. \qquad (37)$$

It is then found that the solutions of Eq. (34) have the form

$$\psi_{\lambda,n}(y) = N(\lambda,n) \xi^{\lambda - n - 1/2} e^{-\xi/2} L_n^{(2\lambda - 2n - 1)}(\xi), \qquad (38)$$

where

$$\xi = 2\lambda e^{-y}, \quad 0 < \xi < \infty \qquad (39)$$

and

$$n = 0, 1, \ldots, [\lambda - 1/2], \qquad (40)$$

with $[x]$ denoting the largest integer smaller than x. The normalization constant has the value

$$N(\lambda,n) = \left[\frac{(2\lambda - 2n - 1)\Gamma(n + 1)}{\Gamma(2\lambda - n)} \right]^{1/2}, \qquad (41)$$

and the Laguerre polynomial is defined by Eq. (30).

Equation (40) shows that the number of bound states is $[\lambda + 1/2]$. The energies are given by the expressions

$$\epsilon_n - 1 = -\frac{1}{\lambda^2} (\lambda - n - 1/2)^2 \qquad (42)$$

and

$$\mathscr{E}_n = \left[(n + 1/2) - \frac{1}{2\lambda} (n + 1/2)^2 \right] \hbar \omega_0, \qquad (43)$$

where

$$\omega_0 = \left[\frac{2D\alpha^2}{m} \right]^{1/2}. \qquad (44)$$

Thus, the parameter χ of Eq. (2) equals $1/(2\lambda)$.

The analytical expression (38) is contained in Morse's original paper.[1] The closed form for the normalization constant (41) was first derived by Scholz[23] and by Pekeris.[5] It has later been rediscovered by several authors, including

Rundgren,[6] Nieto and Simmons,[24] and Birtwistle.[25] Note, however, that some of the authors mentioned use a definition of the Laguerre polynomials different from ours, viz.

$$L_{\alpha+n}^{\alpha}(\xi) = (-1)^{\alpha}\Gamma(\alpha + n + 1)L_n^{(\alpha)}(\xi). \quad (45)$$

This is the definition used in most discussions of the Coulomb problem.[13]

We shall now comment on the numerical evaluation and the graphical representation of the Morse functions (38).

At first sight, the right-hand side of Eq. (38) is a rather innocent expression. The Laguerre polynomial is, however, an alternating series, and a straightforward evaluation is accompanied by a substantial loss of significant figures for larger values of n. This is illustrated in Fig. 4 which shows the number of significant figures lost for $\lambda = 30$ and $y = 0$. This number is defined as $\log|u_{max}/s|$, where u_{max} is the absolute value of the numerically largest term in a sum, and s is the value of the sum itself. Obviously, it is necessary to go beyond double precision on a computer in order to obtain reliable values for the Morse functions for all values of n. The situation is even worse if bilinear expressions are considered, as in the evaluation of matrix elements and Franck–Condon factors. Here it may be necessary to go beyond quadruple precision.

Several methods to circumvent these numerical difficulties have been proposed. We shall merely mention a few recent publications in which further references may be found. For some important operators it is possible to evaluate closed expressions for matrix elements,[26] or semiclassical methods and their extension, the phase-integral method,[27] may be used. Other methods are based on Morse functions determined by expansions in an orthonormal basis set or by numerical integration of the Schrödinger equation.[28] Yet other methods draw on the fact that Morse oscillators with λ values differing by one are connected by a so-called spectrum generating algebra.[29–32]
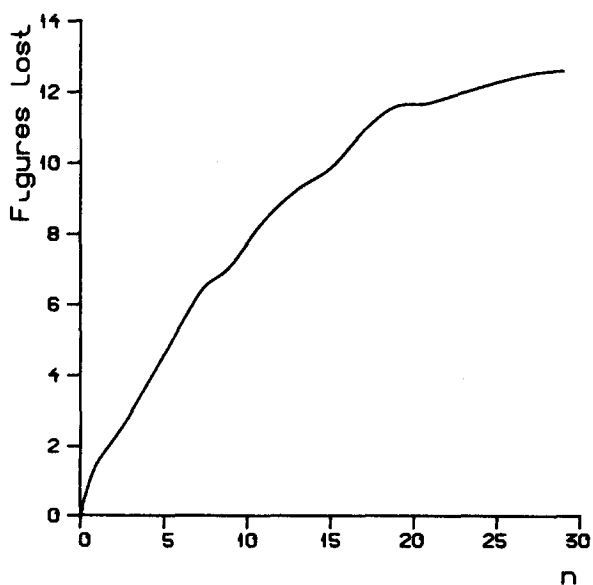
As a variant of the latter methods we have developed a simple and stable method for evaluating the Morse functions be means of a recurrence relation. We define the parameter s by the relation

$$s = 2\lambda - 2n - 1, \quad (46)$$

and write

$$\psi_n^s(\xi) = N(s,n)e^{-\xi/2}\xi^{s/2}L_n^{(s)}(\xi), \quad (47)$$

instead of Eq. (38). Observing Eq. (41) and the recurrence relation

$$nL_n^{(s)}(\xi) = (2n + s - 1 - \xi)L_{n-1}^{(s)}(\xi)$$
$$- (n + s - 1)L_{n-2}^{(s)}(\xi) \quad (48)$$

then gives, after some algebra:

$$\psi_n^s(\xi) = \left\{\frac{1}{n(s+n)}\right\}^{1/2}\left\{(2n + s - 1 - \xi)\psi_{n-1}^s(\xi)\right.$$
$$\left. - [(n-1)(n+s-1)]^{1/2}\psi_{n-2}^s(\xi)\right\}. \quad (49)$$

By defining $\psi_{-1}^s(\xi)$ to be zero, this relation allows us to generate $\psi_n^s(\xi)$ from the simple function

$$\psi_0^s(\xi) = N(s,0)e^{-\xi/2}\xi^{s/2}. \quad (50)$$

Relation (49) is similar to the relation

$$\psi_n(Q) = Q\left[\frac{2}{n}\right]^{1/2}\psi_{n-1}(Q) - \left[\frac{n-1}{n}\right]^{1/2}\psi_{n-2}(Q) \quad (51)$$

for harmonic oscillator wave functions, but it is stressed that keeping s fixed in Eq. (49) implies that λ varies in steps of unity.

A relation related to Eq. (49) has been given by Sension and Strauss.[33] Their expression is, however, more complicated than ours and only approximate. We have found it to be quite inaccurate.

In Sec. II we plotted the potential and the wave functions for the standard harmonic oscillator, and noted that the contours of the associated Wigner functions were circles centered on the origin of phase space. It is convenient and desirable to define standard variables for a given Morse oscillator in such a way that the anharmonicity effects stand out as clearly as possible. This is done by introducing a new position variable Q according to the definition

$$Q = (m\omega_0/\hbar)^{1/2}x, \quad (52)$$

where ω_0 is the angular frequency for small oscillations, as defined by Eq. (44). By combining Eqs. (36) and (44) we also get

$$Q = \alpha\sqrt{\lambda}\,x. \quad (53)$$

The Schrödinger equation (32) then becomes

$$-\frac{1}{2}\frac{d^2\psi}{dQ^2} + \frac{1}{2}\lambda\left[1 - \exp(-Q/\sqrt{\lambda})\right]^2\psi = E\psi, \quad (54)$$

where

$$E = \mathscr{E}/(\hbar\omega_0) = \frac{1}{2}\lambda\epsilon, \quad (55)$$

with ϵ as given by Eq. (35).

Equations (52) and (55) are similar to Eqs. (10) and (9), respectively. The potential energy function is now
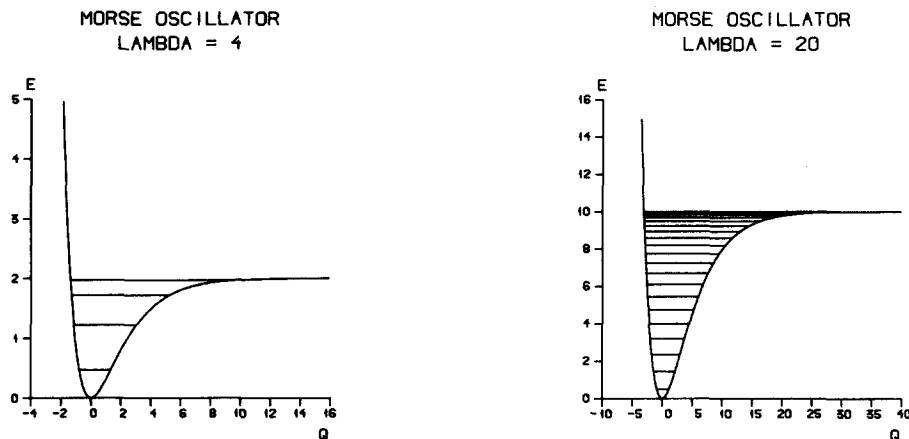

FIG. 4. Number of significant figures lost in the numerical evaluation of Morse functions, for $\lambda = 30$ and $y = 0$.

MORSE OSCILLATOR
LAMBDA = 4

MORSE OSCILLATOR
LAMBDA = 20

FIG. 5. The Morse potentials and bound state energies for $\lambda = 4$ and $\lambda = 20$, according to Eqs. (56) and (57).

$$V(Q) = \tfrac{1}{2}\lambda \left[1 - \exp(-Q/\sqrt{\lambda}\,) \right]^2. \qquad (56)$$

$V(Q)$ contains the harmonic potential function (19) as its leading term when it is expressed as an infinite expansion in powers of $1/\sqrt{\lambda}$. The expression for the admissible energies is

$$E_n = (n + 1/2) - \frac{1}{2\lambda}(n + 1/2)^2. \qquad (57)$$

The first term of this expression is just Eq. (16). These observations have also been made by Cooper who used them as the basis for a recent perturbational treatment of the Morse oscillator.[34]

Figure 5 shows the potential $V(Q)$ for $\lambda = 4$ and

$\lambda = 20$, as well as the bound state energy levels, whose number, according to Eq. (40), just equals λ when λ is an integer. Note that the variable Q has been defined such that Fig. 1 gives the harmonic part of the potential $V(Q)$, for any Morse oscillator.

In Fig. 6 we show the Morse eigenfunctions corresponding to $\lambda = 4$, with Q as the position variable. The functions are normalized according to Eq. (18), and a comparison with Fig. 2 gives a clear and quantitative picture of the anharmonicity effects.

IV. THE MORSE OSCILLATOR IN MOMENTUM SPACE

Corresponding to the position coordinate x in Eqs. (1) and (32) we have a momentum p, with the associated opera-
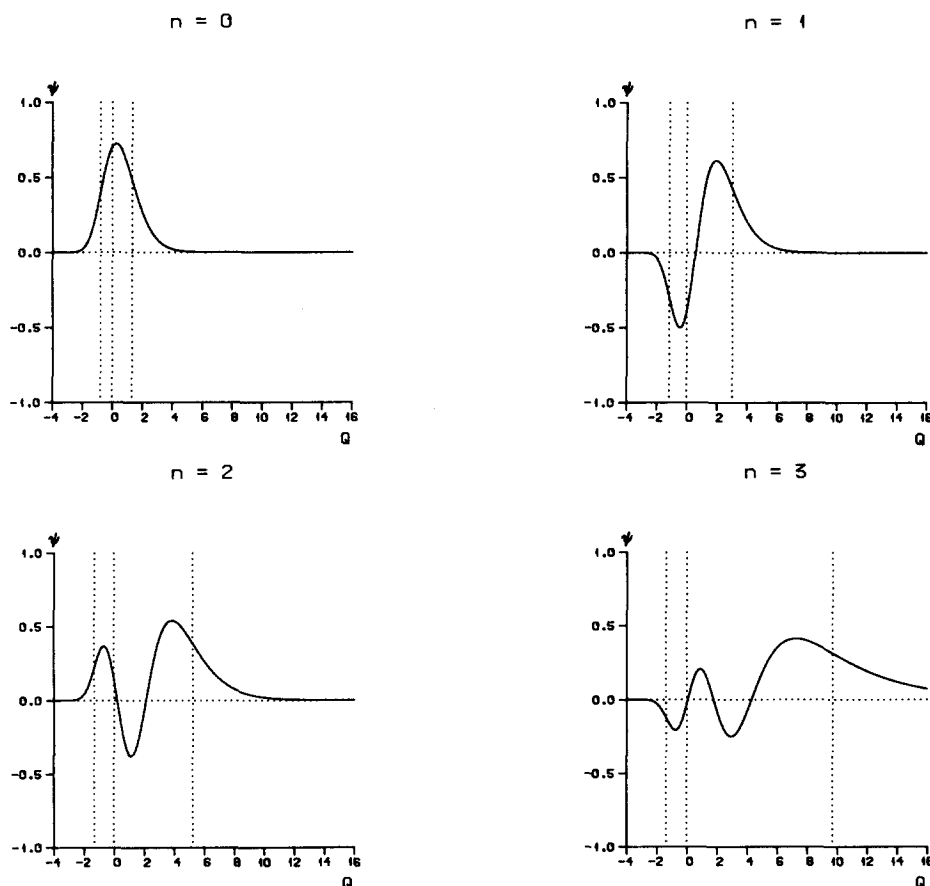
n = 0

n = 1

n = 2

n = 3

FIG. 6. Morse oscillator wave functions in position space. The dotted reference lines mark the $Q = 0$ and $\psi = 0$ axes, and the turning points for a classical vibrator with the same energy.

tors satisfying the commutation relation (5). Let us introduce a dimensionless momentum k corresponding to the dimensionless coordinate y of Eq. (33) by the definition

$$k = p/(\alpha\hbar). \tag{58}$$

The associated operators will then satisfy the commutation relation

$$[\hat{y},\hat{k}] = i. \tag{59}$$

The momentum wave function corresponding to the position wave function $\psi(y)$ is accordingly

$$\phi(k) = (2\pi)^{-1/2}\int_{-\infty}^{\infty}\psi(y)e^{-iky}\,dy. \tag{60}$$

It is normalized such that

$$\int_{-\infty}^{\infty}|\phi(k)|^2\,dk = 1. \tag{61}$$

To determine the analytical form of $\phi(k)$ we write the Laguerre polynomial of Eq. (38) as

$$L_n^{(2\lambda-2n-1)}(\xi) = \sum_{j=0}^{n}b(\lambda,n;j)\xi^j, \tag{62}$$

where

$$b(\lambda,n;j) = \frac{(-1)^j}{j!}\frac{\Gamma(2\lambda-n)}{\Gamma(2\lambda-2n+j)\Gamma(n-j+1)}. \tag{63}$$

Next, we write $\psi(\xi)$ instead of $\psi(y)$ in Eq. (60), observe the definition (39), and get

$$\phi(k) = (2\pi)^{-1/2}(2\lambda)^{-ik}\int_{0}^{\infty}\psi(\xi)\xi^{ik}\frac{d\xi}{\xi}. \tag{64}$$

We then insert the analytical form of $\psi(\xi)$ from Eq. (38) and note the relation[15]

$$\Gamma(z) = \int_{0}^{\infty}e^{-t}t^{z-1}\,dt, \quad \mathrm{Re}(z)>0. \tag{65}$$

Thus, we obtain the final result

$$\phi_{\lambda,n}(k) = N(\lambda,n)(2\pi)^{-1/2}2^{\lambda-n-1/2}\lambda^{-ik}$$
$$\times\sum_{j=0}^{n}2^jb(\lambda,n;j)\Gamma(\lambda-n+j-\tfrac{1}{2}+ik). \tag{66}$$

Using this expression we have plotted the momentum wave functions corresponding to $\lambda = 4$ in Fig. 7, but with

$$P = k/\sqrt{\lambda} \tag{67}$$

as the momentum variable. This momentum variable is conjugate to the position variable Q in Eq. (53), and the associated operators satisfy the commutation relation (12).

Figure 7 is based on the polar representation

$$\phi(P) = |\phi(P)|\exp\{i\arg[\phi(P)]\}, \tag{68}$$

with $|\phi(P)|$ and $\arg(\phi(P))$ plotted on the same diagram. We note that $\phi(P)$ is a nodeless function, the mutual orthogonality of functions with different n being ensured by the phase functions $\arg[\phi(P)]$. Thus, there is an essential difference between these functions and the corresponding func-
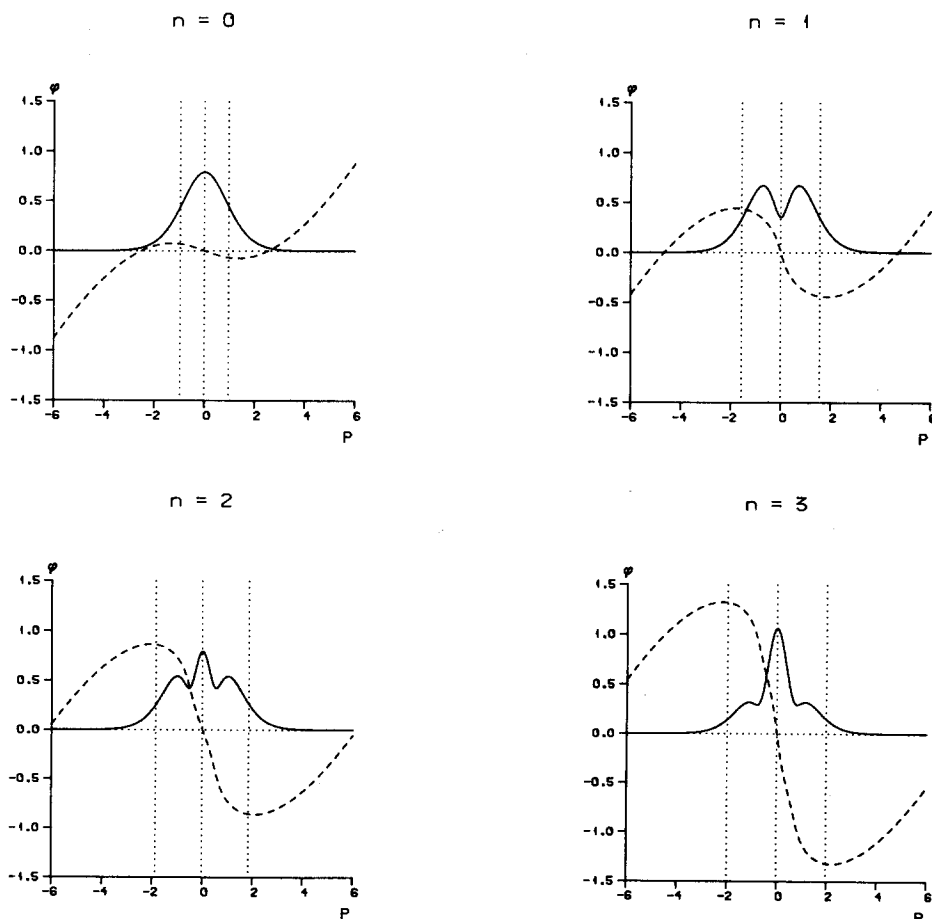
n = 0

n = 1

n = 2

n = 3

FIG. 7. Morse oscillator wave functions in momentum space. The solid curves show $|\phi(P)|$, the dashed curves $\arg[\phi(P)]/(2\pi)$. The dotted reference lines mark the $P=0$ and $\phi=0$ axes, and the turning points for a classical vibrator with the same energy.

tions for the harmonic oscillator which look like the functions in Fig. 2.

We shall now give the momentum-space representation of the Schrödinger equation for the Morse oscillator. It is obtained from Eq. (34) by noting the correspondences:

$$\psi \to \phi, \quad \frac{d^2}{dy^2} \to -k^2,$$

$$e^{-ay}\psi \to (2\pi)^{-1/2}\int_{-\infty}^{\infty} e^{-ay}\psi(y)e^{-iky}\,dy = \phi(k - ia).$$

$$(69)$$

Thus, we get

$$\left\{-\frac{k^2}{\lambda^2} + \epsilon - 1\right\}\phi(k) = \phi(k - 2i) - 2\phi(k - i).\,(70)$$

This is a linear difference equation rather than a differential equation.

The form of Eq. (70) reflects the fact that the operator $\exp(i\kappa\hat{y})$ is a translation operator in momentum space. In the present context κ is imaginary, and the translation is accordingly a translation in the imaginary direction in a complex k space.

When evaluating $\phi(k)$ by Eq. (66) we encounter again the problem of losing significant figures. It would be interesting to study whether a direct attack on Eq. (70) could lead to new and more stable ways of determining Morse wave functions. We have made some introductory studies but have not been able to answer this question in the affirmative.

V. THE MORSE OSCILLATOR WIGNER FUNCTIONS

In this section we shall explore the form of the Morse oscillator Wigner functions

$$f_{mn}^{\lambda}(y,k) = \frac{1}{\pi}\int_{-\infty}^{\infty} \psi_{\lambda,m}(y - y')^*$$

$$\times \psi_{\lambda,n}(y + y')e^{-2iky'}\,dy'. \quad (71)$$

When $m = n$ a Wigner function describes a state and when $m \neq n$ it describes a transition between two states. The functions defined here are thus more general than the functions defined by Eq. (25) and explicitly given for the harmonic oscillator in Eq. (28). Those functions were merely Wigner functions associated with states, but we note that Refs. 8 and 9 also give the more general harmonic oscillator Wigner functions.

As in the previous section we write $\psi(\xi)$ instead of $\psi(y)$, with ξ defined by Eq. (39). We also introduce

$$\tau = e^{-y} \quad (72)$$

as a new integration variable, and get

$$f_{mn}^{\lambda}(y,k) = \frac{1}{\pi}\int_0^{\infty} \psi_{\lambda,m}(\xi/\tau)^*\psi_{\lambda,n}(\xi\tau)\tau^{2ik}\frac{d\tau}{\tau}. \quad (73)$$

It is now a straightforward matter to insert the actual form of the wave functions, as given by Eq. (38). Again, we write the Laguerre polynomials as in Eq. (62) and obtain the following result:

$$f_{mn}^{\lambda}(y,k) = \frac{2}{\pi}N(\lambda,m)N(\lambda,n)\xi^{2\lambda - m - n - 1}$$

$$\times \sum_{r=0}^{m}\sum_{s=0}^{n} b(\lambda,m;r)b(\lambda,n;s)\xi^{r+s}$$

$$\times K_{m-n-r+s+2ik}(\xi), \quad (74)$$

where

$$K_\nu(\xi) = \frac{1}{2}\int_0^{\infty}\tau^\nu \exp\left[-\frac{\xi}{2}\left(\tau + \frac{1}{\tau}\right)\right]\frac{d\tau}{\tau} \quad (75)$$

is the modified Bessel function of the third kind.[35] The evaluation of $K_\nu(\xi)$ is discussed in the Appendix.

In analogy with the notation in Sec. II we write $f_n^{\lambda}(y,k)$ instead of $f_{nn}^{\lambda}(y,k)$, and get in particular:

$$f_o^{\lambda}(y,k) = \frac{2}{\pi}\frac{1}{\Gamma(2\lambda - 1)}\xi^{2\lambda - 1}K_{2ik}(\xi). \quad (76)$$

This expression has previously been derived by Lee and Scully,[36] who also pointed out that "similar expressions for the Wigner distribution function can be obtained through a lengthy algebra for the case when the oscillator is prepared in one of its excited states."

For low values of m and n, Eq. (74) provides a good basis for the calculation of $f_{mn}^{\lambda}(y,k)$. For higher values an increasing number of significant figures are lost. There does not seem to be any easy way to circumvent this problem when $m \neq n$. But when $m = n$ the recurrence relation (49) may be put to use. Let us write it as

$$\psi_n^s(\xi) = (a_n + b_n\xi)\psi_{n-1}^s(\xi) + c_n\psi_{n-2}^s(\xi), \quad (77)$$

where the constants a_n, b_n, and c_n may be read off Eq. (49). Let us also write

$$W(f,g|\xi,k) = \frac{1}{\pi}\int_0^{\infty} f(\xi/\tau)^*g(\xi\tau)\tau^{2ik}\frac{d\tau}{\tau}. \quad (78)$$

The following relations are then easily verified:

$$W(\xi f,g|\xi,k) = \xi W(f,g|\xi,k + i/2), \quad (79)$$

$$W(f,\xi g|\xi,k) = \xi W(f,g|\xi,k - i/2), \quad (80)$$

$$W(\xi f,\xi g|\xi,k) = \xi^2 W(f,g|\xi,k). \quad (81)$$

Using these expressions we get the recurrence relation

$$f_{n,m}^s(\xi,k) = (a_n a_m + b_n b_m\xi^2)f_{n-1,m-1}^s(\xi,k) + c_n c_m f_{n-2,m-2}^s(\xi,k) + a_n b_m\xi f_{n-1,m-1}^s(\xi,k - i/2)$$

$$+ b_n a_m\xi f_{n-1,m-1}^s(\xi,k + i/2) + a_n c_m f_{n-1,m-2}^s(\xi,k) + b_n c_m\xi f_{n-1,m-2}^s(\xi,k + i/2)$$

$$+ c_n a_m f_{n-2,m-1}^s(\xi,k) + c_n b_m\xi f_{n-2,m-1}^s(\xi,k - i/2), \quad (82)$$

where it is understood that $f^s_{l,m}(\xi,k)$ is zero whenever l and/or m is negative.

Equation (82) allows us to calculate $f^s_{n,n}(\xi,k)$ from $f^s_{0,0}(\xi,k+il)$, where $l=0,\pm 1,\ldots,\pm n$. We have found this procedure to be stable towards loss of significant figures. It is again stressed that it is s that is being kept fixed in Eq. (82), and that λ varies in steps of unity. A recurrence relation for f^λ_{mn} with $m\neq n$ would involve two s values according to Eq. (46) and hence be considerably more complicated. We do not explore it here.

On the basis of the above expressions we have made a detailed study of the Wigner functions $f^\lambda_n(y,k)$ for $\lambda=4$ and $n=0,1,2,3$. The results are shown in Fig. 8 as a set of contour diagrams. In accordance with Eqs. (53) and (67) we have again chosen

$$(Q,P) = (\sqrt{\lambda}\,y,k/\sqrt{\lambda}) \tag{83}$$

as the independent variables. This choice has the advantage, as pointed out earlier, that it gives an optimal picture of the anharmonicity effects. In Fig. 8, the anharmonicity effects are given by the way in which the contour curves deviate from circles centered on the origin of phase space.

Figure 8 shows very large anharmonicity effects, especially for the excited states. It must, however, be remembered that the λ values encountered in physical applications are considerably larger than four. They will typically lie in the range from $\lambda=10$ to 100. Thus, the ground state will in general be more harmonic than Fig. 8(a) shows, and it will take the whole range of n vlaues to reach an early dissociating state similar to the one shown in Fig. 8(d).
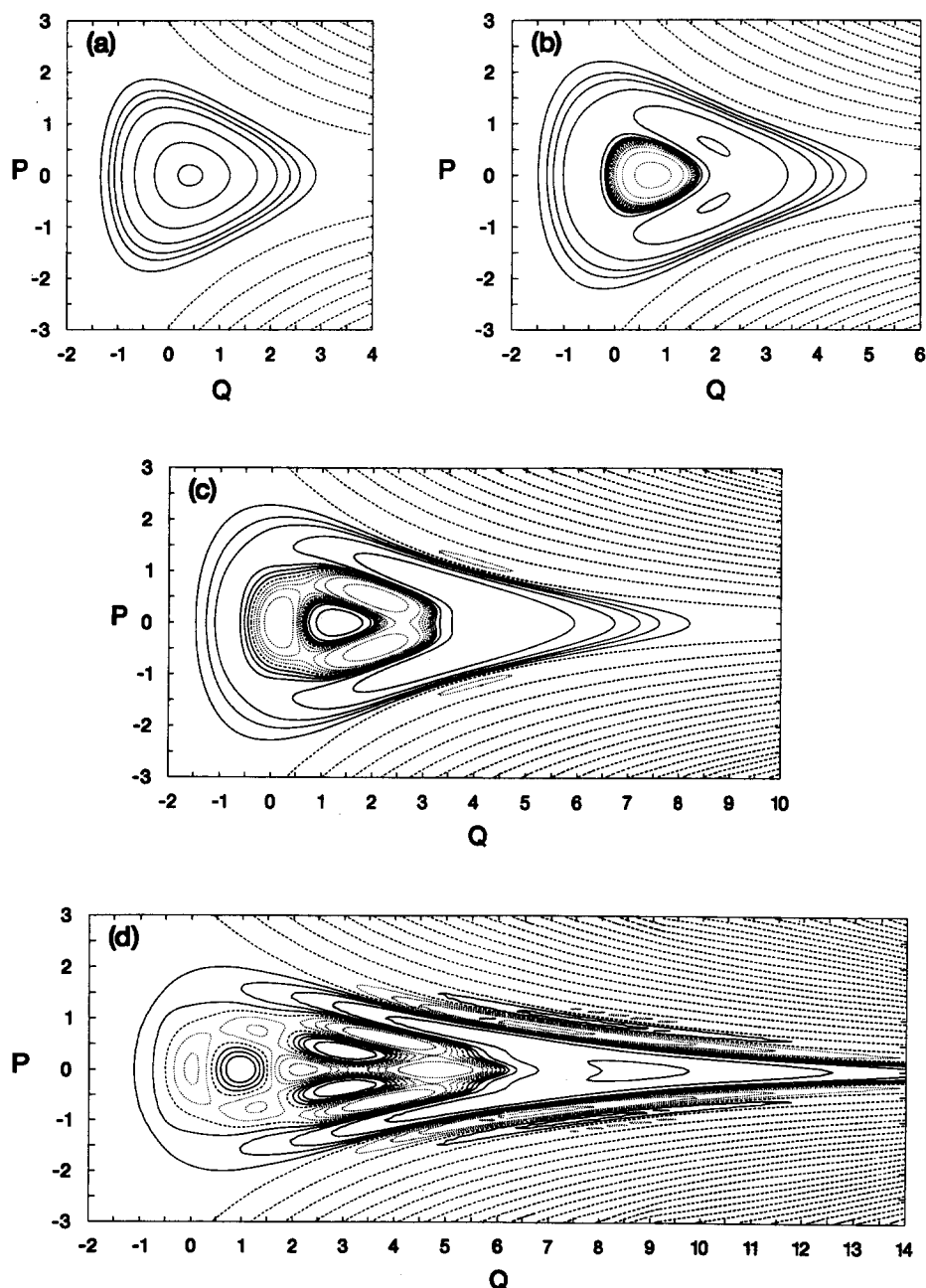

FIG. 8. Wigner's phase space function $F(Q,P)$ for the Morse oscillator with $\lambda=4$ for the ground state $[n=0$ (a)], the first $[n=1$, (b)], the second $[n=2$, (c)], and the third $[n=3$, (d)] excited state. The function is shown as contour curves in a (Q,P) phase plane where Q and P are the renormalized position and momentum coordinates, respectively. Contour values in a.u.: positive (solid curves): 0.30, 0.20, 0.10, 0.05, 0.03, 0.02, 0.01; 0 (dashed curves); negative (dotted curves): -0.30, -0.20, -0.10, -0.05, -0.03, -0.02, -0.01.

TABLE I. Positions, values, and types of some selected local extrema in Fig. 8. $n = 0, 1, 2, 3$ in the table corresponds to a, b, c, d in the figure.

n	Q	P	Value	Type
0	0.40	0.00	0.315	max
1	0.74	0.00	-0.262	min
	1.98	± 0.57	0.208	max
2	0.17	0.00	-0.084	min
	1.33	0.00	0.185	max
	2.10	± 0.54	-0.161	min
	3.54	± 0.66	0.194	max
	4.17	± 1.14	-0.012	min
	4.56	0.00	0.195	max
3	-0.91	0.00	0.012	max
	0.01	0.00	-0.023	min
	0.98	0.00	0.046	max
	1.28	± 0.76	-0.022	min
	2.19	0.00	-0.062	min
	3.02	± 0.36	0.084	max
	3.90	± 0.59	-0.089	min
	4.81	0.00	-0.087	min
	6.36	± 0.90	-0.057	min
	7.63	± 0.96	0.024	max
	8.72	± 0.06	0.215	max

The information displayed in Fig. 8 is supplemented by Table I which gives the positions of some selected maxima and minima of the Wigner functions, and also the value of the Wigner functions at those positions. These values may be compared with the values that can be read off Fig. 3 for the harmonic oscillator. Again, we draw attention to the fact that the values of a Wigner function are bounded by the relation (31).

The Wigner functions for the Morse oscillator have, in particular, been used in studies of collision induced dissociation[37] and photodissociation.[38] In the first of these studies the Wigner functions were obtained by numerical integration of Eq. (71). In the second it was obtained by expanding the Morse eigenfunctions in terms of harmonic oscillator eigenfunctions and evaluating the general Wigner functions for the harmonic oscillator. The expressions derived in the present section allow a much more systematic use of the Morse Wigner functions in molecular problems.

In closing, we would like to draw attention to a recent article by one of us, in which the Morse oscillator is studied in the semiclassical limit, as part of a general discussion of the phase space representation of quantum mechanics and the Bohr–Heisenberg correspondence rules.[39]

VI. CONCLUDING REMARKS

The present paper gives, for the first time, a unified description of the position-space wave functions, the momentum-space wave functions, and the phase-space Wigner functions for the bound states of a Morse oscillator. The position and momentum variables were carefully chosen so as to facilitate a comparison with the corresponding harmonic oscillator functions, thereby clearly demonstrating the effects of the anharmonic parts of the Morse potential. The analytical expressions for the position-space wave functions and the Wigner functions are given in terms of La-

guerre polynomials with rapidly decreasing argument. We have paid attention to the problem of losing significant figures in calculating the resulting alternating series, and we have given algorithms by means of which the functions may be evaluated such that this problem may be circumvented. The algorithms may also be applied for other problems where Laguerre polynomials are to be calculated. Since experience has shown that the Morse potential offers good approximations to the energy levels of a large class of systems in chemical physics, we believe that our analysis will be useful for the solution of a variety of problems.

APPENDIX

In this Appendix we shall discuss the numerical evaluation of the modified Bessel function $K_\nu(R)$, of positive argument and complex order. This is the function which appears in the expression (74) for the Morse oscillator Wigner functions, but to emphasize that the argument of the function is supposed to be real and positive, we write R instead of ξ.

The integral representation of $K_\nu(R)$, as given in Eq. (75), is

$$K_\nu(R) = \frac{1}{2}\int_0^\infty \tau^\nu \exp\left[-\frac{R}{2}\left(\tau + \frac{1}{\tau}\right)\right]\frac{d\tau}{\tau}. \quad (A1)$$

ν may vary over the entire complex plane, but it is readily seen that

$$K_{-\nu}(R) = K_\nu(R) \quad (A2)$$

and

$$K_{\nu^*}(R) = K_\nu(R)^*. \quad (A3)$$

The computational problem is thus reduced to the quadrant $\mathrm{Re}(\nu) \geqslant 0 \wedge \mathrm{Im}(\nu) \geqslant 0$.

Standard computer programs for the calculation of $K_\nu(R)$ exist when ν is a positive integer or zero, but for the general values of ν needed in this work no programs seem available. One might consider using the relation[35]

$$K_\nu(z) = i\frac{\pi}{2}\exp(i\pi\nu/2)\{J_\nu(iz) + iY_\nu(iz)\}, \quad (A4)$$

where $J_\nu(iz)$ and $Y_\nu(iz)$ are Bessel functions of the first and second kind, respectively. Computer programs are available for these functions, but the relation (A4) implies a serious loss of significant figures in our case, and is thus numerically unstable.

For considerable (ν, R) regions, including the transition region described below, a straightforward numerical integration is a good procedure for the evaluation of $K_\nu(R)$, in particular if we introduce the new integration variable

$$u = \ln \tau, \quad (A5)$$

and write, instead of Eq. (A1):

$$K_\nu(R) = \frac{1}{2}\int_{-\infty}^\infty \exp(\nu u - R\cosh u)du, \quad (A6)$$

or

$$e^R K_\nu(R) = \frac{1}{2}\int_{-\infty}^\infty \exp[\nu u - R(\cosh u - 1)]du. \quad (A7)$$

For sufficiently large values of $\mathrm{Im}(\nu)$ the integrand in Eq. (A7) becomes a strongly oscillating function of u, and

numerical integration is no longer feasible. In this case, as well as in many cases where a numerical integration is in fact possible, the proper procedure is to calculate $K_\nu(R)$ from its asymptotic expansions. Such asymptotic expansions have, in particular, been studied by Olver,[40] but the expressions presented by him exclude the important part of the ν plane about the imaginary axis and have to be generalized for our purpose. This generalization is described below. It leads to a fast and reliable procedure for the evaluation of $K_\nu(R)$ in the pertinent (ν,R) regions.

The starting point for Olver's discussion is the differential equation

$$z^2 \frac{d^2 f(z)}{dz^2} + z \frac{df(z)}{dz} - (z^2 + \nu^2) f(z) = 0, \qquad (A8)$$

which the modified Bessel functions $I_\nu(z)$ and $K_\nu(z)$ must satisfy.[35] By a suitable transformation of this equation he derived two independent asymptotic solutions for the function $f(\nu z)$, which we write as

$$S_\nu(\nu z) = \sqrt{\frac{\pi}{2\nu}} \frac{e^{-\nu\varsigma}}{(1+z^2)^{1/4}}$$
$$\times \left\{ 1 + \sum_{k=1}^{\infty} (-1)^k \frac{U_k(t)}{\nu^k} \right\} \qquad (A9)$$

and

$$T_\nu(\nu z) = \sqrt{\frac{\pi}{2\nu}} \frac{e^{\nu\varsigma}}{(1+z^2)^{1/4}} \left\{ 1 + \sum_{k=1}^{\infty} \frac{U_k(t)}{\nu^k} \right\}. \qquad (A10)$$

Here

$$\varsigma = \sqrt{1+z^2} + \ln \frac{z}{1+\sqrt{1+z^2}} \qquad (A11)$$

and

$$t = 1/\sqrt{1+z^2}. \qquad (A12)$$

$U_k(t)$ is a polynomial in t, of order k.

In particular, Olver showed that

$$K_\nu(\nu z) \sim S_\nu(\nu z) \qquad (A13)$$

and

$$I_\nu(\nu z) \sim \frac{1}{\pi} T_\nu(\nu z). \qquad (A14)$$

These expansions are uniformly valid with respect to z when $|\nu|$ is large, with z confined to the half-plane $|\arg z| < \pi/2$, and ν to the half-plane $|\arg \nu| < \pi/2$.

The lowest order polynomials $U_k(t)$ are[40,41]

$$U_1(t) = \frac{t}{8}(3 - 5t^2)/3,$$

$$U_2(t) = \left[\frac{t}{8}\right]^2 (81 - 462t^2 + 385t^4)/18,$$

$$U_3(t) = \left[\frac{t}{8}\right]^3 (30375 - 3\,69603t^2 + 7\,65765t^4 - 4\,25425t^6)/810,$$

$$U_4(t) = \left[\frac{t}{8}\right]^4 (44\,65125 - 941\,21676t^2 + 3499\,22430t^4 - 4461\,85740t^6 + 1859\,10725t^8)/9720,$$

$$U_5(t) = \left[\frac{t}{8}\right]^5 (15190\,35525 - 4\,92869\,48607t^2 + 28\,44997\,69554t^4$$
$$- 61\,41358\,72350t^6 + 56\,60981\,57625t^8 - 18\,86993\,85875t^{10})/2\,04120,$$

$$U_6(t) = \left[\frac{t}{8}\right]^6 (275\,70494\,77875 - 12757\,72983\,54750t^2 + 105076\,07744\,57901t^4 - 3\,36903\,20682\,61860t^6$$
$$+ 5\,10469\,67162\,44125t^8 - 3\,68529\,90061\,38750t^{10} + 1\,02369\,41683\,71875t^{12})/183\,70800. \qquad (A15)$$

The domain of validity for the expressions (A13) and (A14) does not include the important points on and close to the imaginary ν axis. In addition, we have also noted that the expressions are surprisingly inaccurate in certain regions where they might be expected to work well. For our purpose, we must of course choose z such that

$$\nu z = R. \qquad (A16)$$

We have found, that a modification of Olver's results leads to a satisfactory procedure for the computation of $K_\nu(R)$, apart from a "transition" region in which $\mathrm{Re}(\nu^2 + R^2)$ is numerically small. The procedure may be described as follows.

For a given value of R, the transition region divides the first quadrant of the complex ν plane into three domains, A,

B, and C. B is the transition region itself, and in this domain all asymptotic expansions are useless.

A is the domain in which $\mathrm{Re}(\nu^2 + R^2) > 0$. It includes, in particular, the positive real axis. As discussed below we put in this domain

$$K_\nu(\nu z) \sim S_\nu(\nu z), \quad \nu z = R. \qquad (A17)$$

C is the domain in which $\mathrm{Re}(\nu^2 + R^2) < 0$, and here we put

$$K_\nu(\nu z) \sim S_\nu(\nu z) + ie^{i\nu\pi} T_\nu(\nu z), \quad \nu z = R. \qquad (A18)$$

On the imaginary axis the two contributions to $K_\nu(R)$ become the complex conjugates of each other, and the modification is therefore both substantial and essential.

We can justify the above modification by a set of heuris-

tic arguments tied to the method of steepest descent and the integral representation (A6), which we rewrite as

$$K_\nu(\nu z) = \frac{1}{2}\int_{-\infty}^{\infty} \exp[\nu(u - z\cosh u)]du, \quad \nu z = R. \tag{A19}$$

Let

$$F(u) = u - z\cosh u. \tag{A20}$$

Then

$$F'(u) = 1 - z\sinh u, \tag{A21}$$

where a prime denotes differentiation with respect to u. This equals zero when

$$\sinh u = 1/z. \tag{A22}$$

The saddle points of $F(u)$ are accordingly defined by

$$\tau_1 = \frac{1 + \sqrt{1 + z^2}}{z}, \qquad u_1 = \ln\tau_1,$$
$$\tag{A23}$$
$$\tau_2 = \frac{1 - \sqrt{1 + z^2}}{z}, \qquad u_2 = \ln\tau_2.$$

We note that

$$\tau_1\tau_2 = -1, \quad u_1 + u_2 = i\pi. \tag{A24}$$

Furthermore

$$F''(u_1) = -\sqrt{1 + z^2},$$
$$F''(u_2) = \sqrt{1 + z^2}, \tag{A25}$$

and

$$F(u_1) = \ln\frac{1 + \sqrt{1 + z^2}}{z} - \sqrt{1 + z^2},$$
$$\tag{A26}$$
$$F(u_2) = \ln\frac{1 - \sqrt{1 + z^2}}{z} + \sqrt{1 + z^2}.$$

Thus,

$$F(u_1) = -\zeta,$$
$$F(u_2) = \zeta + i\pi. \tag{A27}$$

To estimate the value of the integral (A19) the contour of integration is deformed such that it passes through the maximum number of saddle points in the u plane. Furthermore, it must cross a saddle point along a path where $\mathrm{Re}\{\nu F(u)\}$ varies as steeply as possible and goes through a maximum. With these restrictions, it is possible to take the contour of integration through both saddle points when $\nu \in C$, but only through u_1 when $\nu \in A$. The domain B is the domain where the saddle regions are quite flat. It is only vaguely defined.

By standard methods (see, e.g., Ref. 42) we find

$$K_\nu(\nu z) \sim \sqrt{\frac{\pi}{2\nu}}\frac{1}{(1 + z^2)^{1/4}}e^{\nu F(u_1)}, \quad \nu \in A, \tag{A28}$$

$$K_\nu(\nu z) \sim \sqrt{\frac{\pi}{2\nu}}\frac{1}{(1 + z^2)^{1/4}}e^{\nu F(u_1)} + ie^{\nu F(u_2)},$$
$$\nu \in C. \tag{A29}$$

By introducing ζ via Eq. (24) we rediscover the factors in front of the parentheses in Eqs. (3) and (4), and we are thus

led to take the expressions (12) and (13) as the appropriate approximate solutions of Eq. (1) in the domains A and C, respectively.

These expressions are, of course, not asymptotic expressions because we have not assumed ν to be large. It is, however, easy to see that if $\mathrm{Re}(\nu) < \pi/2$ then the contribution from $e^{i\nu\pi}T_\nu(\nu z)$ becomes vanishingly small for $|\nu|$ becoming very large. In this sense there is complete agreement with Olver's results.

When summing the series (A9) and (A10) it must be remembered that they are asymptotic series. Hence, a series should be terminated with the numerically smallest term. The absolute magnitude of that term is a measure of the accuracy obtained. With the domain B taken sufficiently large, an arbitrarily high degree of accuracy is obtained by using the asymptotic expansions in the domains A and C.

ACKNOWLEDGMENT

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