Phase Space Approach to Solving the Time-independent Schrödinger Equation

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We propose a method for solving the time independent Schrödinger equation based on the von Neumann (vN) lattice of phase space Gaussians. By incorporating periodic boundary conditions into the vN lattice [F. Dimler et al., New J. Phys. 11, 105052 (2009)] we solve a longstanding problem of convergence of the vN method. This opens the door to tailoring quantum calculations to the underlying classical phase space structure while retaining the accuracy of the Fourier grid basis. The method has the potential to provide enormous numerical savings as the dimensionality increases. In the classical limit the method reaches the remarkable efficiency of 1 basis function per 1 eigenstate. We illustrate the method for a challenging two-dimensional potential where the FGH method breaks down.

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The formal framework for quantum mechanics is an infinite dimensional Hilbert space. In any numerical calculation, however, a wave function is represented in a finite dimensional basis set and therefore the choice of basis set determines the accuracy. The optimal basis set should combine accuracy and flexibility, allowing a small number of basis functions to represent the wave functions even in the presence of complex boundary conditions and geometry. Unfortunately, these two criteria—accuracy and efficiency—are usually in conflict, and globally accurate methods [1, 3] lack the flexibility of local methods [2, 7]. For example, in the pseudospectral Fourier grid method the wave function is represented by its values on a finite number of evenly spaced grid points. Due to the Nyquist sampling theorem, this allows for an exact representation of the wave provided the wavefunction is band limited with finite support [8–10]. However, the non-local form of the basis functions in momentum space leads to limited efficiency. On the other hand, in the von Neumann basis set [11, 12] each basis function is localized on a unit cell of size \( h \) in phase space. Despite the formal completeness of the vN basis set [13], attempts to utilize this basis in quantum numerical calculations have been plagued with numerical errors [4, 14].

In this paper we establish a precise mathematical formalism for the vN basis on a truncated phase space. By using periodic boundary conditions in the vN basis, as introduced in the seminal work by Dimler et al. [13], the method achieves Fourier accuracy with Gaussian flexibility. This allows one to tailor the basis in quantum eigenvalue calculations to the underlying classical phase space structure, with the potential for enormous numerical savings. The efficiency of the method relative to the Fourier grid rises steeply with dimensionality, defeating exponential scaling. In the classical limit the method reaches the remarkable efficiency of 1 basis function per 1 eigenstate.

The von Neumann basis set [12] is a subset of the “coherent states” of the form:

\[
g_{nl}(x) = \left( \frac{2\alpha}{\pi} \right)^{\frac{1}{4}} \exp \left( -\alpha(x-na)^2 - il\frac{2\pi}{a}(x-na) \right) \tag{1}\]

where \( n \) and \( l \) are integers. Each basis function is a Gaussian centered at \((na, \frac{2\pi}{a})\) in phase space. Taking \( \Delta x = a, \Delta p = \hbar/a \) as the spacing between neighboring Gaussians in \( x \) and \( p \) space respectively, we note that \( \Delta x \Delta p = \hbar \) so we have exactly one basis function per unit cell in phase space. As shown in [13] this implies completeness in the Hilbert space.

The “complete” vN basis, where \( n \) and \( l \) run over all integers, spans the infinite Hilbert space. In any numerical calculation, however, \( n \) and \( l \) take on a finite number of values, producing \( N \) Gaussian basis functions \( \{g_i\} \), \( i = 1...N \). Since the size of one vN unit cell is \( h \), the area of the truncated vN lattice is given by \( S_{vN} = Nh \).

The pseudospectral Fourier method (also known as the sinc Discrete Variable Representation [16]) is a widely used tool in quantum simulations [17–20]. In this method a function \( \psi(x) \) that is periodic in \( L \) and band limited in \( K = \frac{\pi}{L} \) can be written in the following form: \( \psi(x) = \sum_{n=1}^{N} \psi(x_n)\theta_n(x) \), where \( x_n = \delta_x(n-1) \), and \( \delta_x = \frac{\pi h}{L} \). The basis functions \( \{\theta_n(x)\} \) are given by [21]:

\[
\theta_n(x) = \sum_{j=\delta_x+1}^{\delta_x+L} \frac{1}{\sqrt{LN}} \exp \left( i\frac{2\pi}{L}(x - x_n) \right), \tag{2}
\]

which can be shown to be sinc functions that are periodic on the domain \([0, L]\) [22]. The set \( \{\theta_i(x)\} \) \( i = 1,...,N \) spans a rectangular shape in phase space with area of \( S_{FGH} = 2LP = 2L\frac{\pi}{L} = Nh \). Thus \( N \) unit cells in the vN lattice and \( N \) grid points in the Fourier method cover the same rectangle with an area in phase space of:

\[
S_{vN} = S_{FGH} = Nh \tag{3}
\]
We can write eq.(4) in matrix notation as: Gaussian functions with periodic boundary conditions.

\[ \tilde{g}_m(x) = \sum_{n=1}^{N} \theta_n(x) g_m(x_n) \]  

for \( m = 1, ..., N \). The new basis set is in some sense, the Gaussian functions with periodic boundary conditions. We can write eq.4 in matrix notation as: \( \tilde{G} = \Theta G \) where \( G_{ij} = g_j(x_i) \) By taking the width parameter \( \alpha = \frac{\Delta p}{2 \Delta x} \) we can guarantee that the pvN functions have no linear dependence and that the matrix \( G \) is invertible, that is \( GG^{-1} = \Theta \). The invertibility of \( G \) implies that both bases span the same space.

The representation of \( |\psi\rangle \) in the pvN basis set is given by:

\[ |\psi\rangle = \sum_{m=1}^{N} |\tilde{g}_m\rangle a_m. \]  

To find the coefficients \( a_m \) we first define the overlap matrix, \( S \):

\[ S_{ij} = \langle \tilde{g}_i | \tilde{g}_j \rangle = \int_{-L}^{L} \tilde{g}_i^*(x) \tilde{g}_j(x) dx \]

\[ = \sum_{n=1}^{N} \sum_{m=1}^{N} g_j^*(x_n) g_j(x_m) \int_{-L}^{L} \theta_n^*(x) \theta_m(x) dx \]

\[ = \sum_{n=1}^{N} g_j^*(x_n) g_j(x_n) \]  

or

\[ S = G^\dagger G. \]  

Using the completeness relationship for non-orthogonal bases, \( |\psi\rangle \) can be expressed as

\[ |\psi\rangle = \sum_{n=1}^{N} \sum_{m=1}^{N} |g_m(S^{-1})_{mn}\rangle |\tilde{g}_n\rangle |\psi\rangle. \]  

Comparing with eq.11, we find that \( a_m = \sum_{n=1}^{N} (S^{-1})_{mn} \langle \tilde{g}_m | \psi \rangle \) and \( \langle \tilde{g}_i | \psi \rangle = \sum_{n=1}^{N} g_i^*(x_n) \psi(x_n) \).

Although the periodic von Neumann (pvN) and the Fourier methods span the same rectangle in phase space, the localized nature of the basis functions in the pvN method can lead to significant advantages. In particular, if \( |\psi\rangle \) has an irregular phase space shape we may expect that some of the pvN basis functions will fulfill the relation: \( \langle \tilde{g}_j | \psi \rangle = 0, \quad j = 1, ..., M. \) Due to the non-orthogonality of the basis we cannot simply eliminate the states \( \tilde{g}_j \), since the coefficients of \( \tilde{g}_j \) may include contributions from remote basis functions, but we can take advantage of the vanishing overlaps by defining a bi-orthogonal von Neumann basis (bvN) \( \{ b_i(x) \} \).

\[ |b_i\rangle = \sum_{j=1}^{N} |\tilde{g}_j(S^{-1})_{ji}\rangle \]  

or in matrix notation: \( B = \tilde{G}S^{-1} \). Inserting eq.10 into eq.9 \( |\psi\rangle \) can be written as

\[ |\psi\rangle = \sum_{n=1}^{N} |b_n\rangle c_n = \sum_{n=1}^{N} |b_n\rangle \langle \tilde{g}_n | \psi \rangle. \]  

By assumption, \( M \) of the coefficients are zero, hence in order to represent \( |\psi\rangle \) in the bvN basis set we need only \( N' = N - M \) basis functions. Note that the bvN and pvN are bi-orthogonal bases, meaning that each set taken by itself is non-orthogonal but they are orthogonal to each other. This can be shown easily by:

\[ \langle \tilde{g}_i | b_j \rangle = \sum_{n=1}^{N} g_i^*(x_n) f_j(x_n) \]

\[ = \sum_{m=1}^{N} \sum_{n=1}^{N} g_i^*(x_n) g_m(x_n) (S^{-1})_{mj} \]

\[ = \sum_{m=1}^{N} S_{im} (S^{-1})_{mj} = \delta_{ij}. \]  

For many practical applications the full knowledge of the basis wavefunctions is unnecessary: we need only the value of the basis functions at the sampling points. For example the evaluation of Hamiltonian matrix elements can be performed explicitly by:
$H_{ij}^{\text{pvN}} = \langle \hat{g}_i | H | \hat{g}_j \rangle$

$= \sum_{m=1}^{N} \sum_{n=1}^{N} g_i^*(x_m) \langle \theta_m | H | \theta_n \rangle g_j(x_n)$

$= \sum_{m=1}^{N} \sum_{n=1}^{N} g_i^*(x_m) H_{mn}^{\text{FGH}} g_j(x_n)$

(12)

and similarly:

$H_{ij}^{\text{bvN}} = \sum_{m=1}^{N} \sum_{n=1}^{N} b_i^*(x_m) H_{mn}^{\text{FGH}} b_j(x_n)$

(13)

where $H_{ij}^{\text{FGH}} = V_{ij}^{\text{FGH}} + T_{ij}^{\text{FGH}}$ and the potential and the kinetic matrix are given by: $V_{ij}^{\text{FGH}} \approx V(x_i) \delta_{ij}$ and

$T_{ij}^{\text{FGH}} = \frac{\hbar^2}{2M} \left( \frac{\hbar^2}{M^2} \sin^2(\pi \frac{k \cdot x}{L}) \right)$, if $i = j$

and

$= \frac{\hbar^2}{2M} \left( \frac{\hbar^2}{M^2} - 1 \right)^{-1} \sin^2(\pi \frac{k \cdot x}{L})$, if $i \neq j$

(14)

[23]. The eigenvalue problem in a non-orthogonal basis set becomes $H \psi = s \psi$; in the pvN basis set $\psi$ is given by eq. (7) and in the bvN basis set $\psi$ is given by:

$B^\dagger B = S^{-1} G! G S^{-1} = S^{-1}$.  

(15)

Diagonalization should give accurate results for all wavefunctions localized to the classically allowed region of the rectangle. Note that in the multidimensional implementation, the $S^{-1}$ matrix required in Eq.(9) can be constructed separately for each dimension. As a result, the computational effort to construct the bvN basis set is negligible compared with diagonalizing the Hamiltonian.

As a numerical test of the pvN basis set we studied the standard example of the harmonic oscillator $V(x) = \frac{m \omega^2}{2} x^2$ in units such that $m = \hbar = \omega = 1$. We calculated the seventh excited energy using different number of pvN and conventional Gaussian basis functions. In the Gaussian basis set the Hamiltonian and the overlap matrices were calculated analytically as:

$H_{ij} = \langle g_i | H | g_j \rangle = \int_{-\infty}^{\infty} g_i^*(x) [-\frac{d^2}{dx^2} + V(x)] g_j(x) dx$ and

$S_{ij} = \langle g_i | g_j \rangle = \int_{-\infty}^{\infty} g_i^*(x) g_j(x) dx$.

The results, shown in Fig. 2(a), show the superiority of the pvN basis set compared to the standard Gaussian basis set. In fact, the results obtained with the pvN basis set are exactly as accurate as in the Fourier grid method. The kinetic energy spectra in Fig. 2(b) show that the pvN has a perfect quadratic dependence while the vN spectrum is highly flawed.

In the bvN basis set we are able to remove some of the basis functions and construct lower dimensional $H^{\text{bvN}}$ and $S^{\text{bvN}}$ matrices without losing accuracy. In order to test this claim, we calculated numerically the eigenergies of the Morse oscillator $V(x) = D(1 - e^{-\beta x})^2$ by using both the FGH and bvN basis sets. The Morse parameters were taken to be $D = 12, m = 6, \beta = 0.5$ and $\hbar = 1$. For FGH, 100 grid points between $[-1.6, 20.1]$ were required to get 4 digits of accuracy in energy for all 24 bound states. By using the bvN basis functions (constructed from $10 \times 10$ vN functions with $\alpha = 0.5$) we obtain the same 4 digit accuracy with only 48 basis functions. This is demonstrated graphically in Fig. 3(a). The figure shows the phase space representation of 100 evenly grid points. Although it requires 100 pvN basis functions to span this area in phase space, due to the flexibility of the bvN basis set we can suffice with just the basis functions in the classically allowed region (magenta squares).

FIG. 2: (a) Error in the $7^{\text{th}}$ eigenvalue of the harmonic oscillator as a function of basis set size for vN(dashed) and pvN(solid). (b) Kinetic energy spectra using 16 basis functions. vN(dashed), pvN(solid).

FIG. 3: (a) Phase space area spanned in the bvN method (magenta) and in the pvN (or FGH) method (full rectangle) for Morse. (b) Efficiency ratio (defined as number of basis functions per converged eigenstates) of the pvN (solid) and FGH (dashed) methods for the Morse potential as function of $h$.

The ability to localize a bvN function at a specific point in phase space results in the remarkable concept of 1 basis function per 1 eigenstate. This means that in order to calculate $N$ eigenenergies we need only $N$ basis functions. Obviously, such one per one efficiency, if reachable, will be the ideal efficiency for any basis set. In order to test the ability of the bvN method to reach the ideal efficiency we examined the Morse potential and looked for
the smallest basis that provides 12 digits of accuracy for all the eigenvalues up to \( E = 11.25 \). The bvN method indeed tends to the ideal efficiency in the classical limit \( h \to 0 \) (Fig. 3b). This remarkable result is unique for methods based on phase space localization [24].

The true power of the method is in the application to higher dimensional systems. As an illustration, consider the potential \( V(r, \theta) = (1 - \exp(-\alpha r^2)) \) where \( \alpha = ((1 - \cos(3\theta))/4)^2 + 0.05 \). This 3-fold symmetric potential (Fig. 1), which is a realistic model for a system of three identical particles and fixed hyperradius, is quite challenging for the FGH method. Taking \( m = 96, h = 1 \) gives 760 states below \( E = 0.996 \). In order to get two digits of accuracy for all those states one needs \( \sim 11000 \) FGH grid points, while with the bvN basis set convergence is achieved with only 1500 basis functions. For higher accuracy (four digits), the FGH breaks down completely while the bvN method requires fewer than 3000 basis functions (Fig. 5a-b). Figure 5c shows again that as \( h \to 0 \) the efficiency tends to 1 basis function per 1 eigenstate (because of the size of the calculations we consider just 3 digits of accuracy). In contrast, the FGH efficiency as \( h \to 0 \) is determined by the ratio between the classical phase space and the box that contains it, which we calculate to be \( \sim 10 \) for this system using Monte Carlo integration. Note that in going from 1-d to 2-d the savings provided by the bvN relative to the FGH method has gone from 2 to 7-10 for qualitatively similarly potentials. This suggests that the relative efficiency of the bvN method increases rapidly with dimension.

To explore the scaling with dimensionality more fully, consider a harmonic oscillator with 1-d classical phase space volume \( v \) up to energy \( E \). For the \( D \)-dimensional oscillator, the total phase space volume up to energy \( E \) is \( V = v^{D}/D! \). In the classical limit, the total number of states is determined by \( V/h^{D} \) and therefore in this limit the efficiency of pvN relative to FGH is determined by the ratio of the phase space volumes spanned. Defining \( a \) to be the area of the box surrounding the 1-d oscillator phase space, the volume of the box surrounding the \( D \)-dimensional phase space is \( A = a^{D} \) and the ratio of phase space volumes is \( S = V/A = s^{D}/D! \) where \( s = v/a = \pi/4 \) for the harmonic oscillator. For the Morse, Coulomb and other chemically relevant potentials, the 1-d ratio \( s < \pi/4 \) and the \( D \)-dimensional phase space volume scales more slowly than \( v^{D}/D! \) [22]; these effects combine so that the relative efficiency of the pvN method rises steeply with dimension. As a result of the \( D! \) in the expression for \( V \), the method remarkably defeats exponential scaling. A more detailed analysis [22] shows that for \( D \gg v/h = g \) the method scales polynomially: \( V = D^{g}/g! \).

Work in progress includes application to vibrational eigenvalue calculations for realistic polyatomic molecules, electronic eigenvalues for multielectron atoms and extension of the approach to the time-dependent Schrödinger equation.

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SUPPLEMENTARY MATERIAL

I. THE DIRICHLET OR PERIODIC SINC FUNCTION

In Eqn. (2) of the paper we introduced the pseudospectral functions underlying the FGH/sinc DVR method as a sum of exponentials:

\[
\theta_n(x) = \frac{1}{\sqrt{LN}} \exp \left( \frac{i2\pi j}{L} (x - x_n) \right). \tag{1}
\]

In this section we will show that these pseudospectral functions \( \theta(x) \) are periodic sinc functions, proportional to the Dirichlet functions. We will first replace the index \( j \) with \( k = j + N/2 - 1 \) and define \( A = \frac{\pi j}{\sqrt{LN}} \) (for simplicity we suppress the subscript \( n \) on \( A \)) to obtain:

\[
\theta_n(x) = \sum_{k=0}^{N-1} \frac{1}{\sqrt{LN}} \exp \left( iA(k - N/2 + 1) \right) = \exp \left( iA\left( -\frac{N}{2} + 1 \right) \right) \sum_{k=0}^{N-1} \left( \exp (iA) \right)^k. \tag{2}
\]

For \( A = 2\pi m \), where \( m \) is an integer, \( \theta_n(x) = \frac{L}{\sqrt{N}} \); for \( A \neq 2\pi m \) we use the expression for a geometric series \( \sum_{k=0}^{N-1} r^k = \frac{1 - r^N}{1 - r} \) to get:

\[
\theta_n(x) = \frac{\exp \left( iA\left( -\frac{N}{2} + 1 \right) \right) \left( 1 - \exp(iAN) \right)}{\sqrt{LN}} = \frac{\exp \left( \frac{\pi}{2} \right) \sin \left( \frac{N\pi}{2} \right)}{\sqrt{LN}} = \frac{\exp \left( \frac{\pi}{2} \right) D_N(A),}{\sqrt{LN}}
\]

where \( D_N(A) \) is the Dirichlet function.

II. SCALING OF THE PVN METHOD WITH DIMENSIONALITY

In this section we discuss the scaling of the pvN method with the dimensionality of the system. We begin in Section II A by discussing the scaling of the classical phase space volume \( V \) up to energy \( E \) of a set of \( D \) isotropic harmonic oscillators. We show that \( V \) increases more slowly than exponential with \( D \).

Since the number of states \( G \) is given semiclassically by \( G = \frac{V}{h^D} \), and since in the classical limit the pvN method requires only 1 basis function per eigenstate, we find that the scaling of the pvN method is slower than exponential with \( D \).

In Section II B we note that semiclassically the efficiency of the pvN relative to the FGH method is (the inverse of) the ratio of the classical phase space volume to that of the enclosing box. For harmonic potentials, this relative efficiency increases faster than exponentially with dimension \( D \). For anharmonic potentials, two factors contribute to make the relative efficiency even higher than in the harmonic case.

In Section II C we go beyond the semiclassical formalism. Starting with a fully quantum formula for the number of states of a \( D \)-dimensional isotropic harmonic oscillator, we show that the scaling with \( D \) is sub-exponential, leading in the limit of large \( D \) to polynomial scaling, \( G = D^n/g! \).

A. Phase space volume \( V \) of the \( D \)-dimensional oscillator

The phase space of the \( D \)-dimensional isotropic harmonic oscillator up to energy \( E \), for \( \sum_i \frac{p_i^2}{2m} + \frac{1}{2} \omega_i \) \( (\omega_i = m_i = 1) \) is a sphere with radius \( R = \sqrt{2E} \) and volume \( V = \frac{\pi^D R^D}{D!} = \frac{\pi^D (2E)^D}{D!} \). This gives volume \( v = \pi R^2 \) 1-dimensional and volume

\[
V = \frac{v^D}{D!} \tag{3}
\]

in \( D \)-dimensions (Fig 1).

In 1-d, the relation between states and volume is \( g = \frac{v}{\lambda} \). Thus, we obtain a formula for the scaling of the total number of states similar to that for the phase space volume:

\[
G = \frac{V}{h^D} = g^D/D!. \tag{4}
\]

Because of the \( D! \) in Eqn. (4), \( G \) increases slower than exponentially. In fact according to Eqn. (4) \( G \) decreases for \( D > g \); however as we will show in Section II C this effect is an artifact of using the semiclassical formula outside of its domain of applicability.

![FIG. 1: Log of the volume of the classical phase space below \( E = 8 \) as a function of dimensionality (solid) compared with exponential scaling (dashed).](image-url)
B. Ratio between phase space volume and box

1. Harmonic potentials

The efficiency of the pvN method relative to the FGH in the classical limit is (the inverse of) the ratio of the classical phase space area and the enclosing box. For a 1-d harmonic oscillator, this is the ratio between the area of a circle and the square surrounding it, given by: \( s = \frac{\pi R^2}{(2R)^2} = \frac{\pi}{4} \). In D-dimensions, this ratio is \( S = \frac{\pi^D}{(2R)^D} = \left(\frac{\pi}{4}\right)^D \). Because of the \( D! \), the relative efficiency (the inverse of \( S \)) increases faster than exponentially with dimension \( D \).

2. 1-d anharmonic potentials

For the harmonic oscillator, the packing parameter \( s = \frac{\pi}{4} \approx 0.7854 \) is relatively close to 1. However most chemically relevant potentials have classical phase space shapes that are packed in a much less compact way (Fig.2). For example, for the Morse oscillator shown in Fig.2(b) \( s = 0.4638 \); for the Coulomb potential shown in Fig.2(c) \( s = 0.0321 \).

3. D-d anharmonic potentials

For anharmonic potentials, not only is \( s < \frac{\pi}{4} \), but the multidimensional classical phase space volume scales more slowly than in Eq.3. This can be understood by visualizing figures such as Figs. 2(b)-(c) in multidimensions, and is confirmed numerically using Monte Carlo integration (see Fig.(3)); in Section II C we rationalize this behavior in a different way using state counting arguments. As a consequence, the ratio of phase space volumes \( S_{\text{AHO}} \) is even smaller than \( S_{\text{HO}} = \frac{s^D}{D!} \) (and the efficiency of pvN is therefore larger):

\[
S_{\text{HO}} = \frac{s_{\text{HO}}^D}{D!} > \frac{s_{\text{AHO}}^D}{D!} > S_{\text{AHO}}. \tag{5}
\]

Since the harmonic efficiency (the inverse of \( S_{\text{HO}} \)) increases faster than exponentially with dimension \( D \), clearly the anharmonic efficiency (the inverse of \( S_{\text{AHO}} \)) does as well.

C. Number of states for D-dimensional potential

In Section II A we showed that for the \( D \)-dimensional isotropic harmonic oscillator, in the semiclassical limit, the number of states below energy \( E \) is given by \( G = g^D/D! \) We now reexamine this result starting from a fully quantum treatment. For a 1-d oscillator the number of states below energy \( E \) is \( g_{\text{AHO}} \), since some combinations give energy above \( E \). Computing \( G \) is identical to the number of ways to distribute no more than \( g \) indistinguishable balls (quanta of energy) into \( D \) distinguishable boxes (oscillators). The answer is given by Eq. 4

\[
G = \frac{g}{g_{\text{AHO}}} = \frac{g^D}{g_{\text{AHO}}^D} = (g + D)! \frac{g_{\text{AHO}}^D}{D!}. \tag{6}
\]

We now draw attention to two points about Eqn. 6:

1) Consider the case \( D = 2 \) with \( g \gg 2 \). Then Eqn. 6 becomes

\[
G = \frac{(g + 2)(g + 1)}{2} \approx \frac{g^2}{2}. \tag{7}
\]

The factor \( g^2 \) in the numerator has its origin in the tensor product Hilbert space of the two truncated harmonic oscillators. The factor of 2 in the denominator comes from the fact that about half of the states in the tensor product Hilbert space have energy \( E_1 + E_2 > E \). For a \( D \)-dimensional system the fraction of tensor product states with \( \Sigma_{i=1}^D E_i < E \) is approximately \( 1/N \)!

In the case of an anharmonic potential such as the Morse oscillator, the gaps between energy levels are not equal: the higher energy states are spaced more closely together. As a consequence, for a larger fraction of combinations than in the harmonic case \( \Sigma_{i=1}^D E_i > E \) and the scaling of \( G \) is slower than in Eq.4 (Fig. 3).

2) If we assume \( g \gg D \), Eq. 6 becomes

\[
G = \frac{g^D}{D!}, \tag{8}
\]
which is the same result as Eq. (4). However, in the opposite limit, \( D \gg g \), we obtain

\[
G = \frac{D^g}{g!},
\]

showing that for large enough \( D \) the scaling \( D \) is actually polynomial. Equations 6-9 are plotted in Fig. 4. The true scaling with \( D \) is clearly subexponential. Equation 8 is seen to be a valid approximation for \( g \gg D \), although the turnover at large \( D \) is an artifact of using the semiclassical formula outside of its range of validity.

![Figure 4: Log of the number of states \( G \) that have energy below \( E = gh\omega \), \( (g = 30) \) vs. \( D \) for a \( D \)-dimensional harmonic potential. The figure shows the exact expression (red), the approximations for \( g \gg D \) (blue), for \( D \gg g \) (green) and a comparison with exponential scaling (dashed).](image)

[1] W. Forst, Theory of Unimolecular Reactions: A Concise Introduction (Cambridge University Press, Cambridge, 2003), p. 84. (Forst gives the correct formula but says that the boxes are indistinguishable. This appears to an error; cf. J.E. Mayer and M.G. Mayer, Statistical Mechanics (Wiley, New York, 1966), Appendix A VII (10) p. 438.)