ADVANCED TOPICS SECTION

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Leading quantum correction to the classical free energy

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The quantum free energy of a system governed by a standard Hamiltonian is larger than its classical counterpart. The lowest-order correction, first calculated by Wigner, is proportional to $\hbar^2$ and involves the sum of the mean squared forces. We present an elementary derivation of this result by drawing upon the Zassenhaus formula, an operator-generalization for the main functional relation of the exponential map. Our approach highlights the central role of non-commutativity between kinetic and potential energy and is more direct than Wigner's original calculation, or even streamlined variations thereof found in modern textbooks. We illustrate the quality of the correction for the simple harmonic oscillator (analytically) and the purely quartic oscillator (numerically) in the limit of high temperature. We also demonstrate that the Wigner correction fails in situations with sufficiently rapidly changing potentials, for instance, the particle in a box.
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I. INTRODUCTION

The development of a quantum theory owes much to experimental work on cold systems, as quantum effects manifest most visibly at low temperatures. For instance, the unexpected drop in the heat capacities of solids was a prominent experimental puzzle; Einstein's solution,[1] later refined by Debye,[2] constituted a triumph of the emerging theory. Similarly, Planck's solution to the ultraviolet catastrophe relies on the fact that k_BT is small compared to the photon energy associated with high frequency modes.[3] Bose–Einstein condensation requires very low temperatures in order to simultaneously satisfy the conditions of low density (i.e., ideal gas case) but high phase space density (i.e., degeneracy).[4,5]

Formally, we frequently think of $\hbar \to 0$ as the classical limit, with quantum corrections arising in powers of $\hbar$. However, since the value of $\hbar$ cannot be changed in experiment, tuning the temperature turns out to be the next best option to explore the classical limit. Quantum statistical physics is, hence, the natural framework in which to consider quantum corrections, and $T \to \infty$ has become a frequent proxy for the classical limit. The two limits are not equivalent, though: The fact that the exponent $-\beta H$ in the canonical state becomes small in the high temperature limit does not necessarily imply that the Hamiltonian H is proportional to $\hbar$. Instead, the terms that are small are those that arise because position and momentum contributions to the Hamiltonian do not commute.

More precisely, quantum effects have two different origins. First, quantum operators (representing classical observables) need not commute. Second, the spin-statistics theorem imposes symmetry constraints on multi-particle quantum states, which gives rise to Fermi–Dirac and Bose–Einstein statistics. As it turns out, the former effect creates quantum corrections of order $\hbar^2$, while the latter creates effects of order $\hbar^3$—assuming a three-dimensional system in the non-degenerate limit $\lambda_{\rm th}^3(N/V) \ll 1$, where $\lambda_{\rm th} = h/\sqrt{2\pi m k_B T}$ is the thermal de Broglie wavelength and N/V is the particle density (for details, see Sec. SM 1 in the supplementary material[6]). Under many important conditions, Fermi or Bose considerations are, therefore, subleading to commutation considerations. Remarkably, the lowest order effect is not linear in $\hbar$.

Wigner was the first to present a systematic analysis of the $\hbar^2$-corrections, in a famous 1932 paper.[7] He clearly understood that non-commutativity was central to his result, but this connection is somewhat obscured by his ingenious yet roundabout calculation—so much so that at the end of his paper he muses on the possibility of a more direct derivation. Modern statistical physics textbooks tend to omit the subject; the few that do treat it[8,9] present a streamlined version of Wigner's argument—again leaving the key role of non-commutativity opaque. A very elegant derivation using path integrals can be found in Feynman/Hibbs,[10] and a more formal presentation of Wigner's approach, as further developed by Kirkwood, is given in a textbook by Brack and Bhaduri, which more broadly covers semi-classical methods.[11] Huang (in his textbook[12]) and Harper[13] both approach the question from an operator perspective, but neither author consistently expands the exponential of non-commuting operators to the required order to get the correct result. Our goal is to fill an apparent gap and present a derivation of Wigner's leading order quantum correction highlighting the fundamental role of non-commutativity, while remaining accessible to undergraduates. Our central tool will be a formula typically attributed to Zassenhaus, which disentangles the non-commuting kinetic and potential terms in the Boltzmann factor, thereby allowing for a systematic construction of quantum corrections.[14,15]

The Zassenhaus formula is a sophisticated identity, and proving it in generality requires a deep appreciation of Lie algebras and Lie groups. It might, thus, seem disingenuous to call our derivation of Wigner's result "elementary," but we shall summon the following two points to our defense: First, we find it useful to separate the mathematical idiosyncrasies of non-commuting operators from the physical question at hand. Second, proving Wigner's correction does not require the "full" Zassenhaus formula, i.e., the infinite series expansion. Its first two terms suffice, and we offer a straightforward (albeit not especially elegant) derivation of those.

We investigate how well the correction works by studying several examples. For the simple harmonic oscillator, everything can be calculated analytically. In other cases, calculating the quantum free energy typically requires resorting to numerics, or approximate methods such as WKB. We will also look at an ideal gas in a box and show that in this case the Wigner correction fails.

Systematically expanding exponentials of non-commuting operators is a well-travelled road and has led to many fruitful applications over the years. For instance, Suzuki published a series of articles in the 1990s, applying this procedure to quantum statistical mechanics (see Ref. 16 and references therein). It is also worth emphasizing that this formalism also has numerical applications. Notably, Takahashi and Imada used it to speed up the Monte Carlo evaluation of a quantum path integral.[17] They start with another widely used approach to evaluate the exponential of non-commuting quantum operators—namely, the Lie-Trotter product formula—and then speed up its convergence by an ingenious application of the Wigner correction. Indeed, their derivation relies on the same systematic operator expansions we will discuss here.

II. INTRODUCING WIGNER'S CORRECTION

We will examine quantum corrections arising for standard Hamiltonians of the form

$$H(\{P_i, Q_i\}) = \sum_{i=1}^{N} \frac{P_i^2}{2m} + U(\{Q_i\}) \equiv K + U, \tag{1}$$

where N is the number of particles, all of mass m, and where the potential energy U generally depends on all their coordinates. The position and momentum operators are $\{Q_i\}$ and $\{P_i\}$, respectively. We will use lowercase letters $\{q_i\}$ and $\{p_i\}$ to denote their eigenvalues.

The essence of the order $\hbar^2$ "operator correction" is fully contained in the single-particle situation. As explained in Sec. I (and the supplementary material), the inclusion of multiple particles leads to "exchange corrections," which are typically higher order in $\hbar$. To declutter the math, let us then first consider just a single degree of freedom,

$$H = \frac{P^2}{2m} + U(Q) \equiv K + U. \tag{2}$$

The quantum and classical partition functions for this Hamiltonian are

$$Z_Q = \mathrm{Tr}(e^{-\beta H}), \tag{3a}$$

$$Z_C = \int \frac{dp\,dq}{2\pi\hbar} e^{-\beta h(p,q)}, \tag{3b}$$

where "$\mathrm{Tr}(\cdot)$" denotes the trace over Hilbert space and $\beta = 1/(k_B T)$. Let us recall that $h(p, q)$ is the classical Hamiltonian belonging to the Hamilton operator $H(P, Q)$.

In both cases, the free energy is given by

$$F_{Q/C} = -k_B T \log(Z_{Q/C}). \tag{4}$$

Our goal is to find a relation between F_Q and F_C.

A. Prelude: An inequality between quantum and classical free energy

We begin by noting that the well known trace inequality due to Golden[18] and Thompson[19]

$$\mathrm{Tr}(e^{A+B}) \le \mathrm{Tr}(e^A e^B) \tag{5}$$

(for selfadjoint operators A and B) implies that the classical partition function constitutes an upper bound to the quantum partition function, as can be seen as follows:

$$Z_Q = \mathrm{Tr}(e^{-\beta(K+U)}) \tag{6a}$$

$$\le \mathrm{Tr}(e^{-\beta K} e^{-\beta U}) \tag{6b}$$

$$= \int dq\, \langle q| e^{-\beta P^2/2m} e^{-\beta U(Q)} |q\rangle \tag{6c}$$

$$= \int dq\, dp\, \langle q| e^{-\beta P^2/2m} |p\rangle \langle p| e^{-\beta U(Q)} |q\rangle \tag{6d}$$

$$= \int dq\, dp\, \langle q| e^{-\beta p^2/2m} |p\rangle \langle p| e^{-\beta U(q)} |q\rangle \tag{6e}$$

$$= \int \frac{dq\, dp}{2\pi\hbar} e^{-\beta[p^2/2m + U(q)]} = Z_C. \tag{6f}$$

In Eq. (6c), we evaluate the trace in the position basis; in Eq. (6d), we inserted a momentum-basis representation of unity, $\mathbb{1} = \int dp\, |p\rangle\langle p|$; in Eq. (6e), we replaced operators acting on eigenvectors by their eigenvalues; in Eq. (6f), we used $\langle q|p\rangle = e^{ipq/\hbar}/\sqrt{2\pi\hbar}$ (a plane wave in Dirac normalization). In consequence, we get

$$F_Q \ge F_C. \tag{7}$$

Quantum fluctuations can only increase the free energy compared to the classical limit.

The inequality $F_Q \ge F_C$ (as well as the fact that at large temperatures $F_Q \to F_C$) relies on the use of $2\pi\hbar$ when non-dimensionalizing the phase space volume in Eq. (3b). From a purely classical perspective, any constant with the dimension of an action would do, but picking Planck's constant enables this smooth link to the quantum description. In that sense, even the classical free energy depends (fairly benignly) on $\hbar$.

B. The main result: Wigner's correction

What is the leading correction that quantifies the extent by which the quantum free energy exceeds its classical counterpart?

In 1932, Wigner showed that if we ignore particle exchange complications, the answer for the standard Hamiltonian (1) is[7]

$$F_{\rm Q} = F_{\rm C} + \frac{\hbar^2}{24 m k_{\rm B} T} \sum_{i=1}^{N} \left\langle \frac{\partial^2 U}{\partial q_i^2} \right\rangle + \mathcal{O}(\hbar^4). \quad (8)$$

That this increases the free energy is plausible, considering that we expect a stable potential to be convex up; but it can be made obvious by integrating the expectation value by parts,

$$\begin{aligned} \langle U'' \rangle &= \frac{1}{Z_{\rm C}} \int {\rm d}q\, U''(q)\, {\rm e}^{-\beta U(q)} \\ &= \frac{1}{Z_{\rm C}} \int {\rm d}q\, U'(q) \left(-\frac{\partial}{\partial q} \right) {\rm e}^{-\beta U(q)} \\ &= \frac{1}{Z_{\rm C}} \int {\rm d}q\, U'(q)\, (\beta U'(q))\, {\rm e}^{-\beta U(q)} \\ &= \beta \, \langle (U')^2 \rangle, \end{aligned} \quad (9)$$

which leads to the manifestly positive correction

$$F_{\rm Q} = F_{\rm C} + \frac{\hbar^2}{24 m (k_{\rm B} T)^2} \sum_{i=1}^{N} \left\langle \left(\frac{\partial U}{\partial q_i} \right)^2 \right\rangle + \mathcal{O}(\hbar^4). \quad (10)$$

Our goal is now to provide an elementary derivation of this result.

III. PROVING WIGNER'S CORRECTION

Our main tool in the proof is an operator identity: The "Zassenhaus formula."[14,15] Like its more famous counterpart, the Baker–Campbell–Hausdorff formula,[20–23] the Zassenhaus formula provides corrections to the functional relation ${\rm e}^{x+y} = {\rm e}^x {\rm e}^y$ that arise when non-commuting objects A and B are exponentiated:

$${\rm e}^{t(A+B)} = {\rm e}^{tA} {\rm e}^{tB} \prod_{n=2}^{\infty} {\rm e}^{-t^n C_n / n!}, \quad (11)$$

where t is a constant and the "correction operators" C_n are nested commutators comprising n occurrences of either A or B. The first few are given by

$$C_2 = [A, B], \quad (12a)$$

$$C_3 = [[A, B], A] + 2[[A, B], B], \quad (12b)$$

$$\begin{aligned} C_4 = {} & [[[A, B], A], A] + 3[[[A, B], A], B] \\ & + 3[[[A, B], B], B], \end{aligned} \quad (12c)$$

where as usual $[A, B] = AB - BA$. Higher order C_n involve increasingly cumbersome expressions, which can be obtained recursively.[15,24–26] In the Appendix, we offer an elementary derivation of the correction operators C_2 and C_3, which suffice for our purposes. Observe also that if A and B commute, all C_n vanish and Eq. (11) reduces to the conventional functional relation.

In our case, we need to work with the quantum canonical state, proportional to the operator ${\rm e}^{-\beta(K+U)}$, and this suggests the identification $A = K$, $B = U$, and $t = -\beta$. We will need a few commutators to proceed which follow straightforwardly from the elementary identity $[Q, P] = {\rm i}\hbar$,

$$[K, U] = -\frac{{\rm i}\hbar}{m} U' P - \frac{\hbar^2}{2m} U'', \quad (13a)$$

$$[[K, U], U] = -\frac{\hbar^2}{m} (U')^2, \quad (13b)$$

$$[[K, U], K] = \frac{\hbar^2}{4m^2} (U'' P^2 + 2 P U'' P + P^2 U'') \quad (13c)$$

$$= \frac{\hbar^2}{m^2} U'' P^2 + \mathcal{O}(\hbar^3). \quad (13d)$$

These can be derived swiftly by recalling that $[P, f(Q)] = -i\hbar f'(Q)$ for some function f of the operator Q. Furthermore, from Eq. (13c) to Eq. (13d), we used the fact that switching the order of the P and $U''(Q)$ operators creates extra terms, which however are higher order in $\hbar$. At the relevant order, the key correction operators C_2 and C_3 then become

$$C_2 = -\frac{{\rm i}\hbar}{m} \left[U' P - \frac{{\rm i}\hbar}{2} U'' \right], \quad (14a)$$

$$C_3 = \frac{2\hbar^2}{m} \left[U'' \frac{P^2}{2m} - (U')^2 \right]. \quad (14b)$$

Observe that $C_2 = \mathcal{O}(\hbar)$, while $C_3 = \mathcal{O}(\hbar^2)$. The correction C_4 turns out to be $\mathcal{O}(\hbar^3)$, and since we aim for the leading quantum correction at order $\hbar^2$, we can terminate the Zassenhaus expansion with C_3. To be clear: even though $P = -{\rm i}\hbar(\partial/\partial q)$ in position representation, the occurrence of a momentum operator does *not* by itself signal a factor of $\hbar$. The momentum is not proportional to $\hbar$, for otherwise particles would classically always be at rest. Instead, $\hbar$ only arises whenever we switch the order of a P- and a Q-type operator.

Because the C_n commutators all contain at least one factor of $\hbar$, we can Taylor-expand the exponentials appearing in the Zassenhaus formula for small argument. Considering that we wish to go up to order $\hbar^2$ and that $C_2 = \mathcal{O}(\hbar)$, we need to expand the C_2-exponential up to second order

$${\rm e}^{-\beta^2 C_2/2} = 1 - \frac{1}{2}\beta^2 C_2 + \frac{1}{8}\beta^4 C_2^2 + \mathcal{O}(\hbar^3) \quad (15a)$$

$$\begin{aligned} &= 1 + \frac{{\rm i}\hbar\beta^2}{2m} \left[U' P - \frac{{\rm i}\hbar}{2} U'' \right] \\ &\quad - \frac{\hbar^2 \beta^4}{8m^2} \left[U' P - \frac{{\rm i}\hbar}{2} U'' \right]^2 + \mathcal{O}(\hbar^3) \end{aligned} \quad (15b)$$

$$\begin{aligned} &= 1 + \frac{{\rm i}\hbar\beta^2}{2m} U' P + \frac{\hbar^2 \beta^2}{4m} U'' \\ &\quad - \frac{\hbar^2 \beta^4}{8m^2} (U' P U' P) + \mathcal{O}(\hbar^3). \end{aligned} \quad (15c)$$

The mixed operator term in the last line can be rewritten as $U' P U' P = (U')^2 P^2 + \mathcal{O}(\hbar)$, and so the first factor becomes

$${\rm e}^{-\beta^2 C_2/2} = 1 + \frac{\hbar^2 \beta^2}{2m} \left[\frac{\rm i}{\hbar} U' P + \frac{1}{2} U'' - \frac{\beta^2}{4m} (U')^2 P^2 \right] + \mathcal{O}(\hbar^3). \quad (16)$$

It suffices to expand the exponential of C_3 to first order

$${\rm e}^{-(-\beta)^3 C_3/6} = 1 + \frac{\hbar^2 \beta^3}{3m} \left[U'' \frac{P^2}{2m} - (U')^2 \right] + \mathcal{O}(\hbar^3). \quad (17)$$

Multiplying the C_2- and C_3-exponentials, we obtain the correction factor up to order $\hbar^2$,

$$\mathrm{e}^{-\beta^2 C_2/2}\mathrm{e}^{-\beta^3 C_3/6} = 1 + \frac{\hbar^2\beta^2}{2m}\left[\frac{\mathrm{i}}{\hbar}U'P + \frac{1}{2}U'' - \frac{\beta^2}{2}(U')^2\frac{P^2}{2m} + \frac{2}{3}\beta\left(U''\frac{P^2}{2m} - (U')^2\right)\right] + \mathcal{O}(\hbar^3). \tag{18}$$

Next we evaluate the quantum partition function, using the brute-factorized quantum canonical state amended by the corrections up to order $\hbar^2$. The required steps are closely analogous to Eqs. (6)—except that we have the additional factor from Eq. (18) in the trace. This causes no new complications: we simply arrive at six individual terms, the first of which is the classical partition function. The other terms become *classical canonical averages*, up to a missing factor of $1/Z_\mathrm{C}$. Hence, at order $\hbar^2$,

$$\frac{Z_\mathrm{Q}}{Z_\mathrm{C}} = 1 + \frac{\hbar^2\beta^2}{2m}\left[\frac{\mathrm{i}}{\hbar}\langle U'p\rangle + \frac{1}{2}\langle U''\rangle - \frac{\beta^2}{2}\left\langle (U')^2\frac{p^2}{2m}\right\rangle + \frac{2}{3}\beta\left(\left\langle U''\frac{p^2}{2m}\right\rangle - \langle (U')^2\rangle\right)\right] + \mathcal{O}(\hbar^3), \tag{19}$$

where $\langle\cdots\rangle$ denotes a classical canonical average. Since position and momentum in the classical counterpart of Hamiltonian (2) decouple, we get

$$\langle U'p\rangle = \langle U'\rangle\langle p\rangle = 0, \tag{20a}$$

$$\left\langle (U')^2\frac{p^2}{2m}\right\rangle = \langle (U')^2\rangle\left\langle\frac{p^2}{2m}\right\rangle = \langle (U')^2\rangle\frac{1}{2\beta}, \tag{20b}$$

$$\left\langle U''\frac{p^2}{2m}\right\rangle = \langle U''\rangle\left\langle\frac{p^2}{2m}\right\rangle = \langle U''\rangle\frac{1}{2\beta} = \frac{1}{2}\langle (U')^2\rangle, \tag{20c}$$

where we used the classical equipartition theorem, $\langle p^2/2m\rangle = 1/2\, k_\mathrm{B}T$, as well as Eq. (9) in the last step of Eq. (20c).

Putting everything together, we find

$$\begin{aligned}\frac{Z_\mathrm{Q}}{Z_\mathrm{C}} &= 1 + \frac{\hbar^2\beta^2}{2m}\left[\frac{1}{2}\langle U''\rangle - \frac{\beta}{4}\langle (U')^2\rangle + \frac{2}{3}\beta\left(\langle U''\rangle\frac{1}{2\beta} - \langle (U')^2\rangle\right)\right] + \mathcal{O}(\hbar^3)\\ &= 1 + \frac{\hbar^2\beta^3}{2m}\langle (U')^2\rangle\left[\frac{1}{2} - \frac{1}{4} + \frac{1}{3} - \frac{2}{3}\right] + \mathcal{O}(\hbar^3)\\ &= 1 - \frac{\hbar^2\beta^3}{24m}\langle (U')^2\rangle + \mathcal{O}(\hbar^3).\end{aligned} \tag{21}$$

From there, we readily obtain the free energy

$$\begin{aligned}F_\mathrm{Q} &= -k_\mathrm{B}T\,\log Z_\mathrm{Q}\\ &= -k_\mathrm{B}T\,\log\left\{Z_\mathrm{C}\left[1 - \frac{\hbar^2\beta^3}{24m}\langle (U')^2\rangle + \mathcal{O}(\hbar^3)\right]\right\}\\ &= F_\mathrm{C} - k_\mathrm{B}T\,\log\left[1 - \frac{\hbar^2\beta^3}{24m}\langle (U')^2\rangle + \mathcal{O}(\hbar^3)\right]\\ &= F_\mathrm{C} + \frac{\hbar^2\beta^2}{24m}\langle (U')^2\rangle + \mathcal{O}(\hbar^3).\end{aligned} \tag{22}$$

This proves Wigner's correction for a single degree of freedom.

Ignoring exchange symmetry considerations, the calculation for multiple degrees of freedom—i.e., the Hamiltonian (1)—goes through virtually unchanged. This is because position and momentum operators for different degrees of freedom commute, and so Eqs. (13) simply acquire a sum over all degrees of freedom on the right hand side. Mixed terms can then only arise from squaring, and this only affects one term, $(U')^2p^2$. However, the multi-particle counterpart of its canonical average is

$$\begin{aligned}\sum_{ij}\left\langle\frac{\partial U}{\partial q_i}\frac{\partial U}{\partial q_j}p_ip_j\right\rangle &= \sum_{ij}\left\langle\frac{\partial U}{\partial q_i}\frac{\partial U}{\partial q_j}\right\rangle\frac{m\,\delta_{ij}}{\beta}\\ &= \frac{m}{\beta}\sum_i\left\langle\left(\frac{\partial U}{\partial q_i}\right)^2\right\rangle,\end{aligned} \tag{23}$$

yielding again just a single sum.[30] This then readily generalizes Eq. (22) to Eq. (10).

For the interested reader, we provide an alternative and faster derivation of this result in supplementary material SM 2, which relies on a suitably symmetrized version of the Zassenhaus formula.[6]

IV. EXAMPLE ILLUSTRATIONS

To see how well Wigner's correction works, and when it fails, let us now look at a couple of examples. We will examine the harmonic oscillator and the general $|x|^k$-potential, later specializing to $k=4$ (quartic oscillator) and $k\to\infty$ (particle in a box).

A. The harmonic oscillator

The harmonic oscillator with frequency ω is described by the Hamiltonian

$$H = \frac{P^2}{2m} + \frac{1}{2}m\omega^2Q^2 \tag{24}$$

and has the well-known spectrum[8]

$$E_n = \hbar\omega\left(n+\frac{1}{2}\right), \quad n\in\mathbb{N}_0. \tag{25}$$

Its quantum partition function is

$$Z_\mathrm{Q} = \sum_{n=0}^{\infty}\mathrm{e}^{-\beta\hbar\omega(n+1/2)} = \frac{1}{2\sinh\left(\frac{\beta\hbar\omega}{2}\right)}, \tag{26}$$

and so the quantum free energy turns out to be

$$F_\mathrm{Q} = k_\mathrm{B}T\log\left[2\sinh\left(\frac{\beta\hbar\omega}{2}\right)\right]. \tag{27}$$

Expanding this expression for small $\beta\hbar\omega$, we get

$$F_\mathrm{Q} = k_\mathrm{B}T\log\left(\frac{\hbar\omega}{k_\mathrm{B}T}\right) + \frac{(\hbar\omega)^2}{24\,k_\mathrm{B}T} - \frac{(\hbar\omega)^4}{2880\,(k_\mathrm{B}T)^3} + \mathcal{O}(\hbar^6). \tag{28}$$

The first term is the classical result, and so the next term must be Wigner's correction. Indeed, since $U''(q) = m\omega^2$, we obtain from Eq. (8) the correction

$$\Delta F_{\mathrm{W}} = \frac{\hbar^2}{24 m k_{\mathrm{B}} T} \langle U'' \rangle = \frac{(\hbar\omega)^2}{24\, k_{\mathrm{B}} T}, \tag{29}$$

exactly as expected.

Figure 1 compares the Wigner-corrected free energy with the classical and quantum free energy. For $k_{\mathrm{B}}T/\hbar\omega \gtrsim 1/2$, the leading order correction to the classical result cannot be distinguished from the quantum free energy in this plot. Indeed, examining the next term in the expansion Eq. (28) we see that the leading correction approaches the quantum free energy with rapid $1/T^3$ asymptotics. The subleading term's prefactor is also two orders of magnitude smaller than that of the leading one.

At sufficiently low temperatures, the Wigner-corrected classical free energy fails qualitatively: it diverges from the correct quantum free energy and, for $k_{\mathrm{B}}T/\hbar\omega < 1/\sqrt{12}$, it acquires a positive curvature—and hence a negative heat capacity $C = -T(\partial^2 F/\partial T^2)$. Of course, the correction was derived assuming $\beta\hbar\omega \ll 1$, so we expect the approximation to fail at low temperatures, but it remains impressive how far down it fares well.

B. The power-law oscillator with potential $|x|^k$

1. General considerations

It is instructive and fairly straightforward to extend this reasoning to the monomial oscillator

$$H = \frac{P^2}{2m} + A|x|^k, \tag{30}$$

with $k > 2$. It proves convenient to rescale

$$\varepsilon \equiv \frac{\hbar^2}{2m\ell^2} \equiv A\ell^k \;\Rightarrow\; \begin{cases} \ell = \left(\dfrac{\hbar^2}{2mA}\right)^{\frac{1}{2+k}} \\ A = \dfrac{\varepsilon^{1+\frac{k}{2}}}{(\hbar^2/2m)^{\frac{k}{2}}} \end{cases}, \tag{31}$$

which permits us to write the potential as

$$U(x) = \frac{\hbar^2}{2m\ell^2}\left(\frac{|x|}{\ell}\right)^k. \tag{32}$$

The classical partition function can be calculated easily

$$Z_{\mathrm{C}} = \int_{-\infty}^{\infty} \frac{\mathrm{d}p\,\mathrm{d}q}{2\pi\hbar}\, \mathrm{e}^{-\beta((p^2/2m)+A|q|^k)}$$

$$= \frac{2}{\lambda_{\mathrm{th}}} (\beta A)^{-1/k} \frac{1}{k} \int_0^{\infty} \mathrm{d}t\, t^{1/k-1} \mathrm{e}^{-t} \tag{33}$$

$$= 2\frac{\ell}{\lambda_{\mathrm{th}}} \left(\frac{k_{\mathrm{B}}T}{\varepsilon}\right)^{1/k} \Gamma\left(1+\frac{1}{k}\right), \tag{34}$$

where $\Gamma(x)$ is the Gamma-function (Ref. 27, Chap. 6).

Calculating Wigner's correction of the associated classical free energy involves another straightforward integral that evaluates to a Gamma function

$$\langle U'' \rangle = \frac{\displaystyle\int_0^{\infty} \mathrm{d}q\, k(k-1)Aq^{k-2}\, \mathrm{e}^{-\beta A q^k}}{\displaystyle\int_0^{\infty} \mathrm{d}q\, \mathrm{e}^{-\beta A q^k}} \tag{35a}$$

$$= k_{\mathrm{B}}T \frac{2m\varepsilon}{\hbar^2} (\beta\varepsilon)^{2/k} (k-1) \frac{\Gamma\left(1-\frac{1}{k}\right)}{\Gamma\left(1+\frac{1}{k}\right)}, \tag{35b}$$

which together with Eq. (8) yields

$$\frac{\Delta F_{\mathrm{W}}}{\varepsilon} = \frac{k-1}{12} (\beta\varepsilon)^{2/k} \frac{\Gamma\left(1-\frac{1}{k}\right)}{\Gamma\left(1+\frac{1}{k}\right)}. \tag{36}$$

This reduces to the special case of the harmonic oscillator, Eq. (29), if $k=2$.

Unfortunately, the quantum free energy cannot be obtained so easily, because the spectrum of the $|x|^k$-oscillator is not analytically known for general k. A tempting work-around invokes a semi-classical approximation such as WKB. This seems particularly apt given that WKB is known to become asymptotically exact for large eigenvalues and thus, one would hope, large temperatures. If $a = (E/A)^{1/k}$ is the classical turning point of the potential, then the WKB quantization condition becomes[28]

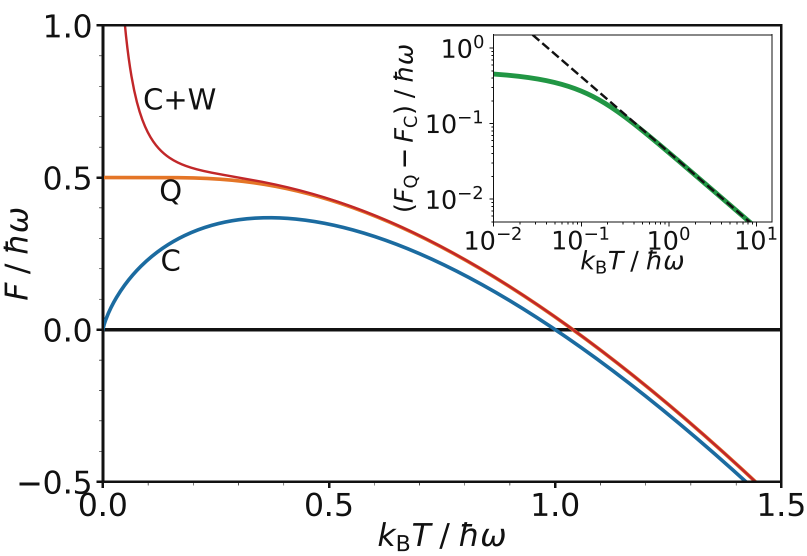

Fig. 1. Free energy of the harmonic oscillator as a function of temperature. The three curves correspond to: Classical result ("C," blue); quantum result ("Q," orange); classical result plus Wigner's leading order correction ("C + W," red). The inset shows a log-log plot of the difference between the quantum and the classical free energy as a solid green curve, and the Wigner correction from Eq. (29), which scales $\sim T^{-1}$, as a black dashed line.

$$\left(n+\frac{1}{2}\right)\pi\hbar = \int_{-a}^{a} \mathrm{d}q\,\sqrt{2m(E_n - A|q|^k)} \tag{37a}$$

$$= \hbar\sqrt{\pi}\left(\frac{E_n}{\varepsilon}\right)^{\frac{1}{2}+\frac{1}{k}} \frac{\Gamma\left(1+\frac{1}{k}\right)}{\Gamma\left(\frac{3}{2}+\frac{1}{k}\right)}, \tag{37b}$$

which yields the spectrum

$$E_n = \varepsilon\left[\frac{\Gamma\left(\frac{3}{2}+\frac{1}{k}\right)}{\Gamma\left(1+\frac{1}{k}\right)}\sqrt{\pi}\left(n+\frac{1}{2}\right)\right]^{2k/(2+k)} \quad \text{with } n\in\mathbb{N}_0. \tag{38}$$

The associated quantum partition function is

$$Z_{\mathrm{Q}} = \sum_{n=0}^{\infty} \mathrm{e}^{-\beta E_n}, \tag{39}$$

which can be approximated numerically with a finite number of terms. To see how well the Wigner approximation (and its WKB competitor) fare, let us now look at two special cases.

2. The purely quartic oscillator

Consider the potential $U(x) = Ax^4$. Specializing Eq. (34) for $k=4$ yields the classical partition function, while the WKB spectrum follows from Eq. (38):

$$\frac{E_n}{\varepsilon} = \alpha\left(n+\frac{1}{2}\right)^{4/3}, \tag{40}$$

with $\alpha = [3\sqrt{\pi}\,\Gamma(3/4)/\Gamma(1/4)]^{4/3} \approx 2.185$. When inserted into Eq. (39), it permits us to numerically evaluate Z_{Q}. The Wigner correction follows from Eq. (36):

$$\frac{\Delta F_{\mathrm{W}}}{\varepsilon} = \frac{\Gamma\left(\frac{3}{4}\right)}{\Gamma\left(\frac{1}{4}\right)}\sqrt{\frac{\varepsilon}{k_{\mathrm{B}}T}} \approx 0.338\sqrt{\frac{\varepsilon}{k_{\mathrm{B}}T}}. \tag{41}$$

Notice that this decays more slowly with temperature than in the case of the harmonic oscillator, where we found a $1/T$ scaling instead—see Eq. (29).

Figure 2 compares the classical result, the Wigner-corrected free energy, and the WKB approximation. Remarkably, the answer perplexes: F_{WKB} matches the Wigner-corrected classical free energy quite poorly, but in the absence of an exact answer it is unclear whether WKB or Wigner are at fault. Nevertheless, the fact that even at large temperatures WKB is closer to the classical than to the Wigner-corrected result does not bode well for WKB, because we know that the Wigner formula is the unique leading order correction. (In Sec. SM 3 of the supplementary material, we argue that the failure of WKB is due to more than just a few incorrectly predicted low-lying energy states.[6])

To perform a true comparison, we need the actual quantum free energy, not just a semi-classical approximation. Luckily, the quartic oscillator has been extensively studied. For instance, Banerjee *et al.* give the first 25 eigenvalues of H in Ref. 29, which is more than enough to calculate $F_{\mathrm{Q}}(T)$ for $0 \le k_{\mathrm{B}}T/\varepsilon \le 10$ at the accuracy we need. The resulting free energy is added as the orange curve into Fig. 2. Once again we see that the Wigner-corrected classical result is an excellent approximation to the true quantum free energy, as long as $k_{\mathrm{B}}T/\varepsilon \gtrsim 0.5$—well below the point where the classical free energy has a positive slope and, thus, a negative entropy $S = -(\partial F/\partial T)_{N,V}$. The Wigner-corrected result is in fact *far* superior to WKB, which—being semi-classical in nature—appears biased towards the classical answer. (To be fair, WKB avoids two major low-temperature sins: It never predicts a negative entropy; and it never becomes convex, unlike the Wigner correction, thus averting a negative heat capacity.)

It is less obvious how to obtain the speed of convergence between the quantum and the Wigner-corrected classical result. However, we can offer the following heuristics: The Wigner correction scales like $\varepsilon^{3/2} \sim \hbar^2$. Wigner's original treatment suggests that the next term in the expansion is in fact of order $\hbar^4$, which would scale like ε^3. Hence, $\Delta F_{\mathrm{W}}/\varepsilon$ is proportional to ε^2 and for dimensional reasons, must scale like $1/T^2$. This is indeed what numerics suggests.

3. The particle in a box

As a second special case, let us look at the limit $k\to\infty$ of Eq. (32). We can easily recognize this as the particle in a box of length $L = 2\ell$, since $U(x)$ converges to zero for $|x| < \ell$ while it diverges to infinity otherwise.

Sending $k\to\infty$ in Eq. (34) yields the classical partition function $Z_{\mathrm{C}} = L/\lambda_{\mathrm{th}}$, which is exactly the right answer for a single gas particle in a box of length L. Taking the limit in the WKB spectrum (38), we get

$$\lim_{k\to\infty} E_n = \frac{\pi^2\hbar^2}{2mL^2}\left(n+\frac{1}{2}\right)^2. \tag{42}$$

This is *almost* the box spectrum, except that we have $(n+1/2)^2$ instead of $(n+1)^2$.[31]

Both results look promising, but our luck runs out when we look at the Wigner correction. Equation (36) shows that for large k,

$$\frac{\Delta F_{\mathrm{W}}}{\varepsilon} \sim \frac{k}{12}, \tag{43}$$

which is divergent. Hence, Wigner's result does not produce a well-defined quantum correction for the infinite square well. However, take note of what we are trying to do here: We are evaluating the (classical) thermal expectation value of $U''(x)$ (see Eq. (35a)), and even though this is perfectly well-defined for all k, the limit $k\to\infty$ is singular because the potential becomes singular. We have no guarantee that this will not interfere with other analytic aspects of the problem—and indeed here it does. The Wigner correction has the form $(1/48\pi)\lambda_{\mathrm{th}}^2\langle U''(x)\rangle$, and this only makes sense as the first term of an expansion as long as the expansion parameter—essentially λ_{th}^2—is small compared to the average (inverse) potential curvature. This evidently fails in view of the diverging curvature at the "corners" of our box.

There is of course a quantum correction to the ideal gas, but it looks quite different from the Wigner expression. It can be obtained analytically from the partition function

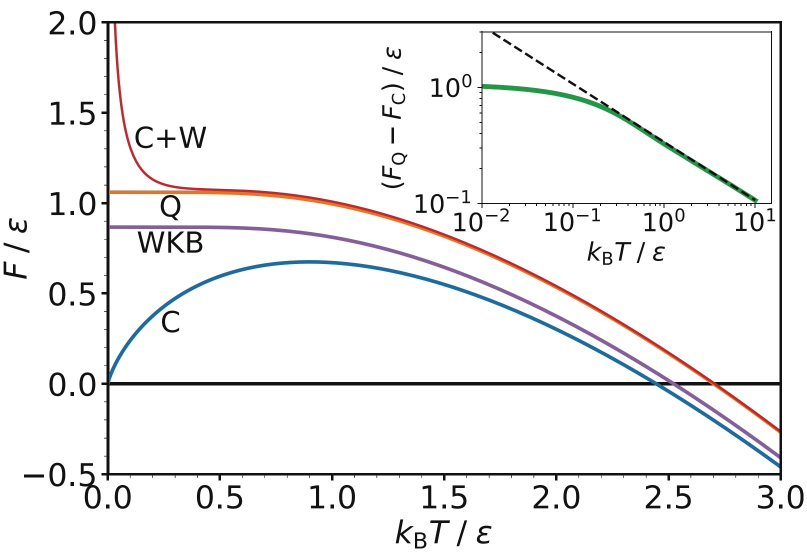

Fig. 2. Free energy of the quartic oscillator as a function of temperature. The four curves correspond to: Classical result ("C," blue); WKB approximation ("WKB," purple); quantum result ("Q," orange); classical result plus Wigner's leading order correction ("C + W," red). The inset shows a log-log plot of the difference between the quantum and the classical free energy as a solid green curve, and the Wigner correction from Eq. (41), which scales $\sim T^{-1/2}$, as a black dashed line.

$$Z_Q = \sum_{n=1}^{\infty} e^{-\beta E_0 n^2}, \tag{44}$$

where the ground state energy is $E_0 = \pi^2\hbar^2/2mL^2$. We can express Z_Q as a Jacobi theta function (Ref. 27, Chap. 16), but this is unwieldy. If we replace the sum by an integral, we get a Gaussian that readily leads to the classical ideal gas law. However, we can also do the replacement more systematically, using the Euler–Maclaurin summation formula,[32] which yields

$$Z_Q \approx \int_0^{\infty} dn\, e^{-\beta E_0 n^2} - \frac{1}{2} = \frac{L}{\lambda_{th}} - \frac{1}{2}. \tag{45}$$

The extra "$-1/2$" shifts the partition function and adds a first quantum correction to the classical free energy

$$F_Q \approx -k_B T \log\left(\frac{L}{\lambda_{th}} - \frac{1}{2}\right) = F_C - k_B T \log\left(1 - \frac{\lambda_{th}}{2L}\right) \approx F_C + \frac{\lambda_{th}\, k_B T}{2L} = F_C + \frac{\hbar}{L}\sqrt{\frac{\pi\, k_B T}{2m}}. \tag{46}$$

Remarkably, this leading correction is *linear* in $\hbar$, unlike the Wigner term. It also depends more weakly on the mass: $1/\sqrt{m}$ as opposed to the $1/m$ Wigner scaling. The existence of this lower order term elucidates the divergence of the Wigner correction: it can by construction not appear in the regular series expansion, and this forces the first allowed term to diverge. As an almost trivial illustration, consider the expansion

$$(a+x)^{3/2} = a^{3/2} + \frac{3}{2}\sqrt{a}\,x + \frac{3}{8\sqrt{a}}\,x^2 + \mathcal{O}(x^3). \tag{47}$$

The constant and linear term converge (here: to zero) in the singular limit $a \to 0$, but the quadratic one diverges—because the function itself approaches $x^{3/2}$ in that limit, which is "of lower order" than x^2.

The limit $k \to \infty$ renders the potential in Eq. (32) *non-analytic*, but it also has a more subtle effect: It *confines* the particle to a finite region (of width 2ℓ). It turns out that this confinement alone, even if done analytically, can cause the Wigner correction to fail. We sketch a proof of this in Sec. SM 4 of the Supplementary Material, where we calculate the large-T asymptotics of the Wigner correction for a particularly easy case of smooth confinement.

Incidentally, difficulties arising from steeply repulsive potentials are the main reason why Feynman and Hibbs consider the Wigner correction to be of limited use (after just having derived it most elegantly using path integrals).[10] They consider a typical "use case" to be colliding molecules in a gas, pointing out that "the potential rises very sharply so that there is a violent repulsion at small distances." We believe their assessment to be too pessimistic, though. If we alternatively consider atoms in a solid, their lattice vibrations are more benign, essentially harmonic, and then Wigner's approximation is applicable.

V. CONCLUSIONS

We have presented a new proof of Wigner's leading order quantum correction to the classical free energy of a standard Hamiltonian. Our approach relies on the Zassenhaus formula, which highlights the role of non-commuting operators. We also offer an elementary proof of the Zassenhaus formula itself in an Appendix—at least to the order required here. Wigner showed that the sub-leading order is quartic in $\hbar$, which is unfortunately difficult to see in our approach: At several places we ignored $\mathcal{O}(\hbar^3)$ contributions, and it is not obvious that these will all cancel. However, since the sub-leading term will generally be preempted by a spin-statistics correction of order $\hbar^3$, this may not be a grievous problem.

We applied the correction to the harmonic and the quartic oscillator, demonstrating it to be an accurate approximation to the full result for a large range of temperatures. In particular, Wigner's correction outperforms the semi-classical WKB approximation in the high-T limit—which is not surprising, given that it is the unique leading order correction.

We have also shown that Wigner's correction does not work in all cases, because the classical canonical expectation values might not converge to a physically permissible result. For instance, the Wigner correction diverges when modeling an ideal gas in a box as the $k \to \infty$ limit of a confining potential $|x|^k$. Furthermore, smoothly confining particles via diverging potentials could give rise to Wigner corrections that dominate the classical result for large enough temperatures.

The mathematics required to follow our operator-based proof is accessible to advanced physics undergraduates. In fact, one of us has successfully test-driven several key ideas of this paper (in homeworks and exams) in the course "Thermal Physics II," aimed at Junior physics students at Carnegie Mellon. Together with the applications, and the comparison to the complementary spin-statistics correction, we feel that this subject could provide valuable insight into some foundational questions—both in Statistical Physics and Quantum Mechanics—that appear to be rarely covered. We would be delighted if our exposition served as an inspiration.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

APPENDIX: THE CLASSICAL ZASSENHAUS FORMULA

The Zassenhaus formula expresses the exponential of the sum of two operators A and B as the product of their exponentials, times an infinite product of exponentials of increasingly higher order nested commutators of A and B,

$$e^{t(A+B)} = e^{tA}e^{tB}\prod_{n=2}^{\infty} e^{-t^n C_n/n!}. \tag{A1}$$

The first few C_n are explicitly given in Eq. (12). Formally, we can think of A and B as elements of a Lie algebra corresponding to some Lie group. Since e^A, e^B, and e^{A+B} then all represent group elements, we know we can transform them into one another by additional group operations, each generated by elements of the Lie algebra spanned by A and B—which is why the C_n in Eq. (A1) must be nested commutators of A and B. In fact, the C_n are all homogeneous Lie polynomials of degree n. Notice, though, that for the infinite product to converge, we must require the Lie algebra elements to be sufficiently small—or here, we need t to be small enough. This will be the limit we care about, so this poses no further restrictions.

Several procedures have been proposed to systematically construct the correction terms C_n.[15,24–26] Since we will only need C_2 and C_3, though, let us show how to calculate them in an elementary way by Taylor-expanding a truncated version of the formula and appending one more correction factor in each step.

To quadratic order, we have

$$e^{A+B} = 1+(A+B)+\frac{1}{2}(A^2+AB+BA+B^2)+\mathcal{O}(3), \tag{A2a}$$

$$e^A e^B = 1+(A+B)+\frac{1}{2}(A^2+2AB+B^2)+\mathcal{O}(3). \tag{A2b}$$

Subtracting these two expressions yields

$$e^{A+B} - e^A e^B = -\frac{1}{2}[A,B]+\mathcal{O}(3). \tag{A3}$$

Observe now that, at the quadratic level, we can fix this discrepancy by multiplying $e^A e^B$ by the factor $e^{-[A,B]/2}$. This leads to the lowest order correction in the Zassenhaus formula,

$$e^{A+B} = e^A e^B e^{-[A,B]/2}+\mathcal{O}(3), \tag{A4}$$

or the identification $C_2 = [A,B]$.

We get the next order by expanding e^{A+B} and $e^A e^B e^{-[A,B]/2}$ up to cubic order and comparing again. Since all terms up to quadratic order by construction cancel, we only need to consider the cubic terms

$$e^{A+B} = \cdots + \frac{1}{6}(A^3+A^2B+ABA+AB^2 + BA^2+BAB+B^2A+B^3)+\mathcal{O}(4), \tag{A5}$$

$$\begin{aligned} e^A e^B e^{-[A,B]/2} &= \Big[1+(A+B)+\frac{1}{2}(A^2+2AB+B^2) + \frac{1}{6}(A^3+3A^2B+3AB^2+B^3)+\mathcal{O}(4)\Big] \\ &\quad \times \Big[1-\frac{1}{2}(AB-BA)+\mathcal{O}(4)\Big] \\ &= \cdots + \frac{1}{6}(A^3+3AB^2+B^3+3B^2A - 3BAB+3ABA)+\mathcal{O}(4). \end{aligned} \tag{A6}$$

Taking the difference between these two terms, we get

$$\begin{aligned} e^{A+B} - e^A e^B e^{-[A,B]/2} &= \frac{1}{6}(A^2B-2ABA+4BAB-2AB^2 + BA^2-2B^2A)+\mathcal{O}(4) \\ &= -\frac{1}{6}([[A,B],A] + 2[[A,B],B])+\mathcal{O}(4). \end{aligned} \tag{A7}$$

The last step is easy to see by working backwards and identifies $C_3 = [[A,B],A]+2[[A,B],B]$. Just as with the quadratic correction term from Eq. (A3), we can fix this cubic term by multiplying with an exponential factor that has this correction term in the exponent. Up to cubic order, we, therefore, get

$$e^{A+B} = e^A e^B e^{-C_2/2} e^{-C_3/6}+\mathcal{O}(4). \tag{A8}$$

This process can be continued to get the higher order corrections, but it obviously will get tedious quite quickly. Moreover, this derivation does not automatically yield the C_n in terms of nested commutators, even though we know they have to be, for they must be part of the Lie algebra in order to represent a group element.

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[30]It is maybe worth pointing out that the untangling happening in Eq. (23) is a consequence of the special form of the multi-particle term. It is by no means obvious that at higher order this continues to work, and so the fact that the correction is just additive in the particles seems really just a quirk of the leading-order.
[31]This is expected, because in the limit $k \to \infty$ the two classically forbidden regions near the turning points shrink to zero, and so their contribution to the wave function's accumulated phase difference across one period vanishes as well. This leads to a replacement of $1/2 \to 1$, as revisited by Geldart and Kiang (Ref. 28). Observe that we would have gotten the $(n+1)^2$ formula right away had we used the slightly more crude Bohr–Sommerfeld quantization condition.
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