Exercise 12

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This is part of an application to work in a group as a doctoral candidate.

1 Path Integral Quantum Statistics

The potential energy of a Morse oscillator is defined as

$$V(x) = D_e(1 - e^{-\alpha(x-x_e)})^2$$

with parameters chosen to represent an OH bond: $D_e = \hbar\omega_e^2/4\omega_e\chi_e$ and $\alpha = \sqrt{2m\omega_e\chi_e/\hbar}$ with $\omega_e/2\pi c = 3737.76$ cm^{-1}, $\omega_e\chi_e/2\pi c = 84.881$ cm^{-1} and $x_e = 0.96966$ Å. For the mass, m, we use the reduced mass as if OH were a diatomic molecule.

We wish to compute the partition function

$$Z(\beta) = \left(\frac{m}{2\pi\beta_N\hbar^2}\right)^{N/2} \int \mathrm{d}\mathbf{x} e^{-\beta_N U_N(\mathbf{x})}$$

where $U_N(\mathbf{x}) = \sum_{n=1}^{N} \frac{m}{2\beta_N^2\hbar^2}(x_n - x_{n-1})^2 + \sum_{n=1}^{N} V(x_n)$ and $\beta_N = \beta/N$. Here the index notation is cyclic such that $x_0 \equiv x_N$ and $\mathbf{x} = \{x_1, ..., x_N\}$.

1.1 a)

Write code to build the $N \times N$ ring-polymer Hessian, $\mathbf{H} = \nabla^2 U_N(\mathbf{x})$, for a ring polymer collapsed at the bottom of the Morse oscillator. Note that because the potential at the bottom of the oscillator is 0, the Taylor expansion of the ring-polymer potential is $U_N(\mathbf{x}) = \frac{1}{2}\mathbf{x}^T\mathbf{H}\mathbf{x} + ...$

1.1.1 Solution

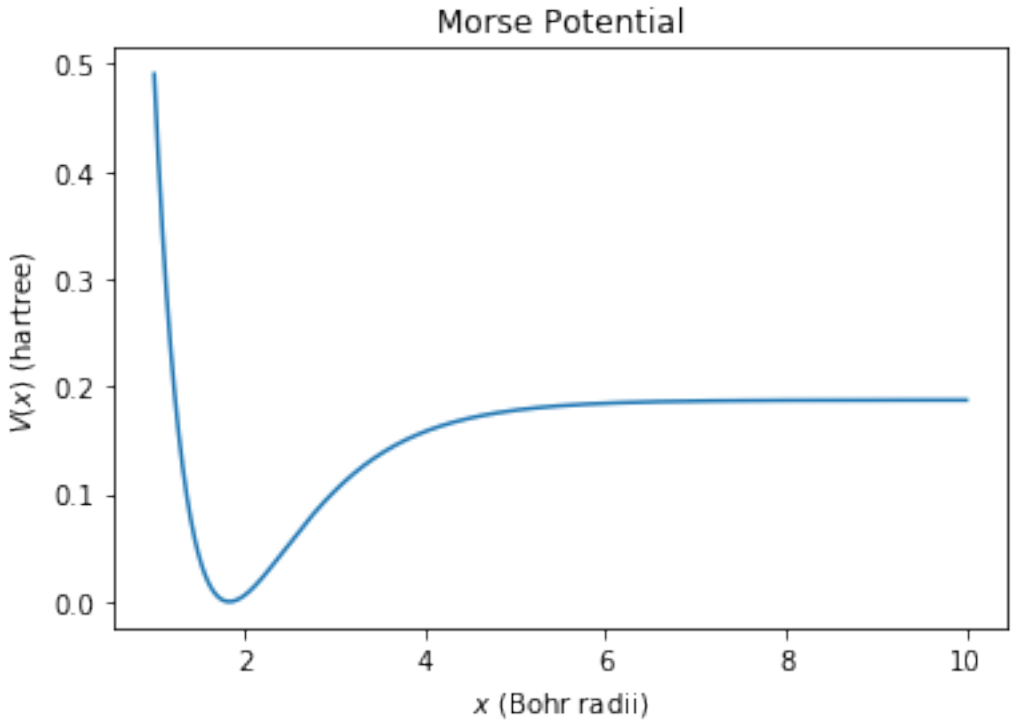
First, let's import the necessary modules and calculate the necessary constants defined in the problem.

NOTE: for convenience (and numerical accuracy), I am using the Hartree atomic units system.

[1]:
```
import numpy as np # used in (b), so presumably allowed
from matplotlib import pyplot as plt
from math import pi

# from mpmath import mp
# mp.dps = 50

# values in units as given
ωe_2pic_cm = 3737.76 # ω_e/2πc, cm^-1
ωχ_2pic_cm = 84.881 # ω_e χ_e/2ωc, cm^-1
```

```
xe_ang = 0.96966 # x_e, Å

# atomic unit conversions
percm_2_pera0 = 5.29177211e-9 # cm^-1 to a0^-1
ang_2_a0 = 1.889726125 # angstrom to Bohr radius

# convert values
ωe_2pic = ωe_2pic_cm * percm_2_pera0 # ω_e/2πc, a0^-1
xe = xe_ang * ang_2_a0 # x_e, a0

# c = 2.998e10 # speed of light, cm/s
# use atomic units
c = 137  # speed of light, a0 Eh / hbar

χ = ωχ_2pic_cm / ωe_2pic_cm # dimensionless
ω = ωe_2pic * 2 * pi * c # Eh/hbar

# NOTE I am assuming that I may just look up the masses for O and H
# I looked them up via Wolfram Alpha
mO = 29164 # mass of Oxygen, m_e
mH = 1837 # mass of Hydrogen, m_e
m = mO*mH/(mO+mH) # reduced mass of OH

# hbar,e,a0,m_e = 1
De = ω/4/χ # well depth, Eh
α = np.sqrt(2*m*ω*χ) # exponent, a0^-1

# Morse oscillator potential energy
V = lambda x: De*(1-np.exp(-α*(x-xe)))**2
```

[2]:
```
# sanity check that the Morse oscillator looks like as expected
xs = np.linspace(1, 10, 1000)
plt.plot(xs, V(xs))
plt.title(r'Morse Potential')
plt.ylabel(r'$V(x)$ (hartree)')
plt.xlabel(r'$x$ (Bohr radii)')
plt.show()
```



Now that we have sorted out units and have a function for the Morse oscillator, we can calculate the Hessian. First, the gradient is easily seen to be

$$\frac{\partial U_N(\mathbf{x})}{\partial x_n} = \frac{m}{\beta_N^2\hbar^2}(-x_{n+1} + 2x_n - x_{n-1}) + \frac{\partial V(x_n)}{\partial x_n}.$$

Similarly, the Hessian can be calculated,

$$\frac{\partial^2 U_N(\mathbf{x})}{\partial x_n \partial x_j} = \frac{m}{\beta_N^2\hbar^2}(-\delta_{n+1,j} + 2\delta_{n,j} - \delta_{n-1,j}) + \delta_{n,j}\frac{\partial^2 V(x_n)}{\partial x_n^2}.$$

where, as usual, δ_{nj} is the Kronecker delta function.

Assuming the Morse potential, it is also easy to calculate the second derivative thereof, via repeated differentiation,

$$V''(x) = 2D_e\alpha^2 e^{-\alpha(x-x_e)}(2e^{-\alpha(x-x_e)} - 1).$$

As described in the question, we are expanding about the bottom of the Morse oscillator, so we evaluate at $x = x_e$ and Taylor expand $U_N(x) \approx \frac{1}{2}(\mathbf{x} - x_e)^T H(\mathbf{x} - x_e)$.

NOTE: In the question, I am given $U_N(\mathbf{x}) = \frac{1}{2}\mathbf{x}^T\mathbf{H}\mathbf{x} + ...$, but since we are evaluating about the minimum, the $\mathbf{x}$ should really be $\mathbf{x} - x_e$, where the notation of subtracting a scalar from a vector means subtracting the scalar from each element.

NOTE: I previously emailed Prof Richardson about a typo later in the exercise. In fact, I think there is no typo there, and that the Taylor approximation above is actually the real culprit.

[3]:
```
# V''(x) as found above
# we are expanding about the *minimum* => don't need as function
# Vpp(x) = lambda x: 2*De*a*a*np.exp(-a(x-xe))*(2*np.exp(-a*(x-xe))-1)
# Vpp(x_e) = 2Da²

# assuming room temperature, T=293 K
βr = 1/9.2787578809e-4 # 1/Eh

# I will write the Hessian as a function of N and x
def Hij(i,j,N,β,potential='morse'):
    """
    returns the value of the N by N Hessian matrix grad^2 U at index i,j
    evaluated at x=x_e (i.e. minimum of Morse potential)

    helper function for hessian function, below
    :param: i row index
    :param: j column index
    :param: size of matrix (number of beads)
    :param: β reciprocal temperature
    :param: potential either 'morse' or 'harmonic'
    :return: $H_{ij}$, value of H at index i,j
    """
    if i==j:
        if potential=='morse':
            return 2*m*N*N/β/β+2*De*α*α
        elif potential=='harmonic':
            return 2*m*N*N/β/β+m*ω*ω
        else:
            print('error: select either morse or harmonic')
    if (i+1)%N==j: # mod N to ensure PBCs
        return -m*N*N/β/β
    if (i-1)%N==j:
        return -m*N*N/β/β
    else:
        return 0

def hessian(N,β,potential='morse'):
    """
    returns the Hessian of size N at reciprocal temp β
    """
    H = np.zeros((N,N))
    for i in range(N):
        for j in range(N):
            H[i,j] = Hij(i,j,N,β,potential=potential)
    return H

# print small example, looks fine
print(hessian(4,βr))
```

```
[[ 0.5485753  -0.02380566  0.         -0.02380566]
 [-0.02380566  0.5485753  -0.02380566  0.        ]
```

```
[ 0.         -0.02380566  0.5485753  -0.02380566]
[-0.02380566  0.         -0.02380566  0.5485753 ]]
```

1.2 b)

Calculate the eigenvalues and eigenvectors of this matrix using

`evals, U = numpy.linalg.eigh(H)`

We use eigh instead of eig because our matrix is hermitian (actually symmetric). If you want, you can check that the eigenvalues are in agreement with the Hückel cyclic alkene formula. The eigenvalues will be stored as a vector and the eigenvectors as a matrix. Show that the eigenvectors are stored in the columns by printing $U^T H U$ and checking if the result is the diagonal matrix with the eigenvalues along the diagonal.

1.3 Solution

[4]:
```
# select some N
N = 16
H = hessian(N,βr)

evals, U = np.linalg.eigh(H)
UHU = (U.T @ H) @ U # U^THU
# If the following line returns True, then they are the same
# up to the tolerance
print(np.all(np.abs(UHU-np.diag(evals))<=1e-10))
```

```
True
```

1.4 c)

We use the eigenvectors to define a set of normal modes for our system. Check (numerically) that for any path-integral configuration, **x**, that $x^T H x = \sum_k \lambda_k q_k^2$ where λ_k are the eigenvalues and $\mathbf{q} = U^T(\mathbf{x} - x_e)$

1.4.1 Solution

Since this is a numerical "proof," I assume that "for any path-integral configuration," we really mean an arbitrary configuration.

[5]:
```
# check for random values between zero and one

x = np.random.rand(N)

xHx = x.T @ H @ x
print(xHx)

rhs = 0 # rhs of the expression, which should equal xHx
q = U.T @ x
for i in range(N):
    rhs += evals[i] * q[i] * q[i]
print(rhs)
```

```
print(abs(xHx-rhs)<=1e-10)
```

```
2.4617365891008727
2.461736589100873
True
```

As one can see above, the true results are identical.

Just for fun Here is a simple analytical proof. Below when I write $\mathbf{x}$, I actually mean $\mathbf{x} - x_e$, since we expand about the minimum

We know that $U^T H U = \text{diag}\lambda$ where λ is the vector of eigenvalues and diag$\mathbf{x}$ is the matrix with the vector $\mathbf{x}$ along the diagonal and zeros everywhere else.

Then, by multiplying $U^T x$ on the right,

$$U^T H x = \text{diag}(\lambda) U^T x$$

and then by $x^T U$ on the left,

$$x^T H x = x^T U \text{diag}(\lambda) U^T x.$$

But we define $\mathbf{q} \equiv U^T x$ so we have

$$x^T H x = q^T \text{diag}(\lambda) q.$$

By simple matrix multiplication rules it is then simple to see $x^T H x = \sum_k \lambda_k q_k^2$.

1.5 d)

Write code to perform Monte Carlo importance sampling of the normal-mode coordinates from the distribution

$$q_k \sim \sqrt{\frac{\beta_N \lambda_k}{2\pi}} e^{-\beta_N \lambda_k q_k^2/2},$$

and hence compute the partition function at room temperature

Hint: First converge with respect to the number of Monte Carlo steps (you could estimate the standard deviation in your result to help with this process). Next, converge the results to about 5% error with respect to N. You can estimate how many beads will be needed from the condition $\beta_N \hbar \omega_e \ll 1$.

Hint: use a sanity check to help you eliminate errors, e.g. change the potential $V(x)$ to that of a harmonic oscillator. In this case the normal modes describe the system exactly and each loop of the Monte Carlo algorithm should give exactly the same result with no statistical error.

1.5.1 Solution

First, as a sanity check, it is worth checking that the distribution is properly normalised (I did so via Wolfram Alpha).

Notice that each q_k has a normal distribution with mean 0 and standard deviation $1/\sqrt{\beta_N \lambda_k}$.

Just for fun, but also for a sanity, check, we can try evaluating this integral analytically making use of further approximations.

We have

$$\begin{aligned} Z(\beta) &= \left(\frac{m}{2\pi\beta_N\hbar^2}\right)^{N/2} \int \mathrm{d}\mathbf{x} \mathrm{e}^{-\beta_N U_N(\mathbf{x})} \\ &\approx \left(\frac{m}{2\pi\beta_N\hbar^2}\right)^{N/2} \int \mathrm{d}\mathbf{x} \mathrm{e}^{-\beta_N \frac{1}{2} x^T H x} \\ &= \left(\frac{m}{2\pi\beta_N\hbar^2}\right)^{N/2} \int \mathrm{d}\mathbf{x} \mathrm{e}^{-\beta_N \frac{1}{2} \sum_k \lambda_k q_k^2} \\ &= \left(\frac{m}{2\pi\beta_N\hbar^2}\right)^{N/2} \int \mathrm{d}\mathbf{x} \prod_k \mathrm{e}^{-\beta_N \frac{1}{2} \lambda_k q_k^2} \end{aligned}$$

From the problem description we sample each q_k from a normal distribution of variance $1/\beta_N\lambda_k$. To do Monte Carlo importance sampling, we first want to express the integrand in terms of the integration variable.

We have $q = U^T x$ and thus (by matrix multiplication and remembering to switch the indices due to transposition)

$$q_k = U_{1k}x_1 + ... + U_{Nk}x_N.$$

Hence, taking the partial derivative we have

$$\frac{\partial q_k}{\partial x_j} = U_{jk} = (U^T)_{kj}.$$

Hence, the Jacobian is U^T. We have from multivariate calculus, $dq_1 dq_2 ... dq_N = |\frac{\partial(q_1,...,q_N)}{\partial(x_1,...,x_N)}| dx_1 dx_2 ... dx_N$.

However,

$$\begin{aligned} \left|\frac{\partial(q_1,...,q_N)}{\partial(x_1,...,x_N)}\right| &= |U^T| \\ &= |U^{-1}| \\ &= 1/|U| \\ &= 1 \end{aligned}$$

since the determinant of a unitary matrix is unity. Hence, we have $dq_1 dq_2 ... dq_N = dx_1 dx_2 ... dx_N$.

Returning to the partition function, we have

$$\begin{aligned} Z(\beta) &= \left(\frac{m}{2\pi\beta_N\hbar^2}\right)^{N/2} \int \mathrm{d}\mathbf{x} \prod_k \mathrm{e}^{-\beta_N \frac{1}{2} \lambda_k q_k^2} \\ &= \left(\frac{m}{2\pi\beta_N\hbar^2}\right)^{N/2} \int \mathrm{d}\mathbf{q} \prod_k \mathrm{e}^{-\beta_N \frac{1}{2} \lambda_k q_k^2} \\ &= \left(\frac{m}{2\pi\beta_N\hbar^2}\right)^{N/2} \left(\int \mathrm{d}q_1 \mathrm{e}^{-\beta_N \frac{1}{2} \lambda_1 q_1^2}\right) \left(\int \mathrm{d}q_2 \mathrm{e}^{-\beta_N \frac{1}{2} \lambda_2 q_2^2}\right) \cdots \left(\int \mathrm{d}q_N \mathrm{e}^{-\beta_N \frac{1}{2} \lambda_N q_N^2}\right). \end{aligned}$$

But now each of these integrals is just a gaussian and the solution is known, so we can find the exact/analytical answer. Use $\int e^{-ax^2/2} \mathrm{d}x = \sqrt{\frac{2\pi}{a}}$:

$$Z(\beta) = \left(\frac{m}{2\pi\beta_N\hbar^2}\right)^{N/2} \frac{(2\pi)^{N/2}}{\beta_N^{N/2}\sqrt{\prod_{k=1}^N \lambda_k}}$$

or

$$Z(\beta) = \frac{m^{N/2}}{\hbar^N \beta_N^N \sqrt{\prod_{k=1}^N \lambda_k}}$$

In the code below, I use this Taylor series estimate to check if the Monte Carlo sampling is giving us reasonable results (while I do not expect them to agree exactly, I expect them to not be ludicrously apart).

[6]:
```
# From correspondence with Prof Richardson:
# The Taylor series may be useful for the derivation,
# but you should look for a numerical result that doesn't actually rely on
# that approximation.
# (I think this resolves the source of my confusion)

# β_N * U_N (i.e. the term in the exponential)
def potential_U(x, β, potential='morse'):
    """
    U_N (i.e. the term in the exponential)

    :param: x vector of positions
    :param: β reciprocal temperature 1/kT
    :param: potential either morse or harmonic
    :return: scalar value in the exponential to be integrated to get Z
    """
    if potential=='morse':
        V = lambda xi: De*(1-np.exp(-α*xi))**2
    elif potential=='harmonic':
        V = lambda xi: m*ω*ω*xi*xi/2
    else:
        print('error: potential is either morse or harmonic')
    N = len(x)
    retval = 0
    βN = β/N
    for n in range(N):
        # NOTE modulo and hence PBCs is dealt with since in Python x[-1]==x[N]
        retval += m*(x[n]-x[n-1])*(x[n]-x[n-1])/2/βN/βN # hbar = 1
        retval += V(x[n])
    return retval

# integrand up to the constant factor at the front
f = lambda x,β,potential: np.exp(-β/N*potential_U(x,β,potential=potential))
```

Below, I implement Monte Carlo importance sampling in the standard way, following instructions from the question and referencing *Understanding Molecular Simulation* by Frenkel and Smit as well as *Statistical Mechanics: Algorithms and Computations* by Krauth.

We have an integral of the form

$$\int \mathrm{d}\mathbf{x} f(\mathbf{x}),$$

a random variable

$$q_k \sim \mathcal{N}(0, \sigma_i^2)$$

where $\mathcal{N}(0, \sigma_i^2)$ is the normal distribution with variance σ_i^2 and mean 0. However, since $\mathbf{q} = U^T\mathbf{x}$ and hence

$$\mathbf{x} = U\mathbf{q},$$

we must use properties of the multivariate normal distribution, in particular under Affine transforms. This can be seen, e.g., here.

If we define σ as the vector outer product $\sigma\sigma^T$ (since the q_k's are each independent, I safely assume there is no covariance among them), we have

$$\mathbf{x} \sim \mathcal{N}(\mathbf{0}, U\sigma U^T).$$

This allows us to continue as usual with Monte Carlo importance sampling. In particular, we have

$$\int \mathrm{d}\mathbf{x} f(\mathbf{x}) = \int \mathrm{d}\mathbf{x} \frac{f(\mathbf{x})}{w(\mathbf{x})} w(\mathbf{x}) \approx \frac{1}{L} \sum_{i=1}^{L} \frac{f(\mathbf{x})}{w(\mathbf{x})}$$

where L is the number of samples, where we sample $\mathbf{x}$ from the distribution above. w is the corresponding probability density function.

In the code below, I implement this importance sampling, converging when the approximate error (found by taking the estimator for the variance) falls below 3%. Furthermore, I introduce a "wobble" parameter, to make sure that I don't "accidentally" fall under this, but rather stay there for a number of iterations.

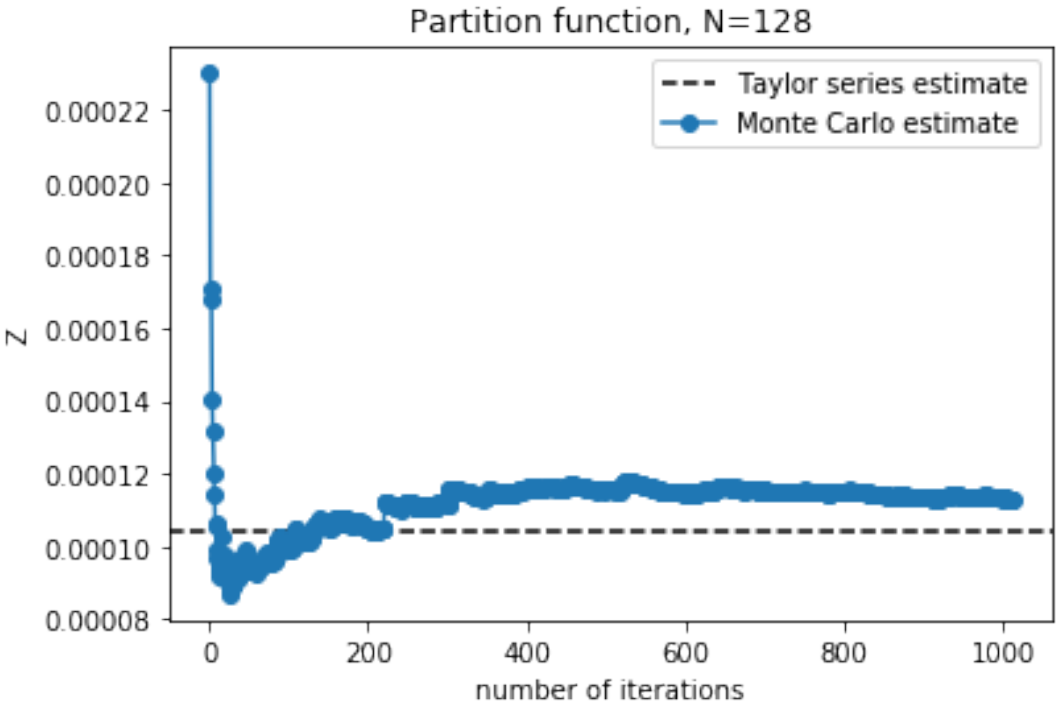
I can plot the results and compare it with the values above. I implement it for both the Morse and harmonic potentials.

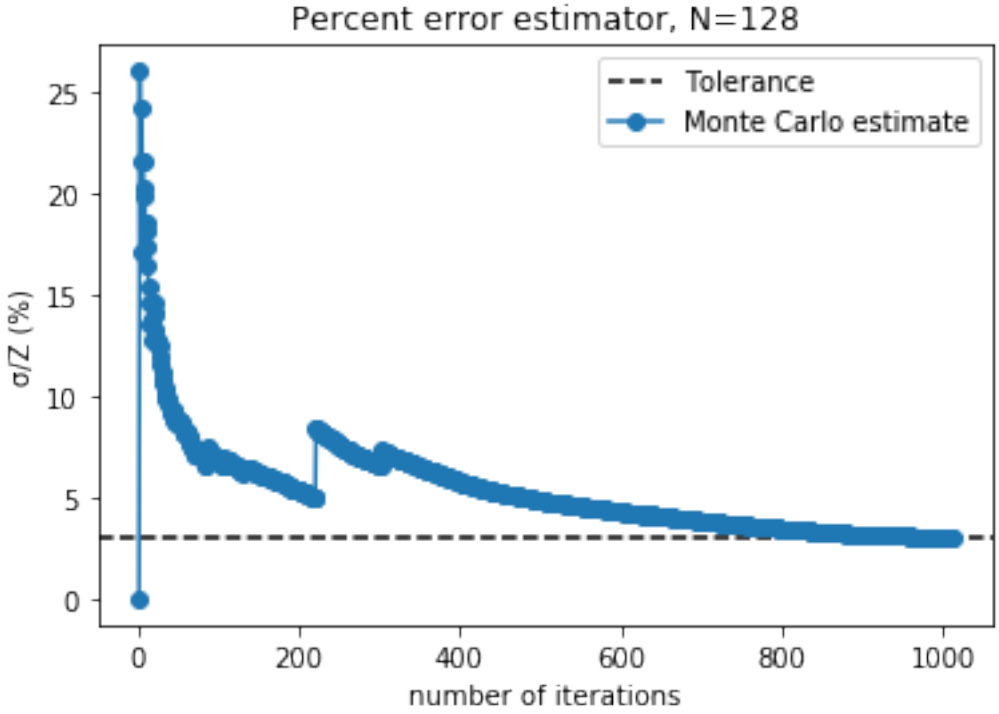
[7]:
```
# Monte Carlo Importance Sampling
# from scipy.stats import norm
from scipy.stats import multivariate_normal

def mc_isampling(N, β=1077.73, potential='morse', max_samples=3000,␣
 ↪verbose=False, taylor_estimate=True):
    """
    performs Monte Carlo importance sampling to calculate the partition
    function given in the exercise, for N beads

    all parameters are in atomic hartree units

    :param: N number of beads
    :param: β inverse temperature 1/kT (default room temp)
    :param: max_samples maximum samples, in case it does not converge
    :param: verbose (T/F) whether or not to print and plot results
    :param: taylor_estimate (T/F) whether or not to include Taylor estimate,␣
 ↪ignored if verbose==False
    :return: Z the partition function, at different # of samples
    :return: σ_pct the estimated percentage error
    """
#     max_samples = 1000 # number of samples (L)
    Z = np.zeros((max_samples,)) # keep track of Z as we sample
    σ = np.zeros((max_samples,)) # error estimate
    # for now, assuming room temperature, T=293 K
    fis = np.zeros((max_samples,))
```

```
# set up with hessian to get U
H = hessian(N,β,potential=potential)
evals, U = np.linalg.eigh(H)

# NOTE this prefactor blows up for large N
prefac = (m*N/(2*pi*β))**(N/2)
i=0
wobble=0 # keep track of how many times it is below
max_wobble=10 # stay below tol_pct max_wobble times
tol_pct=0.03 # 1% error tolerance
# for i in range(max_samples):
while wobble<=max_wobble and i<max_samples:
    # sigma * np.random.randn(...) + mu
    variance = N/β/evals
    # sample q, q_i ~ N(0,σ_i)
    q = np.sqrt(variance) * np.random.randn(N) # + 0
    # assuming q_i's are indep, so covariance matrix is diagonal
    covar = np.diag(variance) # covar for q's
    x = U @ q
    # use Affine transformation of multivariate normal distro
    # cov = U*cov*U.T
    w = multivariate_normal.pdf(x, mean=np.zeros((N,)), cov=U@covar@U.T)
    fis[i] = prefac*f(x,β,potential)/w
    Z[i] = np.sum(fis)/(i+1)
    σ[i] = (1/(i+1)**2)*np.sum(fis*fis)-(1/(i+1))*(np.sum(fis)/(i+1))**2
    σ[i] = np.sqrt(σ[i])
    # print results every 10% of max_samples
    if (i+1) % (max_samples//10) == 0 and verbose:
        print('Z: %.5e at %i samples' % (Z[i],(i+1)))
        print('σ/Z: %.5e at %i samples' % (σ[i]/Z[i], i+1))
        print('wobble:',wobble)
#     Σ += fi
#     σ += fi*fi
#     print('Σ/N: %.4e' % (Σ/(i+1)))
    wobble=wobble+1 if σ[i]/Z[i]<tol_pct else 0
    i=i+1
if verbose:
    print('Z: %.5e at %i samples' % (Z[i-1],i))
    print('σ/Z: %.5e at %i samples' % (σ[i-1]/Z[i-1], i))
    print('wobble:',wobble)
Z = Z[:i-1]
σ = σ[:i-1]

if verbose:
    # while this uses more approximations, it should give an estimate
    # overflow error for lage N though, had to
    # rewrite in a while that will make it work
    if taylor_estimate:
        estimateZ = m**(N/2)/((β/N)**N*np.sqrt(np.prod(evals)))
```

```
            plt.axhline(y=estimateZ, color='k', linestyle='--',label='Taylor␣
 ↪series estimate')
        plt.plot(np.arange(1,i,1),Z,'o-',label='Monte Carlo estimate')
        plt.title('Partition function, N=%i'%N)
        plt.xlabel('number of iterations')
        plt.ylabel('Z')
        plt.legend()
        plt.show()

        plt.axhline(y=100*tol_pct, color='k',␣
 ↪linestyle='--',label='Tolerance')
        plt.plot(np.arange(1,i,1),100*σ/Z,'o-',label='Monte Carlo estimate')
        plt.legend()
        plt.title('Percent error estimator, N=%i'%N)
        plt.xlabel('number of iterations')
        plt.ylabel('σ/Z (%)')
        plt.show()
    return Z, σ/Z

# NOTE for large N, the prefactor is very large as it goes like x^N/2
# and the exponential is very small because it goes like e^(-N)
# so the computer does not handle it well (get overflow errors)
N = 128 # number of beads (to be adjusted)
# β = 1077.73 # 1/Eh
# don't include the Taylor estimate for big N (it blows up, some numerical␣
 ↪issue)
mc_isampling(N, verbose=True, taylor_estimate=True);
```

```
Z: 1.11639e-04 at 300 samples
σ/Z: 6.60743e-02 at 300 samples
wobble: 0
Z: 1.14589e-04 at 600 samples
σ/Z: 4.29146e-02 at 600 samples
wobble: 0
Z: 1.13322e-04 at 900 samples
σ/Z: 3.16074e-02 at 900 samples
wobble: 0
Z: 1.12995e-04 at 1012 samples
σ/Z: 2.98137e-02 at 1012 samples
wobble: 11
```

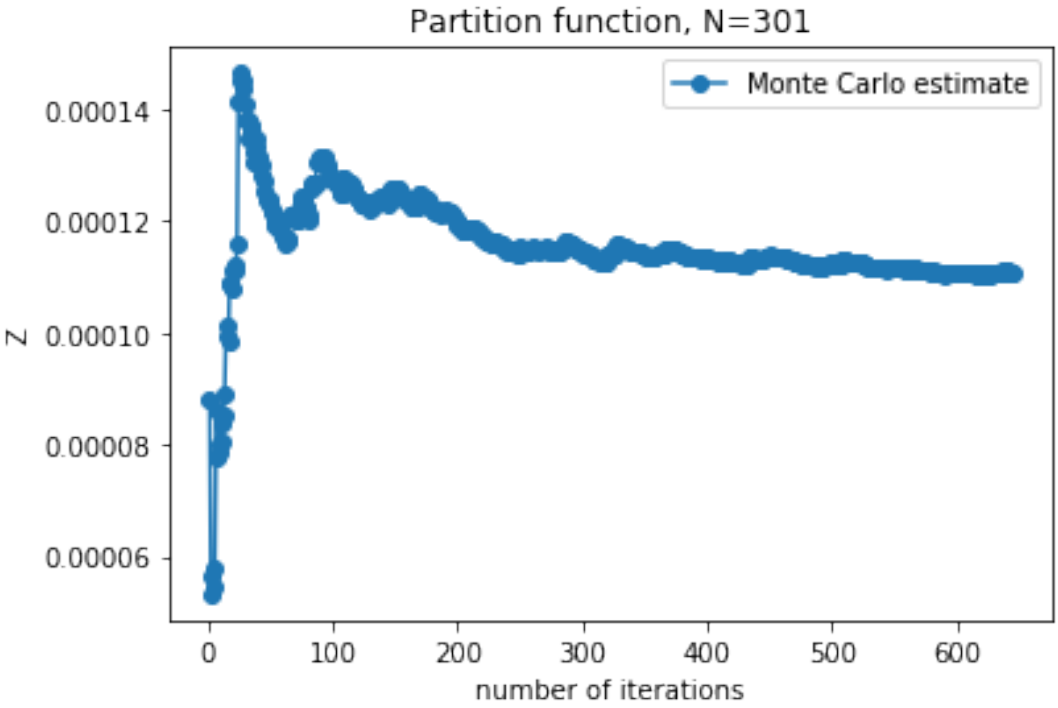


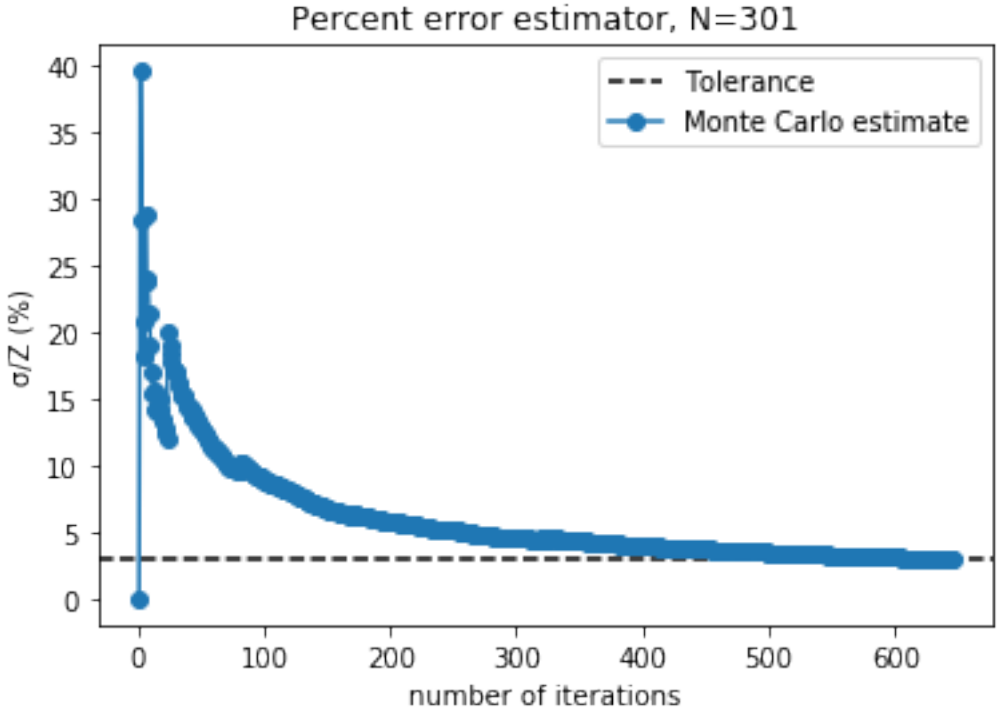


Now, I check convergence with respect to N. That is, I run the function above for a large N and treat this as my "true" result. Then, I keep running the function above for various N, and calculate the error based on the "true" value. When the percent error falls below 5%, it terminates.

[8]:
```
# check convergence wrt N
print('N estimate:',10*1077.73*ω)
Ns = np.arange(1,301+1,10)#2**np.arange(0,lenN+1,1)
lenN = len(Ns)
tol_pct = 0.05 # 5% tolerance

# # # first, get the "true" result
N = Ns[-1]
Z_true,σ_pct_true = mc_isampling(N, verbose=True, taylor_estimate=False)

# print('Z',Z_true)
# print('σ%',σ_pct_true)

wobble = 0
max_wobble = 1 # need at least max_wobble+1 in a row
Z_wrtN = np.zeros((lenN,))
σ_pct_N = np.zeros((lenN,))
# # for i,N in reversed(list(enumerate(Ns))):
for i,N in enumerate(Ns[:-1]): # exclude the last one
    Z,σ_pct = mc_isampling(N, verbose=False, taylor_estimate=False)
    σ_pct_N[i] = (Z_true[-1]-Z[-1])/Z_true[-1]
    Z_wrtN[i] = Z[-1]
    print('percent error wrt N: %.5e at N=%i' % (σ_pct_N[i],N))
    wobble=wobble+1 if abs(σ_pct_N[i])<tol_pct else 0
    if wobble>max_wobble:
        break
# print(σ_pct_N)
```

```
N estimate: 183.49445834227265
Z: 1.14233e-04 at 300 samples
σ/Z: 4.57273e-02 at 300 samples
wobble: 0
Z: 1.10526e-04 at 600 samples
σ/Z: 3.10696e-02 at 600 samples
wobble: 0
Z: 1.10471e-04 at 646 samples
σ/Z: 2.97510e-02 at 646 samples
wobble: 11
```






```
percent error wrt N: -4.89731e+02 at N=1
percent error wrt N: -1.43918e+00 at N=11
percent error wrt N: -3.41972e-01 at N=21
percent error wrt N: -9.82035e-02 at N=31
```

```
percent error wrt N: -8.66498e-02 at N=41
percent error wrt N: -4.20065e-02 at N=51
percent error wrt N: -1.24591e-01 at N=61
percent error wrt N: -6.38624e-02 at N=71
percent error wrt N: -8.04722e-02 at N=81
percent error wrt N: -1.20965e-02 at N=91
percent error wrt N: -6.12280e-02 at N=101
percent error wrt N: -1.25711e-02 at N=111
percent error wrt N: -9.14640e-02 at N=121
percent error wrt N: -4.86420e-02 at N=131
percent error wrt N: 1.45012e-03 at N=141
```

1.6 e)

Look up the Morse-oscillator energy levels and compute the quantum partition function in the standard way to check that your path-integral result is in agreement. Also compute the classical partition function using quadrature.

1.6.1 Solution

From many sources, (e.g. Wikipedia, https://arxiv.org/pdf/quant-ph/0411159.pdf, https://demonstrations.wolfram.com/EnergyLevelsOfAMorseOscillator/, https://scipython.com/blog/the-morse-oscillator/)

$$E_n = \hbar\omega_e(n+1/2) - \hbar\omega_e\chi_e(n+1/2)^2$$

with $n = 0, 1, 2, ...\lfloor 2D_e/\omega_e \rfloor$.

From correspondence with Prof Richardson, "the standard way" is just summing over eigenstates. That is, sum over all $e^{-\beta E_j}$.

First, let's calculate the partition function from the Morse oscillator energy levels.

[9]:
```
# from math import factorial

β = 1077.73 # room temp
def Z_QM(β):
    En = lambda n: ω*(n+1/2)-ω*χ*(n+1/2)**2
    n=0
    newZ = 0
    while n<2*De/ω: # == np.sqrt(2*m*De)/a
        newZ += np.exp(-β*En(n))
    #     print(newZ)
        n+=1
    return newZ
# newZ /= factorial(N) # indistinguishability

# they are in agreement
newZ = Z_QM(β)
print(newZ)
print(Z_true[-1])
```

```
0.00011500347121643913
0.00011061902810707886
```

Next, let's calculate the classical partition function using quadrature.

First, we start with the expression for the classical partition function,

$$Z_{\text{classical}} = \frac{1}{h}\int \mathrm{d}x\mathrm{d}p e^{-\beta[\frac{p^2}{2m}+V(x)]}.$$

With a little effect integrating normal distributions, we get

$$Z_{\text{classical}} = \left(\frac{m}{2\pi\beta\hbar^2}\right)^{1/2} I(x)$$

where

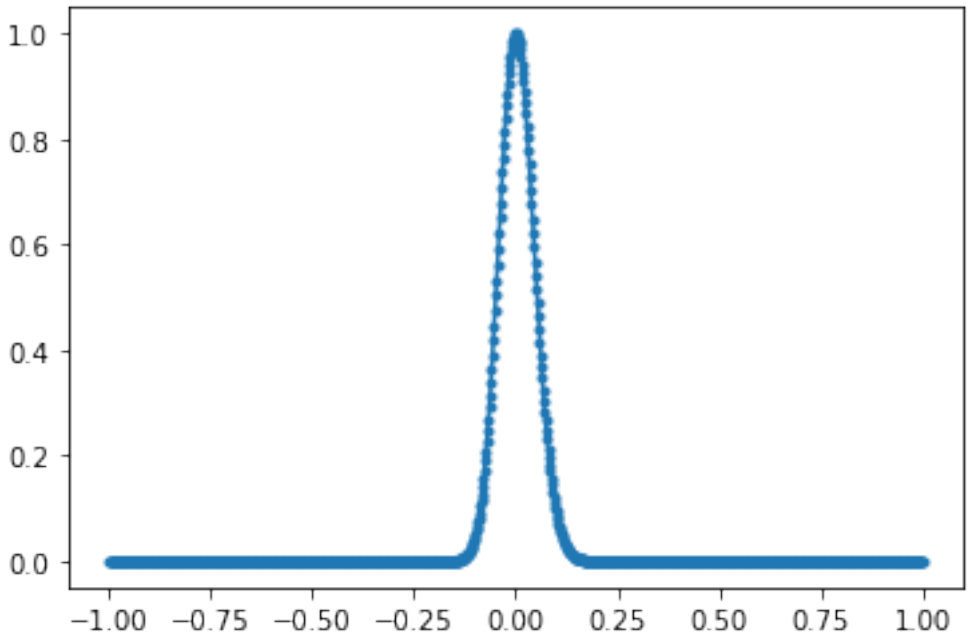
$$I(x) \equiv \int \mathrm{d}x e^{-D_e\beta(1-e^{-\alpha(x-x_e)})^2}.$$

So we must numerically integrate $I(x)$ and then plug it into the equation above.

For ease of implementation, we can make the change of variables $x - x_e \to x$:

$$I(x) = \int \mathrm{d}x e^{-D_e\beta(1-e^{-\alpha x})^2}.$$

[10]:
```
from scipy.integrate import quad

β = 1077.73 # room temp

def integrand(x, β):
    retval = -De*β*(1-np.exp(-α*x))**2
    return np.exp(retval)

# view integrand -- can see it's extremely sharply peaked
# => consider only a small interval around zero
# tested a few intervals and saw this is good enough
tmpx = np.linspace(-1, 1, 1000)
plt.plot(tmpx, integrand(tmpx,β), '.-')
plt.show()

def Z_CM(β):
    I_inZ = quad(lambda x: integrand(x,β), -1, 1)[0]
    return np.sqrt(m/(2*pi*β))*I_inZ

    N=Ns[i]
    # it very quickly approaches zero
    Z_class = Z_CM(β)
    print('Z_class=%.5e for N=%i' % (Z_class, Ns[i]))

print('classical Z=', Z_CM(β))
```




```
classical Z= 0.05463346393288489
```

1.7 f)

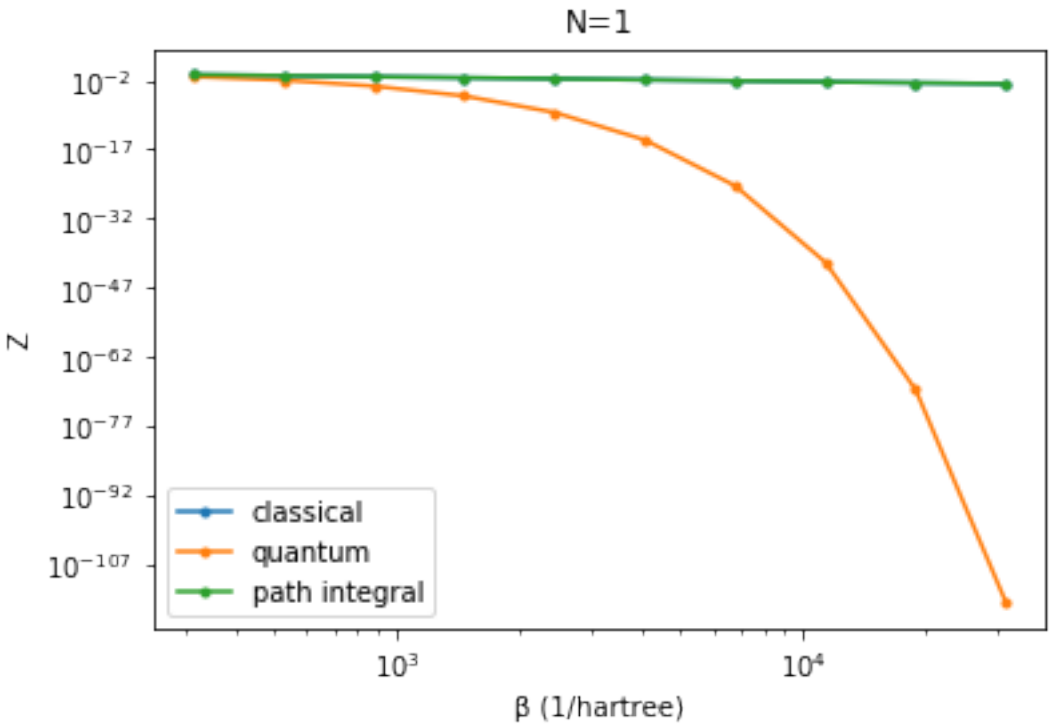
Plot Z against (a few values of) β for quantum, classical and path-integral approaches with various values of N, e.g. $N = 1, 2, 4, 8, 16, ...$ until convergence. In what limits are the $N = 1$ results acceptable?

1.7.1 Solution

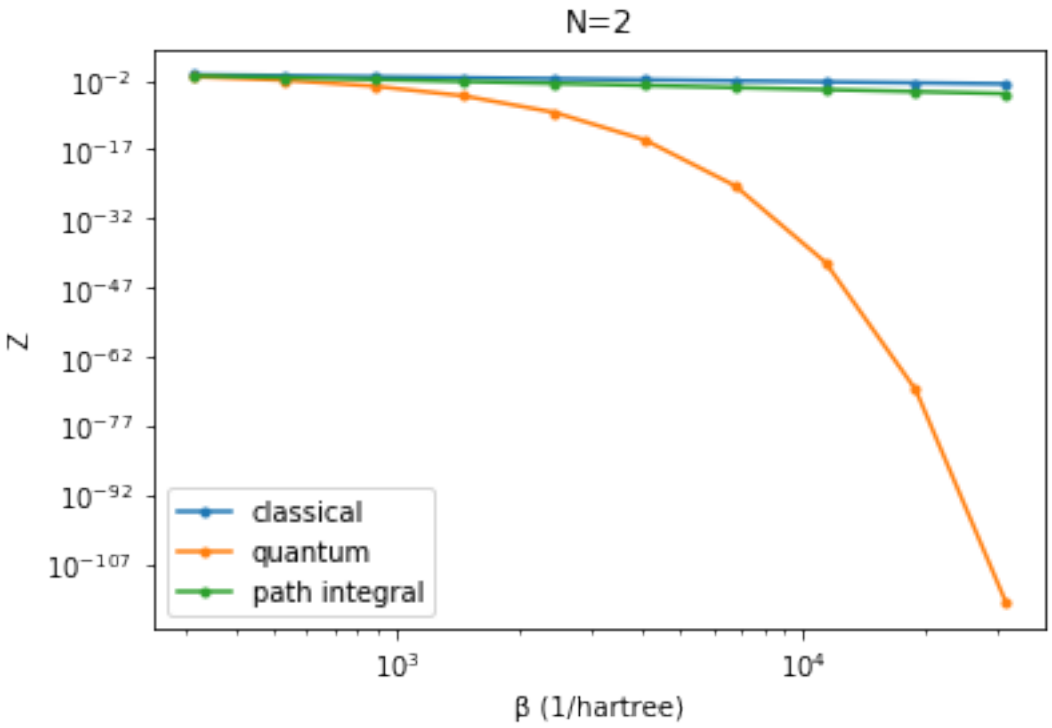
[11]:
```
kB = 3.1668115635e-6 # E_h/K
Ts = np.logspace(1,3,10)
βs = 1/(Ts*kB)
print('Ts')
print(Ts)
Ns = 2**np.arange(0,7,1) # up to 64
lenN = len(Ns)
Z_q = np.zeros((len(βs),))
for i,β in enumerate(βs):
    # QM (does not require N)
    Z_qi = Z_QM(β)
    Z_q[i] = Z_qi

for j,N in enumerate(Ns):
    Z_p = np.zeros((len(βs),))
    Z_c = np.zeros((len(βs),))
    for i,β in enumerate(βs):
#         print('T=%.5e' % Ts[i])
        # path integral
```

```
        Z_pi,σ_pct_pi = mc_isampling(N, β=β, verbose=False,␣
↪taylor_estimate=True)
        # classical
        Z_ci = Z_CM(β)
        Z_p[i] = Z_pi[-1]
        Z_c[i] = Z_ci
    # I'm printing out values to compare them, since the values change
    # so much with temp that it may be hard to read from the graph
    print('N=%i'%N)
    print('Z_c', Z_c)
    print('Z_q', Z_q)
    print('Z_p', Z_p)
    plt.plot(βs,Z_c,'.-',label='classical')
    plt.plot(βs,Z_q,'.-',label='quantum')
    plt.plot(βs,Z_p,'.-',label='path integral')
    plt.legend()
    plt.xscale('log')
    plt.yscale('log')
    plt.title('N=%i' % N)
    plt.ylabel('Z')
    plt.xlabel('β (1/hartree)')
#     plt.xlabel('T (K)')
    plt.show()
```

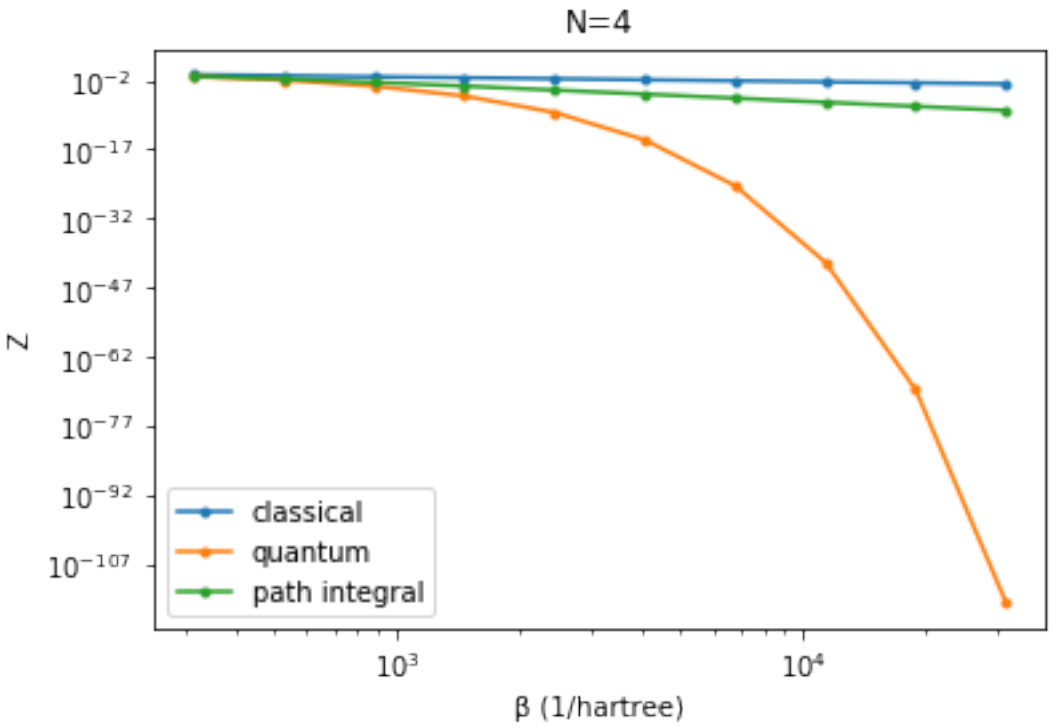
```
Ts
[  10.           16.68100537   27.82559402   46.41588834   77.42636827
  129.1549665   215.443469    359.38136638  599.48425032 1000.        ]
N=1
Z_c [0.00186014 0.00310308 0.00517673 0.00863667 0.01441062 0.02404892
 0.04014548 0.06704918 0.11207661 0.18761128]
Z_q [3.79123952e-116 6.40910211e-070 3.30951754e-042 1.35910256e-025
 1.23815882e-015 1.15705555e-009 4.39158808e-006 6.14237458e-004
 1.18779414e-002 7.05283203e-002]
Z_p [0.00185609 0.00311717 0.00521175 0.0086129  0.01451445 0.02452586
 0.0405967  0.06682835 0.11251619 0.18739772]
```



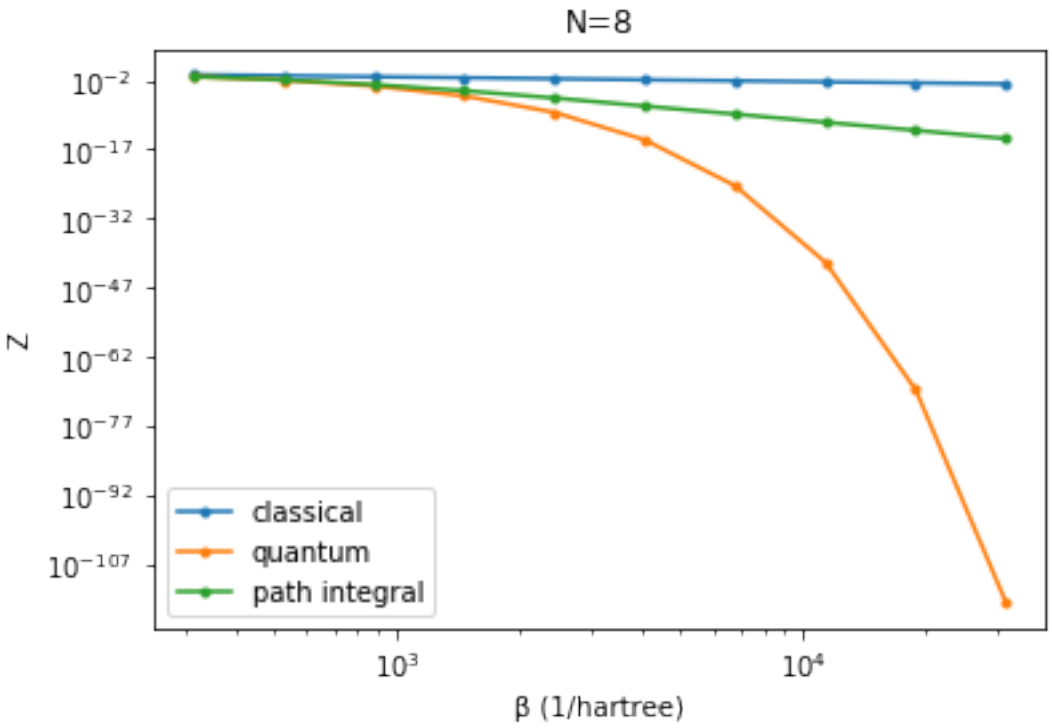

```
N=2
Z_c [0.00186014 0.00310308 0.00517673 0.00863667 0.01441062 0.02404892
 0.04014548 0.06704918 0.11207661 0.18761128]
Z_q [3.79123952e-116 6.40910211e-070 3.30951754e-042 1.35910256e-025
 1.23815882e-015 1.15705555e-009 4.39158808e-006 6.14237458e-004
 1.18779414e-002 7.05283203e-002]
Z_p [1.38095594e-05 3.86139928e-05 1.06640069e-04 2.92274898e-04
 8.59796278e-04 2.38762969e-03 6.15594338e-03 1.70492930e-02
 4.53086197e-02 1.11848977e-01]
```



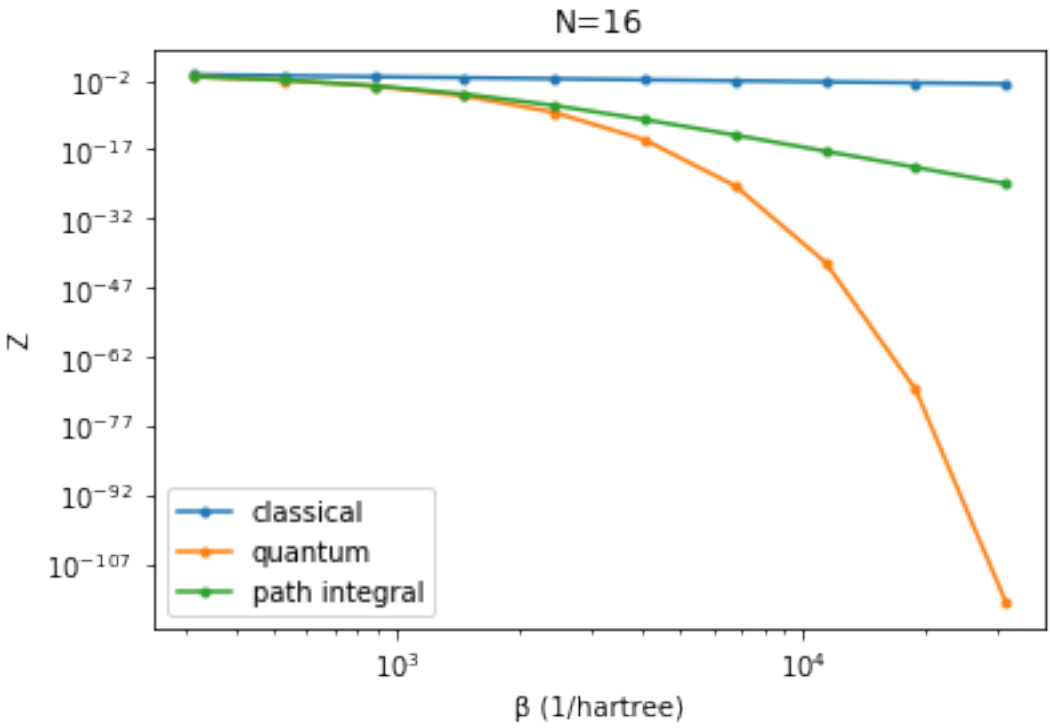

```
N=4
Z_c [0.00186014 0.00310308 0.00517673 0.00863667 0.01441062 0.02404892
 0.04014548 0.06704918 0.11207661 0.18761128]
Z_q [3.79123952e-116 6.40910211e-070 3.30951754e-042 1.35910256e-025
 1.23815882e-015 1.15705555e-009 4.39158808e-006 6.14237458e-004
 1.18779414e-002 7.05283203e-002]
Z_p [3.10465040e-09 2.41236670e-08 1.82904058e-07 1.44059213e-06
 1.10914155e-05 8.16237677e-05 6.17452466e-04 4.16328671e-03
 2.22759515e-02 8.12711224e-02]
```



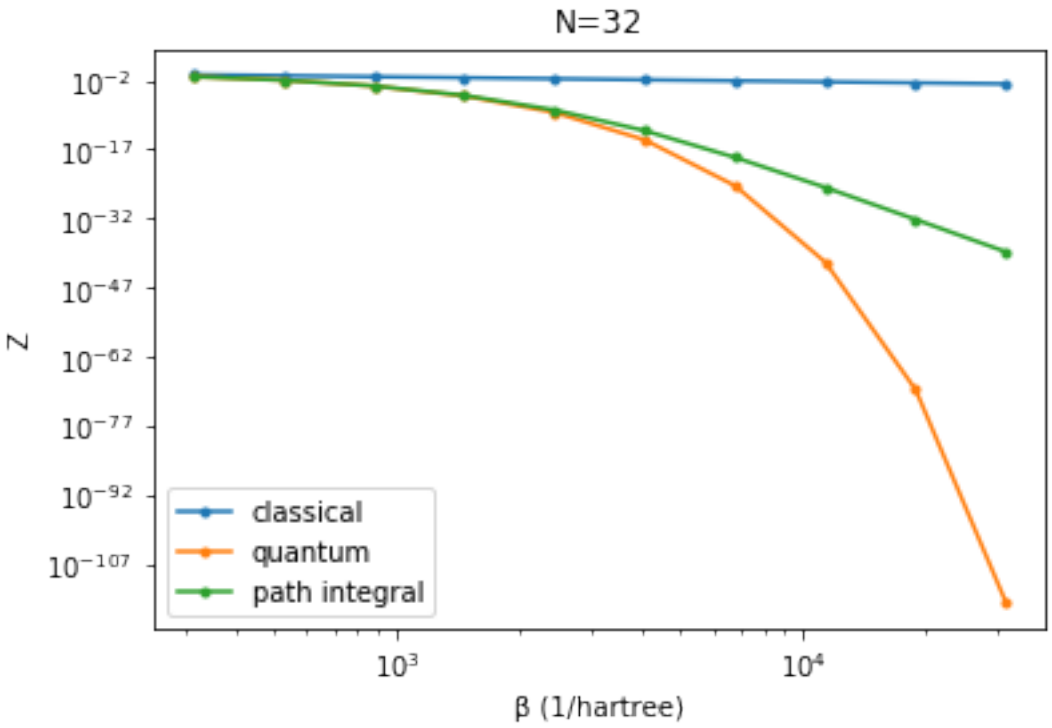

```
N=8
Z_c [0.00186014 0.00310308 0.00517673 0.00863667 0.01441062 0.02404892
 0.04014548 0.06704918 0.11207661 0.18761128]
Z_q [3.79123952e-116 6.40910211e-070 3.30951754e-042 1.35910256e-025
 1.23815882e-015 1.15705555e-009 4.39158808e-006 6.14237458e-004
 1.18779414e-002 7.05283203e-002]
Z_p [2.33234457e-15 1.48043253e-13 8.40230911e-12 4.95297434e-10
 2.75784665e-08 1.54865904e-06 6.13498050e-05 1.30294728e-03
 1.38580897e-02 7.30913851e-02]
```



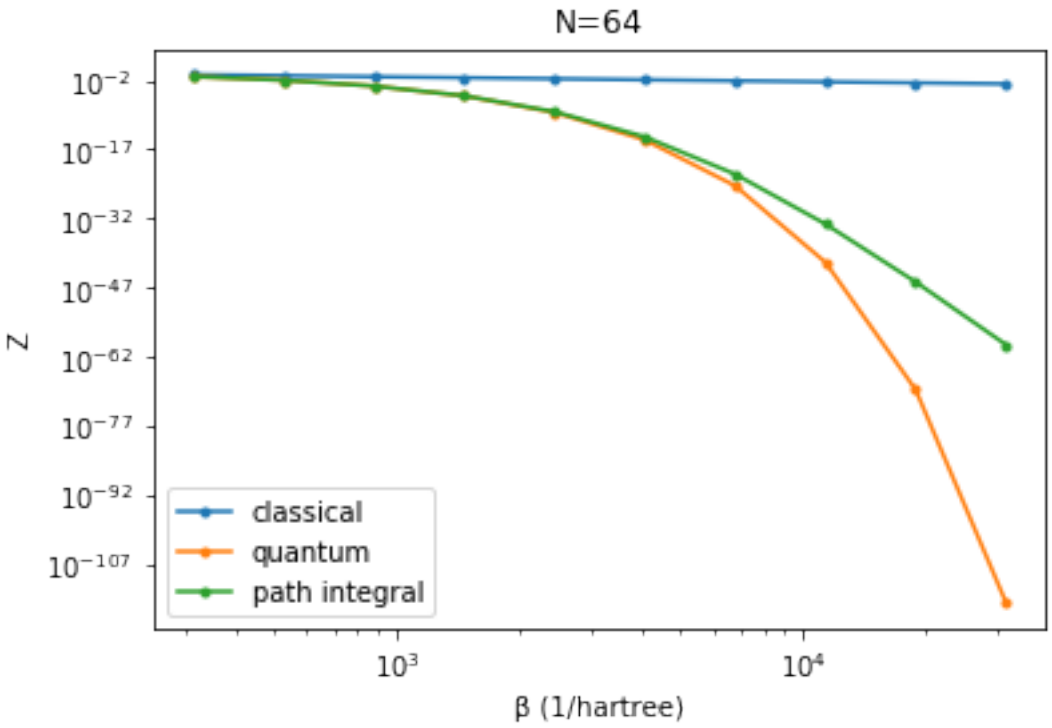

```
N=16
Z_c [0.00186014 0.00310308 0.00517673 0.00863667 0.01441062 0.02404892
 0.04014548 0.06704918 0.11207661 0.18761128]
Z_q [3.79123952e-116 6.40910211e-070 3.30951754e-042 1.35910256e-025
 1.23815882e-015 1.15705555e-009 4.39158808e-006 6.14237458e-004
 1.18779414e-002 7.05283203e-002]
Z_p [3.75501437e-25 1.38100008e-21 4.42861010e-18 1.39686473e-14
 3.21484465e-11 3.67968051e-08 1.18682521e-05 7.57609447e-04
 1.25142620e-02 6.99460935e-02]
```




```
N=32
Z_c [0.00186014 0.00310308 0.00517673 0.00863667 0.01441062 0.02404892
 0.04014548 0.06704918 0.11207661 0.18761128]
Z_q [3.79123952e-116 6.40910211e-070 3.30951754e-042 1.35910256e-025
 1.23815882e-015 1.15705555e-009 4.39158808e-006 6.14237458e-004
 1.18779414e-002 7.05283203e-002]
Z_p [5.83436029e-40 6.29886599e-33 5.71157751e-26 1.90945731e-19
 1.22974774e-13 3.97342106e-09 5.96007295e-06 6.71589138e-04
 1.16753838e-02 6.96624214e-02]
```




```
N=64
Z_c [0.00186014 0.00310308 0.00517673 0.00863667 0.01441062 0.02404892
 0.04014548 0.06704918 0.11207661 0.18761128]
Z_q [3.79123952e-116 6.40910211e-070 3.30951754e-042 1.35910256e-025
 1.23815882e-015 1.15705555e-009 4.39158808e-006 6.14237458e-004
 1.18779414e-002 7.05283203e-002]
Z_p [3.89049591e-60 1.69743128e-46 6.78114025e-34 4.54696717e-23
 5.75465917e-15 1.68240460e-09 4.89542312e-06 6.18890674e-04
 1.15916285e-02 7.34847176e-02]
```



$N = 1$ results are acceptable in the high-T limit (makes sense because at high temperature, the details shouldn't matter). It seems the path-integral approach agrees with the classical case for small N and approaches the quantum case for large N.

1.8 g)

Also consider the harmonic-oscillator approximation. Put these approximations in the order of how accurately they predict the correct partition function:

- quantum harmonic oscillator,
- classical harmonic oscillator,
- large but finite N path-integral calculation of the harmonic oscillator,
- classical Morse oscillator,
- large but finite N path-integral calculation of the Morse oscillator.

The real advantage of the path-integral method is that it can be easily applied to more complicated problems than the Morse oscillator, including high-dimensional systems, without needing to sovle the Schrödinger equation at all.

1.8.1 Solution

The harmonic oscillator potential is

$$V(x) = \frac{1}{2} m\omega^2 (x - x_e)^2.$$

I've already implemented this as an option in the path integral code above, so I shall just call these functions.

The quantum and classical partition functions can easily be solved exactly for the harmonic oscillator, and is done in any standard textbook on statistical mechanics.

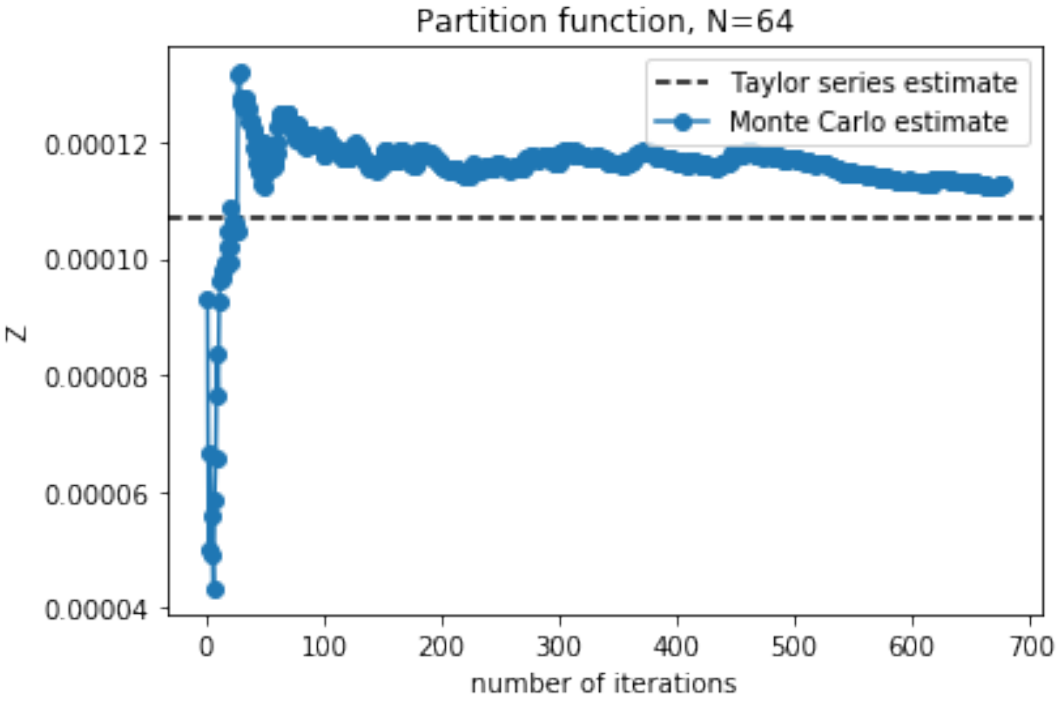
$$Z_{\text{classical}} = \frac{1}{\hbar\beta\omega},$$

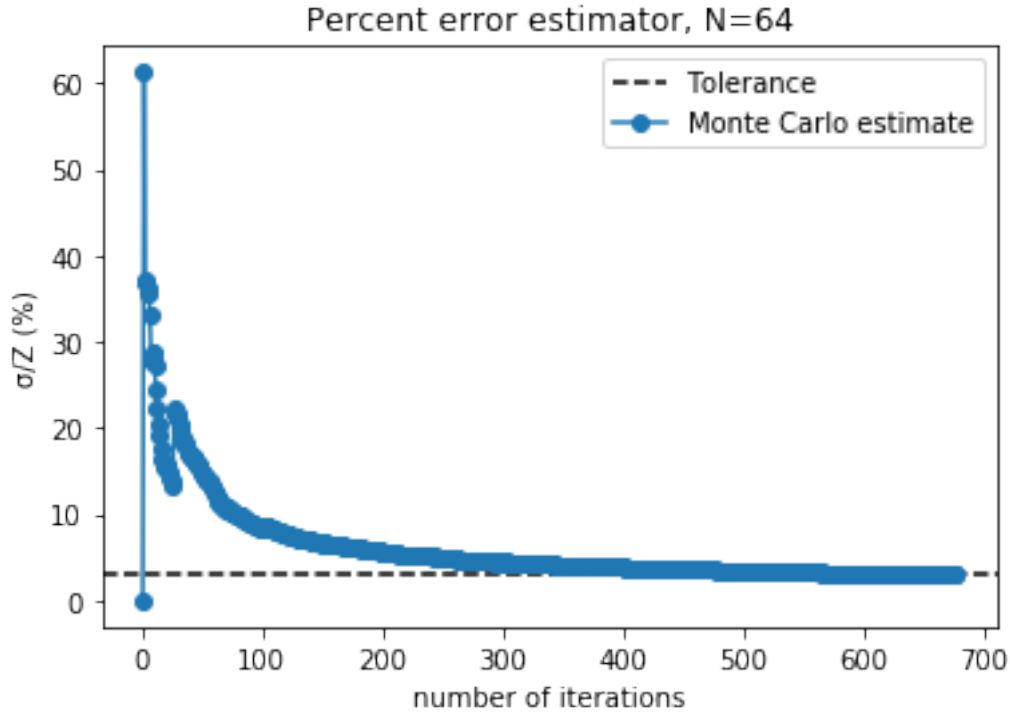
$$Z_{\text{quantum}} = \frac{1}{2\sinh(\hbar\beta\omega/2)}.$$

The quantum Morse oscillator should be the best approximation since we are dealing with unbound states. The rest can be checked with numerics, but in general I suspect the quantum case to be the best, then path integral, then classical, and in general Morse to be more accurate than harmonic oscillator. I will check the values for each at room temperature.

[12]:
```
N = 64
β = 1077.73 # room temp
Z_morse_path, _ = mc_isampling(N, β=β, potential='morse',verbose=True)
Z_harm_path, _ = mc_isampling(N, β=β, potential='harmonic',verbose=False) #␣
 ↪all fall on same spot, not exciting
# good to see that the Taylor approximation works nicely also for the␣
 ↪harmonic case though
Z_morse_qm = Z_QM(β)
Z_morse_cm = Z_CM(β)
# now just need classical and quantum harmonic oscillators
# they are both exactly solved!
from math import sinh
Z_harm_qm = 1/(2*sinh(β*ω/2)) # **N
Z_harm_cm = 1/(β*ω) # **N
```

```
Z: 1.17893e-04 at 300 samples
σ/Z: 4.50294e-02 at 300 samples
wobble: 0
Z: 1.13334e-04 at 600 samples
σ/Z: 3.13279e-02 at 600 samples
wobble: 0
Z: 1.12802e-04 at 678 samples
σ/Z: 2.96289e-02 at 678 samples
wobble: 11
```





[13]:
```
print('Morse:')
print('\tQM: Z=%.5e; %% error=0' % Z_morse_qm)
print('\tPath: Z=%.5e, %% error=%.5e' % (Z_morse_path[-1],␣
 ↪(Z_morse_qm-Z_morse_path[-1])/Z_morse_qm))
```

```
print('\tCM: Z=%.5e, %% error=%.5e' % (Z_morse_cm, (Z_morse_qm-Z_morse_cm)/
 ↪Z_morse_qm))

print('Harmonic:')
print('\tQM: Z=%.5e, %% error=%.5e' % (Z_harm_qm, (Z_morse_qm-Z_harm_qm)/
 ↪Z_morse_qm))
print('\tPath: Z=%.5e, %% error=%.5e' % (Z_harm_path[-1],␣
 ↪(Z_morse_qm-Z_harm_path[-1])/Z_morse_qm))
print('\tCM: Z=%.5e, %% error=%.5e' % (Z_harm_cm, (Z_morse_qm-Z_harm_cm)/
 ↪Z_morse_qm))
```

```
Morse:
        QM: Z=1.15003e-04; % error=0
        Path: Z=1.12811e-04, % error=1.90642e-02
        CM: Z=5.46335e-02, % error=-4.74059e+02
Harmonic:
        QM: Z=1.03626e-04, % error=9.89321e-02
        Path: Z=1.06903e-04, % error=7.04339e-02
        CM: Z=5.44976e-02, % error=-4.72878e+02
```

The above shows, at least for room temperature, that the order from most to least accurate is:

- Quantum Morse oscillator
- Path-integral Morse oscillator
- Path-integral harmonic oscillator
- Quantum harmonic oscillator
- Classical harmonic oscillator
- Classical Morse oscillator

Though of course this will also depend on temperature. The two classical approximations are very similar (and both far from the true value), so distinguishing between them is perhaps not very meaningful. In theory, I would expect the classical Morse oscillator in better, but it seems to not make much difference.

That's all! It was an interesting problem set and gave me a better idea of what research in the group would be like.