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Mohamad Toutounji

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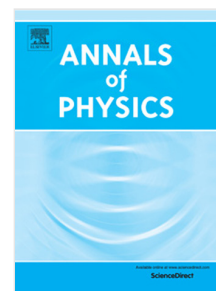
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The Off-diagonal Propagator of Morse Oscillator

$$\mathcal{F}(x, y; t) = \frac{aM\sqrt{\sigma\delta}}{2\pi\hbar} \int_{-\infty}^{+\infty} dE \left[i^{-(p(E)-1)} K_{p(E)} \left(\sqrt{2A \left(\sqrt{B^2 + C^2} + B \right)} \right) \right]$$

This article

1. derives the quantum propagator of Morse oscillator in the high temperature limit;
2. uses the resulting diagonal propagator to derive a closed form of Morse oscillator partition function; and
3. provides a more sophisticated formula of the quantum propagator to test the accuracy of the herein results.

Morse Oscillator Propagator in the High Temperature Limit I: Theory

Mohamad Toutounji

Mtoutounji@uaeu.ac.ae

College of Science, P. O. Box 15551, UAE University, Al Ain, UAE

Abstract

In an earlier work of the author the time evolution of Morse oscillator was studied analytically and exactly at low temperatures whereupon optical correlation functions were calculated using Morse oscillator coherent states were employed. Morse oscillator propagator in the high temperature limit is derived and a closed form of its corresponding canonical partition function is obtained. Both diagonal and off-diagonal forms of Morse oscillator propagator are derived in the high temperature limit. Partition functions of diatomic molecules are calculated.

I. Introduction

Anharmonic behavior of systems often starts to predominate as the ambient temperature increases. As such, harmonic approximation would not seem to be as operative at high temperatures, for which the reason several anharmonic oscillators have been adopted for modeling molecular vibrations at high temperatures. However, this article will only focus on the Morse oscillator time evolution (propagator) since it seems to be the most accurate model in handling molecular vibration. For this reason, chemists and physicists tend to employ the Morse oscillator to model vibrations. This employment, and hence accuracy, comes at a price: Morse oscillator eigenfunctions and propagator [1] are complex functional and unstable numerically. As such, the Morse oscillator propagator has not been utilized despite its availability, [1] as it tends to be complicated and thus does not lend itself readily to use. Although a few people have tried to derive the exact form of the propagator of Morse oscillator, the final result was left as an unevaluated triple-integral form. Therefore, scientists have avoided utilizing it.

Although one may employ Wigner [3, 4], Liouville, or canonical transformation [5] in order to map the Morse oscillator into a harmonic form, Morse oscillator eigenfunctions are tricky to deal with due to the arising divergent integrals and numerical uncertainties. Thus employing them for the purpose of monitoring the temporal evolution of an anharmonic system is difficult. Mukamel and coworkers exploited the Liouville space generating function (LGF) approach to avoid having to deal with Morse oscillator eigenfunctions to probe the spectroscopy and dynamics of anharmonic systems in condensed systems, rendering sound results. [2] The LGF approximation starts with initial Gaussian function of matrices (initial conditions) which is then substituted into equations of motion leading to a system of five nonlinear differential equations that may be solved numerically. Pollak [6] and Tanimura [7] have used closely related methods.

Computing dynamical time correlation functions (two-, four-, or six-point dipole moment time correlation function (DMTCF)) [8–12] in anharmonic systems involves time evolution of the Heisenberg operators in which the corresponding propagator plays a central role. Toutounji [14–19] however has developed several analytical techniques (void of numerical instabilities) that deal with anharmonic systems time evolution, and one of these methods is exact (in the low temperature limit) which utilizes Morse oscillator *coherent states* of which some properties had been developed by the author. [18, 19, 20] For example the linear DMTCF was calculated exactly at $T = 0$ K in a system anharmonically coupled to phonons. [19] The other two methods were developed using cumulant expansion and partial differential equations. [16, 17] In fact nonlinear DMTCFs in anharmonic systems were calculated analytically using cumulant expansion theory of Kubo [17] rendering good results, and no numerical problems. [16] Dealing with the time evolution operator while doing these calculations is formidable. While path integral technique is one common methodology to handle the time evolution operator, other methodologies such as algebraic treatment whereby matrices, Campbell-Baker Hausdorff theory, [16, 17] and differential equations are utilized in order to deal with the resulting nested operators. This article

is probably the first work that deals with Morse oscillator propagator, derived in [1], both numerically and analytically.

This article evaluates the Morse oscillator propagator to be utilized analytically and numerically when calculating physical quantities. Since evaluating the propagator involves multiple-integration with respect to the order of the modified Bessel functional which is not feasible, therefore it has not yet been put to use. For this reason, one way to handle the Morse oscillator propagator analytically, and numerically, is to consider dynamical observables in the high temperature limit, whereby a closed form for the respective canonical partition function may be derived. This will further show the applicability of the Morse oscillator propagator. While Part I of this series requires using the diagonal propagator to carry out calculations, Part II (in progress) will derive time correlation functions of anharmonic systems using the off-diagonal propagator, leading to real molecular spectroscopic applications. Both forms of propagators are derived herein.

II. Morse Oscillator Quantum Mechanical Profile

The vibrational Morse oscillator Hamiltonian reads

$$\hat{H} = \frac{P^2}{2M} + D_e \left(e^{-2a(x-x_0)} - 2e^{-a(x-x_0)} \right) \quad (1)$$

defined over $-\infty < x < \infty$, with P and x being the momentum and position. The eigenfunctions of \hat{H} are expressed in terms of the generalized Laguerre polynomials

$$\Phi_m(x) = \sqrt{\frac{a\Gamma(m+1)2s}{\Gamma(2\alpha-m)}} (2\alpha e^{-a(x-x_0)})^{\alpha-(m+\frac{1}{2})} e^{-\alpha e^{-a(x-x_0)}} L_m^{2\alpha-2m-1}(2\alpha e^{-a(x-x_0)}), \quad (2)$$

where $\alpha \equiv \sqrt{2MD_e}/a$. (It should be noted the constraint condition for this system is $2s = 2\alpha - 2m - 1$ as dictated by Landau and Lifshitz. [11] The normalization condition is

$$\int_{-\infty}^{+\infty} |\Phi_m(x)|^2 dx = 1 \quad (3)$$

To simplify notation and the forthcoming mathematical operations, we set $y \equiv 2a e^{-a(x-x_0)}$ (often called *Morse coordinate*)

$$\Phi_m(y) = \sqrt{\frac{a\Gamma(m+1)2s}{\Gamma(2\alpha-m)}} (y)^s e^{-\frac{y}{2}} L_m^{2s}(y), \quad (4)$$

of which the normalization condition with respect to *Morse coordinate* becomes

$$\int_0^{+\infty} \frac{|\Phi_m(y)|^2}{a y} dy = 1. \quad (5)$$

Note the set $\{\Phi_m\}_{m=0}$ are only the bound states, as the continuum states of Morse oscillator are unnormalizable. While this set is incomplete, it still forms basis in its respective discrete subspace in terms of which the vibrational wavefunction at hand may be expanded.

The eigenvalues of Morse oscillator are

$$E_m = \hbar\omega_e(m + 1/2) - \frac{1}{4D_e} [\hbar\omega_e(m + 1/2)^2] \quad (6)$$

where m is the number of *anharmonic* phonons with $m = 0, 1, \dots, (\alpha-1)$, i.e. m cannot exceed α . Additionally, $a \equiv \sqrt{k_e / 2D_e}$ with k_e being the force constant at the minimum of the Morse potential; and while D_e signifies the depth of Morse well, or the dissociation energy of a diatomic molecule, the parameter a (often called Morse parameter) denotes its breadth and shape. Spectroscopically, Eq. 6 can be recast as

$$E_m = \omega_e \left[\left(m + \frac{1}{2} \right) - \chi \left(m + \frac{1}{2} \right)^2 \right], \quad (7)$$

where the anharmonicity constant $\chi\omega_e = \frac{\omega_e^2}{4D_e}$. The force constant k_e for Morse well is different

from that for harmonic system since k_e is given by the second derivative of the potential. The number of states is then given by $N = [\alpha + 1/2] = [(1-\chi)/2\chi]$, where $[.]$ denotes maximum integer. Hence number of bound states increases as anharmonicity decreases; when $\chi \rightarrow 0$, N is infinite, the system is now harmonic which possesses infinite number of bound states and no continuum. Interestingly, one may observe that the anharmonicity constant χ is totally governed by the number of bound states: $\chi = 1/2N$.

II. Background on the Green function of Morse oscillator

A stationary system with an energy E and Hamiltonian \hat{H} , of which basic information is contained in its Green function, $G(E) = 1/(E - \hat{H})$. The Green function may be expressed in coordinate representation as

$$G(x, y; E) = \left\langle x \left| \frac{1}{E - \hat{H}} \right| y \right\rangle = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{\frac{iEt}{\hbar}} \mathcal{F}(x, y; t) dt. \quad (8)$$

where the propagator $\mathcal{F}(x, y; t) = \left\langle x \left| e^{-\frac{i\hat{H}t}{\hbar}} \right| y \right\rangle$.

The propagator of Morse oscillator may be defined as [21, 22, 23]

$$\mathcal{F}(x, y; t) = \left\langle x \left| e^{-\frac{i\hat{H}t}{\hbar}} \right| y \right\rangle = \sum_{m=0}^N e^{-\frac{iE_m t}{\hbar}} \Phi_m^*(x) \Phi_m(y). \quad (9)$$

A closed form of the Green function of Morse oscillator has been reported [24] as

$$G(x, y; \eta(E)) = \left(-\frac{a}{2\hbar} \right) \frac{(\eta + \mu - \frac{1}{2})!}{(2\mu)!} \exp\left(\frac{a(x-y)}{4}\right) \exp\left(\frac{a(x+y)}{2}\right) \\ \times W_{\eta, \mu} \left(\frac{M\omega}{\hbar} e^{-ay} \right) M_{\eta, \mu} \left(\frac{M\omega}{\hbar} e^{-ax} \right) \quad (10)$$

where $W_{\eta, \mu}$ and $M_{\eta, \mu}$ are the special type of confluent hypergeometric functions, namely the Whittaker functions, and $\eta(E) = -\tilde{E}/2\tilde{\omega}\hbar$ and $\mu = i\sqrt{8ME}/2a\hbar$. This form of Morse oscillator Green function in Eq. 10 is too complicated (both analytically and numerically) to lend itself to use, particularly there is not a sufficient, sound mathematical account of Whittaker functions in the literature.

The Morse oscillator Green function was first derived by Duru [1] through canonically transforming Morse potential to a centrifugal potential whose Green function was available. A handful of physicists [24–26] used different methods to reproduce the Green function obtained by Duru. However, their results, including that of Duru, have never been utilized in applications and therefore it is not clear how readily their results lend themselves to use. Additionally, neither Duru nor anyone else did report the Morse oscillator propagator in a closed form. This article will derive the diagonal and off-diagonal forms of Morse oscillator propagator are derived here in the high temperature limit (HTL) whereby applicability of Morse oscillator propagator is tested as this is not reported in the literature.

One may obtain the propagator from Eq.10 by performing Fourier transform with respect to the energy E which is embedded in the index η . This alone makes analytical integrating Eq. 10 impossible, even carrying out the integration numerically poses a real numerical challenge. Although the analytical solution for Morse Green function has been around for over three decades, it has never been utilized in any applications due to its complexity; nor have its correctness and applicability been tested. In the next section the propagator is evaluated at high temperatures as this will invoke a tremendous simplification on to the pure quantum mechanical propagator. The result will further be used to evaluate the Morse oscillator partition function, which will serve as first-time application of Morse oscillator propagator.

III. Time Evolution of Morse oscillator in the High Temperature Limit

Having the propagator/Green function of any system at one's disposal is a great asset, especially when it lends itself readily to use. It turns out that the propagator of Morse oscillator in the HTL is much easier to handle than at intermediate temperatures. Our starting point would be that expression given by Duru [1]

$$\mathcal{F}(x, y; t) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dE e^{iEt/\hbar} \frac{a}{2} \int_0^{+\infty} dS e^{2iD_e S/\hbar} \mathcal{M}(\sigma, \delta; S), \quad (11)$$

where $\mathcal{M}(x, y; S)$ is given by [1]

$$\mathcal{M}(\sigma, \delta; S) = \frac{M\omega}{i\hbar} \sqrt{\sigma\delta} \csc(\omega S) I_p \left[\frac{M\omega}{i\hbar} \sigma\delta \csc(\omega S) \right] \exp \left[\frac{iM\omega}{2\hbar} (\sigma^2 + \delta^2) \cot(\omega S) \right] \quad (12)$$

where $I_p(\cdot)$ is the modified Bessel function of the first kind and $p = \sqrt{2ME}$, and

$$\sigma = \exp(-ax/2) \text{ and } \delta = \exp(-ay/2). \quad (12a)$$

Although one can evaluate the inner integral

$$\int_0^{\infty} dS e^{2iD_e S/\hbar} \mathcal{M}(\sigma, \delta; S) \quad (13)$$

exactly analytically, the end result being a product of Gamma functions and Whittaker functions makes it not much of use, which will even be impossible (analytically) to follow up with outer integral over the index. However, one can take the classical limit (HTL) by expanding the trigonometric functions to their first terms yielding

$$\mathcal{M}(\sigma, \delta; S) = \frac{M}{i\hbar S} \sqrt{\sigma\delta} I_p[M\sigma\delta/i\hbar S] \exp[iM(\sigma^2 + \delta^2)/2\hbar S]. \quad (14)$$

Inserting Eq. 14 in Eq. 13 and using integration by substitution by letting $u = 1/S$ leads to

$$\mathcal{M}(\sigma, \delta; S) = \frac{iM}{\hbar} \sqrt{\sigma\delta} \int_0^\infty \frac{du}{u} e^{2iD_e/uh} I_p[M\sigma\delta u/i\hbar] \exp[iM(\sigma^2 + \delta^2)u/2\hbar]. \quad (15)$$

Employing the definition of I_p [27, 28] in Eq. 15 and resuming again yields

$$= \frac{2M\sqrt{\sigma\delta}}{\hbar i^{p-1}} K_p \left(\sqrt{2A(\sqrt{B^2 + C^2} + B)} \right) J_p \left(\sqrt{2A(\sqrt{B^2 + C^2} - B)} \right) \quad (16)$$

where K_p and J_p are the modified Bessel function of the second type (MacDonald function) and the ordinary Bessel function, [28] respectively. Here

$$A = 2iD_e/\hbar \quad (16a)$$

$$B = iM(\sigma^2 + \delta^2)/2\hbar \quad (16b)$$

$$C = M\sigma\delta/i\hbar. \quad (16c)$$

Now that the inner integral has been evaluated the outer integral over the index of both Bessel functions must be carried out. So the propagator now looks like

$$\begin{aligned} \mathcal{F}(x, y; t) = & \frac{aM\sqrt{\sigma\delta}}{2\pi\hbar} \int_{-\infty}^{+\infty} dE \left[i^{-(p(E)-1)} K_{p(E)} \left(\sqrt{2A(\sqrt{B^2 + C^2} + B)} \right) \right. \\ & \left. \times J_{p(E)} \left(\sqrt{2A(\sqrt{B^2 + C^2} - B)} \right) e^{iEt/\hbar} \right] \end{aligned} \quad (17)$$

where

$$z_1 = \sqrt{2A(\sqrt{B^2 + C^2} - B)} \quad (17a)$$

$$z_2 = \sqrt{2A(\sqrt{B^2 + C^2} + B)}. \quad (17b)$$

With the momentum $p = \sqrt{2ME}$ being the order of Bessel functions. Note Eq. 17 requires carrying out the integration with respect to the index (order) of Bessel functions. This is a formidable challenge as this type of integral is as if yet remains unfamiliar even to mathematicians and falls far short in the literature. [27] As such, we shall avoid doing the integration as it stands in Eq. 17. One way to work around it is to take the asymptotic limit of both Bessel functions. In fact, taking the asymptotic limit here is physically well-justified within the high temperature regime in which case the molecular system would be in high energy states, which might even be near the maximum value of the momentum p or the energy E . As stated above, one would be able to identify the high energy limit by looking at high Morse oscillator bound quantum vibrational states determined by the shape and breadth of the Morse potential through the relationship $(1 - \chi)/2\chi$. Thus, taking the large-order asymptotic limit of Bessel functions appearing in Eq. 17 leads to

$$\mathcal{F}(x, y; t) = \frac{aM\sqrt{\sigma\delta}}{2\pi\hbar} \int_{-\infty}^{+\infty} dE \frac{i^{-(p+1)}}{2p} \left(\frac{z_1}{z_2}\right)^p e^{iEt/\hbar}. \quad (18)$$

This tremendous simplification which has transpired upon going from Eq. 17 to Eq. 18 is attributed to the fact that the MacDonald function K_p may be thought of as very much the inverse of the Bessel function J_p (within an order of constants only). As stated earlier, an analytical solution to Eq. 17 is not possible because the integration with respect to the *order* (index) of Bessel functions requires solving nonlinear differential equation analytically. Evaluating the integral in Eq. 18 yields the propagator of Morse oscillator

$$\mathcal{F}(x, y; t) = \frac{a\sqrt{\sigma\delta}}{4\pi\hbar} \left\{ \frac{\sqrt{\pi}(1+i)}{2\sqrt{2k}} e^{i(2\varepsilon + i\pi)^2/16k} [\varphi(k, \varepsilon) + \psi(k, \varepsilon)] \right\}, \quad (19)$$

where

$$\varepsilon = \ln \frac{z_1}{z_2}, k = \frac{t}{2M\hbar} \quad (19 a)$$

$$\varphi(k, \varepsilon) = \text{Erfi} \left[\frac{(1+i)}{4\sqrt{k}} (2i\varepsilon - \pi) \right], \quad (19 b)$$

$$\psi(k, \varepsilon) = e^{\pi\varepsilon/2k} \text{Erfi} \left[\frac{(1+i)}{4\sqrt{k}} (2i\varepsilon + \pi) \right]. \quad (19 c)$$

Erfti [...] in Eqs. 19 refer to the complementary error function. [27, 28] Equation 19 is the final form of the propagator of Morse oscillator in the HTL where the molecule at hand still has not yet dissociated. One may note that Eq. 19 is purely thermal and free of quantum effects as expected.

$\mathcal{F}(x, y; t)$ may be called off-diagonal propagator, whereas the diagonal propagator $\mathcal{F}(x, x; t)$ may be obtained by going back to Eq. 15 and setting $\sigma = \delta$ whereupon evaluating the integral yields

$$\mathcal{F}(x, x; t) = -\frac{Ma\sigma}{4\hbar} \int_{-\infty}^{\infty} dE J_p(\sqrt{2\xi D_e}) Y_p(\sqrt{2\xi D_e}) e^{iEt/\hbar}, \quad (20)$$

where

$$\xi = M\sigma^2/\hbar, \quad (20 \text{ a})$$

Y_p is the second type of ordinary Bessel function, and D_e is the depth Morse potential well. Once again, the integration in Eq. 20 with respect to the order of Bessel functions is infeasible, *vide supra*. Invoking the asymptotic limit of high momentum p in the HTL gives

$$\mathcal{F}(x, x; t) = \frac{a}{2\pi\hbar} e^{-ax/2} \sqrt{\frac{\pi}{2}} \left((i-1) \sqrt{\frac{2M\hbar}{t}} \right). \quad (21)$$

The form of Eq. 21 interestingly reflects features of thermal effects whereby the quantum behavior has completely been diminished in the wake of taking the HTL. In the next section a real example of evaluating the canonical partition function will be given whereby Morse oscillator propagator is utilized for the first time. The prime motivation of this article is to put the Morse oscillator propagator to use, despite its complexity at intermediate temperatures, under certain conditions—HTL in this case.

VI. Morse Oscillator Canonical Partition Function

Equation 19 is the Morse oscillator propagator in the HTL that may be utilized for evaluating different time correlation functions in semiclassical systems, mixed quantum-classical systems, [29] or classical systems. As a point of interest, in the future, Part II of this series, optical DMTCF of anharmonic quantum systems will be calculated in the HTL using Eq. 19. This will require using the off-diagonal propagator in the HTL, Eq. 19. In this section it suffices to provide examples of quantities of which calculating will require the use of Eqs. 20 and 21. An interesting quantity is the canonical partition function, for which the diagonal propagator $\mathcal{F}(\sigma, \sigma; t)$ will be needed. As such, the Morse oscillator partition function is

$$Q = \text{Tr}[e^{-\beta\hat{H}}] = \int \langle x | e^{-\beta\hat{H}} | x \rangle dx = \int_{-\infty}^{\infty} \mathcal{F}(\sigma, \sigma; t = -i\hbar\beta) dx. \quad (22)$$

Using change of variables $\sigma = \exp(-ax/2)$ leads to

$$Q = \text{Tr}[e^{-\beta\hat{H}}] = \frac{-2}{a} \int_0^\infty \mathcal{F}(\sigma, \sigma; t = -i\hbar\beta) \frac{d\sigma}{\sigma}. \quad (23)$$

$$Q = \frac{1}{a\pi\hbar} \sqrt{\frac{\pi}{2}} \left((1-i) \sqrt{\frac{2M\hbar}{-i\hbar\beta}} \right). \quad (24)$$

With little algebra Eq. 24 simplifies to

$$Q = \frac{\sqrt{2\pi M/\beta}}{a\pi\hbar}. \quad (25)$$

Tables 1-4 show calculations of Q of HCl, N_2 , CO, and I_2 molecules at various temperatures classically and using Eq. 25 (HTL). An interesting observation may be drawn from these tables: One can see that the classical value approaches the values calculated by Eq. 25 as the temperature increases and starts nearing the HTL. For this reason, one may infer that employing the exact form of propagator may not bring in any improvement either in the HTL. Conversely, as the molecules tables 1-4 start at low temperature significant deviation between the classical and HTL arises.

V. Checking Strategy (Confirmatory Strategy)

Despite the numerics generated in the tables of different molecules, a step (more sophisticated) further was taken to substantiate the above methodology by expressing the second type of ordinary Bessel function, Y_p , in Eq. 20 as [27]

$$Y_p(r) = \frac{1}{\pi} \left\{ 2J_p(r) \ln \frac{r}{2} - \sum_{k=0}^{\infty} \frac{(p-k-1)!}{k!} \left(\frac{r}{2} \right)^{2k-p} + \dots \text{terms} \right\}. \quad (26)$$

The integral in Eq. 20 is to be evaluated with respect to the index p of Y_p , which is not possible at this time. Besides taking the asymptotic limit of J_p in Eq. 26, only the first term in the sum in Eq. 26 in which the result is substituted, we obtain this integral

$$\mathcal{F}(\sigma, \sigma; t) = \frac{Ma\sigma}{4\hbar} \int_{-\infty}^{\infty} dE e^{iEt/\hbar} \frac{1}{p(E)} \left[\left(\frac{er}{p(E)\pi} \right)^{2p(E)} \ln \frac{r}{2} - \frac{\Gamma(p(E))}{\sqrt{2}} (2e)^{p(E)} \left(\frac{1}{p(E)\pi} \right)^{p(E)+\frac{1}{2}} \right]. \quad (27)$$

where $r = \sqrt{2\xi D_e}$. Within the high temperature regime, one may use the following asymptotic identity for the Gamma function to speed up the integration in Eq. 27,

$$\Gamma(p) \sim \left(\frac{p}{e}\right)^p \frac{1}{\sqrt{2\pi p}}. \quad (27a)$$

Although Eq. 27 is more sophisticated than Eq. 21, there was not much improvement for the Q for the same parameters used in tables 1-4.

An interesting observation may be drawn from these tables: One can see that the classical value approaches the values calculated by Eq. 25 as the temperature increases and starts nearing the HTL. For this reason, one may infer that employing the exact form of propagator may not bring in any improvement either in the HTL. Conversely, as the molecules tables 1-4 start at low temperature significant deviation between the classical and HTL arises.

VI. Concluding Remarks

The propagator of the Morse oscillator was derived a few decades ago through some nifty transformation by Duru [1], and was left in an unevaluated multiple-integral-form. The reason for leaving it unevaluated is the integral has to be evaluated with respect to the index (degree) of Bessel functional. As such, it has been shown in this work that one could obtain a closed form, of which applicability is straightforward, in the HTL. As a physical realization of this applicability, the partition function for Morse oscillator has been derived using the HTL propagator in Eq. 19 which in turn was employed to calculate the partition function of several diatomic molecules as displayed in the tables reported herein. In those tables at high enough temperature the classical value perfectly matches the calculated value of the partition function.

While diagonal propagator has been used to carry out calculations herein, Part II (in progress) will derive time correlation functions of anharmonic systems using the off-diagonal propagator, leading to real molecular spectroscopic applications. For this reason, Part II should serve wider interest of scientists as it involves calculation in non-equilibrium statistical mechanics.

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Table 1: Calculated values of Morse oscillator partition function classically and in the HTL at various temperatures of HCl molecule.

Table 2: Calculated values of Morse oscillator partition function classically and in the HTL at various temperatures of N₂ molecule.

Table 3: Calculated values of Morse oscillator partition function classically and in the HTL at various temperatures of CO molecule.

Table 4: Calculated values of Morse oscillator partition function classically and in the HTL at various temperatures of I₂ molecule.

Table 1	T (K)	Classical	HTL
	3000	0.35698	1.25484
	3500	0.463386	1.35538
	4000	0.574524	1.44896
	4500	0.689525	1.53686
	5000	0.807854	1.61999
	5500	0.929192	1.69906
	6000	1.05336	1.77461
	6500	1.18025	1.84707
	7000	1.30983	1.9168
	7500	1.44208	1.98408
	8000	1.57697	2.04915
	8500	1.71449	2.11221
	9000	1.85459	2.17345
	9500	1.99721	2.233
	10 000	2.14226	2.29101
	10 500	2.28963	2.34759
	11 000	2.4392	2.40284
	11 500	2.59081	2.45684
	12 000	2.74432	2.50968

Table 2

T (K)	Classical	HTL
3000	0.770742	2.16681
3500	0.967944	2.34043
4000	1.17314	2.50202
4500	1.38615	2.65379
5000	1.6069	2.79734
5500	1.83521	2.93388
6000	2.07076	3.06434
6500	2.31301	3.18946
7000	2.56127	3.30986
7500	2.81474	3.42603
8000	3.07256	3.53839
8500	3.33382	3.64729
9000	3.59766	3.75303
9500	3.86321	3.85587
10 000	4.1297	3.95604

Table 3

T (K)	Classical	HTL
3000	0.581738	1.75445
3500	0.73254	1.89502
4000	0.887025	2.02586
4500	1.04434	2.14875
5000	1.20395	2.26498
5500	1.36548	2.37553
6000	1.5287	2.48116
6500	1.69344	2.58248
7000	1.85958	2.67996
7500	2.02703	2.77402
8000	2.19575	2.865
8500	2.36571	2.95317
9000	2.53687	3.03879
9500	2.70925	3.12206
10 000	2.88283	3.20317
10 500	3.05763	3.28227
11 000	3.23368	3.35951
11 500	3.411	3.43501
12 000	3.58961	3.50889

Table 4

T (K)	Classical	HTL
300	1.11803	2.80664
400	1.63399	3.24082
500	2.16725	3.62335
600	2.7163	3.96918
700	3.28169	4.28721
800	3.86464	4.58322
900	4.46622	4.86124
1000	5.08687	5.12419