

Scattering contributions to the internal partition function of a diatomic molecular system*

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Abstract. An analytical expression for the phase shift contribution to the internal partition function for the Morse potential is derived by using an approximate Jost function. This function is shown to be a convergent sum. The numerical results obtained for H_2 and HCl show the partition function to be a monotonically increasing function of temperature. This observation agrees with the results of Rogers and co-workers.

Keywords. Internal partition function; diatomic molecules; phase-shift contribution.

1. Introduction

The total energy of a molecular system can be expressed in terms of its contributing energies:

- (i) the energy associated with the translation of its mass through space, and
- (ii) energy arising due to the internal motion of the molecule.

Typically, for visualising the internal motion, the geometry of a diatomic molecule may be approximated by two point masses attached by a massless spring. The molecule is free to rotate about its centre of gravity and may also vibrate along the line of the centres. It is customary to associate a partition function with the internal contribution to the energy. This is commonly known as the internal partition function. The complete internal partition function requires scattering (phase shift) contributions in addition to the usual bound state sum. The internal partition function is given by

$$z_{\text{int}} = \sum_l (2l + 1) [z_l^B + z_l^S]. \quad (1)$$

The bound state and scattering state contributions z_l^B and z_l^S can be written as (Landau and Lifshitz 1959)

$$z_l^B = \sum_n \exp(-\beta E_{nl}). \quad (2a)$$

and
$$z_l^S = \frac{1}{\pi} \int_0^\infty \exp(-\beta \hbar^2 k^2 / 2m) \frac{d}{dk} n_l(k) dk. \quad (2b)$$

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Here E_{nl} represents the binding energy of the n th state with orbital angular momentum l . Also $\beta = (K_B T)^{-1}$ and $n_l(k)$, the phase shift of the l th partial wave. The object z_l^S will be discontinuous when the density or temperature of the gas molecules changes so as to admit a new bound state. These discontinuities affect all the thermal properties such as pressure and specific heat. The awkward discontinuities in z_{int} can be removed (Rogers *et al* 1971; Petschek 1971; Petschek and Cohen 1972) by taking proper account of the scattering contribution. It is therefore of some interest to evaluate z_l^S in a relatively non-complicated manner by using simple and physically founded assumptions for the molecular potential.

In this paper we present a method for computing z_l^S for diatomic molecular systems. The vibration as well as the rotation of a diatomic molecule are excellently represented by the Morse function

$$V(r) = D [\exp(-2\alpha x) - 2 \exp(-\alpha x)]. \quad (3)$$

We shall therefore base our treatment on the use of an approximate solution of the Schrödinger equation for the potential given in (3). The symbol D stands for the depth of the Morse potential, $x = (r - r_0)/r_0$ and α , a constant.

All these parameters depend on the typical molecule under consideration. The distance r_0 corresponds to the separation of the atomic centres when the potential energy is minimum. The potential $V(r)$ is attractive for $r > r_0$ and produces a strong repulsion if the two nuclei approach each other closer than r_0 . In § 2 we derive an analytic expression for z_l^S . Based on this, numerical results are presented in § 3 for H_2 and HCl . Usefulness of the present approach is also discussed.

2. Theory

2.1. Continuum partition function and Jost function

The proof regarding continuity (Petschek and Cohen 1972) of the internal partition function has been given by writing z_l^S in terms of the Jost function. Using the relation between the S -matrix and Jost function

$$S_l = \exp(-2in_l) = f_l(k)/f_l(-k). \quad (4)$$

Equation (2b) can be written in the form

$$z_l^S = \frac{1}{2\pi i} \int_{-\infty}^{+\infty} \exp(-\beta \hbar^2 k^2 / 2m) \frac{d}{dk} \ln f_l(k) dk. \quad (5)$$

Here we have followed the convention of Newton (1966). The upper half of the k -plane refers to the physical sheet and the phase shift n_l is the negative of the phase of the Jost function. Equation (5) could very well form the basis for computing the scattering contribution to the internal partition function for a system consisting of interacting particles, provided the Jost function for all partial waves would be known for the interaction. Unfortunately, the Schrödinger equation cannot be solved in closed form for the so-called realistic potentials. For this reason the Jost function

approach to the continuum partition function has been confined to the s -wave case only (Petschek 1971; Petschek and Cohen 1972). Reasonably, therefore, one may be interested to introduce approximation techniques for deriving the l -wave Jost function in analytical form. Assuming that the atoms of a diatomic molecule are bound together by Morse type interactions, we derive an analytic expression for $f_l(k)$ by replacing the centrifugal term by an approximate one. This approach, in a natural way, incorporates the rotational correction to the Morse formula (Flügge 1971). One can deal with the problem without meeting any fresh mathematical difficulties as compared to the s -wave problem. Before such a study is made it will be useful to know if the approximate treatment of the centrifugal term affects the continuity of the partition function. To that end we partially integrate (2b), make use of the Levinson's (1949) theorem and use the resulting equation in (1) to write z_{int} in the form

$$z_{\text{int}} = \sum_l (2l+1) \left\{ \sum_n [\exp(-E_{nl}/K_B T) - 1] + \frac{1}{m\pi K T} \times \int_0^\infty k dk n_l(k) \exp(-k^2/2mKT) \right\}.$$

The third term in the right hand side of the above equation stands for the scattering contribution made by the zero energy part of the phase shift, which exactly cancels the zero energy part of the bound state sum and thereby removes the discontinuity. Here we approximate the centrifugal term by a superposition of Morse-type function and thus convert the l -wave problem formally to an s -wave one to write simple analytical solutions. The Levinson's theorem is valid under extremely general conditions like the existence of first and second absolute moments of the interaction (Newton 1966). Fortunately, the effective potential obtained in our approximation satisfies these conditions. Thus our approximation of the centrifugal term will not affect the continuity of the partition function.

2.2. l -wave Jost function for the Morse potential

The l -wave Schrödinger equation for the potential in (3) is given by

$$\left[\frac{d^2}{dr^2} + k^2 - \frac{2mD}{\hbar^2} [\exp(-2ax) - 2 \exp(-ax)] - \frac{l(l+1)}{r^2} \right] f_l(kr) = 0. \quad (6)$$

It is well known that for $l > 0$, equation (1) does not admit of an analytical solution due to the presence of the singular term $l(l+1)/r^2$. To incorporate the effect of the centrifugal barrier we introduce the identity

$$\frac{1}{r^2} = \frac{1}{r_0^2} [1 + x]^{-2} = \frac{1}{r_0^2} [C_0 + C_1 \exp(-ax) + C_2 \exp(-2ax)]. \quad (7)$$

This identity has been devised by Flügge *et al* (1967). Following their viewpoint we assume that in the region of physical interest the two expressions in (7) deviate only in the order x^3 . We thus obtain

$$C_0 = 1 - 3/a + 3/a^2. \quad (8a)$$

$$C_1 = 4/a - 6/a^2, \quad (8b)$$

$$C_2 = -1/a + 3/a^2. \quad (8c)$$

The series in (7) attempts to include in some way the effect of centrifugal term as a part of the potential. This approach thus bears an analogy with the method of Martin (1960) and of Alfaro and Rossetti (1968) for solving the radial Schrödinger equations with Yukawian potentials. Inserting (7) in (6) and changing the variable r to x we obtain

$$\left[\frac{d^2}{dx^2} + k_1^2 r_0^2 + 2\gamma_1^2 \exp(-ax) - \gamma_2^2 \exp(-2ax) \right] f_l(k_1 x) = 0, \quad (9)$$

where $k_1^2 = k^2 - C_0 \frac{l(l+1)}{r_0^2}, \quad (10a)$

$$\gamma_1^2 = \frac{2mDr_0^2}{\hbar^2} - C_1 \frac{l(l+1)}{2}, \quad (10b)$$

and $\gamma_2^2 = \frac{2mDr_0^2}{\hbar^2} + C_2 l(l+1). \quad (10c)$

We transform the variable in (9) by substituting

$$y = \delta \exp(-ax), \quad (11)$$

and get $\left[y \frac{d}{dy} y \frac{d}{dy} + r_0^2 \frac{k_1^2}{\alpha^2} + y \frac{2\gamma_1^2}{\delta \alpha^2} - \frac{1}{4} y^2 \right] f_l(k_1 y) = 0. \quad (12)$

Here $\delta = \frac{2\gamma_2}{\alpha} = \frac{2}{\alpha} \left\{ \frac{2mDr_0^2}{\hbar^2} + l(l+1) C_2 \right\}^{1/2}. \quad (13)$

To reduce (12) to a known form we proceed as follows.

(i) We note that for large r (i.e. for small y) it has a solution

$$y^{-lk_1 r_0 / \alpha},$$

and (ii) for small r the equation has a solution of the form $\exp(-\frac{1}{2}y)$.

From (i) and (ii) we see that the exact solution of (12) can be put in the form

$$f_i(k_1 y) = \exp(-\frac{1}{2}y) y^{-ik_1 r_0/a} G(y), \quad (14)$$

where $G(y)$ is asymptotically normalised such that

$$f_i(k_1 r) \underset{r \rightarrow \infty}{\sim} \exp(ik_1 r). \quad (15)$$

Substitution of (14) in (12) yields

$$yG''(y) + (c - y) G'(y) - aG(y) = 0, \quad (16)$$

$$\text{where } C = 1 - (2ik_1 r_0/a), \quad (17a)$$

$$\text{and } a = \frac{1}{2} - (2\gamma_1^2/\delta a^2) - (ik_1 r_0/a). \quad (17b)$$

The general solution of (16) is given by

$$G(y) = A_1 {}_1F_1(a, c; y) + A_2 y^{1-c} {}_1F_1(a - c + 1; 2 - c; x), \quad (18)$$

where ${}_1F_1(\dots)$ is the so-called confluent hypergeometric function. We note that only the first term in (18) together with (14) satisfies the asymptotic boundary condition prescribed for the Jost function provided

$$A_1 = \delta^{ik_1 r_0/a} \exp(ik_1 r_0). \quad (19)$$

Therefore the normalised Jost solution is

$$f_i(k_1 y) = \delta^{ik_1 r_0/a} \exp(ik_1 r_0) \exp(-\frac{1}{2}y) y^{-ik_1 r_0/a} {}_1F_1(a, c; y). \quad (20)$$

For $l \neq 0$, the point $r=0$ is a regular singular point of the Schrödinger equation and $l(l+1)$ multiplies the term of the highest singularity in it. In other words, for small r , the centrifugal term dominates over the potential (Newton 1966) so that $f_i(kr)$ behaves as r^{-l} as r approaches zero. For higher angular momenta, therefore, the Jost function is obtained from the Jost solution by taking the limit $r^l f_i(kr)$

and then multiplying the latter by the appropriate normalisation term. In our case we have incorporated the effect of the centrifugal barrier by writing it as a part of the potential. This necessarily implies that the centrifugal term is no longer more singular than the Morse potential. We therefore compute the Jost function from the behaviour of (20) near the origin. The Morse Jost function is found to be

$$f_i(k_1) = \exp(-\frac{1}{2}\delta e^a) {}_1F_1(a, c; \delta e^a). \quad (21)$$

The s -wave limit (Talukdar *et al* 1975) and the high energy behaviour (Newton 1966)

of $f_l(k_1)$ immediately follows from (21). Equation (21) can be well approximated by replacing the hypergeometric function by its asymptotic expansions

$${}_1F_1(a, c; z) \longrightarrow \frac{\Gamma(c)}{\Gamma(a)} e^z z^{a-c}. \quad (22)$$

We have verified this for the parameters of the Morse potential given in table 1. In this table the values of the parameters C_0 , C_1 and C_2 are also included. To be more specific the values of δe^a for some of the partial waves are given in table 2. We have numerically checked that the error is less than 0.1% for each of the partial waves. In view of (22), (21) takes the form

$$f_l(k_1) = H(a, \delta; \gamma_1) \delta^{ik_1 r_0/a} \exp(ik_1 r_0) \times \frac{\Gamma[1 - (2ik_1 r_0/a)]}{\Gamma[\frac{1}{2} - (2\gamma_1^2/\delta a^2) - (ik_1 r_0/a)]}, \quad (23)$$

where $H(a, \delta; \gamma_1) = \exp[(\frac{1}{2}\delta e^a) - (\frac{1}{2}a) - (2\gamma_1^2/\delta a^2)] \delta^{-\frac{1}{2} - 2\gamma_1^2/\delta a^2}$. (24)

As noted by Flügge the approximation in (7) is quite reasonable for the computation of bound states of the Morse potential. One may ask: How good is this approximation for estimating scattering contributions to the partition function? Understandably, the validity of the approximation depends on the region of important k values which contribute significantly to the integrand of (5). As a useful check one may compare the phase of the approximate Jost function, which by definition is the phase shift $[n_l(k)]$ with the accurate value of $n_l(k)$ obtained by numerically integrating (6). To facilitate this we have calculated the phase of the Jost function in (23) with the help of the standard decomposition

$$\Gamma(x + iy) = \xi \exp(i\eta),$$

Table 1. Values of Morse parameters and the constants C 's
 $E(\text{eV}) = E(\text{cm}^{-1}) \times 1.2398 \times 10^{-4}$

Molecule	$\hbar^2/2 m r_0^2$ cm ⁻¹	D cm ⁻¹	a	C_0	C_1	C_2
H ₂	60.8296	38292	1.440	0.363426	-0.1157407	0.7523148
HCl	10.5930	37244	2.380	0.26912	0.621425	0.1094555

Table 2. Values of δe^a

Molecule	l					
	0	1	2	3	4	5
H ₂	147.08	147.25	147.60	148.13	148.83	149.69
HCl	538.38	538.40	538.43	538.49	538.55	538.64

for the gamma function with complex argument.

$$\text{Here } \xi = \Gamma(x) \prod_{n=0}^{\infty} \left\{ 1 + \frac{y^2}{(x+n)^2} \right\}^{-1/2},$$

$$\text{and } \eta = y \left\{ -\gamma + \sum_{n=1}^{\infty} \left(\frac{1}{n} - \frac{1}{y} \tan^{-1} \frac{y}{x+n-1} \right) \right\},$$

with $\gamma=0.577215$, the Euler constant. We have calculated the accurate value of the phase shifts by employing the variable phase approach to the potential scattering (Calogero 1967). This approach consists in transforming (6) to a first order non-linear differential equation, the solution of which yields in the asymptotic limit the value of the phase shift. The mathematical foundation of the variable phase approach is based on the well-known connection between second order differential equations and first order equations of the Ricatti type (Davis 1957). The numerical integration of the non-linear equation under consideration was done by using the algorithms of the Runge-Kutta method with an appropriate stability check. It is seen that for $T \leq 0.2$ Ry, the exact and approximate phases agree to within 1%. However the error increases significantly at temperatures higher than this. Thus the approximation in (7) seems to be valid only at low temperatures.

2.3. Partition function

The Jost function $f_i(k_1)$ in (23) together with (5) can now be used to derive an analytical expression for the continuum partition function. To facilitate this we require (23) by introducing the well-known infinite product representation for gamma function

$$\frac{1}{\Gamma(1+z)} = \exp(\gamma z) \prod_{n=1}^{\infty} \left(1 + \frac{z}{n} \right) \exp(-z/n). \quad (25)$$

This yields

$$\begin{aligned} f_i(k_1) &= H(\alpha, \delta; \gamma_1) \delta^{ik_1 r_0 / \alpha} \times \\ &\exp \gamma \left[\left(-\frac{1}{2}\right) - (2\gamma_1^2 / \delta \alpha^2) + (ik_1 r_0 / \alpha) + (ik_1 r_0 / \gamma) \right] \times \\ &\prod_{n=1}^{\infty} \frac{[n - \frac{1}{2} - (2\gamma_1^2 / \delta \alpha^2) - (ik_1 r_0 / \alpha)]}{[n - (2ik_1 r_0 / \alpha)]} \times \\ &\exp \left[\left(\frac{1}{2}\right) + (2\gamma_1^2 / \delta \alpha^2) - (ik_1 r_0 / \alpha) \right] / n. \end{aligned} \quad (26)$$

Inserting (26) in (5) we get

$$z_l^S = -\frac{1}{2\pi i} \exp\left(-\frac{\beta\hbar^2}{2m} C_0 \frac{l(l+1)}{r_0^2}\right) \int_{-\infty}^{+\infty} \exp\left(-\frac{\beta\hbar^2 k_1^2}{2m}\right) \times \\ \left\{ i\gamma \left(1 + \frac{\ln \delta}{\alpha} + \frac{\gamma}{\alpha}\right) + \sum_{n=1}^{\infty} \left[\frac{1}{k_1 + (i\alpha/r_0) [n - \frac{1}{2} - (2\gamma_1^2/\delta\alpha^2)]} \right. \right. \\ \left. \left. - \frac{1}{k_1 + (i\alpha/2r_0)} - \frac{ir_0}{n\alpha} \right] \right\} dk_1. \quad (27)$$

The integrals in (27) can be related to tabulated results to get

$$z_l^S = \frac{1}{2} \exp[-l(l+1) C_0 \beta X] \left\{ \frac{1}{\alpha} (\alpha + \ln \delta + \gamma) \times \right. \\ \left. \left(\frac{1}{\pi\beta X} \right)^{1/2} - \sum_{n=1}^{\infty} \left[W\left(\alpha \left(n - \frac{1}{2} - \frac{2\gamma_1^2}{\delta\alpha^2}\right) (\beta X)^{1/2}\right) \right. \right. \\ \left. \left. - W\left(\frac{n\alpha}{2} (\beta X)^{1/2}\right) + \frac{1}{n\alpha} \left(\frac{1}{\pi\beta X}\right)^{1/2} \right] \right\}, \quad (28)$$

where $W(z) = \exp(z^2) (1 - \operatorname{erf} z)$, $X = \hbar^2/2mr_0^2$ (29)

The convergence of the sum in (28) may be explicitly demonstrated by using the Pande' approximants* for W i.e.

$$W(z) = \frac{a_0 + a_1 z + a_2 z^2}{1 + b_1 z + b_2 z^2 + b_3 z^3}, \quad (30)$$

where

$$\left. \begin{aligned} a_0 &= 1 \\ a_1 &= b_2 \pi^{-1/2} = 0.936438 \\ a_2 &= b_3 \pi^{-1/2} = 0.329897 \\ b_1 &= (4 - \pi) \pi^{1/2} = 2.064817 \\ b_2 &= b_1 \pi^{1/2} - 2 = 1.659793 \\ b_3 &= -2\pi^{1/2} + 2b_1 = 0.5847278 \end{aligned} \right\} \quad (31)$$

For large z , therefore, (32)

$$W(z) \rightarrow \pi^{-1/2} z^{-1}$$

*Equations (30)-(32) are from Appendix A of Petschek and Cohen (1972)

With the help of (32) it is easy to see that the n th term T_n of the sum in (28) goes to zero as $n \rightarrow \infty$. It is interesting to note that $W(z)$ evaluated by means of (30) does not introduce error more than 0.2% for all physical values of z . Thus (28) together with (30) forms a basis of calculating scattering contributions to the internal partition function of a diatomic molecular system.

3. Results and discussion

Table 3 illustrates the results of our partition function (z_l^S) calculation for H_2 and HCl. In this table we have included the results for the lowest ten partial waves for $T=0.002$ Ry to 0.2 Ry varying in multiples of ten. From our results we could see that the contributions of z_l^S to the total partition function become pronounced at high temperatures. A similar observation has been made by Rogers *et al* (1971). Both for H_2 and HCl the values of z_l^S exhibit convergence with respect to the partial wave l . The rate of convergence in both cases appears to be slow for higher temperatures. This represents the general trend of the numbers presented. However, $T=0.2$ entry for HCl is an exception which shows rapid convergence with l . This point is not clear to us and deserves to be closely examined. Looking into the table we further see that the values of z_l^S for HCl at $T=0.02$ Ry and 0.2 Ry exhibit a relatively rapid convergence with l than the corresponding numbers for H_2 . This behaviour may be attributed to the existence of a longer tail of the H_2 potential as compared to that associated with the HCl molecule. Understandably, a relatively long tail makes significant contributions to higher partial waves since the region of the potential sampled by a scattering lies at larger distance for greater l .

Since the continuity of the total partition function is associated with accurate numerical values of z_l^S , we would venture to suggest that special caution must be taken to compute this frequently elided contribution to the former. One may then reasonably ask: How realistic is the model presented in this paper? Our model has the obvious virtue of simplicity although it involves a number of approximations. For example, we have used an approximate form of the l -wave Morse Jost function

Table 3. Values of z_l^S as a function of l and T for H_2 and HCl

T in Rydberg	H_2			HCl		
	l	0.002	0.02	0.2	0.002	0.02
0	0.967	-0.830	-1.890	2.848	12.360	14.470
1	0.866	-0.459	-1.002	2.913	12.579	13.703
2	0.676	0.184	0.806	2.741	13.042	12.370
3	0.448	0.966	3.703	2.635	13.805	10.754
4	0.248	1.788	8.254	2.498	14.982	9.093
5	0.115	2.630	16.463	2.335	16.815	7.531
6	0.055	3.050	20.623	2.115	17.513	6.005
7	0.027	3.251	22.251	1.890	17.050	4.651
8	0.012	3.373	23.470	1.652	15.825	3.372
9	0.006	2.511	24.082	1.373	14.234	2.201
10	0.002	1.955	23.423	1.012	12.501	1.152

$f_i(k_1)$ to derive an analytical expression for z_1^S . The estimation of the partition function based on $f_i(k_1)$ is a convergent sum and has correct limits. Our expression is thus expected to yield reasonably accurate numbers. However we feel that our numbers should be compared with the results of an exact numerical calculation. Admittedly, the object in this paper is partly pedagogical to see how far one could go by using a simple analytical procedure; the inevitable numerical routine being invoked only at a later stage of the game. Hopefully, by making a few judicious approximations we could focus attention on the basic conceptual aspect of the problem and obtain some physical weight without straying way off the mark with regard to the numerical accuracy.

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References

- Alfaro V de and Rossetti C 1968 *Nuovo Cimento* **18** 83
 Calogero F 1967 *Mathematics in science and engineering* (New York: Academic Press) Vol. 35
 Davis H T 1957 *Introduction to non-linear differential and integral equations* (New York: Dover)
 Flugge S 1971 *Practical quantum mechanics I* (New York: Springer-Verlag) p 186
 Flugge S, Walger P and Weiguni A 1967 *J. Mol. Spectrosc.* **23** 243
 Landau L D and Lifshitz E M 1959 *Statistical Physics* (Transl. by E Peierls and R F Peierls (London: Pergamon Press) p. 238
 Levinson N 1949 *Kgl. Danske Videnskab. Selskab, Mat. fys. Medd.* **25** 9
 Martin A 1969 *Nuovo Cimento* **15** 99
 Newton R G 1966 *Scattering theory of waves and particles* (New York: McGraw Hill) pp 334, 372 340 and 374
 Petschek A G 1971 *Phys. Lett.* **A34** 411
 Petschek A G and Cohen H D 1972 *Phys. Rev.* **A5** 383
 Rogers F J, Graboske Jr H Ca and Dewitt H E 1971 *Phys. Lett.* **A34** 127
 Talukdar B, Sinha Roy M N, Mallick N and Nayek D K 1975 *Phys. Rev.* **C12** 370