Phase Shifts of Bound State Waves Scattered at Classical Turning Points: Morse Potential

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The analytical transfer matrix method suggests a new quantization condition for calculating bound state eigenenergies exactly. In the quantization condition, the phase shifts of bound state wave functions scattered at classical turning points are explicitly introduced. We calculate the phase shifts of eigenfunctions of the Morse potential with various boundary conditions in order to understand the physical meaning of phase shifts. The Morse potential is known to adequately describe the interaction energy between two atoms and, therefore, it is frequently used to determine the vibrational energy levels of diatomic molecules. The variation of Morse potential eigenenergies influenced upon by changing boundary conditions is also investigated.

Key Words : Morse potential, Phase shifts, ATMM, WKB, Vibration

Introduction

The Morse potential energy function has been used to describe the potential energy between two atoms.[1] In spectroscopy, though it is not exact, the Morse potential is frequently used to mimic the vibrational motion of covalent diatomic molecules or very weak van der Waals complexes.[2-7] From a theoretical point of view, the Morse potential is of great interest because the Morse potential problem can be analytically solved when the vibrational angular momentum is neglected. The eigenfunctions of the Morse potential are expressed in terms of the well-known confluent hypergeometric functions and the exact eigenenergies are obtained in a closed form.[1,8]

The original form of the Morse potential has a finite value at zero atom-atom internuclear distance. But for real diatomic molecules, the potential should be infinite when two atoms are in contact. Therefore, the realistic Morse potential whose value is infinite at the zero internuclear distance is chosen and extensively examined. With the potential the eigenenergies are computed in order to see the difference between the original Morse potential and the realistic one. The calculations are performed for various diatomic pairs and we have found that the difference is negligible for real diatomic molecules.

For a one-dimensional system, when a particle is moving between two classical turning points, its kinetic energy cannot be larger than the potential energy at the turning points. Therefore the particle cannot escape out from the potential well and oscillates between the two turning points. But quantum mechanically the particle can enter the classically forbidden region. The exponentially decaying wave function in the classically forbidden region should be connected smoothly to the oscillating wave function in the classically allowed region at classical turning points. The wave reflected at the turning point has a different phase, relative to the incoming wave traveling towards the turning point. Therefore the phase of wave function should change through the turning points and the change is called a phase loss. Furthermore, there should be a scattering phenomenon unless a potential is constant between the two turning points. The scattering also causes a phase change, and the additional scattering-led phase change is called a phase shift.

The recently developed analytical transfer matrix method (ATMM) suggests a formally exact quantization condition for nonrelativistic quantum systems.[9,10] The quantization condition has been applied to various potentials and is considered to be exact.[9-12] And in the ATMM quantization condition, the concept of phase shift is formally introduced. In this work, the ATMM is applied to the Morse potential problem in order to understand the nature of phase shifts of bound state eigenfunctions. By successively changing the boundary conditions, the original form of Morse potential is altered to generate various Morse potentials. For each altered potential the phase shifts of ground and excited state wave functions are numerically calculated. These calculations should reveal how the phase shifts vary due to a potential change.

The existence of phase shift is ignored in the well-known WKB (Wentzel-Kramers-Brillouin) approximation.[13,14] The WKB approximation is found to be exact for the harmonic oscillator potential and also for the Morse potential. The reason behind this success is that the phase shifts for the harmonic oscillator or the Morse potential happen to be $\frac{1}{2}\pi$.[15-18] But the newly calculated phase shifts for the altered Morse potentials show that the WKB approximation is not valid for the altered potentials. The more advanced quantization conditions beyond the WKB, for example, the WKB with Maslov index[19,20] and the supersymmetric WKB,[21,22] are also qualitatively examined in terms of the ATMM phase shifts.

In the next section, we introduce the Morse potential. And the calculated eigenenergy differences between the original Morse potential and the realistic Morse potential are

presented. In the following section, the ATMM phase shift is formally defined. And the phase shifts for various Morse potentials are presented and analyzed. The information obtained from this work is summarized in the final section.

Morse Potential and Eigenenergy Deviations

The Morse potential energy function $V_M(x)$ for a diatomic molecule A-B is[1,2]

$$V_M(x) = D_e(e^{-2\beta(x-x_e)} - 2e^{-\beta(x-x_e)}). \quad (1)$$

where x is the internuclear distance between atom A and atom B. D_e is the dissociation energy, x_e is the equilibrium bond length of A-B, and β is an adjustable range parameter. The Morse potential, Eq. (1) has a minimum value of $-D_e$ at $x = x_e$ and it is zero at $x = \infty$. It should be noted that the Morse potential becomes infinite when x goes to the negative infinity, *i.e.*, $V_M(x) \to \infty$ as $x \to -\infty$. At $x = 0$, $V_M(0)$ has a finite value of $D_e(e^{2\beta x_e} - 2e^{x_e})$ that is positive when $\beta x_e > \ln2$. $V_M(0)$ is always positive and usually very large for covalent diatomic molecules.[23,24]

The Schrödinger equation for the vibrational motion of A-B, without vibrational angular momentum, is

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\Psi_n(x) + V(x)\Psi_n(x) = E_n\Psi_n(x)$$

$$(-\infty < x < \infty) \quad (2)$$

where $V(x)$ is approximately equal to $V_M(x)$. m is the reduced mass of atoms A and B. The Eq. (2) can be rewritten in terms of a new dimensionless variable r for convenience,

$$\left[-\frac{d^2}{dr^2} + V_M(r)\right]\Psi_n(r) = \varepsilon_n\Psi_n(r) \quad (-\infty < r < \infty) \quad (3)$$

where the new dimensionless quantities are

$$r = \beta x, \; r_e = \beta x_e, \; \lambda = \frac{\sqrt{2mD_e}}{\beta\hbar}, \; \varepsilon_n = \frac{2m}{\beta^2\hbar^2}E_n. \quad (4)$$

And the dimensionless Morse potential is

$$V_M(r) = \lambda^2(e^{-2(r-r_e)} - 2e^{-(r-r_e)}). \quad (5)$$

$V_M(r)$ has a minimum value of $-\lambda^2$ at $r = r_e$. Note that m, D_e, and λ are positive. ε_n (or E_n) are negative for bound states.

The dimensionless Schrödinger Eq. (3) for the Morse potential can be exactly solved and the bound state eigenfunction Ψ_n is, in terms of a new variable $z = 2\lambda e^{-(r-r_e)}$,

$$\Psi_n(z) = N_n z^{\sqrt{-\varepsilon_n}} e^{-\frac{1}{2}z} M(\alpha,\beta;z). \quad (6)$$

$M(\alpha,\beta;z)$ is the confluent hypergeometric function,[25] *i.e.*,

$$M(\alpha,\beta;z) = 1 + \frac{\alpha}{\beta}z + \frac{\alpha(\alpha+1)}{\beta(\beta+1)2!}z^2$$
$$+ \frac{\alpha(\alpha+1)(\alpha+2)}{\beta(\beta+1)(\beta+2)3!}z^3 + \cdots. \quad (7)$$

where $\alpha = \frac{1}{2} + \sqrt{-\varepsilon_n} - \lambda$ and $\beta = 2\sqrt{-\varepsilon_n} + 1$. When the boundary conditions of $\Psi_n(r = \infty \text{ or } z = 0) = 0$ and $\Psi_n(r = -\infty \text{ or } z = \infty) = 0$ are imposed, α turns out to be zero or a negative integer, *i.e.*, $\alpha = -n$. Then the eigenenergy is

$$\varepsilon_n = -\left(\lambda - n - \frac{1}{2}\right)^2 \quad (8)$$

where n is a (vibrational) quantum number, *i.e.*, $n = 0, 1, 2, \ldots, n_{max}$. n_{max} is the largest integer less than $\lambda - \frac{1}{2}$. Inserting Eqs. (7) and (8) into Eq. (6), the better known form of Ψ_n is obtained, *i.e.*,

$$\Psi_n(z) = N_n z^{\lambda - n - \frac{1}{2}} e^{-\frac{1}{2}z} L_n^{2\lambda - 2n - 1}(z). \quad (9)$$

The normalization constant is $N_n = [\Gamma(n+1)\Gamma(2\lambda-n)]^{-1/2}$ where $\Gamma(z)$ is a gamma function. The Laguerre polynomial is defined as

$$L_n^a(z) = z^{-a}e^z\frac{d^n}{dz^n}(z^{n+a}e^{-z}). \quad (10)$$

The eigenenergy Eq. (8) was obtained from the boundary condition of $\Psi_n(r = -\infty \text{ or } z = \infty) = 0$. We call this case V_M^{ideal}. For real diatomic molecules, however, the distance r cannot be negative. It should be always positive so that the correct boundary condition must be $\Psi_n(r = 0 \text{ or } z = z_0) = 0$ where $z_0 = 2\lambda e^{r_e}$. We call this case V_M^{real} as listed in Table 1.

Table 1. Brief notations for the altered Morse potentials used in this work. All potentials have the same form of $V_M(r) = \lambda^2(e^{-2(r-r_e)} - 2e^{-(r-r_e)})$ but their boundary conditions vary

Notation	Form of potential	Boundary condition
V_M^{ideal}	$V_M(r)$ for $-\infty < r < \infty$	$\Psi(-\infty) = \Psi(\infty) = 0$
V_M^{real}	$V_M(r)$ for $0 \leq r < \infty$ and ∞ for $r < 0$	$\Psi(0) = \Psi(\infty) = 0$
V_M^{d1}	$V_M(r)$ for $0.1 \leq r < \infty$ and ∞ for $r < 0.1$	$\Psi(0.1) = \Psi(\infty) = 0$
V_M^{d2}	$V_M(r)$ for $0.2 \leq r < \infty$ and ∞ for $r < 0.1$	$\Psi(0.2) = \Psi(\infty) = 0$
V_M^{d3}	$V_M(r)$ for $1 - \ln2 \leq r < \infty$ and ∞ for $r < 1 - \ln2$	$\Psi(1-\ln2) = \Psi(\infty) = 0$

The correct boundary condition for real diatomic molecules, of course, gives the different eigenenergy and it can be determined by solving the equation[26]

$$M(\alpha, \beta; z_0) = 0 \qquad (11)$$

Consequently the eigenenergies in Eq. (8) are approximate when the eigenenergies of real diatomic molecules are desired. The deviation (the eigenenergy difference between V_M^{ideal} and V_M^{real}) depends on how large z_0 is. When z_0 is infinite (*i.e.*, V_M^{ideal}), we obtain the Eq. (8).

For real diatomic molecules it has been argued that z_0 is large enough to neglect the deviations.[8,23] In this work we examine whether the argument is valid or not. Since $z_0 = 2\lambda e^{r_e}$, z_0 depends on parameters λ and r_e. But the deviation of the eigenenergies of V_M^{real} from those of V_M^{ideal} depends solely on z_0, not on the details of a system. The Eq. (11) is a transcendental equation so that it cannot be solved analytically. We solve it numerically for various values of z_0. The choice of z_0 is rather arbitrary. We start the calculations

for small z_0 (*i.e.*, $z_0 = 5.4$ with $\lambda = 1$, $r_e = 1$) and repeat the same calculations by increasing z_0 until the deviation becomes negligible. The results are tabulated in Table 2.

As seen in Table 2, when z_0 is small, the deviation is very large. The deviation becomes larger as n becomes higher. It is because the inner classical turning point of higher n state lies closer to $r = 0$. As z_0 increases, the deviation becomes smaller as expected. And when z_0 is ~80 (see the $z_0 = 76$ case in Table 2), the deviation becomes virtually zero. For typical covalent diatomic molecules, the dissociation energy (D_e) ranges from 0.01 to 0.4 au, the equilibrium internuclear distance (x_e) ranges from 1 to 5 au, the reduced mass (m) ranges from 1800 to 200000 au, and the range parameter (β) is 0.5-1.5 au^{-1}. When we convert them into the dimensionless parameters, λ ranges from ~6 to ~400 and r_e ranges from ~1 to ~5. For example, for the $X^1\Sigma_g^+$ state of H$_2$, λ is ~18 and r_e is ~1.4. The last entry of $z_0 = 150$ ($\lambda = 18$, $r_e = 1.4$) in Table 2 can be regarded as the case for diatomic molecule H$_2$. Since, in this work, we want only to examine the difference between V_M^{ideal} and V_M^{real}, the very accurate parameter values are not necessary.

For H$_2$, the deviation is completely negligible so that $z_0 = 150$ is large enough to be considered as infinity. For other covalent diatomic molecules, D_e might be smaller than that of H$_2$, so λ is smaller (see Eq. 4). But m of other diatomic molecules is always much larger than that of H$_2$, so λ becomes larger. And x_e is also larger but β is about the same. Overall, it turns out that z_0 of other diatomic molecules is always larger than z_0 of H$_2$. For example, for the $X^1\Sigma_g^+$ state of I$_2$, λ is ~115 and r_e is ~5.0 so that $z_0 = 34000$. Therefore, in conclusion, the V_M^{ideal} potential is quite suitable for describing the vibrational motion of covalent diatomic molecules. For diatomic van der Waals complexes, D_e is very small but m is usually large. Consequently, λ turns out to be larger than 100 so that the above conclusion is also valid for van der Waals complexes. The purpose of the current calculations is not to show that the Morse potential itself is a good approximation to a real potential. Rather, the calculations confirm the longstanding belief − the fact that the Morse potential (V_M^{ideal}) is not infinite at $r = 0$ does not pose any problem when it is applied to real diatomic molecules.

Table 2. Eigenenergies (ε_n) of V_M^{ideal} and V_M^{real} at various z_0 ($=2\lambda e^{r_e}$)

$z_0 = 5.4(\lambda = 1, r_e = 1)$			$z_0 = 11(\lambda = 2, r_e = 1)$		
n	V_M^{ideal}	V_M^{real}	n	V_M^{ideal}	V_M^{real}
0	−2.25	−2.17999	0	−2.25	−2.17475
1	−0.25	−0.20649			

$z_0 = 16(\lambda = 3, r_e = 1)$			$z_0 = 27(\lambda = 5, r_e = 1)$		
n	V_M^{ideal}	V_M^{real}	n	V_M^{ideal}	V_M^{real}
0	−6.25	−6.21226	0	−20.25	−20.24484
1	−2.25	−2.19187	1	−12.25	−12.23321
2	−0.25	−0.22305	2	−6.25	−6.22335
			3	−2.25	−2.22500
			4	−0.25	−0.23987

$z_0 = 76(\lambda = 14, r_e = 1)$			$z_0 = 150(\lambda = 18, r_e = 1.4)$		
n	V_M^{ideal}	V_M^{real}	n	V_M^{ideal}	V_M^{real}
0	−182.25	−182.2500	0	−306.25	−306.2500
1	−156.25	−156.2500	1	−272.25	−272.2500
2	−132.25	−132.2500	2	−240.25	−240.2500
3	−110.25	−110.2500	3	−210.25	−210.2500
4	−90.25	−90.2500	4	−182.25	−182.2500
5	−72.25	−72.2499	5	−156.25	−156.2500
6	−56.25	−56.2499	6	−132.25	−132.2500
7	−42.25	−42.2498	7	−110.25	−110.2500
8	−30.25	−30.2497	8	−90.25	−90.2500
9	−20.25	−20.2496	9	−72.25	−72.2500
10	−12.25	−12.2496	10	−56.25	−56.2500
11	−6.25	−6.2496	11	−42.25	−42.2500
12	−2.25	−2.2497	12	−30.25	−30.2500
13	−0.25	−0.2499	13	−20.25	−20.2500
			14	−12.25	−12.2500
			15	−6.25	−6.2500
			16	−2.25	−2.2500
			17	−0.25	−0.2500

ATMM and Phase Shifts

Very recently the analytical transfer matrix method (ATMM) has been suggested to effectively determine the eigenenergy of bound states of non-relativistic quantum systems.[9-12] The method is based on two conditions; i) the bound state wave function must exponentially decay beyond classical turning points and ii) the wave function and its first order derivative must be continuous at the turning points.

The ATMM quantization condition, for one-dimensional system, can be summarized as[10]

$$\int_{r_L}^{r_R} \kappa_n(r) dr + \delta(n) = (n+1)\pi \quad n = 0, 1, 2, \dots \qquad (12)$$

where n is the quantum number. r_L and r_R are inner (short distance) and outer (long distance) classical turning point, respectively, *i.e.*, $V(r_L) = V(r_R) = \varepsilon_n$. κ_n is the momentum, *i.e.*,

$$\kappa_n(r) = \sqrt{2m[\varepsilon_n - V(r)]}/\hbar \tag{13}$$

where $V(r)$ is the potential, m is the mass and ε_n is the eigenenergy of the n-th state. $\kappa_n(r)$ is always positive between r_L and r_R.

The phase shift $\delta(n)$ is

$$\delta(n) = \int_{r_L}^{r_R} -\kappa_n'(r) \frac{P_n(r)}{P_n'(r)} dr \tag{14}$$

where $\kappa_n'(r) = d\kappa_n(r)/dr$ and $P_n'(r) = dP_n(r)/dr$. $P_n(r)$ is the (minus) log derivative of the n-th state wave function $\Psi_n(r)$, *i.e.*, $P_n(r) = -d\ln\Psi_n(r)/dr$. Of course, $P_n(r)$ satisfies the following Riccati equation,

$$\frac{dP_n(r)}{dr} = [P_n(r)]^2 + \kappa_n^2(r). \tag{15}$$

Since the integrand in Eq. (14), $-\kappa_n'(r)P_n(r)/P_n'(r)$ has a dimension of momentum, we can also consider it as a momentum complementary to the momentum κ_n. The sum of two momenta, $\kappa_n - \kappa_n'(r)P_n(r)/P_n'(r)$ is called the quantum momentum function that includes the effect of phase shifts occurring at the classical turning points. That is, in addition to the phase loss, the phase shift $\delta(n)$ appears in the ATMM quantization condition, Eq. (12). It can be interpreted as the phase change resulting from the wave scattered at the turning points. In general $\delta(n)$ depends on n or eigenenergy ε_n.

The well-known semiclassical WKB method is one of the useful approximations for calculating eigenenergies of the Schrödinger equation.[13,14] Its quantization condition is

$$\int_{r_L}^{r_R} \kappa_n(r)dr = \left(n + \frac{1}{2}\right)\pi. \tag{16}$$

In Eq. (16), the $1/2\pi$ in the right hand side represents the phase loss under the WKB approximation. Of course this phase loss of $1/2\pi$ is only approximate. However, the WKB method is exact for the harmonic oscillator or the Morse potential[15-18] so that their phase loss is definitely $1/2\pi$.

The ATMM quantization condition Eq. (12) can be rewritten as

$$\int_{r_L}^{r_R} \kappa_n(r)dr = [n + 1 - \delta(n)/\pi]\pi. \tag{17}$$

Here we see that the term $[1 - \delta(n)/\pi]\pi$ in ATMM represents the sum of phase loss and phase shift. If $\delta(n)$ is $1/2\pi$, Eq. (17) becomes identical with Eq. (16). For both of the harmonic oscillator potential[9] and the Morse potential $(V_{\mathrm{M}}^{\mathrm{ideal}})$,[27] the $\delta(n)$ is calculated to be $1/2\pi$. Therefore we can say that the phase loss is $1/2\pi$ and the phase shift is $1/2\pi$ for the harmonic oscillator or the Morse potential. It indirectly proves that there should exist a phase shift.

In our previous work,[27] we exactly (analytically) deter-

mine the phase shift, eigenenergy, etc. of the Morse potential, *i.e.*, $V(r) = V_{\mathrm{M}}^{\mathrm{ideal}}$, by using the ATMM method with the aid of supersymmetry algebra.[28,29] The phase integral for momentum part is analytically obtained as

$$\int_{r_L}^{r_R} \kappa_n(r)dr = [\lambda - n - (-\varepsilon_n)^{1/2}]\pi, \tag{18}$$

and the phase shift is also analytically derived to be $\delta(n) = 1/2\pi$ for any n. And the ATMM quantization condition of Eq. (12) produces the eigenenergy $\varepsilon_n = -(\lambda - n - 1/2)^2$ that is identical with the previously known expression of Eq. (8).

The discussions above are on the original Morse potential, $V_{\mathrm{M}}^{\mathrm{ideal}}$. And the conclusion was $\delta(n) = 1/2\pi$ for any n. In order to understand the phase shift more deeply we have calculated the phase shifts for variously altered Morse potentials by numerically solving the Riccati equation (15). The phase shift under discussion is the scattering-led phase change of bound state wave at the classical turning points, which is different from the phase shift of scattered wave in continuum. For continuum state phase shifts of the Morse potential, see Ref. 30.

The test system chosen is the case of $z_0 = 27$ ($\lambda = 5$, $r_e = 1$). Here $z_0 = 27$ is a bit smaller than the usual z_0 value for real diatomic molecules. But the purpose of calculations is only to examine the change of phase shifts, not to obtain the realistic values. The altered Morse potentials for which calculations are performed are i) $V_{\mathrm{M}}^{\mathrm{real}}$ defined previously, ii) $V_{\mathrm{M}}^{\mathrm{dl}}$ in which the potential is infinite when $r < 0.1$, iii) $V_{\mathrm{M}}^{\mathrm{d2}}$ in which the potential is infinite when $r < 0.2$, and iv) $V_{\mathrm{M}}^{\mathrm{d3}}$ in which the potential is infinite when $r < 1 - \ln2$. Note that $V_{\mathrm{M}}(r) = 0$ when $r = 1 - \ln2$. The altered potentials are basically Morse type potentials but they are slightly different to each other. In this way, we believe, the change of phase shifts can be systematically investigated. The altered potentials are summarized in Table 1.

The calculated phase shifts (in units of π) are tabulated in Table 3. As the potential varies from $V_{\mathrm{M}}^{\mathrm{ideal}}$ to $V_{\mathrm{M}}^{\mathrm{d3}}$, *i.e.*, $V_{\mathrm{M}}^{\mathrm{ideal}} \rightarrow V_{\mathrm{M}}^{\mathrm{real}} \rightarrow V_{\mathrm{M}}^{\mathrm{dl}} \rightarrow V_{\mathrm{M}}^{\mathrm{d2}} \rightarrow V_{\mathrm{M}}^{\mathrm{d3}}$, the infinite wall of potential ($V(r) = \infty$) comes closer to the left (inner) turning point r_L to increase the eigenenergy (higher). Since all of the altered potentials are the same between the two turning points, the kinetic energy (or momentum) of a particle under $V_{\mathrm{M}}^{\mathrm{ideal}}$ potential is smallest and the kinetic energy (or momentum) under $V_{\mathrm{M}}^{\mathrm{d3}}$ potential is largest. Given a potential, a particle with a large momentum is weakly scattered so that the phase shift of scattered wave should be small. Therefore the phase shifts must keep decreasing as the potential varies from $V_{\mathrm{M}}^{\mathrm{ideal}}$ to $V_{\mathrm{M}}^{\mathrm{d3}}$. This trend is clearly manifested in Table 3. It also verifies that the phase shift under discussion must be scattering-led phase change at the classical turning points.

As n increases, the phase shifts decrease. The higher n state has a larger total energy and the kinetic energy becomes much larger than the potential energy. It certainly diminishes the scattering so that the phase shift for higher n state is small. This trend is also shown in Table 3.

Table 3. Phase shifts ($\delta(n)$ in units of π) of the altered Morse potentials for the case of $z_0 = 27$ ($\lambda = 5$, $r_e = 1$). For notations, see Table 1

n	$V_{\mathrm{M}}^{\mathrm{ideal}}$	$V_{\mathrm{M}}^{\mathrm{real}}$	$V_{\mathrm{M}}^{\mathrm{d1}}$	$V_{\mathrm{M}}^{\mathrm{d2}}$	$V_{\mathrm{M}}^{\mathrm{d3}}$
0	0.5	0.499	0.497	0.491	0.474
1	0.5	0.498	0.490	0.471	0.428
2	0.5	0.495	0.481	0.448	0.383
3	0.5	0.492	0.472	0.428	0.349
4	0.5	0.490	0.466	0.418	0.334

For the altered potentials, of course, the WKB approximation is not valid. The WKB quantization condition with the Maslov index is[19,20]

$$\int_{r_L}^{r_R} \kappa_n(r)\,dr = \left(n + \frac{\mu}{4}\right)\pi \tag{19}$$

The Maslov index μ is the total phase loss during one period in units of $1/2\pi$. For the Morse potential $V_{\mathrm{M}}^{\mathrm{ideal}}$, μ is exactly 2. μ is, in general, non-integral and depends on a potential. A wave function is required to evaluate an exact μ. If we consider μ as an n-dependent parameter that makes the quantization condition Eq. (19) exact, we can equate Eq. (12) with Eq. (19) to have

$$\mu(n) = 4(1 - \delta(n)/\pi) \tag{20}$$

With the phase shifts in Table 3, we can calculate the Maslov index for our altered Morse potentials. The μ for the $n = 0$ state are 2, 2.00, 2.01, 2.04, 2.10 for $V_{\mathrm{M}}^{\mathrm{ideal}}$, $V_{\mathrm{M}}^{\mathrm{real}}$, $V_{\mathrm{M}}^{\mathrm{d1}}$, $V_{\mathrm{M}}^{\mathrm{d2}}$, and $V_{\mathrm{M}}^{\mathrm{d3}}$, respectively. The Maslov index becomes further off from 2 as the potential gets more altered. This simple observation does not offer any new concept but it confirms that one has to know a wave function beforehand when the exact results are desired. And the phase shift $\delta(n)$ must be dependent on the wave function as given in Eq. (14).

The supersymmetric WKB (SWKB) method,[21,22] based on supersymmetric quantum mechanics,[28,29] has also been suggested. The lowest order form of SWKB for unbroken supersymmetry to which the Morse potential belongs is

$$\int_{r_L'}^{r_R'} \kappa_n^{(s)}(r)\,dr = n\pi \quad n = 0, 1, 2, \ldots. \tag{21}$$

$\kappa_n^{(s)}(r)$ is defined for the hierarchy of Hamiltonians $H^{(s)}$ ($s = 1, 2, 3\ldots$) as

$$\kappa_n^{(s)}(r) = \sqrt{2m\{\varepsilon_n^{(s)} - \varepsilon_0^{(s)} - [W^{(s)}(r)]^2\}}/\hbar \tag{22}$$

The two turning points r_L' and r_R' are given by $\kappa_n^{(s)}(r_L') = \kappa_n^{(s)}(r_R') = 0$. $W^{(s)}(r)$ is a superpotential for hierarchy s. For details, please consult Refs. 28 and 29. The Eq. (21) is proved to be exact for the ground state ($n = 0$) of each $H^{(s)}$ for a shape invariant potential. Note that for a shape invariant potential, the ground state energy can be shifted to zero. Because $\varepsilon_{n+1}^{(s)} = \varepsilon_n^{(s+1)}$ for unbroken supersymmetry, the SWKB quantization condition gives the exact eigener-

gies for all n states of a shape invariant potential ($H^{(1)}$).[17] The lowest order SWKB quantization condition Eq. (21) is exact for the Morse potential ($V_{\mathrm{M}}^{\mathrm{ideal}}$) because the Morse potential is shape invariant. For the altered potentials ($V_{\mathrm{M}}^{\mathrm{real}}$, etc.), we find that the SWKB is not exact though our altered potentials are still the shape invariant Morse potential. That is because the wave functions of the altered potentials are different from that of $V_{\mathrm{M}}^{\mathrm{ideal}}$. Note that the SWKB quantization condition depends on $W^{(s)}(r)$, *i.e.*, consequently on the ground state wave function.

The above analyses shed a light for understanding the nature of phase shift. The scattering-led phase shift of bound state wave function occurs at classical turning points when a particle is oscillating between the two turning points. This phase shift must be non-zero when the potential in the classically allowed region is not constant.

Conclusion

Through the analytical transfer matrix method, we have examined the phase shifts of bound state wave functions of the Morse potential appearing in the quantization condition. During the course of work we have learned the followings. i) In addition to the phase loss emanating from the quantum effect that a wave function should exist in a classically forbidden region, there should be another term (called phase shift) accounting for the phase change. ii) The phase shift in ATMM quantization condition is none other than the phase change of scattered wave at classical turning points. iii) For the Morse potential $V_{\mathrm{M}}^{\mathrm{ideal}}$, the phase shifts are $1/2\pi$ for all bound states. For this case the WKB method is exact. The WKB method is not exact for potentials like $V_{\mathrm{M}}^{\mathrm{real}}$, etc. where the phase shifts are not exactly $1/2\pi$, while ATMM is still exact.

The potential function for real diatomic molecules should be infinite when the two atoms are in contact, *i.e.*, the potential should satisfy the boundary condition of $V(r) \to \infty$ as $r \to 0$. However, the frequently used form of Morse potential ($V_{\mathrm{M}}^{\mathrm{ideal}}$, Eq. 5) does not possess correct boundary conditions for real diatomic molecules. The Morse potential with the correct boundary condition ($V_{\mathrm{M}}^{\mathrm{real}}$) has been examined by calculating the eigenenergies of various diatomic pairs. And it is found that for real diatomic molecules, the eigenenergies of $V_{\mathrm{M}}^{\mathrm{ideal}}$ are virtually identical with those of $V_{\mathrm{M}}^{\mathrm{real}}$. iv) Therefore the original Morse potential can be, without a loss of accuracy, applied to real diatomic molecules.

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