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Modified shifted-large-N approach to an exponential potential

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The modified shifted-large-N approach proposed by Bag *et al.* [Phys. Rev. A **46**, 6059 (1992)] for the Morse potential is applied to the exponential (6) [exp(6)] potential, i.e., a potential with an exponential repulsion and an attraction in r^{-6}. Although the method does not provide the exact analytic expressions of the vibrational eigenvalues and eigenfunctions as in the Morse case, it is shown to predict quite accurate results for both the energy eigenvalues and eigenfunctions for the vibrational and rovibrational states of the exp(6) potential. In particular, the wave functions are much more accurate than those provided by the usual shifted-$1/N$ method, which fails to yield their correct behavior. Moreover, in the modified approach, the exp(6) eigenfunctions are given in the same analytical form as the Morse ones.

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Recently, Bag *et al.* [1] have pointed out that, while producing accurate eigenvalues, the well-known shifted-large-N technique (SLNT) proposed by Imbo, Pagnamenta, and Sukhatme [2] failed to yield the correct behavior of the bound-state wave function for the Morse oscillator. To remedy this drawback, they have proposed a modified SLNT, which leads first to the exact eigenvalues and eigenfunctions of the Morse potential, and second to accurate results for both the rovibrational eigenenergies and wave functions without invoking the rearrangement of the centrifugal barrier by an expansion about the equilibrium distance, r_e, or some other values of r [3].

This difficulty is likely to be encountered for other realistic diatomic potentials of similar shape. Thus it is worthwhile to investigate if this modified SLNT can be applied to other usual potential forms. In this Brief Report, we show that this modified scheme can also be applied to the exponential (6) [exp(6)] potential, i.e., a potential with an exponential repulsion and an attraction in r^{-6}. Although in this case, we do not obtain exact expressions for the nonrotating oscillator, we shall see that the method provides quite accurate results for the vibrational and rovibrational eigenenergies and eigenfunctions in comparison to the exact numerical or WKB values.

The modified SLNT consists in using the usual large-N expansion to a transformed Schrödinger equation in a new variable. We start from the usual radial Schrödinger equation for the rotating exp(6) oscillator

$$-\frac{d^2\chi}{dx^2}+\left\{\frac{3\gamma^2}{\alpha-3}\left[e^{-2\alpha x}-\frac{\alpha}{3(1+x)^6}\right]+\frac{j(j+1)}{(1+x)^2}\right\}\chi(x)=-\beta^2\chi(x)\ , \qquad (1)$$

in which

$$\gamma^2=2mDr_e^2/\hbar^2,\quad \beta^2=-2mE_{vj}r_e^2/\hbar^2\ ,$$
$$x=(r-r_e)/r_e\ , \qquad (2)$$

where v and j are the vibrational and rotational quantum numbers, respectively, m is the reduced mass, D is the dissociation energy, r_e is the equilibrium internuclear distance, and α is a parameter that measures the steepness of the repulsive potential energy chosen to reproduce the Morse repulsion term. We now perform the same change of variable and function as in [1]

$$y=(2\gamma/\alpha)e^{-\alpha x},\quad \phi(y)=y^{1/2}\chi(y)\ , \qquad (3)$$

which leads to the transformed Schrödinger equation

$$\left[-\frac{d^2}{dy^2}+\frac{L(L+1)}{y^2}+V(y)\right]\phi(y)=\eta\phi(y)\ , \qquad (4)$$

where

$$L=(\beta/\alpha)-\tfrac{1}{2}\ , \qquad (5)$$

$$V(y)=-\frac{\gamma^2}{\alpha(\alpha-3)y^2\left[1-\frac{1}{\alpha}\ln\left[\frac{\alpha y}{2\gamma}\right]\right]^6}+\frac{j(j+1)}{\alpha^2y^2\left[1-\frac{1}{\alpha}\ln\left[\frac{\alpha y}{2\gamma}\right]\right]^2}\ , \qquad (6)$$

$$\eta=-\frac{3}{4(\alpha-3)}\ . \qquad (7)$$

Equation (4) is the starting equation for the modified SLNT as applied to the exp(6) potential. It has the same structure as the one obtained for the Morse potential with a different constant value for η and a different expression for the first term of $V(y)$, which comes from the r^{-6} dependence of the exp(6) potential. However, this term has the same form as the centrifugal term [second term of $V(y)$]; it can thus be treated in the same way.

We now apply the usual SLNT to Eq. (4), in which the energy of the original problem is contained in the variable angular momentum L. As this procedure has already been described in Ref. [1], we omit the intermediate steps and indicate here only the expressions useful for the calculations of the eigenvalues and eigenfunctions. To apply the SLNT, Eq. (4) is written

$$-\frac{d^2\phi}{dy^2}+\bar{k}^2\left\{\frac{1}{4y^2}\left[1-\frac{(1-a)}{\bar{k}}\right]\left[1-\frac{(3-a)}{\bar{k}}\right]+\frac{V(y)}{Q}\right\}\phi(y)=\eta\phi(y)\ , \quad (8)$$

where

$$\bar{k}=K-a=N+2L-a\ . \quad (9)$$

N is the number of spatial dimensions, Q is a rescaling constant, which is set equal to $\bar{k}^2$ at the end of the calculation, and a is the shift parameter given by

$$a=2-(2v+1)\omega\ , \quad (10)$$

$$\omega=\{3+[y_0V''(y_0)/V'(y_0)]\}^{1/2}\ . \quad (11)$$

y_0 is the position of the minimum of the effective potential

$$V_{\rm eff}(y)=(1/4y^2)+V(y)/Q\ . \quad (12)$$

at which the particle is trapped in the limit $N\to\infty$; it is given by

$$\bar{k}^2=2y_0^3V'(y_0)\ . \quad (13)$$

With $\hbar=2m=1$, Eq. (8) is the same as the one used by Imbo, Pagnamenta, and Sukhatme to implement the usual SLNT, which leads here in the modified scheme to an analytic expression for η in terms of y_0. In order to derive conveniently this expression for the exp(6) potential, we can take advantage of the fact that the usual SLNT has already been used to obtain analytic expressions of $\epsilon_{vj}=E_{vj}/D$ for the LJ$(n,6)$ (LJ denotes Lennard-Jones) [4] and Varshni [5] potentials. The formulas derived for these two similar diatomic potentials are almost identical. Their differences stem only from a small number of terms, which depend on the specific form of $V(r)$. Here we want to use the expressions given in Refs. [4,5] suitably modified to take into account the fact that we are working with the transformed Schrödinger Eqs. (4) or (8) with the exp(6) potential. For this purpose, we shall give the general expressions of these few potential dependent terms. Following Ref. [2], we can express η as a sum of three terms

$$\eta=\eta^{(0)}+\eta^{(1)}+\eta^{(2)}=-\frac{3}{4(\alpha-3)}\ , \quad (14)$$

where

$$\eta^{(0)}=\tfrac{1}{2}y_0V'(y_0)+V(y_0)\ , \quad (15)$$

$$\eta^{(1)}=\frac{4}{y_0^2}\left[\frac{(1-a)(3-a)}{16}-\frac{3(2-a)(1+2v)}{8\omega}+\frac{3(1+2v+2v^2)}{\omega^2}g_2-\frac{(2-a)^2}{4\omega^2}-\frac{6(2-a)(1+2v)}{\omega^3}g_1-\frac{4(11+30v+30v^2)}{\omega^4}g_1^2\right]\ . \quad (16)$$

Before giving information on $\eta^{(2)}$, we note that $\eta^{(0)}$ and g_i are the terms mentioned above, which specifically depend on $V(y)$. If one is working on the usual Schrödinger equation, $\eta^{(i)}$ is replaced by $E_{vj}^{(i)}=\epsilon_{vj}^{(i)}D$ and $V(y)$ by $V(r)$. The expression of $\eta^{(1)}$ is the one given in Refs. [4,5] for $\epsilon_{vj}^{(1)}=E_{vj}^{(1)}/D$ with the overall multiplicative factor $2\hbar^2/(mr_0^2D)$ replaced by $4/y_0^2$, since $\hbar=2m=1$. The terms g_i can be calculated from Refs. [1,2] in terms of $V(y)$ as

$$g_i=(-1)^i\frac{i+3}{16}+\frac{y_0^{i+4}V^{(i+2)}(y_0)}{8(i+2)!y_0^3V'(y_0)}\ , \quad (17)$$

where the superscripts on V indicate the order of derivation with respect to y. According to this prescription, the term $\eta^{(2)}$ is given by the formula of Refs. [4,5] with g_3 and g_4 expressed by (17) and an overall multiplicative factor $4/(y_0^2\bar{k})$ instead of $2\hbar^2/(mr_0^2D\bar{k})$. For brevity we do not reproduce it here. Equations (15) and (17) with $V(y)$ and $\eta^{(i)}$ replaced, respectively, by $V(r)$ and $E_{vj}^{(i)}$ are also convenient to calculate the energy eigenvalues of the exp(6) potential or any other potential $V(r)$ of similar shape using the usual SLNT. In this case the formulas of Refs. [4,5] can be used directly. This calculation will also be done here to compare the usual and modified SLNT eigenenergies.

Now through a, ω, $V(y_0)$ and its derivatives at y_0, η is a rather complicated function of v, j, and y_0. However, it is easy to determine for a given v and j the value of y_0 which gives $\eta=-3/[4(\alpha-3)]$. The corresponding values of a, ω, and $\bar{k}$ are determined from (10), (11), and (13), respectively. The energy eigenvalues are then obtained from (2), (5), and (9) with $N=3$ as [1]

$$E_{vj}=-(\hbar^2\alpha^2/8mr_e^2)[\bar{k}-(2-a)]^2\ . \quad (18)$$

We now focus our attention on the radial wave function $\chi(r)$. For any spherically symmetric potential, the leading-order usual SLNT wave function is given by [6]

$$\chi(r)=Nr^{(K-1)/2}e^{-(\bar{k}/2\tilde{\omega})(r/r_0)^{\tilde{\omega}}}\times F\left[-v,\frac{K-2}{\tilde{\omega}}+1,\frac{\bar{k}}{\tilde{\omega}}\left[\frac{r}{r_0}\right]^{\tilde{\omega}}\right]\ , \quad (19)$$

where r_0, $\bar{k}$, $\tilde{\omega}$, etc., are defined in Ref. [6], and F is the confluent hypergeometric function. The modified SLNT wave function is then written [1]

TABLE I. Reduced energy eigenvalues $(-\epsilon_{vj}=-E_{vj}/D)$ of the exp(6) potential with $\gamma=50$, $\alpha=6.886$, $j=0$ and 25. Entries in columns (a) and (b) correspond to the modified and usual SLNT results, respectively. The exact results are from Ref. [7].

j	v	(a)	(b)	$-\epsilon_{\rm WKB}$	$-\epsilon_{\rm exact}$	$10^4(\epsilon_{vj}-\epsilon_{\rm ex})$ (a)	(b)
0	0	0.8841	0.8840	0.8840	0.884 095	0	1
	1	0.6773	0.6765	0.6772	0.677 375	1	9
	2	0.5021	0.5004	0.5026	0.502 845	7	24
	3	0.3566	0.3545	0.3588	0.359 075	25	46
	4	0.2384	0.2374	0.2442	0.244 255	59	69
	5	0.1456	0.1474	0.1560	0.156 065	105	87
	6	0.0765	0.0831	0.0916	0.091 705	152	86
25	0	0.6337	0.6337	0.6336		−1	−1
	1	0.4431	0.4430	0.4429		−2	−1
	2	0.2868	0.2859	0.2858		−10	−1
	3	0.1642	0.1615	0.1612		−30	−3
	4	0.0755	0.0692	0.0677		−78	−15

$$\chi(y)=Ny^{(K-2)/2}e^{-(\bar{k}/2\omega)(y/y_0)^{\omega}} \times F\left[-v,\frac{K-2}{\omega}+1,\frac{\bar{k}}{\omega}\left[\frac{y}{y_0}\right]^{\omega}\right], \quad (20)$$

where $\bar{k}$ and ω are given by (13) and (11). For the Morse potential with $j=0$, Eq. (20) yields the exact analytical wave function, while Eq. (19) differs significantly from the exact one [1]. If the modified SLNT restores the exact wave function for the Morse potential, it is our hope that it will considerably improve the usual SLNT wave function for other potential forms of similar shape as the exp(6) potential, for which the change in variable and function (3) is successful. In order to obtain (20) in a more convenient form, which is similar to the one usually given for the Morse potential, we carry out the change of variable

$$t=(\bar{k}/\omega)(y/y_0)^{\omega}, \quad (21)$$

take $N=3$, and use (9), (2), (18), and (10) to express $2\lambda=(K-2)/\omega$ as

$$2\lambda=(K-2)/\omega=2\beta/(\alpha\omega)=(\bar{k}/\omega)-2v-1, \quad (22)$$

so that (20) becomes

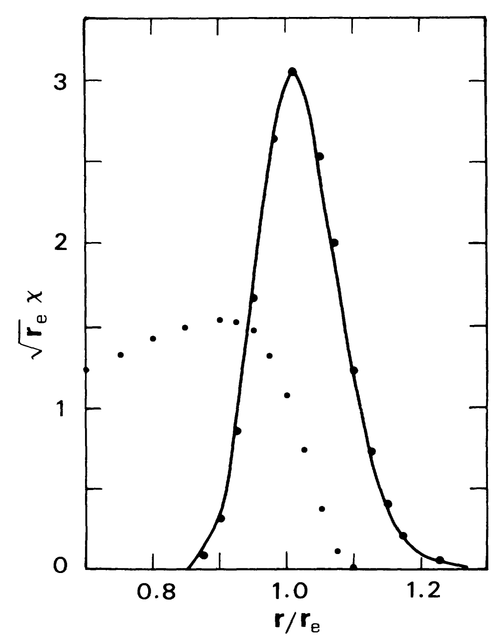

FIG. 1. Normalized exp(6) wave function for $\gamma=50$, $\alpha=6.886$, and $v=j=0$: small dots, usual SLNT [Eq. (19)]; ——, modified SLNT [Eq. (23)]; large dots on curve, uniform WKB [8].

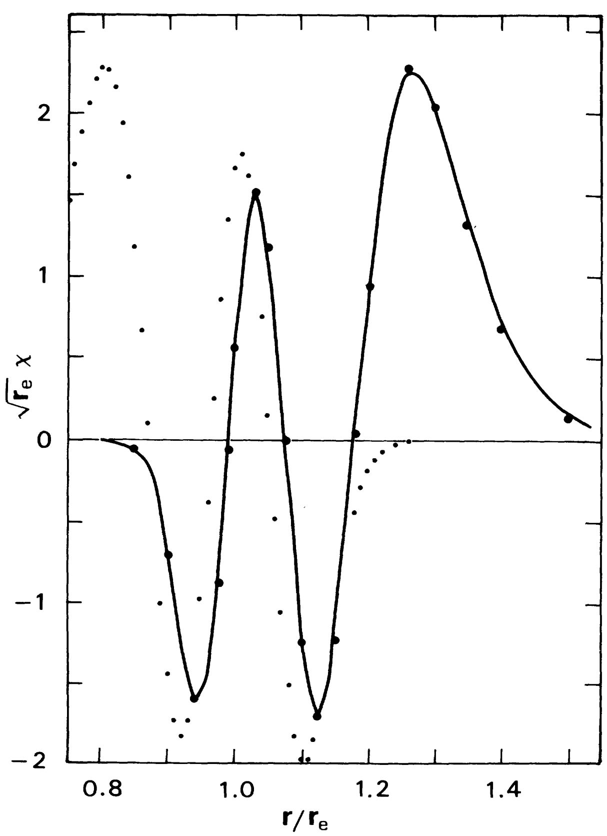

FIG. 2. Same as Fig. 1 for $v=3$ and $j=25$.

$$r_e^{1/2}\chi(t)=\left[\frac{\alpha\omega\Gamma(2\lambda+v+1)}{v!2\lambda\Gamma^2(2\lambda)}\right]^{1/2} t^{\lambda}e^{-t/2} \times F(-v,2\lambda+1,t) . \quad (23)$$

This expression is valid for any v and j, since the quantities λ, t, ω are obtained for a given v, j, through Eq. (14) when the modified SLNT eigenvalues are calculated. Also, as in the Morse case, the centrifugal term is automatically taken care of without any expansion about a value of r.

We now test the accuracy of the preceding equations by presenting for $\gamma=50$ and $\alpha=6.886$ the energy eigenvalues for $j=0$ and 25 (Table I) and the normalized wave functions $v=0$, $j=0$ (Fig. 1) and $v=3$, $j=25$ (Fig. 2) obtained from the usual and modified SLNT. The value of α corresponding to an exp(6) potential, which has the same curvature at the minimum as the LJ (12,6) potential [7].

The eigenenergies are compared to the exact numerical [7] or WKB eigenvalues. It appears that both methods give results of comparable accuracy. However, it can be noted that for $j=0$ the modified eigenvalues are more accurate for small v with a positive deviation, while as j increases they become less accurate with a negative deviation than the usual SLNT results, which tend closely to the WKB eigenvalues.

The eigenfunctions are compared to the accurate uniform WKB wave functions of Miller and Good [8]. It is clear from the figures that the modified SLNT wave functions are much better than those obtained from the usual SLNT, which are shifted toward the origin with the wrong sign for the state $v=3$, $j=25$. As additional information, we give in Table II the values of ω, $\bar{k}$, and y_0 necessary to calculate the modified SLNT wave functions. It is instructive to compare them to the values that we would obtain from a nonrotating Morse potential with the same values of the parameters γ and α; in this case $\omega=1$, $\bar{k}=y_0=2\gamma/\alpha=100/6.886=14.522\,219$ [1]. These values are quite close to those shown in Table II, and their differences could be considered as a measure of how much the exp(6) potential differs from the Morse shape.

TABLE II. Values of ω, $\bar{k}$, and y_0 necessary to construct the exp(6) wave functions $v=0$, $j=0$, and $v=3$, and $j=25$.

State	ω	$\bar{k}$	y_0
$v=0$, $j=0$	0.871 366	14.526 098	14.532 440
$v=3$, $j=25$	0.948 695	12.525 787	13.822 637

In conclusion, we find that the modified SLNT works quite well for the exp(6) potential. This is due to the presence of the exponential repulsive term, which upon the transformation (3) turns out to be given by Eq. (7), while the r^{-6} attraction gives a term similar to the centrifugal one. This means that the modified SLNT is also applicable to the Buckingham type of potentials $\exp(m,n)$, which include attractive contributions proportional to r^{-m} and r^{-n}. Also, the fact that the wave functions are sufficiently accurate and in the Morse form makes the modified scheme valuable for the calculation of the matrix elements and Franck-Condon factors for these potential forms.

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