PHYSICAL REVIEW A VOLUME 49, NUMBER 6 JUNE 1994

Application of a two-step method to the vibrational rotational spectrum of diatomic molecules

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(Received 9 November 1993)

We present a two-step method to calculate the vibrational-rotational spectrum of diatomic molecules in general. The aim of the method is to solve the radial part of the Schrödinger equation with the effective potential in the general form of $V = \sum_n a_n r^n$, where n may be a positive or negative number. The flexibility of the form of the prototype potential used enables us to describe accurately the interatomic potential in general. The method of solution is composed mainly of two steps. In the first step, we introduce a transformation so that the domain of the wave function is the whole real axis. The operator formalism is used to carry through the variational conditions analytically for the ground state of the system. In the second step, we improve the ground-state energy by a standard diagonalization procedure around the ground state using the harmonic oscillator basis obtained from the first step. In this way, we also obtain the low-lying excited states accurately. The method is applied to the following systems explicitly: (1) the lower-energy levels of the H atom or Kratzer's potential in molecular problems, (2) the vibrational-rotational spectrum of the $^2\Sigma_g$ state of the $H_2{}^+$ ion, and (3) the so-called spiked oscillator harmonic system. The results of all these calculations demonstrate that the two-step method is very powerful in the solution of one-dimensional problems, in particular for cases where the effective potential has only one minimum.

PACS number(s): 31.15.+q, 03.65.Ge, 31.50.+w

I. INTRODUCTION

In the vibrational-rotational spectrum of diatomic molecules one tries to solve the radial part of the Schrödinger equation in the form

$$\left[\frac{-1}{2mr^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right)+V_{\text{eff}}(r)\right]\Psi(r)=E\Psi(r), \qquad (1.1)$$

where the effective potential V_{eff} includes the contribution of the angular momentum

$$V_{\text{eff}}(r)=V(r)+\frac{J(J+1)}{2mr^2}. \qquad (1.2)$$

In this paper, we use atomic units so that $\hbar = 1$. The general form of the interatomic potential $V(r)$ essentially consists of a short distance repulsive part and a long distance attractive part. The sharp rising short distance repulsive potential arises essentially from the Coulomb repulsive force of the nuclei and the increase of the electronic energies due to the localization of electrons in the core area and the Pauli exclusion principle. On the other hand, the long distance attractive potential is due to the induced instantaneous dipole-dipole dispersive forces and other tunneling phenomena of the electrons. Both of the above mentioned effects tend to zero as the interatomic distance approaches infinity. Therefore, in general, the interatomic potential has a minimum at the equilibrium position of the diatomic molecules. The simplest approach to solve the Schrödinger equation (1.1) is to use the distance

$$x = r - r_0$$

from the equilibrium interatomic distance r_0 as the new variable and expand the effective potential in a Taylor series of x around the equilibrium position. By retaining only the lowest order term, which is quadratic, the Schrödinger equation (1.1) reduces to the textbook problem of simple harmonic oscillators [1]. The higher order nonlinear terms of the potentials are then used as perturbations for improvement.

There are obvious difficulties in this approach: First of all, interatomic potentials are complicated in shape and many terms in the power series expansion are needed in order to obtain accurate results. In particular, it is difficult to use simple power series to describe correctly the sharp rising repulsive part of the interatomic potential at small r. In addition, for rotational spectra, the interatomic distance r appears in the denominator of the effective potential due to the angular momentum. The power series around the equilibrium position needs many terms to describe the effective potential correctly and sometimes the series may even be divergent.

Recently, we have proposed a two-step approach to treat the anharmonic oscillators [2] and vibrational problems [3,4]. The method is straightforward and has a clear physical picture. It can compete with existing methods in obtaining accurate results with ease.

In this paper, we apply the two-step approach to solve the vibrational-rotational spectrum of diatomic molecules. We first fit the effective interatomic potential in powers of positive and negative integer order of r,

$$V_{\text{eff}}(r) = \sum_n a_n r^n . \tag{1.3}$$

An important point to be emphasized here is that, since we include terms with negative integer powers of r to deal with the sharp rising repulsive potential, only a small number of terms is needed to describe accurately the interatomic potential. Furthermore the contribution of the angular momentum is already of the right form. The widely used Lenard-Jones 6-12 potential consists of course of two terms only:

$$V(r) = C_{12} r^{-12} - C_6 r^{-6} . \tag{1.4}$$

In Sec. II we describe our general approach in detail. As a demonstration, in Sec. III we apply the method to the textbook problem of energy levels of the hydrogen atom, which is a special case of the Kratzer potential [5]. In Sec. IV we apply the method explicitly to the energy levels of the $H_2{}^+ \, {}^2\Sigma_g$ state [6, 7]. In Sec. V we apply the method to the so-called spiked oscillators [8, 9]. A discussion and conclusion are given in Sec. VI.

II. THE TWO-STEP METHOD

We start with the Hamiltonian

$$H = \frac{-1}{2mr^2} \frac{d}{dr} \left(r^2 \frac{d}{dr} \right) + V_{\text{eff}}(r), \tag{2.1}$$

where

$$V_{\text{eff}}(r) = \sum_n a_n r^n \tag{2.2}$$

with n being either positive or negative numbers. In order to use basis-set functions of harmonic oscillators, our first step is to employ a transformation [10] so that the domain of the wave function is the whole real axis. A convenient way is to set

$$r = e^x , \tag{2.3a}$$

i.e.,

$$x = \ln r . \tag{2.3b}$$

The domain of definition is changed from the positive real axis of $\{r\colon\ 0 \le r \le \infty\}$ to the whole real axis of $\{x\colon\ -\infty \le x \le \infty\}$. From Eq. (2.3a) or (2.3b), the Schrödinger equation becomes

$$\left[\frac{-1}{2m} e^{-3x} \frac{d}{dx} \left(e^x \frac{d}{dx} \right) + V_{\text{eff}}(x) \right] R(x) = E R(x). \tag{2.4}$$

In other words, the Hamiltonian (2.1) now becomes

$$H = \frac{-1}{2m} e^{-3x} \frac{d}{dx} \left(e^x \frac{d}{dx} \right) + V_{\text{eff}}(x) \tag{2.5}$$

with

$$V_{\text{eff}}(x) = \sum_n a_n e^{nx} . \tag{2.6}$$

At this point, we should take into account the fact that the transformed Hamiltonian operator H in (2.5) is no longer Hermitian. In order to obtain a Hermitian operator $\bar{H}$, we introduce the new wave function $\phi(x)$ related to the old wave function $R(x)$ by the transformation

$$\phi(x) = Q R(x), \tag{2.7}$$

with the operator

$$Q = e^{\frac{3}{2}x} . \tag{2.8}$$

We now carry through a similarity transformation between the new Hamiltonian operator $\bar{H}$ and the original operator H by

$$\bar{H} = Q H Q^{-1} , \tag{2.9}$$

i.e.,

$$\begin{aligned} \bar{H} &\equiv e^{\frac{3}{2}x} H e^{-\frac{3}{2}x} \\ &= \frac{-1}{2m} e^{-\frac{3}{2}x} \frac{d}{dx} \left(e^x \frac{d}{dx} e^{-\frac{3}{2}x} \right) + V_{\text{eff}}(x) \\ &= \frac{-1}{2m} \left[\frac{d}{dx} e^{-2x} \frac{d}{dx} + \frac{3}{4} e^{-2x} \right] + V_{\text{eff}}(x). \end{aligned} \tag{2.10}$$

Then, for two arbitrary wave functions ϕ and ϕ', and the corresponding wave functions R and R', we have

$$\begin{aligned} \langle \phi' | \bar{H} | \phi \rangle &= \int_{-\infty}^{\infty} (\phi')^* \left[e^{\frac{3}{2}x} H e^{-\frac{3}{2}x} \phi \right] dx \\ &= \int_{-\infty}^{\infty} e^{\frac{3}{2}x} (\phi')^* \left[H e^{-\frac{3}{2}x} \phi \right] dx \\ &= \int_{-\infty}^{\infty} (R')^* [HR] e^{3x} dx \\ &= \int_{0}^{\infty} (R')^* [HR] r^2 dr = \langle R' | H | R \rangle , \end{aligned} \tag{2.11}$$

where R and R' are given, respectively, by

$$R' = e^{-\frac{3}{2}x} \phi' \tag{2.12a}$$

and

$$R = e^{-\frac{3}{2}x} \phi . \tag{2.12b}$$

Furthermore, the original eigenvalue problem $HR = ER$ now takes the form $\bar{H}\phi = E\phi$. From (2.10), it is easy to prove that $\bar{H}$ is a Hermitian operator since it satisfies

$$\bar{H}^\dagger = \bar{H} . \tag{2.13}$$

Following the procedures described in Ref. [2], we now write the Hamiltonian in a second quantized form by introducing the creation operator $a^\dagger$ and the corresponding annihilation operator a into (2.10). We set

$$x = \frac{1}{\sqrt{2m\omega}} (a + a^\dagger) + \tau , \tag{2.14a}$$

$$\frac{d}{dx} = \sqrt{\frac{m\omega}{2}} (a - a^\dagger). \tag{2.14b}$$

The two parameters ω and τ in (2.14a) and (2.14b) are the frequency and the displacement of the origin of the harmonic oscillator system we intend to use. Clearly, the operators a and $a^\dagger$ have the following commutation relations:

$$[a, a^\dagger] = 1, \tag{2.15a}$$

$$[a, a] = 0, \tag{2.15b}$$

$$[a^\dagger, a^\dagger] = 0. \tag{2.15c}$$

To proceed the calculation we now follow the step taken in Ref. [2] by rewriting the Hamiltonian of (2.10) in a normal ordered form where all the creation operators are pushed to the left of the annihilation operators. We have

$$\begin{aligned}\bar{H} = {} & \frac{-1}{2m} e^{-\frac{3}{2}\left[\frac{1}{\sqrt{2m\omega}}(a+a^\dagger)+\tau\right]} \left[\sqrt{\frac{m\omega}{2}}(a-a^\dagger)\right] \\ & \times e^{\frac{1}{\sqrt{2m\omega}}(a+a^\dagger)+\tau} \left(\sqrt{\frac{m\omega}{2}}(a-a^\dagger)\right) e^{-\frac{3}{2}\left[(\frac{1}{\sqrt{2m\omega}})(a+a^\dagger)+\tau\right]} + V_{\mathrm{eff}} \\ = {} & \frac{-\omega}{4} e^{-2\tau+\frac{1}{2}\left(\frac{-2}{\sqrt{2m\omega}}\right)^2} e^{\frac{-2}{\sqrt{2m\omega}}a^\dagger} \left[(a^\dagger)^2 + a^2\right] e^{\frac{-2}{\sqrt{2m\omega}}a} + \frac{\omega}{2} e^{-2\tau+\frac{1}{2}\left(\frac{-2}{\sqrt{2m\omega}}\right)^2} e^{\frac{-2}{\sqrt{2m\omega}}a^\dagger} [a^\dagger a] e^{\frac{-2}{\sqrt{2m\omega}}a} \\ & + \left[\frac{\omega}{4} + \frac{1}{8m}\right] e^{-2\tau+\frac{1}{2}\left(\frac{-2}{\sqrt{2m\omega}}\right)^2} e^{\frac{-2}{\sqrt{2m\omega}}a^\dagger} e^{\frac{-2}{\sqrt{2m\omega}}a} + V_{\mathrm{eff}}\ ,\end{aligned} \tag{2.16}$$

where

$$V_{\mathrm{eff}} = \sum_n a_n e^{n\tau+\frac{1}{2}\left(\frac{n}{\sqrt{2m\omega}}\right)^2} e^{\frac{n}{\sqrt{2m\omega}}a^\dagger} e^{\frac{n}{\sqrt{2m\omega}}a}\ . \tag{2.17}$$

In the above derivation, we have used the following special case of the Campbell-Baker-Hausdorff formula:

$$e^{A+B} = e^A e^B e^{-\frac{1}{2}[A,B]},$$

which holds when the commutator of the two operators $[A, B]$ is a c number [1]. We now introduce the harmonic oscillator eigenstates as our basis set, i.e.,

$$\langle a|0\rangle = 0, \tag{2.18a}$$

$$|u\rangle = \frac{(a^\dagger)^u}{\sqrt{u!}}|0\rangle. \tag{2.18b}$$

In the first step we first take $|0\rangle$ as the trial wave function of the ground state and determine the parameters ω and τ of the ground state by the variation principle. The expectation value of the ground state is

$$\begin{aligned}E_0 &= \langle 0|\bar{H}|0\rangle \\ &= \left(\frac{\omega}{4} + \frac{1}{8m}\right) e^{-2\tau+\frac{1}{2}\left(\frac{-2}{\sqrt{2m\omega}}\right)^2} + \sum_n a_n e^{n\tau+\frac{1}{2}\left(\frac{n}{\sqrt{2m\omega}}\right)^2}.\end{aligned} \tag{2.19}$$

We now impose the following variation conditions for τ and ω:

$$\frac{\partial E_0}{\partial \tau} = 0, \tag{2.20a}$$

$$\frac{\partial E_0}{\partial \omega} = 0. \tag{2.20b}$$

Explicitly, after some simplification, we have

$$\left(\frac{\omega}{2} + \frac{1}{4m}\right) e^{-2\tau+\frac{1}{2}\left(\frac{-2}{\sqrt{2m\omega}}\right)^2} - \sum_n n a_n e^{n\tau+\frac{1}{2}\left(\frac{n}{\sqrt{2m\omega}}\right)^2} = 0, \tag{2.21a}$$

$$m\omega^2 e^{-2\tau+\frac{1}{2}\left(\frac{-2}{\sqrt{2m\omega}}\right)^2} - \sum_n n(n+2) a_n e^{n\tau+\frac{1}{2}\left(\frac{n}{\sqrt{2m\omega}}\right)^2} = 0. \tag{2.21b}$$

The solutions of τ and ω may be conveniently obtained by iteration or standard Newton-Raphson method.

In the second step we can improve the energy level of the ground state by adding the "perturbation corrections" around the ground state $|0\rangle$ using standard perturbation methods. Conceptually the simplest and most straightforward way is to use a truncated basis set consisted of $\{|u\rangle$: $u \leq N$ for a fixed $N\}$ and calculate all the Hamiltonian matrix elements $\langle u|\bar{H}|v\rangle$ in this basis sets. Then the Hamiltonian matrix can be diagonalized by the Jacobi diagonalization method in order to solve for the eigenenergies and eigenvectors. Using a general form of the matrix element in the form

$$\begin{aligned}\langle u|e^{\alpha a^\dagger}(a^\dagger)^j a^k e^{\alpha a}|v\rangle &= \sum_{s=0}^{u-j}\sum_{t=0}^{v-1} \frac{\alpha^{s+t}}{s!t!} \left(\frac{u!v!}{(u-j-s)!(v-k-t)!}\right)^{1/2} \langle u-j-s|v-k-t\rangle \\ &= \sum_{s=0}^{u-j} \frac{(v!\ u!)^{1/2}}{s!(u-j-s)!(v-k-u+j+s)!} \alpha^{v-k-u+j+2s} \\ &= \sum_{q=0}^{u-j} \left[(u-j-q)!(v-k-q)!q!\right]^{-1} (u!v!)^{1/2} \alpha^{v+u-k-j-2q},\end{aligned} \tag{2.22}$$

we can represent the matrix element of the Hamiltonian $\langle u|\bar{H}|v\rangle$ as

$$\langle u|\bar{H}|v\rangle = \frac{-\omega}{4} e^{-2\tau+\frac{1}{m\omega}} \langle u|e^{\alpha_0 a^\dagger} \left[(a^\dagger)^2 + a^2\right] e^{\alpha_0 a}|v\rangle + \frac{\omega}{2} e^{-2\tau+\frac{1}{m\omega}} \langle u|e^{\alpha_0 a^\dagger} a^\dagger a e^{\alpha_0 a}|v\rangle + \left(\frac{\omega}{4} + \frac{1}{8m}\right) e^{-2\tau+\frac{1}{m\omega}} \langle u|e^{\alpha_0 a^\dagger} e^{\alpha_0 a}|v\rangle + \sum_n a_n e^{n\tau+\frac{1}{2}\left(\frac{n}{\sqrt{2m\omega}}\right)^2} \langle u|e^{\beta_n a^\dagger} e^{\beta_n a}|v\rangle , \tag{2.23}$$

where

$$\alpha_0 = \frac{-2}{\sqrt{2m\omega}}, \tag{2.24a}$$

$$\beta_n = \frac{n}{\sqrt{2m\omega}}. \tag{2.24b}$$

Of course by increasing the value of N we recover the whole Hilbert space of the wave function. As will be demonstrated in the following sections, the advantage of our approach is that, in general, we need only very small basis sets for accurate results.

III. APPLICATION TO THE ENERGY LEVELS OF THE HYDROGEN ATOM

As a test of our approach, we first apply the two-step method to solve the textbook problem of the radial part of the energy spectrum of the hydrogen atom. This problem is a special case of the Kratzer potential in the molecular vibrational problem [5]. We start with the Hamiltonian

$$H = \frac{-1}{2r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right) + V_{\text{eff}}(r), \tag{3.1}$$

where

$$V_{\text{eff}}(r) = \frac{-1}{r} + \frac{l(l+1)}{2r^2}. \tag{3.2}$$

Following the step taken in Sec. II, we insert in Eq. (2.17)

$$a_{-1} = -1 \tag{3.3}$$

and

$$a_{-2} = \frac{l(l+1)}{2}. \tag{3.4}$$

We now follow the steps described in Sec. II. We obtain from variation conditions (2.20) the following values of ω and τ for each angular momentum:

	$l=0$	$l=1$	$l=2$
ω	0.8090169944	1.770690633	2.762468905
τ	0.5031802721	1.566302861	2.303745890

It is instructive to know that with these values of ω and τ, we obtain from (2.19) the following unperturbed ground-state energies for different l:

	$l=0$	$l=1$	$l=2$
E_0	-0.4117617151	-0.1202404016	-0.05467250676
E_{exact}	-0.5	-0.125	-0.05555555555

Considering the fact that the transformation

$$r = e^x$$

is quite arbitrary, these values are very impressive. We can improve these results by including the corrections from the truncated basis vectors around these ground states as described in Sec. II. The numerical results are presented in Table I. Notice the extremely fast rate of convergence for all the cases with the angular momentum $l \neq 0$. It is noteworthy that with only a 5×5 matrix we obtain the energy level for the lowest state with an error less than 0.5% for $l = 1$ and with an error even less than 0.02% for $l \geq 2$. In general, the rate of convergence of the series increases as the angular momentum l increases. This is due to the effective repulsive angular potential that forces the wave function to stay away from the origin $r = 0$, which corresponds to $x = -\infty$ for the transformed variable. In principle one needs an infinite number of harmonic basis functions, which are only Hermite functions, with suitably chosen frequency and origin, to effectively describe the behavior at $x = -\infty$. Another success of the method is that even for the case of $l = 0$, which has a pure Coulomb potential with a shape that does not resemble the harmonic potential at all, we still obtain a series with an acceptable degree of convergence.

IV. APPLICATION TO THE VIBRATION-ROTATIONAL ENERGY LEVELS OF THE $H_2{}^+\ {}^2\Sigma_G$ STATE

In this section, we apply our method to calculate the vibrational rotational energy levels of the $H_2{}^+\ {}^2\Sigma_g$ state. We start by fitting the published adiabatic potential of Bishop [6] with the following terms:

$$\begin{aligned} U(r) = {} & 0.001\,470\,89r^3 - 0.025\,732\,87r^2 \\ & +0.168\,192\,2r - 0.883\,832\,1 \\ & -0.231\,036\,3r^{-1} + 0.698\,371\,2r^{-2} \\ & -0.183\,251\,9r^{-3} + 0.004\,396\,873r^{-6} . \end{aligned}$$

The fitted function has error $\leq 6.23\times10^{-7}$ throughout the published range in Ref. [6]. With this trial potential we can then calculate the vibrational-rotational energy levels following the steps described in Sec. II. Table II gives the results calculated with our two-step method. As can be seen in the table, a basis of 10 already yields very accurate results. For comparison, we also list in Table III the calculated result of Hunter and Pritchard [7]. Our results are in good agreement with theirs. To conclude this section we would like to point out that our accuracy of the vibrational-rotational energies is really limited by the accuracy of the published potential data used which has only six digits of accuracy. Because of the fast convergence of our approach we could turn the procedure around and give an accurate representation of the

TABLE I. Energy levels of the H atom calculated with the two-step method (in atomic units).

State	Size of basis	v=0	v=1	v=2
J=0	1	-0.4117617151		
	5	-0.4768172894	-0.1021400099	
	10	-0.4929293606	-0.1222993568	-0.0486263492
	20	-0.4991402530	-0.1248449940	-0.0549109917
	30	-0.4998214128	-0.1249768894	-0.0555010067
	40	-0.4999523168	-0.1249942691	-0.0555493683
	50	-0.4999850738	-0.1249982031	-0.0555545030
	60	-0.4999947705	-0.1249993617	-0.0555553001
	70	-0.4999980074	-0.1249997538	-0.0555554724
J=1	1	-0.1202404016		
	5	-0.1244728750	-0.0527994198	
	10	-0.1249578808	-0.0554628267	-0.0305459624
	20	-0.1249993633	-0.0555545560	-0.0312350807
	30	-0.1249999718	-0.0555555370	-0.0312497856
	40	-0.1249999980	-0.0555555547	-0.0312499921
	50	-0.1249999998	-0.0555555555	-0.0312499997
	60	-0.1250000000	-0.0555555555	-0.0312500000
	70	-0.1250000000	-0.0555555555	-0.0312500000
J=2	1	-0.0546725068		
	5	-0.0554923201	-0.0305658262	
	10	-0.0555532731	-0.0312392606	-0.0198625744
	20	-0.0555555457	-0.0312499589	-0.0199989652
	30	-0.0555555554	-0.0312499998	-0.0199999948
	40	-0.0555555555	-0.0312500000	-0.0199999999
	50	-0.0555555555	-0.0312500000	-0.0200000000
	60	-0.0555555556	-0.0312500000	-0.0200000000
	70	-0.0555555556	-0.0312500000	-0.0200000000

TABLE II. Vibrational-rotational eigenenergies of the $H_2{}^+ \, {}^2\Sigma_g$ state calculated with the two-step method (in atomic units).

State	Size of basis	v=0	v=1	v=2	v=3
J=0	5	-0.5971382158	-0.5871485934	-0.5776161238	-0.5671315359
	10	-0.5971384753	-0.5871540411	-0.5777491563	-0.5688995567
	15	-0.5971384758	-0.5871540672	-0.5777494212	-0.5689037269
	20	-0.5971384758	-0.5871540672	-0.5777494215	-0.5689037302
	25	-0.5971384758	-0.5871540672	-0.5777494215	-0.5689037302
J=1	5	-0.5968728832	-0.5868972495	-0.5773790999	-0.5669098405
	10	-0.5968731407	-0.5869026736	-0.5775112734	-0.5686747544
	15	-0.5968731412	-0.5869026993	-0.5775115360	-0.5686788801
	20	-0.5968731412	-0.5869026994	-0.5775115363	-0.5686788834
	25	-0.5968731412	-0.5869026994	-0.5775115364	-0.5686788834
J=2	5	-0.5963443333	-0.5863965882	-0.5769069757	-0.5664682596
	10	-0.5963445867	-0.5864019656	-0.5770374505	-0.5682270109
	15	-0.5963445872	-0.5864019907	-0.5770377088	-0.5682310492
	20	-0.5963445872	-0.5864019908	-0.5770377092	-0.5682310524
	25	-0.5963445872	-0.5864019908	-0.5770377092	-0.5682310524

TABLE III. The nonadiabatic vibrational-rotational eigenenergy data of the $H_2{}^+ \, {}^2\Sigma_g$ state from Ref. [7] (in atomic units).

State	v=0	v=1	v=2	v=3
J=0	-0.59713873	-0.58715477	-0.57775080	-0.5689070
J=1	-0.59687339	-0.58690341	-0.57751275	-0.56868221
J=2	-0.59634483	-0.58640266	-0.57703894	-0.56823446

TABLE IV. The ground-state eigenvalues for the effective potential $V_{\text{eff}}(r) = r^2 + \lambda r^{-5/2}$ with a small basis of size $n = 1, 2, 3, 4, 5$.

λ	n=1	n=2	n=3	n=4	n=5
1000	47.05216415	45.69872984	45.29296739	45.11745318	45.02872555
100	17.79206926	17.61000440	17.60401631	17.55931024	17.54614547
10	7.863260313	7.863260313	7.861584844	7.748053221	7.745459998
1	4.630565477	4.625574007	4.624185060	4.370980278	4.366055340
0.1	3.793859589	3.793474951	3.793379314	3.428807286	3.404993877
0.01	3.668123158	3.668117869	3.668116525	3.277929848	3.245566494
0.001	3.654648849	3.654648794	3.654648780	3.261504743	3.228025413
0	3.653140284	3.653140284	3.65140284	3.259662384	3.226055328

TABLE V. The energy levels for the effective potential $V_{\text{eff}}(r) = r^2 + \lambda r^{-5/2}$. The data in parentheses are the so-called exact values in Table I of Ref. [8].

λ	Size of basis	v=0	v=1	v=2	v=3
1000	10	44.95665329	49.19695450	53.45488529	57.76290195
	20	44.95548513	49.18637920	53.40678110	57.61773426
	30	44.95548479	49.18637443	53.40674658	57.61756136
	40	44.95548479	49.18637443	53.40674656	57.61756121
		(44.955485)			
100	10	17.54198882	21.75488562	25.94647158	30.13117606
	20	17.54189023	21.75406316	25.94338634	30.11450465
	30	17.54189018	21.75406266	25.94338402	30.11448618
	40	17.54189018	21.75406266	25.94338402	30.11448614
		(17.541889)			
10	10	7.735509397	11.91621330	16.13766716	20.64985495
	20	7.735111823	11.90635159	16.04242601	20.16855994
	30	7.735111107	11.90629966	16.04155754	20.15415750
	40	7.735111104	11.90629916	16.04154376	20.15377173
	50	7.735111103	11.90629915	16.04154343	20.15375983
	60	7.735111103	11.90629915	16.04154341	20.15375941
		(7.735111)			
1	10	4.322657082	8.499250773	13.10098094	18.77358554
	20	4.317394214	8.423344741	12.53023946	16.79978596
	30	4.317314035	8.421255664	12.49580192	16.57759398
	40	4.317311775	8.421170909	12.49305495	16.55208019
	50	4.317311693	8.421165219	12.49282232	16.54860468
	60	4.317311690	8.421164658	12.49280197	16.54803999
	80	4.317311689	8.421164603	12.49279875	16.54795329
	100	4.317311689	8.421164603	12.49279869	16.54795056
		(4.317311)			
0.1	10	3.306362789	7.491640507	12.37487900	18.67913170
	20	3.271021203	7.317164096	11.42823441	15.87062046
	30	3.267428695	7.305347000	11.33916454	15.45101857
	40	3.266947599	7.304173016	11.32948122	15.36919740
	50	3.266882416	7.304040190	11.32837644	15.35043123
	80	3.266873037	7.304022879	11.32812008	15.34625652
	110	3.266873026	7.304022836	11.32811848	15.34621351
		(3.266873)			
0.01	10	3.122071712	7.307492494	12.21570500	18.61258869
	20	3.057625399	7.082862071	11.18103966	15.64737355
	30	3.043650310	7.054453505	11.07016757	15.18671733
	40	3.039278980	7.047379639	11.05402752	15.08536075
	50	3.037715675	7.045039695	11.05027337	15.05913723
	100	3.036737565	7.043574404	11.04803915	15.05142854

TABLE V. *(Continued)*.

λ	Size of basis	v=0	v=1	v=2	v=3
	150	3.036729497 (3.036729)	7.043562198	11.04802339	15.05140499
0.001	10	3.101099879	7.286498114	12.19626428	18.60289292
	20	3.031550554	7.053954469	11.14976131	15.61816566
	30	3.014839465	7.021468576	11.03426336	15.15096915
	40	3.008904488	7.012104231	11.01563477	15.04549559
	50	3.006417517	7.008416661	11.01028735	15.01683363
	60	3.005263579	7.006710346	11.00783769	15.00966413
	70	3.004689097	7.005848549	11.00665477	15.00744213
	80	3.004388407	7.005394776	11.00607171	15.00665412
	90	3.004225253	7.005149327	11.00576853	15.00627958
	100	3.004134344	7.005013020	11.00559946	15.00605704
	110	3.004082668	7.004935509	11.00550180	15.00593576
	120	3.004052866	7.004890744	11.00544552	15.00587069
	130	3.004035513	7.004864682	11.00541301	15.00583323
	140	3.004025358	7.004849438	11.00539398	15.00581061
	150	3.004019406 (3.004022)	7.004840503	11.00538278	15.00579742
0	10	3.098734060	7.284129392	12.19405285	18.60177089
	20	3.028576680	7.050654014	11.14617892	15.61480736
	30	3.011518609	7.017655474	11.03010423	15.14682101
	40	3.005369231	7.007978710	11.01113424	15.04081810
	50	3.002742931	7.004088431	11.00554697	15.01180966
	60	3.001494954	7.002244038	11.00292390	15.00440882
	70	3.000855120	7.001285245	11.00161752	15.00203997
	80	3.000507991	7.000762166	11.00094766	15.00115758
	90	3.000311277	7.000466600	11.00058255	15.00071304
	100	3.000195799	7.000293610	11.00036798	15.00043624
	110	3.000125955	7.000188944	11.00023637	15.00027472
	150	3.000025632	7.000038447	11.00004806	15.00005597

potential curve by fitting the very accurate experimental energy levels if they were available.

V. APPLICATION OF THE TWO-STEP METHOD TO THE CASE OF A SPIKED OSCILLATOR

If we look carefully at the derivation in Sec. II we can easily see that in our prototype of the potential

$$a_n r^n$$

in Eq. (2.2), the exponent n need not be restricted to either positive or negative integers. In fact, the whole derivation and formulas in Sec. II can be repeated without change for exponents with any real values of n. In this section we apply our method to the so-called spiked harmonic oscillator with the effective potential

$$V_{\text{eff}}(r) = r^2 + \lambda r^{-5/2} + \frac{l(l+1)}{r^2}, \tag{5.1}$$

which has been studied by several authors [8, 9]. We present in Table IV the calculated results with basis size ≤ 5 and in Table V results from a larger basis. As can be seen from the tables, the rate of convergence is very fast for large and moderate values of the coupling constant λ. For very small values of the coupling constant the rate of convergence is much slower. But throughout the whole range of values of λ, the result from one basis function, the "bare ground state," always gives a very respectable approximation. It is instructive to compare our results with the work in Ref. [8], which used unmodified Hermite polynomials with odd degree in order to satisfy the Dirichlet boundary condition

$$u(0) = 0$$

at the origin $r = 0$. This selection of the basis functions accounts for the fact that for a very small value of λ, the value in Table I of Ref. [8] gives the wrong impression that the variational method behaves properly in that work. As pointed out in Refs. [8] and [9], the energy eigenvalues in that approach decrease very slowly when increasing the number of basis states. For moderate and large values of λ, we obtain in general a faster rate of convergence. The "exact" value can easily be read off from the table. In our approach the slower rate of convergence for the small coupling constant λ shows up explicitly. We can always be certain about how close our calculated result is to the exact value by looking at the rate of convergence as the size of the basis is increased. There is no abnormal behavior that we can detect. The slow convergence for very small λ is due to the fact that

TABLE VI. The ground-state and first-excited-state eigenvalues of the potential form $V_{\text{eff}}(r) = r^2 + 0.4r^{-4}$. We compare our results with those of Ref. [11].

Size of basis	E_0	E_1
1	4.248960615	
10	4.033245178	8.364117224
20	4.031984855	8.315811300
30	4.031971811	8.314610746
40	4.031971457	8.314566572
50	4.031971440	8.314564429
60	4.031971440	8.314564228
70	4.031971440	8.314564274
80	4.031971440	8.314564272
90	4.031971440	8.314564272
100	4.031971440	8.314564272
Ref. [11]	4.03197134	8.31456538

we need many basis functions to access effectively the region $x = -\infty$ for the transformed variable, which corresponds to $r = 0$. Related to this behavior is the fact that in our approach, the Dirichlet boundary condition at the origin $r = 0$ is automatically taken care of by this transformation.

VI. CONCLUSION AND COMMENTS

In this paper we have described a powerful two-step method to solve the diatomic vibrational-rotational problem with a potential of the form (2.2)

$$V(r) = \sum_n a_n r^n \ ,$$

where the exponents n can be any real numbers. As mentioned in Refs. [2] and [4], the physics of the fast convergence of the numerically calculated results is due to the fact that we have, in the first step, used an operator formalism to carry through analytically the variation principle for the "bare" ground state. Any "large coherent" effect is believed to have been taken care of by this first variational step. The remaining corrections are believed to be small. Notice that in addition to the ground state, we also obtained from the diagonalization process accurate results for the low-lying excited states. As demonstrated in Ref. [4], since we have also obtained converged eigenstates in terms of a harmonic basis, we can easily obtain accurate Frank-Condon factors for rotational-vibrational transitions.

Our method is expected to be very efficient for any potential that has only one minimum. For the more difficult case of tunneling where the potential has two or more deep minima, the rate of convergence is expected to be slower. However, as has been shown in Ref. [2], a modified version of our method can easily furnish accurate results even in this case.

To conclude this paper, we would like to point out that a class of problems called singular anharmonicities, with the effective potential

$$V_{\text{eff}}(r) = ar^2 + br^{-4} + cr^{-6},$$

which have been discussed by several authors recently, coincides with our prototype potentials. Our method provides a uniformly simple, straightforward and very efficient way of yielding accurate energies (Tables VI and VII). We can easily detect some of the numerical errors from the Runge-Kutta method, which was used for the

TABLE VII. The ground-state and first-excited-state eigenvalues of the potential $V_{\text{eff}}(r) = r^2 + br^{-4} + 0.8r^{-6}$. We compare our results with Table I of Ref. [12].

State	No. of basis		b=1.00	b=1.02	b=1.04	b=1.06
ground state	1		5.027246147	5.033808881	5.040343902	5.046851456
	10		4.934905169	4.941459452	4.947987153	4.954488501
	20		4.934720931	4.941276026	4.947804530	4.954306675
	30		4.934719669	4.941274776	4.947803293	4.954305450
	40		4.934719655	4.941274762	4.947803279	4.954305436
	50		4.934719654	4.941274761	4.947803279	4.954305436
Ref. [12]	r_0	r_∞	b=1.00	b=1.02	b=1.04	b=1.06
ground state	0.3	3.5	4.87670	4.88368	4.89063	4.89754
	0.25	4.0	4.87598	4.88295	4.88989	4.89680
	0.2	4.5	4.87593	4.88294	4.88986	4.89677
State	No. of basis		b=1.00	b=1.02	b=1.04	b=1.06
first excited state	10		9.468702927	9.475079026	9.481432857	9.487764583
	20		9.449604002	9.456067353	9.462507935	9.468925909
	30		9.449471368	9.455935682	9.462377220	9.468796142
	40		9.449469378	9.455933714	9.462375273	9.468794216
	50		9.449469325	9.455933661	9.462375221	9.468794165
Ref. [12]	r_0	r_∞	b=1.00	b=1.02	b=1.04	b=1.06
first excited state	0.3	3.5	9.4414	9.4487	9.4560	9.4631
	0.25	4.0	9.3787	9.3857	9.3926	9.3995
	0.2	4.5	9.3736	9.3806	9.3875	9.3944

"reference" exact energies in Refs. [11–13]. By its very nature, the Runge-Kutta method is well known to be difficult in providing extremely accurate results. Details of this work will be presented in a future publication.

The generalization of our two-step method to systems with two or more degrees of freedom is straightforward. In that case, the first step of carrying out the variation principle analytically also eliminates the need of a very time-consuming selection of basis sets by numerical trial-and-error methodology.

ACKNOWLEDGMENTS

This work is supported by the The National Council of the Republic of China.

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