Two-step approach to the Morse-potential derivation of the energy spectrum and its application to Frank-Condon factors

Chen-Shiung Hsue
*Institute of Physics, National Tsing Hua University, Hsin-Chu, Taiwan, Republic of China**
and Institut für Theoretische Physik II, Ruhr-Universität Bochum,
D-4630 Bochum 1, West Germany
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A recently proposed two-step method is applied to the quantum-mechanical problem of one-dimensional Morse potential. The method is composed of two steps. In the first step a variational principle is applied to a generalized coherent-state ansatz which in the present case is nothing but a Gaussian with a shifted origin and modified frequency. Correlation corrections are then added in the second step by standard perturbation. The "rigorous formula" for the energy spectrum is derived by a lowest-order perturbation calculation. As a severe test of the theory, we have applied the method to calculate the Frank-Condon factors. The agreement with numerical calculation is excellent over eight orders of magnitude.

I. INTRODUCTION

The Morse potential[1] and its superpositions have been widely used as an approximation to interatomic potentials. The vibrational energy spectrums were usually obtained by approximating pole conditions on the gamma functions. But the eigenfunctions obtained[2] are difficult to be used for evaluating Frank-Condon factors.[2-6] In an attempt to study the unharmonic effects, Kono, Huo, and Lin[6] showed that straightforward harmonic approximations usually yield unreliable results for the Frank-Condon factors in comparison with numerical integrated values.

Recently, we have proposed a two-step method to solve the anharmonic oscillators.[7] The method is heavily influenced by the coupled-cluster method (CCM)[8] of the many-body problems. In the first step a generalized coherent-states ansatz of SUB 2 approximation in the language of CCM is introduced. The variational principle is then applied and is solved via a Hartree-Bogoliubov transformation. In the present case this is equivalent to an optimized Gaussian with shifted origin and modified frequency.[7,9-12] Correlation corrections are then added in the second step by CCM or various methods of perturbation, with the confidence that all the disastrous coherent effects have been taken care of in the first step. The method is simple, straightforward, and has a clear physical picture. It has been successfully applied to the ϕ_2^4 quantum field theory,[9-11] coupled oscillators,[12] and electron correlations.[13]

In Sec. II we apply the two-step method to solve the vibration spectrum of the Morse potential. The widely used "exact" expression for the energy spectrum is derived by keeping terms up to first order in the anharmonicity. The best harmonic approximation to the Morse potential is one with shifted origin and modified frequency. In Sec. III we calculate the Frank-Condon factors. It is shown that the corrections in the second step are very important in obtaining satisfactory results. The conclusion and discussions are also given in that section.

II. THEORY

The Hamiltonian for a one-dimensional vibration for the Morse potential can be written as[14]

$$H=\frac{\hbar^2}{Mr_0^2}\left[-\frac{1}{2}\frac{\partial^2}{\partial x^2}+\frac{1}{2}\gamma^2(1-2e^{-\alpha x}+e^{-2\alpha x})\right], \quad (1)$$

where

$$\gamma^2=2MDr_0^2/\hbar^2 . \quad (2)$$

To write (1) in a second quantized form we face the problem with the choice of the correct origin and the frequency. However, this problem can be put in a form of a generalized coherent-state ansatz of the SUB 2 approximation in the language of CCM.[7-12] The Hamiltonian can then be transformed by a Hartree-Bogoliubov transformation,[7,9-12] and as already mentioned the only result in our case is a change of the origin and the frequency. We can therefore skip the whole step by just introducing the creation and annihilation operators through

$$\begin{aligned} x&=(1/\sqrt{2\gamma\alpha\omega})(a+a^\dagger)+\tau, \\ \frac{1}{i}\frac{\partial}{\partial x}&=i\left(\frac{\gamma\alpha\omega}{2}\right)^{1/2}(a^\dagger-a), \end{aligned} \quad (3)$$

where the creation and annihilation operators $a^\dagger$ and a satisfy the commutator relation

$$[a,a^\dagger]=1 . \quad (4)$$

The frequency ω and the shift of the origin τ are to be determined by the variational principle. With use of the operator identity

$$e^{A+B}=e^Ae^Be^{-[A,B]/2} , \quad (5)$$

which holds when $[A,B]$ is a c number. We may write the Hamiltonian (1) in a normal ordered form:

$$\begin{aligned} M=\hbar\omega_0\Bigg[&-\frac{\omega}{4}(a^{\dagger 2}+a^2-2a^\dagger a-1)+\frac{\eta}{4}\Bigg\{1-2\exp\left[-\alpha\tau+\frac{1}{2\eta\omega}\right]\exp\left[-\left(\frac{1}{\eta\omega}\right)^{1/2}a^\dagger\right] \\ &\times\exp\left[-\left(\frac{1}{\eta\omega}\right)^{1/2}a\right]+\exp\left[-2\alpha\tau+\frac{2}{\eta\omega}\right]\exp\left[-2\left(\frac{1}{\eta\omega}\right)^{1/2}a^\dagger\right]\exp\left[-2\left(\frac{1}{\eta\omega}\right)^{1/2}a\right]\Bigg\}\Bigg], \end{aligned} \quad (6)$$

where

$$\hbar\omega_0=\hbar^2\gamma\alpha/Mr_0^2 \ , \tag{7}$$

and

$$\eta=2\gamma/\alpha \ . \tag{8}$$

In the standard treatment, the fact that η is a big number plays an important role. This fact will also show up in our treatment. The bare ground state for (6) satisfies

$$a|0\rangle=0 \ . \tag{9}$$

Its expectation value is given by

$$E=\langle 0|H|0\rangle$$
$$=\hbar\omega_0\left\{\frac{\omega}{4}+\frac{\eta}{4}\left[1-2\exp\left(\alpha\tau+\frac{1}{2\eta\omega}\right)+\exp\left(-2\alpha\tau+\frac{2}{\eta\omega}\right)\right]\right\} \ . \tag{10}$$

Application of the variational principle now yields

$$\partial E/\partial\tau=0=\exp(-\alpha\tau+1/2\eta\omega)-\exp(-2\alpha\tau+2/\eta\omega) \ , \tag{11}$$

or

$$\alpha\tau=3/2\eta\omega \ , \tag{12}$$

and

$$\partial E/\partial\omega=0 \ , \tag{13}$$

which leads to

$$\omega^2=e^{-1/\eta\omega} \ . \tag{14}$$

Inserting (12) and (14) into the Hamiltonian (6) and keeping only the diagonal terms up to $1/\eta$ and off-diagonal terms up to $1/\sqrt{\eta}$, we can simplify (6) and arrive at

$$H=\hbar\omega_0\left[\frac{\omega}{4}+\frac{\eta}{4}\left(\frac{1}{\eta\omega}+\frac{1}{2(\eta\omega)^2}\right)+\omega a^\dagger a+\frac{7}{8\eta}(a^{\dagger 2})a^2-\frac{1}{4}\left(\frac{\omega}{\eta}\right)^{1/2}[(a^{\dagger 3})+3(a^{\dagger 2})a+3a^\dagger a^2+a^3]\right] \ . \tag{15}$$

Notice the absence of the linear and the quadratic terms in the creation and annihilation operators. This is an essence of the Hartree approximation. The advantage of our Hartree-Bogoliubov transformation lies in the physical interpretation of the generalized coherence ansatz.[7] Any disastrous coherent effect has been taken care of in the first step. Further perturbation around this coherent state is expected to be small and harmless. We therefore apply the standard perturbation theory. The zeroth-order eigenvector of (15) is given by

$$|n\rangle=\frac{(a^\dagger)^n}{\sqrt{n!}}|0\rangle \ , \tag{16}$$

and the first-order approximation is given (keeping only the lowest order in $1/\sqrt{\eta}$) by

$$1/12\sqrt{\eta}[\sqrt{(n+1)(n+2)(n+3)}|n+3\rangle-\sqrt{n(n-1)(n-2)}|n-3\rangle]+3/4\sqrt{\eta}[n\sqrt{n+1}|n+1\rangle-(n-1)\sqrt{n}|n-1\rangle] \ . \tag{17}$$

With use of (17) and the expansion from (14)

$$\omega=1-1/2\eta+O(1/\eta^2) \ , \tag{18}$$

we obtain for the energy spectrum by a second-order perturbation keeping terms up to order $1/\eta$, the "rigorous result":

$$E_n=\hbar\omega_0[(n+\tfrac{1}{2})-(1/\eta)(n+\tfrac{1}{2})^2] \ . \tag{19}$$

Systematical improvement is straightforward. In most cases, this is not necessary due to the smallness of $1/\eta$.

III. APPLICATION TO FRANK-CONDON FACTORS AND DISCUSSIONS

As a severe test of our theory, we have applied it to calculate the Frank-Condon factors $|\langle\nu'|\nu''\rangle|^2$, recently treated by Kondo, Huo, and Lin.[6] The original frequencies are $\omega_1=1160$ cm^{-1}, $\omega_2=870$ cm^{-1}, $\omega_1/\eta_1=1$ cm^{-1}, and $\omega_2/\eta_2=2$ cm^{-1}. In addition to the corrected frequencies due to Eq. (14), the original shift $d=0.825$ is now changed, because of Eq. (12), to

$$d'=\sqrt{(\omega_1'/\omega_1)}\{d+(3/4\sqrt{2})[(1/\sqrt{\eta_2})-(1/\sqrt{\eta_1})]\} \ . \tag{20}$$

The results of the calculation are given in Table I. The first entry is the harmonic approximation with the correct frequency and shift. In the second entry, we include via (17) the lowest correction in order of $1/\sqrt{\eta}$, or $1/\sqrt{\eta_2}$. The comparison with the numerical results (last entries) is very satisfactory.[15] In the third entries we include the whole first-order correction to the Hamiltonian (15). The agreement with the numerical results is excellent over eight orders of magnitude. If necessary, a systematic improvment can be obtained with use of our method.

We conclude our paper by a few observations: Although the first-order correction to the wave function is very small in amplitude, sometimes it is the dominating term in the Frank-Condon factors due to its rapidly changing in magnitude. Any harmonic approximation to nonlinear potentials is doomed to fail sooner or later. One should be very cautious in treating the corrections. Similary, the Hamiltonian (15) may be obtained by retaining the correct order from a truncation in the expansion of (1) in powers of x up to the sixth order. But due to the rapid cancellation, the energy obtained by directly diagonalizing the truncated Hamiltonian is usually worse than the "rigorous" result (19). In conclusion, we have shown in this paper and a related series of papers[7,9,11,12] that the two-step method is simple, straightforward, and yet very powerful in yielding accurate results. It is appealing because of its clear physical picture. The extension of our method to superpositions of the Morse potential and other nonlinear potentials is straightforward.

TABLE I. Frank-Condon factors $|\langle\nu'|\nu''\rangle|^2$ for Morse potentials. The suitable parameters are given in the text. In our notation, ν' and ν'' represent the ν'th and ν''th vibrational level corresponding to ω_1 and ω_2, respectively. The first entry is the harmonic approximation. The second includes the lowest correction. The third entry contains the whole first-order correction. The last entry is the numerical result from Ref. 6. The entry 2.49(-1) means 2.49×10^{-1}, etc.

	0	1	2	3
	7.29(−1)	1.91(−1)	5.98(−2)	1.52(−2)
	7.31(−1)	2.00(−1)	5.48(−2)	1.21(−2)
0				
	7.31(−1)	2.00(−1)	5.45(−2)	1.20(−2)
	7.27(−1)	2.02(−1)	5.55(−2)	1.24(−2)
	2.55(−1)	3.44(−1)	2.18(−1)	1.20(−1)
	2.47(−1)	3.27(−1)	2.52(−1)	1.22(−1)
1				
	2.46(−1)	3.27(−1)	2.51(−1)	1.20(−1)
	2.49(−1)	3.20(−1)	2.52(−1)	1.24(−1)
	1.55(−2)	4.13(−1)	1.30(−1)	1.67(−1)
	2.39(−2)	3.97(−1)	9.44(−2)	2.06(−1)
2				
	2.35(−2)	3.94(−1)	9.36(−2)	2.06(−1)
	2.42(−2)	3.95(−1)	9.03(−2)	2.02(−1)
	2.74(−4)	4.92(−2)	4.86(−1)	3.14(−2)
	1.11(−4)	8.11(−2)	4.42(−1)	5.86(−3)
3				
	1.26(−4)	7.61(−2)	4.37(−1)	5.26(−3)
	1.67(−4)	7.94(−2)	4.30(−1)	5.12(−3)
	4.13(−4)	5.00(−4)	1.00(−1)	4.91(−1)
	2.96(−4)	1.63(−3)	1.72(−1)	3.98(−1)
4				
	2.45(−4)	1.28(−3)	1.52(−1)	3.96(−1)
	1.64(−4)	2.01(−3)	1.61(−1)	3.73(−1)
	1.06(−5)	1.88(−3)	3.86(−4)	1.64(−1)
	8.43(−5)	1.18(−3)	8.64(−3)	2.87(−1)
5				
	8.36(−5)	1.04(−3)	5.08(−3)	2.39(−1)
	4.60(−5)	4.84(−4)	9.60(−3)	2.52(−1)
	3.51(−6)	7.82(−5)	5.02(−3)	5.78(−5)
	5.07(−7)	5.93(−4)	2.56(−3)	2.87(−2)
6				
	2.90(−6)	5.30(−4)	2.68(−3)	1.29(−2)
	1.29(−6)	2.82(−4)	6.23(−4)	2.92(−2)
	7.21(−7)	2.00(−5)	3.20(−4)	1.03(−2)
	1.97(−6)	9.97(−6)	2.33(−3)	3.81(−3)
7				
	6.25(−7)	2.31(−5)	1.84(−3)	5.48(−3)
	1.72(−7)	1.73(−5)	9.20(−4)	2.69(−4)
	5.38(−9)	5.83(−6)	6.34(−5)	9.61(−4)
	3.46(−7)	1.53(−5)	7.93(−5)	6.71(−3)
8				
	3.53(−7)	4.93(−6)	9.04(−5)	4.69(−3)
	1.03(−7)	4.74(−7)	1.06(−4)	2.07(−3)
	1.67(−8)	2.30(−8)	2.61(−5)	1.47(−4)
	6.93(−9)	3.84(−6)	6.44(−5)	3.96(−4)
9				
	5.91(−9)	3.11(−6)	2.21(−5)	2.37(−4)
	5.91(−9)	8.72(−7)	9.89(−8)	4.22(−4)

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*Permanent address.
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[15]The only marked difference is the entry $|\langle 9|2\rangle|^2$. The numerical result given in Ref. 6 changes very rapidly here. We do not know at this moment whether this discrepancy is a real one or is only due to a numerical cancellation.