

An application of hypervirial perturbation theory to calculate energy eigenvalues of the Morse potential for various diatomic molecules

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Abstract. The Schrödinger equation with the potential $V(r) = D[\exp(-2\beta(r - r_e)) - 2\exp(-\beta(r - r_e))]$ is treated in the framework of the hypervirial-renormalization parameter scheme. The energy eigenvalues of various eigenstates for different molecules are calculated.

Keywords. Schrödinger equation; Morse potential; eigenvalues.

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1. Introduction

The Schrödinger equation with the potential

$$V(r) = D[\exp(-2\beta(r - r_e)) - 2\exp(-\beta(r - r_e))] \quad (1)$$

has frequently been used to describe vibrating molecules. In quantum mechanics textbooks, the energy levels of potential (1) are often derived to the second order of the approximation within the framework of the Rayleigh-Schrödinger perturbation theory [1–3]. On the other hand, the Schrödinger equation with potential (1) has been studied by Hajj *et al* [4] using the Numerov finite difference approach to calculate the eigenvalues for the first five states. Also, Adam *et al* [5] have used a perturbative numerical technique to compute the energy levels for various eigenstates. Johnson [6] applied the Numerov–Cooley integration method to the Morse potential and obtained good results for the energy eigenvalues. Fernandez and Castro [7] applied diagonal and off-diagonal hypervirial relationships in order to obtain recursion formulae for matrix elements related to the perturbed Morse oscillator model. Their results simplify the variational and perturbative calculation of the energy eigenvalues for the Morse potential. Fernandez and Ogilvie [8] developed an approach to calculate analytic perturbation corrections of large order to the vibrational-rotational energies; their approach is based on a combination of perturbation theory and the hypervirial and Hellmann–Feynman theorems. Bonatsos *et al* [9] have shown that the quantum algebra $SU_q(1, 1)$ can be used for the description of the vibrational spectra of diatomic molecules, in the same way as the quantum algebra $SU_q(2)$ can be used for the description of the rotational spectra of molecules.

In this paper we outline the formalism for the hypervirial calculation and obtain recurrence relations involving the energy perturbation coefficients. The renormalization parameter K plays an important role in ensuring the convergence of our

calculations. We list the results of the calculated energy eigenvalues for many molecules for various eigenstates in tables (1–3) and compare our results with those available in the literature. Our calculation intends to test HVPT for a case where the $V(x)$ is an infinite series (not polynomial of low order) and where the numerical accuracy can be tested against an exact formula. K gives convergence- exact formula checks that the converged results is indeed the desired energy value.

2. The Schrödinger equation with the Morse potential

In connection with the description of the vibrational bound states of diatomic molecules, Morse [10] defined the following Schrödinger equation problem.

$$-\frac{d^2\psi(x)}{dx^2} + D[\exp(-2\beta x) - 2\exp(-\beta x)] \psi(x) = E\psi(x) \quad (2)$$

where

$$x = r - r_e \quad (3)$$

The notation for the constants in (2) is the one customarily employed in spectroscopic works, D is the dissociation energy in Å^{-2} referred to the minimum of the potential, r is the internuclear separation in Å , r_e the equilibrium value of r , and β is an adjustable parameter. The vibrations of various diatomic molecules are reasonably well described by the Morse potential. To study small vibrations we can expand $V(x)$ in a series of powers of $x = r - r_e$, where r_e is the value of r for which $V(r)$ has a minimum. The potential in (1) can be rewritten in the form

$$\begin{aligned} V(x) &= D[\exp(-2\beta x) - 2\exp(-\beta x)] \\ &= 4D\exp(-\beta x) \left[\frac{\exp(-\beta x/2) - \exp(\beta x/2)}{2} \right]^2 - D \\ &\equiv 2D\exp(-\beta x)[\cosh(\beta x) - 1] - D \end{aligned} \quad (4)$$

to facilitate its expansion as Taylor series. Truncating this expansion at the x^2 term produces the familiar harmonic oscillator potential. Taking terms up to (say) x^{15} provides an improved fit close to the bottom of the well, but at higher distances the fit becomes unrealistic. We find

$$V(x) = D[-1 + \beta^2 x^2 - \beta^3 x^3 + V_4 \beta^4 x^4 + \dots + V_{14} \beta^{14} x^{14} + V_{15} \beta^{15} x^{15}] \quad (5)$$

with

$$\begin{aligned} V_0 &= -1, \quad V_1 = 0, \quad V_2 = 1, \quad V_3 = -1, \quad V_4 = \frac{7}{12}, \quad V_5 = -\frac{1}{4}, \quad V_6 = \frac{31}{360}, \quad V_7 = -\frac{1}{40}, \\ V_8 &= \frac{127}{20160}, \quad V_9 = -\frac{17}{12096}, \quad V_{10} = \frac{73}{259200}, \quad V_{11} = -\frac{31}{604800}, \quad V_{12} = \frac{2047}{239500800}, \\ V_{13} &= -\frac{1}{760320}, \quad V_{14} = \frac{8191}{43589145600}, \quad V_{15} = \frac{5461}{217945728000} \end{aligned}$$

The coefficients given by (5) alternate in sign; even coefficients take (+ sign) and odd coefficients take (-) sign. We have expanded the potential (5) to a limit in which

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any term beyond that limit makes no difference to our eigenvalues. For our calculations this limit was reached for (15).

In this way the Hamiltonian for this potential can be written in a form which has the unperturbed part

$$H_0 = -\frac{d^2}{dx^2} - D + D\beta^2 x^2. \quad (6)$$

The total Hamiltonian takes the form

$$H = H_0 + D[-\beta^3 x^3 + V_4 \beta^4 x^4 + V_5 \beta^5 x^5 + \dots + V_{14} \beta^{14} x^{14} + V_{15} \beta^{15} x^{15}] \quad (7)$$

The central idea of this work is to expand the potential $V(r)$ in a Taylor series about its minimum value, and solve the resulting approximate problem by hypervirial perturbation theory physically, as the potential well is very deep, the classical turning points for the lowest bound states are very close to the minimum of the well; therefore the particle, even quantum mechanically, can in the main see only the region of the potential near the minimum. We thus expect that the eigenvalues obtained in this way will certainly be accurate only for the first few states. For higher bound states, with their classical turning points further from the minimum, we expect that the accuracy of the approximation will decrease progressively relative to that for the lowest bound states. This is indeed confirmed by the explicit results obtained.

3. Formulation of the problem

The Hamiltonian for the potential described by (1) is

$$H = -\frac{d^2}{dx^2} + V(x) \quad (8)$$

where the potential $V(x)$ can be rewritten in terms of the single perturbation parameter

$$V(x) = \sum_{I=0}^J \lambda V(I) x^I \quad (J = 15) \quad (9)$$

The coefficients $\beta^J V_J D$ given by (7) are replaced by $\lambda V(I)$ in (9). From the hamiltonian given by (8) and using the basic relations for the commutator,

$$\left[\frac{d}{dx}, H \right] = \frac{dV}{dx} \quad (10)$$

$$[x^N, H] = \frac{N}{2}(N-1)x^{N-2} + Nx^{N-1} \frac{d}{dx} \quad (11)$$

we obtain the result

$$\left[x^N \frac{d}{dx}, H \right] = x^N \frac{dV}{dx} + \frac{N}{2}(N-1)x^{N-2} \frac{d}{dx} + 2Nx^{N-1}(V-H). \quad (12)$$

The diagonal hypervirial requirement that $\left\langle \left[x^N \frac{d}{dx}, H \right] \right\rangle$ shall vanish for the bound

states of (7) leads to the result

$$2E(N+1)\langle x^N \rangle = \sum_{I=0}^J \lambda V(I)(2N+2+I)\langle x^{N+I} \rangle - \frac{N}{2}(N^2-1)\langle x^{N-2} \rangle \quad (13)$$

The Hellmann–Feynman theorem and the virial theorem provide relationships between the energy E and the expectation values $\langle x^N \rangle$. Let us assume that the energy E and the expectation values $\langle x^N \rangle$ can be expanded in power series of the perturbation parameter λ as

$$E = \sum E(I)\lambda^I, \quad (14)$$

$$\langle x^N \rangle = \sum A(N, M)\lambda^M. \quad (15)$$

In order to improve the convergence properties of the perturbation series we used a rearrangement of terms in the potential as given by (8). To illustrate this technique it is necessary to write the potential appearing in (5) in a renormalized form involving a parameter K

$$V(x) = V(0) + [\mu - \lambda K]x^2 + \sum_{I=3}^J V(I)\lambda \quad (16)$$

where

$$\mu = V(2) + \lambda K. \quad (17)$$

The use of the renormalization parameter K is helpful in improving convergence. If we use the perturbation expansions (14 and 15) in the hypervirial relation given by (13), we obtain recurrence relations corresponding to the $V(x)$ given by (16) as follows:

$$\begin{aligned} (2N+2)\sum_0^M E(I)A(N, M-I) &= -\frac{N}{2}[N^2-1]A(N-2, M) \\ &- (2N+4)[\mu A(N+2, M) - KA(N+2, M-1)] \\ &+ \sum_{I=3}^J V(I)(2N+2+I)A(N+I, M-1) \end{aligned} \quad (18)$$

Applying the Hellmann–Feynman theorem in the form

$$\frac{\partial E}{\partial \lambda} = \left\langle \frac{\partial H}{\partial \lambda} \right\rangle = \left\langle \frac{\partial V}{\partial \lambda} \right\rangle \quad (19)$$

we obtain a recurrence relation for the energy coefficients in the form

$$(M+1)E(M+1) = \sum_{I=0}^J V(I)A(I, M) - KA(2, M). \quad (20)$$

The unperturbed energy corresponding to the Morse potential can be expressed as

$$E = V(0) + (2n+1)\sqrt{\mu} \quad (n = 0, 1, 2, \dots) \quad (21)$$

The analytic eigenvalues for the Morse potential for bound states are given by Landau (19)

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$$E = -D \left[1 - \frac{\beta}{\sqrt{D}} \left(n + \frac{1}{2} \right) \right]^2 \quad (22)$$

The pure vibrational spectrum (22) is very simple. The spacing between vibrational levels decreases with increasing vibrational quantum number n , and goes to zero when $E = 0$. The number of vibrational levels, however, is finite and can easily be seen to be equal to

$$N = \frac{\sqrt{D}}{\beta} - \frac{1}{2} \quad (23)$$

According to the results (23) there are 19 bound states for the diatomic molecule H_2^+ , and this is confirmed by Adam *et al* [5]. Our method is adequate to calculate the first six bound states, with some convergence problems for higher states. From the recurrence relations (18 and 20) together with the unperturbed energy (21) and initial coefficient $A(0, 0) = 1$, we can calculate the perturbation series for the energy.

4. Discussion and conclusion

We have used the hypervirial-renormalization method to calculate the eigenvalues of the Morse potential for different molecules and for various vibrational quantum numbers n . We diminish convergence problems by using the adjustable renormalization parameter K ; this parameter has been used widely by Witwit [11, 12]. Both the convergence and the accuracy of the results can be controlled by varying the values of K .

We list our results in tables 1–3. We present the eigenvalues for various molecules, as described by the appropriate values of D and β . In tables 1 and 2 we list the energy eigenvalues for the diatomic molecules H_2^+ and HCl; the potential parameters corresponding to these molecules are ($D = 188 \cdot 4355 \text{ \AA}^{-2}$, $\beta = 0 \cdot 711248 \text{ \AA}^{-1}$, $r_e = 1 \cdot 3 \text{ \AA}$) and ($D = 2000 \text{ \AA}^{-2}$, $\beta = 1 \cdot 7 \text{ \AA}^{-1}$, $r_e = 1 \cdot 3 \text{ \AA}$), respectively. Our results are given for the first seven energy levels. The results for H_2^+ are compared with the results of Hajj *et al* [4] and Adam *et al* [5]. It is clear from the listed results in table 1 that there is agreement between our results and their results. For higher states it was found that the renormalized series method faced increasing convergence difficulties, and in general the results decreased in accuracy. We list in table 2 the results for HCl. The results can be compared with corresponding results calculated from the exact formula (22) for the bound states.

We used two different ranges of Taylor series coefficients $\sum_{I=0}^{J=7,15} V(I)$ in order to check the effect on the calculated eigenvalues. The best accuracy was obviously achieved with $J = 15$, with accuracy being reduced with other values of ($J = 7$), this situation was more noticeable at high state numbers such as $n = 5, 6$; We should note that the present technique works equally well for the two forms $V(x) = \sum_{I=0}^J \lambda V(I) x^I$, $\lambda = 1$ and $V(x) = \sum_{I=0}^J \lambda^I V(I) x^I$; $\lambda = \beta$. We used both forms in numerical calculations but for the Morse potential we found that use of the form with various powers of λ did not improve the numerical accuracy.

Table 1. Eigenvalues of Morse potential for H_2^+ . First line represents the present result, second line Adam *et al* [5], third line Hajj *et al* [4]. Our calculations carry out for two different terms number of perturbation expansion. The empty spaces mean these are not reported.

n	$-E_n(n_0 = 15)$	N	K	$-E_n(n_0 = 6)$	N	K
0	178-79853835103	198	400	178-7986447313	155	400
	178-79853835			178-79853835		
	178-79853			178-79853		
1	160-283425629	240	400	160-278522266	220	400
	160-28342563			160-28342563		
	160-28342			160-28342		
2	142-7800603	260	400	142-7947516	230	400
	142-780060347			142-78060347		
	142-78004			142-78004		
3	126-2884425	264	450	126-36845	230	450
	126-28844249			126-28844249		
	126-28840			126-28840		
4	110-80857	220	460	111-260	230	460
	110-80857207			110-80857207		
	110-80849			110-80849		
5	96-3404	240	500	97-78	166	450
	96-340449093			96-340449093		
6	82-884	280	550	80-785	220	600
	82-884073546			82-884073546		

Table 2. First eleven eigenvalues of Schrödinger equation with Morse potential for HCl, first line represents the present calculations, the second line calculations computed from analytic solution given by equation (22).

n	$-E_n$	N	K	$-E_{analytic}$
0	1924-696198876	42	6500	1924-696198876
1	1778-423566295	166	12550	1778-423566295
2	1637-930943825	167	12500	1637-930943825
3	1503-2183213	170	13000	1503-218321355
4	1374-285698	224	18000	1374-285698885
5	1251-13307	240	19000	1251-133076415
6	1133-7604	270	23000	1133-760453945
7	1022-167	270	26000	1022-167831475
8	916-355	272	26000	916-3552090051
9	816-32	275	25000	816-3225865351
10	722-06	300	27000	722-0699640651

The results in table 3 are calculated for the H_2 , HCl, I_2 molecules (for various vibrational quantum numbers ($n = 0$ to 6)); the energy is given in cm^{-1} . Again, our results can be compared with those produced by the exact formula, equation (22). We note that the energy levels calculated by the exact equation (22) agree formally

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Table 3. The eigenvalues of Schrödinger equation with Morse Potential for various molecules, the numerical results yielded by renormalized series, and analytic results computed from equation (22). The potential parameters are given by Siegfried [1]. The empty spaces mean the results cannot be calculated by the renormalized series method.

n	molecules	Numerical (cm^{-1})	N	K	Analytic (cm^{-1})
0	HCl	-35764-09225012	81	12000	-35764-09225012
	H ₂	-36125-80569054	195	2500	-36125-80569054
	I ₂	-12442-90131346	32	8000	-12442-90131346
1	HCl	-32894-28123766	122	13000	-32894-28123766
	H ₂	-31982-62147534	210	2200	-31982-62147534
	I ₂	-12230-08075308	48	8000	-12230-08075308
2	HCl	-30144-47620872	187	16000	-30144-47620872
	H ₂	-28091-709799	233	2400	-28091-709798
	I ₂	-12019-09594289	77	9000	-12019-09594298
3	HCl	-27514-67716145	199	17000	-27514-67716195
	H ₂	-24453-0706587	216	2200	-24453-0706597
	I ₂	-11809-94688324	185	12000	-11809-94688314
4	HCl	-25004-88409880	225	20000	-25004-88409870
	H ₂	-21066-70405955	229	2200	-21066-70405942
	I ₂	-11602-63357346	96	60000	-11602-63357356
5	HCl	-22615-09701356	221	21000	-22615-09701851
	H ₂	-17932-60988	228	2200	-17932-60999
	I ₂	-11397-15601446	132	8000	-11397-15601426
6	HCl	-20345-31592249	210	22000	-20345-31592139
	H ₂	-15050-7866	238	2500	-15050-7854
	I ₂	-11193-5142062	166	100000	-11193-51420522

with the second order of approximation within the framework of standard Rayleigh–Schrödinger perturbation theory. Our results for the renormalized series use different potential and perturbation expansions and this leads to a slight difference in the numerical results.

Our calculated values of the energy levels at low values of n are excellent as compared with the results of Adam *et al* [5] and Hajj *et al* [4]. From our results it can be seen that the hypervirial method with a renormalization parameter K is sufficient to calculate the energy eigenvalue of the first few states without using Padé approximants to overcome the convergence problem. We illustrated the effect of use the of renormalization parameter K on the convergence rate in the following table

K	E_0
0	178.79
10	178.798
50	178.79853
100	178.798538
150	178.7985384
200	178.79853809
400	178.798538103

It is clear from the above table how the renormalization parameter K can be used to give perturbation series with a better convergence.

Although the renormalized series method has calculational elegance at low values of n , it suffers from a drawback that the numerical accuracy and the rate of convergence falls off very rapidly with increasing value of the vibrational quantum number n .

It is interesting to note that the renormalized series method has not been used before to treat Morse potential for various diatomic molecules.

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