Expectation values for Morse oscillators

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Several exact recursion relations for expectation values of different operators are derived for the Morse potential using the hypervirial and Hellmann–Feynman theorems. These results enable one to express the expectation values of other useful operators as series expansions in terms of the dimensionless anharmonicity parameter $\omega_e X_e/\omega_e$. The present results, obtained without explicit use of the eigenfunctions, are compared with similar results derived by other techniques, and it is illustrated how accurate values can be obtained with very little computational effort.

I. INTRODUCTION

Since its introduction over 50 years ago,[1] the Morse potential has proved useful for a wide variety of problems in many diverse fields. It is one of the simplest, two-parameter anharmonic potentials for which one can obtain exact eigenenergies. For many purposes, however, one requires expectation values or matrix elements of various operators, and there exists in the literature a large number of papers devoted to the derivation and applications of these quantities.[2–16] Many of the previous workers have made explicit use of the eigenfunctions expressed in terms of associated Laguerre polynomials and have generated complicated closed form expressions for the various matrix elements. This complexity, however, had deterred their use, and in some cases, because of serious round-off errors incurred in the numerical evaluation, leads to erroneous results.[16] As a consequence, simple asymptotic approximations have been derived that are not only much more convenient, but also have sufficient accuracy for most problems.[15,16]

In the present paper, we first derive several exact recursion relations between expectation values of different operators; these derivations are based on two general quantum mechanical relations (the Hellmann–Feynman[17] and hypervirial[18] theorems) that do not require explicit use of the eigenfunctions.[18,19] These results can then be used in an iterative way to obtain power series expansions in terms of the dimensionless anharmonicity parameter $\omega_e X_e/\omega_e$ for the expectation values of a variety of operators to any degree of accuracy required. We illustrate the method by deriving expressions for several of the more useful operators and compare these results with those obtained via other techniques. Modest accuracy can be obtained with very minimal computational effort, and because of the iterative nature of the algorithm, the present method is ideally suited for calculations carried out on programmable hand calculators.

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II. THEORY

In the present paper, we consider the nonrotating Morse oscillator having a reduced mass μ. (If need be, rotational corrections can be included in a formal but approximate way by defining rotationally dependent parameters[20,21].) The vibrational eigenfunctions $\psi_v(R)$ satisfy the radial Schrödinger equation

$$H\psi_v(R) = -\frac{\hbar^2}{2\mu}\frac{d^2\psi_v(R)}{dR^2} + V(R)\psi_v(R) = E_v\psi_v(R) \tag{1}$$

for the Morse potential

$$V(R) = D_e\{1-\exp[-a(R-R_e)]\}^2 , \tag{2}$$

where D_e and R_e are the depth and the position of the minimum of the well. Introducing the following notation:

$$q = R - R_e , \tag{3}$$

$$y = (1-e^{-aq}) = 1 - Z , \tag{4}$$

$$S = \left(\frac{8\mu D_e}{\hbar^2}\right)^{1/2}\frac{1}{a} = \frac{\omega_e}{\omega_e X_e} , \tag{5}$$

and

$$u = v + 1/2 , \tag{6}$$

the eigenenergies can be written as

$$E_v = 4D_e\left(\frac{u}{S} - \frac{u^2}{S^2}\right) . \tag{7}$$

The diagonal hypervirial theorem[18] for any time-independent operator W expresses the general commutator result

$$\int \psi_v [H, W]\psi_v dR \equiv \langle v|\,[H, W]|v\rangle$$
$$= \langle v|HW - WH|v\rangle = 0 , \tag{8}$$

where H is the Hamiltonian operator in Eq. (1). By choosing

$$W = y^i \frac{d}{dq} \tag{9}$$

and

TABLE I. Expectation values of $y^k = (1-e^{-\alpha q})^k$.

k	$\langle v \mid y^k \mid v \rangle$
0	1
1	$2u/S$
2	$2u/S$
3	$(6u^2-1/2)/S^2+(-4u^3+u)/S^3$
4	$(6u^2+3/2)/S^2+(-4u^3-3u)/S^3$
5	$(20u^3-15u)/S^3+\left(-30u^4+45u^2-\frac{27}{8}\right)/S^4 + \left(12u^5-30u^2+\frac{27}{4}u\right)/S^5$
6	$(20u^3+25u)/S^3+\left(-30u^4-75u^2+\frac{245}{8}\right)/S^4 + \left(12u^5+50u^3-\frac{245}{4}u\right)/S^5$
7	$\left(70u^4-175u^2-\frac{525}{8}\right)/S^4+\left(-168u^5+700u^3-\frac{385}{2}u\right)/S^5 + \left(140u^6-875u^4+\frac{3885}{4}u^2-\frac{1125}{16}\right)/S^6 + \left(-40u^7+350u^5-\frac{1295}{2}u^3+\frac{1125}{8}u\right)/S^7$
8	$\left(70u^4+245u^2+\frac{315}{8}\right)/S^4+\left(-168u^5-980u^2+\frac{3311}{2}u\right)/S^5 + \left(140u^6+\frac{1225}{7}u^4-\frac{20811}{4}u^2+\frac{18\,207}{16}\right)/S^6 + \left(-40u^7-490u^5+\frac{6937}{2}u^2-\frac{18\,207}{8}u\right)/S^7$

$$W = y^j \ , \tag{10}$$

one can derive the following exact recursion relation[12,19]:

$$\langle v|\ y^{k+2}|\,v\rangle = \langle v|\ y^{k+1}|\ v\rangle + \frac{k}{(k+1)S^2}\left\{k^2+4uS\left(1-\frac{u}{S}\right)\right\}\langle v|\ y^k|\ v\rangle - \frac{k}{(k+1)S^2}\left\{(3k^2-3k+1)+4uS\left(1-\frac{u}{S}\right)\right\}\langle v|\ y^{k-1}|\,v\rangle + \frac{3k(k-1)^2}{(k+1)S^2}\langle v|\ y^{k-2}|\,v\rangle - \frac{k(k-1)(k-2)}{(k+1)S^2}\langle v|\ y^{k-3}|\,v\rangle\ , \quad k=0,1,2\ldots\ . \tag{11}$$

This result is equivalent to the expression derived by Requena *et al.*[12] except for two minor misprints: The left-hand side of their Eq. (9) should be multiplied by α, and the coefficient of the next to last term should read αa^3 not $\alpha^3 a$.

Inspection of Eq. (11) reveals that expectation values for all powers of y can be deduced if one knows that for y^2 (or y).

The easiest way to find this expectation value is through the Hellmann–Feynman theorem[17]

$$\frac{\partial E_v}{\partial D_e} = \langle v|\ \frac{\partial H}{\partial D_e}\ |v\rangle = \langle v|\ y^2|\,v\rangle = \frac{2u}{S}\ , \tag{12}$$

where we have used Eqs. (5) and (7). Explicit results for the first few powers of y are given in Table I. These results for $k=0$–4 agree with those derived by Huffaker and Tran[14] by a factorization technique and can easily be extended if higher powers are required.

We note, in addition, that for the special case $v=0\,(u=1/2)$, Eq. (11) reduces to the simpler result

$$\langle 0|\ y^k|\,0\rangle = -\frac{(k-2)}{S}\langle 0|\ y^{k-1}|\,0\rangle + \frac{(k-1)}{S}\langle 0|\ y^{k-2}|\,0\rangle \tag{13}$$

as given in Ref. 14.

By analogous methods, with alternate choices for W, one can deduce the two similar relations

$$\langle v|Z^{k+2}|\,v\rangle = \left(\frac{2k+1}{k+1}\right)\langle v|Z^{k+1}|v\rangle + \left(\frac{k}{k+1}\right)\left(\frac{k-S+2u}{S}\right)\left(\frac{k+S-2u}{S}\right)\langle v|Z^k|\,v\rangle\ , \tag{14}$$

where

$$\langle v|Z|\,v\rangle = \langle v|(1-y)|\,v\rangle = 1-\frac{2u}{S}$$

and

$$\langle v|q^{k-1}y(y-1)|\,v\rangle = \frac{(k-1)}{a}\langle v|q^{k-2}y^2|\,v\rangle - \frac{(k-1)}{a}\frac{4u}{S}\left(1-\frac{u}{S}\right)\langle v|q^{k-2}|\,v\rangle - \frac{(k-1)(k-2)(k-3)}{aS^2}\langle v|q^{k-4}|\,v\rangle\ . \tag{15}$$

The application of the above results to the calculation of expectation values of different operators will now be illustrated. For this purpose we consider the choice of operators recently discussed by Vasan and Cross[16]; specifically

$$M_{vv}^{(l)} = \langle v|q^l|\,v\rangle = \langle v|(R-R_e)^l|\,v\rangle \tag{16}$$

and

$$Y_{vv}^{(l)} = \langle v|qZ^l|\,v\rangle = \langle v|(R-R_e)\exp[-la(R-R_e)]|\,v\rangle \tag{17}$$

for $l=1$, 2, and

$$M_{vv}^{(\mathrm{exp})}(\beta) = \langle v|Z^\beta|\,v\rangle = \langle v|\exp[-\beta a(R-R_e)]|\,v\rangle \tag{18}$$

for an arbitrary β.

From Eq. (4), one can write the series expansion for the displacement coordinate q

$$q = \frac{1}{a}\sum_{j=1}\frac{y^j}{j} \tag{19}$$

and thus express $M_{vv}^{(l)}$ as

$$M_{vv}^{(l)} = \frac{1}{a^l}\langle v|\left(\sum_{j=1}\frac{y^j}{j}\right)^l|v\rangle\ . \tag{20}$$

Using the results from Table I, one finds the asymptotic expansion

$$M_{vv}^{(1)} = \frac{1}{aS}\left\{3u+\left(\frac{7}{2}u^2+\frac{5}{24}\right)\Big/S + \left(5u^3+\frac{3u}{4}\right)\Big/S^2 + \left(\frac{31}{4}u^4+\frac{17}{8}u^2-\frac{23}{960}\right)\Big/S^3+\cdots\right\}\ . \tag{21}$$

The first two terms are identical to those given by Vasan

TABLE II. Numerical comparison of asymptotic formulas for various expectation values with exact values for H_2.[a]

v	$M_{vv}^{(1)}$	$M_{vv}^{(2)}$	$M_{vv}^{(\exp)}$	$Y_{vv}^{(1)}$
0	2.199-2[b]	8.486-3	1.085	7.026-3
	2.199-2	8.486-3	1.085	7.026-3
	2.199-2	8.476-3	1.087	7.033-3
1	6.802-2	2.911-2	1.282	2.022-2
	6.802-2	2.911-2	1.282	2.022-2
	6.799-2	2.911-2	1.289	2.025-2
2	0.1173	5.594-2	1.527	3.218-2
	0.1173	5.598-2	1.529	3.219-2
	0.1172	5.575-2	1.542	3.230-2
3	0.1703	9.024-2	1.838	4.288-2
	0.1702	9.001-2	1.841	4.288-2
	0.1703	8.964-2	1.859	4.320-2
4	0.2275	0.1336	2.237	5.224-2
	0.2273	0.1327	2.239	5.225-2
	0.2281	0.1325	2.260	5.293-2
5	0.2896	0.1881	2.759	6.022-2
	0.2890	0.1856	2.746	6.024-2
	0.2917	0.1867	2.769	6.150-2
6	0.3574	0.2563	3.453	6.676-2
	0.3559	0.2582	3.391	6.680-2
	0.3626	0.2549	3.420	6.892-2

[a] $S = 37.1586$, $a = 1.8719$ Å^{-1}.
[b] Top line is numerical integration (Ref. 16); the second line is from formulas (21), (22), (29), and (30); the bottom line is from the corresponding approximate formulas given in Ref. 16. The notation 2.199-2 indicates 2.199×10^{-2}.

and Cross, while these authors approximated the third term as $(u+1/2)^4/S^2$ by neglecting higher-order terms and fitting to results obtained by direct numerical integration. Similarly, one obtains for $M_{vv}^{(2)}$

$$M_{vv}^{(2)} = \frac{1}{a^2S}\left\{2u + \left(\frac{23}{2}u^2 + \frac{7}{8}\right)\Big/S + \left(\frac{218}{9}u^3 + \frac{43}{9}u\right)\Big/S^2 + \left(\frac{1117}{24}u^4 + \frac{803}{48}u^2 + \frac{95}{1152}\right)\Big/S^3 + \cdots\right\} . \tag{22}$$

Again, comparison of this result with the analogous expression from Ref. 16 reveals some small differences: they give the coefficient of S^{-1} as $12u^2 + 3/4$, while they approximated the third term by $15(u+1/2)^4/4$ and neglected higher-order contributions. These differences are negligible for low vibrational levels, but increase as v increases, and become significant especially in those cases for which the expansion parameter $S^{-1} = (\omega_e X_e/\omega_e)$ is appreciable. In this event, additional terms in the series [Eqs. (21) and (22)] may be required if high accuracy is desired.

Using the numerical values for S and a appropriate to H_2 as given by Vasan and Cross[16] (37.1586 and 1.8719 Å^{-1}, respectively), we obtain the values through Eqs. (21) and (22) as presented in Table II. Also shown are the results obtained by numerical integration and through the approximate formulas of Vasan and Cross.[16]

One can also compare the above results [Eqs. (21) and (22)] with similar expressions derived for the more general Dunham potential[19,22]

$$V(R) = a_0 x^2\left(1 + \sum_{j=1} a_j x^j\right) , \tag{23}$$

where

$$x = \frac{R - R_e}{R_e} \tag{24}$$

by using the following identifications[19] in the Dunham results:

$$a_0 = D_e a_M^2 , \quad a_i = \frac{2^{i+2} - 2}{(i+2)!}(-a_M)^i , \quad a_M = aR_e \tag{25}$$

and

$$\gamma \equiv 2B_e/\omega_e = \frac{2R_e^2}{a^2 S} .$$

As expected, the results are identical to the order of approximation carried out.

Next, consider the expectation values $Y_{vv}^{(l)}$. From Eq. (15) with $k=2$, one obtains the exact result

$$\langle v|q(y^2 - y)|v\rangle = \frac{1}{a}\langle v|\, y^2|v\rangle - \frac{4u}{aS}\left(1 - \frac{u}{S}\right) = \frac{2u}{aS}\left(\frac{2u}{S} - 1\right) . \tag{26}$$

Thus, from Eqs. (17) and (26), one has the identity

$$Y_{vv}^{(2)} = Y_{vv}^{(1)} + \frac{2u}{aS}\left(\frac{2u}{S} - 1\right) \tag{27}$$

and, therefore, we will only consider $Y_{vv}^{(1)}$ explicitly. Rewriting Eq. (17) and substituting in for q the expansion in terms of y, one obtains

$$\begin{aligned} Y_{vv}^{(1)} &= \frac{1}{a}\langle v|(1-y)\sum_{j=1}\left(\frac{y^j}{j}\right)|v\rangle \\ &= \frac{1}{a}\langle v|\; y - \frac{y^2}{1\cdot 2} - \frac{y^3}{2\cdot 3} - \frac{y^4}{3\cdot 4} - \cdots |v\rangle . \end{aligned} \tag{28}$$

Again, using the results from Table I, this becomes

$$Y_{vv}^{(1)} = \frac{1}{aS}\left\{u + \left(-\frac{3u^2}{2} - \frac{1}{24}\right)\Big/S + (-\tfrac{2}{3}u^3)/S^2 + \left(-\frac{5}{12}u^4 + \frac{1}{24}u^2 + \frac{7}{960}\right)\Big/S^3 + \cdots\right\} \tag{29}$$

that differs from the corresponding expression published by Vasan and Cross in that these latter authors give the coefficient of the second term as $(-\frac{3}{2}u^2 - \frac{1}{40})$ and neglect higher-order terms. Numerical comparisons of these results for H_2 are also presented in Table II.

Finally, consider the expectation values $M_{vv}^{(\exp)}(\beta)$. For integer β, one can obtain an exact result through Eq. (14). For the noninteger value ($\beta = 1.35424$) considered by Vasan and Cross that is appropriate to the repulsive potential for $H_e + H_2$,[16] one can use the binomial expansion

$$\begin{aligned} M_{vv}^{(\exp)}(\beta) &= \langle v|Z^\beta|v\rangle = \langle v|(1-y)^\beta|v\rangle \\ &= \langle v|\,1 - \beta y + \frac{\beta(\beta-1)}{2!}y^2 - \cdots |v\rangle \\ &= 1 + \beta(\beta-3)\,u/S + \frac{\beta(\beta-1)(\beta-2)}{24S^2} \\ &\quad\times[(\beta-3)(6u^2+\tfrac{3}{2}) + (-24u^2+2)] + \cdots . \end{aligned} \tag{30}$$

Expansion of the result given in Ref. 16

$$M_{vv}^{(\exp)}(\beta) = \exp\left\{\frac{\beta(\beta-3)u}{S} + \frac{(4\beta+11)(u+1/2)^2}{S^2}\right\} \simeq 1 + \frac{\beta(\beta-3)u}{S} + \frac{1}{S^2}\left[(4\beta+11)(u+1/2)^2 + \frac{\beta^2(\beta-3)^2u^2}{2}\right] + \cdots \tag{31}$$

again reveals slight differences in the coefficients of the S^{-2} and higher terms. Keeping the contributions through S^{-4}, we obtain the numerical results shown in Table II.

III. DISCUSSION AND CONCLUSIONS

By means of the diagonal hypervirial and Hellmann–Feynman theorems, one can generate simple closed form expressions for the expectation values of $(e^{-aq})^l$ and $(1-e^{-aq})^l$ for the Morse oscillator by a recursive method that obviates the need for explicit eigenfunctions or complicated integrations. These results can then be used to generate series expansions for other expectation values of interest. As can be seen from the numerical values in Table II, accurate results can be obtained with relative ease. Furthermore, since the expansion parameter S^{-1} is larger for H_2 than for most other realistic problems of interest, the results given by Eqs. (21), (22), (29), and (30) should provide sufficient accuracy for low or moderate $(u<S)$ vibrational quantum numbers for most applications.

Finally, before concluding, we would like to point out that since the algorithms for calculating $\langle v|y^k|v\rangle$, $M_{vv}^{(l)}$, $Y_{vv}^{(l)}$, etc. are recursive, they are easily programmed. One can make use of this method not only to avoid numerical complications arising from multiple summations and cancellations occurring in some of the closed form representations of the expectation values,[10,11,16] but also by means of computer algebra,[23–26] derive alternative analytical expressions. Extensive results obtained in this manner will be published elsewhere.[25]

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