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We have derived exact analytic expressions for the following matrix elements for a Morse oscillator: $\langle m|\exp[\gamma(r-r_0)]|n\rangle$, $\langle m|(r-r_0)\exp[-a(r-r_0)]|n\rangle$, and $\langle m|(r-r_0)\exp[-2a(r-r_0)]|n\rangle$, where a is the Morse range parameter and γ is an arbitrary constant. We have found that several of the commonly used expressions for various diagonal matrix elements of the Morse oscillator involve considerable roundoff error. Due to near cancellation of terms the result may be many orders of magnitude lower than any of the terms. We obtain simple yet accurate asymptotic approximations for the diagonal elements which avoid these problems. These approximations are obtained for $\langle m|(r-r_0)|m\rangle$, $\langle m|(r-r_0)^2|m\rangle$, and the cases mentioned above.

The Morse oscillator is one of the simplest anharmonic potentials and is very useful in doing model calculations in spectroscopy, molecular scattering, and other fields. In our work on the theory of vibrationally inelastic scattering[1] we require a fast yet accurate method of calculating the following matrix elements for Morse oscillators: $(r-r_0)$, $(r-r_0)^2$, $\exp[\gamma(r-r_0)]$, $(r-r_0)\exp[-a(r-r_0)]$, and $(r-r_0)\exp[-2a(r-r_0)]$, where r_0 is the position of the potential minimum. Expressions for the first two cases have been obtained previously.[3-5] However, the diagonal matrix elements for state $|n\rangle$ consist of $(n+1)^2$ terms of alternating sign, laced with gamma and psi functions. This, in itself, poses serious roundoff errors. For cases which are roughly harmonic the final result may be many orders of magnitude less than the largest term so that even a long calculation in double precision is seriously in error. It therefore becomes difficult or impossible to obtain the harmonic limit of these matrices. We have obtained simple asymptotic approximations for the diagonal matrix elements which are accurate for many practical cases. Simple methods exist for using wave functions, eigenvalues, and matrix elements for the nonrotating Morse oscillator in the more general case,[5,6] and thus our results can be used in spectroscopic problems involving rotation as well.

The Morse potential is[3-7]

$$V(r)=D\{1-\exp[-a(r-r_0)]\}^2 . \tag{1}$$

D is the dissociation energy from the minimum in the potential well and a is related to the force constant and the anharmonicity. The normalized wave functions are

$$\Psi_n = N_n\, e^{-z/2} z^{b/2} L_n^b(z) , \tag{2}$$

where

$$N_n=[abn!/\Gamma(k-n)]^{1/2} , \tag{3}$$

$$z=k\exp[-a(r-r_0)] , \tag{4}$$

$$b=k-2n-1 , \tag{5}$$

$$k=\omega_e/\omega_e x_e = 0.487\,118(\mu D)^{1/2}/a , \tag{6}$$

$$L_n^b(z)=\sum_{i=0}^{n}\frac{\Gamma(b+n+1)(-1)^i z^i}{\Gamma(b+i+1)\,i!(n-i)!}=\frac{e^z}{n!z^b}\frac{d^n}{dz^n}(e^{-z}z^{n+b}) \tag{7}$$

is the associated Laguerre polynomial.[8] Note that in the harmonic limit, $k\to\infty$ and $\omega_e x_e\to 0$. By using the finite power series and the Rodrigues formula for L, Gallas[3] obtained the following matrix elements for $(r-r_0)$ and $(r-r_0)^2$:

$$M_{mn}^{(1)}=\langle m|(r-r_0)|n\rangle=\frac{\ln k}{a}\delta_{mn}+\frac{N_m N_n}{a^2}\sum_{i=0}^{m}\sum_{j=0}^{n}\frac{(-1)^{i+j+1}}{i!\,j!}\binom{m+b'}{m-i}\binom{n+b}{n-j}\Gamma(k+i+j-n-m-1)\psi(k+i+j-n-m-1) , \tag{8}$$

where ( ) is a binomial coefficient and $\psi(z)=d[\ln\Gamma(z)]/dz$.[8]

$$M_{mn}^{(1)}=\frac{(-1)^{n-m+1}}{a(n-m)(k-n-m-1)}\left[\frac{n!\Gamma(k-n)bb'}{m'\Gamma(k-m)}\right]^{1/2} \quad (n>m) , \tag{9}$$

$$M_{mn}^{(2)}=\langle m|(r-r_0)^2|n\rangle=\frac{N_m N_n}{a^3}\sum_{i=0}^{m}\sum_{j=0}^{n}\frac{(-1)^{i+j}}{i!\,j!}\binom{m+b'}{m-i}\binom{n+b}{n-j}\Gamma(k+i+j-n-m-1)$$
$$\{[\psi(k+i+j-n-m-1)-\ln k]^2+\psi^{(1)}(k+i+j-n-m-1)\} , \tag{10}$$

where $\psi^{(1)}$ is the derivative of ψ,[8]

$$M_{mn}^{(2)}=\frac{2\ln k}{a}M_{mn}^{(1)}+\frac{2(-1)^{n-m-1}}{a^2}\left[\frac{m!\Gamma(k-m)bb'}{n!\Gamma(k-n)}\right]^{1/2}$$
$$\times\sum_{i=0}^{m}\frac{\Gamma(k+i-n-m-1)(n+i-m-1)!}{\Gamma(k+i-2m)\quad i!}[\psi(m-i+1)-\psi(n+i-m)-\psi(k+i-n-m-1)] \quad (n>m) . \tag{11}$$

Using similar techniques, we have obtained

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$$M_{mn}^{(\exp)}(\beta)=\langle m|\exp[\gamma(r-r_0)]|n\rangle=\frac{N_mN_n}{ak^\beta}\sum_{i=0}^{m}\sum_{j=0}^{n}\frac{(-1)^{i+j}}{i!\,j!}\binom{m+b'}{m-i}\binom{n+b}{n-j}\Gamma(k-m-n+\beta+i+j-1)\,, \tag{12}$$

$$M_{mn}^{(\exp)}(\beta)=\frac{N_mN_n(-1)^n}{ak^\beta n!}\sum_{i=0}^{m}\binom{m+b'}{m-i}\frac{(-1)^i\Gamma(n+i-m+\beta)\Gamma(k-n-m+i+\beta-1)}{i!\,\Gamma(i-m+\beta)}\quad(n\geq m)\,, \tag{13}$$

where $\beta=-\gamma/a$. This is analogous to the Rapp–Sharp matrix for harmonic oscillators.[9] All three matrices are symmetric. Equation (13) is equivalent to an expression derived by Clark and Dickinson.[2] The diagonal elements of Eq. (13) are related to expressions obtained by Gallas.[10] Two special cases of Eq. (13) are of interest. When $\beta=1$, the matrix elements of $\exp[-a(r-r_0)]$ are obtained. Only the term for $i=m$ contributes. When $\beta=2$, the matrix elements for $\exp[-2a(r-r_0)]$ are obtained, and only two terms of the sum in Eq. (13) contribute. The results are

$$X_{mn}^{(1)}=\langle m|\exp[-a(r-r_0)]|n\rangle=\frac{(-1)^{n+m}}{k}\left[\frac{(k-2n-1)(k-2m-1)n!\,\Gamma(k-n)}{m!\,\Gamma(k-m)}\right]^{1/2}\quad(n\geq m)\,, \tag{14}$$

$$X_{mn}^{(2)}=\langle m|\exp[-2a(r-r_0)]|n\rangle=\frac{(-1)^{n+m}}{k^2}\left[\frac{(k-2n-1)(k-2m-1)n!\,\Gamma(k-n)}{m!\,\Gamma(k-m)}\right]^{1/2}[(n+1)(k-n)-m(k-m-1)]\quad(n\geq m)\,. \tag{15}$$

Two other matrices are useful, the products of $M^{(1)}$ with $X^{(1)}$ and $X^{(2)}$. Let

$$Y_{mn}^{(1)}=\langle m|(r-r_0)\exp[-a(r-r_0)]|n\rangle\,. \tag{16}$$

Using Eqs. (2)–(7), the finite power series for L_n^b in $|n\rangle$, and the Rodrigues formula for L in $\langle m|$, we obtain

$$Y_{mn}^{(1)}=\frac{\ln k}{a}X_{mn}^{(1)}-\frac{N_mN_n}{ka^2}\sum_{i=0}^{m}\frac{\Gamma(b'+m+1)(-1)^i}{\Gamma(b'+i+1)(m-i)!\,i!\,n!}\int_0^\infty z^p\ln z\,\frac{d^n}{dz^n}(e^{-z}z^{n+b})\,dz\,, \tag{17}$$

where $p=n-m+i\leq n$. The integral in Eq. (7) can be evaluated by successive integrations by parts. After p integrations, we obtain

$$(-1)^p p!\int_0^\infty[\ln z+A_p]\frac{d^{n-p}}{dz^{n-p}}(e^{-z}z^{n+b})\,dz\,, \tag{18}$$

where

$$A_p=\sum_{i=1}^{p}\frac{1}{i}=\gamma+\psi(p+1) \tag{19}$$

and $\gamma=0.5722\cdots$ is the Euler's constant.[8] When $n=p$ the evaluation of Eq. (18) is trivial. For the terms where $n>p$ we integrate Eq. (18) by parts $n-p$ times to get the final result

$$Y_{mn}^{(1)}=\frac{\ln k}{a}X_{mn}^{(1)}+\frac{N_mN_n}{ka^2}(-1)^{n-m}\times\left\{\frac{\Gamma(k-m)}{n!}\sum_{i=0}^{m-1}\frac{(n-m+i)!(m-i-1)!\,\Gamma(k-n-m+i)}{(m-i)!\,i!\,\Gamma(k+i-2m)}-\frac{\Gamma(k-n)}{m!}[\psi(k-n)+\psi(n+1)+\gamma]\right\}\quad(n\geq m)\,. \tag{20}$$

The sum over i is not present for $m=0$. Using the same procedure we obtain

$$Y_{mn}^{(2)}=\langle m|(r-r_0)\exp[-2a(r-r_0)]|n\rangle=\frac{\ln k}{a}X_{mn}^{(2)}+\frac{N_mN_n}{k^2a^2}(-1)^{n-m-1}\frac{\Gamma(k-m)}{n!}\times\left\{\sum_{i=0}^{m-2}\frac{(n+i-m+1)!(m-i-2)!\,\Gamma(k+i-n-m+1)}{(m-i)!\,i!\,\Gamma(k+i-2m)}-\frac{n!\,\Gamma(k-n)[\psi(k-n)+\psi(n+1)+\gamma]}{(m-1)!\,\Gamma(k-m-1)}+\frac{(n+1)!\,\Gamma(k-n+1)[\psi(k-n+1)-1+\psi(n+2)+\gamma]}{m!\,\Gamma(k-m)}\right\}\quad(n\geq m)\,. \tag{21}$$

The sum over i does not contribute when $m=0$ or 1. The same methods can be applied to higher powers of $(r-r_0)$ or to other cases of $\exp[-\lambda a(r-r_0)]$ for integer λ.

In the limit of large k, each term in Eq. (8) is proportional to $k^n\ln k$, but the final result is proportional to k^{-1}, so that, for a heavy molecule like Br_2, the result for $n=6$ is 18 *orders of magnitude* smaller than the largest term. The resulting roundoff error makes computation of these matrix elements difficult or impossible. Even double precision may not be sufficient for the higher states! We have obtained simple approximations for the diagonal elements of these five matrices which are very useful, especially in the harmonic limit. They were obtained from exact algebraic evaluation of the respective diagonal expressions for $m=0$, 1, 2 and then fitting the higher coefficients to results obtained by numerical integration[11] for the higher states. For example,

$$M_{00}^{(1)}=[\ln k-\psi(k-1)]/a\sim 3/(2ak)+13/(12ak^2)+1/(k^3a)+\cdots\,. \tag{22}$$

The formulas are

TABLE I. Numerical test of the asymptotic approximation for H_2.[a]

m	$M^{(1)}_{mm}$	$M^{(2)}_{mm}$	$M^{(\exp)}_{mm}$[b]	$Y^{(1)}_{mm}$	$Y^{(2)}_{mm}$
0	2.199–2[c]	8.486–3[c]	1.085[c]	7.026–3[c]	−6.963–3[c]
	2.199–2[c]	8.476–3[c]	1.087[c]	7.033–3[c]	−6.956–3[c]
	2.199–2[c]	8.486–3[c]	1.085[c]	7.026–3[c]	−6.963–3[c]
1	6.802–2	2.911–2	1.282	2.022–2	−1.943–2
	6.799–2	2.911–2	1.289	2.025–2	−1.940–2
	6.802–2	2.911–2	1.282	2.022–2	−1.943–2
2	0.1173	5.594–2	1.527	3.218–2	−3.003–2
	0.1172	5.575–2	1.542	3.230–2	−2.990–2
	0.1173	5.594–2	1.527	3.218–2	−3.002–2
3	0.1703	9.024–2	1.838	4.288–2	−3.880–2
	0.1703	8.964–2	1.859	4.320–2	−3.848–2
	0.1703	9.023–2	1.839	4.286–2	−3.880–2
4	0.2275	0.1336	2.237	5.224–2	−4.581–2
	0.2281	0.1325	2.260	5.293–2	−4.512–2
	0.3343	0.1342	2.193	5.224–2	−4.581–2
5	0.2896	0.1881	2.759	6.022–2	−5.110–2
	0.2917	0.1867	2.769	6.150–2	−4.982–2
	−0.3743	0.1818	2.016	6.022–2	−5.110–2
6	0.3574	0.2563	3.453	6.676–2	−5.474–2
	0.3626	0.2549	3.420	6.892–2	−5.259–2
	−30.41	2.63–3	−13.3	6.677–2	−5.474–2

[a] $k = 37.1586$, $a = 1.8719$ Å^{-1}, $D = 8.1220\times10^{-12}$ ergs, $r_0 = 0.7416$ Å.

[b] The value for $\gamma = 2.535$ Å^{-1} is appropriate for the potential for $He + H_2$.

[c] The top line is obtained by a numerical integration. The second line is from the asymptotic approximations (23)–(27). The bottom line is obtained from Eqs. (8), (10), (12), (20), and (21) using double precision. All lengths are in Å. The notation 2.199–2 means 2.199×10^{-2}.

$$M^{(1)}_{mm} = \{[(3/2)+3m] + [13/12+(7/2)(m^2+m)]/k + (m+1)^4/k^2\}/(ka) , \quad (23)$$

$$M^{(2)}_{mm} = [2m+1+15/(4k) + 12(m^2+m)/k + 15(m+1)^4/(4k^2)]/(ka^2) , \quad (24)$$

$$M^{(\exp)}_{mm}(\beta) = \exp[\beta(\beta-3)(2m+1)/(2k) + (4\beta+11)(m+1)^2/k^2] , \quad (25)$$

$$Y^{(1)}_{mm} = \frac{(2m+1)}{2ak} - [2/5+3m(m+1)/2]/(ak^2) , \quad (26)$$

$$Y^{(2)}_{mm} = -\frac{(2m+1)}{2ak} + [3/5+5m(m+1)/2]/(ak^2) . \quad (27)$$

The approximate formulas were tested against a numerical integration[11] for four systems commonly used in scattering theory: H_2, Br_2, HBr, and N_2 with k ranging from 37–301 and $m = 0$–6. The asymptotic formulas are accurate to within 4% with the highest errors for H_2. Needless to say, they are very much faster computationally than even a single-precision evaluation of the corresponding analytic expressions. Table I shows the accuracy for the worst case of H_2. The value of γ used in $M^{(\exp)}$ is appropriate for the repulsive potential[2] for $He + H_2$. In the case of the off-diagonal elements, Eqs. (9), (11), (13)–(15), (20) and (21) are accurate to better than 1%, in double precision. It is recommended that double precision be used in their evaluation. The calculation is reasonably fast so that no attempt was made to derive asymptotic approximations for them. Our method may be contrasted with that of Gallas and Chakraborty[4] who used a term-by-term asymptotic expansion of Eqs. (8) and (10). Their result, however, still contains the double sum and its attendant roundoff errors.

Beginning with the original paper by Morse,[7] a number of authors[3,4,10,12] have devised analytic expressions for various matrix elements for Morse oscillators. However, their final expressions were often sufficiently complex to deter their usage. The harmonic limit to the Morse oscillator is often important in model calculations and yet it is often very difficult to obtain simple expressions which show how it is approached. It is our hope that our simple asymptotic approximations for the diagonal matrix elements and the single-sum expressions for the off-diagonal matrix elements will alleviate this problem.

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