Analytical and algebraic solutions of the rotating Morse oscillators: Matrix elements of arbitrary powers of $(r-r_e)^l\exp[-ma(r-r_e)]$

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Analytical expressions for the matrix elements $\langle v'J|(r-r_e)^l\exp[-ma(r-r_e)]|vJ\rangle$ of a rotating Morse oscillator are obtained, where l is a non-negative integer and m is any number. These matrix elements are also obtained by a recursive method that obviates the need for using explicit eigenfunctions. This procedure is based on the hypervirial theorem together with the second-quantization formalism. The results permit the diagonal ($v=v',J=J'$) and off-diagonal ($v\neq v',J=J'$) matrix elements of the operator $(r-r_e)^l$ to be calculated.

I. INTRODUCTION

There are many problems of interest to chemists and physicists, such as molecular-scattering transition probabilities, oscillator strengths, or the study of the interaction of coherent radiation with molecules, where it is necessary to determine rapidly and accurately the matrix elements of an operator of the form $(r-r_e)^l\exp[-ma(r-r_e)]$.[1-3]

Because the most popular potential model in the theory of diatomic molecules is the Morse potential,[4-7] many authors have given general expressions for the matrix elements of different quantum-mechanical operators of the Morse oscillator.[8-18] However, the use of the results obtained in these papers to calculate the matrix elements of higher vibrational levels usually involves computational difficulties due alternation of signs in the summations.[11,12] Analytical expressions for the diagonal matrix elements of $(r-r_e)^l$ ($l=1,2$) and an algorithm for computing the matrix elements of arbitrary powers of $\langle v'J|(r-r_e)^l|vJ\rangle$ have been published recently.[17] The authors themselves note that the results of the algorithm seem to be quite poor.

In this paper we evaluate matrix elements of the operator $(r-r_e)^l\exp[-ma(r-r_e)]$, where r_e and a are the parameters of the Morse potential, l is a non-negative integer, and m is any real number. We first obtain for these elements analytical expressions which avoid the difficulties due to the alternating sign. Second, using operator algebra, we obtain recursion relations which facilitate these calculations especially when many matrix elements are needed, because we only have to evaluate a few matrix elements analytically to run the recursion relations up to any value of l, m, and the vibrational and rotational quantum numbers. Our expressions can be used to calculate both diagonal and off-diagonal rotational-vibrational matrix elements.

II. ROTATING MORSE OSCILLATOR

A. Eigenvalues and eigenvectors

If we write the Morse oscillator in the form

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

where D_e is the dissociation energy from the minimum in the potential well and a is related to the force constant and anharmonicity, the effective vibrational-rotational potential keeping the Morse form will be

$$V_{\text{eff}}(r)=P_0+P_1y+P_2y^2\ , \tag{2}$$

with $y=1-\exp[-a(r-r_e)]$. The first term of Eq. (2) represents the unperturbed Morse potential and the following three terms are the approximation to the centrifugal component $\hbar^2(J+1)/(2\mu r^2)$. We define the coefficients P_0, P_1, and P_2 to be

$$\begin{aligned}P_0&=Q_0+Q_1(1-f)+Q_2(1-f)^2\ ,\\ P_1&=Q_1f+2Q_2f(1-f)\ ,\\ P_2&=D_e+Q_2f^2\ ,\end{aligned} \tag{3}$$

with

$$\begin{aligned}Q_0&=D_eJ(J+1)/(\sigma^2\rho^2)\ ,\\ Q_1&=-2Q_0/\rho\ ,\\ Q_2&=Q_0(3/\rho^2-1/\rho)\ ,\end{aligned} \tag{4}$$

where $\sigma=(2\mu D_e)^{1/2}/a\hbar$, J is the rotational quantum number, and the parameters ρ and f adopt different values depending on whether we use the Pekeris or the Elsum and Gordon models.[13,14]

Likewise the corresponding eigenfunctions can be written as

$$\Psi_{vJ}(z)=N_{vJ}\exp(-z/2)z^{b/2}L_{b,v}(z)\ , \tag{5}$$

where

$$\begin{aligned}z&=2\sigma_J\exp[-a(r-r_e)]\ ,\\ b&=2\sigma_{JJ}-2v-1\ ,\\ \sigma_J&=(2\mu P_2)^{1/2}/(a\hbar)\ ,\\ N_{vJ}&=[abv!/\Gamma(b+v+1)]^{1/2}\ ,\end{aligned} \tag{6}$$

and $L_{b,v}(z)$ are the Laguerre polynomials given by[19]

$$L_{b,v}(z)=\sum_{i=0}^{v}\frac{(-1)^i}{i!}\begin{pmatrix}v+b\\ v-i\end{pmatrix}z^i \tag{7}$$

or alternatively by the Rodrigues formula

$$L_{b,v}(z)=\frac{1}{v!}\exp(z)z^{-b}\frac{d^v}{dz^v}[\exp(-z)z^{v+b}] . \tag{8}$$

The eigenvalues can be written as

$$E_{vJ}=\frac{F_1}{\sigma_J}u-\frac{F_2}{\sigma_J^2}u^2+F_0-\frac{F_1^2}{4} , \tag{9}$$

where $u=v+1/2$, $F_0=P_0+P_1+P_2$, $F_1=P_1+2P_2$, and $F_2=P_2$.

B. Ladder Operators

We use the factorization method proposed by Infeld and Hull[20] in which we consider the Schrödinger equation as a class I, F-type factorization problem (a procedure described by Huffaker and Dwivedi[21] for the unperturbed Morse oscillator) to obtain a set of raising and lowering operators which act on the vibrational quantum numbers v. These operators are given by

$$G^+(v)=A_v\left[2\sigma_J bx^{-1}-\frac{2\sigma_{JJ}}{b-1}-4a^{-1}\sigma_J x^{-1}\frac{d}{dr}\right] , \tag{10}$$

$$G^-(v)=B_{v-1}\left[2\sigma_J bx^{-1}-\frac{2\sigma_{JJ}}{b+1}+4a^{-1}\sigma_J x^{-1}\frac{d}{dr}\right] , \tag{11}$$

where

$$A_v=\frac{b-1}{2}\left[\frac{b+2}{b(b+v)(v+1)}\right]^{1/2} , \tag{12}$$

$$B_{v-1}=\frac{b+1}{2}\left[\frac{b-2}{b(b+v+1)v}\right]^{1/2} , \tag{13}$$

with $x=\exp[-a(r-r_e)]$.

The action of these operators on the vibrational wave function is given by Eq. (14),

$$\begin{aligned}G^+(v)\Psi_v&=\Psi_{v+1} ,\\ G^-(v-1)\Psi_v&=\Psi_{v-1} ,\end{aligned} \tag{14}$$

with $G^-\Psi_0=0$.

III. MATRIX ELEMENT CALCULATIONS

A. Analytical expressions for the $\langle v'J|(r-r_e)^l\exp[-ma(r-r_e)]|vJ\rangle$ matrix elements

Setting $(r-r_e)^l\exp[-ma(r-r_e)]=q^lx^m$, we can write the corresponding matrix elements as

$$\langle q^lx^m\rangle_{v'J,vJ}=(-1)^l a^{-l}(2\sigma_J)^{-m}\frac{\partial^l}{\partial s^l}\bigg|_{s=0}\times(2\sigma_J)^{-s}\langle z^{m+s}\rangle_{v'J,vJ} . \tag{15}$$

If we now use Eq. (7) for $\Psi_{v'J}$ and Eq. (8) for Ψ_{vJ} we obtain the equation

$$\langle q^lx^m\rangle_{v'J,vJ}=\frac{(-1)^l N_{v'J}N_{vJ}}{a^{l+1}(2\sigma_J)^m v!}\times\sum_{i=0}^{v'}\frac{(-1)^i}{i!}\begin{pmatrix}b'+v'\\ v'-i\end{pmatrix}\frac{\partial^l}{\partial s^l}\bigg|_{s=0}\times(2\sigma_J)^{-s}\int_0^\infty z^t\frac{d^v}{dz^v}z^{v+b}e^{-z}dz , \quad v\ge v' \tag{16}$$

where we have replaced $2\sigma_J\exp(ar_e)$ by infinity[8] and $t=v-v'+i+s-1$. This integral can be evaluated by means of v integrations by parts. If $m\neq 0$, after differentiating, the results are

$$\langle q^lx^m\rangle_{v'J,vJ}=\frac{(-1)^{v+l}N_{v'J}N_{vJ}}{a^{l+1}(2\sigma_J)^m v!}\times\sum_{i=0}^{v'}\frac{(-1)^i}{i!}\begin{pmatrix}v'+b'\\ v'-i\end{pmatrix}(t_0+1-v)\times\Gamma(b+t_0+1)\Omega(b,t_0,l) , \tag{17}$$

where $t_0=v-v'+i+m-1$, and

$$(t_0-v+1)_v=\begin{cases}1 & \text{if } v=0\\ t(t-1)\cdots(t-v+1) & \text{if } v\neq 0 ,\end{cases} \tag{18}$$

and the $\Omega(b,t_0,l)$ function is defined for values of $l\le 4$ by the following equations:

$$\begin{aligned}\Omega(b,t_0,1)&=\Psi(b+t_0+1)-\ln(2\sigma_J)+\sum_{k=0}^{v-1}\frac{1}{t_0-k} ,\\ \Omega(b,t_0,2)&=[\Omega(b,t_0,1)]^2+\Omega(b,t_0,1) ,\\ \Omega(b,t_0,3)&=[\Omega(b,t_0,1)]^2+3\Omega(b,t_0,1)\Omega'(b,t_0,1)\\ &\quad+\Omega''(b,t_0,1) ,\\ \Omega(b,t_0,4)&=[\Omega(b,t_0,1)]^4+6[\Omega(b,t_0,1)]^2\Omega'(b,t_0,1)\\ &\quad+3[\Omega'(b,t_0,1)]^2+4\Omega(b,t_0,1)\Omega''(b,t_0,1)\\ &\quad+\Omega'''(b,t_0,1) .\end{aligned} \tag{19}$$

Here Ω', Ω'', and Ω''' denote the first, second, and third derivatives. In general, we can write

$$\Omega^{(n)}(b,t_0,1)=\Psi^{(n)}(b+t_0+1)+(-1)^n n\sum_{k=0}^{v-1}\frac{1}{(t_0-k)^n} , \tag{20}$$

where $\Psi^{(n)}$ is the polygamma function of order n. It should be easy to obtain expressions for l values higher than 4, but of course the complexity rises with the l

value. However, we would emphasize that our expressions reduce the rounding errors because we only have one summation over an alternating sign. Also many of these quantities only need to be evaluated once for the different powers of q.

Maybe the most interesting case is when $m=0$ and then we can evaluate the matrix elements $\langle q^l \rangle_{v'J,vJ} = \langle v'J|(r-r_e)^l|vJ\rangle$. Some recently published papers obtained expressions for the diagonal ($v=v'$, $J=J'=0$) (Refs. 8, 17, and 18) and off-diagonal ($v \neq v'$, $J=J'=0$) (Refs. 8 and 17) cases. These expressions are somewhat complicated and require a great deal of computation to obtain only one matrix element. Our procedure permits both diagonal and off-diagonal matrix elements to be derived from less sophisticated expressions as well as being useful for values of $J \neq 0$. So, setting $m=0$ and calculating the successive derivatives, after solving the integral in Eq. (16) and some algebraic manipulation we obtain analytical expressions for the powers of q.

We present in the following expressions values corresponding to the first power

$$\langle q \rangle_{vJ} = a^{-1} \left[\ln(2\sigma_J) - \Psi(b) + \sum_{i=1}^{v} \frac{1}{b+1} \right] ,$$

$$\langle q \rangle_{v'J,vJ} = \frac{(-1)^{v-v'+1}}{a(v-v')(b+v-v')} \times \left[\frac{v!\Gamma(b+v+1)bb'}{v'!\Gamma(b'+v'+1)} \right]^{1/2} , \quad v > v' . \tag{21}$$

For the other powers we use the following notation:

$$\kappa = \ln(2\sigma_J) ,$$

$$\beta_{vv'} = \left[\frac{v'!bb'\Gamma(b'+v'+1)}{v!\Gamma(b+v+1)} \right]^{1/2} , \tag{22}$$

$$\alpha_i = \frac{\Gamma(b+t_0+1)}{\Gamma(b'+i+1)} , \quad c = b+t_0+1 .$$

The powers of the matrix elements of q^l $(1 < l \leq 4)$ have therefore the following form:

$$\langle q^2 \rangle_{vJ} = 2a^{-1}\kappa \langle q \rangle_{vJ} + a^{-2} \left\{ -\kappa^2 + \Psi^2(b) + \Psi'(b) - 2\Psi(b) \sum_{i=1}^{v} (b+i)^{-1} + 2 \sum_{k<l=1}^{v} \frac{1}{kl} + 2b \sum_{i=1}^{v} [i(b+i)]^{-1} \left[\left[\sum_{k=1}^{i-1} \frac{1}{k} - \sum_{k=1}^{v-i} \frac{1}{k} \right] + \Psi(b+i) \right] \right\} , \tag{23}$$

$$\langle q^2 \rangle_{v'J,vJ} = 2a^{-1}\kappa \langle q \rangle_{v'J,vJ} + a^{-2}(-1)^{v-v'} \beta_{vv'} \sum_{i=0}^{v'} \frac{t_0!}{i!} \alpha_i \left[2\Psi(c) + 2 \sum_{k=1}^{t_0} \frac{1}{k} - 2 \sum_{k=1}^{v'-i} \frac{1}{k} \right] , \tag{24}$$

$$\begin{aligned} \langle q^3 \rangle_{vJ} = {} & 3a^{-1}\kappa \langle q^2 \rangle_{vJ} - 3a^{-2}\kappa^2 \langle q \rangle_{vJ} \\ & + a^{-3} \left\{ \kappa^3 - \Psi^3(b) - 3\Psi(b)\Psi'(b) - \Psi''(b) + 3[\Psi^2(b) + \Psi'(b)] \sum_{k=1}^{v} \frac{1}{k} - 6\Psi(b) \sum_{k<l=1}^{v} \frac{1}{kl} \right. \\ & + 6 \sum_{k<l<m=1}^{v} \frac{1}{klm} - 3b \sum_{i=1}^{v} [i(b+i)]^{-1} \left[\Psi^2(b+i) + \Psi'(b+i) + 2\Psi(b+i) \left[\sum_{k=1}^{i-1} \frac{1}{k} - \sum_{k=1}^{v-i} \frac{1}{k} \right] \right. \\ & \left. \left. + 2 \sum_{k<l=1}^{v-i} \frac{1}{kl} + 2 \sum_{k<l=1}^{i-1} \frac{1}{kl} - 2 \sum_{k=1}^{i-1} \sum_{l=1}^{v-i} \frac{1}{kl} \right] \right\} , \end{aligned} \tag{25}$$

$$\begin{aligned} \langle q^3 \rangle_{v'J,vJ} = {} & 3a^{-1}\kappa \langle q^2 \rangle_{v'J,vJ} - 3a^{-2}\kappa^2 \langle q \rangle_{v'J,vJ} \\ & + a^{-3}(-1)^{v-v'+1} \times \beta_{vv'} \sum_{i=0}^{v'} \frac{t_0!}{i!} \alpha_i \left[3\Psi^2(c) + 3\Psi'(c) + 6\Psi(c) \left[\sum_{k=1}^{t_0} \frac{1}{k} - \sum_{k=1}^{v'-i} \frac{1}{k} \right] \right. \\ & \left. - 6 \sum_{k<l=1}^{v'-i} \frac{1}{kl} + 6 \sum_{k<l=1}^{t_0} \frac{1}{kl} - 6 \sum_{k=1}^{t_0} \frac{1}{k} \sum_{l=1}^{v'-i} \frac{1}{l} \right] , \end{aligned} \tag{26}$$

$$\begin{aligned}
\langle q^4\rangle_{vJ} =& 4a^{-1}\kappa\langle q^3\rangle_{vJ}-6a^{-2}\kappa^2\langle q^2\rangle_{vJ}+4a^{-3}\kappa^3\langle q\rangle_{vJ} \\
&+a^{-4}\Bigg\{-\kappa^4+\Psi^4(b)+6\Psi^2(b)\Psi'(b)+3[\Psi'(b)]^2+4\Psi(b)\Psi''(b)+\Psi'''(b)-[4\Psi^3(b)+12\Psi(b)\Psi'(b)]\sum_{k=1}^{v}\frac{1}{k} \\
&\quad +12[\Psi^2(b)+\Psi'(b)]\sum_{k<l=1}^{v}\frac{1}{kl}-24\Psi(b)\sum_{k<l<m=1}^{v}\frac{1}{klm}+24\sum_{k<l<m<n=1}^{v}\frac{1}{klmn} \\
&\quad +\sum_{i=1}^{v}b[i(b+i)]^{-1}\Bigg[4\Psi^3(b+i)+12\Psi(b+i)\Psi'(b+i)+4\Psi''(b+i) \\
&\qquad +[12\Psi^2(b+i)+12\Psi'(b+i)]\left[\sum_{k=1}^{i-1}\frac{1}{k}-\sum_{k=1}^{v-i}\frac{1}{k}\right] \\
&\qquad +24\Psi(b+i)\left[\sum_{k<l=1}^{i-1}\frac{1}{kl}+\sum_{k<l=1}^{v-i}\frac{1}{kl}-\sum_{k=1}^{i-1}\sum_{l=1}^{v-i}\frac{1}{kl}\right] \\
&\qquad +\sum_{k<l<m=1}^{i-1}\frac{1}{klm}+\sum_{k=1}^{i-1}\sum_{l<m=1}^{v-i}\frac{1}{klm}-\sum_{k<l=1}^{i-1}\sum_{m=1}^{v-i}\frac{1}{klm}-\sum_{k<l<m=1}^{v-i}\frac{1}{klm}\Bigg]\Bigg\}\,,
\end{aligned} \tag{27}$$

$$\begin{aligned}
\langle q^4\rangle_{v'J,vJ} =& 4a^{-1}\kappa\langle q^3\rangle_{v'J,vJ}-6a^{-2}\kappa^2\langle q^2\rangle_{v'J,vJ} \\
&+4a^{-3}\kappa^3\langle q\rangle_{v'J,vJ}+a^{-4}(-1)^{v-v'}\beta_{vv'} \\
&\times\sum_{i=0}^{v'}\frac{t_0!}{i!}\alpha_i\Bigg[\Psi^3(c)+12\Psi(c)\Psi'(c)+4\Psi''(c)+12[\Psi^2(c)+\Psi'(c)]\left[\sum_{k=1}^{t_0}\frac{1}{k}-\sum_{k=1}^{v'-i}\frac{1}{k}\right] \\
&\quad +24\Psi(c)\left[\sum_{k<l=1}^{t_0}\frac{1}{kl}+\sum_{k<l=1}^{v'-i}\frac{1}{kl}-\sum_{k=1}^{t_0}\sum_{l=1}^{v'-i}\frac{1}{kl}\right]+24\sum_{k<l<m=1}^{t_0}\frac{1}{klm} \\
&\quad +24\sum_{k=1}^{t_0}\frac{1}{k}\sum_{l<m=1}^{v'-i}\frac{1}{lm}-24\sum_{l<m=1}^{t_0}\sum_{k=1}^{v'-i}\frac{1}{klm}-24\sum_{k<l<m=1}^{v'-i}\frac{1}{klm}\Bigg]
\end{aligned} \tag{28}$$

where $v>v'$ in all the previous equations. For Eqs. (21) and (23)–(28) the summation vanishes when the index is greater than the upper limit.

Using this procedure we could obtain expressions for higher powers of q. One sees, however, that the complexity of the equations is rising with l. Our expressions avoid the rounding-error inconvenience, but require too much calculation to determine only some matrix elements. In conclusion, we feel that it is necessary to find another procedure which would facilitate extension of the computation both with the order of the power of q and with the rotational and vibrational quantum numbers, and then to use exclusively the analytical equations for lower powers of the operators.

B. Recursion relations for the $\langle v'J|(r-r_e)^l\exp[-sa(r-r_e)]|vJ\rangle$ matrix elements

If we use the off-diagonal hypervirial theorem, with x^s as operator, we obtain

$$ka^2s^2\langle x^s\rangle_{v'J,vJ}-2kas\left\langle x^s\frac{d}{dr}\right\rangle_{v'J,vJ}-(E_{v'J}-E_{vJ})\langle x^s\rangle_{v'J,vJ}=0\,, \tag{29}$$

where $k=\hbar/(2\mu)$.

Using the expressions for the ladder operators [Eqs. (10) and (11)], we can derive the following relationships:

$$\left\langle x^s\frac{d}{dr}\right\rangle_{v'J,vJ}=-\frac{ab}{2}\langle x^s\rangle_{v'J,vJ}+\frac{2a\sigma_J\sigma_{JJ}}{b+1}\langle x^{s+1}\rangle_{v'J,vJ}+a\sigma_J B_{v-1}^{-1}\langle x^{s+1}\rangle_{v'J,v-1J}\,, \tag{30}$$

$$\left\langle x^s\frac{d}{dr}\right\rangle_{v'J,vJ}=\frac{ab}{2}\langle x^s\rangle_{v'J,vJ}-\frac{2a\sigma_J\sigma_{JJ}}{b-1}\langle x^{s+1}\rangle_{v'J,vJ}-a\sigma_J A_v^{-1}\langle x^{s+1}\rangle_{v'J,v+1J} \tag{31}$$

which together with Eq. (29) permits us to obtain the recursion relation for x^s operators:

$$\frac{4\sigma_{JJ}b}{b^2-1}(s^2+s+F)\langle x^{s+1}\rangle_{v'J,vJ}+B_{v-1}^{-1}[s(s-b)+F]\langle x^{s+1}\rangle_{v'J,v-1J}+A_v^{-1}[s(s+b)+F]\langle x^{s+1}\rangle_{v'J,v+1J}=0\,, \tag{32}$$

where

$$F=\frac{\sigma_J^2(E_{v'J}-E_{vJ})}{D_e} .$$

Taking into consideration the identity

$$\frac{\partial^l}{\partial s^l}x^s=(-a)^l q^l x^s , \tag{33}$$

the successive derivatives permit to obtain recursion relations for the matrix elements $\langle q^l x^s\rangle$ and their lower powers. So, differentiating l times, we obtain for $l\in N$ and $s\in R$

$$\begin{aligned}
&\frac{4\sigma_{JJ}b}{b^2-1}\left[(-a)^l[(s-1)s+F]\langle q^l x^s\rangle_{v'J,vJ}+(-a)^{l-1}l(2s-1)\langle q^{l-1}x^s\rangle_{v'J,vJ}+2(-a)^{l-2}\sum_{k=1}^{l-1}{}' k\langle q^{l-2}x^s\rangle_{v'J,vJ}\right]\\
&\quad+B_{v-1}^{-1}\Bigg[(-a)^l[(s-1)(s-1-b)+F]\langle q^l x^s\rangle_{v'J,v-1J}\\
&\qquad+(-a)^{l-1}l[2(s-1)-b]\langle q^{l-1}x^s\rangle_{v'J,v-1J}+2(-a)^{l-2}\sum_{k=1}^{l-1}{}' k\langle q^{l-2}x^s\rangle_{v'J,v-1J}\Bigg]\\
&\quad+A_v^{-1}\Bigg[(-a)^l[(s-1)(s-1+b)+F]\langle q^l x^s\rangle_{v'J,v+1J}+(-a)^{l-1}l[2(s-1)+b]\langle q^{l-1}x^s\rangle_{v'J,v+1J}\\
&\qquad+2(-a)^{l-2}\sum_{k=1}^{l-1}{}' k\langle q^{l-2}x^s\rangle_{v'J,v+1J}\Bigg]=0 .
\end{aligned} \tag{34}$$

The steps for computing with Eq. (34) are (a) setting $l=1$ and knowing the matrix elements $\langle x^s\rangle_{v'J,vJ}$ and $\langle qx^s\rangle_{0J,0J}$, one obtains all matrix elements of the form $\langle qx^s\rangle_{v'J,vJ}$ step by step, using the recursion relation given by Eq. (34); and (b) setting $l=2$ and knowing the matrix elements $\langle q^2x^s\rangle_{0J,0J}$, one obtains all matrix elements of the form $\langle q^2x^s\rangle_{v'J,vJ}$. Repeating the process, one can obtain all the matrix elements for any value of l and s. The initial matrix elements can be derived easily. For the $\langle x^s\rangle_{v'J,vJ}$ matrix elements, one only needs to know $\langle x^s\rangle_{0J,0J}$ and then to use Eq. (32) repeatedly with $s+1=s$. If s is an integer power, we can evaluate all the matrix elements without knowing any initial matrix element.[16] However, if $s\in R$ in general, from Eq. (16) (with $v=v'=0$ and $l=0$), one obtains

$$\langle x^s\rangle_{0J,0J}=\frac{b\Gamma(b+s)}{(2\sigma_J)^s\Gamma(b+1)} , \tag{35}$$

and differentiating with respect to s the rest of the necessary matrix elements $\langle qx^2\rangle_{0J,0J}$ are

$$\begin{aligned}
\langle qx^s\rangle_{0J,0J}&=(-a)^{-1}\frac{\partial}{\partial s}\Big|\langle x^s\rangle_{0J,0J}\\
&=a^{-1}[\ln(2\sigma_J)-\Psi(b+s)]\langle x^s\rangle_{0J,0J} ,
\end{aligned} \tag{36}$$

$$\begin{aligned}
\langle q^2x^s\rangle_{0J,0J}&=(-a)^{-2}\frac{\partial^2}{\partial s^2}\Big|\langle x^s\rangle_{0J,0J}\\
&=(-a)^{-2}\\
&\quad\times\{a[\ln(2\sigma_J)-\Psi(b+s)]\langle qx^s\rangle_{0J,0J}\\
&\qquad-\Psi'(b+s)\langle x^s\rangle_{0J,0J}\} .
\end{aligned} \tag{37}$$

In general, for the lth power, we can write

$$\begin{aligned}
\langle q^l x^s\rangle_{0J,0J}&=\sum_{i=0}^{l-1}\binom{l-i}{i}\Psi^i(b+s)a^{-(i+1)}\\
&\quad\times\langle q^{l-i-1}x^s\rangle_{0J,0J} ,
\end{aligned} \tag{38}$$

where

$$\begin{aligned}
&\Psi^0(b+s)=\Psi(b+s)-\ln(2\sigma_J)\\
&\Psi^i(b+s)=\frac{d^i}{ds^i}\Psi(b+s),\quad \text{with } i>0 .
\end{aligned} \tag{39}$$

To compute with these equations one uses the asymptotic expansions for gamma and polygamma functions where, due to the higher values of b for the fundamental state of diatomic molecules, we only need a few terms in those expansions.

When $s=0$, our recursion relation is even more economical because $\langle x^0\rangle_{v'J,vJ}=\delta_{vv'}$, and we only need to know initially the elements $\langle q^l\rangle_{0J,0J}$ which we can derive from Eq. (38) with $s=0$. In this case, we cannot obtain the diagonal and off-diagonal matrix elements simultaneously by Eq. (34), because if we make $v=v'$ then $F=0$, and if we make $v'=v+1$ then $F=b+1$. These results cancel the coefficients of the matrix elements and so we cannot evaluate them. If we need to calculate the diagonal matrix elements, we must evaluate the off-diagonal elements of the higher powers, and setting $v=v'=0$ ($F=0$) in Eq. (34), we can obtain the $\langle q^l\rangle_{vJ,vJ}$ in terms of the $\langle q^{l+1}\rangle_{v'J,vJ}$ and $\langle q^{l-1}\rangle_{v'J,vJ}$.

IV. CONCLUDING REMARKS

We have derived analytical expressions for the matrix elements of arbitrary powers of $(r-r_e)^l\exp[-ma(r-r_e)]$ for the rotating Morse oscillator. Our procedure permits us to obtain analytical expressions for the matrix elements of the powers of the $(r-r_e)$ operator, both diagonal and off-diagonal with respect to the vibrational quantum number and diagonal only for the rotational quantum number. These expressions have been obtained easily, and their computational treatment is straightforward. The only difficulty is the algebraic complexity if it is to be done by hand. This difficulty too is avoided if algebraic processors are used.

Using the operator algebra we have generated a recursion relation which makes it to obtain matrix elements of the powers of the internuclear distance without any computational difficulty (i.e., to calculate up to the lth power, we only need to evaluate initially l polygamma functions). This expression [Eq. (34)] is very useful when we need many matrix elements or higher powers of $(r-r_e)$.

We have checked the results obtained using the analytical equations and the recursion relation, and they coincide. As to the results from numerical integration of the Schrödinger equation with a rotating Morse oscillator with the centrifugal term $J(J+1)/r^2$, we obtain the same numbers up to $v=5$, $J=5$, and $l=4$ (if $J=0$ we can raise the vibrational quantum number up to $v=10$ and $l=10$ with really good results), using the H_2 molecule as an example [our numerical results completely agree with those obtained from Eqs. (4) and (5) of Ref. 17]. However, our procedure has the important advantage that we can compute with our expressions on a hand calculator. Moreover, they can be used in problems which need analytical solutions for these matrix elements. The next step in our research will be to introduce the necessary modifications to the Pekeris potential to obtain good values for the matrix elements with high values of the rotational and vibrational quantum numbers, with the goal of comparing them to the approximation-free numerical integration of the rotating Morse oscillator.

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