Ladder operators for the rotating Morse oscillators: Matrix element calculations

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We describe a simple method based on the hypervirial theorem along with a second-quantization formalism, which allows us to obtain recursion relations without using explicit wave functions for the calculation of matrix elements such as $\{\exp[-a(r-r_e)]\}^n$, $(r-r_e)^n$, $(r-r_e)^n\exp[-a(r-r_e)]$, and $\{\exp[-a(r-r_e)]\}^n(d/dr)$ for the rotating Morse oscillator.

I. INTRODUCTION

There are, principally, two standard theoretical approaches to solving the vibrational-rotational Schrödinger equation of a diatomic molecule using the Morse potential.[1] These are the Pekeris[2] and Elsum and Gordon[3] approximations. Both are based on keeping the Morse form for the effective vibrational-rotational potential,

$$V_{\text{eff}}(r)=D_e y^2+P_0+P_1 y+P_2 y^2 , \tag{1}$$

with $y=1-\exp[-a(r-r_e)]$, and where the first term of Eq. (1) represents the unperturbed Morse potential, and the following three terms are the approximation for the centrifugal term $\hbar^2 J(J+1)/(2\mu r^2)$.

We define the P_0, P_1, and P_2 coefficients to be

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

with

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

where $\rho=ar_e$ and $\sigma=(2\mu D_e)^{1/2}/(a\hbar)$. The f parameter will be equal to 1 or $\exp[-a(r-r_e)]$, depending on whether we use the Pekeris[4] or the Elsum and Gordon[5] approximations, respectively.

Many efforts have been made in order to obtain matrix elements analytically[6–9] as well as through recursion relations[4,5,7,10] from quantum theorems such as the hypervirial and Hellmann-Feynman theorems. However, owing to the computational difficulties [see Eq. (2.2) in Ref. 5 and Eq. (11) in Ref. 4] of using analytical equations, it is preferable, when $J\neq J'$, to use recursion relations. So, starting from some analitically calculated matrix elements, we can obtain the others by a recurrence method.

In this paper we obtain recursion relations for the vibration-rotational matrix elements of the $x^n=\{\exp[-a(r-r_e)]\}^n$ operator. The procedure used, if $J=J'$, does not need the explicit use of the wave functions, although it is necessary to first evaluate the overlap integrals between $|v'J'\rangle$ and $|vJ\rangle$ for the $J\neq J'$ case. The same method give us recursion relations for the matrix elements of the xq^n, q^n, and $q^n d/dr$ operators in terms of the matrix elements of x. The procedure utilized consists of using certain ladder operators, which modify the wave-function quantum numbers in such a way as to cover all the spectrum. Once these ladder operators are known, we can calculate matrix elements between any two states of the system of any operator which can be expressed in terms of the corresponding raising and lowering operators. This method has been successfully applied to several systems,[11–14] but it is the first time for the rotating Morse oscillator case.

II. LADDER OPERATORS FOR THE ROTATING MORSE POTENTIAL

In general, the description of the nuclear motion of a diatomic molecule is represented by the Schrödinger equation

$$\left[\frac{-\hbar^2}{2\mu}\frac{d^2}{dr^2}+V_{\text{eff}}(r)\right]\Psi_{vJ}=E_{vJ}\Psi_{vJ} . \tag{4}$$

Substituting $V_{\text{eff}}(r)$, defined in Eq. (1), and after some algebraic manipulations, we obtain the differential equation

$$\left[\frac{d^2}{dz^2}-n^2+\sigma_{JJ}e^z-\tfrac{1}{4}e^{2z}\right]R_{vJ}(z)=0 , \tag{5}$$

where

$$\begin{aligned} z&=-a(r-r_e)+\ln(2\sigma_J) ,\\ \sigma_J&=(2\mu F_2)^{1/2}/(a\hbar) ,\\ \sigma_{JJ}&=F_1\sigma_J/(2F_2) ,\\ n^2&=2\mu(F_0-E_{vJ})/(a^2\hbar^2) , \end{aligned} \tag{6}$$

and

$$F_0=P_0+P_1+P_2+D_e\ ,\quad F_1=P_1+2(P_2+D_e)\ ,\quad F_2=P_2+D_e\ . \tag{7}$$

Equation (5) can be solved using the factorization method proposed by Infeld and Hull.[15] So, following the procedure described by Huffaker and Dwivedi[13] for the unperturbed Morse oscillator, we obtain a set of raising and lowering operators, which act on the vibrational quantum numbers v

$$G^+(v)\Psi_v=\Psi_{v+1}\ ,\quad G^-(v)\Psi_{v+1}=\Psi_v\ , \tag{8}$$

where

$$G^+(v)=A_v\left[be^{-z}-\frac{2\sigma_{JJ}}{b-1}+2e^{-z}\frac{d}{dz}\right], \tag{9}$$

$$G^-(v)=B_v\left[(b-2)e^{-z}-\frac{2\sigma_{JJ}}{b-1}-2e^{-z}\frac{d}{dz}\right], \tag{10}$$

with $b=2\sigma_{JJ}-2v-1$ and,

$$A_v=\frac{1}{2}\left[\frac{(b-2)(b-1)^2}{b(b+v)(v+1)}\right]^{1/2}, \tag{11}$$

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

III. MATRIX ELEMENTS

A. Recursion relations for the $\langle v'J'|x^\alpha|vJ\rangle$ matrix elements

Making $x=\exp[-a(r-r_e)]$ and using Eqs. (9) and (10) to derive expressions for the differential operator in terms of $G^+(v)$ and $G^-(v)$, we can obtain the recursion relation

$$\frac{b}{\sigma_J}\langle x^{\alpha-1}\rangle_{v'J',vJ}=\frac{4\sigma_{JJ}b}{b^2-1}\langle x^\alpha\rangle_{v'J',vJ}+A_v^{-1}\langle x^\alpha\rangle_{v'J',vJ}+B_{v-1}^{-1}\langle x^\alpha\rangle_{v'J',v-1J}\ , \tag{13}$$

with $\alpha=0,\pm1,\pm2,\ldots$.

If $J=J'$, using the results $\langle d/dz\rangle_{vJ}=0$, we derive from Eqs. (9) and (10) the following equations, respectively:

$$\frac{b}{2\sigma_J}=\frac{2\sigma_{JJ}}{b-1}\langle x\rangle_{vJ,vJ}+A_v^{-1}\langle x\rangle_{vJ,v+1J}\ , \tag{14}$$

$$\frac{b}{2\sigma_J}=\frac{2\sigma_{JJ}}{b+1}\langle x\rangle_{vJ,vJ}+B_{v-1}^{-1}\langle x\rangle_{vJ,v-1J}\ . \tag{15}$$

Finally, combining appropriately the expressions obtained from the equation

$$\langle v'J'|H'x^\alpha-x^\alpha H|vJ\rangle=(E_{v'J'}-E_{vJ})\langle v'J'|x^\alpha|vJ\rangle \tag{16}$$

with Eqs. (9), (10), and (13), we obtain

$$\left[\frac{4\sigma_J\sigma_{JJ}}{b^2-1}K_\alpha-\Delta F_1+\frac{4\alpha F_2\sigma_{JJ}}{\sigma_J(b-1)}\right]\langle x^{\alpha+1}\rangle_{v'J',vJ}+\frac{\sigma_J}{bA_v}K_\alpha\langle x^{\alpha+1}\rangle_{v'J',v+1J}+\left[\frac{\sigma_J}{bB_{v-1}}K_\alpha+\frac{2F_2\alpha}{\sigma_J B_{v-1}}\right]\times\langle x^{\alpha+1}\rangle_{v'J',v-1J}+\Delta F_2\langle x^{\alpha+2}\rangle_{v'J',vJ}=0\ , \tag{17}$$

with $\alpha=0,\pm1,\pm2,\ldots$, and where

$$K_\alpha=\left[\Delta F_0-\Delta E-\frac{F_2}{\sigma_J^2}\alpha(\alpha+b)\right],$$

and $\Delta F_0=F_0'-F_0$, $\Delta F_1=F_1'-F_1$, $\Delta F_2=F_2'-F_2$, and $\Delta E=E_{v'J'}-E_{vJ}$.

If we know the overlap integral between the $|vJ\rangle$ and $\langle v'J'|$ states, we can obtain the successive powers of x (positive or negative) using Eqs. (13) and (17), repeatedly. The improvement over our previous results[4,5] is that we need only know one power of x to evaluate the rest.

For the diagonal case, $J=J'$, the results are better. Firstly, we use Eqs. (14) and (15) to obtain all the matrix elements $\langle x\rangle_{v'J,vJ}$. Then, we can derive the matrix elements of the negative powers from Eq. (13), making $J=J'$ and $\alpha=0,-1,-2,\ldots$. We cannot use Eq. (17) for the positive powers because this equation is a recursion relation between matrix elements of the same power of x. To solve this problem, we use the off-diagonal hypervirial theorem with the following commutator:

$$\left\langle v'J\left|\left[H,x^\alpha\frac{d}{dr}\right]\right|vJ\right\rangle=(E_{v'J}-E_{vJ})\left\langle v'J\left|x^\alpha\frac{d}{dr}\right|vJ\right\rangle \tag{18}$$

together with the ladder operators defined previously. So, we obtain two possible recursion relations depending on which operator [$G^+(v)$ or $G^-(v)$] we use,

$$\left[\frac{b}{2}\left[\frac{F_2}{\sigma_J^2}+\Delta E\right]+2\alpha(F_0-E_v)\right]\langle x^\alpha\rangle_{v'J,vJ}-\left[(2\alpha+1)F_1-\frac{2\sigma_J\sigma_{JJ}}{b-1}\left[\frac{F_2}{\sigma_J^2}+\Delta E\right]\right]\langle x^{\alpha+1}\rangle_{v'J,vJ}-\sigma_J A_v^{-1}\left[\frac{F_2}{\sigma_J^2}+\Delta E\right]\langle x^{\alpha+1}\rangle_{v'J,v+1J}+2(\alpha+1)F_2\langle x^{\alpha+2}\rangle_{v'J,vJ}=0\ , \tag{19}$$

and

$$\left[\frac{b}{2}\left[\frac{F_2}{\sigma_J^2}+\Delta E\right]+2\alpha(F_0-E_v)\right]\langle x^\alpha\rangle_{v'J,vJ}-\left[(2\alpha+1)F_1+\frac{2\sigma_J\sigma_{JJ}}{b+1}\left[\frac{F_2}{\sigma_J^2}+\Delta E\right]\right]\langle x^{\alpha+1}\rangle_{v'J,vJ}$$
$$-\sigma_J B_{v-1}^{-1}\left[\frac{F_2}{\sigma_J^2}+\Delta E\right]\langle x^\alpha\rangle_{v'J,v-1J}+2(\alpha+1)F_2\langle x^{\alpha+2}\rangle_{v'J,vJ}=0\ , \quad (20)$$

with $\Delta E=E_{v'J}-E_{vJ}$.

Then we would straightforwardly calculate the successive powers of x^α, $\alpha=2,3,\ldots$, using Eqs. (14), (19), and (20), starting with $\alpha=0$ and taking into account the orthonormality condition.

For the diagonal case ($J=J'$), we can obtain all the matrix elements $\langle v'J|x^\alpha|vJ\rangle$ for any value of α (positive or negative), without using the explicit form of the wave functions, working with Eqs. (13)–(15), (19), and (20). The results of this section will be used later to derive the matrix elements of other interesting operators.

B. Recursion relations for matrix elements related to the q and x operators

Using the off-diagonal hypervirial theorem with the commutator

$$\langle v'J|[H,q^\alpha]|vJ\rangle=(E_{v'J}-E_{vJ})\langle v'J|q^\alpha|vJ\rangle\ , \quad (21)$$

together with the expressions for the ladder operators [Eqs. (9) and (10)], we obtain, after some algebraic manipulations, the following recursion relations:

$$\begin{aligned}\Delta E\langle q^\alpha\rangle_{v'J,vJ}&=\alpha ab\langle q^{\alpha-1}\rangle_{v'J,vJ}\\&+\alpha(\alpha-1)\langle q^{\alpha-2}\rangle_{v'J,vJ}\\&-2A_v^{-1}a\sigma_J\langle q^{\alpha-1}x\rangle_{v'J,v+1J}\\&-\frac{4a\alpha\sigma_J\sigma_{JJ}}{b-1}\langle q^{\alpha-1}x\rangle_{v'J,vJ},\end{aligned} \quad (22)$$

and

$$\begin{aligned}\Delta E\langle q^\alpha\rangle_{v'J,vJ}&=-\alpha ab\langle q^{\alpha-1}\rangle_{v'J,vJ}\\&+\alpha(\alpha-1)\langle q^{\alpha-2}\rangle_{v'J,vJ}\\&+\frac{4a\alpha\sigma_J\sigma_{JJ}}{b+1}\langle q^{\alpha-1}x\rangle_{v'J,vJ}\\&+2B_{v-1}^{-1}a\sigma_J\langle q^{\alpha-1}x\rangle_{v'J,v-1J}\ ,\end{aligned} \quad (23)$$

with $\alpha=1,2,3,\ldots$.

If we know the expectation values of $\langle q^{\alpha-1}\rangle_{vJ,vJ}$, which can be derived from the analytical expressions given in the literature,[16,17] we can evaluate the matrix elements $\langle q^\alpha\rangle_{v'J,vJ}$ and $\langle q^{\alpha-1}x\rangle_{v'J,+1J}$, using Eqs. (22) and (23), alternatively. The matrix elements $\langle q\rangle_{v'J,vJ}$ are obtained by setting $\alpha=1$ in Eqs. (22) and (23), in terms of the $\langle x\rangle_{v'J,v+1J}$ matrix elements. This procedure permits us to evaluate exact matrix elements ($v\neq v', J=J'$) of the q^α and xq^α operators without the explicit use of the wave functions and avoids working with complicated analytical expressions.

Finally, we can obtain the matrix elements of the $x^\alpha(d/dr)$ operator, using the definitions of the ladder operators $G^+(v)$ and $G^-(v)$ [see Eqs. (9) and (10)]. Thus combining adequately both equations, we deduce

$$\begin{aligned}\left\langle x^\alpha\frac{d}{dr}\right\rangle_{v'J',vJ}&=\frac{2a\sigma_J\sigma_{JJ}}{b^2-1}\langle x^\alpha\rangle_{v'J',vJ}\\&-\frac{a}{2}\sigma A_V^{-1}\langle x^\alpha\rangle_{v'J,v+1J}\\&+\frac{A}{2}\sigma_J B_{v-1}^{-1}\langle x^{\alpha+1}\rangle_{v'J',v-1J}\ .\end{aligned} \quad (24)$$

If $J=J'$, we can use the hypervirial theorem alternatively to get these matrix elements. So, by the following equation:

$$\left\langle v'J\left|\left[H,x^\alpha\frac{d}{dr}\right]\right|vJ\right\rangle=\Delta\left\langle v'J\left|\frac{d}{dr}\right|vJ\right\rangle\ , \quad (25)$$

we derive

$$\begin{aligned}\left\langle x^\alpha\frac{d}{dr}\right\rangle_{v'J,vJ}\left[\Delta+\alpha^2\frac{F_2}{\sigma_J^2}\right]&=-2a\alpha(E_{vJ}-F_0)\langle x^\alpha\rangle_{v'J,vJ}\\&-a(2\alpha+1)F_1\langle x^{\alpha+1}\rangle_{v'J,vJ}\\&+2a(\alpha+1)F_2\langle x^{\alpha+2}\rangle_{v'J,vJ}\ .\end{aligned} \quad (26)$$

If we make $\Delta=E_{v'J}-E_{vJ}=0$ and $\alpha=0$, we find that $\langle d/dr\rangle_{vJ}=0$. This result was used previously to derive Eqs. (14) and (15).

IV. CONCLUDING REMARKS

By means of the operators algebra, we can generate simple closed-form expressions for the matrix elements of the x^α, $x^\alpha(d/dr)$, q^α, and $q^\alpha x$ operators for the rotating Morse oscillator by a recursive method that obviates the need for using explicit eigenfunctions (if $J=J'$). We feel our equations improve the previous results[4,5] because we only need the overlap integrals to evaluate all the matrix elements when $J\neq J'$, but we do not need to know any expression for the wave functions when $J=J'$.

These matrix elements can be used in perturbations expansions in which the Morse vibrational-rotational states are used as a starting point. These are utilized in spectroscopic problems for polyatomics molecules.[18,19] In the case of dynamics problems such as the vibrational energy transfer for simple molecules or collinear reactive collisions a better approximations is usually required.

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