Journal of Mathematical Chemistry 25 (1999) 383–391

Algebraic derivation of Franck–Condon overlap integrals for diatomic molecules

A. Frank [a,b], R. Lemus [a] and F. Pérez-Bernal [c]

[a] *Instituto de Ciencias Nucleares, UNAM, Apdo. Postal 70-543, Circuito Exterior, C.U., 04510 México, D.F., México*

[b] *Centro de Ciencias Físicas, UNAM, Apdo. Postal 139-B, Cuernavaca, Morelos, México*

[c] *Departamento de Física Atómica, Molecular y Nuclear, Facultad de Física, Universidad de Sevilla, Apdo. 1065, 41080 Sevilla, Spain*

Received 24 November 1998; revised 23 June 1999

We derive a new formula for Franck–Condon harmonic-oscillator overlap integrals using an algebraic procedure based on a Bogoliubov transformation. We discuss how the formulation may be generalized to SU(2)-based descriptions of anharmonic oscillator wave functions.

1. Introduction

Within the Born–Oppenheimer approximation the dipole transition strengths of absorption or emission of light in a molecule are proportional to the overlap integral between vibrational states in the ground and excited electronic states. In addition, for this approximation to be valid, the electronic dipole transition moment must vary slowly as a function of internuclear distance [12]. Since a vast amount of spectroscopic measurements in molecules involve the excitation and subsequent de-excitation of electronic states, the calculation of vibrational overlap integrals is of great interest. A first approximation for diatomic molecules is to consider both electronic states as harmonic oscillator potentials. Although this is usually a crude approximation, it constitutes the starting point for corrections which include anharmonic behavior [6,8]. Several authors have derived formulas for the harmonic oscillator overlaps using different methods, including analytic and generating function approaches, which usually lead to recurrence relations [2,7,16,21,23,24]. In a recent paper, an algebraic method was used to evaluate the overlap integral in closed form by defining translation and dilatation operators in terms of the creation and annihilation harmonic oscillator operators [13]. It was stressed in this work that this derivation can in principle be generalized to anharmonic Pöschl–Teller and Morse oscillators via the Lie algebra of U(2) [1,3]. A modified harmonic oscillator formula was subsequently used with great success to describe the Franck–Condon emission spectrum of S_2O [4,10,19,20]. The purpose of this paper is to present a new algebraic derivation of harmonic-oscillator overlap integrals which

relies entirely upon the commutator relations for the Weyl–Heisenberg algebra and which may thus be generalized to anharmonic U(2) overlaps by an appropriate change in the commutator relations. Although the overlap expression we find is equivalent to the one derived in [13], the procedure is simpler and better suited for its extension to the Morse and Pöschl–Teller systems.

In this paper we shall concentrate on the harmonic oscillator case and only indicate the steps required to derive the corresponding result for the U(2) potentials.

The rest of the paper is organized as follows. In section 2 we show that the dilatation and translation operations on the harmonic oscillator states translate into a Bogoliubov transformation on the corresponding creation and annihilation operators. In section 3 we carry out the evaluation of the overlap integrals by applying this transformation, while in section 4 we describe the procedure to generalize our result for the anharmonic systems. Finally, in section 5 we present our conclusions.

2. Bogoliubov transformation

Consider two one-dimensional harmonic potentials

$$V_1(x) = \frac{\mu\omega^2}{2}\,x^2, \qquad V_2(x') = \frac{\mu\omega'^2}{2}\,x'^2, \tag{1}$$

where μ is the reduced mass and ω, ω' the corresponding frequencies. The potentials are centered on $x = 0$ and $x' = 0$, respectively, where

$$x' = x - x_0 \tag{2}$$

and x_0 is the displacement between the two. The ground state wave functions for these potentials are given by

$$|0\rangle = \sqrt{\frac{\alpha}{\pi^{1/2}}}\,\mathrm{e}^{-1/2\alpha^2x^2}, \qquad |0\rangle\rangle = \sqrt{\frac{\alpha'}{\pi^{1/2}}}\,\mathrm{e}^{-1/2\alpha'^2x'^2}, \tag{3}$$

where $\alpha \equiv (\mu\omega/\hbar)^{1/2}$ and we used a double ket to denote the displaced state. The overlap integral of these states can be obtained simply by substituting (2) and completing squares in the exponential. The result is

$$\langle\langle 0|0\rangle = \sqrt{\frac{2(\omega\omega')^{1/2}}{(\omega+\omega')}}\,\exp\left[\frac{-\mu}{2\hbar}\,\frac{\omega\omega' x_0^2}{(\omega+\omega')}\right]. \tag{4}$$

Equation (4) is the only integral that must be evaluated in the algebraic procedure. We now define creation and annihilation operators for the x and x' variables,

$$x = \sqrt{\frac{\hbar}{2\mu\omega}}\,\left(a + a^\dagger\right), \qquad x' = \sqrt{\frac{\hbar}{2\mu\omega'}}\,\left(b + b^\dagger\right), \tag{5}$$

where $[a, a^\dagger] = 1$, $[b, b^\dagger] = 1$. From (5) we find

$$a + a^\dagger = \sqrt{\frac{2\mu\omega}{\hbar}}\, x, \tag{6a}$$

$$b + b^\dagger = \sqrt{\frac{2\mu\omega'}{\hbar}}\, x' = \sqrt{\frac{2\mu\omega'}{\hbar}}\, (x - x_0), \tag{6b}$$

which imply that

$$b + b^\dagger = \sqrt{\frac{\omega'}{\omega}}\, \big(a + a^\dagger\big) - \sqrt{\frac{2\mu\omega'}{\hbar}}\, x_0. \tag{7}$$

Likewise, since

$$\frac{\partial}{\partial x} = \sqrt{\frac{m\omega}{2\hbar}}\big(a - a^\dagger\big) \quad \text{and} \quad \frac{\partial}{\partial x'} = \sqrt{\frac{m\omega'}{2\hbar}}\big(b - b^\dagger\big),$$

we find

$$b - b^\dagger = \sqrt{\frac{\omega}{\omega'}}\, \big(a - a^\dagger\big). \tag{8}$$

Solving (7) and (8),

$$b = ua + va^\dagger - \beta', \tag{9a}$$

$$b^\dagger = ua^\dagger + va - \beta', \tag{9b}$$

where

$$u = \frac{\omega + \omega'}{2\sqrt{\omega\omega'}}, \qquad v = \frac{\omega' - \omega}{2\sqrt{\omega\omega'}}, \qquad \beta' = \sqrt{\frac{\mu\omega'}{2\hbar}}\, x_0. \tag{10}$$

The inverse form of (9) can be readily evaluated:

$$a = ub - vb^\dagger + \beta, \tag{11a}$$

$$a^\dagger = ub^\dagger - vb + \beta, \tag{11b}$$

where

$$\beta = \sqrt{\frac{\mu\omega}{2\hbar}}\, x_0. \tag{12}$$

The transformations (9) and (11) are Bogoliubov (particle-hole) transformations supplemented by translations by β' and β, respectively, since

$$u^2 - v^2 = 1. \tag{13}$$

We conclude that this simple transformation connects the states of the displaced (and dilatated) potentials (1). Since the harmonic oscillator eigenfunctions are monomials in $a^\dagger$ (or $b^\dagger$), we exploit this fact in the next section to evaluate closed expressions for their general overlaps.

3. Harmonic oscillator overlaps

The states associated to the harmonic oscillator wells (1) are given by

$$|\nu\rangle = \frac{1}{\sqrt{\nu!}} \left(a^\dagger\right)^\nu |0\rangle \tag{14}$$

and

$$|\nu'\rangle\!\rangle = \frac{1}{\sqrt{\nu'!}} \left(b^\dagger\right)^{\nu'} |0\rangle\!\rangle. \tag{15}$$

Our task is thus to evaluate the overlap

$$\langle\!\langle \nu'|\nu\rangle = \frac{1}{\sqrt{\nu!\nu'!}} \langle\!\langle 0\big| b^{\nu'} \left(a^\dagger\right)^\nu \big|0\rangle, \tag{16}$$

which we can accomplish by substitution of the transformation (9) in (16) and using a binomial expansion

$$\begin{aligned}\langle\!\langle \nu'|\nu\rangle &= \frac{1}{\sqrt{\nu!\nu'!}} \langle\!\langle 0\big| \left(ua + va^\dagger - \beta'\right)^{\nu'} \left(a^\dagger\right)^\nu \big|0\rangle \\ &= \sqrt{\frac{\nu!}{\nu'!}} \sum_{k=0}^{\nu'} \frac{(-\beta')^{\nu'-k}}{k!(\nu'-k)!} \langle\!\langle 0\big| \left(ua + va^\dagger\right)^k \left(a^\dagger\right)^\nu \big|0\rangle. \end{aligned} \tag{17}$$

Before proceeding with the calculation, we require a normal order expansion of the binomial $(ua + va^\dagger)^k$. This is a simple expansion which has been previously obtained by other authors [9]. We find the result

$$\left(ua + va^\dagger\right)^k = \sum_{s=0}^{[k/2]} \sum_{t=0}^{k-2s} \frac{(-)^s k! u^{k-s-t} v^t}{2^s s!(k-2s-t)!t!} (a)^{k-2s-t} \left(a^\dagger\right)^t, \tag{18}$$

substituting back in (17) we obtain a triple sum and the overlap

$$\langle\!\langle 0\big| (a)^{k-2s-t} \left(a^\dagger\right)^{\nu+t} \big|0\rangle \equiv A_{\nu+t}^{k-2s-t}, \tag{19}$$

which we now evaluate by solving a recurrence relation. Applying the a, $a^\dagger$ commutation relation we find

$$\begin{aligned} A_l^m &= \langle\!\langle 0\big| a^m \left(a^\dagger\right)^l \big|0\rangle = \langle\!\langle 0\big| a^m a^\dagger \left(a^\dagger\right)^{l-1} \big|0\rangle \\ &= \langle\!\langle 0\big| a^\dagger a^m \left(a^\dagger\right)^{l-1} \big|0\rangle + m \langle\!\langle 0\big| a^{m-1} \left(a^\dagger\right)^{l-1} \big|0\rangle. \end{aligned} \tag{20}$$

The action on the left of $a^\dagger$ on the displaced vacuum $|0\rangle\!\rangle$ can be evaluated by means of the inverse transformation (11). Taking the Hermitean conjugate of $\langle\!\langle 0|a^\dagger$ we find

$$a|0\rangle\!\rangle = \left(ub - vb^\dagger + \beta\right)|0\rangle\!\rangle = \left(-vb^\dagger + \beta\right)|0\rangle\!\rangle, \tag{21}$$

since $b|0\rangle\rangle = 0$. Applying again relation (9) for $b^\dagger$ and solving for $a|0\rangle\rangle$ gives

$$a|0\rangle\rangle = \left(-ga^\dagger + f\right)|0\rangle\rangle, \tag{22}$$

where

$$g = \frac{v}{u}, \qquad f = \frac{v\beta' + \beta}{u^2}. \tag{23}$$

Inserting the Hermitean conjugate of (22) in the first term of (20) we readily find the recurrence relation

$$A_l^m = mA_{l-1}^{m-1} - gA_{l-1}^{m+1} + fA_{l-1}^m, \tag{24}$$

where $A_0^0 = \langle\langle 0|0\rangle$ is given by (4). The recurrence relation (24) can be used in conjunction with (17) and (18) to find to general overlap (16). Although numerical evaluation of (24) is quite simple, we have also solved it explicitly:

$$A_l^m = \sum_{j=0}^{[(l-m)/2]} \frac{(-)^j l! f^{l-m-2j} g^j}{(l-m-2j)!2^j j!} \langle\langle 0|0\rangle. \tag{25}$$

The final result for the overlap is given by

$$\langle\langle \nu'|\nu\rangle = \sum_{k,s,t} \sqrt{\frac{\nu'!}{\nu!}} \frac{(-)^{\nu'-k+s}(\beta')^{\nu'-k} u^{k-s-t} v^{t+s}}{(\nu'-k)!2^s s!(k-2s-t)!t!} A_{\nu+t}^{k-2s-t}, \tag{26}$$

where the limits in the sums were defined in (17) and (18). To check our formula we have compared it with the expression derived in [9], finding full accord.

Formula (26) was arrived at by purely algebraic means through the Bogoliubov transformations (9) and (10). In the next section we briefly discuss its generalization to U(2) anharmonic potentials.

4. Anharmonic overlap

It is well known that a number of exactly solvable one-dimensional potentials, including the Morse and Pöschl–Teller (P.T.) potentials, can be associated to a U(2) algebraic structure [1,3,11]. This fact has been exploited in the description of vibrational spectra in polyatomic molecules by means of local-mode vibron models that arise from the coupling of anharmonic U(2) oscillators [4,10,15,19,20,22,25]. This approach has been very successful in providing accurate fits to energies and transition intensities in these systems. We refer the reader to the literature for a detailed description of these methods [4,10,11,14,15,18–20,22,25]. Since the wave functions arising from the fits are expressed as linear combinations of products of one-dimensional U(2) eigenstates [4,10,14,15,19–22,25], it is then possible to compute Franck–Condon factors in polyatomic molecules as linear combinations of products of overlap integrals for each U(2) oscillator. For this reason it is necessary to evaluate such integrals, in order to

avoid the computer intensive (and often unstable) calculations associated with overlaps of Morse (or Pöschl–Teller) wave functions in configuration space [13]. An important step in this direction was accomplished in [13], where closed Franck–Condon expressions were derived for a "dynamically adapted" harmonic oscillator overlap. The nth energy level Morse wave function is substituted by a harmonic wave function, where the frequency and position of the corresponding potential are adjusted to best approximate the Morse potential for each n. Coupled with a U(2)-model fit to the ground and excited vibrational levels of S_2O, the method successfully describes the observed Franck–Condon emission spectrum in this molecule [17]. This constitutes a computationally efficient method which opens the way to the study of transition amplitudes in polyatomic molecules.

In this section we indicate an alternative way to evaluate anharmonic overlaps, starting from the derivation of the harmonic Franck–Condon factors discussed in the previous sections.

We begin by introducing an SU(2) algebra

$$\big[\widehat{J}_+, \widehat{J}_-\big] = 2\widehat{J}_0, \qquad \big[\widehat{J}_0, \widehat{J}_\pm\big] = \pm\widehat{J}_\pm \tag{27}$$

and consider a fixed representation $j = N/2$, where N is an integer. We can now define the renormalized operators

$$c = \frac{\widehat{J}_+}{\sqrt{N}}, \qquad c^\dagger = \frac{\widehat{J}_-}{\sqrt{N}}, \qquad \widehat{\nu} = \frac{N}{2} - \widehat{J}_0, \tag{28}$$

which from (27) can be seen to satisfy the commutation relations

$$\big[c, c^\dagger\big] = 1 - \frac{2\widehat{\nu}}{N}, \qquad \big[c, \widehat{\nu}\big] = c, \qquad \big[c^\dagger, \widehat{\nu}\big] = -c^\dagger, \tag{29}$$

which are similar to the (Weyl–Heisenberg) harmonic oscillator relations ($\widehat{n} = a^\dagger a$)

$$\big[a, a^\dagger\big] = 1, \qquad \big[a, \widehat{n}\big] = a, \qquad \big[a^\dagger, \widehat{n}\big] = -a^\dagger, \tag{30}$$

except for the $2\widehat{\nu}/N$ correction in (29). We note that in the limit of $N \to \infty$ we recover (30). This is the contraction limit of SU(2) to the Weyl–Heisenberg algebra. The operators (28) have as wave functions the usual $|jm\rangle$ states, which we can rewrite as $|Nv\rangle$:

$$|Nv\rangle = \sqrt{\frac{N^v(N-v)!}{N!v!}}\,\big(c^\dagger\big)^v|N0\rangle, \tag{31}$$

where $N = 2j$ and $v = N/2 - m$. The matrix elements of $c^\dagger$ and c are then given by

$$\big\langle Nv+1\big|c^\dagger\big|Nv\big\rangle = \sqrt{(v+1)(1-v/N)}, \tag{32a}$$

$$\big\langle Nv-1|c|Nv\big\rangle = \sqrt{v\left(1 - \frac{v+1}{N}\right)}, \tag{32b}$$

which again reduce to the harmonic oscillator results for $N \to \infty$, but that include corrections for finite N consistent with the anharmonic character of the Morse potential [5].

To illustrate the connection of these operators with anharmonic potentials, consider the simple Hamiltonian

$$\mathcal{H} = \frac{\hbar\omega}{2}\left(c^\dagger c + cc^\dagger\right). \tag{33}$$

Using (29) we find the energy eigenspectrum of (33) to be

$$E_\nu = \hbar\omega\left(\nu + 1/2 - \nu^2/N\right), \tag{34}$$

$$= \hbar\omega_e(\nu + 1/2) - \frac{\omega_e}{N+1}(\nu + 1/2)^2 - \frac{\hbar\omega}{4N}, \tag{35}$$

where $\omega_e = (1 + 1/N)\omega_0$. Except for the unimportant constant $\hbar\omega/(4N)$, this is the exact form of the Morse spectrum. Child and Halonen [5] have analyzed the coupling of Morse oscillators and defined the anharmonicity parameter k, which from (35) is seen to be given by

$$k = N + 1. \tag{36}$$

The integer N can be shown to be directly related with the depth and range of the Morse potential $D(1 - \mathrm{e}^{-ax})^2$ by the relation [11]

$$N + 1 = \left(\frac{8\mu D}{a^2\hbar^2}\right)^{1/2}, \tag{37}$$

where μ is the reduced mass of the diatomic system.

There are other ways to establish the close link between U(2) (or SU(2)) and the Morse potential [1,3], but perhaps this is a simpler method. Having shown this correlation, we are now in a position to enumerate the necessary steps for the evaluation of the U(2) overlaps

$$I^{NN'}_{\nu\nu'} = \langle\langle N'\nu'|N\nu\rangle. \tag{38}$$

The main idea is to substitute in (9), (11), (14) and (15) the SU(2) operators and states (28) and (31) for their harmonic counterparts. This "anharmonization" must be carried out before any commutator has been calculated, taking into account the modified expressions (29). Relation (17) will essentially be preserved for the c and $c^\dagger$ operators, except for the different normalization in (31), but a generalization of (18) is required for $\widehat{J}_+$ and $\widehat{J}_-$ and the recurrence relation (24) will have a more complex form. The procedure, however, can be implemented following the steps used in the derivation of equation (26). The results and their comparison with numerical results for Morse and P.T. potentials will be presented in a forthcoming publication.

5. Conclusions

We have presented a new closed formula for Franck–Condon overlap integrals for harmonic oscillator states, following a purely algebraic procedure based on the particle-hole transformations (9) and (11), which relate the creation and annihilation operators of displaced oscillators with different frequencies. The result depends crucially on formula (18), which is simple to derive by repeated use of the Heisenberg–Weyl $[a, a^\dagger] = 1$ commutator. In order to generalize this result to the case of SU(2) operators (28), which are associated to anharmonic potentials, several modifications are required, including the normal expansion formulas for SU(2) equivalent to (18). The use of such formulas in conjunction to vibron model molecular structure fits should contribute to the establishment of an algebraic framework for the evaluation of Franck–Condon intensities in polyatomic molecules.

Acknowledgement

This work was supported in part by DGAPA-UNAM under project IN101997.

References

[1] Y. Alhassid, F. Gursey and F. Iachello, Ann. Phys. (N.Y.) 148 (1983) 346.
[2] F. Ausbacher, Z. Naturforsch. 14a (1959) 589.
[3] M. Berrondo and A. Palma, J. Phys. A: Math. Gen. 13 (1980) 773.
[4] R. Bijker, A. Frank, R. Lemus, J.M. Arias and F. Pérez-Bernal, A comparison between algebraic models of molecular spectroscopy, in: *Symmetries in Science X*, Bregenz, Austria (July 13–18, 1997) (Plenum Press) pp. 37–46.
[5] M.S. Child and L. Halonen, Adv. Chem. Phys. 57 (1984) 1.
[6] P.J. Drallos and S.M. Wadebra, J. Chem. Phys. 85 (1986) 6524.
[7] F. Fernandez and E. Castro, *Algebraic Methods in Quantum Chemistry and Physics* (CRC Press, 1995).
[8] F.M. Fernandez and J.T. Ogilvie, Chem. Phys. Lett. 169 (1990) 292.
[9] G.F. Filippov, V.I. Ovcharenko and Y.F. Smirnov, *Microscopic Theory of Collective Excitations of Atomic Nuclei* (Kiev, 1981) p. 302.
[10] A. Frank, R. Lemus, R. Bijker, F. Pérez-Bernal and J.M. Arias, Rev. Mex. Fís. 42 (1996) 73; Ann. Physics 252 (1996) 211.
[11] A. Frank and P. Van Isacker, *Algebraic Methods in Molecular and Nuclear Structure Physics* (Wiley Interscience, 1994).
[12] G. Herzberg, *Spectra of Diatomic Molecules* (Van Nostrand, New York, 1950).
[13] F. Iachello and M. Ibrahim, Analytic and algebraic evaluation of Franck–Condon overlap integrals, J. Phys. Chem., to appear.
[14] F. Iachello and R.D. Levine, *Algebraic Theory of Molecules* (Oxford University Press, Oxford, 1995).
[15] F. Iachello and S. Oss, J. Chem. Phys. 9 (1993) 7337; J. Mol. Spectrosc. 153 (1992) 225; Phys. Rev. Lett. 66 (1991) 2976; Chem. Phys. Lett. 187 (1991) 500.
[16] S. Koide, Z. Naturforsch. 15a (1960) 123.
[17] T. Müller, P. Dupré, P.H. Vaccaro, F. Pérez-Bernal, M. Ibrahim and F. Iachello, Chem. Phys. Lett. 292 (1998) 243.

[18] S. Oss, *Algebraic Models in Molecular Spectroscopy*, Advances in Chemical Physics, Vol. 93 (1996).
[19] F. Pérez-Bernal, J.M. Arias, A. Frank, R. Lemus and R. Bijker, J. Mol. Spectrosc. 184 (1997) 1; Czechoslovak J. Phys. 48 (1998) 782; A symmetry adapted approach to molecular spectroscopy: the anharmonic oscillator symmetry model, in: *Symmetries in Science IX*, Bregenz, 1996.
[20] F. Pérez-Bernal, R. Bijker, A. Frank, R. Lemus and J.M. Arias, Chem. Phys. Lett. 258 (1996) 301.
[21] L. Sandoval, A. Palma and F. Rivas-Silva, Int. J. Quant. Chem. 23 (1989) 183.
[22] O.S. van Roosmalen, I. Benjamin and R.D. Levine, J. Chem. Phys. 81 (1984) 5986.
[23] M. Wagner, Z. Naturforsch. 14a (1959) 81.
[24] S. Waldenstrom and K. Razi, Chem. Phys. Lett. 85 (1982) 581; J. Chem. Phys. 77 (1982) 1614.
[25] L. Wiesenfeld, J. Mol. Spectrosc. 184 (1997) 277.