Properties of the Quantum Double Oscillator

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A formalism is presented to obtain approximate analytic expressions for the eigenstates and eigenvalues of a quantum double oscillator (QDO). The matrix elements of a large class of operators with respect to states of different double oscillators result as finite sums of explicit functions of the respective parameters. Matrix elements between states of a harmonic oscillator and a double oscillator are also determined. The analytic expressions were used to calculate Franck-Condon factors for electronic transitions including double oscillator anharmonicities.

I. Introduction

A great variety of problems in physics and chemistry can be described in terms of a quantum mechanical particle or quasiparticle oscillating around two different equilibrium positions with the possibility of interchange. One of the first applications of such a double oscillator (DO) was given by Hund[1] and other authors[2] to analize the inversional motion of the NH_3-molecule[3]. The mechanisms of direct intramolecular rearrangements in other molecular complexes can also be discussed in terms of a quantum double oscillator[4]: Examples are the inversion of molecules and molecular parts[5], the pseudorotation of the ring puckering amplitudes in cyclic systems[6], the Berry-pseudorotation[7] of trigonal bypyramidal molecules[8] and the alternative "turnstile" rotation[9]. The motion of protons in hydrogen bonds in molecular systems[10—12] and microbiological systems[13] can also be described with this model. In molecular spectroscopy and in recent concepts of radiationless transitions the double oscillator appears as a special kind of anharmonicity[14, 15]. The appearance of a double oscillator potential in an excited electronic state generated by Jahn-Teller interaction has a characteristic influence on the electronic absorption and emission spectra of the corresponding molecular system[14, 15]. In solid state physics the DO-model is used to represent the orientational relaxation of polar impurities[16, 17] and to analyze the properties of ice and other hydrogen bonded complexes[18]. Ferroelectric phase transitions can also be described in terms of a double oscillator model[19]. In nuclear physics, the DO-concept can be used to analyze the asymetric mass distribution of fragments after fission of actinide nuclei[20—22].

In most of the chemical and physical systems cited above quantum effects cannot be neglected, and one has to solve some of the following problems

(i)   Determination of eigenstates and eigenvalues of the quantum double oscillator (QDO)

(ii) Coupling of the double oscillator to a photon or a phonon field

(iii) Calculation of matrix elements of several operators, like position, momentum, and kinetic energy with respect to double oscillator states

(iv) Transitions between different double oscillators or between a double oscillator and an oscillator

(v)   Adiabatic changes of double oscillator states as an analytic function of time.

There is no problem in principle to solve the Schrödinger equation for a QDO by numerical or quasiclassical methods and many authors have done this considering different model potentials and physical realizations[3, 7, 13, 21—27]. Even more, a formal analytic solution of the Schrödinger equation with a two-center oscillator potential can be obtained[21], which reduces the problem of solving the differential equation to the problem of finding the zeros of Kummers confluent hypergeometric functions. However, the disadvantage of such a procedure is that it is impossible or at least very complicated to obtain matrix elements of physical operators with respect to the eigenstates of the QDO as analytic functions of the parameters of the system. Such analytic properties are important for example in the study of non-stationary phenomena, where the parameters such as the oscillatory frequency ω and the displacement $2 \cdot d$ of the two equilibrium positions are functions of time. The calculation of matrix elements between eigenstates of different double oscillators

(or double oscillator and single oscillator) as in (iv) is a second example.

In the present paper a formalism is presented to obtain approximate analytic expressions for the eigenstates and eigenvalues of a double oscillator. The matrix elements of the position operator, the momentum operator, and the kinetic energy with respect to two different QDOs result as finite sums of explicit functions of the respective parameters. Matrix elements between states of a single oscillator and a double oscillator are also determined.

II. Model and Basic Results

A) Formal Solution of the Schrödinger Equation of the QDO

The double oscillator can be represented by a Hamiltonian $\mathbf{H}(\xi)$ for the motion of a particle with effective mass in a potential field depicted schematically in Figure 1.
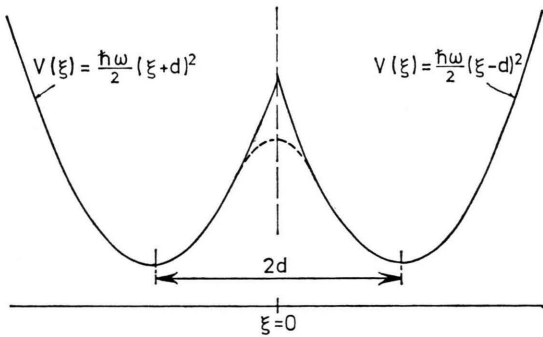

Fig. 1. Potential energy of a double oscillator (schematically); 2d: Separation of the two wells in generalized units.

The Schrödinger equation

$$\mathbf{H}\,\psi_\lambda(\xi) = \frac{\hbar\,\omega}{2}\left(-\frac{d^2}{d\xi^2} + V(\xi)\right)\psi_\lambda(\xi) = E_\lambda\,\psi_\lambda(\xi) \tag{1}$$

with

$$V(\xi) = (|\xi| - d)^2 = \begin{cases} (\xi+d)^2 & \text{for } \xi \leqq 0 \\ (\xi-d)^2 & \text{for } \xi \geqq 0 \end{cases} \tag{2}$$

is solved by the non normalized functions [21, 22]

$$\psi_\lambda(\xi) = \{\Theta(\xi) + P\,\Theta(-\xi)\} \tag{3}$$

$$\cdot \exp\left[-\tfrac{1}{2}(|\xi|-d)^2\right] U\left(-\frac{\lambda}{2}, \frac{1}{2}, (|\xi|-d)^2\right)$$

where $U(a, b\,z)$ is the confluent hypergeometric function, $\Theta(\xi)$ the heaviside step function, and $P = \pm 1$ the parity of the wave functions. The eigenvalues are [21]

$$E_\eta = \hbar\,\omega\,(\eta + \tfrac{1}{2}) \tag{4}$$

where the non integer parameter η is related to the displacement d by the relations [21]

$$\begin{cases} U\left(-\dfrac{\eta}{2}, \dfrac{1}{2}, d^2\right) = 0 & \text{for } P = -1 \\[2mm] \dfrac{d}{d\xi} \exp\left[-\dfrac{1}{2}(\xi-d)^2\right] \\[2mm] \cdot U\left(-\dfrac{\eta}{2}, \dfrac{1}{2}, (\xi-d)^2\right)\Bigg|_{\xi=0} = 0 & \text{for } P = 1. \end{cases} \tag{5}$$

The solutions of these equations, i. e. the determination of E as a function of d, can only obtained by numerical methods [21].

B) Approximate Solution of the Schrödinger Equation of the Double Oscillator

For large values of d and small vibrational quantum numbers the solution of Eq. (1) can be approximated by

$$\psi_n^{\pm d}(\xi) = \frac{1}{\sqrt{2}}\left[u_n(\xi+d) \pm u_n(\xi-d)\right] \tag{6}$$

with the energies

$$E_n^\pm = \hbar\,\omega\,(n + \tfrac{1}{2}) + \Delta E_n/2. \tag{7}$$

Here $u_n(\xi)$ is the eigenfunction of an oscillator of frequency ω with the vibrational quantum number n. $\mathbf{H}(\xi)$, $\psi_n^\pm(\xi)$ are again given in terms of generalized coordinates [21, 25]

$$\xi = (m\,\omega/\hbar)^{1/2}\,x. \tag{8}$$

The energy split ΔE_n of the two adjacent states ψ_n^+ and and ψ_n^- [22]

$$\Delta E_n = 2\left|\int_{-\infty}^{+\infty} d\xi\,u_n(\xi+d)\,\mathbf{H}(\xi)\,u_n(\xi-d)\right| \tag{9}$$

can be roughly estimated with the aid of the quasi-classical JWKB-method [28]

$$\Delta E_0 = \frac{\hbar\,\omega}{2}\exp\left[-\left|\int_{-\xi_u}^{+\xi_u}\sqrt{V(\xi)-1}\,\right|d\xi\right] \tag{10}$$

where $-\xi_u$ and $+\xi_u$ are the classical turning points to the left and the right of the barrier separating the two harmonic wells. In this approximation several types of barrier functions $V_B(\xi)$ (see Fig. 1,

dotted line) can be used. For small values of d or (and) large quantum numbers the overlap integral

$$S_n = \int_{-\infty}^{+\infty} u_n(\xi + d) u_n(\xi - d) \, \mathrm{d}\xi \qquad (11)$$

can no longer be neglected. Instead of (7) one has approximately

$$E_n^{\pm}(1 \pm S_n) = a_n \pm \beta_n \qquad (12)$$

with

$$a_n = \int_{-\infty}^{+\infty} u_n(\xi + d) \mathbf{H}(\xi) u_n(\xi + d) \, \mathrm{d}\xi \qquad (13)$$

and

$$\beta_n = \int_{-\infty}^{+\infty} u_n(\xi + d) \mathbf{H}(\xi) u_n(\xi - d) \, \mathrm{d}\xi . \qquad (14)$$

a_n is now different from $\hbar \omega \ (n + \frac{1}{2})$ because of the special form of $\mathbf{H}(\xi)$. To get analytic expressions for $E_n^{\pm} \equiv E_n^{\pm} \ (d, \omega, m)$ we have to evaluate (11), (13), and (14).

For $d = 0$ the secular matrix, which is the basis of (9), becomes singular and one obtains only one energy (see Figure 2).
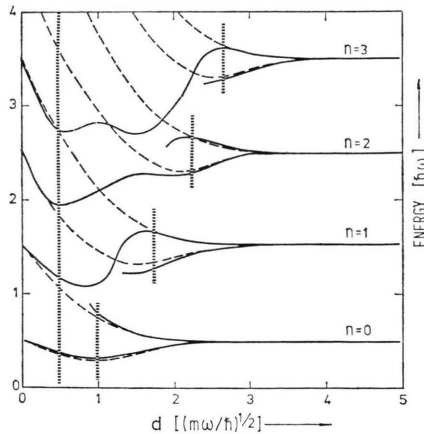

Fig. 2. Eigenvalues $E_n^{\pm}$ of a double oscillator as function of d (full line: approximate values from Eq. (13); dashed line: exact energies).

From $S_n = 1$, $a_n = \beta_n = \hbar \omega \ (n + \frac{1}{2})$ follows directly

$$E_n^+ (d = 0) = \hbar \omega (n + \frac{1}{2}) . \qquad (15)$$

For $d \neq 0$ is $|S_n| < 1$ and therefore

$$E_n^{\pm} = \frac{a_n \pm \beta_n}{1 \pm S_n} = \frac{a_n - \beta_n S_n \pm (\beta_n - a_n S_n)}{1 - S_n^2} . \qquad (16)$$

The lowest energies as functions of d are drawn in Figure 2. The renormalized double oscillator wave functions are now

$$\psi_n^{\pm d}(\xi) = (2 \pm 2 \, S_n)^{-1/2} [u_n(\xi + d) \pm u_n(\xi - d)] . \qquad (17)$$

With the aid of the translational shift operator $\mathbf{T}_s(\lambda)$ [29, 30]

$$\mathbf{T}_s(\lambda) f(x) = \exp\left(\lambda \frac{\mathrm{d}}{\mathrm{d}x}\right) f(x) = f(x + \lambda) \qquad (18)$$

expression (17) becomes

$$\psi_n^{\pm d}(\xi) = 2^{-1/2} (1 \pm S_n)^{-1/2} [\mathbf{T}_s(d) \pm \mathbf{T}_s(-d)] u_n(\xi) \qquad (19)$$

i. e. the approximate wave functions of the double oscillator can be formally derived by the action of a linear operator $\mathbf{D}_n^+$ on the harmonic oscillator wave functions:

$$\psi_n^{\pm d}(\xi) = \mathbf{D}_n^+(\pm d) u_n(\xi) . \qquad (20)$$

C) Second Quantization

The Hamiltonian for a harmonic oscillator of frequency ω in second quantized form is given by

$$\mathbf{H}_{\mathrm{osc}} = \hbar \omega (\mathbf{a}^+ \mathbf{a} + \frac{1}{2}) \qquad (21)$$

with the creation operator $\mathbf{a}^+$ and the annihilation operator $\mathbf{a}$

$$\mathbf{a} = 2^{-1/2} \cdot (\boldsymbol{\xi} + i \, \mathbf{p}) , \quad \mathbf{a}^+ = 2^{-1/2} (\boldsymbol{\xi} - i \, \mathbf{p}) \qquad (22)$$

where $\mathbf{p}$ is the generalized momentum operator

$$\mathbf{p} = -i \, \partial / \partial \xi . \qquad (23)$$

$\mathbf{a}$ and $\mathbf{a}^+$ have the well known properties [30]

$$\begin{cases} [\mathbf{a}, \mathbf{a}^+] = 1 , \\ (\mathbf{a}^+)^n |0\rangle = (n!)^{1/2} |n\rangle , \\ \mathbf{a} |0\rangle = 0 , \\ \langle 0 | 0 \rangle = 1 , \\ \mathbf{H}_{\mathrm{osc}} |n\rangle = \hbar \omega (n + \frac{1}{2}) |n\rangle \end{cases} \qquad (24)$$

where $|0\rangle$ is the so called no-phonon state or oscillator ground state. Using the relations (24) we can write in coordinate free representation

$$|\psi_n^{\pm d}\rangle = \mathbf{B}_n^+(\pm d) |0\rangle \qquad (25)$$

where

$$B_n^+(\pm d) = 2^{-1/2} (1 \pm S_n)^{-1/2} (n!)^{-1/2} \cdot$$
$$\cdot [\mathbf{T}_s(d) \pm \mathbf{T}_s^+(d)] (\mathbf{a}^+)^n . \qquad (26)$$

From (18), (22), and (23) we have

$$\mathbf{T}_s(\lambda) = \exp(i\,\lambda\,\mathbf{p}) = \exp[\lambda'(\mathbf{a} - \mathbf{a}^+)] \quad (27)$$

with

$$\lambda' = 2^{-1/2}\,\lambda \quad (28)$$

and therefore

$$\begin{cases} \mathbf{T}_s^+(d) \equiv \mathbf{T}_s(-d)\,, \\ \mathbf{T}_s(d_1)\,\mathbf{T}_s(d_2) = \mathbf{T}_s(d_1 + d_2)\,, \\ \mathbf{T}_s^+(d_1)\,\mathbf{T}_s^+(d_2) = \mathbf{T}_s(-d_1 - d_2)\,, \\ \mathbf{T}_s(d)\,\mathbf{T}_s^+(d) = \mathbf{T}_s(d)\,\mathbf{T}_s(-d) \equiv 1\,. \end{cases} \quad (29)$$

We obtain from (26)

$$\mathbf{B}_n(\pm d) = 2^{-1/2}\cdot$$
$$\cdot\,(1 \pm S_n)^{-1/2}\,(n!)^{-1/2}\,\mathbf{a}^n[\mathbf{T}_s^+(d) \pm \mathbf{T}_s(d)]\,. \quad (30)$$

The overlap integrals between the two displaced oscillators can simply be written with the aid of the operator $\mathbf{T}_s$

$$\begin{aligned} S_n &= \langle n\,|\,\mathbf{T}_s(2\,d)\,|\,n\rangle = \langle n\,|\,\mathbf{T}_s^+(2\,d)\,|\,n\rangle \\ &= (n!)^{-1}\,\langle 0\,|\,\mathbf{a}^n\,\mathbf{T}_s(2\,d)\,\mathbf{a}^{+n}\,|\,0\rangle \\ &= (n!)^{-1}\,\langle 0\,|\,\mathbf{a}^n\,\mathbf{T}_s^+(2\,d)\,\mathbf{a}^{+n}\,|\,0\rangle\,. \end{aligned} \quad (31)$$
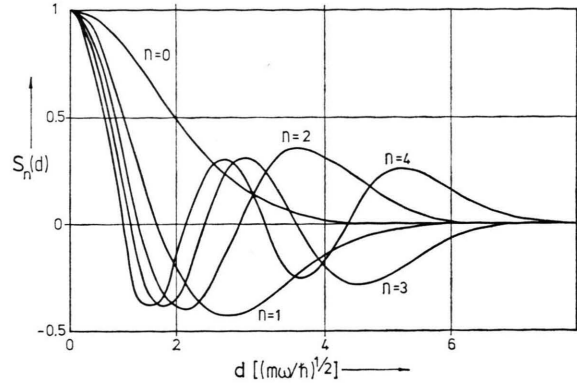

Fig. 3. Overlap-integrals $S_n(d)$ between two oscillator eigenfunctions of the same quantum number n, but displaced by d.

In Fig. 3 some overlap integrals $S_n(d)$ are depicted as functions of d. The approximate double oscillator states (25) are not strongly orthogonal as can been shown by calculating the overlap integrals. One has

$$\begin{aligned} \langle \psi_m^{\pm d}\,|\,\psi_n^{\pm d}\rangle &= \langle 0\,|\,\mathbf{B}_m(\pm d)\,\mathbf{B}_n^+(\pm d)\,|\,0\rangle = [(1 \pm S_m)\,(1 \pm S_n)\,m!\,n!]^{-1/2} \\ &\quad \times \{\langle 0\,|\,\mathbf{a}^m\,\mathbf{a}^{+n}\,|\,0\rangle \pm \tfrac{1}{2}(\langle 0\,|\,\mathbf{a}^m\,\mathbf{T}_s^+(2\,d)\,\mathbf{a}^{+n}\,|\,0\rangle + \langle 0\,|\,\mathbf{a}^m\,\mathbf{T}_s(2\,d)\,\mathbf{a}^{+n}\,|\,0\rangle)\} \\ &= [(1 \pm S_m)\,(1 \pm S_n)]^{-1/2}\{\delta_{mn} \pm \tfrac{1}{2}[1 + (-1)^{m-n}]\,\langle m\,|\,\mathbf{T}_s(2\,d)\,|\,n\rangle\}\,. \end{aligned} \quad (32)$$

Respectively

$$\begin{aligned} \langle \psi_m^{\pm d}\,|\,\psi_n^{\mp d}\rangle &= \pm\tfrac{1}{2}[(1 \pm S_m)\,(1 \mp S_n)]^{-1/2}\,(\langle m\,|\,\mathbf{T}_s(2\,d)\,|\,n\rangle - \langle m\,|\,\mathbf{T}_s^+(2\,d)\,|\,n\rangle) \\ &= \pm\tfrac{1}{2}[(1 \pm S_m)\,(1 \mp S_n)]^{-1/2}\,[1 - (-1)^{m-n}]\,\langle m\,|\,\mathbf{T}_s(2\,d)\,|\,n\rangle\,. \end{aligned} \quad (33)$$

Here we used the relation

$$\langle m\,|\,\mathbf{T}_s^+(d)\,|\,n\rangle = \langle m\,|\,\mathbf{T}_s(-d)\,|\,n\rangle = (-1)^{m-n}\,\langle m\,|\,\mathbf{T}_s(d)\,|\,n\rangle \quad (34)$$

which will be derived in Part IV.

Generally the deviation from orthogonality is relatively small if d is large enough. With the aid of the algebraic formalism presented above it is possible to calculate matrix elements of linear operators with respect to the approximate eigenstates of a double oscillator if one knows the overlap integrals between the eigenstates of two oscillators which are displaced against each other. In the following chapter such matrix elements of some representative operators will be determined.

III. Matrix Elements of Some Operators with Respect to Double Oscillator States

Let $\mathbf{O} \equiv \mathbf{O}(\mathbf{a}, \mathbf{a}^+)$ be a linear operator which can be written as a polynomial of the creation operator $\mathbf{a}^+$ and the annihilation operator $\mathbf{a}$. The matrix element

$$\begin{aligned} \langle \psi_m^{\pm d}|\,\mathbf{O}\,|\,\psi_n^{\pm d}\rangle &\equiv \langle 0\,|\,\mathbf{B}_m(\pm d)\,\mathbf{O}\,\mathbf{B}_n^+(\pm d)\,|\,0\rangle \\ &= \tfrac{1}{2}[(1 \pm S_m)\,(1 \pm S_n)]^{-1/2}\,\langle m\,|\,[\mathbf{T}_s^+(d) \pm \mathbf{T}_s(d)]\,\mathbf{O}\,[\mathbf{T}_s(d) \pm \mathbf{T}_s^+(d)]\,|\,n\rangle \end{aligned} \quad (35)$$

can be determined, if integrals of the type

$$\langle m\,|\,\mathbf{T}_s^+\,\mathbf{O}\,\mathbf{T}_s\,|\,n\rangle \quad \text{and} \quad \langle m\,|\,\mathbf{T}_s\,\mathbf{O}\,\mathbf{T}_s\,|\,n\rangle \quad (36)$$

are known. These expressions can simply be solved with the aid of the commutation relations (see appendix B):

$$\begin{cases} \mathbf{T}_s(d)\,\mathbf{a}^n = (\mathbf{a}+d')^n\,\mathbf{T}_s(d)\ , \\ \mathbf{T}_s^+(d)\,\mathbf{a}^n = (\mathbf{a}-d')^n\,\mathbf{T}_s^+(d)\ , \\ \mathbf{T}_s(d)\,\mathbf{a}^{+n} = (\mathbf{a}^++d')^n\,\mathbf{T}_s(d)\ , \\ \mathbf{T}_s^+(d)\,\mathbf{a}^{+n} = (\mathbf{a}^+-d')^n\,\mathbf{T}_s^+(d)\ , \qquad d' = 2^{-1/2}\,d\ . \end{cases}$$

(37)

Applications to some special operators may illustrate the procedure.

A) Momentum and Position (Dipole transition-) operator

With the definition of $\mathbf{T}_s(d)$ [Eq. (24)] the momentum operator

$$\mathbf{p} = -i\,2^{-1/2}\,(\mathbf{a}-\mathbf{a}^+) \tag{38}$$

commutes with $\mathbf{T}_s(d)$ and $\mathbf{T}_s^+(d)$ and one obtains

$$\begin{aligned} \langle \psi_m^{\pm d}\,|\,\mathbf{p}\,|\,\psi_n^{\pm d}\rangle &= -i\,2^{-3/2}\,[(1\pm S_m)(1\pm S_n)]^{-1/2}\,\langle m\,|\,[\mathbf{T}_s^+(d)\pm\mathbf{T}_s(d)]\,[\mathbf{T}_s(d)\pm\mathbf{T}_s^+(d)]\,(\mathbf{a}-\mathbf{a}^+)|\,n\rangle \\ &= -i\,[2(1\pm S_m)(1\pm S_n)]^{-1/2}\,\{n^{1/2}\,\delta_{mn-1}-(n+1)^{1/2}\,\delta_{mn+1} \\ &\quad \pm \tfrac{1}{2}[n^{1/2}\,\langle m\,|\,\mathbf{T}_s^+(2\,d)+\mathbf{T}_s(2\,d)\,|\,n-1\rangle-(n+1)^{1/2}\,\langle m\,|\,\mathbf{T}_s^+(2\,d)+\mathbf{T}_s(2\,d)\,|\,n+1\rangle]\} \\ &= -i\,[2(1\pm S_m)(1\pm S_n)]^{-1/2}\,\{n^{1/2}[\delta_{mn-1}\pm\tfrac{1}{2}(1+(-1)^{m-n-1})\,\langle m\,|\,\mathbf{T}_s(2\,d)\,|\,n-1\rangle] \\ &\quad -(n+1)^{1/2}[\delta_{mn+1}\pm\tfrac{1}{2}(1+(-1)^{m-n-1})\,\langle m\,|\,\mathbf{T}_s(2\,d)\,|\,n+1\rangle]\}\ . \end{aligned}$$

(39)

If we use the overlap integrals of the double oscillator states, eq. (32), relation (39) leads to

$$\langle \psi_m^{\pm d}\,|\,\mathbf{p}\,|\,\psi_n^{\pm d}\rangle = -i\left\{\left[\frac{n}{2}\,\frac{1\pm S_{n-1}}{1\pm S_n}\right]^{1/2}\cdot\langle \psi_m^{\pm d}\,|\,\psi_{n-1}^{\pm d}\rangle-\left[\frac{(n+1)}{2}\,\frac{1\pm S_{n+1}}{1\pm S_n}\right]^{1/2}\,\langle \psi_m^{\pm d}\,|\,\psi_{m+1}^{\pm d}\rangle\right\}. \tag{40}$$

For $\langle \psi_m^{\pm d}\,|\,\hat{\mathbf{p}}\,|\,\psi_n^{\mp d}\rangle$ we obtain analogously

$$\langle \psi_m^{\pm d}\,|\,\mathbf{p}\,|\,\psi_n^{\mp d}\rangle = \mp\frac{i}{2}\,[2(1\pm S_m)(1\mp S_n)]^{-1/2}\,[1-(-1)^{m-n-1}]\,[n^{1/2}\,\langle m\,|\,\mathbf{T}_s(2\,d)\,|\,n-1\rangle-(n+1)^{1/2} \\ \cdot\langle m\,|\,\mathbf{T}_s(2\,d)\,|\,n+1\rangle] \tag{41}$$

or

$$\langle \psi_m^{\pm d}\,|\,\mathbf{p}\,|\,\psi_n^{\mp d}\rangle = -i\left\{\left[\frac{n}{2}\,\frac{1\mp S_{n-1}}{1\mp S_n}\right]^{1/2}\,\langle \psi_m^{\pm d}\,|\,\psi_{n-1}^{\mp d}\rangle-\left[\frac{(n+1)}{2}\,\frac{1\mp S_{n-1}}{1\mp S_n}\right]^{1/2}\,\langle \psi_m^{\pm d}\,|\,\psi_{n-1}^{\mp d}\rangle\right\}. \tag{42}$$

The position operator is [see Eq. (22)]

$$\boldsymbol{\xi} = 2^{-1/2}\,(\mathbf{a}+\mathbf{a}^+)\ . \tag{43}$$

With the aid of Eq. (37) one has

$$(\mathbf{a}+\mathbf{a}^+)\,[\mathbf{T}_s(d)\pm\mathbf{T}_s^+(d)] = \mathbf{T}_s(d)\,(\mathbf{a}+\mathbf{a}^+-2\,d')\pm\mathbf{T}_s^+(d)\,(\mathbf{a}+\mathbf{a}^++2\,d') \tag{44}$$

and therefore

$$\begin{aligned} \langle \psi_m^{\pm d}\,|\,\boldsymbol{\xi}\,|\,\psi_n^{\pm d}\rangle &= 2^{-3/2}\,[(1\pm S_m)(1\pm S_n)]^{-1/2}\,\{\langle m\,|\,[\mathbf{T}_s^+(d)\pm\mathbf{T}_s(d)]\,\mathbf{T}_s(d)\,(\mathbf{a}+\mathbf{a}^+-2\,d')\,|\,n\rangle \\ &\pm\langle m\,|\,[\mathbf{T}_s^+(d)\pm\mathbf{T}_s(d)]\,\mathbf{T}_s^+(d)\,(\mathbf{a}+\mathbf{a}^++2\,d')\,|\,n\rangle\} = [2(1\pm S_m)(1\pm S_n)]^{-1/2} \\ &\cdot\{n^{1/2}[\delta_{mn-1}\pm\tfrac{1}{2}(1+(-1)^{m-n-1})\,\langle m\,|\,\mathbf{T}_s(2\,d)\,|\,n-1\rangle] \\ &+(n+1)^{1/2}[\delta_{mn+1}\pm\tfrac{1}{2}(1+(-1)^{m-n-1})\,\langle m\,|\,\mathbf{T}_s(2\,d)\,|\,n+1\rangle]\mp2^{-1/2}\,d\,[1-(-1)^{m-n}]\,\langle m\,|\,\mathbf{T}_s(2\,d)\,|\,n\rangle\} \end{aligned}$$

(45)

and

$$\langle \psi_m^{\pm d}\,|\,\boldsymbol{\xi}\,|\,\psi_n^{\mp d}\rangle = \pm[2(1\pm S_m)(1\mp S_n)]^{-1/2}\,\{\tfrac{1}{2}[1-(-1)^{m-n-1}]\,[n^{1/2}\,\langle m\,|\,\mathbf{T}_s(2\,d)\,|\,n-1\rangle+(n+1)^{1/2} \\ \cdot\langle m\,|\,\mathbf{T}_s(2\,d)\,|\,n+1\rangle]-[1+(-1)^{m-n}]\,\langle m\,|\,\mathbf{T}_s(2\,d)\,|\,n\rangle\mp2^{1/2}\,d\,\delta_{mn}\}\ . \tag{46}$$

The matrix elements, Eqs. (45, 46), can also be given with respect to the double oscillator overlap integrals

$$\langle \psi_m^{\pm d}\,|\,\boldsymbol{\xi}\,|\,\psi_n^{\pm d}\rangle = \left[\frac{n}{2}\,\frac{1\pm S_{n-1}}{1\pm S_n}\right]^{1/2}\,\langle \psi_m^{\pm d}\,|\,\psi_{n-1}^{\pm d}\rangle+\left[\frac{n+1}{2}\,\frac{1\pm S_{n+1}}{1\pm S_n}\right]^{1/2}\,\langle \psi_m^{\pm d}\,|\,\psi_{n+1}^{\pm d}\rangle-d\,\langle \psi_m^{\pm d}\,|\,\psi_n^{\mp d}\rangle \tag{47}$$

and

$$\langle \psi_m^{\pm d} \mid \boldsymbol{\xi} \mid \psi_n^{\mp d} \rangle = \left[\frac{n}{2} \frac{1 \mp S_{n-1}}{1 \mp S_n} \right]^{1/2} \langle \psi_m^{\pm d} \mid \psi_{n-1}^{\mp d} \rangle + \left[\frac{n+1}{2} \frac{1 \mp S_{n+1}}{1 \mp S_n} \right]^{1/2} \langle \psi_m^{\pm d} \mid \psi_{n+1}^{\mp d} \rangle - d \, \langle \psi_m^{\pm d} \mid \psi_n^{\pm d} \rangle \,. \tag{48}$$

In Fig. 4 the squares of the dipole transition matrix elements are displayed for a special case.
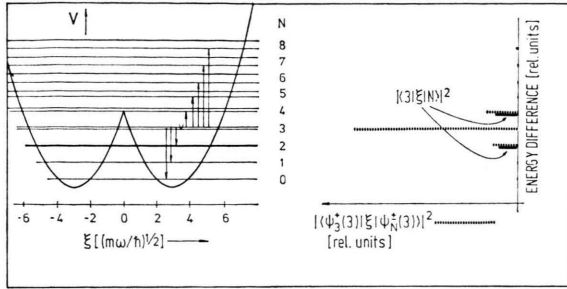

Fig. 4. Squares of dipole transition matrix elements between different double oscillator states.

B) Kinetic Energy

With

$$\mathbf{E}_{\mathrm{kin}} = (\hbar\,\omega/2)\,\mathbf{p}^2 = - (\hbar\,\omega/4)\,(\mathbf{a} - \mathbf{a}^+)^2 \tag{49}$$

and the commutation relations (38) one obtains

$$\begin{aligned}
\langle \psi_m^{\pm d} \mid \mathbf{E}_{\mathrm{kin}} \mid \psi_n^{\pm d} \rangle &= -\frac{\hbar\,\omega}{4} \frac{1}{2} \left[(1 \pm S_m)(1 \pm S_n) \right]^{-1/2} \langle m \mid [\mathbf{T}_s^+(d) \pm \mathbf{T}_s(d)][\mathbf{T}_s(d) \pm \mathbf{T}_s^+(d)](\mathbf{a} - \mathbf{a}^+)^2 \mid n \rangle \\
&= \frac{\hbar\,\omega}{4} \left[(1 \pm S_m)(1 \pm S_n) \right]^{-1/2} \big\{ (2\,n+1)\,[\delta_{mn} \pm \tfrac{1}{2}(1 + (-1)^{m-n})] \langle m \mid \mathbf{T}_s(2\,d) \mid n \rangle \\
&\quad - [n(n-1)]^{1/2}\,[\delta_{mn-2} \pm \tfrac{1}{2}(1 + (-1)^{m-n})]\,\langle m \mid \mathbf{T}_s(2\,d) \mid n-2 \rangle \\
&\quad - [(n+1)(n+2)]^{1/2}[\delta_{mn+2} \pm \tfrac{1}{2}(1 + (-1)^{m-n})]\,\langle m \mid \mathbf{T}_s(2\,d) \mid n+2 \rangle \big\} \\
&= \frac{\hbar\,\omega}{4} \big\{ (2\,n+1)\,\langle \psi_m^{\pm d} \mid \psi_n^{\pm d} \rangle - \left[\frac{1 \pm S_{n-2}}{1 \pm S_n} \right]^{1/2} \cdot \langle \psi_m^{\pm d} \mid \psi_{n-2}^{\pm d} \rangle - \left[\frac{1 \pm S_{n+2}}{1 \pm S_n} \right]^{1/2} \cdot \langle \psi_m^{\pm d} \mid \psi_{n+2}^{\pm d} \rangle \,.
\end{aligned} \tag{50}$$

For $\langle \psi^{\pm d} \mid \mathbf{E}_{\mathrm{kin}} \mid \psi^{\pm d} \rangle$ an analogous expression results.

IV. Matrix Elements Between an Oscillator and a Double Oscillator

A) Quantization of an Oscillator with Different Frequency

In analogy to Eq. (21) an oscillator of effective mass M and frequency Ω can be described by

$$\mathbf{H}_{\mathrm{osc}} = \hbar\,\Omega\,(\mathbf{A}^+\mathbf{A} + \tfrac{1}{2}) \tag{51}$$

where the creation operator $\mathbf{A}^+$ and the annihilation operator $\mathbf{A}$ obey the relations [30]

$$\begin{cases} [\mathbf{A}, \mathbf{A}^+] = 1 \,, \\ (\mathbf{A}^+)^N \mid 0 \rangle\rangle = (N!)^{1/2} \mid N \rangle\rangle \,, \\ \mathbf{A} \mid 0 \rangle\rangle = 0 \,, \\ \mathbf{H}_{\mathrm{OSC}} \mid N \rangle\rangle = \hbar\,\Omega\,(N + \tfrac{1}{2}) \mid N \rangle\rangle \end{cases} \tag{52}$$

and can be expressed in terms of $\mathbf{a}$ and $\mathbf{a}^+$ [30]

$$\mathbf{A} = \delta\mathbf{a}^+ + \varepsilon\,\mathbf{a} \,, \quad \mathbf{A}^+ = \delta\mathbf{a} + \varepsilon\,\mathbf{a}^+ \,, \tag{53}$$

$$[\mathbf{a}, \mathbf{A}] = [\mathbf{A}^+, \mathbf{a}^+] = \delta \,, \quad [\mathbf{a}, \mathbf{A}^+] = [\mathbf{A}, \mathbf{a}^+] = \varepsilon \tag{54}$$

with

$$\delta = \frac{1}{2} \left\{ \left(\frac{M\,\Omega}{m\,\omega} \right)^{1/2} - \left(\frac{m\,\omega}{M\,\Omega} \right)^{1/2} \right\} \tag{55}$$

and

$$\varepsilon = \frac{1}{2} \left\{ \left(\frac{M\,\Omega}{m\,\omega} \right)^{1/2} + \left(\frac{m\,\omega}{M\,\Omega} \right)^{1/2} \right\} \,. \tag{56}$$

It could be shown by Katriel [30] with the aid of an algebraic formalism that the overlap integrals between two harmonic oscillator wave functions on

different centers and with different force constants can be calculated in closed form. If the center of the $|N\rangle\rangle$ — states is located at the origin while the $|n\rangle$ — states are displaced by d (in generalized coordinates) one has

$$\langle\langle M\,|\,\mathbf{T}_s(d)\,|\,n\rangle = \varepsilon^{-1/2} \sum_{ijk} \frac{(M!\,n!)^{1/2} \exp\left[-\tfrac{1}{2}\,d'^2(\varepsilon+\delta)/\varepsilon\right]}{i!\,j!\,k!\,(M-2\,i-k)!\,(n-2\,j-k)!}$$
$$\times \left(\frac{1}{2}\,\frac{\delta}{\varepsilon}\right)^i \left(-\frac{1}{2}\,\frac{\delta}{\varepsilon}\right)^j \left(\frac{1}{\varepsilon}\right)^k \left(\frac{-d'}{\varepsilon}\right)^{M-2i-k} \left(d'\,\frac{\varepsilon+\delta}{\varepsilon}\right)^{n-2j-k}. \qquad (57)$$

This is a more general result than that obtained by several authors for two oscillators with the same frequency [22, 31].

From Eq. (57) results directly

$$\langle\langle M\,|\,\mathbf{T}_s(-d)\,|\,n\rangle = \langle\langle M\,|\,\mathbf{T}_s^+(d)\,|\,n\rangle = (-1)^{M-n}\langle\langle M\,|\,\mathbf{T}_s(d)\,|\,n\rangle. \qquad (58)$$

In Fig. 5 the dependence of these matrix elements on d and the ratio Ω/ω is illustrated.
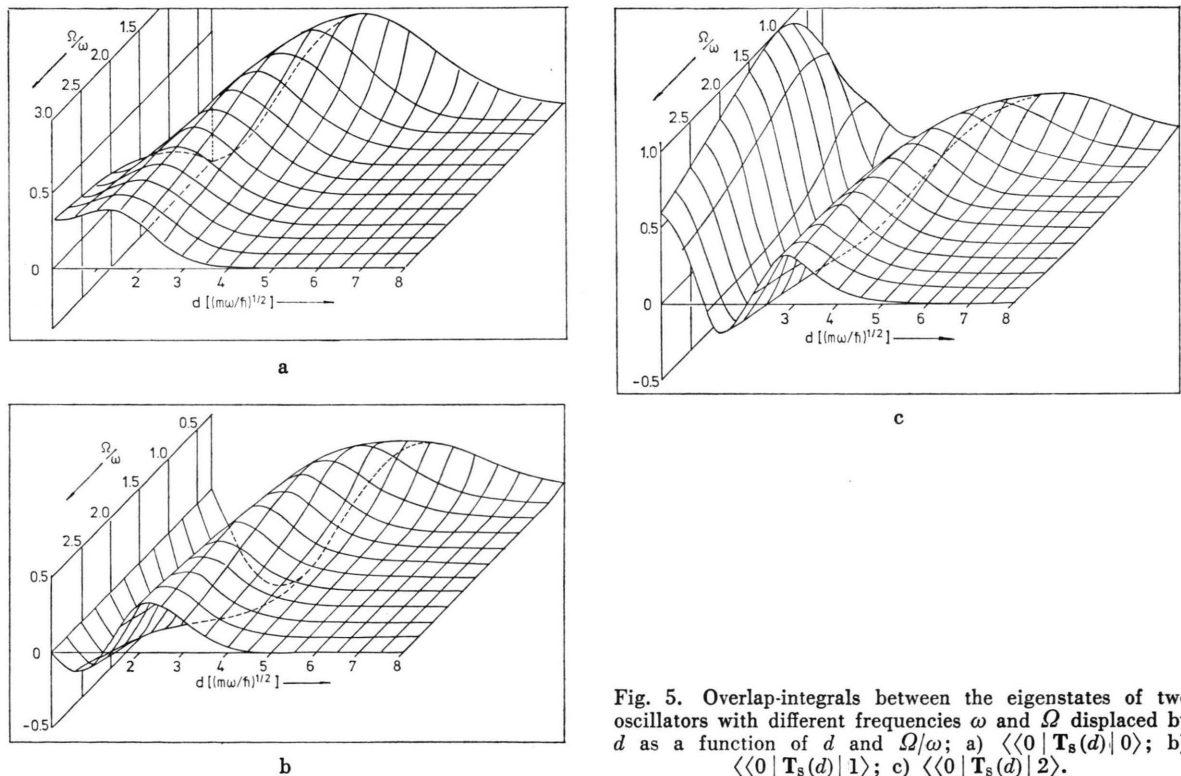
Fig. 5. Overlap-integrals between the eigenstates of two oscillators with different frequencies ω and Ω displaced by d as a function of d and Ω/ω; a) $\langle\langle 0\,|\,\mathbf{T}_s(d)\,|\,0\rangle$; b) $\langle\langle 0\,|\,\mathbf{T}_s(d)\,|\,1\rangle$; c) $\langle\langle 0\,|\,\mathbf{T}_s(d)\,|\,2\rangle$.

B) Matrix Elements for $\mathbf{p}$, ξ, and $\mathbf{E}_{kin}$ with Respect to Single and Double Oscillator States

The matrix elements of the form $\langle\langle M\,|\,\mathbf{O}\,|\,\psi_n^{\pm d}\rangle$ can be evaluated with the aid of Eqs. (57 − 58) in a similar way as in § III.

The overlap integrals become

$$\langle\langle M\,|\,\psi_n^{\pm d}\rangle = [2\,(1\pm S_n)]^{-1/2}\,[1\pm(-1)^{M-n}]\,\langle\langle M\,|\,\mathbf{T}_s(d)\,|\,n\rangle \qquad (59)$$

The Franck-Condon factors $|\langle\langle 0\,|\,\psi_m^\pm(d)\rangle\rangle|^2$ and $|\langle\langle n\,|\,\psi_0^+(d)\rangle\rangle|^2$ for some characteristic model systems are depicted in Fig. 6 a − d in comparison with Franck-Condon factors $|\langle n\,|\,\mathbf{T}(d)\,|\,0\rangle|^2$ between two displaced oscillators of the same frequency and of different frequencies.
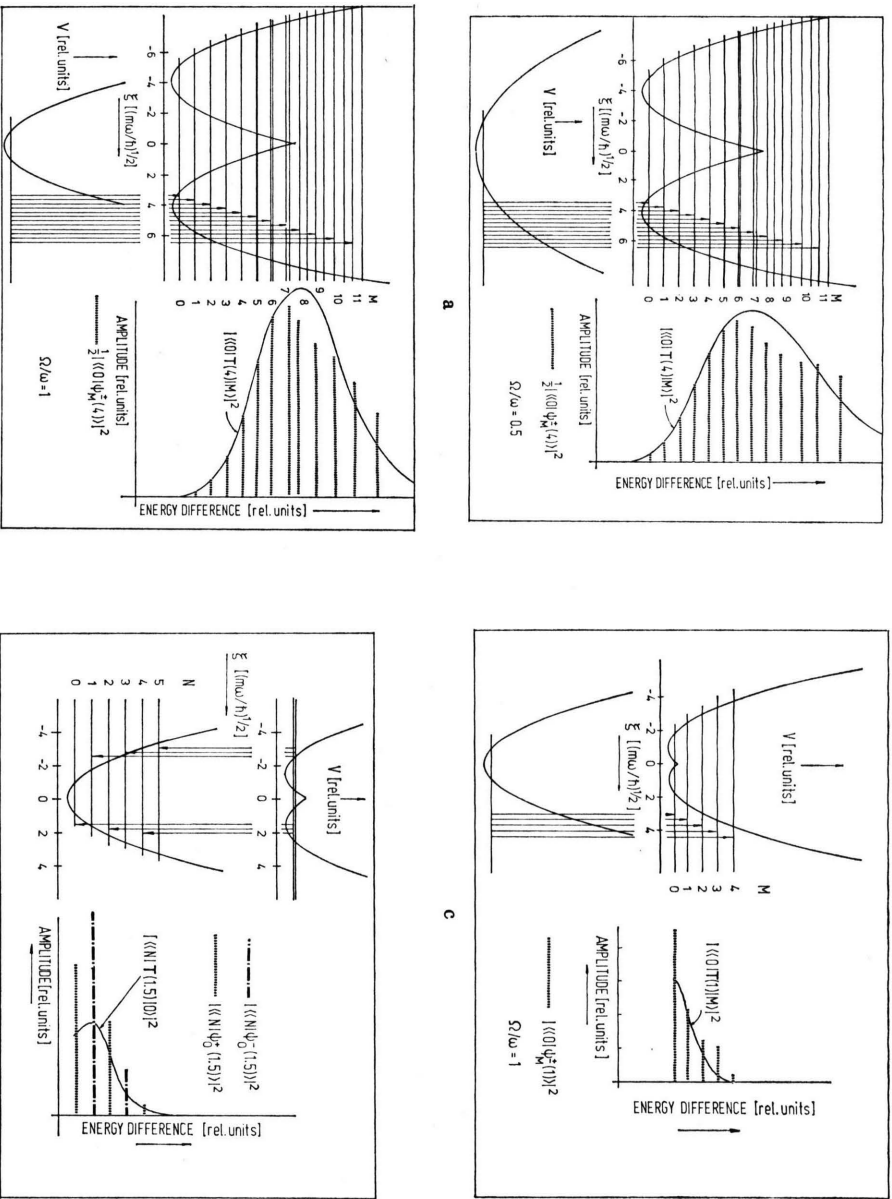
In analogy to Eq. (39) one obtains for the momentum operator

$$\langle\langle M|\mathbf{p}|\psi_n^{\pm d}\rangle = -\frac{i}{2}[1\pm S_n]^{-1/2}\langle M|\mathbf{T}_s(d)\pm\mathbf{T}_s^+(d)|n\rangle$$

$$= -\frac{i}{2}[1\pm S_n]^{-1/2}[1\pm(-1)^{M-n-1}]n^{1/2}\langle M|\mathbf{T}_s(d)|n-1\rangle -(n+1)^{1/2}\langle M|\mathbf{T}_s(d)|n+1\rangle] \tag{60}$$

and further for the dipole transition operator

$$\langle\langle M|\boldsymbol{\xi}|\psi_n^{\pm d}\rangle = \frac{1}{2}[1\pm S_n]^{-1/2}\{\langle\langle M|(\mathbf{T}_s(d)\pm\mathbf{T}_s^+(d))(\mathbf{a}+\mathbf{a}^+)|n\rangle - 2d'\langle\langle M|\mathbf{T}_s(d)|n\rangle\}$$
$$= \frac{1}{2}[1\pm S_n]^{-1/2}\{[1\pm(-1)^{M-n-1}[n^{1/2}\langle M|\mathbf{T}_s(d)|n-1\rangle + (n+1)^{1/2}\langle\langle M|\mathbf{T}_s(d)|n+1\rangle]$$
$$- 2d'[1\pm(-1)^{M-n}]\langle M|\mathbf{T}_s(d)|n\rangle\}. \tag{61}$$

The matrix elements of the kinetic energy result as

$$\langle\langle M|\mathbf{E}_{\mathrm{kin}}|\psi_n^{\pm d}\rangle = \frac{\hbar\omega}{4}[2(1\pm S_n)]^{-1/2}\langle\langle M|(\mathbf{T}_s(d)\pm\mathbf{T}_s^+(d))(2\mathbf{a}^+\mathbf{a}+1-\mathbf{a}^2-\mathbf{a}^{+2})|n\rangle$$
$$= \frac{\hbar\omega}{4}[2(1\pm S_n)]^{-1/2}[1\pm(-1)^{M-n}\{(2n+1)\langle\langle M|\mathbf{T}_s(d)|n\rangle$$
$$-[n(n-1)]^{1/2}\langle\langle M|\mathbf{T}_s(d)|n-2\rangle -[(n+1)\cdot(n+2)]^{1/2}\langle\langle M|\mathbf{T}_s(d)|n+2\rangle\}. \tag{62}$$

Fig. 6. Franck-Condon factors for transitions between a single oscillator ground state and a double oscillator excited state for different choises of the parameters d and Ω/ω.

V. Transitions Between the States of two Different Double Oscillators

The eigenstates of a double oscillator $|\psi_N^{\pm D}\rangle$ with effective mass M and frequency Ω can be evaluated in the same manner as described in § II. We will calculate the overlap integrals and dipole transition matrix elements between the eigenstates of the two different double oscillators. If the minima of the two wells of the oscillators are separated by d and D [in units of $(m\,\omega/\hbar)^{1/2}$], respectively, the overlap integrals become

$$\langle\psi_M^{\pm D}|\psi_n^{\pm d}\rangle = \tfrac{1}{2}\left[(1\pm\bar{S}_M)\,(1\mp S_n)\right]^{-1/2}\langle\langle M|(\mathbf{T}_s^+(D)\pm\mathbf{T}_s(D))\,(\mathbf{T}_s(d)\pm\mathbf{T}_s^+(d))|n\rangle \tag{63}$$
$$= \tfrac{1}{2}\left[(1\pm\bar{S}_M)\,(1\pm S_n)\right]^{-1/2}\left[1+(-1)^{M-n}\right]\left\{\langle\langle M|\mathbf{T}_s(d-D)|n\rangle\pm\langle\langle M|\mathbf{T}_s(d+D)|n\rangle\right\}$$

and

$$\langle\psi_M^{\pm D}|\psi_n^{\mp d}\rangle = \tfrac{1}{2}\left[(1\pm\bar{S}_M)\,(1\mp S_n)\right]^{-1/2}\left[1-(-1)^{M-n}\right]\left\{\langle\langle M|\mathbf{T}_s(d-D)|n\rangle\pm\langle\langle M|\mathbf{T}_s(d+D)|n\rangle\right\}. \tag{64}$$

The overlap integral $\bar{S}_M$ of two displaced eigenstates of the Ω-oscillator is given by [see Eq. (31)]

$$\bar{S}_M = \langle\langle M|\mathbf{T}_s(2\,D)|M\rangle\rangle = \langle M|\mathbf{T}_s[2\,(\varepsilon+\delta)D]|M\rangle. \tag{65}$$

The results of some numerical calculations of Franck-Condon factors from (55) and (56) are depicted in Figure 7. Again, significant differences between the double oscillator transitions and related single oscillator transitions appear.
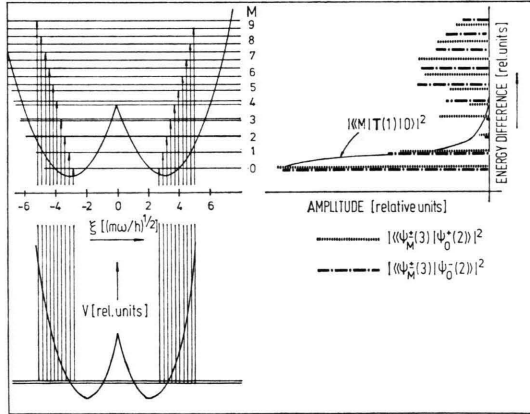

Fig. 7. Franck-Condon factors for a transition between two double oscillator states with different parameters ($\Omega/\omega=0.5$, $d=2$, $D=3$).

VI. Discussion

The approximate eigenstates of a QDO-system presented in this paper are well suited to calculate analytic expressions for matrix elements of a large class of operators. Transitions between two different QDO-systems or between a QDO state and a harmonic oscillator state can also be obtained as analytic functions of QDO parameters. The validity

of the approximation is restricted to values of the parameters, where the relations

$$\text{sign}\left[(S_n(d)\right] = \text{sign}\left[\lim_{d\to\infty}S_n(d)\right] \tag{66}$$

and

$$\text{sign}\left[(S_n(d)\right] = \text{sign}\left[\lim_{d\to 0}S_n(d)\right] \tag{67}$$

hold. For $d\lesssim 0.5$ and $d\gtrsim(2n+1)^{1/2}$ the relative error of the energy eigenvalues $[E_n-E_n(\text{approx})]/E_n$ is less than 1 percent while the splitting of two adjacent states can be given within less than 10 percent. The splitting is important for dynamical studies of transitions from one localized oscillator of the QDO-system to another [23].

Outside of the parameter range described by (66) and (67) the QDO wave functions and related matrix elements can only be obtained by numerical methods. This is also true for the "exact" solutions of the Schrödinger equation for the QDO-system [21]. For each value of d the values of the noninteger quantum number η [see Eq. (5)] can be calculated by numerical iteration. Even if exact values of η could be obtained, this would still not lead to a simple analytic expression for the eigenfunctions, Eq. (3), because the confluent hypergeometric functions $U(-a,\tfrac{1}{2},Z^2)$ can only be given as finite sums,

if $a = n/2$ with $n = 0, 1, 2, 3 \ldots$, corresponding to the relation [32]

$$H_n(Z) = 2^n U(-n/2, 1/2, Z^2) . \qquad (68)$$

respective to $d \to \infty$.

For all other values of a, the wave functions (3) can only be defined by infinite series.

As cited above, the QDO-model system can be used to interpret a lot of physical and chemical phenomena. As a demonstration calculations of Franck-Condon factors were carried out for different model situations (see Figs. 6 and 7). The band profile for an electronic transition between a single oscillator ground state and a QDO excited state differs characteristically from the profile of a transition between two displaced oscillators. The large anharmonicity of the QDO leads to an asymmetric double hump profile of the absorption spectrum (Fig. 6 a − c) while the fluorescence spectrum has no such remarkable changes (Figure 6 d). These results are in qualitative agreement with extensive calculation of other authors [14, 15]. The double hump character of the electronic spectrum is even more distinct in a QDO − QDO transition as can be seen in Figure 7. The amplitudes depicted in Fig. 6 and Fig. 7 were obtained with the aid of a small calculator using the analytic formulas (59), (63), and (64).

The main advantage of the presented analytic formulas for matrix elements of several operators is not the application to stationary problems but the possibility to handle time dependent changes of the QDO-Hamiltonian as a function of d and ω. Such a situation appears for example in numerical exchange reactions of light particles. In a subsequent paper [33] the proton exchange reaction between equivalent complexes will be investigated in terms of a time dependent QDO-model.

The numerical calculations were carried out on a Hewlett-Packard HP 65 and on the UNIVAC 1106/II of the Universität Freiburg.

Appendix A

Calculation of a_n and β_n

The QDO-Hamiltonian can be written as

$$\mathbf{H}(\xi) = H_{osc}(\xi + d) - \begin{cases} (2 \hbar \omega d) \xi & \text{for } \xi \geqq 0 \\ (2 \hbar \omega) \xi & \text{for } \xi \geqq 0 \end{cases}$$
$$(A\,1)$$

with the Hamiltonian $\mathbf{H}_{osc}$ of the harmonic oscillator in generalized coordinates. The matrix elements a_n and β_n Eqs. (3 − 4) become

$$a_n = \hbar \omega \left\{ (n + \tfrac{1}{2}) - 2 d \int_0^\infty d\xi \, u_n(\xi + d) \, \xi \, u_n(\xi + d) \right\},$$
$$(A\,2)$$

$$\beta_n = \hbar \omega \left\{ (n + \tfrac{1}{2}) S_n - 2 d \int_0^\infty d\xi \, u_n(\xi + d) \, \xi \, u_n(\xi - d) . \right.$$
$$(A\,3)$$

The integrals in (A 2) and (A 3) can be solved in closed form. By definition one has

$$u_n(\xi) = N_n H_n(\xi) \exp \left\{ -\tfrac{1}{2} \xi^2 \right\} \qquad (A\,4)$$

with the normalizing factors

$$N_n = [2^n n! \, \pi^{1/2}]^{-1/2} \qquad (A\,5)$$

and the orthogonal Hermitean functions $H_n(\xi)$

$$H_n(\xi) = (-1)^n \exp \left\{ \xi^2 \right\} (d^n/d\xi^n) \exp \left\{ -\xi^2 \right\} .$$
$$(A\,6)$$

Therefore

$$I_n^+ = \int_0^\infty d\xi \, u_n(\xi + d) \, \xi \, u_n(\xi + d)$$
$$= N_n^2 \int_0^\infty \exp \left\{ -(\xi + d)^2 \right\} \xi H_n^2(\xi + d) \, d\xi . \quad (A\,7)$$

With the recursions [34]

$$\xi H_n(\xi) = \tfrac{1}{2} H_{n+1}(\xi) + n H_{n-1}(\xi) \qquad (A\,8)$$

and

$$H_n'(\xi) = (d/d\xi) H_n(\xi) = 2 n H_{n-1}(\xi) \qquad (A\,9)$$

one obtains

$$I_n^+ = N_n^2 \Big\{ \tfrac{1}{2} \int_d^\infty d\eta \, \exp \left\{ -\eta^2 \right\} H_{n+1}(\eta) H_n(\eta)$$
$$+ n \int_d^\infty d\eta \, \exp \left\{ -\eta^2 \right\} H_{n-1}(\eta) H_n(\eta) \qquad (A\,10)$$
$$- d \int_d^\infty d\eta \, \exp \left\{ -\eta^2 \right\} H_n^2(\eta) \Big\}$$
$$= N_n^2 \Big\{ \tfrac{1}{2} H_n^2(d) \exp \left\{ -d^2 \right\} + 2 n I_{nn-1}^d - d I_{nn}^d \Big\}$$

where the last equality results from partial integration. The integrals I_{nn-1}^d **and** I_{nn}^d can be solved in a successive manner in analogy to a method published earlier [25]

$$I_{n+1\,n}^d = \sum_{i=0}^{n} \frac{n!}{i!} 2^{(n-i)} H_i^2(d) \exp\{-d^2\} \quad (A\,11)$$

and

$$I_{nn}^d = \sum_{i=1}^{n} \frac{n!}{i!} 2^{(n-i)} H_i(d) H_{i-1}(d) \exp\{-d^2\}$$
$$+ n!\, 2^n \frac{\sqrt{\pi}}{2} [1 - \mathrm{erf}(d)] \quad (A\,12)$$

with the error function

$$\mathrm{erf}(d) = \frac{2}{\sqrt{\pi}} \int_0^d \exp\{-\eta^2\}\, d\eta . \quad (A\,13)$$

With $(A\,10 - A\,13)$ the matrix elements $(A\,2)$ can be calculated. The integral in $(A\,3)$ can be solved with the aid of the expansion [34] for the Hermitean polynomials and the recursion $(A\,8)$

$$H_n(\xi+d) = \sum_{m=0}^{n} \binom{n}{m} H_m(\xi) (2\,d)^{n-m} \quad (A\,14)$$

$$I_n^{\pm} = \int_0^\infty d\xi\, u_n(\xi+d)\, \xi\, u_n(\xi-d)$$

$$= N_n^2 \exp\{-d^2\} \int_0^\infty d\xi \exp\{-\xi^2\}$$
$$\cdot H_n(\xi+d)\, \xi\, H_n(\xi-d)$$

$$= N_n^2 \exp\{-d^2\} \sum_{i=0}^{n} \sum_{k=0}^{n} (-1)^{n-k} \binom{n}{i}\binom{n}{k} (2\,d)^{2n-i-k}$$

$$\cdot \Big\{ \tfrac{1}{2} \int_0^\infty d\xi \exp\{-\xi^2\} H_i(\xi) H_{k+1}(\xi)$$

$$+ k \int_0^\infty d\xi \exp\{-\xi^2\} H_i(\xi) H_{k-1}(\xi) \Big\} . \quad (A\,15)$$

The last integrals were calculated in closed form in a earlier paper [25]. One obtains

$$I_{ii}^0 = N_i^2/2 = (2^{i+1} i!\, \pi^{1/2})^{-1} , \quad (A\,16)$$

$$I_{2i2j}^0 = I_{2i+1\,2j+1}^0 = 0 \quad \text{for all} \ i \neq j , \quad (A\,17)$$

and for $I_{2n\,2k+1}^0$ one has the recursion

$$I_{2n\,2k+1}^0 = (-1)^{n+k} \frac{(2\,n)!\,(2\,k)!}{n!\,k!} + 4\,n\, I_{2n-1\,2k}^0 \quad (A\,18)$$

with the "initial integrals"

$$I_{2j-1\,0}^0 = H_{2j-2}(0) = (-1)^{j-1} \frac{(2\,j-2)!}{(j-1)!} . \quad (A\,19)$$

With the relations $(A\,15 - A\,19)$ the integrals $(A\,3)$ are also determined.

Appendix B

Calculation of $[\mathbf{T}_s(\lambda), \mathbf{a}^n]$ *and* $[\mathbf{T}_s(\lambda), \mathbf{a}^{+n}]$

By definition of $\mathbf{T}_s(\lambda)$ Eq. (27) one has

$$\mathbf{T}_s(\lambda) \cdot \sum_{n=0}^{\infty} \frac{\mathbf{a}^n t^n}{n!} = \exp\{\lambda'(\mathbf{a} - \mathbf{a}^+)\} \exp\{t\,\mathbf{a}\} \quad (B\,1)$$

where t is an expansion parameter. Using the Zassenhaus formula [35] for operators $\mathbf{A}$ and $\mathbf{B}$

$$\exp\{\mathbf{A}\} \exp\{\mathbf{B}\} = \exp\{\mathbf{A}+\mathbf{B}\} \exp\{\tfrac{1}{2}[\hat{\mathbf{A}}, \hat{\mathbf{B}}]\} \quad (B\,2)$$

the right hand side of $(B\,1)$ reads

$$\exp\{\lambda'(\mathbf{a}-\mathbf{a}^+)\} \exp\{t\,\mathbf{a}\} =$$
$$= \exp\{\lambda'(\mathbf{a}-\mathbf{a}^+) + t\,\mathbf{a}\} \exp\{\tfrac{1}{2}\lambda' t\}$$
$$= \exp\{\tfrac{1}{2}\lambda' t\} \exp\{t\,\mathbf{a} + \lambda'(\mathbf{a}-\mathbf{a}^+)\}$$
$$= \exp\{\lambda' t\} \exp\{t\,\mathbf{a}\} \exp\{\lambda'(\mathbf{a}-\mathbf{a}^+)\} \quad (B\,3)$$
$$= \exp\{(\lambda'+\mathbf{a})t\} \exp\{\lambda'(\mathbf{a}-\mathbf{a}^+)\}$$
$$= \sum_{n=0}^{\infty} \frac{(\lambda'+\mathbf{a})^n t^n}{n!} \mathbf{T}_s(\lambda) .$$

Comparison of $(B\,1)$ and $(B\,3)$ gives

$$\mathbf{T}_s(\lambda)\, \mathbf{a}^n = (\mathbf{a}+\lambda')^n\, \mathbf{T}_s(\lambda) \quad (B\,4)$$

and in the same way one obtains the commutation relations (37).

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