On a Unified Theory of Twocentre Harmonic Oscillator Integrals

I. The Onedimensional Oscillator

W. WITSCHEL

Physikalisch-Technische Bundesanstalt, Braunschweig

(Z. Naturforsch. 26 a, 940—942 [1971]; received 3 March 1971)

Twocentre harmonic oscillator overlap integrals, arbitrary transition integrals and collision energy exchange integrals for equal and different frequencies of the oscillators are contained in a generalized Franck-Condon-integral which is solved by operator methods in the second quantization representation.

Introduction

A generalized Franck-Condon-integral of the form

\[ I = \langle m, \omega, 0 | x^l | r, \Omega, 0 + b \rangle \] (1)

is important in the theory of electronic transitions in molecular spectroscopy \(^1\) and in the theory of the optical properties of colour centres \(^2\). For brevity a double bracket is introduced to indicate that the basis set for the frequencies \(\omega\) and \(\Omega\) is different. The integral reads now:

\[ I = \langle m | x^l | r + b \rangle . \] (2)

The integral with \(l = 0\) is the usual twocentre overlap integral which was calculated by HUTCHINSON \(^3\). The theory of this integral was investigated with sophisticated analytical techniques by WAGNER \(^4\) and ANSCHER \(^5\), KOIDE \(^6\) introduced the occupation number representation in the calculation of the integral but he did not recognize that for different frequencies the basis systems of the oscillators are different.

Recently the interest in operator methods was renewed by KATRIEL \(^7\) who essentially gave an operator proof of Hutchison’s calculations.

In Part 1 the present article aims at a new elementary solution of the generalized Franck-Condon-integral by applying a recently published operator method \(^8\). Part 2 discusses the generalized transition and kinetic energy integral and the collision energy exchange integral which are implicitly contained in the integral of Eq. (1).

1. Solution of the Integral I

Following the notation of MESSIAH \(^9\) and KATRIEL \(^7\) the Hamiltonians of both oscillators are given by:

\[ \hat{H} = h \omega \left( \hat{a}^\dagger \hat{a} + \frac{1}{2} \right), \]
\[ \hat{H} = h \Omega \left( \hat{A}^\dagger \hat{A} + \frac{1}{2} \right). \]

The creation and annihilation operators are:

\[ \hat{a} = \left( \frac{M \omega}{2 \hbar} \right)^{1/4} \left( \hat{x} + \frac{i \hat{p}}{M \omega} \right), \]
\[ \hat{a}^\dagger = \left( \frac{M \omega}{2 \hbar} \right)^{1/4} \left( \hat{x} - \frac{i \hat{p}}{M \omega} \right), \]
\[ \hat{A} = \left( \frac{M \Omega}{2 \hbar} \right)^{1/4} \left( \hat{x} + \frac{i \hat{p}}{M \Omega} \right), \]
\[ \hat{A}^\dagger = \left( \frac{M \Omega}{2 \hbar} \right)^{1/4} \left( \hat{x} - \frac{i \hat{p}}{M \Omega} \right). \]

The commutators are:

\[ [\hat{a}, \hat{a}^\dagger] = [\hat{A}, \hat{A}^\dagger] = 1 . \] (9)

Introducing abbreviations

\[ \varepsilon = \frac{1}{2} \left\{ \left( \omega/\Omega \right)^{1/2} + \left( \Omega/\omega \right)^{1/2} \right\} \]
\[ \delta = \frac{1}{2} \left\{ \left( \varpi/\Omega \right)^{1/2} - \left( \Omega/\varpi \right)^{1/2} \right\} \]

yields

\[ \hat{A} = \delta \hat{a}^\dagger + \varepsilon \hat{a}, \]
\[ \hat{A}^\dagger = \delta \hat{a}^\dagger + \varepsilon \hat{a}^\dagger \]

with the commutation relations

\[ [\hat{a}, \hat{A}]_+ = [\hat{A}, \hat{a}^\dagger]_+ = \delta , \]
\[ [\hat{a}, \hat{A}^\dagger]_+ = [\hat{A}, \hat{a}^\dagger]_+ = \varepsilon . \] (14)


\(^3\) E. HUTCHINSON, Phys. Rev. 36, 410 [1930].

\(^4\) M. WAGNER, Z. Naturforsch. 14 a, 81 [1959].


\(^6\) S. KOIDE, Z. Naturforsch. 15 a, 123 [1960].


The operators $\hat{a}$ and $\hat{a}^\dagger$ generate the complete eigenvector system of the oscillators
\[
|m\rangle = (m!)^{-\frac{1}{2}} \hat{A}^m |0\rangle, \quad (m) = (m!)^{-\frac{1}{2}} \hat{a}^m |0\rangle.
\]
(15)
(16)
In the derivation of the Franck-Condon-integral the same commutations will be used as in the derivation of the equal frequencies integral.

The integral to be solved is [see 8, Eq. (4)]
\[
I_1 = \langle m | \hat{a}^\dagger \exp \{ i b \hat{a} / \hbar \} | r \rangle. \quad (17)
\]
The operator $\hat{p}$ is expressed by:
\[
\hat{p} = i \left( \frac{\hbar}{\omega} \right)^{\frac{3}{2}} (\hat{a}^\dagger - \hat{a}).
\]
(18)
which is introduced in Eq. (17). The result is:
\[
I_1 = \langle m | \hat{a}^\dagger \exp \{ - \alpha (\hat{a}^\dagger - \hat{a}) \} | r \rangle
\]
(19)
with
\[
\alpha = (M \omega / 2 \hbar)^{\frac{3}{2}} b.
\]
(20)
Applying Weyl's formula [see Appendix (A 3)] yields:
\[
I_1 = \exp \{ - \alpha^2 / 2 \} (m! r!) \left( \frac{\hbar}{2 M \omega} \right)^{\frac{3}{2}} \langle 0 | \hat{a}^m (\hat{a}^\dagger + \hat{a}) \rangle \exp \{ - \alpha \hat{a} \} \exp \{ \alpha \hat{a} \hat{A}^r | 0 \rangle \}. \quad (21)
\]
The essential point in the calculation of Eq. (21) is the commutation of $\exp \{ - \alpha \hat{a} \}$ to the left and $\exp \{ \alpha \hat{a} \}$ to the right so that only the first terms of the series expansion will survive if they are working on the vacuum state. As $|0\rangle$ is different from $|0\rangle$, $\alpha \hat{a}$ is expressed by Eq. (12)
\[
\alpha \hat{a} = (\alpha / \epsilon) (\hat{A} - \delta \hat{a}^\dagger).
\]
(22)
The Weyl-formula is applied again:
\[
I_1 = \exp \{ - \alpha^2 / 2 \} \exp \{ - \alpha \delta / 2 \} \langle m! r! \rangle^{-\frac{3}{2}} \left( \frac{\hbar}{2 M \omega} \right)^{\frac{3}{2}} \langle 0 | \hat{a}^m (\hat{a}^\dagger + \hat{a}) \rangle \exp \{ - \alpha \hat{a} \} \exp \{ \alpha \hat{a} \hat{A}^r | 0 \rangle \}. \quad (23)
\]
The commutations can be easily performed by introducing the identity operator between $|0\rangle$ and $\hat{a}^m$ and between $|0\rangle$ and $\hat{A}^r$ [see Appendix (A 1)].
\[
I_1 = \exp \left[ - \alpha^2 / 2 \left( 1 + \frac{\delta}{\epsilon} \right) \right] (m! r!)^{-\frac{3}{2}} \left( \frac{\hbar}{2 M \omega} \right)^{\frac{3}{2}} \langle 0 | \hat{a}^m \hat{A}^r | 0 \rangle \cdot \sum_s C_{0s} \langle s | \hat{a}^s \rangle \langle \hat{a}^s | \hat{A}^r | 0 \rangle
\]
(32)
As there is only a limited number of annihilation operators available the series breaks off after few terms. The matrix elements can be calculated by elementary algebra:
\[
\langle 0 | \hat{a}^m \hat{a}^s | 0 \rangle = m!. \quad \text{[see Appendix (A 2)].}
\]
(33)
Eq. (31) contains the result for the equal frequencies Franck-Condon-integral $^8$ as a special case:
\[
I_2 = \exp \{ - \alpha^2 / 2 \} (m! r!)^{-\frac{3}{2}} \left( \frac{\hbar}{2 M \omega} \right)^{\frac{3}{2}} \langle 0 | (\hat{a} - \alpha)^m (\hat{a}^\dagger + \alpha) \hat{A}^r \rangle \langle 0 | (\hat{a} - \alpha)^m (\hat{a}^\dagger + \alpha) \hat{A}^r \rangle.
\]
(33)
2. Integrals Related to the Generalized Franck-Condon-Integral

2.1. Transition Integral

If \( \alpha = 0 \) the integral is reduced to a transition integral between oscillators of different frequencies but equal equilibrium distances.

\[
\mathcal{I}_3 = \langle m | \hat{\mathbf{x}}^\dagger | r \rangle = (m! r!)^{-\frac{1}{2}} \left( \frac{\hbar}{2 M \omega} \right)^{\frac{1}{2}} \cdot \left\{ \sum_s C_{0s}(s!)^{-\frac{1}{2}} \left\langle 0 \left| \hat{\mathbf{a}}^m (\hat{\mathbf{a}} + \hat{\mathbf{a}}^\dagger)^l (\hat{\mathbf{a}} + \epsilon \hat{\mathbf{a}}^\dagger)^r \hat{\mathbf{a}}^{ts} \right| 0 \right\rangle \right\}.
\]

For equal frequencies the result is:

\[
\mathcal{I}_4 = \langle m | \hat{\mathbf{x}}^\dagger | r + b \rangle = (m! r!)^{-\frac{1}{2}} \left( \frac{\hbar}{2 M \omega} \right)^{\frac{1}{2}} \cdot \left\{ \sum_s C_{0s}(s!)^{-\frac{1}{2}} \left\langle 0 \left| \hat{\mathbf{a}}^m (\hat{\mathbf{a}} + \hat{\mathbf{a}}^\dagger)^l (\hat{\mathbf{a}} + \epsilon \hat{\mathbf{a}}^\dagger)^r \hat{\mathbf{a}}^{ts} \right| 0 \right\rangle \right\}.
\]

2.2. Kinetic Energy Integral

In some spectroscopic applications the kinetic energy integral is important. This integral can be generalized for arbitrary powers of the momentum operator.

\[
\mathcal{I}_5 = \langle m | \hat{\mathbf{p}}^\dagger | r + b \rangle.
\]

By a slight change of notation in Eq. (31) the result is:

\[
\mathcal{I}_5 = \exp \left\{ -\frac{x^2}{2} \left( 1 + \frac{\delta}{\epsilon} \right) \right\} (m! r!)^{-\frac{1}{2}} \left( \frac{\hbar}{2 M \omega} \right)^{\frac{1}{2}} \cdot \left\{ \sum_s C_{0s}(s!)^{-\frac{1}{2}} \left\langle 0 \left| \hat{\mathbf{a}}^m (\hat{\mathbf{a}} + \hat{\mathbf{a}}^\dagger)^l (\hat{\mathbf{a}} + \epsilon \hat{\mathbf{a}}^\dagger)^r \hat{\mathbf{a}}^{ts} \right| 0 \right\rangle \right\}.
\]

For equal frequencies this result simplifies to:

\[
\mathcal{I}_6 = \langle m | \hat{\mathbf{p}}^\dagger | r + b \rangle = \exp \left\{ -\frac{x^2}{2} \right\} (m! r!)^{-\frac{1}{2}} \left( \frac{\hbar}{2 M \omega} \right)^{\frac{1}{2}} \cdot \left\{ \sum_s C_{0s}(s!)^{-\frac{1}{2}} \left\langle 0 \left| \hat{\mathbf{a}}^m (\hat{\mathbf{a}} + \hat{\mathbf{a}}^\dagger)^l (\hat{\mathbf{a}} + \epsilon \hat{\mathbf{a}}^\dagger)^r \hat{\mathbf{a}}^{ts} \right| 0 \right\rangle \right\}.
\]

2.3. Collision energy-exchange Integral

A convenient interaction in collision processes leads to interaction integrals of the form

\[
\left( \frac{\hbar}{2 M \omega} \right)^{\frac{1}{2}} \langle m | (\hat{\mathbf{a}}^\dagger + \hat{\mathbf{a}})^l \exp (\gamma (\hat{\mathbf{a}}^\dagger + \hat{\mathbf{a}}) | r \rangle \right\} (39)
\]

(\( \gamma \) is an arbitrary constant)

(Takayanagi\textsuperscript{18}). Similar integrals are important if an interatomic potential like the Morse-potential is calculated in an harmonic oscillator basis. Again the results can be written down using Eq. (31) after a slight change of notation:

\[ I_7 = \exp \left\{ \frac{r^2}{2} \left( 1 + \frac{\delta}{\epsilon} \right) \right\} (m! r!)^{-\frac{1}{2}} \left( \frac{\hbar}{2 M \omega} \right)^{\frac{1}{2}} \cdot \left\{ \sum_s C_{0s}(s!)^{-\frac{1}{2}} \left\langle 0 \left| \hat{\mathbf{a}} + \gamma (1 + \frac{\delta}{\epsilon}) \right|^m \hat{\mathbf{a}}^{ts} \right| 0 \right\}.
\]

For equal frequencies Eq. (40) simplifies to

\[
I_8 = \exp \left\{ \frac{r^2}{2} \right\} (m! r!)^{-\frac{1}{2}} \left( \frac{\hbar}{2 M \omega} \right)^{\frac{1}{2}} \cdot \left\{ \left\langle 0 \left| (\hat{\mathbf{a}} + \gamma)^m (\hat{\mathbf{a}} + \gamma)^r \right| 0 \right\rangle \right\}.
\]

3. Conclusion

Second quantization and operator technique leads to elementary expressions for some important harmonic oscillator integrals which simplify the calculation of transition probabilities between arbitrary oscillator states considerably. It is difficult to treat \( n \)-dimensional oscillators in a similar manner because additional angular momentum quantum numbers are important. A simple expression can be given if only integrals of the type

\[
I = \langle m \left| \hat{x}_k^b \right. \rangle \right\} (42)
\]

are considered; \( x_k \) is the normal coordinate of mode \( k \) and the state vectors \( | m \rangle \) and \( | r \rangle \) are of the form:

\[
| m \rangle = | m_1 \ldots m_k \ldots \rangle,
| r \rangle = | r_1 \ldots r_k \ldots \rangle.
\]

In this case the generalized Franck-Condon-integrals for \( n \)-dimensional oscillators are products of the linear harmonic oscillator integral Eq. (31).

Discussion with Professors Reich and Richter are gratefully acknowledged.

Appendix

Collection of Some Operator Formulas Used in the Text

\[ \exp{\beta \hat{B}} \hat{C} \exp{-\beta \hat{B}} = \hat{C} + \beta [\hat{B}, \hat{C}] - \frac{\beta^2}{2} [\hat{B}, [\hat{B}, \hat{C}]] - \ldots \right\} = \sum_{n=0}^{\infty} \frac{\beta^n}{n!} [\hat{B}, \hat{C}] - \exp{\beta \hat{B}} \hat{C} \exp{-\beta \hat{B}} = (\exp{\beta \hat{B}} \hat{C} \exp{-\beta \hat{B}})
\]

\[
\hat{a}^m \hat{a}^{tm} = \prod_{p=1}^{m} (\hat{a}^p \hat{a} + p),
\]

\[
\hat{a}^m \hat{a}^{tm} = \prod_{p=1}^{m} (\hat{a}^p \hat{a} + 1 - p),
\]

(41)

This formula is named occasionally Weyl-, Zassenhaus-, Baker-Hausdorff-Campbell- or, after a clear proof\textsuperscript{9}, Glauber-formula.

\textsuperscript{9} K. Takayanagi, Advances Atomic Molecular Physics 1, 149 [1965].
On a Unified Theory of Twocentre Harmonic Oscillator Integrals

II. The Twofold Degenerate Oscillator

W. Witschel

Physikalisch-Technische Bundesanstalt, Braunschweig

(Z. Naturforsch. 26 a, 945—946 [1971] ; received 3 March 1971)

Twocentre harmonic oscillator overlap integrals (Franck-Condon-integrals) are calculated in a simple way for twodimensional oscillators of different frequencies. Second quantization and operator technique are applied. It is further shown that transition and kinetic energy integrals can be derived in the same representation.

Introduction

Transition- and overlap integrals for the two-dimensional oscillator are important in the theory of electronic and infrared transitions in polyatomic molecules, in the theory of nuclear models, in quantum chemistry and in the theory of charged scalar boson fields. Recently Bell treated some integrals by analytical methods but they are very complicated.

In the present article, Part 1, second quantization and operator technique are applied in the straightforward calculation of the twocentre integral which was apparently not given in the literature. In Part 2 transition and overlap integrals for one centre are derived. The paper closes with a discussion of advantages, applications and limitations of the techniques presented here.

1. The Twocentre Overlap Integral (Franck-Condon-Integral) for Different Frequencies

This integral is a generalization of the well known linear Franck-Condon-integral for two dimensions. It reads in spectroscopic notation:

\[ I = \langle v \ l \ | v' \ l' \ | \omega \ | 0 + d \rangle. \] (1)

The quantum numbers \( v, l \) and \( v', l' \) are the vibration and angular momentum quantum numbers, \( \omega \) and \( \Omega \) are oscillator frequencies and \( d \) is the displacement of the equilibrium distance from 0 (zero). For brevity we use the angular momentum occupation number representation given by Messiah which may be consulted for details.

In the new notation the integral has the form:

\[ I = \langle n_+ \ n_- | m_+ \ m_- | 0 + d \rangle. \] (2)

The double bracket indicates that the basis sets are different for \( \omega \) and \( \Omega \). The quantum numbers \( v, l \) and \( v', l' \) are expressed by

\[
\begin{align*}
   v &= n_+ + n_- , \\
   l &= n_+ - n_- , \\
   v' &= m_+ + m_- , \\
   l' &= m_+ - m_- , \\
   n_+ , n_- &= 0 , 1 , 2 , \ldots 
\end{align*}
\] (3)

In usual cartesian occupation number representation the Hamiltonian can be written:

\[
\begin{align*}
   H_\omega &= \hbar \omega (\hat{a}_1^\dagger \hat{a}_1 + \frac{1}{2}) + \hbar \omega (\hat{a}_2^\dagger \hat{a}_2 + \frac{1}{2}), \\
   H_\Omega &= \hbar \Omega (\hat{b}_1^\dagger \hat{b}_1 + \frac{1}{2}) + \hbar \Omega (\hat{b}_2^\dagger \hat{b}_2 + \frac{1}{2}).
\end{align*}
\] (4)

The angular momentum properties of the oscillator can be expressed by introducing appropriate linear combinations of the \( a \)-type and \( b \)-type operators.

\[
\begin{align*}
   \hat{A}_+ &= (\sqrt{2}/2) (\hat{a}_1^\dagger - i \hat{a}_2), \\
   \hat{A}_- &= (\sqrt{2}/2) (\hat{a}_1 + i \hat{a}_2), \\
   \hat{A}_+^\dagger &= (\sqrt{2}/2) (\hat{a}_1^\dagger + \hat{a}_2), \\
   \hat{A}_-^\dagger &= (\sqrt{2}/2) (\hat{a}_1^\dagger - \hat{a}_2).
\end{align*}
\] (5 a)

\[
\begin{align*}
   \hat{A}^+_1 &= (\sqrt{2}/2) (\hat{a}_1^\dagger + i \hat{a}_2^\dagger), \\
   \hat{A}^-_1 &= (\sqrt{2}/2) (\hat{a}_1^\dagger - i \hat{a}_2^\dagger), \\
   \hat{A}^+_2 &= i(\sqrt{2}/2) (\hat{A}_+^\dagger + \hat{A}_1), \\
   \hat{A}^-_2 &= i(\sqrt{2}/2) (\hat{A}_-^\dagger - \hat{A}_1).
\end{align*}
\] (5 b)

---