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On a Unified Theory of Harmonic Oscillator Two-Centre Integrals

III. The Gauss-Potential

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Occupation number representation and operator-technique are used in the calculation of harmonic oscillator matrixelements for one and two centres and for equal and different frequencies. The potentials treated are generalized Gauss-potentials of the form $\hat{p}^k \hat{x}^l \exp\{\alpha \hat{x}^2\}$, $\hat{x}^k \hat{p}^l \exp\{\alpha \hat{p}^2\}$, and $\hat{p}^k \hat{x}^l \exp\{\alpha \hat{x} \hat{p}\}$ which by application of an operator identity could be reduced to the same form. Applications in nuclear and molecular physics, in molecular spectroscopy and in quantum chemistry are discussed briefly.

1. Introduction

In two short notes cited as I¹ and II² formulae for two-centre and one-centre harmonic oscillator integrals were derived for the one dimensional and two dimensional case and for equal and different frequencies. Second quantization and operator-technique were applied in an algebraic calculation. The most general matrixelement was of the form

$$\langle k | \hat{p}^m \hat{x}^r \exp\{\alpha \hat{x}\} | l + d \rangle \quad (1.1)$$

where the notation of the double bracket means an oscillator of frequency Ω . Its equilibrium position is displaced a distance d from the origin. In the present paper a derivation of integrals for potentials of the Gauß-type for two centres will be given. They have the general form

$$\langle k | \hat{p}^m \hat{x}^r \exp\{\alpha \hat{x}^2\} | l + d \rangle, \quad (1.2)$$

$$\langle k | \hat{p}^m \hat{x}^r \exp\{\alpha \hat{x} \hat{p}\} | l + d \rangle, \quad (1.3)$$

$$\langle k | \hat{p}^m \hat{x}^r \exp\{\alpha \hat{p}^2\} | l + d \rangle, \quad (1.4)$$

and are thus more general than similar integrals already given in the literature. A short survey on previous Gauß-integral calculations may show this

generalization. The first solution of the Gauß-integral for one centre was apparently given by SACK³ who used an operator identity derived from his "Taylor theorem for shift operators". As the same identity will be used later, no detailed explanation will be given. Introducing intermediate states he got a condensed result in form of hypergeometric function. A different treatment was given by CHAN and STELMAN⁴ using conventional integration techniques. They got recursion formulae and relations between matrixelements which could be used in the computerdiagonalization of a vibrational Hamilton-matrix. Along similar lines a derivation of one centre Gauß-integrals in one, two and three dimensions was given by BELL⁵. Instead of Hermite-functions he used Laguerre-functions as radial wave functions and applied complex integration methods. His article is especially valuable for a thorough discussion on the applications of Gauß-integrals in the spectroscopy of polyatomic molecules. A different attack to the problem of one centre Gauß-integrals was made by WILCOX⁶ who introduced a Fourier-transform technique in the solution for various potential types.

$$\langle m | V(\hat{x}) | n \rangle = \sum_{r=0}^m \frac{\alpha (m! n!)^{1/2}}{r! (m-r)! (n-r)!} \left\{ \int_{-\infty}^{+\infty} dy g(\alpha y) e^{-1/2 y^2} \times (i y)^{m+n-2r} \right\} \quad (1.5)$$



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where $\alpha \equiv (2\omega/\hbar)^{1/2}$ and $g(\alpha y)$ is the Fourier-transform of $V(\hat{x})$, which in his work is \hat{x} , $\hat{x}^j \exp\{-1/2\gamma\hat{x}^2\}$, $\exp\{i\alpha z\hat{x}\}$, and $\hat{x}^{-1} \sin(\alpha\lambda\hat{x})$. He mentioned that this method will be applicable to all potentials which have a Fourier-transform, and he proposed a double Fourier-transform in \hat{x} and \hat{p} in the WEYL⁷ manner for the calculation of momentum dependent matrixelements. This will always be difficult if analytical methods are used, whereas with algebraic methods the inclusion of momentum dependent terms because of the similarity between \hat{x} and \hat{p} in occupation number representation is always possible. The two centre Gauß-integral seems to be derived for the first time by ROBERTS⁸, who borrowed an expansion method from nuclear physics. Since the pioneering work by TALMI⁹ it is well known in nuclear physics that so called Slater-integrals for two centres can be reduced to a one centre expansion. SMIRNOV¹⁰ generalized Talmi's method for two particles of different mass in an oscillator well.

Though this one centre-expansion is only formally identical with a one centre-expansion for different oscillator frequencies ROBERTS⁸ applied this expansion to oscillator integrals in quantumchemistry. He got condensed results, but for practical applications the calculation of the Talmi-coefficients in the expansions may be complicated and tedious. A disadvantage of the method is that the derivations are not straight forward and difficult to follow.

It may therefore be valuable to have a clear derivation of generalized Gauß-integrals which uses simple algebra only. The widespread applications in several fields of physics and chemistry will be given in the conclusion.

2. Gauss-Potentials in Second Quantization

For convenience the defining equations of I are repeated, as they will be important in the further calculation. The formulae for the twodimensional oscillator follow II and will not be given here for brevity; the operators \hat{a}^+ , \hat{a} belonging to the oscillator with frequency ω , the operators \hat{A}^+ , \hat{A} to the oscillator with frequency Ω . They are related to each other by

$$\hat{A} = \delta \hat{a}^+ + \varepsilon \hat{a}, \quad (2.1)$$

$$\hat{A}^+ = \delta \hat{a} + \varepsilon \hat{a}^+, \quad (2.2)$$

and have the commutators

$$[\hat{a}, \hat{A}]_- = [\hat{A}^+, \hat{a}^+]_- = \delta, \quad (2.3)$$

$$[\hat{a}, \hat{A}^+]_- = [\hat{A}, \hat{a}^+]_- = \varepsilon \quad (2.4)$$

where

$$\varepsilon = (1/2) \left\{ \left(\frac{\omega}{\Omega} \right)^{1/2} + \left(\frac{\Omega}{\omega} \right)^{1/2} \right\}, \quad (2.5)$$

$$\delta = (1/2) \left\{ \left(\frac{\Omega}{\omega} \right)^{1/2} - \left(\frac{\omega}{\Omega} \right)^{1/2} \right\}. \quad (2.6)$$

The main tool in treating generalized Gauß-potentials will be an operator identity which was derived by SACK³. A proof can be found in a review article by WILCOX¹¹ which may be consulted for all details of operator calculus. For "shift operators" with the commutator

$$[\hat{X}, \hat{Y}]_- = y \hat{Y} \quad (2.7)$$

where y is a c -number Sack's identity is:

$$\begin{aligned} \exp\{\xi(\hat{X} + \lambda \hat{Y})\} &= \exp\left\{\frac{\lambda \hat{Y}}{y} [\exp\{\xi y\} - 1]\right\} \exp\{\xi \hat{X}\} \\ &= \exp\{\xi \hat{X}\} \exp\{(\lambda \hat{Y}/y) [1 - \exp\{-\xi y\}]\} \\ &\quad (\lambda, \xi = \text{constants}). \end{aligned} \quad (2.8)$$

The problem is the factorization of the Gauß-type exponential operators

$$\begin{aligned} V_1(\hat{x}^2) &= \exp\{a \hat{x}^2\}, \\ V_2(\hat{p}^2) &= \exp\{a \hat{p}^2\}, \\ V_3(\hat{x}\hat{p}) &= \exp\{a \hat{x}\hat{p}\}. \end{aligned} \quad (2.9)$$

The first potential was already factorized by SACK³ with the simplification $\hbar = m = \omega = 1$. In the general case some additional numerical factors arise. The shift operators for the potentials will be given in the ω -representation.

$$[\hat{a} \hat{x}, \hat{x}^2]_- = 2(\hbar/2m\omega)^{1/2} \hat{x}^2, \quad (2.10)$$

$$\begin{aligned} [\hat{a} \hat{p}, \hat{p}^2]_- &= 2i(m\hbar\omega/2)^{1/2} \hat{p}^2, \\ [\hat{x}^2, \hat{x}\hat{p}]_- &= 2i\hbar \hat{x}^2, \end{aligned} \quad (2.11)$$

$$[\hat{a}^+ \hat{a}, \hat{a}^{+m}]_- = m \hat{a}^{+m}, \quad (2.12)$$

$$[\hat{a}^+ \hat{a}, \hat{a}^m]_- = -m \hat{a}^m, \quad (2.13)$$

m is a positive integer.

The application of Sack's identity will be demonstrated for the potential $V_1(\hat{x}^2)$. The potentials $V_2(\hat{p}^2)$ and $V_3(\hat{x}\hat{p})$ are factorized in an analogous way. As the result for all the potentials will be given in the same algebraic form the constants are

labelled by indices corresponding to the potentials V_1, V_2 or V_3 . It is:

$$\begin{aligned} & \exp\{K_1[\hat{a}\hat{x} - (\hbar/2m\omega)^{-1/2}]\hat{x}^2\} \\ &= \exp\{-K_1(\hbar/2m\omega)^{1/2}(\hat{a}^+\hat{a} + \hat{a}^{+2})\} \\ &= \exp\{(m\omega/\hbar)(1 - \exp\{K_1(2\hbar/m\omega)^{1/2}\})\hat{x}^2\} \\ &\quad \times \exp\{K_1(\hbar/2m\omega)^{1/2}(\hat{a}\hat{a}^+ + \hat{a}^2)\}. \end{aligned} \quad (2.14)$$

Multiplication from the right with

$$\exp\{-K_1^*(\hat{a}\hat{a}^+ + \hat{a}^2)\}$$

where K_1^* abbreviates $[(\hbar/2m\omega)^{1/2}K_1]$ yields:

$$\begin{aligned} & \exp\{(m\omega/\hbar)[1 - \exp\{K_1(2\hbar/m\omega)^{1/2}\}]\hat{x}^2\} \\ &= \exp\{-K_1^*(\hat{a}^+\hat{a} + \hat{a}^{+2})\}\exp\{-K_1^*(\hat{a}^+\hat{a} + \hat{a}^2)\} \\ &\quad \times \exp\{-K_1^*\}. \end{aligned} \quad (2.15)$$

By comparison of the coefficients of $\exp\{\hat{x}^2\}$, K_1 is related to α by:

$$K_1 = (m\omega/2\hbar)^{1/2} \log(1 - \alpha\hbar/m\omega). \quad (2.16)$$

The exponential operators on the right side are factorized with Eqs. (2.8), (2.12) and (2.13) so that

the final result can be written as

$$V_\gamma = \exp\{w_{\gamma 1}\hat{a}^{+2}\}\exp\{w_{\gamma 2}\hat{a}^+\hat{a}\} \times \exp\{w_{\gamma 3}\hat{a}^2\}\exp\{w_{\gamma 4}\} \quad (2.17)$$

where the coefficients for the potential with $\gamma=1$ are:

$$\begin{aligned} w_{11} &= (1/2)(\exp\{-2K_1^*\} - 1), \quad w_{12} = -2K_1^*, \\ w_{13} &= (1/2)(\exp\{-2K_1^*\} - 1), \quad w_{14} = -K_1^*. \end{aligned} \quad (2.18)$$

For the potential with $\gamma=2$, $V_2(\hat{p}^2)$ the coefficients are:

$$\begin{aligned} w_{21} &= (1/2)(1 - \exp\{-2K_2^*\}), \quad w_{22} = -2K_2^*, \\ w_{23} &= (1/2)(1 - \exp\{-2K_2^*\}), \quad w_{24} = -K_2^*. \end{aligned} \quad (2.19)$$

with

$$\begin{aligned} K_2^* &= i(m\hbar\omega/2)^{1/2}K_2, \\ K_2 &= -i(2m\hbar\omega)^{1/2} \log(1 + \alpha m\hbar\omega). \end{aligned} \quad (2.20)$$

For the potential $V_3(\hat{x}\hat{p})$ the factorization reduces to the factorization of the already known potential $V_1(\hat{x}^2)$ if Eq. (2.11) is used.

$$\exp\{\alpha(\hat{x}\hat{p} - im\omega\hat{x}^2)\} = \exp\left\{\left(\frac{m\omega}{2\hbar}\right)\hat{x}^2[\exp\{-2i\hbar\alpha\} - 1]\right\} \exp\{\alpha\hat{x}\hat{p}\}, \quad (2.21)$$

$$\exp\{\alpha\hat{x}\hat{p}\} = \exp\{-(m\omega/2\hbar)\hat{x}^2[\exp\{-2i\hbar\alpha\} - 1]\}\exp\{-i\hbar\alpha(\hat{a}^+\hat{a} + \hat{a}^2)\}. \quad (2.22)$$

The last factor in Eq. (2.22) will be factorized and ordered to the form of Eq. (2.17).

$$\exp\{\alpha\hat{x}\hat{p}\} = \exp\{\alpha_1^*\hat{x}^2\}\exp\{-i\alpha\hbar\hat{a}^+\hat{a}\}\exp\{(-1/2)\hat{a}^2(1 - \exp\{-2i\hbar\alpha\})\} \quad (2.23)$$

with

$$\alpha_1^* = -(m\omega/2\hbar)[\exp\{-2i\hbar\alpha\} - 1]. \quad (2.24)$$

The coefficients for $V_3(\hat{x}\hat{p})$ are:

$$\begin{aligned} w_{31} &= w_{11}(\alpha_1^*), \quad w_{32} = w_{12}(\alpha_1^*) - i\alpha\hbar, \\ w_{33} &= w_{13}(\alpha_1^*)\exp\{-2i\hbar\alpha\} + (1/2) \\ &\quad (\exp\{-2i\hbar\alpha\} - 1), \quad w_{34} = w_{14}(\alpha_1^*). \end{aligned} \quad (2.25)$$

It may be remarked that $V_3(\hat{x}\hat{p})$ can be used in a similarity transformation generating a transformed oscillator Hamiltonian of a different mass.

$$\hat{H} = \exp\{\alpha\hat{x}\hat{p}\}[(\hat{p}^2/2m) + m\omega^2\hat{x}^2]\exp\{-\alpha\hat{x}\hat{p}\}, \quad (2.26)$$

$$\begin{aligned} \hat{p}^2 &= \hat{p}^2 \exp\{2i\hbar\alpha\}, \\ \hat{x}^2 &= \hat{x}^2 \exp\{-2i\hbar\alpha\}. \end{aligned} \quad (2.27)$$

A "transformed" mass can be defined as

$$m^* = m \exp\{-2i\hbar\alpha\}. \quad (2.28)$$

The transformed eigenvector is:

$$|\tilde{n}\rangle = \exp\{\alpha\hat{x}\hat{p}\}|n\rangle. \quad (2.29)$$

Particles of different mass in an oscillator well are sometimes treated in nuclear physics.

3. Calculation of Matricelements

The most general onedimensional matrixelement of the Gaussian type will be:

$$\begin{aligned} I_1 &= \exp\{w_4 - w_5^2/2\} \langle r | \hat{p}^k \hat{x}^l \exp\{w_1\hat{a}^{+2}\} \\ &\quad \times \exp\{w_2\hat{a}^+\hat{a}\} \exp\{w_3\hat{a}^2\} \exp\{-w_5\hat{a}^+\} \\ &\quad \times \exp\{w_5\hat{a}\} | t \rangle \rangle. \end{aligned} \quad (3.1)$$

The double bracket means a state belonging to the oscillator with Ω , the constant w_5 contains the shift of the origin.

$$w_5 = (\omega m/2\hbar)^{1/2}d. \quad (3.2)$$

If $\exp\{w_3\hat{a}^2\}$ and $\exp\{-w_5\hat{a}^+\}$ are commuted and if the Zassenhaus formula of the appendix is applied, Eq. (3.1) reads in occupation number representation:

$$I_1 = T_1 \cdot \langle 0 | \hat{a}^r (\hat{a}^+ - \hat{a})^k (\hat{a}^+ + \hat{a})^l \exp\{w_1 \hat{a}^{+2}\} \\ \times \exp\{w_2 \hat{a}^+ \hat{a}\} \exp\{-w_3 \hat{a}^+\} \\ \times \exp\{g_1 \hat{a}\} \exp\{w_3 \hat{a}^2\} (\hat{A}^+)^t | 0 \rangle \rangle$$

with

$$T_1 = (r! t!)^{-1/2} i^k (m \hbar \omega / 2)^{k/2} (\hbar / 2 m \omega)^{l/2} \quad (3.4) \\ \times \exp\{w_4 + w_5^2 w_3 - w_5^2 / 2\}, \quad g_1 = w_5 - 2 w_3 w_5.$$

The main problem will be to express $\exp\{w_3 \hat{a}^2\}$ by a product of exponential operators which contain powers of \hat{a}^+ and \hat{A} separately. By a suitable definition of shift operators it is possible to apply Sack's identity repeatedly. These shift operators are defined as

$$[\hat{a} \hat{A}, \hat{A}^2]_- = 2 \delta \hat{A}^2, \quad (3.5)$$

$$[\hat{a}^+ \hat{A}, \hat{A}^2]_- = -2 \varepsilon \hat{A}^2, \quad (3.6)$$

$$[\hat{a}^+ \hat{a}, \hat{a}^m]_- = -m \hat{a}^m,$$

$$[\hat{a}^+ \hat{a}, \hat{a}^{+m}]_- = m \hat{a}^{+m}, \quad (3.7)$$

$$[\hat{a} \hat{A}, \hat{a}^2]_- = -2 \delta \hat{a}^2. \quad (3.8)$$

It is

$$\exp\{-g_2(\hat{a} \hat{A} - \varepsilon \hat{a}^2)\} = \exp\{-g_2 \delta\} \exp\{-g_2 \delta \hat{a}^+ \hat{a}\} \\ = \exp\{(\varepsilon/2 \delta) [\exp\{2 g_2 \delta\} - 1] \hat{a}^2\} \exp\{-g_2 \hat{a} \hat{A}\}. \quad (3.9)$$

Equation (3.9) is multiplied from the right with $\exp\{+g_2 \hat{a} \hat{A}\}$ so that the coefficients of \hat{a}^2 in Eqs. (3.9) and (3.3) can be compared.

$$g_2 = (1/2 \delta) \log[(2 \delta w_3/\varepsilon) + 1]. \quad (3.10)$$

The next step is the splitting of the mixed exponential operator with $\hat{a} \hat{A}$ into expressions which contain \hat{a}^+ and \hat{A} operators separately. This can be achieved by using Eq. (3.5).

$$\exp\{g_2(\hat{a} \hat{A} - (1/\varepsilon) \hat{A}^2)\} = \exp\{(-g_2 \delta/\varepsilon) \hat{a}^+ \hat{A}\} \\ = \exp\{g_2 \hat{a} \hat{A}\} \quad (3.11) \\ \times \exp\{-(2 \varepsilon \delta)^{-1} [1 - \exp\{-2 g_2 \delta\}] \hat{A}^2\}.$$

Equation (3.11) is multiplied from the right with $\exp\{+g_3 \hat{A}^2\}$, where g_3 abbreviates

$$g_3 = (2 \varepsilon \delta)^{-1} [1 - \exp\{-2 g_2 \delta\}], \quad (3.12)$$

$$\exp\{g_2 \hat{a} \hat{A}\} = \exp\{(-g_2 \delta/\varepsilon) \hat{a}^+ \hat{A}\} \exp\{g_3 \hat{A}^2\}. \quad (3.13)$$

In the first exponential on the right side the operator \hat{A} is replaced by Eq. (2.1) leading to an expres-

sion which can be factorized.

$$(3.3) \exp\{(-g_2 \delta/\varepsilon) \hat{a}^+ \hat{A}\} = \exp\{(-g_2 \delta/\varepsilon) (\delta \hat{a}^{+2} + \varepsilon \hat{a}^+ \hat{a})\} \\ = \exp\{-g_2 \delta \hat{a}^+ \hat{a}\} \exp\{g_4 \hat{a}^{+2}\}, \quad (3.14)$$

$$g_4 = (\delta/2 \varepsilon) (1 - \exp\{2 g_2 \delta\}). \quad (3.15)$$

The final result is:

$$\exp\{w_3 \hat{a}^2\} = \exp\{-g_2 \delta\} \exp\{-2 g_2 \delta \hat{a}^+ \hat{a}\} \\ \times \exp\{g_4 \hat{a}^{+2}\} \exp\{g_3 \hat{A}^2\}. \quad (3.16)$$

The usual commutations as in I and II can be performed, according to the formulae given in the appendix; $\exp\{g_1 \hat{a}\}$ will be commuted to the right to complete the separation of creation and annihilation operators.

$$\exp\{g_1 \hat{a}\} \exp\{-2 g_2 \delta \hat{a}^+ \hat{a}\} \exp\{g_4 \hat{a}^{+2}\} \\ = \exp\{-2 g_2 \delta \hat{a}^+ \hat{a}\} \exp\{g_4 \hat{a}^{+2}\} \\ \times \exp\{2 g_1 \exp\{-2 g_2 \delta\} g_4 \hat{a}^+\} \quad (3.17) \\ \times \exp\{g_1 \exp\{-2 g_2 \delta\} \hat{a}\} \exp\{g_1^2 \exp\{-4 g_2 \delta\} g_4\}.$$

Now, $\exp\{g_1 \exp\{-2 g_2 \delta\} \hat{a}\}$ is substituted by Eq. (2.1) and the Zassenhaus-formula is applied:

$$\exp\{(-g_1/\varepsilon) \exp\{-2 g_2 \delta\} (\delta \hat{a}^+ - \hat{A})\} \\ = \exp\{-(g_1/\varepsilon) \exp\{-2 g_2 \delta\} \delta \hat{a}^+\} \\ \times \exp\{(g_1/\varepsilon) \exp\{-2 g_2 \delta\} \hat{A}\} \quad (3.18) \\ \times \exp\{(-g_1^2/2 \varepsilon^2) \exp\{-4 g_2 \delta\} \delta \varepsilon\}.$$

The matrixelement is after collecting all terms

$$I_1 = T_1 T_2 \langle 0 | \hat{a}^r (\hat{a}^+ - \hat{a})^k (\hat{a}^+ + \hat{a})^l \exp\{w_1 \hat{a}^{+2}\} \\ \times \exp\{w_2 \hat{a}^+ \hat{a}\} \exp\{-w_5 \hat{a}^+\} \exp\{-2 g_2 \delta \hat{a}^+ \hat{a}\} \\ \times \exp\{g_4 \hat{a}^{+2}\} \exp\{g_5 (2 g_4 - \delta/\varepsilon) \hat{a}^+\} \quad (3.19) \\ \times \exp\{(g_5/\varepsilon) \hat{A}\} \exp\{g_3 \hat{A}^2\} (\hat{A}^+)^t | 0 \rangle \rangle$$

$$\text{with} \quad g_5 = g_1 \exp\{-2 g_2 \delta\} \quad (3.20)$$

and

$$T_2 = \exp\{-g_2 \delta + g_4 g_5^2 - \delta g_5^2 / 2 \varepsilon\}. \quad (3.21)$$

The \hat{A} -operators are commuted to the right according to the formulae of the appendix.

$$\exp\{(g_5/\varepsilon) \hat{A}\} \exp\{g_3 \hat{A}^2\} (\hat{A}^+)^t | 0 \rangle \rangle \\ = [\hat{A}^+ + 2 g_3 \hat{A} + (g_5/\varepsilon)]^t | 0 \rangle \rangle. \quad (3.22)$$

The \hat{A} -type operators are replaced by Eqs. (2.1) and (2.2) and the vacuum state $|0\rangle$ is expanded in terms of the eigenstates of the operator \hat{H} with frequency ω . The derivation of the expansion coefficients was already given in I.

$$|0\rangle\rangle = \sum_s C_{0s} (s!)^{-1/2} \hat{a}^{+s} |0\rangle, \\ C_{0s} = \langle s | 0 \rangle\rangle. \quad (3.23)$$

Equation (3.22) is, therefore:

$$\sum_s C_{0s}(s!)^{-1/2} [\hat{a}^+(2g_3\delta + \varepsilon) + \hat{a}(2g_3\varepsilon + \delta) + (g_5/\varepsilon)]^t (\hat{a}^+)^s | 0 \rangle. \quad (3.24)$$

The \hat{a}^+ -type operators are commuted to the left where no difficulties will arise. The final result will be:

$$\begin{aligned} I_1 = T_1 T_2 \sum_s C_{0s}(s!)^{-1/2} \langle 0 | \{ \hat{a} \exp\{w_2 - 2g_2\delta\} \\ + [2g_4 \exp\{w_2 - 2g_2\delta\} + 2w_1 \exp\{-w_2 + 2g_2\delta\}] \hat{a}^+ \\ - w_5 \exp(w_2) + g_5(2g_4 - \delta/\varepsilon) \exp\{w_2 - 2g_2\delta\} \}^r \\ \{ [\exp\{2g_2\delta - w_2\}(1 - 2w_1) - 2g_4 \exp\{w_2 - 2g_2\delta\}] \hat{a}^+ \\ - \exp\{w_2 - 2g_2\delta\} \hat{a} + w_5 \exp(w_2) - g_5(2g_4 - \delta/\varepsilon) \exp\{w_2 - 2g_2\delta\} \}^k \\ \{ [\exp\{2g_2\delta - w_2\}(1 + 2w_1) + 2g_4 \exp\{w_2 - 2g_2\delta\}] \hat{a}^+ \\ + \exp\{w_2 - 2g_2\delta\} \hat{a} - w_5 \exp(w_2) + g_5(2g_4 - \delta/\varepsilon) \exp\{w_2 - 2g_2\delta\} \}^l \\ [\hat{a}^+(2g_3\delta + \varepsilon) + \hat{a}(2g_3\varepsilon + \delta) + g_5/\varepsilon]^t (\hat{a}^+)^s | 0 \rangle. \end{aligned} \quad (3.25)$$

It can be seen from Eq. (3.25) that only a limited number of annihilation operators is available. The series expansion breaks off after a finite number of terms. The evaluation of the matrixelements is straightforward, only multiplications and some commutations are necessary. A more elegant treatment will be the use of a normal ordering formula, which is given in the appendix. In a normal ordered operator product all creation operators stand left from all annihilation operators. The vacuum expectation value of a normal ordered product is zero. The method will be given in the following example for the Gauß-potential between undisplaced oscillator states of equal frequencies.

$$\begin{aligned} I_2 = \langle r | \exp\{w_1 \hat{a}^{+2}\} \exp\{w_2 \hat{a}^+ \hat{a}\} \exp\{w_3 \hat{a}^2\} | t \rangle \exp\{w_4\} \\ = (r! t!)^{-1/2} \exp\{w_4\} \langle 0 | (\hat{a} + 2w_1 \hat{a}^+)^r (\hat{a}^+ \exp\{w_2\} + 2w_3 \exp\{-w_2\} \hat{a})^t | 0 \rangle. \end{aligned} \quad (3.26)$$

New operators are introduced having the same properties as \hat{a}^+ and \hat{a} .

$$\hat{D}_1^+ = 2w_1 \hat{a}^+, \quad \hat{D}_1 = \hat{a}, \quad (3.27) \quad \hat{D}_2^+ = \hat{a}^+ \exp\{w_2\}, \quad \hat{D}_2 = 2w_3 \exp\{-w_2\} \hat{a}. \quad (3.28)$$

With the normal ordering formula of the appendix the result is:

$$\begin{aligned} I_2 = (r! t!)^{-1/2} \exp\{w_4\} \sum_{k=0}^{[r/2]} \sum_{s=0}^{r-2k} \sum_{l=0}^{[t/2]} \sum_{m=0}^{t-2l} \frac{(w_1)^k r!}{k! s! (r-2k-s)!} \frac{(w_3)^l t!}{l! m! (t-2l-m)!} \\ \times \langle 0 | \hat{D}_1^+{}^s \hat{D}_1^{r-2k-s} \hat{D}_2^+{}^m \hat{D}_2^{t-2l-m} | 0 \rangle. \end{aligned} \quad (3.29)$$

The matrixelement vanishes for all non zero powers of \hat{D}_1^+ and \hat{D}_2 so that the labor of calculating the Gauß-matrixelement is reduced even for large numbers r and t .

4. The Gauss-Potential for the Twodimensional Oscillator

As no physical or chemical applications of the Gauß-potential for the displaced twodimensional oscillator with different frequencies could be found and as no new methods will be applied, only the matrixelement for equal frequencies will be given.

$$\hat{V} = \exp\{\alpha(\hat{x}_1^2 + \hat{x}_2^2)\}. \quad (4.1)$$

As \hat{x}_1 and \hat{x}_2 commute the potential will be written as a product of two onedimensional Gauß-potentials in the ordinary second quantized form.

$$\begin{aligned} \hat{V} = \exp\{w_1(\hat{a}_1^{+2} + \hat{a}_2^{+2})\} \exp\{w_2(\hat{a}_1^+ \hat{a}_1 + \hat{a}_2^+ \hat{a}_2)\} \\ \times \exp\{w_3(\hat{a}_1^2 + \hat{a}_2^2)\} \exp\{2w_4\}. \end{aligned} \quad (4.2)$$

By the well known transformation from the cartesian to the angular momentum representation (see II) the potential is:

$$\begin{aligned} \hat{V} = \exp\{2w_1 \hat{A}_+^+ \hat{A}_-^+\} \exp\{w_2(\hat{A}_+^+ \hat{A}_+ \\ + \hat{A}_-^+ \hat{A}_-)\} \exp\{2w_3 \hat{A}_+ \hat{A}_-\} \exp\{2w_4\}. \end{aligned} \quad (4.3)$$

The shift operator in two dimensions is:

$$\begin{aligned} \hat{S} = \exp\{-w_5^2\} \exp\{-(w_5 \sqrt{2}/2) \\ \times [(1-i) \hat{A}_+^+ + (1+i) \hat{A}_-^+]\} \\ \times \exp\{(w_5 \sqrt{2}/2) [(1+i) \hat{A}_+ + (1-i) \hat{A}_-]\}. \end{aligned} \quad (4.4)$$

The matrixelement

$$I_3 = \langle N L | \hat{V} \hat{S} | N' L' \rangle \quad (4.5)$$

can be written with the abbreviations

$$\begin{aligned} w_6 &= (w_5 \sqrt{2}/2) (1-i), \\ w_7 &= (w_5 \sqrt{2}/2) (1+i), \end{aligned} \quad (4.6)$$

$$\begin{aligned} I_3 &= \exp\{2w_4\} \exp\{-w_5^2\} (m_+! m_-! n_+! n_-!)^{-1/2} \\ &\times \langle 00 | \hat{A}_+^{n_+} \hat{A}_-^{n_-} \exp\{2w_1 \hat{A}_+^+ \hat{A}_-^+\} \\ &\times \exp\{w_2(\hat{A}_+^+ \hat{A}_+ + \hat{A}_-^+ \hat{A}_-)\} \\ &\times \exp\{2w_3 \hat{A}_+ \hat{A}_-\} \exp\{-w_6 \hat{A}_+^+\} \\ &\times \exp\{-w_7 \hat{A}_-^+\} \exp\{w_7 \hat{A}_+\} \\ &\times \exp\{w_6 \hat{A}_-\} \hat{A}_+^{+m_+} \hat{A}_-^{+m_-} | 00 \rangle. \end{aligned} \quad (4.7)$$

The result can be written down after the commutation of the \hat{A}_\pm -type operators:

$$\begin{aligned} I_3 &= \exp\{2w_4\} \exp\{-w_5^2\} (m_+! m_-! n_+! n_-!)^{-1/2} \\ &\times \exp\{2w_3 w_6 w_7\} \langle 00 | (\hat{A}_+ \exp\{w_2\} - w_6 \exp\{w_2\} \\ &+ 2w_1 \exp\{-w_2\} \hat{A}_-^+)^{n_+} (\hat{A}_- \exp\{w_2\} - w_7 \exp\{w_2\} \\ &+ 2w_1 \exp\{-w_2\} \hat{A}_+^+)^{n_-} (\hat{A}_+^+ + 2w_3 \hat{A}_- - 2w_3 w_7 + w_7)^{m_+} \\ &\times (\hat{A}_-^+ + 2w_3 \hat{A}_+ - 2w_3 w_6 + w_6)^{m_-} | 00 \rangle. \end{aligned} \quad (4.8)$$

These results are important for a mathematical application. It will be remarked, that hydrogenic radial functions can be reduced to the radial wavefunction of the twodimensional isotropic harmonic oscillator. Hydrogenic matrixelements can therefore be derived from Eq. (4.8).

5. Conclusion and Discussion

Second quantization and few operator formulae enable the algebraic solution of harmonic oscillator matrixelements of the form

$$I_4 = \langle r | \hat{p}^k \hat{x}^l \exp\{a(\hat{p} + \hat{x})\} | t+d \rangle \quad (5.1)$$

and

$$\begin{aligned} I_5 &= \langle r | \hat{p}^k \hat{x}^l \exp\{a\hat{p}^2\} \\ &\times \exp\{\beta\hat{x}^2\} \exp\{\gamma\hat{p}\hat{x}\} | t+d \rangle \end{aligned} \quad (5.2)$$

for one and two dimensions. The double bracket means an oscillator state which is displaced a distance d , with different mass m^* or frequency Ω compared to the state $\langle r |$. As already mentioned the integrals were not yet known with such generality. The further generalization would be the inclusion of exponential operators with higher powers of \hat{x} or \hat{p} than quadratic ones. This is not possible depending on the Lie-algebraic structure of the har-

monic oscillator. Finite Lie-algebras can be constructed with \hat{x} , \hat{p} , $\hat{x}\hat{p}$, \hat{x}^2 and \hat{p}^2 , higher powers of \hat{x} or \hat{p} which arise in the theory of the anharmonic oscillator lead to infinite Lie-algebras. It may be possible to define a similar occupation number representation for related problems with hypergeometric functions so that matrixelements can be calculated with the same technique.

As the present results were derived by fairly long calculations the question may arise if the calculation of oscillator Gauß-matrixelements by algebraic techniques is of only formal interest or if it is of practical importance. This will be answered by the following applications.

A) Molecular Potentials

Some interactions in molecules and between molecules are described by a Gauß-potential. As the Schrödinger-equation cannot be solved in closed form, the Hamilton-matrix is computed in the oscillatorbasis and diagonalized.

B) Theoretical Spectroscopy

This topic was discussed thoroughly by BELL⁵ who gave a long list of references. In addition to molecular spectroscopy some integrals derived here are important for phononassisted optical transitions in solids.

C) Theoretical Chemistry

The applications of the two centre Gauß-integral were already mentioned in the introduction. In his treatment of energy surfaces from cusplless wavefunctions WULFMAN¹² proposed to use harmonic oscillator wavefunctions as basis sets instead of Gauß-wavefunctions, as these do not form a complete orthonormal basis. In quantum chemical calculations two centre integrals like the overlap and the kinetic energy integral arise which are in Robert's notation

$$KEI(n, a, A, N, b, B) = \iiint dx dy dz \Phi_n(a, \mathbf{r}_A) \nabla^2 \Phi_N(b, \mathbf{r}_B) \quad (5.3)$$

$$\text{and} \quad OVP(n, a, A, N, b, B) = \iiint dx dy dz \Phi_n(a, \mathbf{r}_A) \Phi_N(b, \mathbf{r}_B). \quad (5.4)$$

Both integrals are of the type (5.1) and are already given in I. The three centre nuclear integral can be reduced by an integral transform to a Gauß-integral

$$NAI(n, a, A, N, b, B) = \iiint dx dy dz \Phi_n(a, r_A) \mathbf{r}^{-1} \Phi_N(b, r_B) \quad (5.5)$$

with

$$\mathbf{r}^2 = x^2 + y^2 + z^2$$

and

$$\mathbf{r}^{-1} = 2\pi^{-1/2} \int_0^\infty du \exp\{-u r^2\}. \quad (5.6)$$

NAI factorizes to a product of three one dimensional Gauß-integrals. By one centre expansions three and four centre electron integrals can be reduced to products of the overlap, the kinetic energy and the nuclear attraction integral. First calculations on atomic and molecular few electron systems by MO-SHINSKY and NOVARO¹³ show that harmonic oscillator techniques may improve conventional quantum chemical calculations.

D) Nuclear Physics

Slater-integrals in nuclear shell theory by the Talmi-expansion technique are derived by several authors so that the present results may only be a supplement. It may be more interesting to have matrixelements for velocity dependent potentials available. A momentum dependent potential which was often used¹⁴ is

$$V(r, \nabla^2) = -A \exp\{-\alpha^2 r^2\} - B(\nabla^2 \exp\{-\beta r^2\} - \exp\{-\beta r^2\} \nabla^2) \quad (5.7)$$

with the integral representation

$$V(r, \nabla^2) = \left\{ \int V(\hat{r}, \hat{r}') \exp\{i(\hat{r}' - \hat{r})\hat{p}/\hbar\} d\mathbf{r}' \right\}. \quad (5.8)$$

For both cases matrixelements in a cartesian oscillator basis can be derived from Eq. (5.2).

E) Hydrogenic Matrixelements

LOUCK¹⁵ has shown in a series of papers how the two dimensional harmonic oscillator can be related to the hydrogen atom. After a simple substitution all results derived in the present paper can be transferred to hydrogenic radial integrals. It can be shown that matrixelements of the type

$$K_{nn' ll', s} \equiv \int_0^\infty 1/r^s R_{nl}(r) R_{n'l'}(r) r^2 dr \quad (5.9)$$

treated some time ago by PASTERNAK and STERNHEIMER¹⁶ are contained implicitly in Eq. (4.8).

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Appendix

All commutations of the preceeding text are special cases of well known formulae¹¹, which will be repeated for convenience.

$$\begin{aligned} & \exp\{\alpha \hat{X}\} \hat{Y}^k \exp\{-\alpha \hat{X}\} \\ &= (Y + \alpha [\hat{X}, \hat{Y}]_- + (\alpha^2/2!) [\hat{X}, [\hat{X}, \hat{Y}]_-] + \dots)^k \\ &= (\tilde{Y}(\alpha))^k \\ &= \left(\sum_{m=0}^{\infty} \frac{\alpha^m}{m!} \{\hat{X}^m, \hat{Y}\}_- \right)^k. \end{aligned} \quad (A.1)$$

The curly bracket with the minus sign is an often used abbreviation of the repeated commutator. By series expansion and final resummation it can be derived from (A.1)

$$\exp\{\alpha \hat{X}\} \exp\{\hat{Y}\} \exp\{-\alpha \hat{X}\} = \exp\{\tilde{Y}(\alpha)\}. \quad (A.2)$$

The Zassenhaus-formula is

$$\exp\{\hat{X} + \hat{Y}\} = \exp\{\hat{X}\} \exp\{\hat{Y}\} \exp\{C_2^*\} \exp\{C_3^*\} \dots \quad (A.3)$$

where

$$C_2^* = (-1/2) [\hat{X}, \hat{Y}]_-, \quad (A.4)$$

$$C_3^* = (1/6) [\hat{X}, [\hat{X}, \hat{Y}]_-] + (1/3) [\hat{Y}, [\hat{X}, \hat{Y}]_-]_-. \quad (A.5)$$

If \hat{X} , \hat{Y} commute with $[\hat{X}, \hat{Y}]_-$ all terms higher than the second vanish.

The normal ordering formula given by WILCOX¹¹ is

$$(\hat{P} + \hat{Q})^n = \sum_{k=0}^{[n/2]} \sum_{s=0}^{n-2k} \frac{(c/2)^k n!}{k! s! (n-2k-s)!} \hat{Q}^s \hat{P}^{n-2k-s} \quad (\text{A. 6})$$

with $[\hat{P}, \hat{Q}]_- = c$, c is a c -number, \hat{P} and \hat{Q} can be realized by \hat{a} and \hat{a}^+ , thus leading to:

$$(\hat{a} + \hat{a}^+)^n = \sum_{k=0}^{[n/2]} \sum_{s=0}^{n-2k} \frac{(1/2)^k n!}{k! s! (n-2k-s)!} \hat{a}^{+s} \hat{a}^{n-2k-s}. \quad (\text{A. 7})$$

In the commutations six different types of (A. 1) and (A. 2) are necessary which will be collected:

$$\begin{aligned} \exp\{\alpha \hat{a}^+\} \hat{a} \exp\{-\alpha \hat{a}^+\} &= (\hat{a} - \alpha), \\ \exp\{\alpha \hat{a}^+ \hat{a}\} \hat{a} \exp\{-\alpha \hat{a}^+ \hat{a}\} &= \hat{a} \exp\{-\alpha\}, \end{aligned} \quad (\text{A. 8})$$

$$\exp\{\alpha \hat{a}^{+2}\} \hat{a} \exp\{-\alpha \hat{a}^{+2}\} = (\hat{a} - 2\alpha \hat{a}^+),$$

$$\exp\{\alpha \hat{a}\} \hat{a}^+ \exp\{-\alpha \hat{a}\} = (\hat{a}^+ + \alpha),$$

$$\exp\{\alpha \hat{a}^+ \hat{a}\} \hat{a}^+ \exp\{-\alpha \hat{a}^+ \hat{a}\} = \hat{a}^+ \exp\{\alpha\}, \quad (\text{A. 9})$$

$$\exp\{\alpha \hat{a}^2\} \hat{a}^+ \exp\{-\alpha \hat{a}^2\} = (\hat{a}^+ + 2\alpha \hat{a}).$$

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