

Conclusion

The information " $M(A) = \text{Tr}(WA) = m$, m finite" determines a unique *quantum state with maximum information entropy* if and only if one of the following conditions is fulfilled

(a) A is *thermodynamically regular* and m satisfies the equation $\underline{\sigma}(A) < m \leq \hat{m}_A$ or $\bar{\sigma}(A) > m \geq \hat{m}_A$

depending on whether A is bounded from below or above.

(b) m equals $\bar{\sigma}(A)$ or $\sigma(A)$ and is coincidently an eigenvalue of A with finite multiplicity.

The generalisation of this result to the case in which the mean values of several quantities are given will be treated in a subsequent paper.

¹ E. T. Jaynes, Phys. Rev. **106**, 620 [1957]; **108**, 171 [1957].

² R. S. Ingarden and K. Urbanik, Acta Phys. Polon. **21**, 281 [1962].

³ E. T. Jaynes, Information Theory and Statistical Physics, in: 1962 Brandeis Lectures, Vol. 3, Benjamin, New York 1963.

⁴ For further references to this subject we refer to a recent monograph: A. Hobson, Concepts in Statistical Mechanics, Gordon and Breach, New York 1971.

⁵ J. v. Neumann, Mathematische Grundlagen der Quantenmechanik, Springer-Verlag, Berlin 1932.

⁶ G. Ludwig, Die Grundlagen der Quantenmechanik, Springer-Verlag, Berlin 1954.

⁷ J. Langerholc, J. Math. Phys. **6**, 1210 [1965].

⁸ For simplicity we denote q.m. observables and quantum states by the same symbol as the respective representing s. a. operators and state operators.

⁹ U. Fano, Rev. Mod. Phys. **29**, 74 [1957].

¹⁰ This formula was first derived by v. Neumann¹¹ for the thermodynamic entropy of a q.m. system in thermal equilibrium by means of thermodynamic arguments.

¹¹ J. v. Neumann, Gött. Nachr. **1**, 273 [1927].

¹² A. Stahl, Z. Naturforsch. **15 a**, 655 [1960].

¹³ R. S. Ingarden and A. Kossakowski, Bull. Acad. Polon. Sci., Ser. Sci. Math. **16**, 61 [1968].

¹⁴ F. Engelmann, M. Feix, E. Minardi, and J. Oxenius, Z. Naturforsch. **16 a**, 1223 [1961].

¹⁵ A comparison of these two entropy concepts is found in^{12,13} and in: H. Schwegler, Z. Naturforsch. **20 a**, 1543 [1965]; F. Schlögl, A. Stahl, and R. Bausch, Z. Phys. **187**, 290 [1965].

¹⁶ E. H. Wichmann, J. Math. Phys. **4**, 884 [1963].

¹⁷ Whereas the normal text refers to a regular operator bounded from below, the insertions in square brackets refer to an A bounded from above.

¹⁸ F. N. Ramsey, Phys. Rev. **103**, 20 [1956]. — Y. P. Terletsii, Statistical Physics, North-Holland, Amsterdam 1971.

Coherent States and the Magnetic Operators

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In the present paper a method of calculation of the density matrix in the Schrödinger picture is given, in terms of the known creation and annihilation operators a^+ and a . New magnetic operators are given with the help of the coherent states, which depend on two free parameters μ and ν . For the case $\mu=\nu=(eH)/(2\hbar c)$, these operators lead to the well-known magnetic operators, as they are given in the current literature.

§ 1. Introduction

The physical significance of the coherent states is very important. They are, not only the states of oscillations that we encounter in nature, but also the states which are produced when an oscillator is coupled linearly with a prescribed classical force. They are also emitted by a classical current source. Therefore, they have many significant applications.

The coherent states were first introduced by Glauber¹, as eigenkets of the lowering operator a , defined by the equation:

$$a|a\rangle = a|a\rangle. \quad (1)$$

Applications of the coherent states to the density operator of boson amplitude operators, have been given by Cahill and Glauber². Also by Grosiqueni and Solimeto³, to the master equation for the p -representation in the Schrödinger picture.

The equation of motion of the density matrix in the Schrödinger picture, is of the form:

$$i\hbar \cdot \partial \rho / \partial t = \{H, \rho\}. \quad (2)$$

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The Hamiltonian $\mathcal{H}$ can be developed in a form of convergent series of the creation a^+ and annihilation a operators, namely:

$$\mathcal{H} = \sum_{m,n} \mathcal{H}_{mn} (a^+)^m a^n. \quad (3)$$

Also the operator ϱ can be expanded in a form of convergent series of the operators a^+ and a , as:

$$\varrho = \sum_{l,r} F_{lr}(t) a^{+l} a^r. \quad (4)$$

As an example, we mention the case of the harmonic oscillator with:

$$\mathcal{H} = \hbar \omega (a^+ a + \frac{1}{2}). \quad (5)$$

For this case, the coefficients F_{lr} verify the differential equation:

$$i \partial F_{lr} / \partial t = \omega (l - r) F_{lr}. \quad (6)$$

The solution of the above equation has the form:

$$F_{lr} = c e^{-i\omega t(l-r)} \quad (7)$$

and the operator ϱ for this case is of the form:

$$\varrho = \sum_{l,r} e^{-i\omega t l} a^{+l} e^{i\omega t r} a^r. \quad (8)$$

Malkin and Man'ko⁴ and Feldman and Kahn⁵ have studied the application of the coherent states for the free electron in a uniform magnetic field, by making use of the operators a^+ and a .

In what follows, it will be shown that the up to now used magnetic operators are partial cases of our new operators, for which, instead of having free parameters (such as the magnetic field), we introduce two new parameters, namely μ and ν .

The physical significance in this case corresponds to the movement of the electron in a magnetic field with a vector potential of the form:

$$\mathbf{A}: (A_x = -(\hbar c/e) \nu y, A_y = (\hbar c/e) \mu x, A_z = 0). \quad (9)$$

Where, from the known equation $\mathbf{H} = \text{rot } \mathbf{A}$, we have the relation:

$$H = (\mu + \nu) \hbar c/e \quad \text{or} \quad \mu + \nu = e H / \hbar c = B. \quad (10)$$

The corresponding Hamiltonian operator for this case, has the following form:

$$\mathcal{H} = (1/2 m) \{ (p_x - (e/c) A_x)^2 + (p_y - (e/c) A_y)^2 + p_z^2 \}. \quad (11)$$

In the next chapter, we define the new operators a^+ , a and b^+ , b of creation and annihilation.

§ 2. The new Operators a^+ , a and b^+ , b

The new operators a^+ , a and b^+ , b are defined as:

$$a = \frac{1}{\sqrt{2(\mu + \nu)}} \left\{ \frac{\partial}{\partial x} + i \frac{\partial}{\partial y} + \mu x + i \nu y \right\},$$

$$a^+ = \frac{1}{\sqrt{2(\mu + \nu)}} \left\{ \frac{\partial}{\partial x} - i \frac{\partial}{\partial y} - \mu x + i \nu y \right\}, \quad (12)$$

$$b = \frac{1}{\sqrt{2(\mu + \nu)}} \left\{ \frac{\partial}{\partial x} - i \frac{\partial}{\partial y} + \mu x - i \nu y \right\},$$

$$b^+ = \frac{1}{\sqrt{2(\mu + \nu)}} \left\{ \frac{\partial}{\partial x} + i \frac{\partial}{\partial y} - \mu x - i \nu y \right\}, \quad (13)$$

$$(b^+)^* = a^+ \quad \text{and} \quad (b)^* = a. \quad (14)$$

From the above definition, the following commutation relations result easily

$$\{a^+, a\} = 1, \{a^+, b\} = (\mu - \nu) / (\mu + \nu),$$

$$\{a^+, b^+\} = 0, \{a, b\} = 0, \quad (15)$$

$$\{a, b^+\} = -(\mu - \nu) / (\mu + \nu), \{b^+, b\} = 1.$$

In the case that

$$\mu = \nu = e H / 2 \hbar c = B/2 \quad (16)$$

the operators (12) and (13) become the known magnetic operators of the free electron in a uniform magnetic field. These operators have been studied by several authors⁴⁻⁷.

The Hamiltonian $\mathcal{H}$ of the free electron in an external magnetic field, is

$$\mathcal{H} = (1/2 m) \{ (p_x - (e/c) A_x)^2 + (p_y - (e/c) A_y)^2 + (p_z - (e/c) A_z)^2 \}. \quad (17)$$

For the case (9), (17) takes the form:

$$\mathcal{H} = -\frac{\hbar^2}{2m} \left\{ \left(\frac{\partial}{\partial x} + i \nu y \right)^2 + \left(\frac{\partial}{\partial y} - i \mu x \right)^2 + \frac{\partial^2}{\partial z^2} \right\}. \quad (18)$$

And since the motion along the z -axis is free, we consider the operator:

$$\mathcal{H}_\perp = \frac{\hbar^2}{2m} \left\{ \left(\frac{\partial}{\partial x} + i \nu y \right)^2 + \left(\frac{\partial}{\partial y} - i \mu x \right)^2 \right\}. \quad (19)$$

This operator can be expressed in terms of the operators a and a^+ (12) as:

$$\mathcal{H}_\perp = -\frac{\hbar^2}{2m} 2(\mu + \nu) (a a^+ + \frac{1}{2})$$

$$= -\frac{\hbar^2}{2m} 2(\mu + \nu) (a^+ a - \frac{1}{2}). \quad (20)$$

However, because of (10), it is:

$$\mathcal{H}_\perp = -\hbar \omega (a a^+ + \frac{1}{2}) = -\hbar \omega (a^+ a - \frac{1}{2}) \quad (21)$$

with $\omega = eH/mc$. (22)

It is easy to prove that the eigenvalues of $a^+ a$ are $-n$ and of $a a^+$ are $-(n+1)$. The eigenvalues of the Hamiltonian operator $\mathcal{H}_\perp$ are given by:

$$E = \hbar \omega (n + \frac{1}{2}). \quad (23)$$

§ 3. Eigenfunctions of the Operator $\mathcal{H}$

The eigenvalue equation of the operator $\mathcal{H}_\perp$ is given by:

$$\left\{ \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + 2i \left(\nu y \frac{\partial}{\partial x} - \mu x \frac{\partial}{\partial y} \right) - \mu^2 x^2 - \nu^2 y^2 \right\} \Psi + \frac{2m}{\hbar^2} E \Psi = 0. \quad (24)$$

By substitution

$$\Psi(x, y) = \exp\left\{-\frac{1}{2}(\mu x^2 + \nu y^2)\right\} \Phi(x, y) \quad (25)$$

we obtain

$$\frac{\partial^2 \Phi}{\partial x^2} + \frac{\partial^2 \Phi}{\partial y^2} - 2(\mu x - i\nu y) \cdot \left(\frac{\partial \Phi}{\partial x} + i \frac{\partial \Phi}{\partial y} \right) + \left(\frac{2m}{\hbar^2} E - \mu - \nu \right) \Phi = 0. \quad (26)$$

The solution of the above equation is obtained by the transformation:

$$\Phi(x, y) = \frac{\exp\{i k_x x + i k_y y\}}{2\pi i} \int_c e^{s(\mu x + i\nu y)} f(s) ds \quad (27)$$

where the function $f(s)$ verifies the following differential equation

$$2\{(\mu + \nu)s + i k_x - k_y\} df/ds + \{2mE/\hbar^2 + \mu + \nu + ((\mu + \nu)s + i k_x - k_y) \cdot ((\mu - \nu)s + i k_x + k_y)\} f = 0 \quad (28)$$

from which we have:

$$f(s) = \text{const} [s + (i k_x - k_y)/(\mu + \nu)]^{-1/2 - mE/\hbar^2(\mu + \nu)} \exp\left\{-\frac{1}{4}(\mu - \nu)s^2 - \frac{1}{2}(i k_x + k_y)s\right\}. \quad (29)$$

Therefore the solution (25) is written:

$$\Psi(x, y) \sim \exp\left\{-\frac{1}{2}(\mu x^2 + \nu y^2) + i k_x x + i k_y y\right\} (1/2\pi i) \int_c \exp\left\{-\frac{1}{4}(\mu - \nu)s^2 + [(\mu x - k_y/2) - i(\nu y + k_x/2)]s\right\} \cdot \{s + (i k_x - k_y)/(\mu + \nu)\}^{-1/2 - mE/\hbar^2(\mu + \nu)} ds. \quad (30)$$

The function under the integral has a pole and the following condition must hold:

$$\frac{1}{2} + mE/\hbar^2(\mu + \nu) = n + 1, \quad (n = 0, 1, \dots) \quad (31)$$

from which we obtain the eigenvalues

$$E = [\hbar^2(\mu + \nu)/m] (n + \frac{1}{2}) = \hbar \omega (n + \frac{1}{2}). \quad (32)$$

The above relation is the relation (23).

If we make the transformation

$$u = [s + (i k_x - k_y)/(\mu + \nu)]^{1/2} \sqrt{\mu - \nu} \quad (33)$$

then the eigenfunctions (30) take the form:

$$\Psi(x, y) \sim \exp\left\{-\frac{1}{2}[\mu x^2 + \nu y^2] + (x + i y)(\mu k_y + i\nu k_x)/(\mu + \nu) - [1/4(\mu + \nu)^2] [(3\mu + \nu)k_y^2 + (3\nu + \mu)k_x^2 - 2i(\mu - \nu)k_x k_y]\right\} \cdot \left(\frac{\sqrt{\mu - \nu}}{2}\right)^n \int_c \frac{1}{2\pi i} \exp\{-u^2 + [2u/\sqrt{\mu - \nu}]\} \cdot [(\mu x - k_y/2) - i(\nu y + k_x/2)] \cdot (1/u^{n+1}) du. \quad (34)$$

After integration we take finally the eigenfunctions, which depend upon the parameter $\mathbf{k} = (k_x, k_y)$ and the integer n :

$$\Psi_{\mathbf{k}, n}(x, y) \sim \exp\left\{-\frac{1}{2}(\mu x^2 + \nu y^2) + (x - i y)(\mu k_y + i\nu k_x)/(\mu + \nu) - [1/4(\mu + \nu)^2] [(3\mu + \nu)k_y^2 + (3\nu + \mu)k_x^2 - 2i(\mu - \nu)k_x k_y]\right\} \cdot \left(\frac{\sqrt{\mu - \nu}}{2}\right)^n H_n\{1/\sqrt{\mu - \nu} [(\mu x - k_y/2) - i(\nu y + k_x/2)]\} \quad (35)$$

where $H_n(x)$ are the Hermite polynomials.

We observe that, for $\mu = \nu = eH/2\hbar c = B/2$, the eigenfunctions (35) tend to the well-known Schrauben-functions⁸.

§ 4. Coherent States of the Operators a and b

The coherent states of the operators a and b are defined as follows:

$$a \Psi = [\alpha/\sqrt{2(\mu + \nu)}] \Psi, \quad (36)$$

$$b \Psi = [\beta/\sqrt{2(\mu + \nu)}] \Psi \quad (37)$$

or, by the definitions (12) and (13), we have:

$$(\partial/\partial x + i\partial/\partial y + \mu x + i\nu y) \Psi = \alpha \Psi, \quad (38)$$

$$(\partial/\partial x - i\partial/\partial y + \mu x - i\nu y) \Psi = \beta \Psi \quad (39)$$

where:

$$\Psi = A \exp\left\{-\frac{1}{2}(\mu x^2 + \nu y^2) + \lambda x + \varrho y\right\}. \quad (40)$$

By substitution of (40) into (38) and (39), we obtain:

$$\lambda + i\varrho = \alpha, \quad \lambda - i\varrho = \beta \quad (41)$$

from which we take

$$\lambda = (\alpha + \beta)/2, \quad \varrho = (\alpha - \beta)/2 i = \frac{1}{2} (\beta - \alpha) i \quad (42)$$

and the function we wish to find, is:

$$\Psi = A \exp\left\{-\frac{1}{2}(\mu x^2 + \nu y^2) + (a/2)(x - i y) + (\beta/2)(x + i y)\right\}. \quad (43)$$

The normalisation constant A , is

$$A = \sqrt{V\mu\nu/\pi} \exp\left\{-(\alpha_1 + \beta_1)^2/8\mu - (\alpha_2 - \beta_2)^2/8\nu\right\} \quad (44)$$

and eigenfunctions (43) take the final form:

$$\Psi = \sqrt{V\mu\nu/\pi} \exp\left\{-\frac{1}{2}(\mu x^2 + \nu y^2) + (a/2)(x - i y) + (\beta/2)(x + i y) - (\alpha_1 + \beta_1)^2/8\mu - (\alpha_2 - \beta_2)^2/8\nu\right\} \quad (45)$$

$$\text{where } a = \alpha_1 + i\alpha_2 \quad \text{and} \quad \beta = \beta_1 + i\beta_2. \quad (46)$$

Instead of using the known operators a^+ and a of the harmonic oscillator [Eqs. (5)], we can use the new operators (12) for the case of the magnetic field; we may also construct from them several operators in the meaning of Cahill and Glauber², namely in a form of power series.

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Ab Initio-Rechnungen zum F₂-Molekül

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Different ab-initio calculations for the ground-state and some excited states of the F₂-molecule

For the ground-state and the lower lying excited states of the fluorine-molecule VB—CI calculations with Slater-type orbitals and SCF—CI calculations with contracted Gauß-Lobe functions have been carried out. The SCF—CI method yields a fairly good description of the ground-state. But it is rather difficult to decide whether the SCF—CI calculations of the excited states are accurate or not. The discussion of the potential-curves of some higher excited states leads to the conjecture that the experimentally observed orange band-systems may belong to two transitions

$$^1\Sigma_g^- \rightarrow ^1\Pi_u \quad \text{and} \quad ^1\Sigma_u^+ \rightarrow ^1\Pi_g.$$

But this should be checked in further calculations which must include higher orbitals as basis-functions.

Über das F₂-Molekül ist sowohl experimentell als auch theoretisch relativ wenig bekannt. Im sichtbaren Wellenlängenbereich wurden im wesentlichen zwei Bandensysteme in Emission beobachtet^{1–5}, deren Zuordnung zu Elektronenübergängen noch nicht eindeutig gelungen ist. Auf Grund eingehender Analysen der Rotationsstruktur schloß Porter⁴, daß dabei Übergänge vom Typ $^1\Sigma_g^- \rightarrow ^1\Pi_u$ oder $^1\Sigma_u^+ \rightarrow ^1\Pi_g$ vorliegen sollten. Sicher handelt es sich hierbei nicht um Übergänge in den Grundzustand.

Die Bestimmung der Dissoziationsenergie des F₂-Moleküls ist mit erheblichen Schwierigkeiten verbunden. Die mit Hilfe verschiedener Verfahren erhaltenen Werte schwanken zwischen 1,39 eV und 2,17 eV^{5–10}. Man nimmt zur Zeit an, daß der wirkliche Wert bei etwa 1,6 eV liegen sollte^{11, 12}. Es gibt zwar eine Reihe von theoretischen Arbeiten über das F₂-Molekül, diese befassen sich aber mit Ausnahme der Rechnungen von Hijikata¹³ vorwiegend mit dem Grundzustand. Auch hier ergaben sich z. Tl. schlechte Werte für die Dissoziationsenergie.

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