Der zu 3,4 Å gefundene Abstand der Ladungsschwerpunkte $H_3^+O-Cl^-$ in der Salzsäurespezies ist wesentlich kleiner als der aus dem Molvolumen folgende mittlere Radius von 5,4 Å eines kugelförmigen Moleküls. Eine sterische Betrachtung zeigt, daß die vier Isobutylreste das zentrale Hydroniumion H_3^+O nicht vollständig umhüllen; das Chloridion kann also nahe an die positive Ladung herantreten. Wahrscheinlich liegen das zentrale Hydroniumion und die Hydroxylgruppen der beiden Carbinolmoleküle sowie das verbleibende Wassermolekül in einer Ebene, über und unter der sich die vier Isobutylreste befinden. Legt man das Chloridion ebenfalls in die zentrale Ebene und setzt als O – H-Abstand 1,4 Å, als Cl^--Ionenradius 1,8 Å ein, so sind die Ladungsschwerpunkte 3,5 Å voneinander entfernt, in guter Übereinstimmung mit dem gefundenen Wert. Somit stützen auch die Leitfähigkeitsdaten den hier abgeleiteten Mechanismus der Salzsäureextraktion durch Diisobutylcarbinol.

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On the Lattice-cell-volume Dependence in the Calculation of the Two-point Function in Quantum Mechanics by the Method of Functional Integration

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It is shown that the transition from lattice space, where the two-point functions were calculated by means of functional integration, to continuous space $\varepsilon \to 0$, which requires in field theories some kind of renormalization, is practicable in quantum mechanics after reordering of series without renormalization. An ambiguity, which occurs, is discussed.

In the calculation of two-point functions for models of field theory by means of functional integration the transition from lattice space, where the functional integrals were calculated, to continuous space was practicable only with difficulties. These difficulties were overcome by means of some kind of renormalization [1–5]. In this connection the question occurs, if also in quantum mechanics in calculations by means of functional integration the mentioned transition requires renormalization or if the ε-dependence is of another kind than in field theory and permits the transition $\varepsilon \to 0$ (ε is the volume of an elementary cell in the lattice space, in quantum mechanics the corresponding space is the time axis and ε is a time difference). To clarify this question we calculate the two-point function

$$\chi(u_1, z_1) = \chi(u_1 - z_1) = \langle \psi_0 | T(x(u_1)\, x(z_1)) | \psi_0 \rangle \tag{1}$$

in analogy to the mentioned field theory works by functional integration and examine the ε-dependence. By standard methods we get the FOURIER transform $\tilde{\chi}(\omega)$ of $\chi(u_1 - z_1)$

$$\tilde{\chi}(\omega) = \frac{1}{\sqrt{2\pi}} \int \chi(u_1 - z_1)\, e^{-i\omega(u_1 - z_1)}\, \mathrm{d}(u_1 - z_1) = \frac{2i}{\sqrt{2\pi}} \sum_n \frac{|\langle \psi_0 | x | \psi_n \rangle|^2\, \omega_{n0}}{\omega^2 - \omega_{n0}^2}. \tag{2}$$

ψ_n are the stationary states of the quantum mechanical system and ω_{n0} are the transition-frequencies between the states ψ_n and ψ_0. $x(t)$ in (1) is the position-operator in the HEISENBERG-picture, x in (2) is the position-operator in the SCHRÖDINGER-picture. u_1 and z_1 are fixed times. The formulation of (1) by functional integrals yields

$$\chi(u_1, z_1) = \frac{\int x(u_1)\, x(z_1)\, \exp\{i \int L\, \mathrm{d}t\}\, \delta x}{\int \exp\{i \int L\, \mathrm{d}t\}\, \delta x}, \tag{3}$$

[1] G. HEBER and H. J. KAISER, Z. Naturforschg. **19 a**, 828 [1964].
[2] G. HEBER and A. KÜHNEL, Z. Naturforschg. **19 a**, 1245 [1964].
[3] G. HEBER, A. KÜHNEL, and H. J. KAISER, Z. Naturforschg. **20 a**, 498 [1965].
[4] G. HEBER, M. HOFFMANN, and G. RÖPKE, Z. Physik **190**, 191 [1966].
[5] A. KÜHNEL, Habilitationsschrift, Leipzig 1966, to be published in Soviet Phys.—JETP, Moskow.

at which we have used $\hbar = 1$ and the LAGRANGian L in the form

$$L = -\tfrac{1}{2} m x \ddot{x} - V(x) = L_0 + L_w \tag{4}$$

with $$L_0 = -\tfrac{1}{2} m x \ddot{x}, \quad L_w = -V(x). \tag{5}$$

$V(x)$ contains a parameter λ in the considered cases.

In the numerator of (3) we expand the term with L_0 and then we perform the functional integrations in the lattice space. The resulting contributions can be represented by graphs. We take into consideration the denominator by the fact that in the numerator the factor φ_0 (see below), which is contained in each term, and terms corresponding to unconnected graphs are neglected. The denominator of (3) was introduced in order to remove these terms (cf. [1–6]). We get at last

$$\chi(u_1, z_1) = \sum_{n=0}^{\infty} \frac{i^n}{n!} \left(\frac{m}{2}\right)^n \int G(u_2, z_2) \dots G(u_{n+1}, z_{n+1}) \cdot \varphi_{n+1}\, du_2\, dz_2 \dots du_{n+1}\, dz_{n+1} \tag{6}$$

with $$\varphi_n = \int x(u_1)\, x(z_1) \dots x(u_n)\, x(z_n) \cdot \exp\{-i \int V(x(t))\, dt\}\, \delta x \tag{7}$$

and $$G(u_i, z_i) = -\delta(u_i - z_i) \frac{d^2}{dz_i^2}. \tag{8}$$

We have already mentioned that we calculate in the lattice space, at which we have in quantum mechanics a one-dimensional lattice space (t axis). (7) yields in lattice space

$$\varphi_n = \lim_{\varepsilon \to 0} \int_{-\infty}^{\infty} x_{u_1} x_{z_1} \dots x_{u_n} x_{z_n} \prod_k e^{-i\varepsilon V(x_k)}\, dx_k. \tag{9}$$

Here we have used in each point t_k of the lattice space

$$x_{u_1} = x(u_1), \quad x_{z_1} = x(z_1), \quad x_k = x(t_k).$$

"lim" in (9) means transition from lattice to continuous space. For symmetrical potentials with $V(-x) = V(x)$ we get from (9) nonvanishing contributions only in the case of coinciding lattice-points $(u_1, \dots, u_n, z_1, \dots, z_n)$ in pairs.

For further considerations we need the expressions

$$M_r = \frac{\int_{-\infty}^{\infty} x^{2r} e^{-i\varepsilon V(x)}\, dx}{\int_{-\infty}^{\infty} e^{-i\varepsilon V(x)}\, dx} \tag{10}$$

and

$$\begin{aligned} f_1 &= M_1, \\ f_2 &= M_2 - 3 M_1^2, \\ f_3 &= M_3 - 15 M_2 M_1 + 30 M_1^3, \\ &\dots\dots\dots\dots\dots \\ &\text{etc.} \end{aligned} \tag{11}$$

and the relations

$$\delta(u - z) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega\, e^{i\omega(u-z)}, \tag{12}$$

with the help of this we perform the FOURIER transformation, and

$$\delta^{(2k)}(0) = \lim_{\varepsilon \to 0} \left\{ (-1)^k \binom{2k}{k} \Big/ (2^{2k} \varepsilon^{2k+1}) \right\}. \tag{13}$$

(13) means the second derivative of the function $\delta(t)$ at $t = 0$ and was calculated in lattice space [7]. For technical details we refer again to the cited literature.

$\tilde{\chi}(\omega)$ contains the following contributions, at which we have left out numerical factors consisting of weight factors, manifolds, expansion-coefficients from (6), numerical factors in the f_r and numerical factors from (13):

$n = 0$: $f_1 \varepsilon$ (see Fig. 1);

Fig. 1.

$n = 1$:

a) $i m f_2 \varepsilon^3 \delta''(0)$; b) $i m f_1^2 \varepsilon^2 \omega^2$ (Fig. 2); (14)

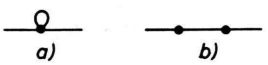

Fig. 2.

$n = 2$:

a) $i^2 m^2 \varepsilon^5 f_3 (\delta''(0))^2$, b) $i^2 m^2 \varepsilon^4 f_1 f_2 \delta''(0)\, \omega^2$,
c) $i^2 m^2 \varepsilon^3 f_1^3 (\omega^2)^2$, d) $i^2 m^2 \varepsilon^4 f_1 f_2 \delta''''(0)$,
e) $i^2 m^2 \varepsilon^4 f_1 f_2 \delta''(0)\, \omega^2$ (Fig. 3);

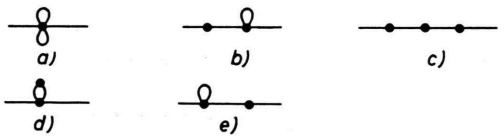

Fig. 3.

etc.

[6] G. RÖPKE, Dissertation, Leipzig 1966; Z. Naturforschg. **22 a**, 860 [1967].

[7] Follows from $f'(0) = [f(\varepsilon) - f(-\varepsilon)]/(2\varepsilon)$
and $f''(0) = (1/4\varepsilon^2)\,(f(2\varepsilon) - 2f(0) + f(-2\varepsilon))$
etc. with $\delta(m\varepsilon) = \begin{cases} 0 & m \neq 0, \\ 1/\varepsilon & m = 0. \end{cases}$

If we change the order of the series resulting from (6) and collect the terms with equal power of ω we get

$$\sqrt{2\pi}\,\tilde{\chi}(\omega) = -i\sum_{k=0}^{\infty}\alpha_k(\omega^2)^k\,. \tag{15}$$

The graphs which contribute to the α_k are pictured in Fig. 4 [6].

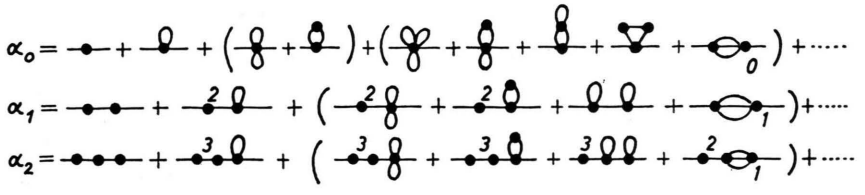

Fig. 4.

The numbers above the horizontal lines denote the manifold of the corresponding graphs, the numbers below mean that we must use only that part of the graph which contributes to the considered α_k (see projection operators below) [3, 5].

The graphs in brackets have equal powers of m, λ and $(i\varepsilon)$ and differ only in numerical factors, so we must use in general considerations only one graph of each bracket. If one defines a multiplication of graphs [3, 6] we can write

$$\alpha_0 = \alpha, \quad \alpha_1 = m\,\alpha^2 + m\,\alpha\,\beta, \quad \alpha_2 = m^2\,\alpha^3 + m^2\cdot 2\,\alpha^2\,\beta + m^2\,\alpha^2\,\gamma, \quad \text{etc.} \tag{16}$$

and we have to consider only the contributions to α, β, γ, which are pictured in Fig. 5.

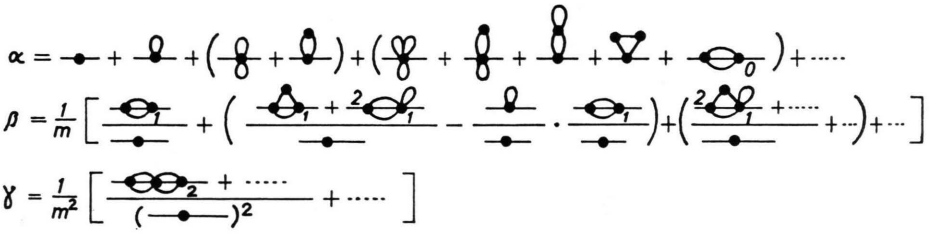

Fig. 5.

By the rules described in the literature [1, 5] we get for the necessary graphs the following expressions (see Fig. 6):

$$\begin{aligned}
&\text{a)}\quad f_1\,\varepsilon\,\delta(u_1-z_1),\\
&\text{b)}\quad i\,m\,\varepsilon^3 f_2\,\delta''(0)\,\delta(u_1-z_1),\\
&\text{c)}\quad i^2 m^2 \varepsilon^5 f_3(\delta''(0))^2\,\delta(u_1-z_1),\\
&\text{d)}\quad i^3 m^3 \varepsilon^7 f_4(\delta''(0))^3\,\delta(u_1-z_1),\\
&\text{e)}\quad i^3 m^3 \varepsilon^6 f_2^2 P_1\left[\left(\frac{\mathrm{d}^2}{\mathrm{d}z_1^2}\,\delta(u_1-z_1)\right)^3\right],\\
&\text{f)}\quad i^4 m^4 \varepsilon^7 f_2^2 f_1 P_1\left[\left(\frac{\mathrm{d}^2}{\mathrm{d}z_1^2}\,\delta(u_1-z_1)\right)^2 \frac{\mathrm{d}^4}{\mathrm{d}z_1^4}\,\delta(u_1-z_1)\right],\\
&\text{g)}\quad i^5 m^5 \varepsilon^9 f_1 f_2 f_3\,\delta''(0)\,P_1\left[\left(\frac{\mathrm{d}^2}{\mathrm{d}z_1^2}\,\delta(u_1-z_1)\right)^2 \frac{\mathrm{d}^4}{\mathrm{d}z_1^4}\,\delta(u_1-z_1)\right],\\
&\text{h)}\quad i^6 m^6 \varepsilon^{11} f_2^2 f_3 P_2\left[\int\left(\frac{\mathrm{d}^2}{\mathrm{d}u_4^2}\,\delta(u_1-u_4)\right)^3\left(\frac{\mathrm{d}^2}{\mathrm{d}z_1^2}\,\delta(u_4-z_1)\right)^3 \mathrm{d}u_4\right].
\end{aligned} \tag{17}$$

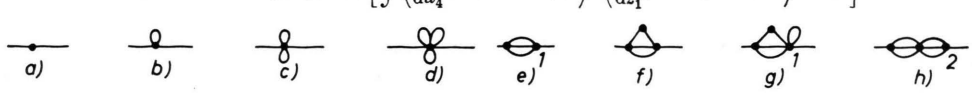

Fig. 6.

We have again left out numerical factors. The projections P_1 and P_2 are calculated in lattice space [5] and yield

$$\begin{aligned} P_1\left[\left(\frac{\mathrm{d}^2}{\mathrm{d}z_1^2}\,\delta(u_1-z_1)\right)^3\right] &= c_1\,\frac{1}{\varepsilon^6}\,\frac{\mathrm{d}^2}{\mathrm{d}z_1^2}\,\delta(u_1-z_1), \\ P_1\left[\left(\frac{\mathrm{d}^2}{\mathrm{d}z_1^2}\,\delta(u_1-z_1)\right)^2\frac{\mathrm{d}^4}{\mathrm{d}z_1^4}\,\delta(u_1-z_1)\right] &= c_2\,\frac{1}{\varepsilon^8}\,\frac{\mathrm{d}^2}{\mathrm{d}z_1^2}\,\delta(u_1-z_1), \\ P_2\left[\int\left(\frac{\mathrm{d}^2}{\mathrm{d}u_4^2}\,\delta(u_1-u_4)\right)^3\left(\frac{\mathrm{d}^2}{\mathrm{d}z_1^2}\,\delta(u_4-z_1)\right)^3\mathrm{d}u_4\right] &= c_3\,\frac{1}{\varepsilon^{12}}\,\frac{\mathrm{d}^4}{\mathrm{d}z_1^4}\,\delta(u_1-z_1), \end{aligned} \tag{18}$$

at which c_1, c_2 and c_3 are numerical factors. The FOURIER transformation of (17) can be done with relation (12) and the derivatives of the δ-function are given by (13).

The Potentials $V(x)=\lambda\,|x|^p$

We carry out the outlined programme for the symmetrical potentials

$$V(x)=\lambda\,|x|^p \qquad p>0, \quad \lambda>0\,. \tag{19}$$

By the relation

$$\int_0^\infty x^{r'}\exp\{-i\,\varepsilon\,\lambda\,x^p\}\,\mathrm{d}x = p^{-1}(i\,\varepsilon\,\lambda)^{-(r'+1)/p}\,\Gamma((r'+1)/p) \tag{20}$$

we get

$$M_r=(i\,\varepsilon\,\lambda)^{-2r/p}\,\frac{\Gamma((2\,r+1)/p)}{\Gamma(1/p)} \sim (i\,\varepsilon\,\lambda)^{-2r/p} \tag{21}$$

and

$$f_r \sim (i\,\varepsilon\,\lambda)^{-2r/p}\,. \tag{22}$$

In (20) we have to demand $r'>-1$ for convergence at zero, which is fulfilled in our theory, for convergence at infinity we have to replace for $r'\geqq p-1$ λ by $\lambda-i\,\lambda'$ $(\lambda'>0)$ and after integration letting $\lambda'\to 0$.

With (22) we get for α

$$\alpha=\sum_{j=1}^{\infty} a_j\,\frac{m^{j-1}}{\lambda^{2j/p}\,(i\,\varepsilon)^{2j/p+j-2}}, \tag{23}$$

at which a_j are all mentioned numerical factors. This expression we can replace by [6]

$$\alpha=\sum_{\nu=1}^{\infty}\frac{i^2\,\varepsilon^2\,A_\nu}{m}\left[\left(1+\left(\frac{m}{\lambda^{2/p}\,(i\,\varepsilon)^{2/p+1}}\right)^\nu\right)^{2/[\nu\,(2/p+1)]}-1\right]. \tag{24}$$

With

$$(1+x)^n=1+\binom{n}{1}x+\binom{n}{2}x^2+\ldots=\sum_{j=0}^{\infty}\binom{n}{j}x^j \tag{25}$$

each term in (24) yields

$$\begin{aligned} \left[\left(1+\left(\frac{m}{\lambda^{2/p}\,(i\,\varepsilon)^{2/p+1}}\right)^\nu\right)^{2/[\nu\,(2/p-1)]}-1\right]\frac{i^2\,\varepsilon^2\,A_\nu}{m} &= \frac{i^2\,\varepsilon^2\,A_\nu}{m}\sum_{j'=1}^{\infty}\binom{2}{\nu\,(2/p+1)}{j'}\left(\frac{m^\nu}{\lambda^{2\nu/p}\,(i\,\varepsilon)^{2\nu/p+\nu}}\right)^{j'} \\ &= \sum_{j'=1}^{\infty}\binom{2}{\nu\,(2/p+1)}{j'}\frac{A_\nu\,m^{j'\nu-1}}{\lambda^{2\nu j'/p}\,(i\,\varepsilon)^{2\nu j'/p+\nu j'-2}} = \sum_{j=\nu,\,2\nu,\,3\nu}\binom{2}{\nu\,(2/p+1)}{j/\nu}A_\nu\,\frac{m^{j-1}}{\lambda^{2j/p}\,(i\,\varepsilon)^{2j/p+j-2}}\,. \end{aligned} \tag{26}$$

$$(j=j'\cdot\nu)$$

After summation over ν the last expression of (26) corresponds to (23) at which the A_ν are determined by the a_j in the following way:

$\nu=1$ contributes to $j=1$,

$\nu=1$, $\nu=2$ contributes to $j=2$,

$\nu=1$, $\nu=3$ contributes to $j=3$,

$\nu=1$, $\nu=2$, $\nu=4$ contributes to $j=4$ etc.,

consequently we have the relations

$$\begin{aligned}
&\binom{2/(2/p+1)}{1} A_1 = a_1 ,\\
&\binom{2/(2/p+1)}{2} A_1 + \binom{2/(2(2/p+1))}{1} A_2 = a_2 ,\\
&\binom{2/(2/p+1)}{3} A_1 + \binom{2/(3(2/p+1))}{1} A_3 = a_3 ,\\
&\binom{2/(2/p+1)}{4} A_1 + \binom{2/(2(2/p+1))}{2} A_2 + \binom{2/(4(2/p+1))}{1} A_4 = a_4 ,\\
&\qquad \text{etc.}
\end{aligned} \tag{27}$$

Expression (24) permits the transition $\varepsilon \to 0$ which yields

$$\alpha = \left(\sum_{\nu=1}^{\infty} A_\nu \right) \frac{1}{\lambda^{4/(2+p)}\, m^{(2-p)/(2+p)}} . \tag{28}$$

For β, γ etc. we get in analogous manner

$$\begin{aligned}
\beta &= \sum_{j=3}^{\infty} b_j \, \frac{m j^{-1}}{\lambda^{2j/p}\,(i\,\varepsilon)^{2j/p+j-2}} \\
&= \sum_{\nu=3}^{\infty} (i^2\,\varepsilon^2\, B\,\nu/m) \times \\
&\qquad \times \left[\left(1 + \left(\frac{m}{\lambda^{2/p}\,(i\,\varepsilon)^{2/p+1}} \right)^{\nu} \right)^{2/[\nu\,(2/p+1)]} - 1 \right],
\end{aligned} \tag{29}$$

$$\beta = \left(\sum_{\nu=3}^{\infty} B_\nu \right) \frac{1}{\lambda^{4/(2+p)}\, m^{(2-p)/(2+p)}} , \tag{30}$$

$$\gamma = \left(\sum_{\nu=5}^{\infty} C_\nu \right) \frac{1}{\lambda^{4/(2+p)}\, m^{(2-p)/(2+p)}} , \qquad \text{etc.} \tag{31}$$

The numbers B_ν are again determined by the numbers b_j by equations similar to (27). The analogue is valid for C_ν etc. The comparison of (2) and (15) shows that the α_k must be real. Because α, β, γ etc. are real expressions the α_k are real indeed [cf. Eqs. (16)]. So the prescribed procedure yields real and ε-independent results for α_k and the comparision of (2) and (15) leads to real energy eigenvalues ω_{n0} (more exactly ω_{n0} is the difference between the energy eigenvalue E_n and the ground-state energy E_0).

Ambiguity of the Transition $\varepsilon \to 0$

The powers of ε in (23) are $-2\,j/p - j + 2$. These powers are always negative for $j \geqq 2$ but we get for $j = 1$, which occurs only in α,

$$-2/p + 1 \lessgtr 0 \quad \text{for} \quad p \lessgtr 2 . \tag{32}$$

That means the power of ε is positive in the term $j = 1$ for $p > 2$. In the cases $p > 2$ there are two possibilities for the transition $\varepsilon \to 0$. We demonstrate the two possibilities in the case $p = 4$. In this case α reads

$$\alpha = \sum_{j=1}^{\infty} a_j \, \frac{m j^{-1}}{\lambda^{j/2}\,(i\,\varepsilon)^{j/2+j-2}} \tag{33}$$

and after transition $\varepsilon \to 0$

$$\alpha = \left(\sum_{\nu=1}^{\infty} A_\nu \right) (m^{1/3}/\lambda^{2/3}) . \tag{34}$$

The equations

$$\begin{aligned}
&\binom{4/3}{1} A_1 = a_1 ,\\
&\binom{4/3}{2} A_1 + \binom{4/6}{1} A_2 = a_2 ,\\
&\binom{4/3}{3} A_1 + \binom{4/9}{1} A_3 = a_3 ,\\
&\binom{4/3}{4} A_1 + \binom{4/6}{2} A_2 + \binom{4/12}{1} A_4 = a_4 , \qquad \text{etc.}
\end{aligned} \tag{35}$$

determine the A_ν by the a_j.

We can perform the transition $\varepsilon \to 0$ also in another way. We write Eq. (33) in the following form:

$$\alpha = \frac{a_1\,(i\,\varepsilon)^{1/2}}{\lambda^{1/2}} + \sum_{j=2}^{\infty} a_j \, \frac{m j^{-1}}{\lambda^{j/2}\,(i\,\varepsilon)^{j/2+j-2}} . \tag{36}$$

Now this expression we can replace after performing the limiting procedure $\varepsilon \to 0$ by

$$\alpha = \sum_{\nu=2}^{\infty} (A_\nu') \, (m^{1/3}/\lambda^{2/3}) . \tag{37}$$

The A_ν' are again determined by the a_j, but now the following equations hold:

$$\begin{aligned}
&\binom{4/6}{1} A_2' = a_2 ,\\
&\binom{4/9}{1} A_3' = a_3 ,\\
&\binom{4/6}{2} A_2' + \binom{4/12}{1} A_4' = a_4 , \qquad \text{etc.}
\end{aligned} \tag{38}$$

If the two ways give the same result the equation

$$\sum_{\nu=1}^{\infty} A_\nu \overset{!}{=} \sum_{\nu=2}^{\infty} A_\nu' \tag{39}$$

must be valid. To see this we compare (35) and (38) and write (35) in the form

$$\begin{aligned}
&\binom{4/3}{1} A_1 = a_1 ,\\
&\binom{4/6}{1} \left[\tfrac{1}{3} A_1 + A_2 \right] = a_2 ,\\
&\binom{4/9}{1} \left[-\tfrac{1}{9} A_1 + A_3 \right] = a_3 ,\\
&\binom{4/6}{2} \left[\tfrac{1}{3} A_1 + A_2 \right] + \binom{4/12}{1} \left[\tfrac{14}{81} A_1 + A_4 \right] = a_4 , \text{ etc.}
\end{aligned} \tag{40}$$

from which follows

$$\begin{aligned} A_2' &= \tfrac{1}{3}\ A_1 + A_2\,, \\ A_3' &= -\tfrac{1}{9}\ A_1 + A_3\,, \\ A_4' &= \tfrac{14}{81} A_1 + A_4\,, \qquad \text{etc.} \end{aligned} \tag{41}$$

From (41) we get the relation

$$\begin{aligned} \sum_{\nu=2}^{\infty} A_\nu' = \sum_{\nu=2}^{\infty} A_\nu + (&0{,}33333 - 0{,}11111 + 0{,}17284 \\ &- 0{,}04115 - 0{,}10562 - 0{,}02347 + 0{,}19184 \\ &+ 0{,}03218 - 0{,}06470 + \ldots)\, A_1\,. \end{aligned} \tag{42}$$

With this nine numbers the coefficient of A_1 is 0,38414, and it is very doubtful if it converges to one as Eq. (39) requires. But at present we have no proof. To clarify the question, which of the two transitions yields the best results in future works we shall calculate by our approximation scheme energy eigenvalues for some in quantum mechanics exactly soluble potentials. Against the second transition $\varepsilon \to 0$ we notice, that in it a_1 and consequently A_1 corresponding to graphs Fig. 1, Fig. 2 b, Fig. 3 c etc., which are the only contributions in the field theory of free fields [2], apparently do not occur. The last remark is important only in the case of noncoincidence of the two transition ways. The question of coincidence or noncoincidence of the two transition ways is closely connected to the question of convergence of the occurring series, which is to answer as difficult as in field theoretical perturbation theory.

The Potential $V(x) = \lambda x^4 + \mu x^2$

For generalization we consider a linear combination of above treated potentials. One of the simplest example is the potential

$$V(x) = \lambda x^4 + \mu x^2, \qquad \lambda > 0\,. \tag{43}$$

The needed integrals are

$$\begin{aligned} \int_0^\infty r'\, e^{-i\varepsilon(\lambda x^4 + \mu x^2)}\, \mathrm{d}x &= \int_0^\infty x^{r'}\, e^{-i\varepsilon\lambda x^4} \sum_{n=0}^{\infty} \frac{(-i\,\varepsilon\,\mu\,x^2)^n}{n!}\, \mathrm{d}x \\ &= \sum_{n=0}^{\infty} \frac{(-i\,\varepsilon\,\mu)^n}{n!} \int_0^\infty x^{r'+2n}\, e^{-i\varepsilon\lambda x^4}\, \mathrm{d}x = \sum_{n=0}^{\infty} \frac{(-i\,\varepsilon\,\mu)^n}{n!}\, \frac{\Gamma((r'+2n+1)/4)}{4\,(i\,\varepsilon\,\lambda)^{(r+2n+1)/4}}\,, \end{aligned} \tag{44}$$

from which follows

$$M_r = \frac{\sum_{n=0}^{\infty} [(-\mu\sqrt{i\,\varepsilon/\lambda})^n/n!] \cdot \Gamma((2\,r+2\,n+1)/4)}{(i\,\varepsilon\,\lambda)^{r/2} \sum_{n=0}^{\infty} [(-\mu\sqrt{i\,\varepsilon/\lambda})^n/n!] \cdot \Gamma((2\,n+1)/4)} = (i\,\varepsilon\,\lambda)^{-r/2} \sum_{n=0}^{\infty} \tilde{F}_n{}^r (-\mu\sqrt{i\,\varepsilon/\lambda})^n \tag{45}$$

and

$$f_r = (i\,\varepsilon\,\lambda)^{-r/2} \sum_{n=0}^{\infty} F_n{}^r (-\mu\sqrt{i\,\varepsilon/\lambda})^n\,. \tag{46}$$

$\tilde{F}_n{}^r$ and $F_n{}^r$ are the occurring numerical factors. Now we get for α

$$\alpha = \sum_{j=1}^{\infty} \left(\frac{m^{j-1}}{\lambda^{j/2}\,(i\,\varepsilon)^{j/2+j-2}} \sum_{n=0}^{\infty} a_n{}^j (-\mu\sqrt{i\,\varepsilon/\lambda})^n \right). \tag{47}$$

The $a_n{}^j$ again contain all numerical factors. We reorder the series (47) in powers of ε and corresponding to the second transition way of the previous section we leave out with regard to $\varepsilon \to 0$ all terms with positive power of ε.

$$\begin{aligned} \alpha = {} & (a_2{}^2(\mu^2 m/\lambda^2) - a_5{}^3(\mu^5 m^2/\lambda^4) + a_8{}^4(\mu^8 m^3/\lambda^6) - \ldots) \\ & + (i\,\varepsilon)^{-1/2} (-a_1{}^2(\mu\, m/\lambda^{3/2}) + a_4{}^3\,(\mu^4 m^2/\lambda^{7/2}) - a_7{}^4\,(\mu^7 m^3/\lambda^{11/2}) + \ldots) \\ & + (i\,\varepsilon)^{-1} (a_0{}^2(m/\lambda) - a_3{}^3(\mu^3 m^2/\lambda^3) + a_6{}^4(\mu^6 m^3/\lambda^5) - \ldots) \\ & + (i\,\varepsilon)^{-3/2} (a_2{}^3(\mu^2 m^2/\lambda^{5/2}) - a_5{}^4\,(\mu^5 m^3/\lambda^{9/2}) + a_8{}^5\,(\mu^8 m^4/\lambda^{13/2}) - \ldots) + \ldots\,, \end{aligned} \tag{48}$$

$$\alpha = a_0{}^* + \sum_{l=1}^{\infty} a_l{}^*/(i\,\varepsilon)^{l/2}\,. \tag{49}$$

a_l^* are infinite series in m, μ and λ. (49) we can replace by

$$\alpha = a_0^* + \sum_{\nu=2}^{\infty} (i\,\varepsilon)^{1/2} A_\nu^* \cdot [(1 + (i\,\varepsilon)^{-\nu/2})^{1/\nu} - 1] \,, \quad (50)$$

at which the A_ν^* are determined by the a_l^* and the following equations are valid:

$$\begin{aligned}
&\binom{1/2}{1} A_2^* = a_1^*, \\
&\binom{1/3}{1} A_3^* = a_2^*, \\
&\binom{1/4}{1} A_4^* + \binom{1/2}{2} A_2^* = a_3^*, \\
&\binom{1/5}{1} A_5^* = a_4^*, \\
&\binom{1/6}{1} A_6^* + \binom{1/3}{2} A_3^* + \binom{1/2}{3} A_2^* = a_5^*, \qquad \text{etc.}
\end{aligned} \quad (51)$$

The transition $\varepsilon \to 0$ yields the real and ε-independent expression

$$\alpha = a_0^* + \sum_{\nu=2}^{\infty} A_\nu^* . \quad (52)$$

(But now the above left out terms with positive power of ε disappear.) Analogous considerations for β yield

$$\begin{aligned}
\beta &= \sum_{j=3}^{\infty} \left(\frac{m^{j-1}}{\lambda^{j/2} (i\,\varepsilon)^{j/2+j-2}} \sum_{n=0}^{\infty} b_n{}^j (-\mu \sqrt{i\,\varepsilon/\lambda})^n \right) \\
&= b_0^* + \sum_{l=1}^{\infty} \frac{b_l^*}{(i\,\varepsilon)^{l/2}} \\
&= b_0^* + \sum_{\nu=2}^{\infty} (i\,\varepsilon)^{1/2} B_\nu^* [(1 + (i\,\varepsilon)^{-\nu/2})^{1/\nu} - 1] \\
&\to b_0^* + \sum_{\nu=2}^{\infty} B_\nu^* .
\end{aligned} \quad (53)$$

The B_ν^* are again determined by the b_l^*.

Field Theory

The step from (23) to (24) to avoid ε-dependence and to get real eigenvalues is not applicable in field theory, because there occur only positive powers of ε [1, 5]. ε is now the volume of the 4-dimensional elementary cell.

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Über eine Erweiterung der ω-Methode

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Electron repulsion and spin properties of π-electrons are explicitely considered in POPLE's SCF-theory; in the ω-method electron interaction is included in a simple way, but there is no physical justification for this procedure. In this paper we describe an LCAO-method ($\omega_{\pi s}$-method), in which π-electron repulsion is explicitely included and spin properties are neglected. Bond lengths, dipole moments, ionisation energies are calculated, and an explanation of the SCHEIBE phenomenon is given.

In den π-Elektronentheorien werden zur angenäherten Beschreibung der Elektronenzustände nur die π-Elektronen explizit behandelt. Die genaueren π-Elektronentheorien (z. B. POPLE-Methode [1]) berücksichtigen sowohl die Abstoßung der π-Elektronen als auch die Antisymmetrieeigenschaften der π-Elektronenwellenfunktionen. Die einfachen π-Elektronentheorien (z. B. HÜCKELsche Theorie [2]) lassen beide Effekte unberücksichtigt und führen daher in vielen Fällen bei der Deutung von Moleküleigenschaften zu Diskrepanzen.

Da die genaueren Theorien kompliziert und dadurch schwer überschaubar sind, ist es unklar, wieweit die Diskrepanzen der einfachen Theorien auf der Nichtberücksichtigung der Antisymmetrie und wieweit sie auf der Vernachlässigung der Elektronenabstoßung beruhen. Man möchte wissen, wie weit von einer Theorie, in der die Elektronenabstoßung berücksichtigt, die Antisymmetriebedingung aber vernachlässigt wird, das physikalisch Wesentliche erfaßt wird.

[1] J. A. POPLE, Trans. Faraday Soc. **49**, 1375 [1953].

[2] A. STREITWIESER, Mol. Orb. Theor. for Org. Chemists, New York—London 1961.