

Original Investigations

On the Representation of Atoms and Molecules as Self-Interacting Field with Internal Structure

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The nonlinear Schrödinger equation with Gaussian convolution kernel K_2 induces the group SU_3 with reference to the classification of the multiplet structure of the eigenstates. Such a field can be used to describe some atoms (where the outermost electrons are related to s -orbitals) as a self-interacting, extended particle with an internal structure. In the case of those atoms, where the valence electrons are described by p -orbitals, and almost all molecules the Gaussian kernel K_2 has to be generalized by Hermite polynomials. By that, we can formulate a nonlinear field theory, establishing the spatial symmetry of a system via basis structure functions. Thus the symmetry represents the most essential starting-point for treating molecules as quasi-particles with an internal structure. It will be shown that there is some connection with the concept of chirality functions and the Ginzburg – Landau theory of superconductivity. The latter theory indicates that we can consider the nonlinear Schrödinger equation and its generalizations as a classical field theory being associated with phase transitions.

Key words: Nonlinear Schrödinger equation – Gaussian kernel – Basis structure functions – Symmetry principles.

1. Introduction

Nonlinear generalizations of the Schrödinger equation for the description of interaction phenomena have become an important tool in many disciplines, e.g. theoretical chemistry, solid-state and nuclear physics. In recent time, they find also applications in plasma and elementary particle physics, and in the theory of

measurement processes, respectively. In this paper, we intend to analyze some mathematical and physical aspects of such generalizations by taking account of problems of molecular physics, but we shall see that the methods under consideration may also be used in other domains of physics.

Because it is not satisfactory to write down "ad hoc" nonlinear field equations, we want to give a sketch of a systematical way of obtaining nonlinear and nonlocal field equations: The usual Schrödinger equation for a charged particle reads

$$i\hbar \frac{\partial \Psi}{\partial t} = \frac{1}{2m} (-i\hbar \nabla - q\mathbf{A})^2 \Psi + q\varphi \Psi, \quad (1.1)$$

whereby the potentials (\mathbf{A} , φ) have to obey the Maxwell equations

$$\left. \begin{aligned} \square \varphi &= -4\pi\rho \\ \square \mathbf{A} &= -4\pi\mathbf{j} \end{aligned} \right\} \quad (1.2)$$

Assuming that the particle is coupled to its own field via charge density $\rho \sim |\Psi|^2$ and current $\mathbf{j} \sim \Psi^* \nabla \Psi - \Psi \nabla \Psi^*$ and substituting (\mathbf{A} , φ) in Eq. (1.1) by the Green's function of Eq. (1.2), we get a nonlocal and nonlinear Schrödinger equation of the form:

$$i\hbar \frac{\partial \Psi}{\partial t} + \frac{\hbar^2}{2m} \Delta \Psi = \int V_{\text{ret}}(x-y, t, \nabla_x, \nabla_y) |\Psi(y)|^2 d^3y \Psi(x), \quad (1.3)$$

where V_{ret} contains besides a convolution kernel the first derivations, and the contribution $\sim \mathbf{A}^2$ has been neglected. However, Eq. (1.3) may bear an inconsistency, as Eq. (1.1) is nonrelativistic and (1.2) is a relativistic equation for the four-potential (\mathbf{A} , φ). Therefore Eq. (1.3) can only be applied

- in the case of static fields (where \square is replaced by Δ),
- when the propagation speed of the field allows a nonrelativistic description.

A further restriction of Eq. (1.3) is obtained by considering only the Poisson equation $\Delta\varphi = -4\pi\rho$, because (1.3) now reads

$$i\hbar \frac{\partial \Psi}{\partial t} + \frac{\hbar^2}{2m} \Delta \Psi = \frac{e^2}{4\pi} \int \frac{|\Psi(y)|^2}{|x-y|} d^3y \Psi(x). \quad (1.4)$$

This approach of Eq. (1.3) is rather familiar, as by considering the variables x and y as co-ordinates in the configuration space and taking Ψ as a simple antisymmetric product, we obtain the Hartree-Fock (HF) equations, if the self-interaction of each charge is omitted. The HF equations can be treated numerically (as often done in theoretical chemistry) with the help of a finite (but arbitrary) basis set

$$\Psi_k = \sum_{l=1}^N c_{kl} \varphi_l, \quad (1.5)$$

where the coefficients c_{kl} are determined by energy variation (Roothaan procedure). The advantages and disadvantages of the approach are well-known; so it cannot be applied to systems with very many interacting particles. It appears that

field theoretical methods are not yet exhausted, but the description of molecular structures by a nonrelativistic, nonlinear field theory cannot be achieved in a simple manner and therefore we shall give an analysis of the problem, in which way the symmetry of a molecular structure can be established in a self-interacting field equation.

In recent time, a further specification of Eq. (1.3) has been discussed by many authors (Ref. [1–8]), the so-called cubic Schrödinger equation

$$E\Psi + \frac{\hbar^2}{2m} \Delta\Psi = \lambda_c |\Psi|^2 \Psi \quad (\lambda_c = \text{coupling constant}), \quad (1.6)$$

because this equation bears particle-like or soliton solutions, which may be considered as a certain approach to describe an extended particle (e.g. an atom or a molecule). A very often discussed soliton solution of Eq. (1.6) is (in one space coordinate):

$$\Psi = A \operatorname{sech} bz : \begin{cases} E = -\hbar^2 b^2 / 2m \\ A^2 = \hbar b^2 / m \lambda_c \end{cases} \quad (1.7)$$

because this wave-function is square-integrable ($\|\Psi\|_2 < \infty$), whereas some other solutions of (1.6) are not [7, 8]. It has been tried to consider the soliton solutions as stable wave-packets [9] – in the usual quantum theory (linear Schrödinger equation) such a property is only known for the harmonic oscillator – but such an interpretation is not quite consistent, because no linear superposition is available for Eq. (1.6), and we shall give another interpretation of Eq. (1.6) and its solitonic solutions in Sect. 3 of this paper.

A further critical point of Eq. (1.6) and its solitonic solutions arises, when one derives the cubic Schrödinger equation (1.6) from Eq. (1.3). Assuming a singular contact potential $V = \lambda_c \delta(x - y)$, (1.3) gets actually the shape of the Eq. (1.6):

$$i\hbar \frac{\partial \Psi}{\partial t} + \frac{\hbar^2}{2m} \Delta\Psi = \lambda_c \int |\Psi(y)|^2 \delta(x - y) d^3y \Psi(x). \quad (1.8)$$

However, it should be noted that a singular contact interaction is not quite consistent with the conception of an extended particle, and in the nonrelativistic domain one has not to consider energies, where a self-interaction δ -function is a good approach. Therefore we have studied in preceding considerations [7, 8] nonlocal generalizations of Eq. (1.8) of the form

$$i\hbar \frac{\partial \Psi}{\partial t} + \frac{\hbar^2}{2m} \Delta\Psi = \lambda_c \int |\Psi(y)|^2 K(k_0, x - y) d^3y \Psi(x), \quad (1.9)$$

which exhibit the property to generate in the local limit ($k_0 \rightarrow \infty$) the cubic Schrödinger equation (1.8). A very promising family is obtained, when the convolution kernel $K(k_0, x - y)$ is a Gaussian kernel function

$$K_2 = \mathcal{N}(k_0) \exp \left\{ -k_0^2 \sum_{i=1}^3 (x_i - y_i)^2 \right\} \\ \mathcal{N}(k_0) = k_0^3 / \pi^{3/2}, \quad (1.10)$$

because the corresponding nonlinear field equation

$$i\hbar \frac{\partial \Psi}{\partial t} + \frac{\hbar^2}{2m} \Delta \Psi = \lambda_c \int K_2(k_0, x-y) |\Psi(y)|^2 d^3y \Psi(x) \tag{1.11}$$

uniformly converges against the local limit, when k_0 increases:

$$\iint [K_2(k'_0, x-y) - K_2(k_0, x-y)] |\Psi(y)|^2 d^3y d^3x < \varepsilon \quad \text{for } k'_0 > k_0. \tag{1.12}$$

This relation yields a self-interaction, smeared out by a Gaussian distribution function, which converges uniformly against the self-interaction of a “point-particle” (see also Appendix A). The cubic Schrödinger equation (1.6) or (1.8) cannot be obtained by a local limit procedure of Eqs. (1.3) and (1.4), as an electrostatic self-interaction is strongly nonlocal due to the long range. The self-interaction term

$$\mathcal{J}_H(x) = \int \frac{|\Psi(y)|^2}{|x-y|} d^3y$$

can be considered as a Hilbert transformation of the density $\rho \sim |\Psi|^2$, which can be approximated by an infinite set of two-point Gaussians:

$$\left. \begin{aligned} \mathcal{J}_H &\approx \sum_{\nu=1}^{\infty} c_{\nu}(k_{0,\nu}) \exp(-k_{0,\nu}^2(\xi - \eta_{\nu})^2) |\Psi(y)|^2 d^3y \\ \xi &= |x-y| \geq 0 \end{aligned} \right\} \tag{1.13}$$

The two-point kernel ξ^{-1} consists of a δ -function (for $\lim \xi \rightarrow 0$) and Gaussian functions with $k_{0,\nu} < \infty$.

2. Some Properties and Applications of a Nonlinear Field Equation with Gaussian Kernel

It is clear that the use of a Gaussian kernel K_2 (or in the local limit a δ -kernel) is not practicable, when the “exact” problem is given by long-range Coulomb interactions (Eq. (1.4)), and the Hilbert transformation $\int \rho(y) |x-y|^{-1} d^3y$ would have to be approximated by a sequence of Gauss transformations. The Gaussian kernel K_2 has the advantage to describe an extended particle with an internal self-interaction, when k_0 in Eq. (1.11) is kept finite and chosen suitably for practical problems. Such an “extended” particle may be a quasi-particle, consisting of many interacting particles, as used in solid-state or nuclear physics. In atomic or molecular physics we meet an analogous situation, because we can regard an atom as an interacting many electron system, attracted by a nuclear charge, and the total system is described by a Schrödinger equation, derived from Eq. (1.4). Such a system can also be described by a nonlocal, self-interacting field of an extended particle, where the nonlocal self-interaction must be of much shorter range than that given by Eq. (1.4). Such a field is characterized by further degrees of freedom, because the excitation of an electron in an atom is now treated as a collective excitation of a particle or quasi-particle with an internal structure. There arises the

question, in which way Eq. (1.11) can satisfy these requirements in atomic physics, as we start with a special two-point kernel. We have already analyzed many properties of Eq. (1.11) [7, 8] and therefore we repeat only those results, necessary for a discussion of the above question. Eq. (1.11) contains the generating function of the Hermite polynomials and therefore the stationary form may be written as [7, 8]

$$E\Psi + \frac{\hbar^2}{2m} \Delta\Psi = \lambda_c \mathcal{N} \cdot \sum_{n_1, n_2, n_3=0}^{\infty} \frac{k_0^{n_1+n_2+n_3}}{n_1! n_2! n_3!} x_1^{n_1} x_2^{n_2} x_3^{n_3} \times \int_{-\infty}^{+\infty} d^3y [\exp\{-k_0^2 y^2\} H_{n_1}(k_0 y_1) H_{n_2}(k_0 y_2) H_{n_3}(k_0 y_3) |\Psi(y)|^2] \Psi(x). \tag{2.1}$$

This equation may be formally integrated to yield an anharmonic oscillator equation of infinite order:

$$E\Psi + \frac{\hbar^2}{2m} \Delta\Psi = \lambda_c \sum_{n_1, n_2, n_3=0}^{\infty} a_{n_1, n_2, n_3}(k_0) x_1^{n_1} x_2^{n_2} x_3^{n_3} \Psi, \tag{2.2}$$

where the coefficients $a_{n_1, n_2, n_3}(k_0)$ are determined according to Eq. (2.1). Eq. (1.11) or (2.1) exhibits for finite k_0 a finite set of bound states with $E < 0$ and an infinite set of scattering states with $E > 0$. In Fig. 1, we can see that the Gaussian distribution function K_2 can be partitioned in a domain A_+ with positive curvature and a domain A_- with negative curvature. In the domain A_+ the distribution function K_2 nearly agrees with an oscillator, whereas in $A_- ((x - y)^2 > 1/2k_0^2)$ the higher order terms are more relevant. This fact yields an approximation method for Eqs. (2.1) and (2.2): The ground state and the lower excited states can be calculated by an oscillator approximation ($n_1 + n_2 + n_3 \leq 2$) and the contribution

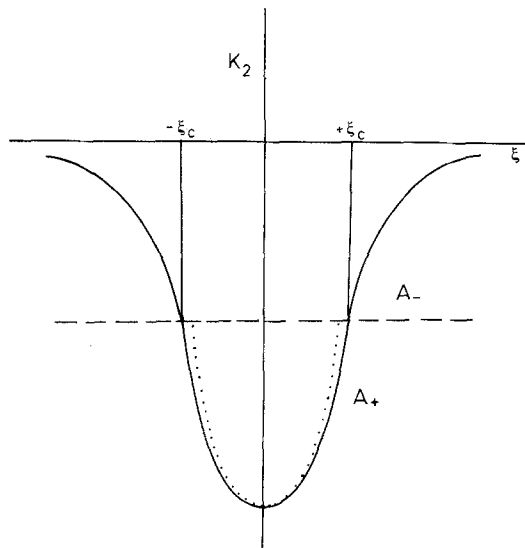


Fig. 1. The Gaussian distribution function $K_2(k_0, x - y)$ and its domains with positive (A_+) and negative (A_-) curvature. At $\xi_c^2 = (x - y)^2 = 1/2k_0^2$ the curvature changes sign. The pointed curve represents the associated oscillator

of the terms with $n_1 + n_2 + n_3 > 2$ can be treated as a perturbation. However, such an approach is insufficient for the excited states in the domain A_- , where the contribution of the terms $\sim x^3$ and $\sim x^4$ becomes essential. The harmonic oscillator approximation of Eq. (2.1) can be brought to the form:

$$E\Psi + \frac{\hbar^2}{2m} \Delta\Psi = \lambda_c [A_0 + A_1(x_1^2 + x_2^2 + x_3^2)]\Psi \quad (2.3)$$

and may be solved with standard methods, but one has to be aware of, that A_0 and A_1 depend on the wavefunction according to Eq. (2.1) and, in particular, the eigenfrequency $\omega (A_1\lambda_c = (m/2)\omega^2)$ is not a free parameter, because we have a self-interacting oscillator, where ω has to be determined for each eigenstate of Eq. (2.3) in the domain A_+ . We do not obtain the energy levels $E_n = \hbar\omega(n + \frac{1}{2})$ of a free oscillator as eigenvalues, but without an explicit calculation of the levels we can make use of group theory to classify the eigenstates in A_+ . It is well-known that a 3-dimensional harmonic oscillator in quantum theory can be classified by SU_3 (see also Appendix B). But this symmetry is also present in Eq. (1.11) or (2.1) and we shall return to this problem. It is also possible to classify Eq. (2.3) according to the angular momentum by the introduction of the spherical harmonics

$$E\Psi + \frac{\hbar^2}{2m} \Delta_{r,\vartheta,\varphi} \Psi = \lambda_c (A_0 + A_1 r^2) \Psi \quad (2.4)$$

and making use of the separation

$$\Psi = f(r)Y_l^m(\cos \vartheta, \varphi), \quad (2.5)$$

but then we do not get an information on the levels of the radial function $f(r)$ in a simple manner and therefore we do not discuss here this classification. The use of a SU_3 -classification exhibits the advantage that we only need consider Eq. (2.3) in one space coordinate

$$E\Psi + \frac{\hbar^2}{2m} \frac{d^2}{dx^2} \Psi = \lambda_c (A_0 + A_1 x^2) \Psi, \quad (2.6)$$

because this symmetry group immediately provides an information about the multiplet structure, when 3 oscillators are combined. The harmonic oscillator approach (2.3) makes also apparent the already indicated physical interpretation of Eq. (1.11): The ground state and the lower excited states represent eigenstates of an extended particle (described by a nonlocal self-interacting field), which may undergo discrete deformations according to Hooke's law. In molecular (but also in solid-state and nuclear) physics we want to relate excited states of particles with an internal structure to collective excitations. The application of the kernel K_2 , exhibiting invariance against rotations (SO_3), is, however, not practicable, when SO_3 is strongly perturbed (e.g. for molecules). Some tests (Table 1) have made clear that the above approach works for the outermost electrons of atoms, where the s -character is dominating. For the ground state of Eq. (2.6) we make the ansatz

$$\left. \begin{aligned} \Psi_0 &= \mathcal{N}(\alpha_0) \exp(-\frac{1}{2}\alpha_0^2 x^2) \\ \|\Psi_0\|_2 = 1 &\Rightarrow \mathcal{N}^2(\alpha_0) = 2\alpha_0/\sqrt{2\pi} \end{aligned} \right\} \quad (2.7)$$

The two parameters k_0 and λ_c can be chosen arbitrarily, but they should be related to properties, which seem reasonable for the specific atom. This request yields $\lambda_c = -Z_{\text{eff}}e^2$ (effective charge of the valence electron) and $k_0 \sim$ reciprocal atomic radius. The subsequent excited states are described by

$$\Psi_n = \mathcal{N}(\alpha_n) H_n(\alpha_n x) \exp(-\frac{1}{2}\alpha_n^2 x^2), \quad n = 1, 2, \dots, \quad (2.8)$$

where $\alpha_n \sim \omega_n$ is different for each eigenstate. Thus we obtain for the ground state:

$$\left. \begin{aligned} E_0 &= \frac{k_0 \lambda_c \alpha_0}{\sqrt{\pi} \sqrt{\alpha_0^2 + k_0^2}} - \frac{\hbar^2 \alpha_0^2}{2m} \\ \alpha_0^2 (\alpha_0^2 + k_0^2)^3 &= \frac{4\lambda_c^2 k_0^6 m^2}{\pi \hbar^4} \end{aligned} \right\} \quad (2.9)$$

By setting $u_0 = \alpha_0^2$ we have to solve a polynomial of degree 4. With respect to the first excited state we have to solve a polynomial of degree 6:

$$\left. \begin{aligned} E_1 &= \frac{3\alpha_1^2 \hbar^2}{2m} + \frac{\lambda_c k_0 \mathcal{N}_1^2(\alpha_1) \Gamma(\frac{3}{2})}{\sqrt{\pi} (\alpha_1^2 + k_0^2)^{3/2}}, \\ \alpha_1^2 (\alpha_1^2 + k_0^2)^5 &= \frac{4m^2 \lambda_c^2 k_0^6 (2k_0^2 - \alpha_1^2)^2}{\pi \hbar^4} \\ \mathcal{N}_1^2 &= \alpha_1^3 / \Gamma(\frac{3}{2}) \end{aligned} \right\} \quad (2.10)$$

In similar fashion we obtain polynomials of higher degree, which have to be solved for the subsequent excited states, but we do not report them, because on the one side these polynomials are simple problems in numerical mathematics and, on the other side, for $k_0^{-1} \approx 10^8 - 10^7 \text{ cm}^{-1}$ we have only a few excited states in the domain A_+ . For $\lambda_c > 0$ Eq. (1.11) yields only scattering states and therefore we have always to put $\lambda_c < 0$ in order to justify the approximation (2.3). But nevertheless we obtain for (2.10) and (2.9) besides one bound state many complex solutions related to scattering states, which are not very meaningful in an oscillator approximation. The ground state of (2.3) results from $3E_0$ of Eq. (2.9) in order to get the SU_3 -singlet. So far we have verified it is reasonable to identify E_0 of (2.3) with the ionization energy I_0 of the outermost electron of an atom. It is possible to use k_0 and λ_c as fitting parameters, but they should have the discussed magnitude. Then the question arises how the lower excited states agree with the experimental results. We have used k_0 and λ_c according to the mentioned proposition without further variation. By that, we have verified in the case of some atoms (Table 1) that the procedure works well for atoms, where the outermost electron is described by an s -function (Li, Be, Na, K, Mg, Ca, etc.), but it does not work in the case of H, He and all atoms, where the outermost electrons are p -functions (or d -functions). For H and He, the first excited states lie already in the domain A_- , and, although the corresponding electrons are described by s -

Table 1. It has been throughout assumed $k_0 = 1/2r_0$ and $\lambda_c = -Z_{\text{eff}} e^2/r_0$ (r_0 is the orbit radius of the outermost electron). The spectral data and further references may be found in Ref. [20]. The excited states of H and He lie in the domain A_- , hence an oscillator approach does not work

		Ground state ^a		Excited states			
H	exp	$1s, {}^2S_{1/2}$	109630				
	cal		98600				
He	exp	$1s, {}^1S_0$	198305				
	cal		170000				
Li	exp	$2s, {}^2S_{1/2}$	43486	$2p, {}^2P_{1/2}$	28582	$3s, {}^2S_{1/2}$	16280
	cal		41750		27410		18520
Na	exp	$3s, {}^2S_{1/2}$	41449	$3p, {}^2P_{1/2}$	24493	$4s, {}^2S_{1/2}$	15709
	cal		40180		24360		17310
K	exp	$4s, {}^2S_{1/2}$	35009	$4p, {}^2P_{1/2}$	22023	$5s, {}^2S_{1/2}$	13982
	cal		34870		22110		14480
Rb	exp	$5s, {}^2S_{1/2}$	33689	$5p, {}^2P_{1/2}$	21110	$6s, {}^2S_{1/2}$	13557
	cal		33610		21130		14270
Be	exp	$2s, {}^1S_0$	75194	$2p, {}^1P_1$	32629		
	cal		77560		36890		
Mg	exp	$3s, {}^1S_0$	61672	$3p, {}^1P_1$	26117		
	cal		62010		28470		
Ca	exp	$4s, {}^1S_0$	49304	$4p, {}^1P_1$	25652	$3d, {}^1D_2$	27455
	cal		50120		27460		27130
Sr	exp	$5s, {}^1S_0$	45925	$5p, {}^1P_1$	24227	$4d, {}^1D_2$	25775
	cal		45980		24420		25625

^a All energy terms in cm^{-1} .

functions, we should note that these electrons “see” the pure Coulomb potential of the nucleus. When the outermost electrons are not described by s -functions, we have to use a more general kernel than (1.10). In the above cases, where the formalism works, the electrons of the outermost shell “see” only a core with an effective potential.

A further interesting aspect of Eqs. (2.3) and (1.11) is that we do not obtain the energy spectrum of the harmonic oscillator with equidistant energy levels. When one considers the term scheme of the atoms and molecules (the H atom inclusive), it is easy to see that in the case of bound states such a situation is indeed realized. We should point out that already the energy spectrum of the self-interacting oscillator (2.3), where the lack of equidistant energy levels is the most significant property, can only be obtained by an anharmonic, but free oscillator obeying the following Schrödinger equation

$$E\Psi + \frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \Psi = \left(\frac{m}{2} \omega_0^2 x^2 + \gamma x^3 + \delta x^4 \right) \Psi. \quad (2.11)$$

Now the parameters ω_0 , γ , and δ do not depend on the wavefunction. Some further properties of Eq. (2.3) are discussed in the appendix B.

3. Generalization of the Gaussian Kernel K_2 and the Relationship to Symmetry Principles

In this section, we discuss the extension of the Gaussian kernel K_2 to arbitrary convolution kernel functions and the symmetry principles involved. Thereby we find a close relationship to the concept of chirality functions, proposed by Ruch *et al.* [10]. A further aspect will be the physical interpretation, as there is some connection with the Ginzburg–Landau theory of superconductivity, and an outlook to other disciplines.

3.1. The Application of Hermite Kernels

Eq. (1.11) and its approximate version (2.3) can only be applied to systems with rotation invariance SO_3 , and the eigenstates are classified by the unitary group SU_3 , whereby it should be noted that the rotation group SO_3 is a little group of SU_3 . Thus the group SO_3 is established by a unitary representation of a continuous group (SU_3). One can hope to describe with such a symmetry group also certain discrete point groups (e.g. T_d): Excitations of the outermost electron (from the HOMO of e.g. CH_4) are considered as collective excitations of an extended particle, but this seems to be a rather rough approach for the discrete T_d symmetry being a little group of SO_3 . In molecules (and nuclei) we do not know the very complicated potential of the outer electrons (or nucleons), but we assume that it stands in a close relationship with the spatial symmetry. Thus the following proposition may lead to a clarification of the situation: For this purpose, we consider a two-atomic molecule, which exhibits a nonvanishing static dipole moment. The spatial symmetry is C_{2v} , and the simplest manner to take account of this request is given by the following equation

$$E\Psi + \frac{\hbar^2}{2m} \Delta\Psi = \lambda_c \int_{-\infty}^{+\infty} H_1(k_0, x_3 - y_3) K_2(k_0, x - y) |\Psi(y)|^2 d^3y \Psi(x). \quad (3.1)$$

$H_1(k_0, x - y_3)$ is the first Hermite polynomial, resulting from $(\partial/\partial x_3)K_2(k_0, x - y)$. By that, the dipole is positioned in the x_3 -axis, whereas in the $(x_1 - x_2)$ -plane the rotation invariance (SO_2) is still present, and the eigenstates of (3.1) are characterized by the symmetry group SU_2 . A completely heteropolar two-atomic molecule, establishing also C_{2v} -symmetry, can be described by the ansatz:

$$E\Psi + \frac{\hbar^2}{2m} \Delta\Psi = \lambda_c \int_{-\infty}^{+\infty} H_2(k_0, x_3 - y_3) K_2 |\Psi(y)|^2 d^3y \Psi(x). \quad (3.2)$$

However, we should note that these two realizations of C_{2v} are indeed very simple, as the two limit cases (polar and heteropolar bond) are also realized in the following nonlinear and nonlocal field equation:

$$E\Psi + \frac{\hbar^2}{2m} \Delta\Psi = \lambda_c \int_{-\infty}^{+\infty} \sum_{n=0}^{\infty} P_n H_n(k_0, x_3 - y_3) K_2 |\Psi(y)|^2 d^3y \Psi(x). \quad (3.3)$$

The heteropolar character is guaranteed by taking account only of P_n with even n , and, on the other hand, a strictly polar character is present for all odd n . With

respect to Eq. (3.3) we are able to make the following statement: The arbitrary convolution kernel K in Eq. (1.9) has been expanded in terms of a Gaussian kernel K_2 and Hermite polynomials H_n , whereby each Hermite polynomial contains the expression $k_0^2(x_3 - y_3)$ as an argument. In the above case, the rotation invariance (SO_2) is preserved. The extension to 3 dimensions, where neither a spatial symmetry (SO_3 or a little group of SO_3) nor a unitary representation of SU_3 or one of its little groups is established in the space of the eigenstates of (1.9), is given by the following equation:

$$E\Psi + \frac{\hbar^2}{2m} \Delta\Psi = \lambda_c \prod_{j=1}^3 \sum_{n=0}^{\infty} P_{nj} \int_{-\infty}^{+\infty} H_n(k_0, x_j - y_j) K_2 |\Psi(y)|^2 d^3y \Psi(x). \quad (3.4)$$

Hereby we have restricted ourselves to a stationary version of the nonlocal and nonlinear Schrödinger equation. The time-dependent version of (3.4) must inevitably be taken into account, when time-dependent external fields are present:

$$\begin{aligned} i\hbar \frac{\partial\Psi}{\partial t} - V_{ex} \Psi - \frac{1}{2m} (-i\hbar\nabla - q\mathbf{A}_{ex})^2 \Psi \\ = \lambda_c \prod_{j=1}^3 \sum_{n=0}^{\infty} P_{nj}(t) \int_{-\infty}^{+\infty} H_n(k_0, x_j - y_j) K_2 |\Psi(y, t)|^2 d^3y \Psi(x, t). \end{aligned} \quad (3.5)$$

However, it appears that such a difficult equation, describing transitions between different eigenstates, is not very interesting in the general form (3.5), as it does not yet exhibit specific symmetries for the characterization of the corresponding transitions, and we shall have to return to this problem after further analysis of Eq. (3.4). In order to reduce the difficulties for obtaining any information on Eq. (3.4), it is necessary to make essential simplifications, e.g. those given by Eq. (3.1) or (3.2). This means that any molecule, described here by a self-interacting field with an internal structure and belonging to a certain symmetry class, has to be treated with a minimal number of Hermite polynomials $H_n(k_0, x_j - y_j)$ being necessary for the representation of the corresponding class. Thus a molecule with T_d symmetry may be treated by the following convolution kernel:

$$\begin{aligned} K_{T_d} = \{P_{01,2,3} + P_{11}H_1P_{12}H_2 + P_{11}H_1P_{13}H_1 + P_{12}H_1P_{13}H_1 \\ + H_2(P_{21} + P_{22} + P_{23})\} K_2 \end{aligned} \quad (3.6)$$

Hereby mean $P_{11}H_1P_{12}H_1 = P_{11}H_1(k_0, x_1 - y_1)P_{12}H_1(k_0, x_2 - y_2)$ and $H_2P_{23} = H_2(k_0, x_3 - y_3)P_{23}$, etc. If T_d represents an exact realization of the spatial symmetry of a molecule, the coefficients P_{nj} of Eq. (3.6) must not be chosen arbitrarily, and the following identities must hold:

$$P_{01} = P_{02} = P_{03}; P_{11} = P_{12} = P_{13}; P_{21} = P_{22} = P_{23}.$$

Nevertheless, (3.6) is only an approach for T_d , because we can add higher order Hermite polynomials, incorporating also representations of the T_d group. The only difficulty, arising from the higher order polynomials, is the finding of proper

solutions. However, the conception to consider a molecule as an extended particle analogous to the quasi-particle concept in other domains of physics, being described by a self-interacting field with an internal structure, underlines the spatial symmetry of a particle as the main starting-point for all other informations. This classification according to the symmetry immediately provides informations about some properties of the molecule. So the Hermite convolution kernel H_1 is related to a dipole, whereas H_2 yields a quadrupole, etc. These spatial symmetries must be reflected in the symmetry classification of the eigenstates of the corresponding field equation being always a specific form of Eq. (3.4). The continuous spatial groups SO_3 and SO_2 exhibit a correspondence to the unitary groups SU_3 and SU_2 . A difficult problem, which we are not yet able to answer, is the finding of a correspondence between a discrete point group (e.g. T_d) and an equivalent unitary representation in the space of the eigenstates. However, we should note that there exists a quite similar approach to such a problem, developed by Ruch *et al.* [10, 11], namely the concept of chirality functions. According to the contention of this concept, a molecular structure is described by an appropriate function, reflecting some molecular properties, being related to the corresponding symmetry class. So far as we can see, the conception of chirality function has not been developed by the authors [10] on the basis of field theory, but we should note that the principles presented here represent a field theoretic realization (or generalization) of Ruch's conception. In the case of the dipole or quadrupole moment etc., we have directly verified the relationship to the above concept. If one considers some mathematical details in Ref. [10, 11], further similarities may be found. So the chirality functions are approached by the minimal order of proper polynomials, reflecting the discrete point group of the molecule, and we have seen that this assumption is also useful in our field theoretic treatment. The fact that we have made use of Hermite convolution kernel instead of usual polynomials in order to give a representation of the internal symmetry, is not of importance, as every Hermite polynomial is a linear combination of usual polynomials, and thus Eq. (3.4) is also equivalent to

$$\left(E + \frac{\hbar^2}{2m} \Delta\right) \Psi = \lambda_c \sum_{j=1}^3 \sum_{n=0}^{\infty} \int C_{nj}(x_j - y_j)^n \cdot K_2 \cdot |\Psi(y)|^2 d^3y \Psi. \quad (3.7)$$

On the other hand, it does not appear that symmetry principles or chirality functions have a relevant meaning, when a molecule is treated numerically on the basis of (1.4) and (1.5).

3.2. Mathematical Aspects of Hermite Kernels

Besides the symmetry principle, which represents a rather heuristic, but powerful motivation for the formulation of a nonlinear field equation describing an internal structure of an extended particle, there is another starting-point leading to some mathematical aspects of the problem: According to Hund [12] we can consider atoms and molecules as classical fields. Because of the short range of the chemical valence forces ($\approx 10^{-8}$ cm) the valence electrons of the atoms can be related to particle-like interactions, where the potential should obey a stationary Klein-

Gordon equation

$$(\Delta - k_0^2)\varphi_{KG} = m^2\varphi_{KG} \quad (k_0^{-1} \approx 10^{-8} \text{ cm}), \quad (3.8)$$

yielding a Youkawa potential of the form

$$\varphi_{KG} \sim r^{-1} \exp(-k_0 r). \quad (3.9)$$

The atoms (or molecules) should obey the strictly classical equation of motion

$$\frac{1}{2m} \left(\frac{\partial W}{\partial x} \right)^2 + \varphi_{KG} = \frac{\partial W}{\partial t}. \quad (3.10)$$

In our approach, we have modified the singular behaviour of (3.9) for $r \rightarrow 0$, which may become crucial for outer valence electrons, by a Gaussian distribution function, and instead of a classical equation we use the Schrödinger equation

$$\left. \begin{aligned} i\hbar \frac{\partial \Psi}{\partial t} + \frac{\hbar^2}{2m} \Delta \Psi &= \varphi \Psi \\ \varphi(x) &= \lambda_c \int_{-\infty}^{+\infty} K_2(k_0, x-y) |\Psi(y)|^2 d^3 y \end{aligned} \right\} \quad (3.11)$$

However, the operator \mathcal{A}_2 , of which the Green's function is given by $K_2(k_0, x-y)$, yielding the "potential" equation

$$\left. \begin{aligned} \mathcal{A}_2 \varphi &= -\rho(x) = \lambda_c |\Psi(x)|^2 \\ \varphi(x) &= \int_{-\infty}^{+\infty} G_{\mathcal{A}_2}(x-y) \rho(y) d^3 y \end{aligned} \right\} \quad (3.12)$$

is not yet defined. We show that \mathcal{A}_2 is given by

$$\begin{aligned} \mathcal{A}_2 &= \exp\{-k_0^{-2} \Delta\} \\ &= 1 - \frac{k_0^{-2}}{1!} \Delta + \frac{k_0^{-4}}{2!} \Delta^2 - + \dots \end{aligned} \quad (3.13)$$

In a rather good approach (3.13) contains the Klein-Gordon equation $k_0^2(1 - k_0^{-2} \Delta)\varphi = -k_0^2 \rho(x)$. The Fourier transformation of φ is given by

$$\varphi = \mathcal{N} \int_{-\infty}^{+\infty} f(\boldsymbol{\lambda}) \exp(i\boldsymbol{\lambda} \mathbf{x}) d^3 \lambda. \quad (3.14)$$

Now we form

$$\left. \begin{aligned} \mathcal{A}_2 \varphi(x) &= \mathcal{N} \int (1 + k_0^{-2} \boldsymbol{\lambda}^2 + \frac{k_0^{-4} \boldsymbol{\lambda}^4}{2!} + \dots +) \\ &\quad \exp(i\boldsymbol{\lambda} \mathbf{x}) f(\boldsymbol{\lambda}) d^3 \lambda = -\rho(x) \\ &= \mathcal{N} \int \exp\{k_0^{-2} \boldsymbol{\lambda}^2\} \exp\{i\boldsymbol{\lambda} \mathbf{x}\} f(\boldsymbol{\lambda}) d^3 \lambda \end{aligned} \right\} \quad (3.15)$$

One should compare this result with the Fourier transform of a Gauss transformation [7], as one observes a complete identity. In order to show this property

we calculate φ via Green's function

$$\begin{aligned}\varphi(x) &= \mathcal{N} \int f(\boldsymbol{\lambda}) \exp \{i\boldsymbol{\lambda}x\} d^3\boldsymbol{\lambda} \\ &= \mathcal{N} \iint G_{\mathcal{A}_2}(x-y) \exp \{k_0^{-2}\boldsymbol{\lambda}^2 + i\boldsymbol{\lambda}y\} f(\boldsymbol{\lambda}) d^3y d^3\boldsymbol{\lambda}.\end{aligned}\quad (3.16)$$

By that, we obtain:

$$\left. \begin{aligned}\exp \{i\boldsymbol{\lambda}x\} &= \int G_{\mathcal{A}_2} \cdot \exp \{k_0^{-2}\boldsymbol{\lambda}^2 + i\boldsymbol{\lambda}y\} d^3y \\ G_{\mathcal{A}_2} &= K_2 = \left(\frac{k_0}{\sqrt{\pi}}\right)^3 \exp \{-k_0^2(x-y)^2\}\end{aligned}\right\}.\quad (3.17)$$

It follows from the preceding considerations that the kernel K_2 does not satisfy all presumptions with respect to a resolution of the problem to describe any extended particle as a self-interacting field with a proper kernel function. We have already verified that the use of K_2 is not sufficient for those atoms, where the outermost electron is related to a p orbital. When one regards the effective potential of a valence electron in a molecule (in the HF approximation this electron is related to the HOMO), then the situation is that one does not know this effective potential. The only available informations are – so far we have already stated – the symmetry of the molecule (clearly the potential depends on it) and the short-range interaction of the valence electron. This situation is quite analogous to crystals, where V_{eff} is completely unknown until its invariance against proper translations

$$\exp\left(\pm a \frac{\partial}{\partial x}\right) V_{\text{eff}}(x-y) = V_{\text{eff}}(x-y \pm a) \quad (3.18)$$

(a is a suitable length). From Eq. (3.18) follows that the translation operator $\exp(\pm a \partial/\partial x)$ has to commute with a certain operator $\mathcal{A}_{\text{eff}}(\partial/\partial x)$, of which the Green's function is $V_{\text{eff}}(x-y)$. In both cases, molecules and solids, it is therefore reasonable to start with an arbitrary operator function $\mathcal{A}(\partial/\partial x)$, being formally considered as an abbreviation of a power series of differential operators

$$\mathcal{A} = \sum_{k=1}^3 \sum_{m=0}^{\infty} a_{m,k} \frac{\partial^m}{\partial x_{k_1} \cdots \partial x_{k_m}}, \quad (3.19)$$

and, in a further step, to put some constraints to (3.19) reflecting the symmetry of the problem. Using the power series of \mathcal{A}_2 (3.13) and multiplying on the left hand side of \mathcal{A}_2 linear combinations of differential operators of arbitrary order, we are able to represent any A (which may be a collection of differential operators of infinite order) by a proper choice of the coefficients B_{nj} :

$$\mathcal{A} = \sum_{k=1}^3 \sum_{m=0}^{\infty} a_{m,k} \frac{\partial^m}{\partial x_{k_1} \cdots \partial x_{k_m}} = \sum_{n=0}^{\infty} \sum_{j=1}^3 B_{nj} \frac{\partial^n}{\partial^n x_j} \mathcal{A}_2. \quad (3.20)$$

In the following, we shall show that we can use $K_2 = G_{\mathcal{A}_2}$ to construct the Green's function $G_{\mathcal{A}}$ of any operator \mathcal{A} , if the coefficients $a_{m,k}$ or B_{nj} do not depend on the coordinates x_k themselves. The potential function φ in Eq. (3.11) now satisfies the

equations

$$\left. \begin{aligned} \mathcal{A}\varphi &= -\rho = \lambda |\Psi(x)|^2 \\ \varphi &= \int G_{\mathcal{A}}(x, y)\rho(y) d^3y \end{aligned} \right\} \quad (3.20a)$$

and therefore we put

$$\left. \begin{aligned} \mathcal{A}_2\varphi &= -\chi(x) \\ (\chi(x) \neq \rho(x), \text{ if } \mathcal{A}_2 \neq \mathcal{A}) \end{aligned} \right\}. \quad (3.20b)$$

For the sake of simplicity we restrict ourselves to one space coordinate, as the extension to 3 dimensions is straightforward. Because the identity

$$\varphi = \int K_2\chi(y) dy = \int G_{\mathcal{A}}\rho(y) dy \quad (3.20c)$$

holds, we obtain by multiplication of Eq. (3.20c) with \mathcal{A} and \mathcal{A}_2 and taking account of the relation

$$\mathcal{A}_2K_2 = \mathcal{A}G_{\mathcal{A}} = -\delta(x - y)$$

the relation

$$\sum_{n=0}^{\infty} B_n \frac{\partial^n}{\partial x^n} \chi(x) = \rho(x). \quad (3.20d)$$

Now we form

$$\mathcal{A}_2\varphi = -\chi(x) = \int \mathcal{A}_2G_{\mathcal{A}} \sum_{n=0}^{\infty} B_n \frac{\partial^n}{\partial y^n} \chi(y) dy, \quad (3.20e)$$

from which results by partial integration

$$K_2(k_0, x - y) = \sum_{n=0}^{\infty} B_n \frac{\partial^n}{\partial x^n} G_{\mathcal{A}}(x, y). \quad (3.21)$$

Because K_2 represents a convolution kernel, which is obtained by differentiations of $G_{\mathcal{A}}$, the kernel $G_{\mathcal{A}}(x, y)$ has also to be a convolution kernel, so far the coefficients B_n are independent of x . In the following, we shall tacitly assume the validity of this fact, since we are able now to expand $G_{\mathcal{A}}$ in terms of K_2 and Hermite polynomials $H_n(k_0, x - y)$:

$$G_{\mathcal{A}}(x - y) = \sum_{n=0}^{\infty} P_n \frac{\partial^n}{\partial x^n} K_2, \quad (3.21a)$$

where

$$H_n(k_0, x - y) \sim \frac{\partial^n}{\partial x^n} K_2(k_0, x - y).$$

Because of the relations

$$\left. \begin{aligned} \mathcal{A}_2K_2 &= -\delta(x - y) \\ \mathcal{A}G_{\mathcal{A}} &= \sum_{n,m=0}^{\infty} P_n B_m \frac{\partial^n}{\partial x^n} \frac{\partial^m}{\partial x^m} \mathcal{A}_2K_2 = -\delta(x - y) \end{aligned} \right\},$$

the coefficients P_n have to satisfy

$$P_0 B_0 = 1, \quad B_m P_0 + B_{m-1} P_1 + \dots + B_0 P_n = 0, \quad \left(\begin{array}{l} m = 1, 2, 3, \dots \\ n = 1, 2, 3, \dots \end{array} \right) \quad (3.21b)$$

e.g.

$$\left. \begin{array}{l} P_0 = B_0^{-1} \\ P_1 = -B_1 \cdot B_0^{-2} \\ P_2 = -B_2 \cdot B_0^{-2} + B_1^2 \cdot B_0^{-3} \\ P_3 = -B_3 \cdot B_0^{-2} + 2B_1 B_2 \cdot B_0^{-3} - B_1^3 B_0^{-4} \\ P_4 = -B_4 B_0^{-2} - 3B_1^2 B_2 B_0^{-4} + (2B_1 B_3 + B_2^2) B_0^{-3} + B_1^4 B_0^{-5} \end{array} \right\} \quad (3.21c)$$

The relation (3.21b) provides a way to construct all P_n , if the corresponding B_n are known, but apart from special cases the sequence of the coefficients P_n remains infinite, even if the sequence of the B_n is finite. It follows from (3.21c) that the low order coefficients B_0, B_1, B_2 should be considerable (in particular B_0) in order to give rise to very small P_n , where n is a very large number. In the case of 3 dimensions, (3.21a) assumes the shape

$$G_{\mathcal{A}} = \sum_{n=0}^{\infty} \prod_{j=1}^3 P_{nj} \cdot H_n(k_0, x_j - y_j) K_2(k_0, x - y). \quad (3.21d)$$

These results might be regarded as a justification for our ansatz (3.4), where we have used two-point Hermite functions in order to obtain a generalization of Eq. (1.11). However, we should be aware that with respect to a practical problem we are not blessed with all informations being necessary for a fixation of each P_{nj} (or B_{nj}). We have to restrict ourselves to those P_{nj} , being relevant for the symmetry adaption. Besides this constraint the remaining coefficients $P_{nj} (\neq 0)$ may serve as fitting parameters (similar like λ_c and k_0). It is clear that we are able to expand every Green's function $G_{\mathcal{A}}(x - y)$ in terms of Gaussians, multiplied with Hermite polynomials due to the completeness relation, but such an expansion has not to be useful in every case, e.g. when $\mathcal{A} = \Delta$, and the expansion (3.21) is then reasonable, when the contributions of P_{nj} with very great n are negligible. This presumption is satisfied for short-range fields (chemical forces are of short range or particle-like, when one treats interactions as mediated by the outermost electrons). Hence, k_0^{-1} should stand in a close relationship with the range of the interaction. So far we are obliged to use more general kernels than the Gaussian kernel K_2 in Eq. (1.11), it is, apart from special cases, no longer possible to classify the corresponding eigenstates by SU_3 (or a perturbed SU_3), as the appearance of discrete spatial symmetries expressed by the Hermite kernels $H_n(k_0, x_j - y_j)$ quenches the existence of SU_3 . This fact is easy to see:

\mathcal{A}_2 incorporates an operator, which can be represented by the generators of SU_3 :

$$\exp(-k_0^{-2} \Delta) = \exp\left(-\sum_{j=1}^3 \sum_{k=1}^3 \delta_{jk} (\ell_j - \ell_j^+) (\ell_k - \ell_k^+) \frac{E}{2\hbar^2 k_0^2}\right), \quad (E = \hbar\omega), \quad (3.22)$$

(the generators of SU_3 are stated in Appendix B). In order to give a sketch for obtaining Eq. (3.22), we should recall that $\exp(-k_0^{-2}\Delta)$ follows from

$$\left. \begin{aligned} \mathcal{A}_2 &= \exp(+\not{k}^2/\hbar^2 k_0^2) \\ \not{k} &\Rightarrow \frac{\hbar}{i} \nabla \end{aligned} \right\}, \quad (3.23)$$

and according to appendix B the momentum operator \mathcal{P} can be expressed in terms of creation and annihilation operators

$$\not{k}_k = (\ell_k - \ell_k^+) \frac{\sqrt{2\hbar\omega}}{2i}. \quad (3.24)$$

The Hermite Kernels $H_n(k_0, x_j - y_j)$ can easily be written in terms of ℓ_k and ℓ_k^+ , but if we do so, we find that the generators of SU_3 do not commute with $\mathcal{A}(\ell_k, \ell_k^+)$.

3.3. General Discussion and an Outlook to other Disciplines

The kernel K_2 stands in a close relationship with well elaborated symmetry principles, which provide interesting informations referring to the classification of the eigenstates and being of interest also by taking account of anharmonic terms of Eq. (2.1). But with respect to Eq. (3.4), where we are, in general, not able to use symmetry principles for the characterization of the solutions, it is evident that we are confronted with the treatment of a self-interacting, highly anharmonic oscillator, even if we approximate K_2 according to Eq. (2.3). Simple perturbation theory should, however, be avoided, and it is therefore stimulating that the treatment of highly anharmonic oscillators in quantum theory is attacked by rather sophisticated methods, providing informations about the complete spectrum of energy levels. It appears that these recent developments (see Ref. [21–25]) may have a dominating importance with respect to integration methods in self-interacting field equations. It is not desirable to use only purely numerical methods, e.g. the variation principle of Ritz:

$$\delta E \left(\left\{ \sum_{\nu} c_{\nu} \varphi_{\nu} \right\} \right) = 0.$$

Hereby means $\{\varphi_{\nu}\}$ a finite set of N arbitrary basis functions (see also Eq. (1.5)). If we would perform numerical calculations on the basis of energy variation, the effort would be much smaller than in a many-particle HF equation, as we treat a many-particle problem in a quite different way: we regard such a problem as a self-interacting field for an extended particle with internal structure, and such a conception has been regarded in superconductivity by Bogoljubov, where a many-particle problem is successfully described by a quasi-particle.

It is rather trivial (see Appendix C) that such a field theoretical method of treating a many-particle system (e.g. a molecule) as an extended particle (or quasi-particle)

with further internal degrees of freedom (e.g. collective excitations) cannot provide information on the inner shell electrons: this is a consequence of the fact that even a purely numerical approach of Eq. (3.5) is much easier than a numerical solution of the HF equations. Thus the methods under consideration resemble the semi-empirical MO methods, but those suffer sometimes a lack of consistency: They treat only the outermost electrons with the MO approach by neglecting the integrals of the inner shell electrons without being aware of, that the effective potential for the valence electrons is far away from Coulomb potentials. The relationship to ligand field theory [26, 27] is much closer, because one considers here a one-particle Schrödinger equation for the central ion, whereby the effective potential is additionally perturbed by the multipole contributions of the ligands (in practice: dipole approximation). It appears, that the formalism presented in this paper, is a certain extension of ligand field theory, as the total system “*central atom (or ion) + ligands*” is treated as the quasi-particle and the effective two-point potential is induced by the spatial symmetry of the total system. However, the above mentioned connection with superconductivity is more apparent as stated till now, since the cubic Schrödinger equation (1.6) is equivalent to the Ginzburg–Landau equation [28, 29, 30], because the free energy reads:

$$F = \int d^3x (\alpha |\Psi(x)|^2 + \beta |\Psi(x)|^4 + \gamma |\nabla \Psi|^2). \quad (3.25)$$

Performing $\delta F = 0$ with respect to Ψ^* yields Eq. (1.6).

This fact is remarkable, as it provides a key for the physical interpretation of the nonlinear field equations under consideration. The soliton solution (1.7) can be associated with a collective excitation of Cooper pairs (quasi-particles). These quasi-particles consist of many interacting particles, and according to Feynman [30] the wavefunction has in such a situation a direct physical meaning: In the case of the Bose condensation, as it is realized in superconductivity, the one particle current becomes a real electric current, formed by a many Boson system, and the wavefunction acquires a real physical significance, when very many Bosons are in the same state. On the other side, the Ginzburg–Landau theory can also be considered as a classical field theory, and Feynman’s interpretation of the wavefunction, which may be realized by solitonic solutions, leads directly to a classical field theory. The wavefunction is then associated with a phase transition, as it is actually realized in superconductivity. Hence, Eqs. (1.11), (3.4), and (3.5) may be interpreted in the same sense as Eq. (3.25), since they represent generalizations of it: We may either consider them as field equations for extended particles with an internal structure, and deformations incorporate a further degree of freedom, or (without probability interpretation of $|\Psi|^2$) as phase transitions of structurized compounds. The presence of time-dependent external fields in Eq. (3.5) has then to be associated with changes in the thermodynamical phase(s), induced by external fields, and the internal structure has to undergo modifications, since P_{nj} depends on time. In this sense, chemical processes can be regarded in the framework of a classical field theory. When the structure of spatial extension of the constituents becomes irrelevant, it may become favourable to pass to the local

limit of eqs. (3.4) and (3.5):

$$\begin{aligned}
 i\hbar \frac{\partial \Psi}{\partial t} - V_{\text{ex}} \Psi - \frac{1}{2m} (-i\hbar \nabla - q\mathcal{A}_{\text{ex}}(t))^2 \Psi \\
 = \lambda_1 \prod_{j=1}^3 \sum_{n=\nu}^{\infty} P_{nj}(t) \int \mathbf{H}_n(k_0, x_j - y_j) \mathbf{K}_2 |\Psi(y)|^2 d^3 y \Psi(x) \\
 = \lambda \prod_{j=1}^3 \sum_{n=\nu}^{\infty} P_{nj}(t) \left\{ \frac{\partial^n}{\partial x_j^n} |\Psi(x)|^2 \right\} \Psi(x) \quad (k_0 \rightarrow \infty). \quad (3.26)
 \end{aligned}$$

By that, it may appear that the extended particles (or quasi-particles) become completely structureless. This is, however, not true, because the extended multipoles shrink to “point-multipoles” (e.g. the term $H_1(k_0, x_3 - y_3)$, related to an extended dipole, now becomes a point-dipole). It should once again be emphasized that even by taking the local limit ($k_0 \rightarrow \infty$), we are restricted in practical problems to a finite order of derivatives of the density $|\Psi(x)|^2$ in Eq. (3.26) according to our request that a proper choice of the weight factors P_{nj} has to reflect the symmetry of the molecules. But in view of the enormous problems of the ab initio methods to describe thermodynamical processes, it may be promising to consider field theoretical methods with internal structures being generalizations of the Ginzburg–Landau theory.

Although we have till now considered problems of molecular and solid-state physics, it is clear that the methods may find also applications in other domains, when k_0 and λ_c are appropriately chosen. Though in nuclear physics oscillator models and symmetry principles (e.g. SU_3) are often used, and there have been many attempts to describe the meson clouds of nucleons by Gaussians (as form-factors) [30–33]. So far as we could verify, models of this kind go back to a remarkable paper of Heisenberg [31], who described the nuclear shells by oscillators and the short-range interactions between the nucleons by Gaussians.

In this connection it is justified to note that the formalism presented here may lead to some insights with reference to the methodology in this domain: Assuming $k_0^{-1} \approx 10^{-13} \text{cm}$, then \mathcal{A}_2 is to a rather good approximation $1 - k_0^{-2} \Delta$ (the higher order contributions are small, but they prevent a singular behaviour), and the elimination of the potential of strong interaction yields Eq. (1.11) or Eq. (A.6). On the other side, Eq. (1.11) can be approximated to a certain extent by oscillators. However, by keeping in mind the Ginzburg–Landau theory of phase transitions for superconductivity, there is some reason that for proper k_0 and λ_c (strong interactions) we are able to describe phase transitions in the domain of a many nucleon system (plasma physics). Furthermore, the problem of an extended particle with internal structure has become a main object in particle physics, and even nonrelativistic quark models play an important role (see Ref. [18, 19, 34–36], where further references may be found). It should be noted that the field theoretical means presented in this paper may also provide an access to some problems of particle physics. By that, we observe a possibility to make use of nonlinear and nonlocal generalizations of the Schrödinger equation in many

disciplines. This fact may incorporate a contribution to overcome the occasionally undesirable tendency of too strong a specialization of some disciplines.

A. Appendix: Gauss Transformation of Polynomials

Many mathematical properties of a Gauss transformation can be derived from the consideration of a polynomial $f_n(y) = y^n$ as test function, yielding the evaluation of the following expression:

$$\int_{-\infty}^{+\infty} y^n \mathbf{K}_2(k_0, x-y) dy = \frac{k_0}{\sqrt{\pi}} \sum_{j=0}^n \binom{n}{j} \frac{x^{n-j}}{k_0^{j+1}} \Gamma\left(\frac{j+1}{2}\right) \left(\frac{1+(-1)^j}{2}\right). \quad (\text{A.1})$$

Now we make use of a well-known theorem of Weierstrass, according to which every (*L-measurable*) function $g(y)$ can be uniformly approached by an infinite set of polynomials. In the following, we identify $g(y)$ with the semi-definite function

$$\left. \begin{aligned} \sum_{n=0}^{\infty} b_n y^n = g(y) = |\Psi(y)|^2 \geq 0 \quad \text{for } |y| < \infty \\ |\Psi(y)|^2 = 0 \quad \text{for } \lim |y| \rightarrow \infty \end{aligned} \right\}. \quad (\text{A.2})$$

The substitution of (A.1) into (A.2) yields:

$$\left. \begin{aligned} \int_{-\infty}^{+\infty} |\Psi(y)|^2 \mathbf{K}_2 dy &= \frac{k_0}{\sqrt{\pi}} \sum_{n=0}^{\infty} b_n \sum_{j=0}^n \frac{x^{n-j}}{k_0^{j+1}} \Gamma\left(\frac{j+1}{2}\right) \left(\frac{1+(-1)^j}{2}\right) \binom{n}{j} \\ &= |\Psi(x)|^2 + h(k_0, x) \\ &\quad (j=0) \quad (j>0) \end{aligned} \right\}. \quad (\text{A.3})$$

This expression can also be written in the form

$$\left. \begin{aligned} \int_{-\infty}^{+\infty} |\Psi(y)|^2 \mathbf{K}_2 dy &= |\Psi(x)|^2 + \frac{1}{4k_0^2} \frac{\partial^2 |\Psi(x)|^2}{\partial x^2} + \dots + T_j(k_0) \\ T_j(k_0) &\sim k_0^{-2j} \partial^{2j} |\Psi(x)|^2 / \partial x^{2j} \end{aligned} \right\}. \quad (\text{A.4})$$

With the help of (A.4) we can verify that the Gauss transformation of the nonlinear term of Eq. (1.11) uniformly converges against the local limit ($k_0 \rightarrow \infty$):

$$\left. \begin{aligned} \int \int |\Psi(y)|^2 [\mathbf{K}_2(k'_0, x-y) - \mathbf{K}_2(k_0, x-y)] dy dx \quad (k'_0 > k_0) \\ = \int [|\Psi(x)|^2 - |\Psi(x)|^2] dx + \frac{1}{4} \left(\frac{1}{k_0'^2} - \frac{1}{k_0^2} \right) \int \frac{\partial^2 |\Psi(x)|^2}{\partial x^2} dx \\ + \dots + \int [T_j(k'_0) - T_j(k_0)] dx < \varepsilon \quad \text{for proper } j, k'_0, k_0 \end{aligned} \right\}. \quad (\text{A.5})$$

From (A.4) and (A.5) results that the nonlinear Schrödinger equation with

Gaussian kernel (1.11) can also be written in the form

$$\begin{aligned}
 i\hbar \frac{\partial \Psi}{\partial t} + \frac{\hbar^2}{2m} \Delta \Psi &= \lambda_c \int K_2 |\Psi(y)|^2 d^3y \Psi(x) \\
 &= \lambda_c |\Psi(x)|^2 \Psi + \frac{\lambda_c}{4k_0^2} \{\Delta |\Psi(x)|^2\} \Psi \\
 &\quad + \dots + \sim \frac{\lambda_c}{k_0^{2n}} \{\Delta^n |\Psi(x)|^2\} \Psi (n > 1). \tag{A.6}
 \end{aligned}$$

This is rather interesting with respect to a proposal of Mielnik [13] to generalize the usual Schrödinger equation such that it contains besides the nonlinear term $\sim |\Psi|^2 \Psi$, discussed by the authors [1–6], a term proportional to the derivative $\sim \Delta |\Psi(x)|^2$. Mielnik's proposal, which is based on some considerations on a generalization of the theory of measurement process, can also be derived from (A.6), when k_0 is sufficiently great, but not yet infinite, because the contributions of the higher order derivatives of the density $|\Psi(x)|^2$ become very small (e.g. $k_0^{-1} \approx 10^{-13}$ cm).

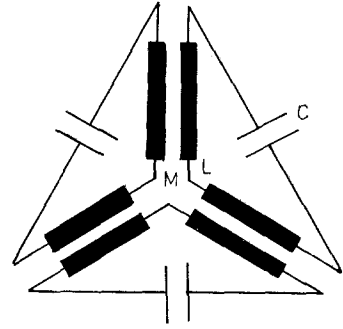
B. Appendix: The Conception of Oscillators in Molecular Systems

Coupled harmonic oscillators are widely used in many disciplines, as the quantization of a Bose field, obeying a linear wave equation of the form

$$\square q = 0 \tag{B.1}$$

(e.g. photons, phonons), is achieved by a treatment of an infinite set of oscillators via Schrödinger equation. However, in the last decade the consideration of anharmonic oscillators has become more and more actual with respect to realistic transport phenomena in solids, and this fact stands in a close relationship to the nonlocal Schrödinger Eq. (1.11), and already an oscillator approach with self-interaction incorporates in reality a Schrödinger equation of an anharmonic oscillator (2.11). In the domain of molecular systems there have been many attempts to use oscillator concepts for the description of dynamical processes [14, 15], and, in particular, Hartmann et al. [14] first considered electric circuits in connection with π -electron systems. The relationship between electric oscillators and molecular processes is actually much closer, since one may regard any state as a certain charge distribution in a capacitance, and the transition between different eigenstates of a molecule as a current, related to an inductivance. Such a transition between different states of a molecule now is treated as a collective excitation in a circuit (or system of coupled circuits), and we can also verify a close connection with the field theory, developed in the preceding sections, according to which an extended particle is described by a self-interacting field and excited states must be viewed as collective excitations. Because we can also verify the symmetry principles in an apparent way, we shall discuss here 3 circuits (see Fig. 2), which may be coupled via a mutual inductivance M . The Lagrangian of the 3

Fig. 2. 3 identical electric circuits with L =inductivance and C =capacitance. The space of eigenstates, being classified by SU_3 multiplets for $M=0$ and by SU_2 for $M \neq 0$, is defined on the charge space



circuits reads:

$$\mathcal{L} = \sum_{k=1}^3 \left(\frac{L}{2} \dot{Q}_k^2 + \frac{M}{2} \sum_{l \neq k=1}^3 \dot{Q}_k \dot{Q}_l - \frac{1}{2C} Q_k^2 \right) \tag{B.2}$$

In order to show the symmetry properties of (B.2) we consider first the case without magnetic interaction ($M=0$). The canonically conjugate momentum is given by

$$P_k = \frac{\partial \mathcal{L}}{\partial \dot{Q}_k} = L \dot{Q}_k \quad (= \text{flux}) \tag{B.3}$$

and therefore the Hamiltonian becomes ($\omega_0^2 = 1/LC$)

$$H = \sum_{k=1}^3 \left(P_k^2 / 2L + \frac{L}{2} \omega_0^2 Q_k^2 \right) \tag{B.4}$$

The canonical commutation relations get the shape

$$\mathcal{P}_k \mathcal{Q}_l - \mathcal{Q}_l \mathcal{P}_k = \frac{\hbar}{i} \delta_{kl} \tag{B.5}$$

(electric charge and magnetic flux are conjugate variables). The solution of the Schrödinger equation related to (B.4) and (B.5) is well-known; we have only to take notice that the wavefunction is now defined in the charge space:

$$\left. \begin{aligned} \mathcal{P}_k &\Rightarrow -i\hbar \partial / \partial Q_k \\ -\frac{\hbar^2}{2L} \sum_{k=1}^3 \frac{\partial^2}{\partial Q_k^2} \Psi + \sum_{k=1}^3 \frac{L}{2} \omega_0^2 Q_k^2 \Psi &= E \Psi \end{aligned} \right\} \tag{B.6}$$

In order to get the generators of SU_3 , we perform the following substitutions

$$\left. \begin{aligned} \ell_k^{(+)} &= \sqrt{\frac{L\omega_0}{2\hbar}} \mathcal{Q}_k^{(+)} i \frac{1}{\sqrt{2\hbar L\omega_0}} \mathcal{P}_k \end{aligned} \right\} \tag{B.7}$$

obeying

$$[\ell_k, \ell_l^+]_- = \delta_{kl}$$

With the help of (B.7) Eq. (B.4) gets the shape:

$$H = \hbar\omega_0 \sum_{k=1}^3 (\ell_k^+ \ell_k + \frac{2}{3}). \quad (\text{B.8})$$

The degeneracy of the eigenstates of the 3 electric circuits is classified by the SU_3 group, of which the generators can be written in terms of Bose operators (Ref. [18, 19]):

$$\left. \begin{aligned} \mathcal{I}_+ &= \ell_1^+ \ell_2, & \mathcal{I}_3 &= \frac{1}{2}(\ell_1^+ \ell_1 - \ell_2^+ \ell_2), \\ \mathcal{I}_- &= \ell_1 \ell_2^+, & \mathcal{U}_+ &= \ell_2^+ \ell_3, & \mathcal{U}_- &= \ell_2 \ell_3^+, \\ \mathcal{U}_3 &= \frac{1}{2}(\ell_2^+ \ell_2 - \ell_3^+ \ell_3), & \mathcal{V}_+ &= \ell_1^+ \ell_3, \\ \mathcal{V}_- &= \ell_1 \ell_3^+, & \mathcal{V}_3 &= \frac{1}{2}(\ell_1^+ \ell_1 - \ell_3^+ \ell_3), \\ \mathcal{Q} &= \frac{2}{3}(\mathcal{I}_3 + 2\mathcal{V}_3), \\ \mathcal{Y} &= \frac{2}{3}(2\mathcal{U}_3 + \mathcal{I}_3) \end{aligned} \right\}. \quad (\text{B.9})$$

It should also be mentioned that the occupation number operator \mathfrak{N} is given by $\mathcal{N} = \ell_1^+ \ell_1 + \ell_2^+ \ell_2 + \ell_3^+ \ell_3$, but in the following we have not to consider it. A more interesting feature is that the Gaussian kernel K_2 (see 3.2) can be expressed in terms of the generators of SU_3 , defined by Eq. (B.9), and therefore this symmetry group is not only important with regard to the oscillator approximation (2.3). A further interesting aspect to be noted is the correspondence $SO_3 \rightarrow SU_3$, because SO_3 is not realized by the isotropy of a 3-dimensional charge space instead of the usual position space. By the introduction of a magnetic interaction ($M \neq 0$) between the circuits according to (B.2) we obtain a reduction of the symmetries: In the charge space we have only invariance against SO_2 , and the corresponding Hamiltonian is characterized by a perturbed SU_3 symmetry. This fact is easy to verify, as the determination of the normal co-ordinates and frequencies involves the resolution of the determinant:

$$\begin{vmatrix} L - \lambda & M & M \\ M & L - \lambda & M \\ M & M & L - \lambda \end{vmatrix} = 0, \quad (\text{B.10})$$

The eigenfrequencies of the 3 coupled circuits now are

$$\left. \begin{aligned} \omega_1^2 &= \omega_2^2 = \omega^2 = 1/[(L-M)C] = 1/\lambda_{1,2}C \\ \omega_3^2 &= 1/\lambda_3 C = 1/(L+2M)C \end{aligned} \right\}, \quad (\text{B.11})$$

and the Hamiltonian assumes the shape

$$\mathcal{H} = \frac{1}{2\lambda_1} (\mathfrak{P}_1^2 + \mathfrak{P}_2^2) + \frac{1}{2\lambda_3} \mathfrak{P}_3^2 + \frac{\lambda_1}{2} \omega^2 (\mathfrak{Q}_1^2 + \mathfrak{Q}_2^2) + \frac{\lambda_3}{2} \omega^2 \mathfrak{Q}_3^2. \quad (\text{B.12})$$

Eq. (B.12) may also be formulated in terms of Bose operators (in Eq. (B.7), we have only to replace L by the appropriate λ):

$$\mathcal{H} = \hbar\omega \sum_{k=1}^2 (\ell_k^+ \ell_k + 1) + \hbar\omega_3 (\ell_3^+ \ell_3 + \frac{1}{2}). \quad (\text{B.13})$$

Both Eq. (B.13) and Eq. (B.12) are equations for a 2-dimensional oscillator in a formal $(x_1 - x_2)$ -plane and an additional oscillator with different ω in the x_3 -plane. The only generators of Eq. (B.9) commuting with the Hamiltonian (B.13) are I_+ , I_- , and I_3 , representing the generators of SU_2 . By that, the system under consideration involves a reduction of the symmetry, if the subsystems (circuits) mutually interact, but SU_2 is exactly preserved.

Models of this kind may find applications in many disciplines and the symmetry groups SU_3 and SU_2 have a meaning for the characterization of the eigenstates of Eqs. (1.11) and (3.3). The advantage of a model with coupled circuits in the molecular domain may be viewed in the description of collective excitations of the electric charge distribution in a molecule, and e.g. a charge transfer between 2 interacting molecules gets an illustrative representation. So it is not surprising that circuits have already been considered as models of molecular processes [14, 15], and it appears to be rather important that the thermodynamics of processes can be founded with the help of circuits [16, 17]. We should also emphasize that the description of molecular processes by coupled circuits stands in a close relationship with our investigations on nonlinear field equations with internal structure: Besides the symmetry principle, which makes already apparent this great similarity, we preferably think of the collective excitations in the coupled circuits. This aspect is to a certain degree equivalent to a field theory of an extended particle with additional degrees of freedom, and we have already discussed the self-interacting oscillator approach of such a theory. However, the use of free (mechanical) oscillators or electric circuits in the molecular domain has to be restricted, because one has not to do with equidistant energy levels in both vibronic and electronic spectra. We have seen that by taking account of the self-interaction of an extended particle it is only possible to fit spectra by rather anharmonic oscillators (without containing the self-interaction). This fact may also be a reason that the theory of *H-bonds* does not yet work in a satisfactory way with the help of simple oscillator models.

C. Appendix: Remarks to Numerical Aspects

As already pointed out in section 3.3, Eq. (3.4) or a specific version of it (e.g. Eq. (3.6)) can be treated as self-interacting, anharmonic oscillators. Such a starting-point favours the use of symmetry principles, which play a dominant role in approximation methods recent developments of perturbation theory. It is also possible to make use of purely numerical methods with reference to the integration of simplified versions of Eq. (3.4), e.g. the variation principle of Ritz.

For this purpose, we write Eq. (3.4) in the form

$$\int E|\Psi|^2 d^3x + \frac{\hbar^2}{2m} \int \Psi^* \Delta \Psi d^3x = \lambda_c \iint |\Psi(y)|^2 G_{\mathcal{A}}(x-y) |\Psi(x)|^2 d^3x dy^3, \quad (\text{C.1})$$

and with respect to actual calculations we have to restrict ourselves to a finite set of basis structure functions (in the following, we consider the kernel (3.6)). By the means of a finite basis set (of arbitrary functions) $\{\varphi_k, k = 1, \dots, N\}$ we perform

$$\left. \begin{aligned} \Psi &= \sum_{k=1}^N b_k \varphi_k, \int \Psi^* \Psi d^3x = 1 \\ \delta E \left(\sum_{k=1}^N b_k \varphi_k \right) &= \sigma \end{aligned} \right\}, \quad (\text{C.2})$$

and the variation of the total energy yields an approximate calculation of a ground state (spin 0) and $N - 1$ excited states of the same multiplicity. Now the question arises, which kind of trial functions may involve simple manipulations of the numerical procedure. So far as we could verify it appears that the use of the kernel (3.21) justifies the application of Hermite polynomials multiplied with a Gaussian as trial functions:

$$\varphi_k = N_k H_k(\alpha_k x) \exp \left\{ -\frac{1}{2} \alpha_k^2 x^2 \right\} \quad (\text{C.3})$$

(α_k is a scaling factor for the trial functions and N_k is defined by the normalization). As $G_{\mathcal{A}}(x-y)$ consists itself of products and sums of two-point Hermite polynomials $H_n(k_0, x_k - y_k)$ multiplied with K_2 , the evaluation of the expression

$$\iint |\Psi(y)|^2 \prod_{j=1}^3 \sum_{n=0}^M H_n(k_0, x_j - y_j) K_2(x-y) |\Psi(x)|^2 d^3x d^3y$$

with the help of (C.3) yields integrals containing products of Gaussians and polynomials. Because of the correspondences

$$\left. \begin{aligned} H_n(\alpha_n x) &= \sum_{l=0}^n C_l(\alpha_n) x^l \\ x^n &= \sum_{l=0}^n d_l(\alpha_l) H_l(\alpha_l x) \end{aligned} \right\}, \quad (\text{C.4})$$

all integrals can be brought to the form

$$I_n(x) = \int_{-\infty}^{+\infty} y^n \exp(-\alpha^2 y^2) \exp(-k_0^2(x-y)^2) dy, \quad (\text{C.5})$$

and this type of integral is easily evaluated by the substitution $\xi = y - k_0^2 x / k_0^2 + \alpha^2$ to yield an integral of the form

$$\int_0^{\infty} y^n \exp(-a^2 y^2) dy = \frac{\Gamma((n+1)/2)}{2a^{n+1}} (a^2 > 0). \quad (\text{C.6})$$

By that, (C.5) assumes the shape

$$I_n(x) = \exp\left(-\frac{\alpha^2 k_0^2 x^2}{\alpha^2 + k_0^2}\right) \sum_{j=0}^n \left\{ \binom{n}{j} \left(\frac{k_0^2 x}{\alpha^2 + k_0^2}\right)^{n-j} \cdot [(\alpha^2 + k_0^2) - (j+1)/2] \cdot \Gamma\left(\frac{j+1}{2}\right) \left(\frac{1+(-1)^j}{2}\right) \right\}. \quad (C.7)$$

(The extension of the integration to 3 dimensions is straightforward). Since the use of trial functions (C.3) implies

$$\int_{-\infty}^{+\infty} H_m(\alpha_m x) H_n(\alpha_n x) \exp\left(-\frac{\alpha_m^2 + \alpha_n^2}{2} x^2\right) dx = 0 \quad \text{for } m \neq n,$$

we are not confronted with a growth of four-center integrals proportional to N^4 as it is the case in *ab initio* calculations. Furthermore, the calculation of excited states is connected to additional numerical effort in *ab initio* methods, whereas in the method presented here we automatically obtain excited states due to the variation principle. In order to give an illustration of the method, we consider the kernel K_{Td} of Eq. (3.6) in connection with the molecule $P(OH)_4^+$, because this molecule can be classified by a weakly perturbed T_d group.

$P(OH)_4^+$ exhibits polar character, and the first excited state is split into 4 energy levels between 5.6 eV and 6.2 eV being associated with $n-\pi^*$ -transitions. For a detailed investigation of the constitutions of phosphoric acid and references to other papers, Ref. [37] should be consulted. We have taken account of the polar character of $P(OH)_4^+$ by the contributions $P_{11} = P_{12} = P_{13}$ in the two-point kernel function K_{Td} (3.6). If we would omit these terms, the kernel of a completely unpolar molecule of the same symmetry class would be obtained (e.g. CH_4). As already mentioned, the coefficients P_{ik} of the basis structure functions may serve as additional parameters of the field equation (3.4). In our calculation, where we only intend to demonstrate the formalism, we have fixed these coefficients till a normalization factor to the ratio $P_{01,2,3} : P_{11,2,3} : P_{21,2,3} = 2 : 1 : 2$ and k_0 was uniquely assumed to $k_0^{-1} = 1.55 \text{ \AA}$, in order to agree with the mean bond length P-O. With respect to the trial functions we have made the following restrictions: We use a finite basis set of 10 functions with the same scaling factor $\alpha_k = \alpha = k_0 \sqrt{2}$, being a free parameter of the trial functions, which we have enumerated as follows:

$$\left. \begin{aligned} u &= \exp(-0.5\alpha^2(x_1^2 + x_2^2 + x_3^2)) \\ \varphi_1 &= \mathcal{N}_0 u; & \varphi_2 &= \mathcal{N}_1 H_1(\alpha x_1) u; \\ \varphi_3 &= \mathcal{N}_1 H_1(\alpha x_2) u; & \varphi_4 &= \mathcal{N}_1 H_1(\alpha x_3) u; \\ \varphi_5 &= \mathcal{N}_2 H_2(\alpha x_1) u; & \varphi_6 &= \mathcal{N}_2 H_2(\alpha x_2) u; \\ \varphi_7 &= \mathcal{N}_2 H_2(\alpha x_3) u; & \varphi_8 &= \mathcal{N}_3 H_1(\alpha x_1) H_1(\alpha x_2) u; \\ \varphi_9 &= \mathcal{N}_3 H_1(\alpha x_1) H_1(\alpha x_3) u; & \varphi_{10} &= \mathcal{N}_3 H_1(\alpha x_2) H_1(\alpha x_3) u. \end{aligned} \right\} \quad (C.8)$$

These trial functions are consistent with the basis structure functions of the kernel K_{Td} . Thus P_{01} and φ_1 can be associated with the central ion (phosphorus),

Table 2. Numerical calculation of the wavefunction of $\text{P}(\text{OH})_4^+$

Normalization factor	1	2	3	4	5	6	7	8	9	10	Energy/eV
1 $(84.3)^{-1/2}$	4.2	1.7	1.7	1.7	4.2	4.2	4.2	1.3	1.3	1.3	-9.46
2 $(54.09)^{-1/2}$	-4.5	2.5	-1.25	-1.25	4.5	0	0	1.7	-1.7	0	-3.94
3 $(59.3)^{-1/2}$	-2.6	0	1.3	-1.3	-2.6	5.2	0	-1.6	-1.6	3.2	-3.80
4 $(12)^{-1/2}$	-1	0	0	0	-1	-1	3	0	0	0	-3.49
5 $(13.74)^{-1/2}$	0	-1.3	-1.3	-1.3	0	0	0	1.7	1.7	1.7	-3.29

$\varphi_2, \varphi_3, \varphi_4$ reflect the dipole structure of the molecule which is expressed by the terms $\text{P}_{1k}H_1(k_0, x_k - y_k)$ of K_{Td} , and $\varphi_5 - \varphi_{10}$ are related to the quadrupole terms $\text{P}_{2k}H_2(k_0, x_k - y_k)$. Using the trial functions (C8) we have calculated via energy variation $\text{P}(\text{OH})_4^+$ on the basis of the kernel K_{Td} without trying to fit the mentioned parameters such that the computed results agree exactly with the corresponding experimental results, because we have to be aware of the fact that $\text{P}(\text{OH})_4^+$ is a constitution of H_3PO_4 being realized in solutions with very strong acids as solvent. Therefore the experimental determination of the ionization energy depends on the solvent [37] (order: 8.5 eV–9.5 eV) and instead of discrete energy levels one observes sometimes a rather continuous absorption of light in the interval 5.6 eV–6.3 eV due to further influences (interaction with the solvent, vibration and rotation spectra). According to Table 2, where some results have been listed, the computed ionization energy amounts to 9.4 eV and the 4 lowest excited states can be roughly classified as $n-\pi^*$ -transitions. But although the formalism presented here exhibits many advantages with respect to computational procedures and avoids the inconsistencies of semi-empirical MO methods (see Sect. 3.3), we should point out that the essential aim of these considerations should not only be viewed in an improvement of numerical methods, because according to Sect. 3.3 Eq. (3.4) can also be viewed under the aspect of the Ginzburg–Landau theory of phase transitions (if $k_0 \rightarrow \infty$ is performed) and symmetry principles, representing a generalization of the Ginzburg–Landau theory to systems with internal structure.

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References

1. Zakharov, V., Shabat, A.: Sov. Phys. JETP, **64**, 1627 (1973)
2. Satsuma, J., Yajima, N.: Prog. Theor. Phys. **55S**, 285 (1974)
3. Kubo, S., Namiki, M., Ohba, I.: Prog. Theor. Phys. **55**, 860 (1976)
4. Jackiw, R.: Rev. Mod. Phys. **49**, 681 (1977)
5. Gupta, M. R.: Phys. Lett. **72A**, 6, 420 (1979)
6. Nonlinear Problems. Lecture Notes in Physics **98**, Heidelberg: Springer Press: 1979
7. Ulmer, W., Hartmann, H.: Nuovo Cimento **47A**, 359 (1978)
8. Ulmer, W.: Nuovo Cimento **51A**, 309 (1979)

9. Yamamoto, H.: *Prog. Theor. Phys.* **58**, 1014 (1977)
10. Ruch, E., Schönhofer, A.: *Theoret. Chim. Acta (Berl.)* **10**, 91 (1968)
11. Ruch, E.: *Angew. Chem. Int. Ed.* **16**, 65 (1977)
12. Hund, F.: *Materie als Feld*. Heidelberg: Springer Press 1954
13. Mielnik, B.: *Com. Math. Phys.* **37**, 221 (1974)
14. Hartmann, H., Stürmer, W.: *Z. Naturforsch.* **5a**, 99 (1950)
15. Huber, W., Simon, G., Kuhn, H.: *Z. Naturforsch.* **17a**, 99 (1962); Seelig, F., Huber, W., Kuhn, H.: *Z. Naturforsch.* **17a**, 114 (1962)
16. Meixner, J.: *J. Math. Phys.* **4**, 154 (1963)
17. Kohler, M.: *Int. Journ. Theor. Phys.* **13**, 38 (1975)
18. Roman, P.: *Int. Journ. Theor. Phys.* **16**, 12, 915 (1977)
19. Fairman, D., Hendry, A. W.: *Phys. Rev.* **173**, 1720 (1968)
20. Landolt-Börnstein: *Atom- und Molekularphysik*. Heidelberg: Springer Press 1950
21. Lakshmanan, N., Prabhakaran, J.: *Lett. Nuovo Cimento* **7**, 689 (1973)
22. Bender, C. M.: *Phys. Rev.* **D7**, 1620 (1973)
23. Shustov, A. P.: *J. Phys. A*, **11**, 1171 (1978)
24. Halpern, F. R.: *J. Math. Phys.* **14**, 219 (1973)
25. Mizrahi, M. M.: *J. Math. Phys.* **20**, 844 (1979)
26. Hartmann, H., Ilse, F.: *Z. Naturforsch.* **6a**, 751 (1951)
27. Schläfer, H. L., Gliemann, G.: *Einführung in die Ligandenfeldtheorie*. Frankfurt am Main: Akademische Verlagsgesellschaft 1967
28. Landau, L. D., Ginzburg, V. L.: *Sov. Phys. JETP*, **20**, 1064 (1950)
29. Graham, R., Haken, H.: *Z. Physik*, **237**, 31 (1970)
30. Feynman, R. P.: *Les Houches Lectures in Theoretical Physics*, p. 163 1976
31. Heisenberg, W.: *Z. Physik*, **96**, 473 (1935)
32. Elliott, J. P.: *The Nuclear Shell Model and its Relation with Other Models*. Wien: International Atomic Energy Agency 1963
33. Meyer, M. G., Jensen, J. H. D.: *Elementary Nuclear Shell Theory*. New York: Wiley 1955
34. Barut, A. O., Raczka, R.: *Nuovo Cimento*, **31B**, 19 (1976)
35. Ivanenko, D. D.: In: *Centenario Einsteiniano*. Firenze: 1979
36. Feynman, R. P.: *Photon-Hadron-Interaction*. New York, N.Y.: 1972
37. Ulmer, W.: *Z. Naturforsch.* **34c**, 658 (1979)

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