Pairing Gaps, Pseudogaps, and Phase Diagrams for Cuprate Superconductors

Yang Sun(1), Mike Guidry(2), and Cheng-Li Wu(3)

(1) Department of Physics, University of Notre Dame, Notre Dame, Indiana 46556, USA
(2) Department of Physics and Astronomy, University of Tennessee, Knoxville, Tennessee 37996, USA
(3) Physics Department, Chung Yuan Christian University, Chung-Li, Taiwan 320, ROC

(Dated: March 23, 2022)

We use a symmetry-constrained variational procedure to construct a generalization of BCS to include Cooper pairs with non-zero momentum and angular momentum. The resulting gap equations are solved at zero and finite temperature, and the doping-dependent solutions are used to construct gap and phase diagrams. We find a pseudogap terminating at a critical doping that may be interpreted in terms of both competing order and preformed pairs. The strong similarity between observation and predicted gap and phase structure suggests that this approach may provide a unified description of the complex structure observed for cuprate superconductors.

PACS numbers:

I. INTRODUCTION

The mechanism responsible for high-temperature superconductivity remains unresolved despite intense study over the past two decades. The observation of pseudogaps and a relatively universal phase diagram are thought to represent key aspects of the solution, but no theory describes all observations in a simple, unified way. Previously we introduced an SU(4) model of competing antiferromagnetism (AF) and d-wave superconductivity (SC), used coherent states to provide a connection to Landau-Ginzburg and symmetry-constrained Hartree-Fock-Bogoliubov theory, and demonstrated that SU(4) symmetry implies no double occupancy. This has defined a new, unconventional method to simplify the otherwise very difficult to solve.

The SU(4) coherent state solution represents a generalization of the BCS pairing theory having Cooper pairs with non-zero momentum and angular momentum. Dynamics of these interacting Cooper pairs at different hole-doping and temperature yields rich phase diagrams that may explain the main features of observations. The occurrence of a pseudogap, a critical value of doping, and splitting of the SC gap at low doping region are all natural consequences of the dynamics.

In this article we extend our previous discussion and compare gap and phase diagrams computed using the formalism developed in Ref[4] with available data. We demonstrate that our analytically-solvable gap equations with doping-independent interactions already describe the basic features of experimental gap and phase diagrams for the cuprates. With addition of simple doping dependence for interaction strengths in the low-doping region, our results can reproduce observed pseudogap transition temperature $T_c$ and the pseudogap transition temperature $T^*$ extracted from a range of cuprate data.

II. GENERALIZED SU(4) COHERENT STATES

In the SU(4) model the configuration space is built from coherent pairs formed from two electrons (or holes) centered on adjacent lattice sites: spin-singlet $D$ and spin-triplet $\pi$ pairs. The 15 generators of SU(4) then consist of two operators for singlet pairs ($D$ and $D^\dagger$), six operators for triplet pairs ($\pi$ and $\pi^\dagger$), three staggered magnetization operators $\mathbf{\hat{S}}$, three spin operators $\mathbf{S}$, and a number operator $\hat{n}$. An SU(4) Hamiltonian restricted to one and two-body interactions can be determined uniquely,

$$H = \epsilon n - G_0 D^\dagger D - G_1 \pi^\dagger \pi - \chi \mathbf{\hat{S}} \cdot \mathbf{\hat{S}} + \kappa \mathbf{S} \cdot \mathbf{S},$$

(1)

where $G_0$, $G_1$, and $\chi$ are effective strengths of d-wave singlet pairing, triplet pairing, and AF correlations, respectively. We shall assume the total spin to be zero and ignore the last term for the present discussion.

The SU(4) coherent state $|0\rangle$ is $|\rangle = \mathcal{F} |0\rangle$, where $|0\rangle$ is the physical vacuum and the unitary operator $\mathcal{F}$ is a 4-dimensional matrix parameterized in terms of variational parameters $u$ and $v$, with $u^2 + v^2 = 1$. It implements a quasiparticle transformation on the $D-\pi$ pair space that preserves SU(4) symmetry (implying no double occupancy)$2$. The corresponding matrix elements for one- and two-body operators are discussed in Ref[2] and matrix elements for the operators appearing in Eq. (1) are easily evaluated in the $\Omega \to \infty$ limit.

III. TEMPERATURE-DEPENDENT GAP EQUATIONS

Introducing the “gaps”

$$\Delta_d = G_0 \langle D^\dagger D \rangle^{\frac{1}{2}} \quad \Delta_\pi = G_1 \langle \pi^\dagger \pi \rangle^{\frac{1}{2}} \quad \Delta_\chi = \chi \langle \mathbf{\hat{S}} \cdot \mathbf{\hat{S}} \rangle^{\frac{1}{2}},$$

representing correlation energies for singlet pairing, triplet pairing, and AF, respectively, the variational Hamiltonian $H' = H - \lambda \hat{h}$ (with chemical potential $\lambda$) is

$$\langle H' \rangle = \langle \epsilon - \lambda \rangle n - \left( \Delta_d^2 / G_0 + \Delta_\pi^2 / G_1 + \Delta_\chi^2 / \chi \right).$$

(2)

Variation of $\langle H' \rangle$ with respect to $u_\pm$ and $v_\pm$ yields

$$2 u_\pm v_\pm (\epsilon_\pm - \lambda) - \Delta_d (u_\pm^2 - v_\pm^2) = 0,$$

(3)

which has the solution

$$u_\pm^2 = \frac{1}{2} \left( 1 + \frac{\epsilon_\pm - \lambda}{\epsilon_\pm} \right) \quad v_\pm^2 = \frac{1}{2} \left( 1 - \frac{\epsilon_\pm - \lambda}{\epsilon_\pm} \right) \quad \Delta_d = \Delta_d \pm \Delta_\pi$$

(4)

$$e_\pm = \left( \epsilon_\pm - \lambda \right)^2 + \Delta_d^2.$$
where we define
\[ \epsilon_{\pm} = \epsilon \mp \Delta q. \] (5)
From Eq. (4), the definitions for \( \Delta_d, \Delta_x, \) and \( \Delta_q \), and a theoretical doping fraction \( x = 1 - n/\Omega \) with \( n \) the electron number, we obtain the temperature-dependent gap equations
\[ \Delta_d = \frac{G_0\Omega}{4} (w_+\Delta_+ + w_-\Delta_-) \] (6)
\[ \Delta_x = \frac{G_1\Omega}{4} (w_+\Delta_+ - w_-\Delta_-) \] (7)
\[ \frac{4\Delta_q}{\chi\Omega} = \frac{w_+ (\Delta_q + \lambda') + w_- (\Delta_q - \lambda')}{e} \] (8)
\[ -2x = \frac{w_+ (\Delta_q + \lambda') - w_- (\Delta_q - \lambda')}{e} \] (9)
where \( \lambda' \equiv \lambda - \epsilon \) and
\[ w_\pm = \frac{1 - \tilde{n}_\pm(T)}{e}. \] (10)
The quasiparticle number densities \( \tilde{n}_\pm(T) \) are assumed to be
\[ \tilde{n}_\pm = \frac{1}{1 + \exp(\beta E_{\pm}/\hbar T).} \] (11)
where \( \tilde{n}_\pm \equiv 0 \) and \( w_\pm = 1/e_{\pm} \) if \( T = 0 \). The gaps and \( \lambda \) follow from the algebraic equations (6)-(9), the energy \( E \) can be calculated from (2) and
\[ E = \langle H' \rangle + n\lambda, \] (12)
and \( e_{\pm}, u_{\pm}, \) and \( v_{\pm} \) are determined by Eqs. (4). This defines a complete formalism permitting calculation of general observables.

These results are similar to the BCS theory but with important differences. Here we have two pairing energy gaps and two kinds of quasiparticles, implying complex behavior (ultimately tracing to the non-abelian commutator algebra for the SU(4) operators). The quantities \( e_{\pm} \) correspond to two sets of single-particle energies \( \{ \epsilon_{\pm} \} \), split by \( 2\Delta_q \) in the AF background. Each level can be occupied by one electron of spin up or down. The corresponding pairing gaps are \( |\Delta_{\pm}| \) and the probabilities for single-particle levels to be unoccupied or unoccupied are \( u_{\pm}^2 \) and \( v_{\pm}^2 \), respectively. When \( G_1 = \chi = \kappa = 0 \), Eq. (11) reduces to a pairing Hamiltonian, \( \Delta_x = \Delta_q = 0 \), and Eqs. (3)-(4) reduce to the usual BCS equations.

IV. SOLUTION OF THE GAP EQUATIONS

We now describe the solution of the gap equations (6)-(9), first for temperature \( T = 0 \) and then for finite \( T \). Data suggest that in hole-doped cuprates the interactions in (6)-(9) are attractive, with AF correlation strongest and triplet pairing weakest. Assuming that \( \chi \geq G_0 \geq G_1 \geq 0 \), we find the general \( T = 0 \) solution
\[ \Delta_q = \frac{1}{4} \chi \Omega [(x_q^{-1} - x) (x_q - x)]^{1/2} \] (13)
\[ \Delta_d = \frac{1}{4} G_0 \Omega [(x^{-1} - x) x_q^{-1} - x_q]^{1/2} \] (14)
\[ \Delta_x = \frac{1}{4} G_1 \Omega [(x^{-1} - x) x_q - x]^{1/2} \] (15)
\[ \lambda' = -\frac{1}{2} \chi \Omega x_q (1 - x_q x) - \frac{1}{2} G_1 \Omega \chi, \] (16)
which exists only for \( x \) less than a critical doping
\[ x_q \equiv \left( \frac{\chi - G_0}{\chi - G_1} \right)^{1/2}. \] (17)
The dependence of \( x_q \) on three elementary interaction strengths shows explicitly that the critical doping point results from competition between correlations. A trivial \( \Delta_q = \Delta_x = 0 \) (pure singlet) solution exists also in the entire physical doping range \( 0 \leq x \leq 1 \),
\[ \Delta_0 \equiv \Delta_q = \frac{1}{2} G_0 \Omega [(1 - x^2)]^{1/2} \] (18)
Trivial solutions valid for \( 0 \leq x \leq 1 \) that correspond to pure triplet pairing, pure AF states, and metallic states (all \( \Delta_i = 0 \)) may be found also, but insertion of \( \Delta_q, \Delta_d \) and \( \Delta_x \) into Eq. (2) indicates that the nontrivial solution is always the ground state where it exists \( (0 \leq x \leq x_q) \), and that for \( x > x_q \), Eq. (18) gives the ground state. Thus, when \( x > x_q \) the ground state is a pure singlet pairing state given by (18), but when \( x \leq x_q \) the solution (13)-(16) (which differs from the singlet pairing state in permitting finite values for \( \Delta_d, \Delta_x, \) and \( \Delta_q \)) is the ground state and (18) defines an excited state. The critical doping point \( x_q \) separates these two qualitatively distinct ground states and marks a quantum phase transition.

V. CUPRATE GAP DIAGRAMS

We now use these results to construct gap diagrams for cuprate superconductors. The parameters \( G_0, G_1, \) and \( \chi \) are effective interaction strengths within a truncated space. In Fig. (1), we first make the simplest possible approximation and assume that they are constants, independent of doping. Four energy scales are shown:
1. \( \Delta_q \), which measures AF correlations;
2. the singlet pairing gap \( \Delta_q \) [Eq. (14)], which is the superconducting gap for \( x < x_q \);
3. the singlet pairing gap \( \Delta_0 = \Delta_d \) [Eq. (18)], which is the superconducting gap for \( x > x_q \) but is not the ground-state order parameter for \( x < x_q \);
4. the triplet pairing gap \( \Delta_x \).

The AF gap \( \Delta_q \) is maximal at \( x = 0 \), decreases rapidly with doping, crosses the pairing gaps, and vanishes at the critical doping \( x_q \). Like \( \Delta_q \), the triplet gap \( \Delta_x \) exists only within the doping range \( 0 \leq x \leq x_q \); it peaks at \( x_q/2 \). For \( x > x_q \), the singlet gap is the curve \( \Delta_q \) but below \( x_q \) it splits into two curves \( (\Delta_x \) and \( \Delta_0 \) having different doping behavior. Also shown in Fig. (1) are gap data from Refs. [11-13] that support the complex gap structure suggested by the SU(4) quasiparticle solutions. In particular, the predicted splitting of the singlet pairing gap and termination of the \( \Delta_q \) gap at a critical doping \( P_q \approx x_q \) are consistent with the data points plotted.

Figure [1] suggests qualitative agreement between predicted and observed gap structure at \( T = 0 \) but there are two quantitative discrepancies: (1) the slope of \( \Delta_q \) is too small at low
doping, and (2) the onset of a pairing gap at zero doping in the calculation contradicts data suggesting that this onset should occur closer to 5% hole doping. These discrepancies indicate that the constant coupling strength assumption gives unrealistic strong pairing and too weak AF strength in the low-doping region. They can be removed by allowing a simple doping dependence for the coupling strengths according to the following physical considerations. First, the SU(4) symmetry requires that the pure AF state can exist only when \( G_0 = 0 \), which suggests that pairing strength must have an onset at \( P > 0 \). Second, to reproduce the experimental Neél temperature, \( \chi \) has to be strongest at \( P = 0 \). These suggest a doping dependence for \( G_0, G_1 \), and \( \chi \) given by the inset to Fig. 1, which implies an onset of pairing strength at \( P = 0.05 \) (in the simplest picture we assume the same onset for singlet and triplet pairing, but with different magnitudes), and a large AF correlation at half-filling that decreases as doping increases, but finally is stabilized as pairing is established. With that change, the more quantitative agreement with data shown in Fig. 1: results.

VI. SCALING BEHAVIOR

In Figs. 1a and 1b: all energies are scaled by \( k(T_c)_{\text{max}} \). The solution [14] indicates that \( \Delta_\ell \) depends only on \( x_q \), once \( G_0 \) is fixed. If the critical doping \( x_q \) has a universal value (for example, see Ref. [5]), the doping dependence for \( \Delta_\ell \) also should be universal if gaps are scaled by the maximum \( T_c \) for each compound, since the maximum \( T_c \) is proportional to \( G_0 \) (see Ref. [5]). It is well known that cuprate SC pairing gaps exhibit such scaling.

VII. COMPETING ORDER AND PREFORMED PAIRS

The emergence of the critical doping \( x_q \) and the splitting of the singlet gap for \( x < x_q \) are a direct consequence of competing pairing and AF correlations below \( x_q \). When doping is low, AF correlations dominate pairing and a state with large AF gap and suppressed pairing is the ground state. Therefore, the superconducting gap for the ground state is small (\( \Delta_\ell < \Delta_0 \)) and the large pairing gap \( \Delta_0 \) is associated with an excited state when \( x < x_q \). However, as doping increases the SU(4) symmetry implies that pairing correlations decrease less quickly than the AF correlations (see Ref. [5]) and they eventually dominate. The energy is then minimized by larger pairing and diminished AF correlation. The critical point \( x_q \) is the hole-doping fraction where the ground-state AF correlations vanish completely in the variational solution.

The competing-order picture assumes that the pseudogap (PG) is an energy scale for order competing with superconductivity that vanishes at a critical doping point where the competition is completely suppressed. From Figs. 1a and 1c, \( \Delta_\ell \) (an order parameter of the AF phase) has precisely these properties. But the AF operators are generators of SU(4), so \( \Delta_\ell \) also is the stabilization energy for a mixture of preformed singlet and triplet SU(4) pairs that condense into a strong superconducting state only after AF and triplet pairing fluctuations are suppressed by hole doping. This represents a non-abelian generalization of the standard phase-fluctuation model [15] for preformed pairs. Thus, the SU(4) pseudogap state results from competing AF and SC order expressed in a basis of singlet and triplet fermion pairs, which may be viewed as a unification of the competing order and preformed pair pictures.

FIG. 1: (Color online) Energy gap diagrams at \( T = 0 \) (a, c) and phase diagrams (b, d) for hole-doped cuprates. The doping rate \( P \) is defined as \( P = (\Omega - n)/\Omega_c \) with \( \Omega_c \) and \( \Omega \) being the number of lattice sites and the maximum allowed number of holes, respectively. In (a) and (b) constant interaction strengths are assumed: \( G_1 = 3.74, G_0 = 8.2, \) and \( \chi = 13, \) while in (c) and (d) doping-dependent strengths indicated by the insets to the figures are used. In all plots \( G_0 = 0.18, \) except for the dotted line in (d) marked \( T'_c \), which illustrates how the phase boundary marked \( T_c \) shifts if \( G_0 = 0.16 \). The green dashed curve in (b) and (d) is the empirical \( T_c \) curve: \( T_c = T_c_{\text{max}}[1 - 0.16(P - 0.16)]^2 \). Data in (a) and (c) are taken from Refs. [6,7], and in (b) and (d) from Refs. [8,9,10,11,12,13], respectively. Note that data in (b) and (d) marked with the legend (Dai) taken from Ref. [14] and include data taken from Refs. [11,12,13].
VIII. THE ROLE OF TRIPLET PAIRS

Triplet pairs are an essential component of the SU(4) many-body wavefunction (for example, the SU(4) algebra, which imposes the no double occupancy condition on the lattice, does not close in the absence of triplet pair operators). However, Fig. 1 indicates that the triplet pair correlation energy is small in the underdoped region and zero for doping larger than $P_q$. The primary role of triplet pairs in the hole-doped cuprates appears to lie in fluctuations mediating the AF–SC competition.

IX. CUPRATE PHASE DIAGRAMS

In Figs. 1b and 1d we show phase diagrams resulting from finite-temperature calculations. Figure 1b assumes the coupling strengths of Fig. 1a, so the only adjustable parameter in either case is $R = 0.6$. The empirical factor $R < 1$ (see Eq. (1)) is introduced because actual single-particle energies due to thermal excitation are non-degenerate and realistic quasiparticle excitation should be easier than in our degenerate approximation. There are four distinct phases in Figs. 1b and 1d:

1. An antiferromagnetic phase (labeled AF).
2. A superconducting phase (labeled SC).
3. A transitional phase with all three correlations present (labeled AF+SC).
4. A metallic phase.

The correlations involved in each phase are indicated in parentheses in Figs. 1b and 1d, and $T_c$, $T^\ast$, and $T_q$ mark the phase boundaries. Data from Refs. 8, 9, 10 are compared with the predicted SU(4) phase structure in Figs. 1b and 1d. The constant coupling approximation (Fig. 1b) reproduces data quantitatively, but the predicted superconductivity extends too low in doping and the upper boundary on the AF phase does not rise steeply enough at low doping (leading to a Néel temperature a factor of 2–3 too low). These discrepancies are removed in Fig. 1d, which allows the evolution of coupling with doping indicated in the inset.

It is commonly believed that in the cuprate phase diagram there is a boundary (for example, the one labeled $T_N$ in Ref. 14) distinguishing an AF long-range ordered state from a disordered one. We do not discuss this possibility here but note that the potential to describe such a boundary is contained in the present model. If (contrary to our minimal assumptions here) we permit onset of the triplet pairing strength at somewhat lower doping than for the singlet pairing, a new boundary will appear in the very-low doping region ($P \approx 0.02–0.05$) that separates a pure AF phase from the PG region.

There are additional (generally higher-temperature) data that have been related to the pseudogap discussion beyond that displayed in Fig. 1. Their physical interpretation is generally unsettled. Our theoretical $T^\ast$ is clearly defined as the temperature at which the PG in the SU(4) model goes to zero. Once the interaction strengths are fitted to the gap data, there are no free parameters to modify the theoretical $T^\ast$ curve. Thus, any reproducible data that lie substantially above our predicted $T^\ast$ curve may be associated either with physics that goes beyond the minimal model that is described here, or with a definition for $T^\ast$ that is inconsistent with ours.

X. DISCUSSION OF SUPPORTING DATA

The results of Fig. 1 are supported by various additional data. We mention a few representative examples. NMR measurements using strong magnetic fields to suppress SC in Bi$_2$Sr$_{2−x}$La$_x$CuO$_{6+δ}$ concluded that the PG coexists with SC and terminates in a critical point near $P \approx 0.21$. Figure 1d could accommodate $P_q \approx 0.21$ with small parameter changes, but also we note that magnetic fields could increase $P_q$ by altering the SC–AF competition. From specific heat, NMR, and transport data, Tallon et al. concluded that high-$T_c$ phase behavior is universal, with a critical doping $P \approx 0.19$ where the PG vanishes and where large changes in quantities like the superfluid density indicate crossover from weak to strong superconductivity, and that this transition implies vanishing short-range magnetic order. A key role for magnetic correlations in PG states also is suggested by the effect of impurities on $c$-axis optical conductivity. In-plane resistivity measurements indicate that the phase diagram is surprisingly universal, with a PG terminating near optimal doping and different electronic states either side of the termination. These measurements also indicate a crossover above $T_c$ between two kinds of PG behavior (see also Ref. 15), which may be explicable in terms of the finite but decreasing pair fluctuations expected in the PG region, as we now discuss.

Figure 1 may explain the vortex-like Nernst signal observed above $T_c$. The singlet pair gap vanishes there but the many-body SU(4) wavefunction has finite pair content between the curves $T^\ast$ and $T_c$ that decreases with increasing $T$ and decreasing doping. Thus, contours for pair fluctuations above $T_c$ will be similar to observed contours for Nernst signal strength, but a Meissner effect is expected only below $T_c$. Recently, Ong et al. concluded that a consistent explanation of pseudogap and Nernst data requires PG and SC pairing states that are distinct but related by symmetry, as proposed here.

More detailed properties of Fig. 1 may be investigated in future work. For example, the transition between the AF+SC and SC phases is 2nd-order if $P_q$ lies at higher doping than the point $b$ (solid curve $T_q$ in Fig. 1d), but is 1st-order if it lies at lower doping (dotted curve $T_q^\ast$, starting from the point $a$). This implies a wealth of testable consequences for the gap and phase structure depending both on global properties and on microscopic details.
XI. SUMMARY AND CONCLUSIONS

In summary, finite-temperature SU(4) coherent states have been used to construct a rich, universal gap and phase structure for hole-doped cuprates that may be expressed in a BCS-like formalism with two kinds of quasiparticles and competing superconducting and antiferromagnetic order. We find a pseudogap of antiferromagnetic character terminating at a critical doping $P \simeq 0.18$ that is distinct from the superconducting state but related to it by a non-abelian symmetry. The corresponding pseudogap states may be interpreted in terms of either SC–AF competition or preformed SU(4) pairs that condense into a singlet $d$-wave superconductor as hole doping suppresses fluctuations. Our results represent a minimal variational solution of competing antiferromagnetism and $d$-wave superconductivity on a fermionic lattice with no double occupancy. Therefore, we believe that the general gap and phase structure presented here will be a necessary consequence of any realistic theory that takes a doped Mott insulator with competing $d-$wave pairing and antiferromagnetism as the basis for describing high-temperature superconductivity.

1. M. W. Guidry, L.-A. Wu, Y. Sun, and C.-L. Wu, Phys. Rev. B 63, 134516 (2001).
2. L.-A. Wu, M. W. Guidry, Y. Sun, and C.-L. Wu, Phys. Rev. B 67, 014515 (2003).
3. M. W. Guidry, Y. Sun, and C.-L. Wu, Phys. Rev. B 70, 184501 (2004).
4. Y. Sun, M. W. Guidry, and C.-L. Wu, Phys. Rev. B 73, 134519 (2006).
5. W.-M. Zhang, D. H. Feng and R. Gilmore, Rev. Mod. Phys. 62, 867 (1990).
6. J. L. Tallon and J. W. Loram, Physica C 349, 53 (2001).
7. J. L. Tallon et al., Phys. Rev. B 68, 180501 (2003).
8. P. Dai, et al., Science 284, 1344 (1999).
9. M. Oda, et al., Physica C 281, 135 (1997).
10. T. Watanabe, et al., Phys. Rev. Lett. 84, 5848 (2000).
11. B. Wuyts, V. V. Moshchalkov, and Y. Bruynseraede, Phys. Rev. B 53, 9418 (1996).
12. M. Takigawa, et al., Phys. Rev. B 43, 247 (1991).
13. T. Ito, K. Takenaka, and S. Uchida, Phys. Rev. Lett. 70, 3995 (1993).
14. T. Timusk and B. Statt, Rep. Prog. Phys. 62, 61 (1999).
15. V. J. Emery and S. A. Kivelson, Nature 374, 434 (1995).
16. G.-q. Zheng et al., Phys. Rev. Lett. 94, 047006 (2005).
17. J. L. Tallon, et al., Physica C 415, 9 (2004).
18. A. V. Pimenov, et al., Phys. Rev. Lett. 94, 227003 (2005).
19. Y. Ando, et al., Phys. Rev. Lett. 93, 267001 (2004).
20. A. N. Lavrov, et al., Europhys. Lett. 57 (2), 267 (2002).
21. Z. A. Xu, et al., Nature 406, 486 (2000).
22. N. P. Ong, et al., Annalen der Physik 13, 9 (2004).