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ARTICLES

Coulomb interactions and generalized pairing in condensed matter

K. Moulopoulos
University of Cyprus, Department of Natural Sciences, P.O. Box 537, 1678 Nicosia, Cyprus

N. W. Ashcroft
Cornell Center for Materials Research and Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York

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Proceeding from a coherent-state functional-integral approach we give a first-principles theory of generalized pairing phases in a dense neutral system of electrons and protons. Apart from a standard stationary phase approximation the approach is general, it requires no adiabatic separation of time scales, and it can be applied for arbitrary temperatures. For the resulting mean-field theory, we show that pairing of *both* electrons *and* protons is possible at low temperatures, and especially so when an appropriately defined electron-proton order parameter becomes sufficiently large. As a preliminary to the experimentally important case where the protons order in a crystalline phase, the case of continuous symmetry is first presented. Among generic results is the prediction, through a stability analysis, of a charge-density wave (and repairing), and the location of a critical point, both discussed in light of recent experiments on the high-pressure states of hydrogen. [S0163-1829(99)05219-4]

I. INTRODUCTION

It is clear experimentally, and also well understood since the initiating paper of Heitler and London[1] that in the four-particle problem represented by two electrons and two protons, the ground state is one in which the protons are strongly paired by the electrons. This pairing is known to persist in the condensed crystalline state of hydrogen to very high densities, approaching 11-fold compression over the self-stabilized density. Given the simplicity and symmetry of the many-body Hamiltonian governing such a system, the question of pairing in a more general sense naturally arises. Put in its simplest form the question could be posed this way: in a dense dual Fermion system of N electrons and N protons, can the protons themselves lead to pairing of electron states? In the context of ordinary superconductivity in simple metals, the answer can be considered well known. Here we will focus specifically on the notion of mutual pairing of electrons and protons, but go one step further and inquire, in the many-particle context about collective quantum states that also involve electron-proton pairing.

Though the system to be discussed is an ensemble of electrons (charge $-e$) and protons (charge $+e$), the problem can be generalized still further to two distinct sets of Fermions of opposite charges and with different masses, examples being electrons and positrons, electrons and μ^+ mesons, etc. The changes required for positive particles of charge $+Ze$ are quite straightforward, provided conditions on density are chosen appropriately. We choose to start with the fundamental Hamiltonian without formally breaking the translational symmetry; this way our results rigorously apply to continuous single-particle states. We then provide the modifications necessary to describe the important class of experimental states where one class of Fermions exhibits crystalline order. The formal changes required to embrace crystalline physics are actually not extensive and can be handled within the same method, but the results are now richer, presenting significant band-mode structure for both components. Although we point to some important changes, expected from the corresponding physical modifications, we argue that some of the general mean-field conclusions are not qualitatively affected.

In approaching the problem of collective quantum states a powerful method is the functional-integral technique,[2,3] where the partition function for the many-body system (in a grand-canonical ensemble at finite temperatures) is written as a coherent-state functional integral.[4] In the case of Fermions this integral is recast in terms of Grassmann variables $\{\Psi^*,\Psi\}$ rather than complex variables, thereby defining an action $S[\Psi^*,\Psi]$ that is generally not expected to be calculable for an arbitrary many-body system. Then the usual procedure is to perform, for the interaction term, an appropriate Hubbard-Stratonovich (HS) transformation[5,6] as dictated by the physics that is being pursued. In this way new collective fields $\{\Delta^*,\Delta\}$ are introduced as well as a new action $\tilde{S}[\Psi^*,\Psi;\Delta^*,\Delta]$ the latter now being quadratic in the Ψ's. By carrying out a Gaussian integration the final action $\overline{S}[\Delta^*,\Delta]$ is obtained in terms of the new fields Δ and up to this point the procedure is exact. From this point on approximation is necessary, one path being to follow a stationary phase approximation (SPA) to the new partition function, i.e., by imposing an extremization of $\overline{S}$ with respect to the Δ's. The extremization of $\overline{S}$ gives the mean-field equations that the new field Δ is obliged to satisfy. As noted, the choice of the HS transformation is dictated by the collective characteristics of the physics considered, while the stationary-phase approximation is merely equivalent to an assumption that the collective character of the physics was indeed correctly chosen and the fluctuations around the mean-field solution for the Δ's are therefore small (and can be ignored as a first step).

The above scheme is directly applicable to a single-component Fermion system with pairing correlations. The appropriate HS transformation for this problem is well known,[2,7] and in this case the new collective field Δ is the corresponding BCS gap parameter. The final equation for Δ resulting from the extremization of $\overline{S}$ is then the BCS gap equation. As background to the electron-proton problem that follows, it is useful to review this continuous phase one-component procedure (Sec. II) since the formal changes required for crystalline phases are not substantially different. In Sec. III we then give a complete generalization to a two-component system of oppositely charged Fermions with different masses (electrons and protons being an example), which leads, not unexpectedly, to four gap equations. These correspond to electron-electron, proton-proton, and electron-proton pairings. Depending on density range these equations have interesting limiting behavior, a matter that is discussed in Sec. IV; by way of application we also consider in Sec. V the modifications required for the standard experimental situation where the proton states possess crystalline symmetry, and we discuss the ensuing results in relation to dense hydrogen. Finally, in Sec. VI we discuss possible generalizations of the method to other physical systems.

II. FUNCTIONAL INTEGRAL APPROACH FOR A ONE-COMPONENT SYSTEM

We start from the grand-partition function Z for a one-component system of identical Fermions in volume V, at temperature T and chemical potential μ (for notational convenience we set $\hbar = 1$ in everything that follows). In terms of a coherent-state functional integral the partition function Z is generally written as[4]

$$Z = \int_{\Psi(x,\beta) = -\Psi(x,0)} D[\Psi^*(x\tau)] D[\Psi(x\tau)] \times \exp(-S[\Psi^*,\Psi]) \tag{1}$$

where S is the action

$$S = \int_0^\beta d\tau \left\{ \int dx \Psi^*(x\tau) \left(\frac{\partial}{\partial\tau} - \mu \right) \Psi(x\tau) + H[\Psi^*(\tau),\Psi(\tau)] \right\} \tag{2}$$

In Eq. (2) we choose a notation that includes spin, namely $x = \{\mathbf{r}, s\}$ in terms of which $\int dx = \Sigma_s \int d^3r$. Generally, the paths in the partition function are constrained by the standard periodic- or antiperiodic-boundary conditions corresponding to Bosons or Fermions, respectively. In our case of Fermions antiperiodic boundary conditions have been used in Eq. (1) as constraints in the selection of paths. The Hamiltonian H in Eq. (2) is assumed to be in normal order (i.e., all Ψ^*'s appear to the left of all Ψ's), and for a one-component system with static pairwise interactions it is given by

$$H[\Psi^*,\Psi] = \int dx \Psi^*(x\tau) \epsilon(-i\nabla) \Psi(x\tau) + \frac{1}{2} \int dx\, dy \Psi^*(x\tau) \Psi^*(y\tau) v(x-y) \times \Psi(y\tau) \Psi(x\tau). \tag{3}$$

A combination of Eqs. (2) and (3) then leads to the separation

$$S[\Psi^*,\Psi] = \int_0^\beta d\tau \int dx\, dy \left\{ \Psi^*(x\tau) \delta(x-y) \times \left[\frac{\partial}{\partial\tau} + \epsilon(-i\nabla) - \mu \right] \Psi(y\tau) + \frac{1}{2} \Psi^*(x\tau) \Psi^*(y\tau) v(x-y) \Psi(y\tau) \Psi(x\tau) \right\} \equiv S_0 + S_{\text{int}} \tag{4}$$

In Eq. (4) the $\epsilon(k)$ are single-Fermion energies (for a translationally invariant system $\epsilon(k) = k^2/2m$, for localized states see below), v is the effective pairwise interaction between the identical Fermions (and not necessarily attractive at this level), the Ψ's are the Grassmann variables parametrizing the Fermion coherent states for this system, and finally S_0 denotes the term not containing v. We next use a Gaussian integration, which is generally valid for Grassmann numbers, namely

$$\exp\left[\int d1\, d2\, f^*(1) C^{-1}(1,2) f(2) \right] = (\det C)^{-1} \int D[\Delta^*] D[\Delta] \times \exp\left(-\int d\bar{1} d\bar{2} \{ \Delta^*(\bar{1}) C(\bar{1},\bar{2}) \Delta(\bar{2}) + \delta(\bar{1}-\bar{2}) \times [f^*(\bar{1}) \Delta(\bar{1}) + f(\bar{1}) \Delta^*(\bar{1})] \} \right). \tag{5}$$

In order to apply Eq. (5) we use variables $1 \equiv xy\tau, 2 \equiv x'y'\tau'$ etc. and make the identifications

$$f(1) \equiv \Psi(x\tau) \Psi(y\tau) \tag{6}$$

and

$$C^{-1}(1,2) = -\frac{\tilde{v}(xy\tau, x'y'\tau')}{2} \tag{7}$$

(the reciprocal being understood in the functional sense) with

$$\tilde{v}(xy\tau, x'y'\tau') = v(x-y) \delta(x-x') \delta(y-y') \delta(\tau-\tau'). \tag{8}$$

Then because of Eq. (5) we may invoke a Hubbard-Stratonovich transformation, namely

$$\exp[-S_{\text{int}}] = (\text{const}) \int D[\Delta^*] D[\Delta] \exp[-S'], \tag{9}$$

with

$$S' = \int d1\, d2 \Delta^*(1) C(12) \Delta(2) - \int d1 [f^*(1)\Delta(1) + f(1)\Delta^*(1)]. \tag{10}$$

Finally, if we rescale $\Delta \rightarrow -\Delta/2$ we obtain in detailed form

$$Z[\Psi^*,\Psi;\Delta^*,\Delta] = (\mathrm{const}) \int D[\Psi^*] D[\Psi] D[\Delta^*] D[\Delta] \times \exp\{\tilde{S}[\Psi^*,\Psi;\Delta^*,\Delta]\}, \tag{11}$$

with

$$\tilde{S}[\Psi^*,\Psi;\Delta^*,\Delta] = \int_0^\beta d\tau \int dx\, dy \Big\{ \Psi^*(x\tau)\delta(x-y) \times \left[-\frac{\partial}{\partial\tau} - \epsilon(-i\nabla) + \mu \right] \Psi(y\tau) - \frac{1}{2}\Delta^*(xy\tau)\Psi^*(x\tau)\Psi^*(y\tau) - \frac{1}{2}\Delta(xy\tau)\Psi(y\tau)\Psi(x\tau) + \frac{1}{2}\frac{1}{v(x-y)}|\Delta(xy\tau)|^2 \Big\}. \tag{12}$$

The quite crucial point for the two-component case to follow is that Eq. (12) can be recast in a compact *matrix form*, namely

$$\tilde{S}[\Psi^*,\Psi;\Delta^*,\Delta] = \int d1\, d2 \left\{ \frac{1}{2}\mathbf{\Phi}^*(1)[-\hat{A}(12)]\mathbf{\Phi}(2) + \frac{1}{2}\Delta^*(12)\frac{1}{v(1-2)}\Delta(12) \right\} \tag{13}$$

where now we have changed notation to local variables $1 \equiv x\tau$ and we have also defined a vector

$$\mathbf{\Phi}(1) \equiv \begin{bmatrix} \Psi(1) \\ \Psi^*(1) \end{bmatrix} \tag{14}$$

and a matrix

$$\hat{A}(12) \equiv \begin{Bmatrix} \delta(1-2)\left[\frac{\partial}{\partial\tau} + \epsilon(-i\nabla) - \mu\right] & \Delta(12) \\ \Delta^*(12) & \delta(1-2)\left[\frac{\partial}{\partial\tau} - \epsilon(-i\nabla) + \mu\right] \end{Bmatrix}. \tag{15}$$

As a consequence the partition function (11) can be written, equally compactly, as

$$Z = (\mathrm{const}) \int D[\Delta^*] D[\Delta] \int D[\mathbf{\Phi}^*] D[\mathbf{\Phi}] \exp\left\{ \int d1\, d2 \left[-\frac{1}{2}\mathbf{\Phi}^*(1).\hat{A}(12).\mathbf{\Phi}(2) \right] \right\} \times \exp\left[\int d1\, d2 \frac{1}{2}\Delta^*(12)\frac{1}{v(1-2)}\Delta(12) \right] \tag{16}$$

and this presents a form where we can once again use the Gaussian integration (5) to eliminate the old fields Ψ. In this case the functional integral over $\mathbf{\Phi}$ in Eq. (16) simply gives $\det(\hat{A}/2)$, which can also be written[2] as $\exp[\mathrm{tr}\ln(\hat{A}/2)]$. The final result is, therefore,

$$Z = (\mathrm{const}) \int D[\Delta^*] D[\Delta] \exp(\bar{S}[\Delta^*,\Delta]), \tag{17}$$

with

$$\bar{S}[\Delta^*,\Delta] = \mathrm{tr}\ln\left(\frac{\hat{A}}{2}\right) + \frac{1}{2}\int d1\, d2 \frac{|\Delta(12)|^2}{v(1-2)}. \tag{18}$$

This result for Z is exact[2] but written in terms of a field Δ, which is unknown. To elucidate the physical meaning to be attached to Δ we proceed with the usual SPA which is embodied in the statements

$$\frac{\delta\bar{S}}{\delta\Delta^*} = \frac{\delta\bar{S}}{\delta\Delta} = 0. \tag{19}$$

This approximation is well known to be very accurate in standard BCS-type theories involving pairing in momentum space, and a physical discussion of its more general validity[8] is given in the next section. If a solution to Eq. (19) exists, it will provide the mean-field result for Δ, and the resulting Δ is the usual BCS gap parameter, as is now demonstrated:

First, extremization of Eq. (18) with respect to the Δ's yields

$$\frac{\delta\bar{S}}{\delta\Delta^*(12)} = \frac{\Delta(12)}{v(12)} + \mathrm{tr}\left[\hat{A}^{-1}(12)\begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}\right] = 0,$$

or

$$\Delta(12) = -v(12)\,\mathrm{tr}\left[\hat{A}^{-1}(12)\begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}\right]. \tag{20}$$

Next, imposition of the condition

$$\frac{\delta\bar{S}}{\delta\Delta(12)} = 0$$

gives

$$\Delta^*(12) = -v(12)\,\mathrm{tr}\left[\hat{A}^{-1}(12)\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}\right]. \tag{21}$$

Now $\hat{A}^{-1}$ is the Green's-function matrix $\hat{G}$ for the fundamental particles moving in the pairing field in the sense that

$$\int d3\,\hat{A}(13)\hat{G}(32) = \delta(12)\hat{1}. \tag{22}$$

We next Fourier transform to **k**-space and Matsubara frequencies ω_n (which account for the antiperiodicity properties of the Grassmann fields as functions of τ with period β), i.e., we write

$$\hat{G}(32) = \frac{1}{\beta}\sum_{\omega_n} e^{-i\omega_n \tau_{32}} \int \frac{d^3k}{(2\pi)^3} e^{i\mathbf{k}\mathbf{r}_{32}} \hat{G}(\mathbf{k},\omega_n), \tag{23}$$

where the Matsubara frequencies for Fermions are the poles of the Fermi function, namely

$$i\omega_n = i(2n+1)\frac{\pi}{\beta}. \tag{24}$$

Then, Eq. (22) reads

$$\frac{1}{\beta}\sum_{\omega_n} \int \frac{d^3k}{(2\pi)^3} e^{i\mathbf{k}\mathbf{r}_{12}} e^{-i\omega_n\tau_{12}} \begin{bmatrix} -i\omega_n + \epsilon(\mathbf{k}) - \mu & \Delta(\mathbf{k}) \\ \Delta^*(\mathbf{k}) & -i\omega_n - \epsilon(\mathbf{k}) + \mu \end{bmatrix} \hat{G}(\mathbf{k},\omega_n) = \delta(12)\hat{1}, \tag{25}$$

and this shows that

$$\hat{G}(\mathbf{k},\omega_n) = \frac{1}{\omega_n^2 + [\epsilon(\mathbf{k}) - \mu]^2 + |\Delta(\mathbf{k})|^2} \begin{pmatrix} i\omega_n + \epsilon(\mathbf{k}) - \mu & \Delta(\mathbf{k}) \\ \Delta^*(\mathbf{k}) & i\omega_n - \epsilon(\mathbf{k}) + \mu \end{pmatrix}. \tag{26}$$

Using this in the Fourier transform of Eq. (20) we obtain

$$\Delta(\mathbf{k}) = -\frac{1}{\beta}\sum_{\mathbf{k}'}\sum_{\omega_n} v(\mathbf{k}-\mathbf{k}') \frac{\Delta(\mathbf{k}')}{\omega_n^2 + [\epsilon(\mathbf{k}') - \mu]^2 + |\Delta(\mathbf{k}')|^2} \tag{27}$$

and in a similar way Eq. (21) gives the complex conjugate equation.

Finally, we are required to carry out the frequency sums over the Matsubara frequencies ω_n in Eq. (27). These are found in Appendix A and the final result is very familiar, namely

$$\Delta(\mathbf{k}) = -\sum_{\mathbf{k}'} v(\mathbf{k}-\mathbf{k}') \frac{\Delta(\mathbf{k}')}{2E(\mathbf{k}')} \tanh\frac{\beta E(\mathbf{k}')}{2}, \tag{28}$$

where

$$E(\mathbf{k}) = \sqrt{[\epsilon(\mathbf{k}) - \mu]^2 + |\Delta(\mathbf{k})|^2}. \tag{29}$$

This is the usual BCS gap equation for the gap parameter Δ at temperature T, together with the standard BCS quasiparticle spectrum (29). It describes Cooper pairs at high densities, and even tightly bound pairs (''Schafroth pairs'') in the low-density limit[9] (where it simply gives the Schrödinger equation for the pair wave function in **k** space). Accordingly, this procedure, which we shall next extend to two components, demonstrates the manner in which the results of standard pairing theories can be derived for a one-component system with some effective static pairing interaction v proceeding from a very compact and general approach within a stationary phase argument. The physical possibility of pairing depends of course on whether the physical nature of v is such that Eq. (28) possesses nonzero solutions for Δ (an attractive interaction, for example, is more likely to yield a solution); and even if this is true, it certainly depends on whether the pairs constitute a stable phase, which in turn requires a positive determinant for the second derivative matrix of $\overline{S}$ with respect to Δ's. This latter point is also of importance in the stability of pairing phases in the two component context (see below).

III. FUNCTIONAL INTEGRAL APPROACH FOR A TWO-COMPONENT SYSTEM

Motivated by the physical example of hydrogen, a dual Fermion system, we now discuss in detail the simplest generalization of the above procedure to the simultaneous formation of all possible pairs (f_af_a, f_af_b, f_bf_b) arising in a neutral and thermodynamic mixture of two different classes of Fermions, but now with the fundamental Coulomb interactions included in all such pairings. As will be seen, the structure of the development closely parallels the one-component case, although the presence of two components and the symmetry of the Hamiltonian leads to a generalized matrix description that has no analog in the one-component case (see below). Once again we start from the grand-partition function Z for this two-component system in volume V, at temperature T and chemical potential $\mu = \mu_e + \mu_p$. The definitions of the chemical potentials in this case involve number variations, which are constrained to neutral fluctuations; this is nontrivial and it results[10] in interesting relations between μ_e, μ_p and linear-response functions. In terms of a coherent-state functional integral the partition function Z is now written as the straightforward parallel of Eq. (1), namely

$$Z=\int D[\Psi_e^*(x\tau)]D[\Psi_e(x\tau)]\int D[\Psi_p^*(x\tau)]D[\Psi_p(x\tau)] \times \exp(-S[\Psi_e^*,\Psi_e,\Psi_p^*,\Psi_p]), \tag{30}$$

where S is the action

$$S=\int_0^\beta d\tau\left\{\int dx\left[\Psi_e^*(x\tau)\left(\frac{\partial}{\partial\tau}-\mu_e\right)\Psi_e(x\tau) + \Psi_p^*(x\tau)\left(\frac{\partial}{\partial\tau}-\mu_p\right)\Psi_p(x\tau)\right] + H[\Psi_e^*(\tau),\Psi_e(\tau),\Psi_p^*(\tau),\Psi_p(\tau)]\right\} \tag{31}$$

again with the notation $\int dx \equiv \Sigma_s \int d^3r$. The standard antiperiodic boundary conditions corresponding to Fermions are once again used in Eq. (30), appearing again as constraints in the selection of paths, but now separately for each component, namely

$$\Psi_e(x,\beta)=-\Psi_e(x,0),$$

and

$$\Psi_p(x,\beta)=-\Psi_p(x,0).$$

(In the case of deuterium the latter must be replaced by periodic-boundary conditions.) As before, the Hamiltonian H is assumed to be in normal order, and in the case of a two-component system with static pairwise interactions of the Coulomb type it is given by

$$\begin{aligned} H[\Psi_e^*,\Psi_e,\Psi_p^*,\Psi_p] = & \int dx \Psi_e^*(x\tau)\epsilon_e(-i\nabla)\Psi_e(x\tau) + \int dx \Psi_p^*(x\tau)\epsilon_p(-i\nabla)\Psi_p(x\tau) \\ & + \frac{1}{2}\int dx\, dy \Psi_e^*(x\tau)\Psi_e^*(y\tau)v_c(x-y)\Psi_e(y\tau)\Psi_e(x\tau) \\ & + \frac{1}{2}\int dx\, dy \Psi_p^*(x\tau)\Psi_p^*(y\tau)v_c(x-y)\Psi_p(y\tau)\Psi_p(x\tau) \\ & - \int dx\, dy \Psi_e^*(x\tau)\Psi_p^*(y\tau)v_c(x-y)\Psi_p(y\tau)\Psi_e(x\tau), \end{aligned} \tag{32}$$

$v_c(x-y)$ being the bare-Coulomb interaction

$$v_c(x-y)=\frac{e^2}{|\mathbf{x}-\mathbf{y}|}. \tag{33}$$

As a consequence of the form of Eq. (32) the action Eq. (31) again takes the separable form

$$\begin{aligned} S[\Psi_e^*,\Psi_e,\Psi_p^*,\Psi_p] = & \int_0^\beta d\tau \int dx\, dy \left\{ \Psi_e^*(x\tau)\delta(x-y)\left[\frac{\partial}{\partial\tau}+\epsilon_e(-i\nabla)-\mu_e\right]\Psi_e(y\tau) + \Psi_p^*(x\tau)\delta(x-y) \right. \\ & \times\left[\frac{\partial}{\partial\tau}+\epsilon_p(-i\nabla)-\mu_p\right]\Psi_p(y\tau) + \frac{1}{2}\Psi_e^*(x\tau)\Psi_e^*(y\tau)v_c(x-y)\Psi_e(y\tau)\Psi_e(x\tau) \\ & + \frac{1}{2}\Psi_p^*(x\tau)\Psi_p^*(y\tau)v_c(x-y)\Psi_p(y\tau)\Psi_p(x\tau) - \frac{1}{2}\Psi_e^*(x\tau)\Psi_p^*(y\tau)v_c(x-y)\Psi_p(y\tau)\Psi_e(x\tau) \\ & \left. - \frac{1}{2}\Psi_p^*(x\tau)\Psi_e^*(y\tau)v_c(x-y)\Psi_e(y\tau)\Psi_p(x\tau) \right\} \\ \equiv & S_0 + S_{\mathrm{int}}, \end{aligned} \tag{34}$$

where S_0 denotes the terms not containing v_c. For a translationally invariant system we again have $\epsilon_a(k)=k^2/2m_a$, with $a=\{e,p\}$. Note that in what follows we take these energy dispersions to be quite general [$\epsilon_e(k)$ for example, could correspond to a band structure, with protons being in an extreme tight-binding or Hubbard limit, see Sec. V].

Next, it is important to observe that S_{int} can be written in a *matrix form* (as noted this has no analog in the one-component case), namely

$$S_{\text{int}}[\boldsymbol{\Psi}^*,\boldsymbol{\Psi}]=\frac{1}{2}\int dx\,dy\int_0^\beta d\tau\boldsymbol{\Psi}^*(xy\tau)\hat{\hat{V}}(xy)\boldsymbol{\Psi}(xy\tau), \tag{35}$$

with

$$\boldsymbol{\Psi}(xy\tau)\equiv\begin{pmatrix}\Psi_e^*(x\tau)\Psi_e^*(y\tau)\\ \Psi_p^*(x\tau)\Psi_p^*(y\tau)\\ \Psi_e^*(x\tau)\Psi_p^*(y\tau)\\ \Psi_p^*(x\tau)\Psi_e^*(y\tau)\end{pmatrix}, \tag{36}$$

and

$$\hat{\hat{V}}(xy)\equiv v_c(x-y)\begin{pmatrix}1&0&0&0\\0&1&0&0\\0&0&-1&0\\0&0&0&-1\end{pmatrix}. \tag{37}$$

The structure of Eq. (35) arises entirely because of the *symmetry* of the Hamiltonian (32) with respect to the Coulomb interactions and is ideally suited to yet another HS transformation of the type (5). Indeed, if we use the notation $1\equiv xy\tau$, $2\equiv x'y'\tau'$, etc., and make the identifications [see Eqs. (6) and (7)]

$$f(1)\equiv\boldsymbol{\Psi}(xy\tau), \tag{38}$$

and

$$C^{-1}(1,2)=-\frac{\hat{\hat{V}}(xy)}{2}\,\delta(x-x')\,\delta(y-y')\,\delta(\tau-\tau'), \tag{39}$$

then Eq. (5) leads to the result [the companion of Eqs. (9) and (10)] that

$$\exp[-S_{\text{int}}]=(\text{const})\int D[\boldsymbol{\Delta}^*]D[\boldsymbol{\Delta}]\exp[-S'], \tag{40}$$

with

$$S'=\int d1\,d2\boldsymbol{\Delta}^*(1)\hat{C}(12)\boldsymbol{\Delta}(2)-\int d1\{\boldsymbol{\Psi}^*(1)\boldsymbol{\Delta}(1)+\boldsymbol{\Psi}(1)\boldsymbol{\Delta}^*(1)\}. \tag{41}$$

Here the ‘‘natural form’’ for $\boldsymbol{\Delta}$ (again with no analogy to the one-component case) is

$$\boldsymbol{\Delta}(1)\equiv\begin{pmatrix}\Delta_{\text{ee}}^*(xy\tau)\\ \Delta_{\text{pp}}^*(xy\tau)\\ \Delta_{\text{ep}}^*(xy\tau)\\ \Delta_{\text{pe}}^*(xy\tau)\end{pmatrix}, \tag{42}$$

and it immediately introduces the four-order parameters that will be essential in the discussion that follows. If as earlier we subsequently rescale $\boldsymbol{\Delta}\rightarrow-\boldsymbol{\Delta}/2$ the partition function then reads

$$Z=(\text{const})\int D[\boldsymbol{\Psi}^*]D[\boldsymbol{\Psi}]D[\boldsymbol{\Delta}^*]D[\boldsymbol{\Delta}]\times\exp\{\tilde{S}[\boldsymbol{\Psi}^*,\boldsymbol{\Psi};\boldsymbol{\Delta}^*,\boldsymbol{\Delta}]\}, \tag{43}$$

with

$$\begin{aligned}\tilde{S}[\boldsymbol{\Psi}^*,\boldsymbol{\Psi};\boldsymbol{\Delta}^*,\boldsymbol{\Delta}]=\int_0^\beta d\tau\int dx\,dy\Bigg\{&\Psi_e^*(x\tau)\,\delta(x-y)\left[-\frac{\partial}{\partial\tau}-\epsilon_e(-i\nabla)+\mu_e\right]\Psi_e(y\tau)\\&+\Psi_p^*(x\tau)\,\delta(x-y)\left[-\frac{\partial}{\partial\tau}-\epsilon_p(-i\nabla)+\mu_p\right]\Psi_p(y\tau)-\frac{1}{2}\boldsymbol{\Delta}^*(xy\tau)\boldsymbol{\Psi}(xy\tau)\\&-\frac{1}{2}\boldsymbol{\Delta}(xy\tau)\boldsymbol{\Psi}^*(xy\tau)+\frac{1}{2}\frac{1}{v_c(x-y)}\boldsymbol{\Delta}^*(xy\tau)\begin{pmatrix}1&0&0&0\\0&1&0&0\\0&0&-1&0\\0&0&0&-1\end{pmatrix}\boldsymbol{\Delta}(xy\tau)\Bigg\},\end{aligned} \tag{44}$$

which is now the analog of Eq. (12).

Once again, Eq. (44) can be recast into a *new* matrix form [which is essentially a generalization of Nambu's procedure,[11] as in Eq. (13)]. Indeed, if we change notation once again to $1\equiv x\tau$, etc. (so that $\int d1\equiv\int_0^\beta d\tau\int dx$, etc.) and if we define [see Eq. (14)]

$$\boldsymbol{\Phi}(1)\equiv\begin{pmatrix}\Psi_e(1)\\ \Psi_e^*(1)\\ \Psi_p(1)\\ \Psi_p^*(1)\end{pmatrix} \tag{45}$$

and

$$\mathbf{\Delta}(12)\equiv\begin{pmatrix}\Delta^*_{\mathrm{ee}}(12)\\ \Delta^*_{\mathrm{pp}}(12)\\ \Delta^*_{\mathrm{ep}}(12)\\ \Delta^*_{\mathrm{pe}}(12)\end{pmatrix}, \tag{46}$$

then Eq. (44) can be written as [see Eq. (13)]

$$\tilde{S}[\mathbf{\Psi}^*,\mathbf{\Psi};\mathbf{\Delta}^*,\mathbf{\Delta}]=\int d1\,d2\left\{\frac{1}{2}\,\mathbf{\Phi}^*(1)[-\hat{A}(12)]\mathbf{\Phi}(2)+\frac{1}{2}\,\mathbf{\Delta}^*(12)\hat{\tilde{V}}^{-1}(12)\mathbf{\Delta}(12)\right\}. \tag{47}$$

In Eq. (47) we have the definitions

$$\hat{\tilde{V}}^{-1}(12)\equiv\frac{1}{v_c(1-2)}\begin{pmatrix}1&0&0&0\\0&1&0&0\\0&0&-1&0\\0&0&0&-1\end{pmatrix}, \tag{48}$$

and

$$\hat{A}(12)\equiv\begin{pmatrix}\delta(12)\left(\dfrac{\partial}{\partial\tau}+\xi_e\right)&\Delta_{\mathrm{ee}}(12)&0&\Delta_{\mathrm{ep}}(12)\\ \Delta^*_{\mathrm{ee}}(12)&\delta(12)\left(\dfrac{\partial}{\partial\tau}-\xi_e\right)&\Delta^*_{\mathrm{ep}}(12)&0\\ 0&\Delta_{\mathrm{pe}}(12)&\delta(12)\left(\dfrac{\partial}{\partial\tau}+\xi_p\right)&\Delta_{\mathrm{pp}}(12)\\ \Delta^*_{\mathrm{pe}}(12)&0&\Delta^*_{\mathrm{pp}}(12)&\delta(12)\left(\dfrac{\partial}{\partial\tau}-\xi_p\right)\end{pmatrix}, \tag{49}$$

where we have used the notation $\xi_a=\epsilon_a(-i\nabla)-\mu_a$. Equation (49) is now clearly the two-component generalization of Eq. (15) that takes into account the symmetry of the two-component Hamiltonian.

The partition function can, therefore, finally be written as

$$Z=(\mathrm{const})\times\int D[\mathbf{\Delta}^*]D[\mathbf{\Delta}]\int D[\mathbf{\Phi}^*]D[\mathbf{\Phi}]\exp\left\{\int d1\,d2\left[-\frac{1}{2}\,\mathbf{\Phi}^*(1)\hat{A}(12)\mathbf{\Phi}(2)\right]\right\}\times\exp\left\{\int d1\,d2\,\frac{1}{2}\,\mathbf{\Delta}^*(12)\hat{\tilde{V}}^{-1}(12)\mathbf{\Delta}(12)\right\}, \tag{50}$$

and this may be compared directly with Eq. (16). Using a Gaussian integration over Grassmann variables, namely

$$\int D[\mathbf{\Phi}^*]D[\mathbf{\Phi}]\exp\left\{\int d1\,d2\,\mathbf{\Phi}^*(1)\left[-\frac{\hat{A}(12)}{2}\right]\mathbf{\Phi}(2)\right\}=\det\left(\frac{\hat{A}}{2}\right)=\exp\left[\mathrm{tr}\ln\left(\frac{\hat{A}}{2}\right)\right] \tag{51}$$

to integrate out the $\mathbf{\Phi}$ field we then obtain

$$Z=(\mathrm{const})\int D[\mathbf{\Delta}^*]D[\mathbf{\Delta}]\exp(\tilde{S}[\mathbf{\Delta}^*,\mathbf{\Delta}]), \tag{52}$$

with

$$\overline{S}[\mathbf{\Delta}^*,\mathbf{\Delta}]=\mathrm{tr}\ln\left(\frac{\hat{A}}{2}\right)+\frac{1}{2}\int d1\,d2\,\mathbf{\Delta}^*(12)\hat{\tilde{V}}^{-1}(2)\mathbf{\Delta}(12), \tag{53}$$

and this can be seen as the parallel of Eq. (18).

After a sequence of exact manipulations we again arrive at a point where the stationary-phase approximation can be implemented [comparison can again be made with steps beginning with Eq. (19)]:

$$\frac{\delta\overline{S}}{\delta\Delta^*_{\mathrm{ee}}(12)}=\frac{\Delta_{\mathrm{ee}}(12)}{v_c(12)}+\mathrm{tr}\left[\hat{A}^{-1}(12)\begin{pmatrix}0&0&0&0\\1&0&0&0\\0&0&0&0\\0&0&0&0\end{pmatrix}\right]=0, \tag{54}$$

$$\frac{\delta\overline{S}}{\delta\Delta^*_{\mathrm{pp}}(12)}=\frac{\Delta_{\mathrm{pp}}(12)}{v_c(12)}+\mathrm{tr}\left[\hat{A}^{-1}(12)\begin{pmatrix}0&0&0&0\\0&0&0&0\\0&0&0&0\\0&0&1&0\end{pmatrix}\right]=0, \tag{55}$$

$$\frac{\delta\overline{S}}{\delta\Delta_{\mathrm{ep}}^{*}(12)}=\frac{-\Delta_{\mathrm{ep}}(12)}{v_c(12)}+\mathrm{tr}\left[\hat{A}^{-1}(12)\begin{pmatrix}0&0&0&0\\0&0&1&0\\0&0&0&0\\0&0&0&0\end{pmatrix}\right]=0, \tag{56}$$

and

$$\frac{\delta\overline{S}}{\delta\Delta_{\mathrm{pe}}^{*}(12)}=\frac{-\Delta_{\mathrm{pe}}(12)}{v_c(12)}+\mathrm{tr}\left[\hat{A}^{-1}(12).\begin{pmatrix}0&0&0&0\\0&0&0&0\\0&0&0&0\\1&0&0&0\end{pmatrix}\right]=0. \tag{57}$$

It is evident that $\delta\overline{S}/\delta\Delta_{\mathrm{ee}}(12)=0$ will yield an equation that is conjugate to Eq. (54), and that $\delta\overline{S}/\delta\Delta_{\mathrm{pp}}(12)=0$ will also yield an equation conjugate to Eq. (55). On the other hand, if we impose the condition that equations $\delta\overline{S}/\delta\Delta_{\mathrm{ep}}(12)=0$ and $\delta\overline{S}/\delta\Delta_{\mathrm{pe}}(12)=0$ must yield equations completely conjugate to Eqs. (56) and (57), respectively, we then obtain the constraint that

$$\Delta_{\mathrm{ep}}\Delta_{\mathrm{pe}}^{*}=\Delta_{\mathrm{pe}}\Delta_{\mathrm{ep}}^{*}, \tag{58}$$

and that they both must be real. This will have simplifying consequences in the calculations that follow (see Appendix C).

As mentioned earlier, the SPA is generally justified for **k**-space pairing, and on general physical grounds it would be expected to be accurate for Δ_{ee}. In addition, we shall see that the results that follow show considerable evidence that the approximation is satisfactory for Δ_{pp} and Δ_{ep} as well,[8] as they approximately reproduce the low-density real-space pairing [see Eq. (82)].

To proceed from this point we are again required to Fourier transform Eqs. (54)–(57) to **k**-space and to Matsubara frequencies ω_n, i.e., we write again [as in Eq. (23)],

$$\hat{G}(32)=\frac{1}{\beta}\sum_{\omega_n}e^{-i\omega_n\tau_{32}}\int\frac{d^3k}{(2\pi)^3}e^{i\mathbf{k}\mathbf{r}_{32}}\hat{G}(\mathbf{k},\omega_n),$$

where the Matsubara frequencies for Fermions are given by Eq. (24). We can now find the Green's-function matrix $\hat{A}^{-1}$ appropriate to fundamental particles moving in the "multipairing" field. Beginning again with [see Eq. (22)]

$$\int d3\hat{A}(13)\hat{G}(32)=\delta(12)\hat{1} \tag{59}$$

and using Eqs. (49) and (23), we obtain

$$\frac{1}{\beta}\sum_{\omega_n}\int\frac{d^3k}{(2\pi)^3}e^{i\mathbf{k}\mathbf{r}_{12}}e^{-i\omega_n\tau_{12}}\hat{\hat{A}}(\mathbf{k},\omega_n)\hat{G}(\mathbf{k},\omega_n)=\delta(12)\hat{1}.$$

This clearly is the analog of Eq. (25), but now with

$$\hat{\hat{A}}(\mathbf{k},\omega_n)=\begin{pmatrix}-i\omega_n+\xi_e(\mathbf{k})&\Delta_{\mathrm{ee}}(\mathbf{k})&0&\Delta_{\mathrm{ep}}(\mathbf{k})\\ \Delta_{\mathrm{ee}}^{*}(\mathbf{k})&-i\omega_n-\xi_e(\mathbf{k})&\Delta_{\mathrm{ep}}^{*}(\mathbf{k})&0\\ 0&\Delta_{\mathrm{pe}}(\mathbf{k})&-i\omega_n+\xi_p(\mathbf{k})&\Delta_{\mathrm{pp}}(\mathbf{k})\\ \Delta_{\mathrm{pe}}^{*}(\mathbf{k})&0&\Delta_{\mathrm{pp}}^{*}(\mathbf{k})&-i\omega_n-\xi_p(\mathbf{k})\end{pmatrix} \tag{60}$$

where $\xi_\alpha(\mathbf{k})\equiv\epsilon_\alpha(\mathbf{k})-\mu_\alpha$. [As will be seen below, the form of $\xi_p(\mathbf{k})$ depends heavily on the choice of conditions (i.e., density) and the mass of the proton]. This result shows that $\hat{G}(\mathbf{k},\omega_n)$ is the inverse of the matrix $\hat{\hat{A}}(\mathbf{k},\omega_n)$ [see also Eq. (26)], and it can be found easily. If we use it in the Fourier transform of Eqs. (54)–(57), we obtain four "gap equations," as follows:

$$\Delta_{\mathrm{ee}}(\mathbf{k})=-\frac{1}{\beta}\sum_{\mathbf{k}'}\sum_{\omega_n}v_c(\mathbf{k}-\mathbf{k}')[\hat{G}(\mathbf{k}',\omega_n)]_{12}, \tag{61}$$

$$\Delta_{\mathrm{pp}}(\mathbf{k})=-\frac{1}{\beta}\sum_{\mathbf{k}'}\sum_{\omega_n}v_c(\mathbf{k}-\mathbf{k}')[\hat{G}(\mathbf{k}',\omega_n)]_{34}, \tag{62}$$

$$\Delta_{\mathrm{ep}}(\mathbf{k})=\frac{1}{\beta}\sum_{\mathbf{k}'}\sum_{\omega_n}v_c(\mathbf{k}-\mathbf{k}')[\hat{G}(\mathbf{k}',\omega_n)]_{32}, \tag{63}$$

and

$$\Delta_{\mathrm{pe}}(\mathbf{k})=\frac{1}{\beta}\sum_{\mathbf{k}'}\sum_{\omega_n}v_c(\mathbf{k}-\mathbf{k}')[\hat{G}(\mathbf{k}',\omega_n)]_{14}, \tag{64}$$

where

$$[\hat{G}(\mathbf{k}',\omega_n)]_{ij}\equiv\frac{X_{ij}(\mathbf{k}',\omega_n)}{\det(\mathbf{k}',\omega_n)}. \tag{65}$$

The definitions of quantities X_{ij} and the determinant det are quite straightforward, but they are also quite lengthy; they are given in Appendix B. Equations (61)–(65) are now seen to be the direct generalizations of Eq. (27).

The final step consists in carrying out the frequency sums. These are also found in detail in Appendix C [and are aided by the constraint (58)]; the gap structure resulting from this procedure is quite rich, as we shall see. Applying the results of Appendices B and C to Eqs. (61)–(64) we can determine the "gap equations," which are also the direct generalizations of Eqs. (28) and (29). They have the following final forms, namely:

$$\Delta_{\rm ee}(\mathbf{k}) = -\sum_{\mathbf{k}'} \frac{v_c(\mathbf{k}-\mathbf{k}')\Delta_{\rm ee}(\mathbf{k}')}{2[r_1^2(\mathbf{k}')-r_3^2(\mathbf{k}')]} \times \left\{ \left[r_1(\mathbf{k}')\tanh\frac{\beta r_1(\mathbf{k}')}{2} - r_3(\mathbf{k}')\tanh\frac{\beta r_3(\mathbf{k}')}{2} \right] + D_{\rm ee}(\mathbf{k}') \left[\frac{\tanh\frac{\beta r_3(\mathbf{k}')}{2}}{r_3(\mathbf{k}')} - \frac{\tanh\frac{\beta r_1(\mathbf{k}')}{2}}{r_1(\mathbf{k}')} \right] \right\}, \tag{66}$$

$$\Delta_{\rm pp}(\mathbf{k}) = -\sum_{\mathbf{k}'} \frac{v_c(\mathbf{k}-\mathbf{k}')\Delta_{\rm pp}(\mathbf{k}')}{2[r_1^2(\mathbf{k}')-r_3^2(\mathbf{k}')]} \times \left\{ \left[r_1(\mathbf{k}')\tanh\frac{\beta r_1(\mathbf{k}')}{2} - r_3(\mathbf{k}')\tanh\frac{\beta r_3(\mathbf{k}')}{2} \right] + D_{\rm pp}(\mathbf{k}') \left[\frac{\tanh\frac{\beta r_3(\mathbf{k}')}{2}}{r_3(\mathbf{k}')} - \frac{\tanh\frac{\beta r_1(\mathbf{k}')}{2}}{r_1(\mathbf{k}')} \right] \right\}, \tag{67}$$

$$\Delta_{\rm ep}(\mathbf{k}) = +\sum_{\mathbf{k}'} \frac{v_c(\mathbf{k}-\mathbf{k}')\Delta_{\rm pe}(\mathbf{k}')}{2[r_1^2(\mathbf{k}')-r_3^2(\mathbf{k}')]} \times \left\{ \left[r_1(\mathbf{k}')\tanh\frac{\beta r_1(\mathbf{k}')}{2} - r_3(\mathbf{k}')\tanh\frac{\beta r_3(\mathbf{k}')}{2} \right] + D_{\rm ep}(\mathbf{k}') \left[\frac{\tanh\frac{\beta r_3(\mathbf{k}')}{2}}{r_3(\mathbf{k}')} - \frac{\tanh\frac{\beta r_1(\mathbf{k}')}{2}}{r_1(\mathbf{k}')} \right] \right\} \tag{68}$$

and

$$\Delta_{\rm pe}(\mathbf{k}) = +\sum_{\mathbf{k}'} \frac{v_c(\mathbf{k}-\mathbf{k}')\Delta_{\rm ep}(\mathbf{k}')}{2[r_1^2(\mathbf{k}')-r_3^2(\mathbf{k}')]} \times \left\{ \left[r_1(\mathbf{k}')\tanh\frac{\beta r_1(\mathbf{k}')}{2} - r_3(\mathbf{k}')\tanh\frac{\beta r_3(\mathbf{k}')}{2} \right] + D_{\rm pe}(\mathbf{k}') \left[\frac{\tanh\frac{\beta r_3(\mathbf{k}')}{2}}{r_3(\mathbf{k}')} - \frac{\tanh\frac{\beta r_1(\mathbf{k}')}{2}}{r_1(\mathbf{k}')} \right] \right\}. \tag{69}$$

Here,

$$D_{\rm ee}(\mathbf{k}') = \xi_p^2(\mathbf{k}') + |\Delta_{\rm pp}(\mathbf{k}')|^2 - \Delta_{\rm pp}^*(\mathbf{k}') \frac{\Delta_{\rm ep}(\mathbf{k}')\Delta_{\rm pe}(\mathbf{k}')}{\Delta_{\rm ee}(\mathbf{k}')}, \tag{70}$$

$$D_{\rm pp}(\mathbf{k}') = \xi_e^2(\mathbf{k}') + |\Delta_{\rm ee}(\mathbf{k}')|^2 - \Delta_{\rm ee}^*(\mathbf{k}') \frac{\Delta_{\rm ep}(\mathbf{k}')\Delta_{\rm pe}(\mathbf{k}')}{\Delta_{\rm pp}(\mathbf{k}')}, \tag{71}$$

$$D_{\rm ep}(\mathbf{k}') = \xi_e(\mathbf{k}')\xi_p(\mathbf{k}') + \Delta_{\rm ep}(\mathbf{k}')\Delta_{\rm pe}^*(\mathbf{k}') - \Delta_{\rm ee}(\mathbf{k}')\Delta_{\rm pp}(\mathbf{k}') \frac{\Delta_{\rm pe}^*(\mathbf{k}')}{\Delta_{\rm pe}(\mathbf{k}')}, \tag{72}$$

and

$$D_{\rm pe}(\mathbf{k}') = \xi_e(\mathbf{k}')\xi_p(\mathbf{k}') + \Delta_{\rm pe}(\mathbf{k}')\Delta_{\rm ep}^*(\mathbf{k}') - \Delta_{\rm ee}(\mathbf{k}')\Delta_{\rm pp}(\mathbf{k}') \frac{\Delta_{\rm ep}^*(\mathbf{k}')}{\Delta_{\rm ep}(\mathbf{k}')}. \tag{73}$$

In the above we also have

$$r_1(\mathbf{k}') = \sqrt{\tilde{D}^2(\mathbf{k}') + \frac{D^2(\mathbf{k}')}{2}} \tag{74}$$

and

$$r_3(\mathbf{k}') = \sqrt{\tilde{D}^2(\mathbf{k}') - \frac{D^2(\mathbf{k}')}{2}}, \tag{75}$$

where

$$\tilde{D}^2 = \frac{1}{2}\{|\Delta_{\rm ee}(\mathbf{k}')|^2 + |\Delta_{\rm pp}(\mathbf{k}')|^2 + 2\,{\rm Re}[\Delta_{\rm ep}(\mathbf{k}')\Delta_{\rm pe}^*(\mathbf{k}')] + [\epsilon_e(\mathbf{k}')-\mu_e]^2 + [\epsilon_p(\mathbf{k}')-\mu_p]^2\} \tag{76}$$

and

$$D^2(\mathbf{k}') = [r_1^2(\mathbf{k}') - r_3^2(\mathbf{k}')] = \Big([|\Delta_{\rm ee}(\mathbf{k}')|^2 - |\Delta_{\rm pp}(\mathbf{k}')|^2 + \xi_e^2(\mathbf{k}') - \xi_p^2(\mathbf{k}')]^2 + 4\Delta_{\rm ep}(\mathbf{k}')\Delta_{\rm pe}^*(\mathbf{k}')\{|\Delta_{\rm ee}(\mathbf{k}')|^2 + |\Delta_{\rm pp}(\mathbf{k}')|^2 + [\xi_e(\mathbf{k}') - \xi_p(\mathbf{k}')]^2\} + 8\,{\rm Re}[\Delta_{\rm ee}(\mathbf{k}')\Delta_{\rm pp}(\mathbf{k}')\Delta_{\rm ep}^*(\mathbf{k}')\Delta_{\rm pe}^*(\mathbf{k}')]\Big)^{1/2}. \tag{77}$$

The above system of simultaneous nonlinear integral equations displays an obvious complexity, but it also clearly demonstrates the expected physics, namely that the presence of the various order parameters determines effective interactions, and these in turn lead to the pairings in a completely *self-consistent* way. In particular, it is crucial to note that the quantities (70) and (71), if assumed real, can take *negative values* if $\Delta_{\rm ep}\Delta_{\rm pe}$ is sufficiently large. An important consequence is that in such a case it is possible to have effective *attractions* between identical particles, and therefore real solutions of the system of integral Eqs. (66)–(69) as we will show below. (The four-particle problem of a Heitler-London H_2 molecule introduced earlier is but the simplest manifestation of this and will be discussed in the next section.)

IV. PHYSICAL INTERPRETATIONS

Before we discuss possible solutions and proceed to crystalline order, we offer a brief comment about the general behavior of Eqs. (66)–(69). These equations have some quite intuitive limits: for example, in the special case $\Delta_{\rm ep}\to 0$ and $\Delta_{\rm pe}\to 0$ we have

$$r_1(\mathbf{k}) \to \sqrt{|\Delta_{\rm ee}(\mathbf{k})|^2 + \xi_e^2(\mathbf{k})}$$

and

$$r_3(\mathbf{k})\rightarrow\sqrt{|\Delta_{\mathrm{pp}}(\mathbf{k})|^2+\xi_p^2(\mathbf{k})},$$

and as a result the first two equations decouple into a pair of BCS-like gap equations, namely

$$\Delta_{\mathrm{ii}}(\mathbf{k})=-\sum_{\mathbf{k}'}\frac{v_c(\mathbf{k}-\mathbf{k}')\Delta_{\mathrm{ii}}(\mathbf{k}')}{2\sqrt{|\Delta_{\mathrm{ii}}(\mathbf{k}')|^2+\xi_i^2(\mathbf{k}')}}\times\tanh\left[\frac{\beta\sqrt{|\Delta_{\mathrm{ii}}(\mathbf{k}')|^2+\xi_i^2(\mathbf{k}')}}{2}\right],$$

with $i=\{e,p\}$. These, of course, have no solution for bare Coulomb repulsions, and this suggests that in the physical case Δ_{ep} *cannot* be identically zero. It is also straightforward although tedious to show[12] that by introducing the $e-p$ coupling (i.e., $\Delta_{\mathrm{ep}}\Delta_{\mathrm{pe}}\neq 0$) to the next nontrivial order [i.e., $0(\Delta_{\mathrm{ep}}^2)$] we obtain an interaction which is *less repulsive* than the bare Coulomb interaction v_c.

In the complementary (and more interesting) special case of $\Delta_{\mathrm{ee}}\rightarrow 0$ and $\Delta_{\mathrm{pp}}\rightarrow 0$ Eqs. (68) and (69) lead to a gap equation of the ''excitonic insulator'' type,[13] namely

$$\Delta_{\mathrm{ep}}(\mathbf{k})=+\sum_{\mathbf{k}'}\frac{v_c(\mathbf{k}-\mathbf{k}')\Delta_{\mathrm{pe}}(\mathbf{k}')}{2[r_1(\mathbf{k}')+r_3(\mathbf{k}')]}\times\left[\tanh\frac{\beta r_1(\mathbf{k}')}{2}+\tanh\frac{\beta r_3(\mathbf{k}')}{2}\right], \tag{78}$$

where

$$r_{1,3}(\mathbf{k}')=\left|\frac{1}{2}\sqrt{4\Delta_{\mathrm{ep}}(\mathbf{k}')\Delta_{\mathrm{pe}}^*(\mathbf{k}')+[\xi_e(\mathbf{k}')+\xi_p(\mathbf{k}')]^2}\pm\frac{1}{2}|\xi_e(\mathbf{k}')-\xi_p(\mathbf{k}')|\right|. \tag{79}$$

From these it follows that

$$[r_1(\mathbf{k}')+r_3(\mathbf{k}')]=\begin{cases}\sqrt{4\Delta_{\mathrm{ep}}(\mathbf{k}')\Delta_{\mathrm{pe}}^*(\mathbf{k}')+[\xi_e(\mathbf{k}')+\xi_p(\mathbf{k}')]^2},\\ |\xi_e(\mathbf{k}')-\xi_p(\mathbf{k}')|,\end{cases} \tag{80}$$

the first being true in case that $\Delta_{\mathrm{ep}}(\mathbf{k}')\Delta_{\mathrm{pe}}^*(\mathbf{k}')+\xi_e(\mathbf{k}')\xi_p(\mathbf{k}')\geqslant 0$, and the second for $\Delta_{\mathrm{ep}}(\mathbf{k}')\Delta_{\mathrm{pe}}^*(\mathbf{k}')+\xi_e(\mathbf{k}')\xi_p(\mathbf{k}')\leqslant 0$. The separate cases of weak and strong Δ_{ep} will be discussed in more detail below, but here we may simply note that for $\Delta_{\mathrm{ep}}\Delta_{\mathrm{pe}}^*\ll\xi_e^2$ or ξ_p^2 we once more obtain for Δ_{ee} or Δ_{pp} the uncoupled BCS gap equations, except that there is now an *effective interaction*, which to the first order of correction is

$$v_{\mathrm{eff}}(\mathbf{k}-\mathbf{k}')=\frac{v_c(\mathbf{k}-\mathbf{k}')}{\sqrt{1+\dfrac{4\Delta_{\mathrm{ep}}(\mathbf{k}')\Delta_{\mathrm{pe}}^*(\mathbf{k}')}{[\xi_e(\mathbf{k}')+\xi_p(\mathbf{k}')]^2}}}. \tag{81}$$

Observe that this is *less* repulsive than $v_c(\mathbf{k}-\mathbf{k}')$, so that in each of these special cases the presence of nonvanishing Δ_{ep} has an *attractive effect.*

In general the Δ's are complex quantities. There are two general cases that respect the constraint (58): If Eq. (68) coincides with Eq. (69), then we have $\Delta_{\mathrm{ep}}=\Delta_{\mathrm{pe}}$ (for which $\Delta_{\mathrm{ep}}\Delta_{\mathrm{pe}}^*=|\Delta_{\mathrm{ep}}|^2$ is indeed real). If on the other hand Eq. (68) is the complex conjugate of Eq. (69), then we obtain $\Delta_{\mathrm{pe}}=\Delta_{\mathrm{ep}}^*$ and Eq. (58) then leads to the conclusion that Δ_{ep}, Δ_{pe}, and $\Delta_{\mathrm{ee}}\Delta_{\mathrm{pp}}$ must be real quantities. For the sake of simplicity let us adopt the second case, with all Δ's being real, and examine whether solutions of Eqs. (66)–(69) can actually exist. [The assumption of real Δ's is especially relevant if we restrict ourselves to *s*-wave pairing; accordingly we will later assume that the Δ's are isotropic, i.e., $\Delta_{ij}(\mathbf{k})=\Delta_{ij}(k)$ It should be noted, however, that the more general case of complex order parameters raises further physical issues such as the manner in which phase coherence can develop in a single component when pairing leads to an overall superconducting state. Another is the general question of phase dynamics when we proceed beyond the SPA. Note that because of the way in which we have defined our order parameters (as elements of a matrix) the separate phases do not necessarily incorporate the notion of correspondingly separate phase coherence as arises in the concept of a Josephson weak link.[14] This is obvious from the fact that the cross-pairing is not merely a linear combination of electron-electron and proton-proton pairings but in fact coexists with them as part of a higher strongly coupled complex. For this reason, the limiting cases of simple pairing and excitonic pairing coexist rather than compete]. As expected intuitively it can be shown[12] that in the high-temperature limit no solutions of the first two equations [Eqs. (66) and (67)] exist. But as temperature is lowered solutions subsequently emerge, especially when the cross-order parameter Δ_{ep} assumes sufficiently large values. This occurs because of the corresponding development of effective *attractions* in certain regions of *k*-space for the $e-e$ and $p-p$ channels as we will discuss below [case (b)].

In more detail, let us focus on the physically expected case $\Delta_{\mathrm{ee}}/\Delta_{\mathrm{ep}}$ and $\Delta_{\mathrm{pp}}/\Delta_{\mathrm{ep}}\rightarrow 0$; then two general classes of solutions develop, depending on whether $|\Delta_{\mathrm{ep}}|^2$ is small or large compared to the product $\xi_\alpha\xi_\beta$, with $\{\alpha,\beta\}=$ any of the $\{e,p\}$. To examine whether solutions to Eqs. (66)–(68) actually do exist in principle we may take all $\Delta_{\alpha\beta}$ to be real and isotropic (corresponding to *s*-wave singlet states). The following results then emerge:

(a) Solutions corresponding to $|\Delta_{\mathrm{ep}}|^2\ll\xi_\alpha\xi_\beta$ for any k are possible but only for sufficiently low densities, particularly when μ_e and μ_p are both negative (for which $\xi_\alpha\xi_\beta$ is then positive for any k). At low density and low temperature the solution to Eq. (78) has the form

$$\Delta_{\mathrm{ep}}(k)=(\mathrm{const})\,\frac{[\xi_e(k)+\xi_p(k)]}{(1+k^2a^2)^2}, \tag{82}$$

with $a=\hbar^2/m^*e^2$ and $m^*=m_em_p/m_e+m_p$. From a canonical analysis[9] of the same problem in terms of the wave function ϕ_k of a single pair it can be shown that the relation between $\Delta(k)$ and ϕ_k is

$$|\Delta(k)|^2=\frac{4\xi(k)^2|\phi_k|^2}{(1-|\phi_k|^2)^2}. \tag{83}$$

In the low-density limit $\phi_k\rightarrow 0$ [and noting that the Fourier transform of $e^{-r/a}$, a 1s state, is proportional to (1

$+k^2a^2)^{-2}$] a comparison with Eq. (82) shows that this solution corresponds to an *atomic* $e-p$ form. The scale of $\Delta_{\rm ep}$ is, therefore, of the order of eV [see also case (b) below]. An important result is that from the *structure* of Eqs. (68) and (72) we can rigorously show[12] that the low-temperature form of Eq. (68) remains unaltered even for small but nonvanishing values of $\Delta_{\rm ee}$ and $\Delta_{\rm pp}$ when they are included to the next nontrivial order. As a consequence, the solution (82) also applies at low temperatures and densities to the case of nonzero $e-e$ and $p-p$ pairings. This is consistent with the Heitler-London form for the H_2 wave function in the limit $m_e/m_p \to 0$. We therefore recover in this limit the expected phase of weakly interacting *hydrogen molecules*.[14] An independent stability analysis of these four-particle units (and one that imposes a positive sign for the determinant of the second derivative matrix of the action with respect to the pairing fields) shows that this solution can only be stable at sufficiently *low densities*. The same stability analysis can also locate the temperature at which the corresponding molecular bond ruptures. This is of the order of a few eV the precise value requiring a knowledge of the temperature dependence of μ_e and μ_p.

(b) The second class of solutions corresponds to $|\Delta_{\rm ep}|^2 \gg \xi_\alpha \xi_\beta$, at least for some $k<k_0$. In this case Eq. (78) has a low-temperature solution, which can be approximated by

$$\Delta_{\rm ep}(k) \simeq \frac{e^2}{\pi} k_0 F(k/k_0), \tag{84}$$

where

$$F(x) = \frac{1}{2} + \frac{1-x^2}{4x} \ln\left|\frac{1+x}{1-x}\right|$$

is recognized as the Lindhard function, and k_0 is determined by

$$2\Delta_{\rm ep}(k_0) \simeq |\xi_e(k_0)+\xi_p(k_0)|. \tag{85}$$

The scale of $\Delta_{\rm ep}$ can easily be estimated from Eq. (84) (by taking $k_0 \sim k_F$) as $2/3r_s$Ry. The form (84) is entirely different from Eq. (82) and is valid only at sufficiently *high* densities [down to the point that Eq. (85) fails to give a real and positive solution for k_0]. We therefore deduce the existence of a *transition* from the low-density molecular phase to a high-density phase described by Eq. (84). This transition was anticipated earlier[9] but through a different procedure. The high-density phase is readily associated with a delocalization of the electronic component (which, however, may still be paired), i.e., a given electronic pair no longer belongs to a particular H_2 molecule. As a result the two components can now be discussed separately in terms of effective one-component problems. Thus, by comparing Eq. (66) (or the corresponding equation for $\Delta_{\rm pp}$) with Eq. (28) we can easily determine the *effective* pairing interaction associated with each component. As a physical criterion for stability of the paired phases we may invoke the requirement that there are at least some regions in **k** space where the effective interactions become negative. It is now *crucial* to observe that for strong $\Delta_{\rm ep}$, the quantity $D_{\rm ee}$ [Eq. (70)] and the corresponding quantity $D_{\rm pp}$ [Eq. (71)], if taken as real, can both assume *negative* values if the product $\Delta_{\rm ep}\Delta_{\rm pe}$ is sufficiently large. From the form of Eqs. (66) and (67) this immediately reveals the existence of effective *attractions* between identical particles and correspondingly self-consistently stable solutions within each component. The point can also be established from the fact that the system possesses a critical point (see below) near which Eq. (66) takes the form

$$\Delta_{\rm ee}(\mathbf{k}) = -\sum_{\mathbf{k}'} \frac{v_c(\mathbf{k}-\mathbf{k}')\Delta_{\rm ee}}{2(r_1+r_3)} \frac{[\xi_p(\xi_e+\xi_p)-(\alpha-1)\Delta_{\rm ep}^2]}{|\Delta_{\rm ep}^2+\xi_e\xi_p|}, \tag{86}$$

where α is the ratio $\Delta_{\rm pp}/\Delta_{\rm ee}$, (r_1+r_3) is given by Eq. (80), and the quantities on the right-hand side of Eq. (86) are all evaluated at $\mathbf{k}'$. Comparison with the low-temperature approximation of Eq. (28) then shows that, for example

$$v_{\rm eff}(\mathbf{k},\mathbf{k}') = \frac{v_c(\mathbf{k}-\mathbf{k}')|\xi_e(\mathbf{k}')|}{[r_1(\mathbf{k}')+r_3(\mathbf{k}')]} \frac{\{\xi_p(\mathbf{k}')[\xi_e(\mathbf{k}')+\xi_p(\mathbf{k}')]-[\alpha(\mathbf{k}')-1]\Delta_{\rm ep}^2(\mathbf{k}')\}}{|\Delta_{\rm ep}^2(\mathbf{k}')+\xi_e(\mathbf{k}')\xi_p(\mathbf{k}')|} \tag{87}$$

indeed plays the role of an effective interaction between two electrons (a corresponding identification being possible for the $p-p$ channel), which under conditions to be discussed below, can also be attractive.

The major results for this case can now be summarized as follows: (i) In the high-temperature limit there are no solutions to Eq. (66), as physically expected. (ii) When temperature is lowered, solutions to Eq. (66) emerge, especially, as noted, when the cross-order parameter $\Delta_{\rm ep}$ is sufficiently large. An accurate low-temperature approximation for $\Delta_{\rm ep}$, which solves Eq. (78), is Eq. (84). We note that solutions to Eq. (66) and to the corresponding equation for $\Delta_{\rm pp}$ then emerge because of the development of effective *attractions* in certain regions of *k* space for the $e-e$ and $p-p$ channels. The attractive regions in *k* space are actually always different for the two channels, and for each component they tend to occur at values of *k* where the order parameter of the *other* component dominates. (iii) A critical point T_c exists where the order parameters $\Delta_{\rm ee}$ and $\Delta_{\rm pp}$ *both* vanish (as $T \to T_c$ from below). At the same time the regions of attraction for $e-e$ and $p-p$ channels intersect at a value $\overline{k}$ of *k*, where the sum of the single-particle energies of an electron and a proton equals the total chemical potential $\mu_e+\mu_p$ [i.e., $\xi_e(\overline{k}) + \xi_p(\overline{k})=0$]. (iv) The self-consistent solution is such that T_c is required to be *small* compared to the energy scales of the problem (in agreement, as it happens, with recent experimental results[15–17] on hydrogen), its actual value depending on the model chosen to describe the protonic phase (oscillator states being the simplest model to address experiments, see the next section). A simple approximation for T_c for strong Δ_{ep} turns out to be

$$k_B T_c \simeq \frac{|\xi_e - \xi_p|}{2} \left[\frac{\dfrac{2\Delta_{\mathrm{ep}}}{|\xi_e - \xi_p|} - 1}{\ln\left(\dfrac{2\Delta_{\mathrm{ep}}}{|\xi_e - \xi_p|} \dfrac{\alpha+1}{|\alpha-1|} \right)} \right], \tag{88}$$

where the ratio $\alpha \equiv \Delta_{\mathrm{pp}}/\Delta_{\mathrm{ee}}$ is close to unity, as can be verified by using the structure of the full equations at low temperature and L'Hospital's rule in the limit that both Δ's vanish. This expression for T_c is a consequence of the requirement that the effective attraction between two electrons vanishes as $T \to T_c$. (v) An *inverse* isotope effect is expected from Eq. (88) for the dependence of T_c on the mass of the heavier component. This is controlled by the prefactor in Eq. (88) and it is generally expected for $\xi_e > \xi_p$ and for $\xi_p > 0$ (as is actually the case for localized proton states discussed in the next section, where $\xi_p \sim \omega \sim 1/\sqrt{m_p}$, so that $|\xi_e - \xi_p|$ increases with m_p resulting in an inverse isotope effect). This general behavior is, therefore, preserved in a coarse-graining manner even for dramatic changes in symmetry (the case of a crystal) and it happens to be in agreement with recent data[17] (the issue of the different symmetry in deuterium is briefly discussed in Sec. VI).

V. APPLICATIONS TO DENSE HYDROGEN

By way of practical application of case (b) two distinct models can be used according to the choice of average density: one for a diffusive state, and another for protons being in localized oscillator states, and vibrating within preformed $p-p$ pairs (the remnants of the low-density Heitler-London fields). The electrons are assumed to be fully degenerate in all cases and the partial chemical potentials necessary for these applications are taken from our earlier paper.[10] The first model is a satisfactory description of possible generalized pairing in systems with continuous symmetry, and a primary result is that pairing of identical particles will *not* occur if the masses of the two species are equal; only simple $e-p$ pairing of the excitonic type is possible. The prediction is, therefore, that no pairing between identical particles will occur in, for example, a dense electron-positron system. However, as m_p/m_e is increased from unity, an increasing region in k-space develops around the Fermi surface where effective *attractions* between identical particles result, and molecular clusters of electrons and positrons may form.

The second model is necessary for cases with $m_p \gg m_e$, where the protons are in localized states to begin with. In this physically realizable case our formulation addresses the general issue of pairing in an initially monatomic crystal (a simple example being paired crystal phases discussed recently[18]).

In order to take account of the symmetry of a putative crystalline phase we now write

$$\Psi_p(\mathbf{r},s) = \sum_{\boldsymbol{\mu},\mathbf{k}} \Phi_{\boldsymbol{\mu}\mathbf{k}}(\mathbf{r}) b_{\boldsymbol{\mu}\mathbf{k}s} \tag{89}$$

for the proton field operators, with

$$\Phi_{\boldsymbol{\mu}\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_n e^{i\mathbf{k}\mathbf{R}_n} f_{\boldsymbol{\mu}}(\mathbf{r}-\mathbf{R}_n) \tag{90}$$

where N is the number of protons and $f_{\boldsymbol{\mu}}(\mathbf{r}-\mathbf{R}_n)$ can be approximated by the $\boldsymbol{\mu}^{\mathrm{th}}$ excited-state eigenfunction of a three-dimensional harmonic oscillator potential centered at $\mathbf{R}_n$ [$\boldsymbol{\mu}$ denotes triplets of quantum numbers, i.e. (μ_x, μ_y, μ_z)].

Correspondingly, the electron-field operators are written as

$$\Psi_e(\mathbf{r},s) = \sum_{\nu,\mathbf{k}} \phi_{\nu\mathbf{k}}(\mathbf{r}) c_{\nu\mathbf{k}s}, \tag{91}$$

with $\phi_{\nu\mathbf{k}}(\mathbf{r})$ being Bloch states corresponding to the band ν. In Eqs. (89) and (91) b and c are $\mathbf{k}$-space proton and electron annihilation operators. Substitution of Eq. (90) into Eq. (89) yields

$$\Psi_p(\mathbf{r},s) = \sum_{\boldsymbol{\mu},n} f_{\boldsymbol{\mu}}(\mathbf{r}-\mathbf{R}_n) d_{\boldsymbol{\mu}s}(\mathbf{R}_n), \tag{92}$$

with the localized operator $d_{\boldsymbol{\mu}s}(\mathbf{R}_n)$ (annihilating a proton of spin s at site $\mathbf{R}_n$, which is found in the $\boldsymbol{\mu}^{\mathrm{th}}$ excited state) defined by

$$d_{\boldsymbol{\mu}s}(\mathbf{R}_n) = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} e^{i\mathbf{k}\mathbf{R}_n} b_{\boldsymbol{\mu}\mathbf{k}s}. \tag{93}$$

For reasons of formal symmetry Eq. (91) is also brought into a similar form with the use of electronic Wannier functions W_ν; by writing the Bloch states as

$$\phi_{\nu\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_n W_\nu(\mathbf{r}-\mathbf{R}_n) e^{i\mathbf{k}\mathbf{R}_n} \tag{94}$$

then Eq. (91) is transformed into

$$\Psi_e(\mathbf{r},s) = \sum_{\nu,n} W_\nu(\mathbf{r}-\mathbf{R}_n) \tilde{d}_{\nu s}(\mathbf{R}_n), \tag{95}$$

with the electron operator $\tilde{d}_{\nu s}$ defined by

$$\tilde{d}_{\nu s}(\mathbf{R}_n) = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} e^{i\mathbf{k}\mathbf{R}_n} c_{\nu\mathbf{k}s}. \tag{96}$$

With these transformations the two-component Hamiltonian (32) takes the form

$$H=\sum_{n}\sum_{\boldsymbol{\mu}_1\boldsymbol{\mu}_2 s} t_{\boldsymbol{\mu}_1\boldsymbol{\mu}_2} d^{\dagger}_{\boldsymbol{\mu}_1 s}(\mathbf{R}_n) d_{\boldsymbol{\mu}_2 s}(\mathbf{R}_n)+\sum_{n}\sum_{\nu_1\nu_2 s}\tilde{t}_{\nu_1\nu_2}\tilde{d}^{\dagger}_{\nu_1 s}(\mathbf{R}_n)\tilde{d}_{\nu_2 s}(\mathbf{R}_n)$$
$$+\frac{1}{2}\sum_{n\neq m}\sum_{ss'}\sum_{\boldsymbol{\mu}_3\boldsymbol{\mu}_4\boldsymbol{\mu}_5\boldsymbol{\mu}_6} v^{nm}_{\boldsymbol{\mu}_3\boldsymbol{\mu}_4\boldsymbol{\mu}_5\boldsymbol{\mu}_6} d^{\dagger}_{\boldsymbol{\mu}_3 s}(\mathbf{R}_n) d^{\dagger}_{\boldsymbol{\mu}_4 s'}(\mathbf{R}_m) d_{\boldsymbol{\mu}_5 s'}(\mathbf{R}_m) d_{\boldsymbol{\mu}_6 s}(\mathbf{R}_n)$$
$$+\frac{1}{2}\sum_{n\neq m}\sum_{ss'}\sum_{\nu_3\nu_4\nu_5\nu_6}\tilde{v}^{nm}_{\nu_3\nu_4\nu_5\nu_6}\tilde{d}^{\dagger}_{\nu_3 s}(\mathbf{R}_n)\tilde{d}^{\dagger}_{\nu_4 s'}(\mathbf{R}_m)\tilde{d}_{\nu_5 s'}(\mathbf{R}_m)\tilde{d}_{\nu_6 s}(\mathbf{R}_n)$$
$$-\sum_{nm}\sum_{ss'}\sum_{\nu_3\boldsymbol{\mu}_4\boldsymbol{\mu}_5\nu_6}\overline{v}^{nm}_{\nu_3\boldsymbol{\mu}_4\boldsymbol{\mu}_5\nu_6}\tilde{d}^{\dagger}_{\nu_3 s}(\mathbf{R}_n) d^{\dagger}_{\boldsymbol{\mu}_4 s'}(\mathbf{R}_m) d_{\boldsymbol{\mu}_5 s'}(\mathbf{R}_m)\tilde{d}_{\nu_6 s}(\mathbf{R}_n). \qquad (97)$$

In Eq. (97) the kinetic (hopping) elements t and $\tilde{t}$ are defined by

$$t_{\boldsymbol{\mu}_1\boldsymbol{\mu}_2}\equiv\int d^3k\,\frac{\hbar^2k^2}{2m_p}\hat{f}_{\boldsymbol{\mu}_1}(\mathbf{k})\hat{f}^{*}_{\boldsymbol{\mu}_2}(\mathbf{k}), \qquad (98)$$

and

$$\tilde{t}_{\nu_1\nu_2}\equiv\int d^3k\,\frac{\hbar^2k^2}{2m_e}\hat{W}_{\nu_1}(\mathbf{k})\hat{W}^{*}_{\nu_2}(\mathbf{k}), \qquad (99)$$

[with $\hat{f}_{\boldsymbol{\mu}}(\mathbf{k})$ and $\hat{W}_{\nu}(\mathbf{k})$ the Fourier transforms of $f_{\boldsymbol{\mu}}(\mathbf{r})$ and $W_{\nu}(\mathbf{r})$]; the potential elements v are defined by

$$v^{nm}_{\boldsymbol{\mu}_3\boldsymbol{\mu}_4\boldsymbol{\mu}_5\boldsymbol{\mu}_6}\equiv\sum_{\mathbf{q}}\frac{4\pi e^2}{Vq^2}e^{i\mathbf{q}(\mathbf{R}_n-\mathbf{R}_m)}\int\int d^3k\,d^3k'\,\hat{f}_{\boldsymbol{\mu}_3}(\mathbf{k})\hat{f}_{\boldsymbol{\mu}_4}$$
$$\times(\mathbf{k}')\hat{f}^{*}_{\boldsymbol{\mu}_5}(\mathbf{k}'+\mathbf{q})\hat{f}^{*}_{\boldsymbol{\mu}_6}(\mathbf{k}-\mathbf{q}), \qquad (100)$$

and the elements $\tilde{v}$ and $\overline{v}$ are given in a similar way by appropriate substitutions of $\hat{f}$'s with $\hat{W}$'s.

The new Hamiltonian (97) is *formally* quite similar to the continuous one [Eq. (32)], but with some important changes: now the space appears as *discrete*, the corresponding field operators are physically richer (containing labels $\boldsymbol{\mu}$ and ν), and the kinetic and potential elements are significantly renormalized from the continuous case. The entire physics of phonons and electron-hole transitions is included in Eq. (97); phonons, in this localized description, are associated with ''proton-hole pairs'' described by combinations of the type $d^{\dagger}_{\boldsymbol{\mu}_1}(\mathbf{R}_n)d_{\boldsymbol{\mu}_2}(\mathbf{R}_m)$ for neighboring sites (nm), and similar combinations of $\tilde{d}$'s contain all the physics of electron-hole pairs. At this point the simplest route is to retain just the oscillator ground states $(\boldsymbol{\mu}=0)$ and the lowest electronic bands $(\nu=0)$. Though not a completely general description this choice at least permits a first assessment of the solution structure for the discrete (crystalline) case.

With this reduced description our real-space analysis actually goes through completely as before but in discrete space, and the HS transformation will now pair the new operators d and $\tilde{d}$ in all four possible combinations. When we again proceed to Fourier transforms, the sums over $\mathbf{k}$ will now be restricted to sums over reciprocal lattice vectors. (These can alternatively be written as sums over $\mathbf{k}$ within the first Brillouin zone). In this formulation, $\xi_e(\mathbf{k})$ is simply substituted by the electronic band energies, while $\xi_p(\mathbf{k})$ will now lack dispersion and in fact equal $\xi_p(\mathbf{k})=3a_0^{*2}/2\sigma^2\mathrm{Ry}^*$, with σ the half width of the ground-state Gaussian $(\sigma=\sqrt{\hbar/m_p\omega}$, which is self-consistently dependent on density and temperature.) Here the proton mass has been used in the definition of a_0^* and Ry^*. Finally, the Coulomb interaction between protons is now changed to $e^2/|\mathbf{R}_{ij}|\mathrm{erf}(|\mathbf{R}_{ij}|/\sqrt{2}\sigma)$, which in turn renormalizes $v_c(\mathbf{q})$ to $v_c(\mathbf{q})e^{-q^2\sigma^2/2}$. (We see here the familiar Debye-Waller factor modifying the interaction). Similar modifications occur for the electron-electron and electron-proton interactions. Although the general conclusions drawn earlier for the simplest possible generalized pairing are not expected to change, the above modifications may have some further nontrivial consequences and an ongoing investigation is currently devoted to them. A preliminary result is that the lack of symmetry in the character of the states of the two Fermionic components may actually change the character of the corresponding T_c. Because the problem is richer, further solutions can also exist in principle for $T<T_c$ (where $\Delta_{\mathrm{ee}}\rightarrow 0$ while Δ_{pp} remains finite), especially if we permit the possibility that Δ_{pp} can vanish on a surface in $\mathbf{k}$ space. These solutions physically correspond to persistent proton-proton pairing in the presence of normal (unpaired) electrons.

The above model is a simplified but reasonable description for dense molecular hydrogen, when the electronic component is in semimetallic or metallic form. Here, as noted, a transition is expected to occur for $T<T_c$ as we move from higher to lower densities, especially to densities beyond the point where the electronic partial chemical potential becomes negative. From this point on we have to deal with case (a) of Sec. IV.

A final point that deserves special mention concerns the *stability* of the generalized paired phases discussed so far, from the point of view of the SPA. A simple stability analysis, already mentioned earlier, and based on the second-derivative matrix of the action with respect to the pairing fields, leads to expressions similar to those found before[3,2] for the collective excitations of the paired phase, but now corresponding to the limit $\omega\rightarrow 0$, namely a static distortion. If we take the particular cases $\Delta_{\mathrm{ee}}/\Delta_{\mathrm{ep}}\rightarrow 0$, $\Delta_{\mathrm{pp}}/\Delta_{\mathrm{ep}}\rightarrow 0$, and approximate Δ_{ep} by a constant, we obtain the expression

$$\sum_{\mathbf{k}}\left\{\frac{E\left(\mathbf{k}-\frac{\mathbf{K}_0}{2}\right)E\left(\mathbf{k}+\frac{\mathbf{K}_0}{2}\right)+\xi\left(\mathbf{k}-\frac{\mathbf{K}_0}{2}\right)\xi\left(\mathbf{k}+\frac{\mathbf{K}_0}{2}\right)}{E\left(\mathbf{k}-\frac{\mathbf{K}_0}{2}\right)E\left(\mathbf{k}+\frac{\mathbf{K}_0}{2}\right)\left[E\left(\mathbf{k}-\frac{\mathbf{K}_0}{2}\right)+E\left(\mathbf{k}+\frac{\mathbf{K}_0}{2}\right)\right]}-\frac{1}{E(\mathbf{k})}\right\}$$

$$=\pm|\Delta_{\mathrm{ep}}|^2\sum_{\mathbf{k}}\frac{1}{E\left(\mathbf{k}-\frac{\mathbf{K}_0}{2}\right)E\left(\mathbf{k}+\frac{\mathbf{K}_0}{2}\right)\left[E\left(\mathbf{k}-\frac{\mathbf{K}_0}{2}\right)+E\left(\mathbf{k}+\frac{\mathbf{K}_0}{2}\right)\right]},\tag{101}$$

which can be used to establish a criterion of *instability* of the generalized paired phase. In Eq. (101) E is approximately given by Eq. (29) with $\Delta=\Delta_{\mathrm{ep}}$, $\mu=\mu_e+\mu_p$, and $\xi(\mathbf{p})=\xi_e(\mathbf{p})+\xi_p(\mathbf{p})$. Whenever Eq. (101) has a real solution for the wave vector $\mathbf{K}_0$, this can be interpreted as a modulation of the paired phase that leads to a competing charge-density wave state (CDW) with the corresponding periodicity. To solve Eq. (101) for $\mathbf{K}_0$ is difficult in general, but we can nevertheless estimate the result with an expansion of Eq. (101) up to order $0(K_0^4)$, namely

$$\left(1+\frac{p_F^2K_0^2}{9m^2\Delta^2}-\frac{p_F^4K_0^4}{100m^4\Delta^4}+\cdots\cdots\right)=\pm\left(1-\frac{p_F^2K_0^2}{18m^2\Delta^2}+\frac{p_F^4K_0^4}{150m^4\Delta^4}+\cdots\cdots\right),\tag{102}$$

with $m\equiv m^*$, $\Delta\equiv\Delta_{\mathrm{ep}}$, and p_F the Fermi momentum. The smallest solution of Eq. (102) is

$$(K_0)^2\simeq\frac{10m^2\Delta^2}{p_F^2},\tag{103}$$

which, if combined with the earlier estimate $\Delta\sim 2/3r_s\mathrm{Ry}$, leads to $K_0\sim 1.6/a_0$. The physical picture is actually a straightforward one; the instability appears as a periodic modulation and is, therefore, consistent with intense infrared activity observed in experiments,[19] which has been associated with a new symmetry breaking[20] in dense hydrogen of a CDW type. This is an additional charge ordering that may formally be described as repairing of the original fields (a pairing of the generalized paired fields). A complete description of such a phase can only be made through a more general HS transformation than the one given here.

VI. CONCLUSION

We have given a natural generalization of the standard pairing theory for simple pairs to a problem of a two-component system with *all* possible kinds of pairings, but starting from fundamental Coulomb interactions. This theory constitutes a quite general treatment of a two-component system with Coulomb interactions and in ranges of density and temperature where generalized pairing structures can be formed. The theory is, therefore, a first-principles treatment of a fundamental many-body system in condensed-matter theory, but it also has an actual physical realization, namely hydrogen. For this system it gives a general account of the existence of a low-temperature critical point, and an inverse isotope effect observed in ultra-high-pressure experiments. It also leads to a prediction of a competing phase, namely a CDW, a result also consistent with recent experimental evidence of a symmetry broken phase leading to asymmetric charge ordering.

It is clear that the symmetry and the lack of spin dependence of the fundamental Coulomb interaction has resulted in highly symmetric equations for the two components, and this has led to a description of spatial characteristics of the order parameters, which are decoupled from the corresponding spin states. Here we have restricted ourselves to *isotropic* order parameters, which should correspond naturally to spin-singlet states. However, it is also possible to address the issue of magnetic ordering at low densities with the same method (although this will require a different HS transformation to account for the additional spin ordering). Further, exactly the same method can be applied to systems of different symmetry, for instance a Fermion-Boson mixture (e.g., deuterium). The only differences for this case are that the original fields for the Boson system will be complex variables (rather than Grassmann), and the final frequency sums are over Bose (i.e., even) Matsubara frequencies. However, the resulting physics is hardly expected to be very different because of the large mass of the nuclei compared with electronic masses. It may also be noted that for either mass, the Hamiltonian (32) describing the two-component system possesses very considerable symmetry leading to important scaling relations for the primary thermodynamic functions.[21] These can be generalized to the case where an external field is imposed;[22] the latter can be chosen as a probe for the existence of macroscopic currents, and hence for the onset of an insulator to metal transition when a control parameter (such as density) is varied. The transition can also be linked to the appearance of a geometric (Berry's) phase associated with the adiabatic parallel transport of the center of mass of the electron system[22] and in this way the insulator-metal transition in dense hydrogen can be put on a quite general footing.

Finally, we should also mention possible generalizations of the method to other systems. A quite straightforward adjustment is all that is necessary to describe generalized pairing in a two-component system with different (i.e., non-Coulombic) interactions (v_{ee}, v_{pp}, and $v_{\mathrm{ep}}=v_{\mathrm{pe}}$), with some of them possibly retaining a Coulombic part but others representing *pseudopotentials* appropriate for the system under consideration. It then transpires that Eqs. (66)–(69) retain their forms with the corresponding interaction appearing in each channel in place of v_c. In principle, this method could, therefore, address issues of pairing in high T_c or other complex materials, if, of course, the appropriate use of pseudopotentials is made from the start. Note, in particular, that for local approximations to pseudopotentials, the quantity $v_{\mathrm{ep}}(k)$ may be expected to vary in sign reflecting a length scale associated with the electronic condensation leading to the formation of ions. In some regions, therefore, the pseudopotential can be considered repulsive, yet it is important to note that self-consistent solutions to Eq. (66) may still exist in principle for particular choices of density (or k_F), and that as a consequence pairing of ions and electrons can still also exist.[23]

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APPENDIX A

We carry out the frequency sums that appear in Eq. (27). For this we first evaluate the frequency sum

$$J(x)=\sum_{\omega_n}\frac{1}{i\omega_n-x}, \tag{A1}$$

and then use this result to evaluate Eq. (27), but after resolving it into partial fractions. To evaluate $J(x)$ we first consider

$$I(x)=\int_C\frac{d\omega}{\omega-x}\frac{1}{e^{\beta\omega}+1} \tag{A2}$$

along a circular contour C in the complex ω plane that contains x and also certain Matsubara frequencies. The denominator $(1+e^{\beta\omega})^{-1}$ has simple poles at the $i\omega_n$'s with residues

$$\lim_{\omega\to i\omega_n}\frac{(\omega-i\omega_n)}{e^{\beta\omega}+1}=-\frac{1}{\beta}, \tag{A3}$$

so that with the residue of the integrand in Eq. (A2) at $\omega=x$ we have

$$I(x)=2\pi i\left[\sum_{\omega_n}\frac{1}{(i\omega_n-x)}\left(-\frac{1}{\beta}\right)+\frac{1}{e^{\beta x}+1}\right]. \tag{A4}$$

If we take the radius $R(C)$ of a circular contour to infinity (so that Σ_{ω_n} contains the entire infinite set of Matsubara frequencies), we must have

$$\lim_{R(C)\to\infty} I(x)=0, \tag{A5}$$

and then Eq. (107) gives

$$\sum_{\omega_n}\frac{1}{i\omega_n-x}=\frac{\beta}{e^{\beta x}+1} \tag{A6}$$

for the frequency sum $J(x)$. By analyzing Eq. (27) into partial fractions and using Eq. (A6) for each term we obtain

$$\sum_{\omega_n}\frac{1}{\omega_n^2+E^2}=\frac{\beta}{2iE}\tan\frac{i\beta E}{2}=\frac{\beta}{2E}\tanh\frac{\beta E}{2}, \tag{A7}$$

which in turn yields Eqs. (28) and (29) of the text.

APPENDIX B

We give below the definitions of the X_{ij}'s and det that appear in Eqs. (61)–(65) of the text; they are

$$X_{12}(\mathbf{k}',\omega_n)=\Delta_{\mathrm{ee}}(\mathbf{k}')\{(\omega_n)^2+[\epsilon_p(\mathbf{k}')-\mu_p]^2+|\Delta_{\mathrm{pp}}(\mathbf{k}')|^2\}-\Delta^*_{\mathrm{pp}}(\mathbf{k}')\Delta_{\mathrm{ep}}(\mathbf{k}')\Delta_{\mathrm{pe}}(\mathbf{k}'), \tag{B1}$$

$$X_{34}(\mathbf{k}',\omega_n)=\Delta_{\mathrm{pp}}(\mathbf{k}')\{(\omega_n)^2+[\epsilon_e(\mathbf{k}')-\mu_e]^2+|\Delta_{\mathrm{ee}}(\mathbf{k}')|^2\}-\Delta^*_{\mathrm{ee}}(\mathbf{k}')\Delta_{\mathrm{ep}}(\mathbf{k}')\Delta_{\mathrm{pe}}(\mathbf{k}'), \tag{B2}$$

$$\begin{aligned}X_{32}(\mathbf{k}',\omega_n)={}&\Delta_{\mathrm{pe}}(\mathbf{k}')\{(\omega_n)^2+[\epsilon_e(\mathbf{k}')-\mu_e][\epsilon_p(\mathbf{k}')-\mu_p]\}+i\Delta_{\mathrm{pe}}(\mathbf{k}')\omega_n\{[\epsilon_e(\mathbf{k}')-\mu_e]-[\epsilon_p(\mathbf{k}')-\mu_p]\}\\&+\Delta_{\mathrm{ep}}(\mathbf{k}')|\Delta_{\mathrm{pe}}(\mathbf{k}')|^2-\Delta^*_{\mathrm{pe}}(\mathbf{k}')\Delta_{\mathrm{ee}}(\mathbf{k}')\Delta_{\mathrm{pp}}(\mathbf{k}'),\end{aligned} \tag{B3}$$

$$\begin{aligned}X_{14}(\mathbf{k}',\omega_n)={}&\Delta_{\mathrm{ep}}(\mathbf{k}')\{(\omega_n)^2+[\epsilon_e(\mathbf{k}')-\mu_e][\epsilon_p(\mathbf{k}')-\mu_p]\}-i\Delta_{\mathrm{ep}}(\mathbf{k}')\omega_n\{[\epsilon_e(\mathbf{k}')-\mu_e]-[\epsilon_p(\mathbf{k}')-\mu_p]\}\\&+\Delta_{\mathrm{pe}}(\mathbf{k}')|\Delta_{\mathrm{ep}}(\mathbf{k}')|^2-\Delta^*_{\mathrm{ep}}(\mathbf{k}')\Delta_{\mathrm{ee}}(\mathbf{k}')\Delta_{\mathrm{pp}}(\mathbf{k}'),\end{aligned} \tag{B4}$$

and

$$\begin{aligned}\det(\mathbf{k}',\omega_n)={}&(\omega_n)^4+(\omega_n)^2\{|\Delta_{\mathrm{ee}}(\mathbf{k}')|^2+|\Delta_{\mathrm{pp}}(\mathbf{k}')|^2+[\epsilon_e(\mathbf{k}')-\mu_e]^2+[\epsilon_p(\mathbf{k}')-\mu_e]^2+\Delta_{\mathrm{ep}}(\mathbf{k}')\Delta^*_{\mathrm{pe}}(\mathbf{k}')+\Delta_{\mathrm{pe}}(\mathbf{k}')\Delta^*_{\mathrm{ep}}(\mathbf{k}')\}\\&+|\Delta_{\mathrm{ep}}(\mathbf{k}')|^2|\Delta_{\mathrm{pe}}(\mathbf{k}')|^2+|\Delta_{\mathrm{ee}}(\mathbf{k}')|^2|\Delta_{\mathrm{pp}}(\mathbf{k}')|^2-2\,\mathrm{Re}[\Delta^*_{\mathrm{ee}}(\mathbf{k}')\Delta^*_{\mathrm{pp}}(\mathbf{k}')\Delta_{\mathrm{ep}}(\mathbf{k}')\Delta_{\mathrm{pe}}(\mathbf{k}')]+[\epsilon_e(\mathbf{k}')-\mu_e]^2[\epsilon_p(\mathbf{k}')\\&-\mu_p]^2+[\epsilon_e(\mathbf{k}')-\mu_e]^2|\Delta_{\mathrm{pp}}(\mathbf{k}')|^2+[\epsilon_p(\mathbf{k}')-\mu_p]^2|\Delta_{\mathrm{ee}}(\mathbf{k}')|^2+2\,\mathrm{Re}[\Delta_{\mathrm{ep}}(\mathbf{k}')\Delta^*_{\mathrm{pe}}(\mathbf{k}')][\epsilon_e(\mathbf{k}')-\mu_e][\epsilon_p(\mathbf{k}')\\&-\mu_p]-\omega_n(\{[\epsilon_p(\mathbf{k}')-\mu_p]-[\epsilon_e(\mathbf{k}')-\mu_e]\}2\,\mathrm{Im}[\Delta_{\mathrm{ep}}(\mathbf{k}')\Delta^*_{\mathrm{pe}}(\mathbf{k}')]).\end{aligned} \tag{B5}$$

APPENDIX C

We carry out below the frequency sums that appear in Eqs. (61)–(64), combining them at the same time with the definitions of Appendix B. Using the constraint (58) we find that the last term of Eq. (B5) vanishes and as a consequence the frequency sums can be carried out relatively easily. For example, the imaginary terms in Eqs. (B3) and (B4) also vanish when we sum over ω_n, and therefore we only need sums of the form

$$\sum_{\omega_n} \frac{\omega_n^2+a}{\omega_n^4+b\omega_n^2+c}. \tag{C1}$$

For their calculation we resort to contour integrals of the form

$$I=\int_C \frac{d\omega(-\omega^2+a)}{(\omega^4-b\omega^2+c)(1+e^{\beta\omega})}. \tag{C2}$$

Note that the signs are appropriately chosen so that the residues at the Matsubara frequencies will give sums of the required form (C1). Carrying out the contour integration and then taking the contour to infinity (so that $I\rightarrow 0$) we finally obtain the result

$$\sum_{\omega_n} \frac{\omega_n^2+a}{\omega_n^4+b\omega_4^2+c}=\beta\left[\frac{(-r_1^2+a)}{(r_1-r_2)(r_1-r_3)(r_1-r_4)}\frac{1}{1+e^{\beta r_1}}+\frac{(-r_2^2+a)}{(r_2-r_1)(r_2-r_3)(r_2-r_4)}\frac{1}{1+e^{\beta r_2}}\right.$$
$$\left.+\frac{(-r_3^2+a)}{(r_3-r_1)(r_3-r_2)(r_3-r_4)}\frac{1}{1+e^{\beta r_3}}+\frac{(-r_4^2+a)}{(r_4-r_1)(r_4-r_2)(r_4-r_3)}\frac{1}{1+e^{\beta r_4}}\right], \tag{C3}$$

where r_1, r_2, r_3, and r_4 are the roots of $\omega^4-b\omega^2+c$, i.e.,

$$\omega^4-b\omega^2+c\equiv(\omega-r_1)(\omega-r_2)(\omega-r_3)(\omega-r_4). \tag{C4}$$

Applying the above results to Eqs. (61)–(64) (once again in combination with the definitions of Appendix B) we obtain

$$r_{1,2,3,4}=\pm\sqrt{\tilde{D}^2\pm\sqrt{\tilde{D}^4-F^4}}, \tag{C5}$$

where it is understood that the four roots can be obtained by taking all four possible combinations of signs in Eq. (120). Here we have defined

$$\tilde{D}^2=\frac{1}{2}\{|\Delta_{\rm ee}(\mathbf{k}')|^2+|\Delta_{\rm pp}(\mathbf{k}')|^2+2\,\mathrm{Re}[\Delta_{\rm ep}(\mathbf{k}')\Delta_{\rm pe}^*(\mathbf{k}')]+[\epsilon_e(\mathbf{k}')-\mu_e]^2+[\epsilon_p(\mathbf{k}')-\mu_p]^2\}, \tag{C6}$$

and

$$F^4=|\Delta_{\rm ee}(\mathbf{k}')|^2|\Delta_{\rm pp}(\mathbf{k}')|^2+|\Delta_{\rm ep}(\mathbf{k}')|^2|\Delta_{\rm pe}(\mathbf{k}')|^2-2\,\mathrm{Re}[\Delta_{\rm ee}(\mathbf{k}')\Delta_{\rm pp}(\mathbf{k}')\Delta_{\rm ep}^*(\mathbf{k}')\Delta_{\rm pe}^*(\mathbf{k}')]+[\epsilon_e(\mathbf{k}')-\mu_e]^2|\Delta_{\rm pp}(\mathbf{k}')|^2$$
$$+[\epsilon_p(\mathbf{k}')-\mu_p]^2|\Delta_{\rm ee}(\mathbf{k}')|^2+[\epsilon_e(\mathbf{k}')-\mu_e]^2[\epsilon_p(\mathbf{k}')-\mu_p]^2+2\,\mathrm{Re}[\Delta_{\rm ep}(\mathbf{k}')\Delta_{\rm pe}^*(\mathbf{k}')][\epsilon_e(\mathbf{k}')-\mu_e][\epsilon_p(\mathbf{k}')-\mu_p]. \tag{C7}$$

The final application of all the above to Eqs. (61)–(65) yields Eqs. (66)–(77) given in the text.

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