Generalized Coulomb Pairing in the Condensed State

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Starting with a view of condensed matter as a neutral assembly of electrons and nuclei, with mutual Coulomb interactions, a coherent-state functional-integral approach gives a first-principles theory of pairing phases that requires no adiabatic separation of time scales. For electrons and protons, both fermions, we show that an *interdependent* pairing of electrons *and* of protons can arise at low temperature with *effective* pairing interactions. A critical point for this system is identified, which is discussed in the light of recent experiments on dense hydrogen.

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A powerful method for dealing with collective quantum states is the functional-integral approach[1,2] in which the partition function Z for the many-body system appears as a coherent-state functional integral.[3] In a single-component fermion system with an *assumed* static pairing interaction v, the partition function then takes the form[3]

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

where $\{\Psi^*,\Psi\}$ are Grassmann variables, and for chemical potential μ the action S is given by

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

Here

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

is the Hamiltonian and $\int dx\equiv\sum_s\int d^3r$. At this point the standard procedure is to perform an appropriate Hubbard-Stratonovich (HS) transformation[4,5] giving

$$Z[\Psi^*,\Psi;\Delta^*,\Delta]=\text{const}\times\int D[\Psi^*]D[\Psi]D[\Delta^*]D[\Delta]\times\exp\{\tilde{S}[\Psi^*,\Psi;\Delta^*,\Delta]/\hbar\}\,, \tag{4}$$

thereby introducing new collective fields $\{\Delta^*,\Delta\}$ and a new action[1,6]

$$\tilde{S}[\Psi^*,\Psi;\Delta^*,\Delta]=\int d1\,d2\left\{\frac{1}{2}\mathbf{\Phi}^*(1)\cdot[-\hat{A}(12)]\cdot\mathbf{\Phi}(2)+\frac{1}{2}\Delta^*(12)\frac{1}{v(1-2)}\Delta(12)\right\}, \tag{5}$$

which is written here in matrix form (analogous to Nambu's description[7]) in order to facilitate comparison with the more general case below. In Eq. (5), $1\equiv s\mathbf{r}\tau$, the transpose of $\mathbf{\Phi}$ is

$$\mathbf{\Phi}^T(1)\equiv(\Psi(1)\;\;\Psi^*(1))\,, \tag{6}$$

and

$$\hat{A}(12)\equiv\begin{pmatrix}\delta(1-2)[\hbar\,\partial/\partial\tau+\epsilon(-i\hbar\nabla)-\mu] & \Delta(12)\\ \Delta^*(12) & \delta(1-2)[\hbar\,\partial/\partial\tau-\epsilon(-i\hbar\nabla)+\mu]\end{pmatrix}. \tag{7}$$

Equation (5) makes clear the fact that the transformed action is quadratic in the Ψ's. Accordingly a Gaussian integration can be carried out leading to

$$Z=\text{const}\times\int D[\Delta^*]D[\Delta]\exp(\bar{S}[\Delta^*,\Delta]/\hbar)\,, \tag{8}$$

with

$$\bar{S}[\Delta^*,\Delta]=\operatorname{tr}\ln\left(\frac{\hat{A}}{2}\right)+\frac{1}{2}\int d1\,d2\frac{|\Delta(12)|^2}{v(1-2)}. \tag{9}$$

Up to this point the procedure is exact. To proceed further requires approximation and it is customary to invoke a stationary phase approximation, an extremization of $\bar{S}$ with respect to the Δ's, which leads to the mean-field equations that the new field Δ must satisfy. Thus from the vanishing of $\delta\bar{S}/\delta\Delta^*$ we obtain

$$\Delta(12)=-v(12)\operatorname{tr}\left[\hat{A}^{-1}(12)\cdot\begin{pmatrix}0&0\\1&0\end{pmatrix}\right], \tag{10}$$

which, after Fourier transformation, and introduction of and summation over Matsubara frequencies, leads to

$$\Delta(\mathbf{k})=-\sum_{\mathbf{k}'}v(\mathbf{k}-\mathbf{k}')\frac{\Delta(\mathbf{k}')}{2E(\mathbf{k}')}\tanh\left(\frac{\beta E(\mathbf{k}')}{2}\right), \tag{11}$$

where

$$E(\mathbf{k})=\{[\epsilon(\mathbf{k})-\mu]^2+|\Delta(\mathbf{k})|^2\}^{1/2}; \tag{12}$$

Equations (11) and (12) are recognized as the familiar BCS equations for the gap parameter Δ and quasiparticle spectrum, respectively. Thus the method leads to a correct description of Cooper pairs at high densities, and even to tightly bound pairs in the low-density limit.[8] In this one-component procedure, the pairing interaction v has been assumed *a priori,* and is usually taken from heuristic arguments defining the fermion problem in the phonon or some other picture.

In this Letter we show that pairing can actually be established at a more fundamental level, starting with the system viewed as a neutral mixture of electrons ($\alpha = e$) and nuclei ($\alpha = p$) (protons will be the example chosen) with bare Coulomb interactions, alone. The equivalent of (3) is then

$$H[\Psi_e^*,\Psi_e;\Psi_p^*,\Psi_p] = \sum_\alpha \left[\int dx\, \Psi_\alpha^*(x\tau)\epsilon_\alpha(-i\hbar\nabla)\Psi_\alpha(x\tau) + \tfrac{1}{2}\sum_{\alpha'} z_\alpha z_{\alpha'} \int dx\, dy\, \Psi_\alpha^*(x\tau)\Psi_{\alpha'}^*(y\tau)v_c(x-y)\Psi_{\alpha'}(y\tau)\Psi_\alpha(x\tau) \right], \tag{13}$$

where $z_p = +1$, $z_e = -1$, and v_c is now $e^2/|\mathbf{x}-\mathbf{y}|$, the fundamental Coulomb term (which is strictly independent of spin s). The action is

$$\begin{aligned} S &= \int_0^{\beta\hbar} d\tau \left\{ \int dx \sum_\alpha \left[\Psi_\alpha^*(x\tau) \left(\hbar\frac{\partial}{\partial\tau} - \mu_\alpha \right) \Psi_\alpha(x\tau) \right] + H[\Psi_e^*(x\tau),\Psi_e(x\tau);\Psi_p^*(x\tau),\Psi_p(x\tau)] \right\} \\ &= \int_0^{\beta\hbar} d\tau \int dx\, dy \sum_\alpha \left\{ \Psi_\alpha^*(x\tau)\delta(x-y) \left(\hbar\frac{\partial}{\partial\tau} + \epsilon_\alpha(-i\hbar\nabla) - \mu_\alpha \right) \Psi_\alpha(y\tau) \right\} \\ &\quad + \tfrac{1}{2} \int dx\, dy \int_0^{\beta\hbar} d\tau\, \mathbf{\Psi}^*(xy\tau)\cdot \hat{\hat{V}}(xy)\cdot \mathbf{\Psi}(xy\tau). \end{aligned} \tag{14}$$

Here [cf. (6)] the transpose of $\mathbf{\Psi}$ is

$$\mathbf{\Psi}^T(xy\tau) \equiv (\Psi_e^*(x\tau)\Psi_e^*(y\tau) \quad \Psi_p^*(x\tau)\Psi_p^*(y\tau) \quad \Psi_e^*(x\tau)\Psi_p^*(y\tau) \quad \Psi_p^*(x\tau)\Psi_e^*(y\tau)), \tag{15}$$

and

$$\hat{\hat{V}}(xy) \equiv v_c(x-y) \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}. \tag{16}$$

The compactness of the form (14) for S is entirely a consequence of the symmetry of the Coulomb interaction. A HS transformation on (14) leads[6] to an immediate generalization of (4), namely,

$$Z = \text{const} \times \int D[\mathbf{\Psi}^*]D[\mathbf{\Psi}]D[\mathbf{\Delta}^*]D[\mathbf{\Delta}] \exp\{\tilde{S}[\mathbf{\Psi}^*,\mathbf{\Psi};\mathbf{\Delta}^*,\mathbf{\Delta}]/\hbar\}, \tag{17}$$

where the companion of (5) is

$$\tilde{S}[\mathbf{\Psi}^*,\mathbf{\Psi};\mathbf{\Delta}^*,\mathbf{\Delta}] = \int d1\, d2 \{ \tfrac{1}{2}\mathbf{\Phi}^*(1)\cdot[-\hat{A}(12)]\cdot\mathbf{\Phi}(2) + \tfrac{1}{2}\mathbf{\Delta}^*(12)\cdot\hat{\hat{V}}^{-1}(12)\cdot\mathbf{\Delta}(12)\}. \tag{18}$$

In (18) $\mathbf{\Phi}$ is the generalization of (6), $\hat{\hat{V}}^{-1}$ is the formal inverse of (16), and $\hat{A}$ is the expected generalization of (7), namely,

$$\hat{A}(12) \equiv \begin{pmatrix} \delta(12)(\hbar\,\partial/\partial\tau + \xi_e) & \Delta_{ee}(12) & 0 & \Delta_{ep}(12) \\ \Delta_{ee}^*(12) & \delta(12)(\hbar\,\partial/\partial\tau - \xi_e) & \Delta_{ep}^*(12) & 0 \\ 0 & \Delta_{pe}(12) & \delta(12)(\hbar\,\partial/\partial\tau + \xi_p) & \Delta_{pp}(12) \\ \Delta_{pe}^*(12) & 0 & \Delta_{pp}^*(12) & \delta(12)(\hbar\,\partial/\partial\tau - \xi_p) \end{pmatrix}, \tag{19}$$

where we have used the notation $\xi_a = \epsilon_a(-i\hbar\nabla) - \mu_a$. Here $\Delta_{\alpha\beta}(12)$ are the components of the vector $\mathbf{\Delta}(12)$ appearing in (18). Gaussian integration over the Grassmann variables leads[6] to the extensions of (8) and (9), which are still exact, and via the stationary phase approximation to *four* gap equations, the immediate generalization of (11), namely,

$$\Delta_{ee}(\mathbf{k}) = -\sum_{\mathbf{k}'} \frac{v_c(\mathbf{k}-\mathbf{k}')\Delta_{ee}(\mathbf{k}')}{2[r_1^2(\mathbf{k}') - r_3^2(\mathbf{k}')]} \{[t_1(\mathbf{k}') - t_3(\mathbf{k}')] + D_{ee}(\mathbf{k}')[y_3(\mathbf{k}') - y_1(\mathbf{k}')]\} \tag{20}$$

and

$$\Delta_{ep}(\mathbf{k}) = +\sum_{\mathbf{k}'} \frac{v_c(\mathbf{k}-\mathbf{k}')\Delta_{pe}(\mathbf{k}')}{2[r_1^2(\mathbf{k}')-r_3^2(\mathbf{k}')]}\{[t_1(\mathbf{k}')-t_3(\mathbf{k}')]+D_{ep}(\mathbf{k}')[y_3(\mathbf{k}')-y_1(\mathbf{k}')]\}\,, \tag{21}$$

with corresponding equations for Δ_{pp} and Δ_{pe}. Here we introduce the notation

$$t_i(\mathbf{k}') \equiv r_i(\mathbf{k}')\tanh[\tfrac{1}{2}\beta r_i(\mathbf{k}')]\,, \tag{22}$$

$$y_i(\mathbf{k}') \equiv \tanh[\tfrac{1}{2}\beta r_i(\mathbf{k}')]/r_i(\mathbf{k}')\,, \tag{23}$$

$$D_{ee}(\mathbf{k}') = \xi_p^2(\mathbf{k}') + |\Delta_{pp}(\mathbf{k}')|^2 - \Delta_{pp}^*(\mathbf{k}')\Delta_{ep}(\mathbf{k}')\Delta_{pe}(\mathbf{k}')/\Delta_{ee}(\mathbf{k}')\,, \tag{24}$$

and

$$D_{ep}(\mathbf{k}') = \xi_e(\mathbf{k}')\xi_p(\mathbf{k}') + \Delta_{ep}(\mathbf{k}')\Delta_{pe}^*(\mathbf{k}') - \Delta_{ee}(\mathbf{k}')\Delta_{pp}(\mathbf{k}')\Delta_{pe}^*(\mathbf{k}')/\Delta_{pe}(\mathbf{k}')\,, \tag{25}$$

again with corresponding equations for D_{pp} and D_{pe}. The quantities r_1 and r_3 are defined by

$$r_{1,3}(\mathbf{k}') = [\tilde{D}^2(\mathbf{k}') \pm D^2(\mathbf{k}')/2]^{1/2}\,, \tag{26}$$

with

$$\tilde{D}^2 = \tfrac{1}{2}\{|\Delta_{ee}(\mathbf{k}')|^2 + |\Delta_{pp}(\mathbf{k}')|^2 + 2\,\mathrm{Re}[\Delta_{ep}(\mathbf{k}')\Delta_{pe}^*(\mathbf{k}')] + \xi_e^2(\mathbf{k}') + \xi_p^2(\mathbf{k}')\} \tag{27}$$

and

$$\begin{aligned} D^2(\mathbf{k}') = r_1^2(\mathbf{k}') - r_3^2(\mathbf{k}') = (\,&[|\Delta_{ee}(\mathbf{k}')|^2 - |\Delta_{pp}(\mathbf{k}')|^2 + \xi_e^2(\mathbf{k}') - \xi_p^2(\mathbf{k}')]^2 \\ &+ 4\Delta_{ep}(\mathbf{k}')\Delta_{pe}^*(\mathbf{k}')\{|\Delta_{ee}(\mathbf{k}')|^2 + |\Delta_{pp}(\mathbf{k}')|^2 + [\xi_e(\mathbf{k}') - \xi_p(\mathbf{k}')]^2\} \\ &+ 8\,\mathrm{Re}[\Delta_{ee}(\mathbf{k}')\Delta_{pp}(\mathbf{k}')\Delta_{ep}^*(\mathbf{k}')\Delta_{pe}^*(\mathbf{k}')])^{1/2}\,. \end{aligned} \tag{28}$$

The above system of equations is necessarily more complex than the one-component case. But, correspondingly, there is a remarkable richness of physical structure in its solutions. Further, the equations possess some formally transparent limits. First, when Δ_{ep} (and Δ_{pe}) approaches 0 there is an expected decoupling of Eq. (20) and of the parallel equation for Δ_{pp} into two BCS gap equations corresponding to *e-e* and *p-p* pairing. These, of course, have no solution, since the interactions are bare Coulomb repulsions. Next, for the complementary case of Δ_{ee} (and Δ_{pp}) approaching 0, Eq. (21) leads to a gap equation of the "excitonic-insulator" type[9] for the cross-order parameter. More generally it is straightforward to show[10] that in *all* cases, a nonvanishing Δ_{ep} always has an attractive effect, i.e., *the effective interactions between identical particles are always less repulsive than the bare Coulomb interaction.*

There are also some physically expected limits of Eqs. (20) and (21), associated with the case Δ_{ee}/Δ_{ep} (and Δ_{pp}/Δ_{ep}) approaching 0. Two general classes of solutions develop, depending on whether $|\Delta_{ep}|^2$ is small or large compared to the product $\xi_\alpha\xi_\beta$, with $\{\alpha,\beta\}=$(any of $\{e,p\}$). To examine whether solutions to (20) and (21) actually exist in principle we may take all $\Delta_{\alpha\beta}$ to be real and isotropic (*s*-wave singlet states). The following results then emerge.[10]

(a) Solutions corresponding to $|\Delta_{ep}|^2 \ll \xi_\alpha\xi_\beta$ for any k are possible only for sufficiently low densities, particularly when μ_e and μ_p are both negative. At low density and low temperature the cross-order parameter has the form

$$\Delta_{ep}(k) = \mathrm{const}\times[\xi_e(k)+\xi_p(k)]/(1+k^2a^2)^2\,, \tag{29}$$

with $a=\hbar^2/m^*e^2$. From a canonical analysis[8] 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

$$|\Delta(k)|^2 = 4\xi(k)^2|\phi_k|^2/(1-|\phi_k|^2)^2\,. \tag{30}$$

In the low-density limit $\phi_k \to 0$, and by noting that the Fourier transform of $e^{-r/a}$ (a 1*s* state) is proportional to $(1+k^2a^2)^{-2}$, a comparison with (29) shows that this solution corresponds to an *atomic e-p* state. This is consistent[10] 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.*

(b) The second class of solutions corresponds to $|\Delta_{ep}|^2 \gg \xi_\alpha\xi_\beta$ for some $k<k_0$. In this case Δ_{ep} can be approximated by[10]

$$\Delta_{ep}(k) \simeq (e^2/\pi)k_0F(k/k_0)\,, \tag{31}$$

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

$$2\Delta_{ep}(k_0) = |\xi_e(k_0)+\xi_p(k_0)|\,. \tag{32}$$

This is entirely different from (29) and is valid[10] only at sufficiently *high* densities [up to the point that (32) actually fails to give a real and positive solution for k_0]. We therefore see the possibility of a *discontinuous transition* from the low-density molecular phase to the high-density phase described by (31). This transition was anticipated recently[8] but through a different procedure. The high-density phase is readily associated with a delocalization of the electronic component, 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 (20) (or the corresponding equation for Δ_{pp}) with (11) we can easily determine the *effective* pairing interaction associated with each component.

As a criterion for stability of the paired phases we invoke the requirement that there are at least *some* regions in k space where the effective interactions become negative. The major results[10] for this case are the following: (i) In the high-temperature limit there are no solutions to (20), as physically expected. (ii) When temperature is lowered, solutions to (20) emerge, especially when the cross-order parameter Δ_{ep} is sufficiently strong. An accurate low-temperature approximation for Δ_{ep} is given by (31). We note that solutions to (20) and to the corresponding equation for Δ_{pp} then do emerge because of the development of effective *attractions* in certain regions of k space for the e-e and p-p channels. (iii) A critical point T_c is found where the order parameters Δ_{ee} and Δ_{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 $\bar{k}$ 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., $\xi_e(\bar{k}) + \xi_p(\bar{k}) = 0$]. (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[11,12] on hydrogen). A simple approximation for T_c for strong Δ_{ep} turns out to be

$$k_B T_c \simeq \left[\Delta_{ep} - \frac{|\xi_e - \xi_p|}{2} \right] \left[\ln \left(\frac{2\Delta_{ep}}{|\xi_e - \xi_p|} \frac{\alpha + 1}{|\alpha - 1|} \right) \right]^{-1}, \tag{33}$$

where the ratio $\alpha \equiv \Delta_{pp}/\Delta_{ee}$ is expected to approach unity as $T \to T_c$ as can be verified by using the structure of the full equations at low temperature and l'Hôspital's rule in the limit that both Δ's vanish. [All quantities in (33) are evaluated at $k = \bar{k}$.] (v) An *inverse* isotope effect is expected for the dependence of T_c on the protonic mass; this also happens to be in agreement with recent data.[13]

By way of practical application of case (b) we analyze two models: one for a diffusive state, and another for protons treated as Einstein oscillators vibrating within *preformed* p-p pairs (remnants of the low-density Heitler-London fields discussed above). The electrons are assumed to be fully degenerate in all cases and the chemical potentials necessary for these applications are taken from our recent work.[14] The first model is a satisfactory description of possible generalized pairing in an electron-hole liquid and a primary result is that pairing of identical particles will *not* occur if the masses are identical; only simple e-p pairing of the excitonic type is predicted. 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 then result. The second model is a possible description for dense molecular hydrogen, with the electronic component being in semimetallic or metallic form. Here, as noted, a discontinuous transition may occur for $T < T_c$ as we move from higher to lower densities, especially to densities beyond the point where the electronic chemical potential becomes negative. From this point on we have to deal with case (a).

To summarize, we have given a generalization of the BCS theory for simple pairs to a problem of a two-component system with *all* possible kinds of pairings, but starting from fundamental Coulomb interactions. So far as we are aware this theory constitutes the most general description to date of a two-component system with Coulomb interactions in ranges of density and temperature where pairing structures can be formed. It is important to emphasize that it does *not* employ the usual Born-Oppenheimer separation, so that fluctuations of both components are treated on the same footing. It is also a first-principles treatment of a many-body system which has an actual physical realization, namely, hydrogen, for which it gives an account of the existence of a relatively low-temperature critical point and an inverse isotope effect, both observed recently.

Finally, the interrelationship demonstrated here between electron pairing and a structural singularity (in the proton pairing) is a matter we are investigating further from the standpoint of its possible application to high-temperature superconductivity.

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