

## New Low Density Phase of Interacting Electrons: The Paired Electron Crystal

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A variational method shows that for a range of densities the compensated low density interacting electron system possesses a ground-state crystalline phase with  $L=0$  spin-singlet pairs and with an energy lower than the Wigner crystal. The physical origin of the additional binding is intrapair exchange resulting from wave-function overlap and cooperative anharmonic behavior.

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The quantum many-body problem of  $N$  interacting electrons confined to a volume  $V$  ( $N/V=\rho_0$ ) containing a rigid continuum of compensating charge has been an important model system in the development of condensed matter physics. The Hamiltonian for this system,

$$H = \sum_{i=1}^N \frac{\hat{p}_i^2}{2m} + \frac{1}{2} \int d^3r \int d^3r' [\hat{\rho}^{(2)}(\mathbf{r}, \mathbf{r}') + \rho_0^2 - 2\rho_0 \hat{\rho}^{(1)}(\mathbf{r})] \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \quad (1)$$

(where  $\hat{\rho}^{(2)}$  and  $\hat{\rho}^{(1)}$  are two- and one-particle density operators), has considerable symmetry, and it is well known that at high densities, or small values of the linear spacing parameter  $r_s$ ,  $[(4\pi/3)r_s^3 a_0^3 = 1/\rho_0]$ , the states correspond to a homogeneous Fermi liquid. However, for quite low densities Wigner proposed [1] in 1934 a ground state that breaks the symmetry of  $H$ , forming a *monatomic* three-dimensional antiferromagnetic crystal. This state appears to emerge in simulation studies [2] at  $r_s \gtrsim 100$ ; unlike classical systems the melting transition to the homogeneous phase has a large value of the Lindemann parameter ( $\sim 0.28$ ) and indicates that anharmonic effects can be important. Independent of phase, the ground-state energy of (1) is bounded below [3] by  $-N \frac{2}{5} r_s \text{ Ry}$ .

The question we pose and answer in this Letter is whether in a range of densities the symmetry of  $H$  can be broken again, by permitting the electrons to condense into a crystal of singlet pairs. Put in other terms, can the energy be lowered further by removing the implied constraint of the Wigner crystal to spatial Bravais lattices? We shall see that the expected electrostatic penalty is more than recouped from exchange resulting in a distinct preference, over monatomic arrangements, for a *paired* crystal. Thus, the proposition is that there exists an antisymmetrized ( $A$ ) many-electron state of (1)

$$\Psi = A \psi_{\mathbf{R}_1}^{(2)}(\mathbf{r}_1 \mathbf{r}_2, \sigma_1 \sigma_2) \psi_{\mathbf{R}_2}^{(2)}(\mathbf{r}_3 \mathbf{r}_4, \sigma_3 \sigma_4) \cdots \times \psi_{\mathbf{R}_{N/2}}^{(2)}(\mathbf{r}_{N-1} \mathbf{r}_N, \sigma_{N-1} \sigma_N) \quad (2)$$

(where the  $\psi^{(2)}$  are singlet pair states localized at the sites of a lattice  $\{\mathbf{R}_i\}$ ) which is energetically lower than the monatomic equivalent. We argue in this Letter that a variational state which ignores interpair exchange *already* gives an energy lower than the conventional crystal. It further suggests a general tendency towards pairing at low densities which, as discussed below, can be established from a state based on (2) possessing clear links to

superconducting order in the delocalized limit.

We will focus on the low density regime ( $r_s \gtrsim 100$ ) and especially on the possible physical realization of a crystal of *rotational pairs*. In this range of densities the success of the original arguments of Wigner lead immediately to a spherical cell variational method with an initial choice of many-particle states that neglect interpair exchange. We will therefore report on a simple  $r$ -space variational determination of the ground-state energy of a proposed paired state of a low density three-dimensional electron system in a uniform positive background. This state consists of spin-singlet electron pairs in rotational ( $L=0$ ) states with their centers of mass vibrating around the sites of a lattice. Though, as stated, interpair exchange is ignored in such a trial state, exchange between the two electrons within each pair, which is a dominant effect, is included and treated through a Heitler-London ansatz. The anharmonicities in the motion of each electron referred to above are also easily taken into account through the use of the lowest single-particle Morse function. For a certain range of low densities we show that this trial state actually has energy *lower* than that of the conventional monatomic lattice proposed by Wigner [1].

The calculation proceeds within the Wigner-Seitz method and the result is therefore independent of the structure of the underlying lattice. The conventional Wigner crystal is also treated within the same method so that a comparison of the two results can be made in a systematic way. As is well known from comparison with lattice summation methods the errors in energy in this approach are small for symmetric structures (less than  $\frac{1}{2}\%$ ) and arise principally from multipole corrections in electrostatic terms. It is important to note that these errors in electrostatic energies are actually *common* to both monatomic and  $L=0$  paired phases and in fact this is rigorously demonstrable [4]; most importantly the energy lowering we find exceeds such errors. The spherical cell

method is basically the one used in the original treatment by Wigner, although in our analysis we shall emphasize the distributed nature of the charge of the electrons rather than proceeding with a simple point-charge approach. What this viewpoint provides is a variational procedure with respect to the width of the smeared charge density, and it can then be applied to both problems. For the monatomic case we recover Wigner's result; for the paired crystal, however, we show that the resulting energy is lower, *except* for extremely low densities. The most conservative estimate for solid phases favors the paired crystal at least for  $r_s < 170$ , when the two phases are treated within corresponding approximations.

Consider first the monatomic lattice, with Gaussian trial states of half-width  $\sigma$  situated around each Wigner-Seitz sphere center. To within the small multipole corrections alluded to above the total energy is found as a sum of contributions from distinct spheres, and per electron is

$$\epsilon = \epsilon_{bb} + \epsilon_{eb} + \epsilon_k, \quad (3)$$

where

$$\epsilon_{bb} = \frac{\frac{1}{5} + \text{erf}(r_{ws}/\sigma)}{r_s} \text{Ry}, \quad (4)$$

$$\epsilon_{eb} = -\frac{3}{r_s} \left[ 1 - \frac{\sigma^2}{2r_{ws}^2} \right] \text{erf} \left( \frac{r_{ws}}{\sigma} \right) - \frac{3}{\sqrt{\pi}} \frac{\sigma}{r_{ws}} \frac{1}{r_s} \exp \left( \frac{-r_{ws}^2}{\sigma^2} \right) \text{Ry}, \quad (5)$$

and

$$\epsilon_k = \frac{3}{2} \frac{a_0^2}{\sigma^2} \text{Ry}. \quad (6)$$

These terms represent the background self-energy, the interaction energy of the electron with the background, and the electron kinetic energy, respectively, all calculated for a single sphere of radius  $r_{ws} = r_s a_0$ . In the case  $\sigma \ll r_{ws}$  (where charge "leakage" out of the sphere is completely negligible) the above results simplify to more familiar forms [5]. Variation of (3) with respect to  $\sigma$  then yields a minimum at  $\sigma_0 = r_s^{3/4} a_0$  and with a corresponding energy

$$\epsilon = -\frac{9}{5r_s} + \frac{3}{r_s^{3/2}} \text{Ry}. \quad (7)$$

Equation (7) agrees with Wigner's result obtained, however, through a point-charge approach [1].

Now consider the possibility of a *paired crystal* where in each neutralizing sphere there is a Heitler-London pair of electrons in a spin-singlet configuration. A self-consistency argument allows us to assume  $L=0$  states; the orientation of the electron pairs is then temporally random, the pairs themselves being uncorrelated. In such a case there are no additional higher multipole contributions (on the average) from each pair, and the assumed rotational pair state can therefore be self-consistently sustained. The total energy per pair can be determined

again by consideration of a single sphere (but now of radius  $r_{ws} = 2^{1/3} r_s a_0$ ), the total energy *per electron* being

$$\epsilon = \frac{1}{2} (\epsilon_{bb} + \epsilon_{eb} + \epsilon_{HL}), \quad (8)$$

where  $\epsilon_{HL}$  is the energy of an assumed two-particle Heitler-London variational state in each pair. To illustrate the physical origin of the terms favoring pairing we begin with Gaussian states, namely,

$$\Psi(\mathbf{r}, \mathbf{r}') = \frac{1}{[2(1+S^2)]^{1/2}} [\psi_1(\mathbf{r})\psi_2(\mathbf{r}') + \psi_1(\mathbf{r}')\psi_2(\mathbf{r})] \quad (9)$$

with

$$\psi_i(\mathbf{r}) = \frac{1}{\pi^{3/4} \sigma^{3/2}} e^{-(\mathbf{r}-\bar{\mathbf{r}}_i)^2/2\sigma^2}, \quad i=1,2. \quad (10)$$

These are symmetrically placed around the center of the cell, they are separated by  $\mathbf{R}$  ( $\equiv \bar{\mathbf{r}}_2 - \bar{\mathbf{r}}_1$ ), and they have overlap

$$S = e^{-R^2/4\sigma^2}. \quad (11)$$

Once again we can determine  $\epsilon_{bb}$  and  $\epsilon_{eb}$  exactly. The term  $\epsilon_{HL}$  can also be determined analytically and consists of a kinetic energy term and direct and exchange electron-electron repulsion energy terms. In the final result Eq. (8) takes the form

$$\epsilon = \frac{1}{2} (\epsilon_2 + \Delta\epsilon_{ex}), \quad (12)$$

where

$$\epsilon_2 = 3 \frac{a_0^2}{\sigma^2} - \frac{9}{5r_s} 2^{5/3} + \frac{3}{r_s^3} \frac{\sigma^2}{a_0^2} + \frac{1}{2r_s^3} \frac{R^2}{a_0^2} + \frac{2a_0}{R} \text{erf} \left( \frac{R}{\sqrt{2}\sigma} \right) \text{Ry} \quad (13)$$

and is just the result we would have obtained had we ignored exchange. The remainder

$$\Delta\epsilon_{ex} = -\frac{S^2}{1+S^2} \left[ 3 \frac{a_0^2}{\sigma^2} \frac{R^2}{6\sigma^2} + \frac{1}{2r_s^3} \frac{R^2}{a_0^2} \right] \text{Ry} \quad (14)$$

is then the (favorable) correction due to the Heitler-London exchange. Minimization of (13) gives at low densities  $\sigma_0 \approx r_s^{3/4} a_0$ ,  $R_0 \approx r_{ws} = 2^{1/3} r_s a_0$ , and an energy

$$\epsilon = -\frac{21/2^{1/3} 10}{r_s} + \frac{3}{r_s^{3/2}} \text{Ry}, \quad (15)$$

but is still *always* higher than its Bravais lattice analog (7). The result (13) is consistent with and in fact generalizes (to  $\sigma \neq 0$ ) a previous result [6] for the Madelung energy of an isotropically averaged *Pa3* structure, obtained with a lattice sum (with the only replacement of the fcc Madelung constant with  $-\frac{9}{5}$ , as should be expected from the use of the Wigner-Seitz sphere method). Inclusion of exchange (14) alters the result for  $\sigma_0$  and  $R_0$  only slightly, except for high densities ( $r_s \sim 10$ ) where pairing is actually favored (see below) but where, however, we have charge leakage out of the sphere. Thus at the

level of Gaussian trial functions exchange is insufficient at low densities to promote pairing.

But the *form* of the potential experienced by each electron is actually quite anharmonic (the combination of  $1/r$  and  $r^2$  behavior), and this observation motivates the use of a variational wave function that finally does lead to a state of lower energy when compared with the Bravais lattice case. To show this replace the Gaussians in (9) with the ground states of two displaced Morse potentials [7] *extending inwards*. This picture is consistent with

$$\begin{aligned} \psi(x) = & \exp \left[ -\frac{1}{2\lambda} \exp \left( -\sqrt{2\lambda} \frac{x}{\sigma} \right) \right] \exp \left[ -\frac{1}{\sqrt{2\lambda}} (1-\lambda) \frac{x}{\sigma} \right] \\ & = \text{const} \times e^{-x^2/2\sigma^2} [1 + a_1(x)\lambda^{1/2} + a_2(x)\lambda + a_3(x)\lambda^{3/2} + a_4(x)\lambda^2], \end{aligned} \quad (16)$$

with  $a_i(x)$  polynomials of  $x/\sigma$ , and where  $x$  is along the direction of the instantaneous pair axis and is measured from the appropriate equilibrium position. The new feature here is that as expected these states are *asymmetric* around their "centers" [ $x=0$  in (16)] and we have to select an orientation for each of them. As discussed above, tunneling arguments suggest that we use orientations pointing to the center of the cell (see upper inset to Fig. 1), while we retain a Gaussian form along the  $y$  and  $z$  directions. With the use of an isotropic average of this trial state over axis orientations, all the relevant quantities can then be determined in closed form, and from the results we can recover the previous results for the Gaussian case in the limit  $\lambda \rightarrow 0$ . For  $\lambda \neq 0$  the energy gain in  $\epsilon_{eb}$  that results from the large overlap of the two Morse functions (or equivalently from the considerable accumulation of charge around the sphere center appearing in the single-particle density [4]) actually prevails in the competition from the energy penalty due to the electron-electron repulsion. The final result for the total energy per particle then drops *below* the monatomic analog even at values of the anharmonicity  $\lambda$  as low as 0.04 (for  $r_s \sim 100$ ). This justifies *ex post facto* our expansion (16) in powers of  $\lambda^{1/2}$  (and small values of  $\lambda$  should certainly be expected since the electrons are deeply localized at low densities).

The *required* value of  $\lambda$  at every density can actually be fixed by using a simple self-consistency argument on the depth of the potential that each electron feels in the presence of the *other* (which is being assigned a similar variational function). In the most conservative case where the "source electron" gives a Gaussian charge distribution, we obtain

$$\lambda(r_s) \approx \frac{3}{5} \frac{2^{1/3}}{r_s^{1/2}}. \quad (17)$$

This is expected to be a lower bound for  $\lambda$ , since the use of the Morse function can numerically be shown to give values a little higher than (17) and correspondingly lower values for the total energy. Using (17), however, as the *least* favorable case, we perform the variation of  $\epsilon$  with respect to  $\sigma$  and  $R$  and at the minimum we obtain a total

tunneling of each electron towards its partner within the pair, and again is completely consistent with the assumed Heitler-London exchange. An entirely *analytical* treatment is possible for relatively small anharmonicities if we use an accurate expansion [8] of the lowest Morse function with respect to the anharmonicity parameter  $\lambda$  [ $=\hbar\omega/4D = \frac{1}{2}(a_0^2/\sigma^2)Ry/D$ ]. Here  $D$  is the depth of the corresponding Morse potential  $D(e^{-2ax} - 2e^{-ax})$ , and  $\omega$  is given in terms of the range parameter  $a$  by  $\omega = (2D/m)^{1/2}a$ . The expansion is

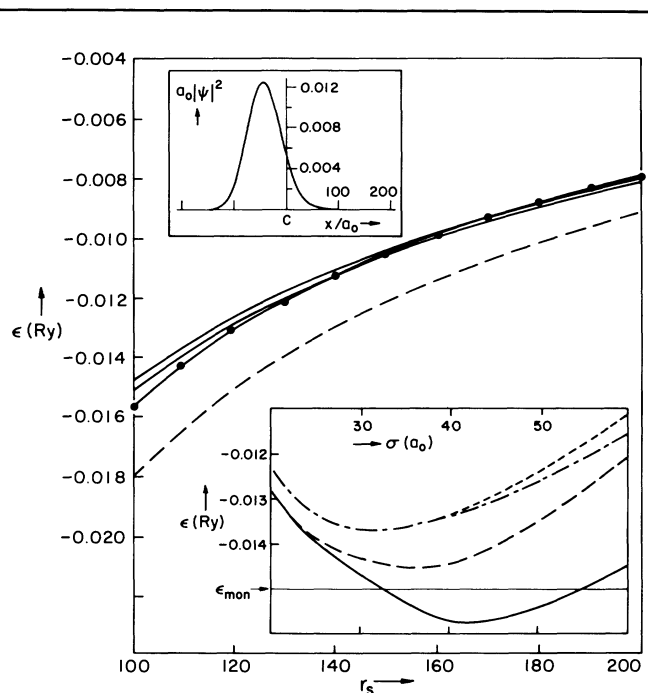


FIG. 1. Total energy per electron as a function of  $r_s$ . Points (including an interpolating curve): the paired electron crystal. Upper solid curve: the monatomic crystal within the Wigner-Seitz method. Lower solid curve: the Wigner crystal but beyond the Wigner-Seitz approximation [2,9]. Dashed curve: the Lieb-Narnhofer lower bound [3]. Upper inset: The probability density  $|\psi|^2$  for a single electron from a given pair (the one centered at  $x = -R/2$ ). Here  $x$  is along the instantaneous pair axis and  $C$  denotes the center of the cell. The wave function  $\psi$  is given by (16) but with  $x$  replaced by  $x + R/2$ . The choice of density corresponds to  $r_s = 100$  (with  $R = 110a_0$ ,  $\sigma = 43a_0$ , and  $\lambda = 0.0756$ ). Lower inset: Effect of exchange and anharmonicity on the total energy per electron, for  $r_s = 100$ . Solid curve: the final result for combined exchange and anharmonicity. Long-dashed curve: including anharmonicity but excluding exchange. Dot-dashed curve: harmonic case including exchange. Short-dashed curve: harmonic case excluding exchange. It is the combination of *both* exchange and anharmonicity that lowers the energy below that of the monatomic Wigner crystal ( $\epsilon_{\text{mon}}$ ).

energy that for  $r_s < 170$  is lower than the monatomic equivalent (7). We note that for  $r_s < 140$  it is even lower than the more accurate energy of the Wigner crystal as given by Carr [9], which from the lattice dynamics viewpoint includes anharmonicities and intracell correlations, the latter being essentially identical to simulation results [2]. Since this result is a variational upper bound, it shows that at least at these densities the paired crystal is energetically favored within the small but common multipole corrections. Pairing is absent at extremely low densities because eventually the anharmonicity is simply too small [Eq. (17)]. A representative result of the minimization procedure for  $r_s = 100$  is given in the lower inset to Fig. 1; the energy of the paired state is compared to the energy of the monatomic state and to a lower bound [3] in Fig. 1 itself.

More interestingly, the results also show that the paired phase is favored when compared to the homogeneous liquid phase at even higher densities. Although at such densities the minimizing values of  $\sigma_0$  begin to approach a considerable fraction of the cell radius implying an eventual leakage of charge out of the sphere, the results nevertheless demonstrate a *tendency* of the paired phase to persist at densities higher than those of the crystal. To investigate such a density range, a detailed many-body description of the paired crystal going well beyond the spherical cell model and taking into account interpair correlations can be given [4]. It is based on the state (2) but rewritten as

$$|\Psi\rangle = \sum_{s_1, \dots, s_N} \int d^3r_1 \cdots d^3r_N F(\mathbf{r}_1 s_1, \dots, \mathbf{r}_N s_N) \times \psi_{s_1}^\dagger(\mathbf{r}_1) \cdots \psi_{s_N}^\dagger(\mathbf{r}_N) |0\rangle, \quad (18)$$

with

$$F = \bar{C} \prod_{l(ij)} f_{ij}^l(\mathbf{r}_i s_i, \mathbf{r}_j s_j), \quad (19)$$

where the product is over distinct pairs [each belonging to a site labeled by  $l$ ; see (2)]. The actual form of  $f_{ij}$  can in principle be determined variationally. The state (18) with  $F$  given by (19) can also be written as

$$|\Psi\rangle = C d_{s_{12}}^\dagger(\mathbf{R}_1) \cdots d_{s_{N-1,N}}^\dagger(\mathbf{R}_{N/2}) |0\rangle, \quad (20)$$

with  $\mathbf{R}_l$  the center of mass of the two electrons constituting a pair localized on site  $l$ . The operators  $d^\dagger$  are given by

$$d_{s_{ij}}^\dagger(\mathbf{R}_l) = \int d^3r_i d^3r_j f_{ij}^l(\mathbf{r}_i s_i, \mathbf{r}_j s_j) \psi_{s_i}^\dagger(\mathbf{r}_i) \psi_{s_j}^\dagger(\mathbf{r}_j) = C \sum_{\mathbf{q}} e^{-i\mathbf{q} \cdot \mathbf{R}_l} \Phi(\mathbf{q}) \sum_{\mathbf{k}} \phi(\mathbf{k}) c_{\mathbf{k}+\mathbf{q}/2, s_i}^\dagger c_{-\mathbf{k}+\mathbf{q}/2, s_j}^\dagger, \quad (21)$$

where in the last line we have separated the motion of the center of mass by writing  $f_{ij} \sim \Phi((\mathbf{r}_i + \mathbf{r}_j)/2) \phi(\mathbf{r}_i, \mathbf{r}_j)$ , with  $\phi$  taken as symmetric with respect to interchange of  $\mathbf{r}_i, \mathbf{r}_j$  as required for spin-singlet pairs. In (21)  $\Phi(\mathbf{q})$  is the wave function describing the motion of the center of mass and  $\phi(\mathbf{k})$  the wave function describing the internal

structure of each pair, all in wave-vector space. [For example, the choice (9) and (10) corresponds to the statements  $\phi(\mathbf{k}) \sim e^{-k^2 \sigma^2} \cos(\mathbf{k} \cdot \mathbf{R})$  and  $\Phi(\mathbf{q}) \sim e^{-\sigma^2 q^2/4}$ ]. This approach provides a unified description not only of the pairs but also of the phonons associated with the motion of their centers of mass; it also suggests new variational states for the paired crystal to be used in Monte Carlo simulations, beyond those that have been used so far [2] that essentially enforce a monatomic crystal. Moreover it can also be shown [4] that *complete delocalization* [where  $\Phi(\mathbf{q}) \sim \delta(\mathbf{q})$ ] of the pairs' centers of mass leads, as density increases, to a superconducting state for an emerging electron liquid. Such a state is anticipated from a generalization of an argument by Leggett [10] and it is an intriguing possibility, since it appears now as an *intrinsic* property of the electron gas problem, at least at low densities. It naturally brings to mind recent claims on universal behavior [11] for *all* exotic low density superconductors; indeed a combination of our results with the system's lower bound on energy [3] actually gives an upper bound for the critical temperature  $T_c$ . In this respect we are also currently investigating the two-dimensional analog of the present calculation where the charge fluctuation effects underlying the effects discussed above are enhanced. Finally, the existence of localized paired states gives at each site of a crystal an object with internal electron dynamics, and this structure can be revealed through a local polarizability. This leads to possible *additional* lowering in correlation energy (and further favoring of the paired state) through the standard fluctuating multipole and polarization wave mechanisms [12], beyond those already present in the conventional Wigner crystal.

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