

Unrestricted Hartree-Fock theory of Wigner crystals

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We demonstrate that unrestricted Hartree-Fock theory applied to electrons in a uniform potential has stable Wigner crystal solutions for $r_s \geq 1.44$ in two dimensions and $r_s \geq 4.5$ in three dimensions. The correlation energies of the Wigner crystal phases are considerably smaller than those of the fluid phases at the same density.

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I. INTRODUCTION

Wigner¹ first predicted that a system of electrons in a uniform potential would crystallize at low densities. Localizing electrons around lattice sites increases their kinetic energy, but at sufficiently low densities the reduction in interaction energy is always greater. The Wigner crystal remains a theoretical prediction in three dimensions (3D), but in 2D Wigner crystals have been created on a liquid helium surface² and at the interface between two semiconductors.^{3,4} It has been suggested that electrons forming a Wigner crystal might eventually be used as quantum bits (qubits) in a quantum computer.^{5,6}

The widely studied model system of electrons in a uniform potential has yielded many insights into electronic many-body phenomena. The most accurate calculations performed to date for the zero-temperature ground-state phases of this system have used the diffusion quantum Monte Carlo (DMC) method.^{7,8} A Wigner crystal may also be described as a vibrating lattice of electrons. When harmonic phonon vibrations and anharmonic terms are included the resulting energies are very similar to DMC ones.⁹ A recent Hartree-Fock study of small numbers of electrons confined by an external potential revealed a transition from a Fermi fluid to a Wigner molecule state.¹⁰ In this paper we also employ the Hartree-Fock approximation which gives a description of Wigner crystals in terms of Einstein oscillators, but including anharmonic and exchange effects.

Within Hartree-Fock theory the paramagnetic (unpolarized) fluid phase is unstable to the ferromagnetic (fully polarized) fluid for values of the density parameter r_s (Ref. 11) greater than 2.01 in 2D and greater than 5.45 in 3D. Hartree-Fock theory also predicts that the paramagnetic fluid is unstable to the formation of a spin density wave.¹² The introduction of electron correlation changes the picture dramatically, with the instability of the paramagnetic to the ferromagnetic fluid being shifted to $r_s \approx 26$ in 2D,¹³ while in 3D a second-order transition to a partially polarized fluid is predicted to occur at $r_s \approx 50$.¹⁴ The spin-density-wave instability may be entirely eliminated. DMC calculations also predict the occurrence of Wigner crystal phases for $r_s > 35$ (Refs. 15 and 16) in 2D and $r_s > 65$ –100 in 3D (Refs. 7 and 17).

Within a mean-field theory of electron systems the interactions are replaced by a potential which acts on each electron orbital separately. The wave function is then simply a

determinant of single-particle orbitals. Two criteria are required for a mean-field description of Wigner crystals. In a Wigner crystal the electrons are localized individually, not in up- and down-spin pairs. To describe this situation we must use a mean-field theory in which the potentials felt by the up- and down-spin orbitals are different. The second issue is that some theories, such as standard implementations of density functional theory, suffer from a spurious effect whereby the electrons interact with themselves, giving a “self-interaction” error. The energy lowering on crystallization derives from the reduction of the interaction energy by spatially separating the electrons. A theory which suffers from self-interaction will tend to overestimate the interaction energy of separated electrons, destabilizing Wigner crystals.¹⁰ The unrestricted Hartree-Fock (HF) theory used here is free of self-interactions and the single-particle orbitals for up and down spins may have different spatial variations, allowing a description of magnetic states and localized electrons.

II. 2D HF CALCULATIONS

For our 2D calculations we wrote a Hartree-Fock code which uses a plane-wave basis set. We considered square and hexagonal lattices with one electron per primitive cell for fully polarized systems and two electrons per primitive cell for unpolarized systems. Basis sets consisting of about 20 plane waves per electron were sufficient to give excellent convergence for $r_s < 10$, while 40 plane waves per electron were required for larger r_s . Highly converged Brillouin-zone integrations were performed using 169 evenly spaced wave vectors for the square and ferromagnetic hexagonal lattices and 153 wave vectors for the antiferromagnetic hexagonal lattice.

We found stable Wigner crystal solutions for $r_s \geq 1.44$. Figure 1 shows the electron density of the 2D ferromagnetic hexagonal Wigner crystal at $r_s = 10$, clearly showing the hexagonal lattice. The ratio of the maximum to minimum charge densities is 13 for this crystal and 17 for the corresponding antiferromagnetic hexagonal crystal.

Figure 2 shows the maximally localized Wannier functions centered on neighboring sites of the antiferromagnetic Wigner crystals at $r_s = 10$. The overlap of the Wannier functions is small, indicating that the electrons are kept far apart. Note also that the parallel-spin Wannier functions have oscillations which maintain their orthogonality.

Figure 3 shows the Hartree-Fock energies of various 2D

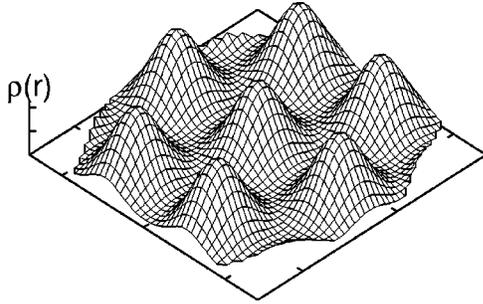


FIG. 1. Hartree-Fock charge density (arbitrary units) of the 2D ferromagnetic hexagonal Wigner crystal at $r_s = 10$.

phases as a function of r_s . The data show a first-order transition from the paramagnetic fluid phase to the antiferromagnetic square Wigner crystal at $r_s = 1.44$ and another first-order transition at $r_s = 2.60$ to the ferromagnetic hexagonal crystal, which remains the most stable phase up to the highest density studied of $r_s = 100$. The ferromagnetic fluid phase is predicted to be unstable at all densities.

III. 3D HF CALCULATIONS

We considered body-centered-cubic (bcc) and face-centered-cubic (fcc) lattices with one electron per primitive cell for fully polarized systems and two electrons per primitive cell for unpolarized systems. For our 3D calculations we used the CRYSTAL (Ref. 18) Gaussian basis set code. We tested many Gaussian basis sets for the different systems, carefully optimizing the Gaussian exponents in each case. For $r_s > 15$ we found no improvement beyond using a single s function on each site. For $r_s \leq 15$ we obtained some improvements from using several functions on each site and our best basis set at these densities consisted of three s functions and a p function on each site. We found that $8 \times 8 \times 8$ wave-vector grids for two-electron unit cells were sufficient to give excellent convergence of the Brillouin-zone integrations.

We found Wigner crystal solutions for $r_s \geq 4.4$. The Hartree-Fock energies (Fig. 4) show first-order transitions from the paramagnetic fluid phase to the antiferromagnetic

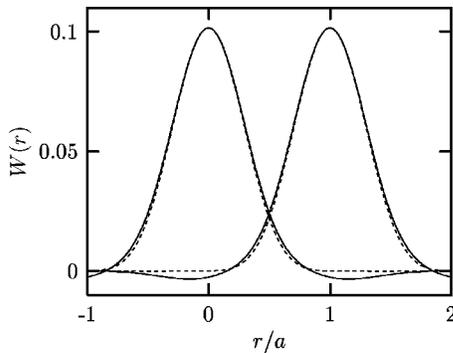


FIG. 2. Maximally localized Wannier functions for the 2D antiferromagnetic hexagonal Wigner crystal at $r_s = 10$ along a line joining two opposite-spin nearest neighbors (dashed line) and joining two parallel-spin nearest neighbors (solid line). The nearest-neighbor distance is a .

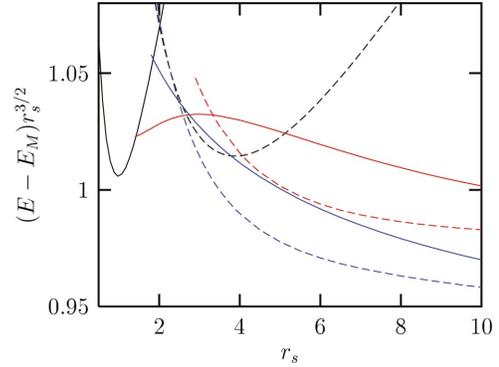


FIG. 3. (Color) Hartree-Fock energies in a.u. per electron of the unpolarized (solid) and fully polarized (dashed) 2D phases as a function of r_s for the square (red) and hexagonal (blue) lattices and for the fluid phases (black). For clarity of presentation we have subtracted the Madelung energy of the hexagonal lattice, $E_M = -1.1061/r_s$, and multiplied by $r_s^{3/2}$.

bcc Wigner crystal at $r_s = 4.4$, then to the ferromagnetic fcc Wigner crystal at $r_s = 9.5$, and finally to the ferromagnetic bcc crystal at $r_s = 13.3$, which remains the most stable phase up to the highest density studied of $r_s = 100$. The ferromagnetic fluid is predicted to be unstable at all densities. We also found a second region ($9.5 < r_s < 9.7$) where the ferromagnetic bcc crystal is extremely close to stability, but the resolution of our data is insufficient to confirm whether it is actually stable in this density range. Note that Hartree-Fock theory predicts (incorrectly) that the electron fluid should crystallize at the average valence charge densities of the heavier alkali metals K, Rb, and Cs.

IV. BROKEN SYMMETRY SOLUTIONS

The Hartree-Fock solutions break the translational invariance of the many-body Hamiltonian. There is an infinite number of degenerate solutions corresponding to arbitrary translations and rotations, but our calculations pick out a particular translational and rotational state. Using a unit cell

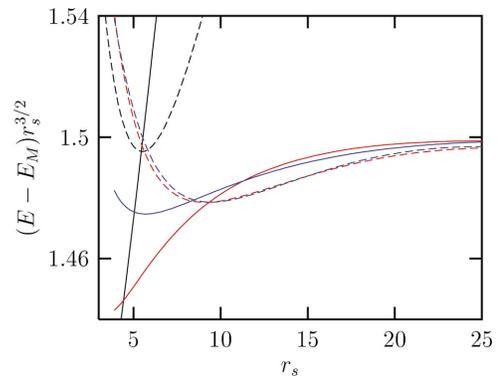


FIG. 4. (Color) Hartree-Fock energies in a.u. per electron of the unpolarized (solid) and fully polarized (dashed) 3D phases as a function of r_s for the bcc (red) and fcc (blue) lattices and for the fluid phases (black). For clarity of presentation we have subtracted the Madelung energy of the bcc lattice, $E_M = -0.89593/r_s$, and multiplied by $r_s^{3/2}$.

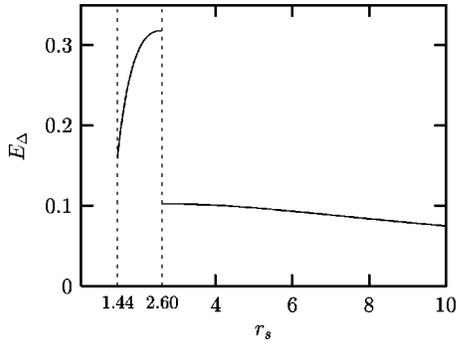


FIG. 5. The HF single-particle band gap E_{Δ} of Wigner crystals in a.u. as a function of r_s . For $1.44 < r_s < 2.6$ the gap of the square antiferromagnetic crystal is plotted, while for $r_s > 2.6$ the gap of the ferromagnetic hexagonal crystal is plotted.

removes the rotational degree of freedom and for the 3D calculations the Gaussian basis set removes the translational degeneracy. The 2D plane-wave calculations also pick out particular translational states, which depend on the starting point of the iterative solution of the equations, but if we artificially translate the final self-consistent solution, we find that the energy only changes by of order the calculational precision ($\sim 10^{-16}$ a.u. per electron). Our calculations therefore lead to broken symmetry solutions which represent “pinned” Wigner crystals. In experiments pinning of Wigner crystals may arise from the presence of impurities or boundaries, and therefore our broken symmetry solutions are physically meaningful.

The broken symmetry Wigner crystals described by Hartree-Fock theory have band gaps for single-electron excitations. Band gaps of the lowest-energy phases of the 2D system are shown in Fig. 5 as a function of r_s . For $r_s < 1.44$ the unpolarized fluid with zero gap has the lowest energy within HF theory. For $1.44 < r_s < 2.6$ the gap of the square antiferromagnetic crystal is plotted, and for $r_s > 2.6$ the gap of the ferromagnetic hexagonal crystal is plotted. At small r_s the band gaps of the crystalline phases rise steeply with increasing r_s . On further increase of r_s the band gaps reach maximum values and then slowly decrease. The HF band gap of the ferromagnetic hexagonal crystal at the density of the transition from the fluid to crystal phases predicted by DMC [$r_s = 35$ (Refs. 15 and 16)] is 0.0303 a.u. = 0.825 eV, which is expected to be a considerable overestimate of the true value as correlation effects normally reduce band gaps.

V. CORRELATION ENERGY OF WIGNER CRYSTALS

Hartree-Fock theory gives the single-determinant approximation to the many-body wave function with the lowest possible energy, which is always greater than (or equal to) the exact energy. We define the correlation energy e_c to be the difference between the exact and unrestricted Hartree-Fock energies. The correlation energy is normally defined as the difference between the exact and restricted Hartree-Fock energies, but this is not appropriate for Wigner crystals because restricted Hartree-Fock theory cannot describe a Wigner

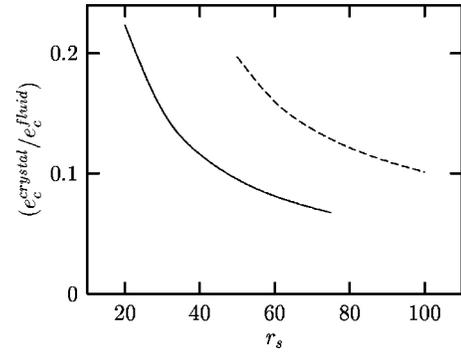


FIG. 6. The ratios of the correlation energies of the 2D hexagonal crystal and ferromagnetic fluid phases (solid line) and of the 3D bcc crystal and ferromagnetic fluid phases (dashed line) as a function of r_s .

crystal. The energies of the Fermi fluid and Wigner crystal phases are known accurately from DMC calculations,^{7,13–17} and therefore we may determine the correlation energies of the different phases. In Fig. 6 we plot the ratio $(e_c^{\text{crystal}}/e_c^{\text{fluid}})$ as a function of r_s , where e_c^{crystal} is the correlation energy of the crystal phase (hexagonal in 2D and bcc in 3D) and e_c^{fluid} is the correlation energy of the ferromagnetic fluid phase. (The energy differences between the ferromagnetic and antiferromagnetic crystals are negligible at these densities.) Figure 6 shows that the correlation energy of the crystalline phase is much smaller than in the fluid in both 2D and 3D. Hartree-Fock theory therefore tends to favor the crystalline phases, which it describes more faithfully than the fluid phases.

The strength of correlations in a system may be measured by the ratio of the correlation energy to the total energy, e_c/E . The DMC results in both 2D and 3D indicate that in the fluid phases e_c/E tends to a positive constant as $r_s \rightarrow \infty$, but for Wigner crystals e_c/E tends to zero as $r_s \rightarrow \infty$. In this sense one may think of the Wigner crystal as being a weakly correlated system at low densities.

VI. ENERGETICS OF WIGNER CRYSTALS

The basic mechanism for electron crystallization within Hartree-Fock theory is that proposed by Wigner; i.e., at sufficiently low densities crystallization greatly reduces the interaction energy with only a small increase in the kinetic energy. The problem can be analyzed more deeply in terms of the Hartree and exchange terms provided by our calculations. In Hartree-Fock theory one normally defines the Hartree energy and potential to include the unphysical self-interaction, which, however, exactly cancels the self-exchange. In Wigner crystals the self-interaction terms are very large and therefore it is more illuminating to discuss the Hartree and exchange terms with the unphysical self-interactions removed. From this viewpoint the essential physics of the Wigner crystal is that the electrons are kept apart by the Hartree potential. Exchange effects are small in Wigner crystals at low densities. The single-particle orbitals obtained at the Hartree-Fock level for a Wigner crystal al-

ready keep the electrons well separated, and therefore their correlation energies are small.

As Wigner argued,¹ at low densities the kinetic energy is unimportant and the many-body wave function of a Wigner crystal is expected to have a large weight for configurations in which the electrons lie far apart on a lattice. The lattice adopted should therefore have the lowest Madelung electrostatic energy—i.e., the hexagonal lattice in 2D and the bcc lattice in 3D. At higher densities the kinetic energy becomes important in determining the structure of the crystal. There are two factors which control the kinetic energy of Wigner crystals. First, crystal structures with larger packing fractions have lower kinetic energies because they allow the electron orbitals to spread out over a greater volume (or area in 2D) without overlap. Second, the kinetic energy of an antiferromagnet tends to be lower than that of the corresponding ferromagnet because in the antiferromagnet the Wannier functions on neighboring sites need not be orthogonal and therefore they can overlap without oscillation, which reduces the kinetic energy.

The relative stabilities of the phases are controlled by the competition between the kinetic and potential energy terms. A detailed study of the numerical values of these terms reveals the following simple picture. In both 2D and 3D the low-density stable phase has the structure with the lowest Madelung energy—i.e., the hexagonal and bcc phases, respectively. The dominant effect at low densities is therefore the Madelung energy, as proposed by Wigner, and ferromagnetism is slightly favored because of the larger exchange interactions. The kinetic energy becomes more important at higher densities, and lattices with higher packing fractions are favored. In 2D the hexagonal crystal has the largest packing fraction and so the stable phase remains unchanged, but in 3D the fcc crystal has the largest packing fraction, and therefore the ferromagnetic fcc crystal becomes the most stable. At still higher densities the reduction in kinetic energy arising from adopting an antiferromagnetic spin configuration dominates. In 2D the hexagonal lattice frustrates antiferromagnetism and therefore a nonfrustrated square lattice becomes more stable. The 2D square lattice with ferromagnetic order along the rows in one direction but antiferromagnetic order in the perpendicular direction is calculated to have a substantially higher energy than the completely antiferromagnetic lattice at high densities, indicating the importance of the spin ordering. The 3D fcc lattice frustrates antiferro-

magnetism, and therefore the antiferromagnetic bcc lattice becomes more stable at higher densities. At the very highest densities the need to reduce the kinetic energy becomes paramount and the crystalline phases become unstable to the formation of paramagnetic fluids. This simple picture explains the occurrence of the different stable phases as a function of density.

VII. CONCLUSIONS

Although Hartree-Fock theory gives a rather approximate description of the electron-electron interaction, we believe it is important to understand how different levels of theory describe such an important model system as electrons in a uniform potential. There are, of course, important corrections to Hartree-Fock theory due to electron correlations. The main effect of adding correlations is to lower the energies of the fluid phases more than the crystalline ones, which moves the transitions to crystalline phases to lower densities. DMC calculations show that only the 2D hexagonal and 3D bcc Wigner crystals are stable when electron correlations are included. In both 2D and 3D Hartree-Fock theory predicts the same stable low-density phases as DMC, which is a further indication that Hartree-Fock theory provides a simple and useful framework for understanding Wigner crystals.

We have shown that unrestricted Hartree-Fock theory is able to describe Wigner crystals in 2D and 3D. We believe this to be important for four reasons. (1) It leads to a picture of Wigner crystals as phases with small correlation energies. (2) It gives simple physical insights into the competition between kinetic and potential energy terms which determines the stability of different phases. (3) Hartree-Fock theory is fairly accurate for Wigner crystals, and because it is computationally inexpensive, it may be used to describe Wigner crystals in more complicated situations, such as when defects or external fields are present or when atomistic effects are important. (4) Hartree-Fock theory forms a natural starting point for more accurate descriptions of Wigner crystals, such as perturbation theory.

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