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Density Functional Theory (DFT) of Quantum Freezing

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Abstract – This paper deals with the density functional theory (DFT) of quantum freezing. The term 'quantum freezing' refers to the freezing /solidification of a quantum-mechanical system. Here, we are interested in the theory of freezing of a quantum many-electron system. From a historical perspective, Wigner [1] predicted theoretically long time back in the year 1934 that at T=0K, a system of interacting electrons embedded in an imaginative charge neutralizing positive charge background should crystallize at sufficiently low electron number densities. The argument given was that with decreasing electron density the electron-electron interaction effects grow over the electron kinetics and at a sufficiently low density, the electrons in an attempt to lower their total energy try to avoid each other by freezing into an electrons' crystal- now known as the Wigner crystal (WC).

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However, till late seventies the prediction of the WC did not attract much attention due mainly to the practical problem of attaining the low electron number densities required for crystallization. For instance, in metals the electron number densities lie in the range $2 < r_s < 6$, where r_s is a dimensionless density parameter defined as

$$r_s = \frac{1}{a_0}\left(\frac{3}{4\pi n}\right)^{1/3}$$

with *n* being the electron number density and a_o the Bohr atomic radius. Physically, it represents the radius of a spherical region occupied on an average by one electron. Thus, it is also a measure of the mean inter-electron separation. Whereas Wigner had predicted that the crystallization would occur at much higher r_s. Notwithstanding all this, the computer simulation experiments performed by Ceperley and Alder [2] established beyond doubt that the electrons would crystallize at r_s=100±20. Sidewise, attempts continued for the experimental realization of the Wigner crystal on one hand, and the development of theory of crystallization on the other hand. The theoretical studies elucidated that the *electron correlations* are at the heart of Wigner crystallization phase transition.

As a notable development towards achieving low electron densities (i.e. high r_s), advances in the material growth technology made it possible to fabricate a two–dimensional (2D) electron system [3] at the interface of semiconductor hetero-structures, with a fine control on the *areal* electron number density. In a 2D electron system, the electrons are free to move within a plane, while their motion perpendicular to the plane is restricted quantum mechanically. The most important advantage of a 2D electron system is that the areal electron number density can be varied by orders of magnitude and also, there lies a choice with the electrons' effective mass and hence, the electron kinetic effects. Moreover, one may further modify/suppress the electron's kinetic energy by applying a strong transverse magnetic field. Low carrier density coupled with the transverse magnetic field have been explored to detect the Wigner crystallization in an electron bi-layer (the system of two parallel and coupled 2D layers) , and its stabilization in the presence of an external magnetic field was reported for the first time by Manoharan et al [4]. Since then there have been many experiments to find evidence of Wigner crystallization without external magnetic field, but the situation is not that clear as even a very small amount of disorder may pin [5] the Wigner crystal state. It is not absolutely clear whether the crystallization is disorder induced or through the electron-electron interactions. Recently, Yoon et al [6] have recorded a convincing evidence of the 2D Wigner crystal in a highly pure 2D hole system at r_s=35.1±0.9 and interestingly, the critical r_s for crystallization has been found to be very close to that predicted (r_s=37±5) by Tanatar and Ceperley [7] by using the quantum Monte Carlo (QMC) simulation.

On the theory side, the DFT has been found to provide a reasonably accurate description of the

Wigner crystal phase transition. In the present work, we shall review the DFT of quantum freezing as put forward by Senatore and Pastore [8], followed by its application to study Wigner crystallization in a 2D electron system. The paper is planned as follows: the rest of this chapter describes a general quantum many-body problem, the Born Oppenheimer approximation, the jellium model and the many-body correlations.

QUANTUM MANY-BODY PROBLEM

The problem of an interacting many-particle system occupies the central stage in condensed matter physics. For studying the solid (crystalline) state, typically we are confronted with the problem of solving a many-particle time-independent Schrodinger wave equation

$$\hat{H}\psi(\mathbf{r}_1,\mathbf{r}_2.............\mathbf{r}_N;\mathbf{R}_1\mathbf{R}_2............\mathbf{R}_N)=E\psi(\mathbf{r}_1\mathbf{r}_2.............\mathbf{r}_N;\mathbf{R}_1\mathbf{R}_2.........\mathbf{R}_N) \qquad (1.1)$$

where $\hat{H}$, $\psi(\mathbf{r}_1,\mathbf{r}_2.............\mathbf{r}_N;\mathbf{R}_1\mathbf{R}_2............\mathbf{R}_N)$ and $E(\mathbf{r}_1\mathbf{r}_2.............\mathbf{r}_N;\mathbf{R}_1\mathbf{R}_2.........\mathbf{R}_N)$ are the Hamiltonian operator, many-body wave function and the total energy of the system, respectively. Quite generally, the Hamiltonian operator is given by

$$\hat{H}=-\sum_{i=1}^{M}\frac{\hbar^2}{2M_Z}\nabla^2_{\mathbf{R}_i}-\sum_{i=1}^{N}\frac{\hbar^2}{2m_e}\nabla^2_{\mathbf{r}_i}+\frac{1}{4\pi\varepsilon_0}\sum_{i}^{M}\sum_{j\neq i}^{M}\frac{Z_iZ_j}{|\mathbf{R}_i-\mathbf{R}_j|}-\frac{1}{4\pi\varepsilon_o}\sum_{i=1}^{N}\sum_{j=1}^{M}\frac{Z_je}{|\mathbf{r}_i-\mathbf{R}_j|}$$
$$+\frac{1}{4\pi\varepsilon_o}\sum_{i=1}^{N}\sum_{j\neq i}^{N}\frac{e^2}{|\mathbf{r}_i-\mathbf{r}_j|} \qquad (1.2)$$

where M and N are the number of nuclei and electrons in the system; M_Z, Z and **R** are the mass, charge and position of nuclei; m_e and e are the mass and charge of an electron and $\mathbf{r}_i$ represents the position of i^{th} electron. The first two terms are the kinetic energy contributions from the nuclei and electrons, respectively and the rest three terms represent columbic potential energy arising from the ion–ion repulsion, ion-electron attraction and electron-electron repulsion, respectively. The Schrodinger wave equation with this Hamiltonian is simply too difficult to solve directly. The quantum many-body problem deals with the development of suitable approximations to the Hamiltonian and the many-body wave function.

BORN OPPENHEIMER APPROXIMATION

The first simplification of the above described Hamiltonian is given by Born and Oppenheimer who recognized that in most cases the nuclear and electronic degrees of freedom can be decoupled since their dynamics involve significantly different time scales. The nuclei are at least thousand times heavier than the electrons and so are considered to be stationary with respect to the electrons – the so-called frozen/static lattice approximation. The electrons can therefore be looked upon as moving in a fixed external potential produced by the lattice of static nuclei. Within the Born Oppenheimer approximation, the complexity of the full many-body Hamiltonian reduces to that of electronic Hamiltonian

$$\hat{H}=-\sum_{i=1}^{N}\frac{\hbar^2}{2m_e}\nabla^2_{\mathbf{r}_i}-\frac{1}{4\pi\varepsilon_o}\sum_{i=1}^{N}\sum_{j=1}^{M}\frac{Z_je}{|\mathbf{r}_i-\mathbf{R}_j|}+\frac{1}{4\pi\varepsilon_o}\sum_{i=1}^{N}\sum_{j\neq i}^{N}\frac{e^2}{|\mathbf{r}_i-\mathbf{r}_j|} \qquad (1.3)$$

Solving the Schrödinger equation with the above Hamiltonian is however still too complex for most cases since the many-electron wave function contains 3N variables, which for a solid is simply a very large number (of the order of Avogadro’s number).

THE JELLIUM MODEL

It turns out that the static lattice of positive ion cores does not play important role in the description of the electronic properties of metallic solids- an important class of solids. Therefore, it is assumed that one may replace the lattice of positive ion cores with a uniform rigid charge neutralizing background, i.e., the positive charge density is taken exactly equal to the electron charge density. This model is known as the jellium model, and it has played a very important role in the development of electron theory of solids. Another main reason for interest in this model is that it has been successfully studied through accurate quantum Monte Carlo simulations, and the simulation results have provided an important benchmark in the development of approximate many-electron theories. In the jellium model, the Hamiltonian is further simplified as

$$\hat{H}=-\sum_{i=1}^{N}\frac{\hbar^2}{2m_e}\nabla^2_{r_i}+\frac{1}{2}\sum_{i\neq j}\frac{e^2}{4\pi\varepsilon_0}\sum_{k\neq 0}\frac{4\pi}{V(k^2+\mu^2)}e^{i\mathbf{k}.(\mathbf{r}_i-\mathbf{r}_j)} \qquad (1.4)$$

Here, V is the volume of the system and μ is a convergence parameter.

At absolute zero temperature, the jellium model is characterized completely in terms of the electron number density n, which is customarily defined through the dimensionless density parameter r_s. It is instructive to rewrite the jellium Hamiltonian in terms of the r_s parameter as

$$\hat{H}=-\frac{1}{r_s^2}\sum_{i=1}^{N}\frac{\hbar^2}{2m_e}\nabla^2_{r_i}+\frac{1}{r_s}\sum_{i\neq j}\frac{e^2}{4\pi\varepsilon_0|\boldsymbol{r}_i-\boldsymbol{r}_j|} \qquad (1.5)$$

where distances are now taken in units of r_s. It may be noted that the ratio of potential and kinetic energies is directly proportional to the r_s parameter. Thus, for $r_s<<1$ (i.e., very high electron density) the kinetic energy dominates completely over the potential energy term, and the system of electrons should behave like an ideal quantum gas. On the other hand, for $r_s>>1$ (i.e., very low electron density) the electron-electron interactions should dominate over the electron kinetics and accordingly, one has a strongly interacting electron system. At intermediate r_s, the kinetic and interaction effects are of comparable magnitude and the system of electrons represents a (quantum) liquid-like situation. The phenomenon of Wigner crystallization has been found to emerge at a sufficiently large value of r_s.

Lying at the heart of the theory of the interacting electrons are the many-particle correlations. The term 'correlation' quite generally describes the inter-dependence of the states of motion of the particles due to their mutual interactions. Thus, one may speak of the correlations in the time space or in the configuration space. Understandably, stronger are the interactions, stronger should be the correlations. For the system of electrons, there exist in addition the correlations due to the requirement of anti-symmetrization of the total wave function. This requirement does not allow two/ more than two electrons of the same spin angular momentum at the same place in the system. In other words, there exists in addition to the coulomb repulsion among electrons in the same spin state the repulsion due to the Pauli exclusion principle- the so-called Pauli repulsion. These correlations are known as *exchange correlations,* while the correlations due to the coulomb repulsion are referred to as the coulomb correlations. Taken together they are called exchange-coulomb correlations. These correlations have been found to be playing a crucial role in determining the physical properties of the electron system. One of the most important effects of correlations has been to change the bare electron-electron interaction potential. This result may be understood as follows: The exchange-coulomb correlations result in a depletion of the local electron charge density surrounding an electron, which may be described as equivalent to a local hole (the so-called exchange-correlation hole). Such a hole is illustrated schematically in Fig.1 for a 3D electron system. The hole present between any two electrons amounts to a modification of the electron interacting potential and it has been a usual practice to represent this modification through a local-field correction to the bare coulomb potential. In literature, much effort has been devoted to the development of more and more refined theories [9] for the description of electron correlations. Apart from these theories, the correlations have been studied by using the quantum Monte Carlo simulation techniques. We shall see in the following chapters that an accurate knowledge of exchange-coulomb correlations for a homogeneous electron system is essential for the implementation of the DFT approach of quantum freezing.

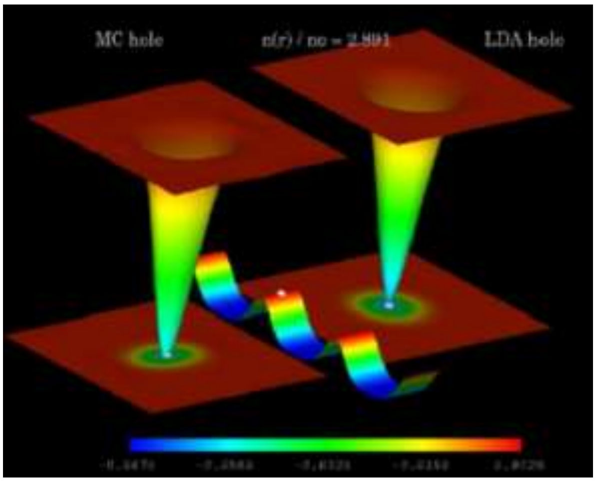

Fig.1: The exchange-correlation hole in a three-dimensional system of electrons. The electron density is indicated by the central ribbon and the white dot shows the position of the electron about which the hole is plotted. The left-hand panel shows the exchange-correlation hole calculated using the variational quantum Monte Carlo method; the right-hand panel shows the approximate hole used in the local density approximation to density functional theory.

TOWARDS THE DENSITY FUNCTIONAL THEORY

Finding accurate schemes to approximate the many-electron problem has been an important goal since the founding of quantum mechanics. In the early 1900s, several notable advances were made, starting from the Thomas–Fermi theory in the late 1920s which established the electron density $n(\mathbf{r})$ as the central unknown variable rather than the complicated many-electron wave function. This approach simplified the problem considerably since the density contains just the three degrees of freedom, namely x, y and z, coordinates of the system, whereas the wave-function involves $3N$ coordinates. In 1930 came the Hartree-Fock theory which was built upon the single-particle approximation given by Hartree, but it took into account correctly the exchange interactions between the electrons arising as a consequence of the Pauli exclusion principle by anti-symmetrizing the many-particle wave function.

The most significant progress in electronic structure theory was made in 1964 with two remarkable theorems of density functional theory given by Hohenberg and Kohn [10]. As we shall see, the density functional theory allows the ground-state properties of many-electron system to be determined exactly through the electron number density. In1965, Kohn and Sham [11] gave the single-particle scheme for performing the DFT calculations. In the Kohn-Sham DFT, the single-particle Hamiltonian is only partly known; in practice, approximation must be made for a single unknown component that accounts for the exchange-coulomb correlations. The DFT approach has emerged as a very powerful theoretical tool, and it has been successfully used for studying a broad class of materials [12], ranging from atoms, molecules and clusters of atoms/molecules to bulk crystalline materials.

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