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# NON-TRIVIAL SOLUTIONS OF THE HARTREE-FOCK EQUATIONS FOR A VERY-MANY-PARTICLE SYSTEM*

## - A SURVEY -

Manuel de Llano

*Instituto de Física, Universidad Nacional de México*

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ABSTRACT: Work related to proofs for the existence of energetically preferred, non-trivial (mostly periodic-density) solutions to the Hartree-Fock equations is reviewed. Both long- and shorth-ranged interacting systems of $N$-bosons or -fermions ($N >> 1$) are considered, and stability criteria discussed. Also, some exact results associated with trivial (plane-wave) solutions are surveyed. The main conclusion is that, for any fixed physical density, a sufficiently strong interparticle coupling can induce the appearance of non-trivial HF states. These solutions provide a first step in studying the properties of many-particle systems, which range from astrophysical plasmas and quantum crystals to nuclear matter and helium at very low temperature.

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## I. INTRODUCTION

Since I have known Professor Marcos Moshinsky, he has emphasized that the study of physical nature can be, not only carried out more simply, but also formulated more elegantly, by finding the "hidden symmetry" in a given situation. I strongly suspect that his beloved late wife, Elena, shared with him this esthetic conviction. This particular out-look has made a lasting impression on me, and it is with deep appreciation towards both that I write this survey.

Both classical and quantum statistical mechanics are in great part concerned with identifying the symmetries characteristic of a given thermodynamic phase, and of elucidating the conditions under which a given symmetry is broken and a new one established, due to a specific system hamiltonian. This is perhaps the most important qualitative aspect of the many-body problem.

Conceptually, at least, the simplest approximation, or rather "first step", to the many-body problem, which allows for *systematic* corrections to be made at successive stages, is perhaps the well-known Hartree-Fock self-consistent field method. Discussing the mathematically very complex many-particle system in terms of the simple idea of a "mean field" is an old procedure: it is found, e.g., in the formulation (1873) of the van der Waals equation of state for a classical fluid of interacting particles. The more recent usefulness of this concept in correlating many phenomena in atomic, molecular, nuclear and solid state physics is hard to exagerate. In the quantum-field-theoretic formulation[1] of the many-body problem in terms of Feynman diagrammatic perturbation theory, the self-consistent HF starting point, (which determines the unperturbed hamiltonian as a one-particle operator), guarantees[2] the mutual cancellation of a very large class of diagrams. A significant simplification of the theory then results.

The first question is whether the HF wave function $\Phi_0$ (determinants or permanents, according as one treats fermions or bosons, respectively) will "carry" the basic symmetries of the phase under consideration, e.g., invariance under translational or rotational or point-group, or etc., transformations.

If $H$ is the $N$-particle hamiltonian, with only pairwise interactions $v_{ij}$, and $\lambda$ is a Lagrange parameter, it is known that under infinitesimal (functional) variation of the orbitals of $\Phi_0$, the stationarity condition

$$\delta\{<\Phi_0|H|\Phi_0> - \lambda<\Phi_0|\Phi_0>\} = 0 \qquad (1)$$

leads to the HF equations for the self-consistent orbitals $\varphi_\alpha(r_i)$ and energies

$\epsilon_\alpha$ (upper case: bosons; lower: fermions)

$$<\alpha| -\frac{\hbar^2}{2m}\nabla^2 |\beta> + \sum_\mu <\alpha\mu| v_{12} |\beta\mu \pm \mu\beta> [n_\mu - \tfrac{1}{2}\delta_{\beta\mu}(n_\mu + 1)] = \epsilon_\alpha \delta_{\alpha\beta} \tag{2}$$

where the $n_\mu$ are occupation numbers subject only to $\sum_\mu n_\mu = N$. A class of trivial solutions to eq. (2) is given by the plane waves (spins suppressed)

$$\varphi_\alpha(\boldsymbol{r}) = \Omega^{-1} \exp(i\boldsymbol{k}\alpha \cdot \boldsymbol{r}) \tag{3}$$

normalized to unity within the volume $\Omega$, and associated with any set of $n_\alpha$ subject only to $\sum_\alpha n_\alpha = N$. This is seen by realizing that the first term in (2) is then diagonal, as is the second (potential energy) term since, using $\boldsymbol{r} \equiv \boldsymbol{r}_1 - \boldsymbol{r}_2$, $\boldsymbol{R} = \tfrac{1}{2}(\boldsymbol{r}_1 + \boldsymbol{r}_2)$, $\boldsymbol{k}_{ij} = \tfrac{1}{2}(\boldsymbol{k}_i - \boldsymbol{k}_j)$, $\boldsymbol{K}_{ij} = \boldsymbol{k}_i + \boldsymbol{k}_j$ we have

$$<\boldsymbol{k}_1\boldsymbol{k}_2 | v_{12} | \boldsymbol{k}_3\boldsymbol{k}_4 \pm \boldsymbol{k}_4\boldsymbol{k}_3> =$$

$$= \Omega^{-1} \int d^3r\, e^{-i\boldsymbol{k}_{12}\cdot\boldsymbol{r}} v(\boldsymbol{r}) [e^{i\boldsymbol{k}_{34}\cdot\boldsymbol{r}} \pm e^{-i\boldsymbol{k}_{34}\cdot\boldsymbol{r}}] \delta_{\boldsymbol{k}_1+\boldsymbol{k}_2, \boldsymbol{k}_3+\boldsymbol{k}_4} \tag{4}$$

so that the matrix element in (2) is *also* diagonal, Q.E.D. The single particle probability density

$$\rho(\boldsymbol{r}) = \sum_\alpha |\varphi_\alpha(\boldsymbol{r})|^2 n_\alpha = N/\Omega \tag{5}$$

will be *homogeneous* (or space-independent, or translational invariant) for any plane-wave set of solutions, called *trivial* solutions. We shall refer to the particular set with

$$n_\alpha = \theta(k_F - k_\alpha);\ \rho = N/\Omega = k_F^3/6\pi^2 \qquad \text{(fermions)} \tag{6a}$$

$$= N\delta_{\boldsymbol{k}_{\alpha,0}} \qquad \text{(bosons)} \tag{6b}$$

as *the* trivial solution. The conditions for the existence of *non-trivial* so-

*lutions* to the HF equations will then be established with the aid of the following

*Theorem*: If a determinant (or permanent) corresponding to a *non*-homogeneous (e.g., periodic or aperiodic) single-particle probability density is found, which has a lower expectation energy than the plane-waves determinant (or permanent) with the (trivial) occupation eq. (6), there exists a lower-energy HF state with the given nonhomogeneous property.

*Proof*: Consider the Hilbert space for the exact ground state eigenfunction of the given hamiltonian. A subspace of this is spanned by the class of all *single* determinantal (or permanental) functions; this class can in turn be divided into three non-intersecting subclasses corresponding to homogeneous, (perfectly) periodic and aperiodic (but nonhomogeneous) probability density. The lowest-valued expectation energy associated with a given one of the three subclasses, being a stationary value, corresponds to a HF solution and will clearly be bounded from above by any trial energy value associated with a member of the same subclass,

$$\therefore\ E^{HF}_{\text{non-triv}} \leqslant E_{\text{non-triv}} < E_{\text{hom}} \equiv E^{HF}_{\text{hom}} .$$

Hence,

$$E_{\text{non-triv}} < E_{\text{hom}} \Longrightarrow E^{HF}_{\text{non-triv}} < E^{HF}_{\text{hom}} ,$$

Q.E.D. We stress again that $E^{HF}_{\text{hom}}$ strictly refers to the *particular* trivial solution specified by eqs. (3) and (6).

## II. TRIVIAL SOLUTIONS

Consider a general hamiltonian

$$H = -\frac{\hbar^2}{2m}\sum_{i=1}^{N}\nabla_i^2 + \sum_{i<j}^{N} v_{ij} , \tag{7}$$

and a determinant (or permanent) $\Phi_0$ with occupation numbers $n_k$. One has the general result

$$< \Phi_0 \mid \sum_{i<j}^{N} v_{ij} \mid \Phi_0 > =$$

$$= \tfrac{1}{2} \sum_{k_1 k_2} < k_1 k_2 \mid v_{12} \mid k_1 k_2 \pm k_2 k_1 > [n_{k_1} n_{k_2} - \delta_{k_1 k_2} n_{k_1} (n_{k_1} + 1)/2] \quad (8)$$

which was in fact used in arriving at eq. (2). Combining this with the trivial solutions eqs. (3) and (6) one obtains

$$\epsilon_{\text{hom}}^{HF} \equiv E_{\text{hom}}^{HF}/N =$$

$$= \begin{cases} \tfrac{1}{2}\rho\nu(0) & \text{(bosons)} \quad (9) \\ C\rho^{2/3} + \tfrac{1}{2}\rho\nu(0) - \dfrac{1}{2\rho(2\pi)^6} \displaystyle\int_{k_1 \leq k_F} d^3k_1 \int_{k_2 \leq k_F} d^3k_2\, \nu(k_1 - k_2) & \text{(fermions)} \quad (10) \end{cases}$$

where we have defined

$$\rho \equiv N/\Omega \, ; \; C \equiv (3\hbar^2/10m)(6\pi^2)^{2/3} \, ; \nu(q) \equiv \int d^3r \, \exp(i\mathbf{q}\cdot\mathbf{r}) \, v(r). \quad (11)$$

1. *Long Range Forces*. We consider first the case of a one-component simple plasma, i. e., $N$ point particles of mass $m$, charge $\pm e$, submersed in a uniform, rigid background carrying the opposite charge so that the system is electrically neutral. This model, sometimes called the "jellium" model, has been used extensively in the study of electrons in metals and insulators[3] as well as in white dwarf stellar structure[4], where one has $N$ charged ions moving in a background of (pressure or temperature) ionized electrons. The presence of the uniform background can be seen[1] to introduce a term $-\tfrac{1}{2}\rho\nu(0)$ into the hamiltonian (7), which refers to the point charges, with

$$v_{ij} = v(r_{ij}) = e^2/r_{ij} \, , \quad (12)$$

$$\nu(q) = 4\pi e^2/q^2 \, . \quad (13)$$

Eqs. (9) and (10) then yield

$$\epsilon_{\text{hom}}^{HF} = \begin{cases} 0 & \text{(bosons)} \quad (14) \\ \\ \dfrac{A}{r_s^2} - \dfrac{B}{r_s} & \text{(fermions)} \quad (15) \end{cases}$$

where

$$A \equiv \frac{3}{5}\,\frac{\hbar^2}{2ma_0^2}\,\frac{1}{\alpha^2}\,;\quad B \equiv \frac{3}{2\pi}\,\frac{e^2}{2a_0}\,\frac{1}{\alpha}\,;\quad a_0 \equiv \frac{\hbar^2}{me^2}\,;\quad \alpha \equiv \left(\frac{4}{9\pi}\right)^{1/3} \qquad (16)$$

$$\rho = N/\Omega = 2\frac{k_F^3}{6\pi^2} \equiv \frac{3}{4\pi a_0^3 r_s^3} \qquad (17)$$

and, clearly, $r_s \equiv r_0/a_0 = r_0 me^2/\hbar^2$ is a dimensionless coupling constant, $r_0$ being simply related to the interparticle distance. The system is then clearly almost ideal at *high* densities and very non-ideal at *low* densities — in exact opposition to the more common case of short-ranged forces as, e.g., a system of argon atoms. Moreover, since $\epsilon_{\text{hom}}^{HF}$ is a rigorous upper bound to the exact ground state energy of $H$, the model system of fermions is not trivial since it can become a self-bound, condensed system (negative energy per particle), as is seen from the fact that eq. (15) can be negative for a range of values of $r_s$ (which can be considered a variational parameter).

For fermions, Gell-Mann & Brueckner[5] have considered the next-order corrections to eq. (15) in terms of the partial sum of all so-called "ring" diagrams, obtaining (in rydberg units, $e^2/2a_0$)

$$\epsilon = \epsilon_{\text{hom}}^{HF} + 0.0622 \ln r_s - 0.094 + \ldots \qquad (18)$$

The "ring" diagrams can be shown to be the most divergent (at small $q$ values) for $r_s \ll 1$; summing the next most divergent diagrams give Du Bois[6] a term $O(r_s \ln r_s)$ as the next correction. Since

$$\frac{0.0622 \ln r_s - 0.094 + O(r_s \ln r_s)}{A/r_s^2 - B/r_s} \xrightarrow[r_s \ll 1]{} \text{const}\; r_s^2 \ln r_s \xrightarrow[r_s \to 0]{} 0 \qquad (19)$$

the HF result for the total energy eq. (15) is *exact* in the high-density, or weak-coupling (small value of $e$) limit.

Indication whether lower-energy non-trivial solutions exist or not can be obtained by considering the problem of *stability*. Iwamoto & Sawada[7] have considered this in terms of whether the *second* variation of the bracketed expression in eq. (1) is positive or negative definite; if the former occurs the solution proposed, which differs infinitesimally from the trivial solution, corresponds to (an at least local) minimum. Their analysis is very elegant, complete and general since various kinds of instabilities (density, spin, etc. fluctuations) are allowed for; however, a very simple *compressibility* criterion[8] for a special but important kind of instability can also be seen. Consider the ground state energy density

$$\mathcal{E}(\rho) \equiv E/\Omega = \rho\epsilon(\rho) \tag{20}$$

and consider a small density inhomogeneity $\rho_1(\boldsymbol{r}) \ll \rho$ defined such that particle number is conserved, i.e.,

$$\int_\Omega d^3r\rho_1(\boldsymbol{r}) = 0\ . \tag{21}$$

Then Taylor-expanding

$$\mathcal{E}(\rho + \rho_1) = \mathcal{E}(\rho) + \mathcal{E}'(\rho)\rho_1 + \frac{1}{2!}\mathcal{E}''(\rho)\rho_1^2 + \ldots \tag{22}$$

and the energy difference between the homogeneous and the inhomogeneous state is

$$\Delta E = E_{\text{inhom}} - E_{\text{hom}} = \int_\Omega d^3r\ [\mathcal{E}(\rho + \rho_1(\boldsymbol{r})) - \mathcal{E}(\rho)] =$$

$$= \frac{1}{2!}\mathcal{E}''(\rho)\int_\Omega d^3r\rho_1^2(\boldsymbol{r}) + \ldots \tag{23}$$

Since the system pressure (free energy $F \equiv E - TS$, $S$ is entropy)

$$P = -\left(\frac{\partial F}{\partial\Omega}\right)_{T,N} = -\left(\frac{\partial E}{\partial\Omega}\right)_{T=0,N} = \rho^2\epsilon'(\rho) \tag{24}$$

eq. (23) immediately leads to

$$\Delta E \gtrless 0 \longleftrightarrow \mathcal{E}''(\rho) \lessgtr 0 \longleftrightarrow \frac{\partial P}{\partial \rho} \lessgtr 0 \ . \tag{25}$$

In short, $\partial P/\partial \rho < 0$ signals the appearance of a lower-energy, inhomogeneous-density ground state. Moreover, the expectation value in *any* state (eigenstate or not) is

$$E = <H> = <T> + <v> \equiv <T> + <U> + <v> - <U> \ . \tag{26}$$

If now $U \equiv \sum_{i=1}^{N} U_i$ is a one-particle operator, and in addition it is the HF field while the state is the HF determinant (or permanant), we have from eq. (2)

$$<\alpha | U_1 | \beta> = \sum_{\mu} <\alpha\mu | v_{12} | \beta\mu \pm \mu\beta> [n_\mu - \tfrac{1}{2}\,\delta_{\beta\mu}(n_\mu + 1)] \tag{27}$$

or, multiplying by $\delta_{\alpha\beta} n_\alpha$ and summing over $\alpha$, by eq. (8),

$$<U> = 2<v> \ . \tag{28}$$

Then, if $W_0$ is the ground state energy of $H_0 \equiv T + U$,

$$E_{HF} = <T> + <U> + <v> - <U> \equiv W_0 + <v> - <U>$$

$$= \tfrac{1}{2} W_0 + \tfrac{1}{2} <T> \tag{29}$$

so that

$$\Delta E_{HF} \gtrless 0 \longleftrightarrow E^{HF}_{\text{inhom}} \lessgtr E^{HF}_{\text{hom}} \longleftrightarrow W_0^{\text{inhom}} + <T>^{\text{inhom}} \lessgtr W_0^{\text{hom}} + <T>^{\text{hom}} \tag{30}$$

but, since the Ritz variational principle states that $<T>^{\text{hom}} \leqslant <T>^{\text{inhom}}$ (the inhomogeneous density state considered as a *trial* state) we have, combining with eq. (25) that

$$\frac{\partial P}{\partial \rho} \leqslant 0 \Longleftrightarrow W_0^{\text{inhom}} \leqslant W_0^{\text{hom}} \tag{31}$$

while noting that $\partial P/\partial \rho > 0$ says nothing definite about the sign of $(W_0^{\text{inhom}} - W_0^{\text{hom}})$. Therefore, the criterion $\partial P/\partial \rho < 0$, which classically corresponds to the longitudinal, compressional wave velocity $C_l \sqrt{(1/m)\, \partial P/\partial \rho}$ becoming pure imaginary (and hence indicating an unstable density fluctuation mode), signals in the HF approximate the ***appearance of a lower energy unperturbed ground state***, which in turn points to a breakdown of a perturbative scheme based on the trivial solution as zero-order state.

Applying the instability criterion to the fermion plasma result eq. (15), using eq. (17), gives

$$\partial P/\partial \rho < 0 \qquad \text{for all} \quad r_s > \pi/\alpha = 6.03 \tag{32}$$

This result agrees with that deduced by the more elaborate analysis of ref. 7. We mention that electron densities in real metals correspond to $2 \lesssim r_s \lesssim 6$ .

2. *Short Range Forces ; An Exact Result .* For either bosons or fermions the HF energies eqs. (9), (10) constitute rigorous upper bounds to the exact ground state energy of $H$. A rigorous *lower* bound can be found[9] by restricting the class of two-body potentials to

$$\text{a) } \nu(\mathbf{q}) \geqslant 0 \text{ all } \mathbf{q} \qquad \text{b) } |v(0)| < \infty \tag{33}$$

but noting that this class does *not* exclude the possibility of producing two-body bound states. The example $\nu(\mathbf{q}) = \nu(0)\,\theta(q_0 - q)$, with $q_0$ constant, gives $v(r) = [\nu(0)\, q_0^3/2\pi^2]\,[j_1(q_0 r)/q_0 r]$ which can evidently have bound states, even if $\nu(0) > 0$, for large enough $\nu(0)\, q_0^3$ . Then the ground state energy is, say

$$E_{\text{exact}} = \left\langle -(\hbar^2/2m) \sum_{i=1}^{N} \nabla_i^2 \right\rangle + \left\langle \sum_{i<j}^{N} v_{ij} \right\rangle \ , \tag{34}$$

where $\left\langle -(\hbar^2/2m) \sum_{i=1}^{N} \nabla_i^2 \right\rangle \geqslant NC\rho^{2/3}$ for fermions and $\geqslant 0$ for bosons, with the constant $C$ given by eq. (11). The last equation in eq. (11) allows us to write the inverse Fourier transform as

$$v(r_{ij}) = \Omega^{-1} \sum_{k} e^{-ik\cdot(r_i - r_j)} \nu(-k) \ . \tag{35}$$

so that, defining $\rho_k \equiv \sum_{i=1}^{N} \exp(-ik\cdot r_i)$ we have

$$\begin{aligned} < \sum_{i<j}^{N} v_{ij} > &= \tfrac{1}{2} < \sum_{i,j=1}^{N} v(r_{ij}) - \sum_{i=j}^{N} v(0) > \\ &= \frac{1}{2\Omega} < \sum_{k} \nu(k) \left|\rho_k\right|^2 > - \frac{N}{2} v(0) \geqslant \tfrac{1}{2} N\rho\nu(0) - \tfrac{1}{2} N v(0) \end{aligned} \tag{36}$$

the inequality following from condition (33a). Thus

$$\epsilon_{\text{exact}} \equiv E_{\text{exact}}/N \geqslant \tfrac{1}{2}\rho\nu(0) - \tfrac{1}{2}v(0) + \begin{cases} 0 & \text{(bosons)} \\ C\rho^{2/3} & \text{(fermions)} \end{cases} \tag{37}$$

and one has a simple *lower* bound. The *upper* bound for fermions eq. (10) can be readily seen to become

$$\epsilon_{\text{hom}}^{HF} \xrightarrow[k_F \gg k_0]{} C\rho^{2/3} + \tfrac{1}{2}\rho\nu(0) - \tfrac{1}{2}v(0) + O(1) \tag{38}$$

where $k_0$ is a characteristic wave number of $\nu(k)$. Therefore, for sufficiently high density the upper and lower bounds *coincide* with each other and must thus become equal to the *exact* energy per particle: the Hartree-Fock energy, for both bosons and fermions, becomes exact at high density for interparticle potentials satisfying *both* conditions (33a) and (33b). (We note that the latter is *not* satisfied by Coulomb forces). This result can be considered a short-ranged-potential analogue of the exactness of HF (with trivial solutions) at high-density for the long-ranged-potential plasma, proved on the basis of the Gell-Mann & Brueckner theory in eq. (19).

Instability can be studied with the Iwamoto & Sawada method[7]; they used a *repulsive* Yukawa potential and found, besides spin-like instabilities, unstable density fluctuations of long-wavelength ($q \to 0$) which appear at *inter-*

*mediate* densities, i.e., not too low nor too high. The compressibility criterion eq. (31) would fail since $\partial P/\partial\rho > 0$ for all $\rho$ for a repulsive Yukawa, but it is found useful[10] for a two body potential with enough attraction to make $\epsilon^{HF}_{\text{hom}}$ negative for some $\rho$ as then $\partial P/\partial\rho$ becomes negative for some $\rho$. In this latter case, the instability is clearly associated with the formation of *liquid* phase in the system; as this state of matter involves strong correlations between the particles, it is not clear which should be the appropriate HF state. What makes this problem particularly difficult is that no known obvious symmetry appears to be broken, in the thermodynamic limit $N \to \infty, \Omega \to \infty, N/\Omega =$ constant, in the passage from gas to liquid or vice versa, even at zero absolute temperature.

## III. NON-TRIVIAL SOLUTIONS

1. *Long Range Forces*. The simplest example of a non-trivial solution is perhaps that discovered by Bloch[11] in 1929: the ferromagnetic fermion gas with net total spin $N\hbar/2$. The HF energy eq. (15) corresponds to a paramagnetic gas, i.e., net total spin zero, namely

$$\epsilon_{\text{para}} = \frac{A}{r_s^2} - \frac{B}{r_s} \tag{39}$$

while the ferromagnetic case is easily obtained from this by just replacing $\rho$ by $2\rho$, so that using eq. (17) gives

$$\epsilon_{\text{ferro}} = \frac{A}{r_s^2}\,2^{2/3} - \frac{B}{r_s}\,2^{1/3} \tag{40}$$

The ferromagnetic (non-trivial) state is clearly *below* the paramagnetic (trivial) state for

$$r_s > \pi/\alpha\ \frac{2(2^{2/3}-1)}{5(2^{1/3}-1)} = 5.45$$

which is *within* the range of metallic densities and below the density instability critical value 6.03, eq. (32).

The classic example of non-trivial HF states, however, is the Wigner lattice[12] which forms in the one-component jellium model for $r_s >> 1$, i.e., low-density and/or strong-coupling. Wigner considers that at sufficiently large interparticle separation the energy per particle is the energy of a single point charge within a sphere of oppositely-charged uniform "jelly" or radius $r_0$. The charge density of the "jelly" is $\pm e/(4\pi/3)\, r_0^3$ while the net charge inclosed in a sphere of radius $r \leqslant r_0$ is

$$q(r) = \mp e \pm \frac{3e}{4\pi r_0^3} \cdot \frac{4\pi}{3} r^3 . \tag{41}$$

The potential at the spherical surface at $r$ is then

$$\phi(r) = q(r)/r \tag{42}$$

while the energy of a shell of thickness $dr$ there is

$$dV(r) = \phi(r)\,[\pm 3e/4\pi r_0^3]\, 4\pi r^2 dr \tag{43}$$

so that the total potential energy becomes

$$V = \int_0^{V(r_0)} dV(r) = -\frac{9}{10}\frac{e^2}{r_0} = -\frac{1.8}{r_s}\,(e^2/2a_0) \tag{44}$$

which is *lower* than the HF trivial state values eqs. (14) and (15), since $A = 2.21(e^2/2a_0)$, $B = 0.916(e^2/2a_0)$. The kinetic energy follows from realizing that the point charge oscillates in a potential energy well

$$-\frac{3}{2}\frac{e^2}{r_0} + \frac{e^2}{2r_0^3} r^2 \tag{45}$$

so that the *kinetic* energy (the first term in (45) must be neglected as it is a self-potential energy) is

$$\frac{3}{2}\hbar\omega = (3/r_s^{3/2})(e^2/2a_0) \ . \qquad (46)$$

Thus, the "Wigner solid" energy per particle becomes

$$\epsilon_{\text{Wigner}} = 3/r_s^{3/2} - 1.8/r_s \ . \qquad \text{(rydbergs)} \qquad (47)$$

This value is a rigorous upper bound to the ground state energy, for $r_s \gg 1$, as can be seen from the following: construct a determinant (or permanant) of single-particle orbitals

$$\varphi(\mathbf{r}_i) = (\beta/\pi)^{3/4} \exp(-\tfrac{1}{2}\beta r_i^2) \ ; \quad \beta = 2\sqrt{me^2/\hbar^2 r_0^3} \qquad (48)$$

localized about the points of a perfect lattice of some given type. The ratio of orbital width to interparticle separation is then $\sqrt{2/\beta}/r_0$ and thus proportional to $r_s^{-1/4}$ so that it tends to zero for $r_s \gg 1$: in this limit, the overlap between orbitals of neighboring sites is negligible and the off-diagonal components of the determinant (or permanent) *vanish* and the expectation energy reduces to a kinetic energy term plus the potential energy of interaction of the charges, which since they have a spherical distribution about each site, becomes just the classical potential energy. The latter is calculable in terms of well-known lattice-summation techniques: Fuchs[13] obtained $-1.79183/r_s$ rydbergs per particle for the bcc lattice and $-1.79172/r_s$ for the fcc, while Carr[14] obtained $-1.760/r_s$ for sc and Kohn & Schechter[15] got $-1.79168/r_s$ for hcp. These results are amazingly close to the Wigner result of $1.8/r_s$ of eq. (47); which of course is based on very simple arguments. The kinetic energy-per-particle term mentioned above is just

$$<\varphi| -\frac{\hbar^2}{2m}\nabla^2 |\varphi> = -\frac{\hbar^2}{2m}(\beta/\pi)^{3/2}\int d^3r\, e^{-\frac{1}{2}\beta r^2}\nabla^2 e^{-\frac{1}{2}\beta r^2}$$

$$= \frac{3}{2}\,\frac{\hbar^2}{2m}\beta = (3/r_s^{3/2})(e^2/2a_0) \ . \qquad (49)$$

Thus, the "Wigner solid" result eq. (47) is, for all practical purposes, the expectation value of the hamiltonian between *legitimate* trial functions, and thus a rigorous upper bound which is *lower* than the trivial solution result

$2.21/r_s^2 - 0.916/r_s$ of (15); hence, using the Theorem of Sec. I a periodic-density HF solution exists which is energetically preferred for $r_s \gg 1$.

Corrections[14] to the Wigner result (47) can be made which extend the validity of $\epsilon(r_s)$ to somewhat smaller $r_s$ values: these appear as a series in powers of $(r_s^{-1/2})^n$, of which the Wigner result gives the first two terms, $n = 2$ and 3.

The instability question is easiest in terms of the compressibility criterion; van Horn[16] gives

$$\partial P/\partial \rho < 0 \quad \text{for} \quad r_s > 6.4 \tag{50}$$

for the corrected Wigner lattice energy of ref. (14). An even more obvious criterion for instability is $P < 0$, which holds for eq. (47) according to

$$P = \rho^2 \frac{\partial \epsilon}{\partial \rho} = \rho^2 \frac{dr_s}{d\rho} \frac{\partial \epsilon}{\partial r_s} < 0 \quad \text{for} \quad r_s > 6.25 \ . \tag{51}$$

This condition gives instability because a ground state with negative pressure can at most be metastable[17,18].

Finally, we mention that Shuster & Kozinskaya[19] have shown that for $r_s$ values somewhat smaller than the limit $r_s \gg 1$ the state with *two* point charges localized about each lattice point has *lower* energy, and conjecture that for successively smaller $r_s$ values states with $n$ point charges, $n = 3, 4, ..$ will have lower energy than the preceeding one, until $n \to N$, which is the fluid phase.

2. *Short Range Forces*. Consider first the case of a purely repulsive barrier of range $a_0$,

$$v(r) = v_0 \theta(a_0 - r) , \qquad v_0 > 0 \ . \tag{52}$$

Define a determinant (or permanent) of orthonormal single-particle, Wannier-like orbitals (no spin)

$$\varphi_{\mathbf{k}_i}(\mathbf{r}_j) = \delta_{ij}\, \varphi_{\mathbf{R}_i}(\mathbf{r}_j) \equiv \delta_{ij} \sqrt{\frac{4\pi}{d^3}}\, \frac{\sin \frac{2\pi}{d} |\mathbf{r}_j - \mathbf{R}_i|}{(2\pi/d)|\mathbf{r}_j - \mathbf{R}_i|}\, \theta\left(d/2 - |\mathbf{r}_j - \mathbf{R}_i|\right) \ , \tag{53}$$

where $i, j = 1, 2, \ldots, N$ and the $\boldsymbol{R}_i$ are the sites of a given perfect lattice while $d$ is the diameter of spheres centered on the sites and within which we place *one* particle. Let the nearest-neighbor distance be $a + d$, so that the surface of the spheres are separated at least a distance $a \geqslant a_0$ apart, i.e., there is *no overlap* of orbitals associated with different particles. The particle density is then given by

$$\rho = \frac{N}{\Omega} = \frac{K_s}{(a+d)^s} \qquad (s = \text{dimensionality}) \tag{54}$$

where $K_s$ is a pure number giving the proportion of the total volume occupied by the spheres, *relative* to that occupied by the simple cubic arrangement. Thus $K_3$ (in three dimensions) equals 1 for sc lattice, $\sqrt{2}$ for fcc or hcp, $3\sqrt{3}/4$ for bcc, and so on. The trial energy per particle (which is a rigorous upper bound) is then just

$$\epsilon_{\text{per}} = 2\pi^2\hbar^2/md^2 \geqslant 2\pi^2\hbar^2/md_0^2 \equiv \epsilon^0_{\text{per}} \tag{55}$$

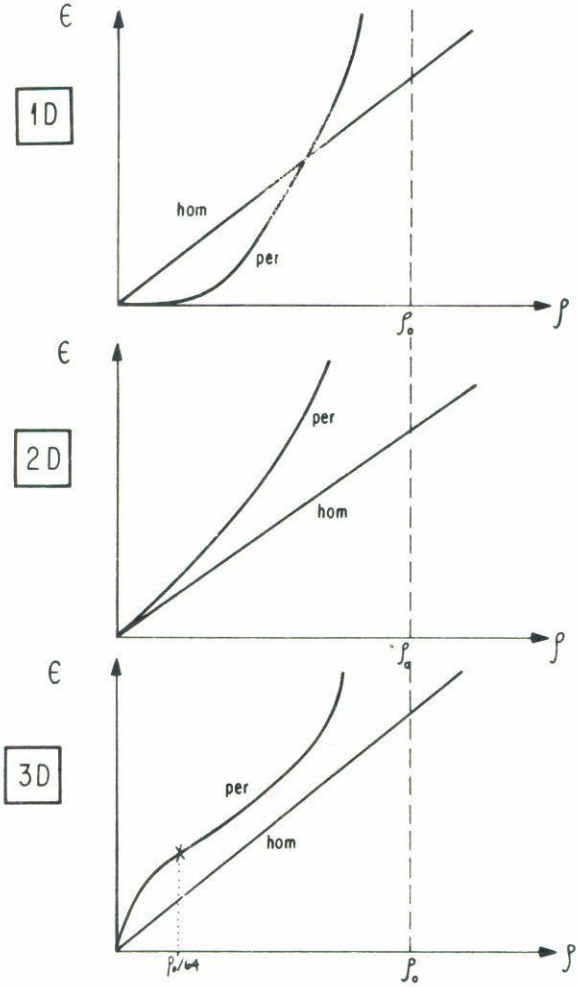
where $d_0 \equiv (K/\rho)^{1/3} - a_0 > (K/\rho)^{1/3} - a = d$ and the subscript "per" stands for "periodic probability density". Defining a "close-packing" density $\rho_0 \equiv K/a_0^3 \geqslant \rho$ one obtains

$$\epsilon^0_{\text{per}}(\rho) = (2\pi\hbar^2/mK^{2/3})\left[1/\rho^{1/3} - 1/\rho_0^{1/3}\right]^{-2} \tag{56}$$

which approaches $|\text{const}|\,\rho^{2/3}$ as $\rho/\rho_0 \ll 1$, diverges as $\rho/\rho_0 \to 1$ and has *one* inflection point at $\rho = \rho_0/64$ (cf. Figure, bottom). On the other hand, the trivial solution for *bosons* gives

$$\epsilon^{HF}_{\text{hom}}(\rho) = \tfrac{1}{2}\rho\nu(0) = \tfrac{2}{3}\pi v_0 a_0^3 \rho \tag{57}$$

and represents the straight line in Figure, bottom. As $v_0$ is allowed to increase this curve touches the curve $\epsilon^0_{\text{per}}(\rho)$ and, as $v_0$ increases further, it *cuts it* at two points: at intermediate densities, a non-trivial, periodic-density solution to the HF equations thus exists if the in interaction is strong enough. This agrees qualitatively with Iwamoto and Sawada[7], who used a repulsive Yukawa force. The situation in one and two dimensions




"Periodic" and "homogeneous" energies per particle compared in 1-, 2- and 3-dimensions (schematic).

is readily seen to be that of the rest of the Figure. Defining the dimensionless coupling constant $\lambda \equiv m v_0 a_0^2/\hbar^2$ and reduced density $\xi = (\rho/\rho_0)^{1/3}$, and bringing in the result eq. (10) for fermions, one finds that $\epsilon^0_{per} < \epsilon_{hom}$ if and only if

$$\lambda > 3\pi/K\xi(1-\xi)^2 \qquad \text{(bosons)} \tag{58}$$

$$\lambda > \{g[2(6\pi^2 K)^{1/3}\xi]\}^{-1}\left\{\frac{2\pi^3}{(1-\xi)^2} - \frac{3\pi(6\pi^2 K)^{2/3}}{10}\right\}\xi^2 \quad \text{(fermions)} \tag{59}$$

$$g(x) \equiv \frac{x^3}{72} - \int_0^x \frac{\sin y}{y}\,dy + \frac{3}{x} + \frac{4}{x^3}\left(\frac{1}{x} + \frac{4}{x^3}\right)\cos x - \frac{4}{x^2}\sin x$$

which, by inspection, are both satisfied for sufficiently large $\lambda$. We thus reach the conclusion of ref. (20), again using the Theorem of Sec. I, that for either bosons or fermions a strong enough repulsive barrier suffices to establish the existence in three-dimensions of non-trivial, periodic-density HF solutions which are energetically preferred at intermediate densities. In one dimension only, an arbitrary weak force, will always give a preferred non-trivial state (cf. Figure, top), whereas in two and three dimensions a critical threshold value of $v_0$ is required. These results corroborate the conjecture of Kohn & Nettel[21], made on the basis of a Hartree treatment in one, two and three dimensions, after they considered the pioneering results of Overhauser's[22] one-dimensional case. They also agree with the long-range force Wigner lattice problem in the sense that a *strong enough coupling* brings about the energetically-preferred non-trivial solutions.

The above corresponds of course only to a non-condensed (positive energy per particle) crystalline state; it can be considered an independent-quasi-particle, quantum mechanical analogue of the so-called Kirkwood[23] hypothesis that a system of hard-spheres undergoes a fluid-solid transition at some finite density, *less than* packing density, at *any* temperature. This appears to have been borne out by computer experiments[24] in two and three dimensions, for $N$ not too large.

Normal crystals are of course condensed, self-bound, $N$-body systems and this can only occur through the presence of attractive forces. For the sake of definiteness, one can take[20] the potential

$$v(r) = v_0\{\theta(a_0 - r) - (\beta/\mu r)\exp(-\mu r)\}; \quad \beta, \mu, v_0 > 0 \ . \tag{60}$$

Using again the determinant (or permanent) of orbitals eq. (53) one has

$$\epsilon^0_{per} = 2\pi^2\hbar^2/md_0^2 + (\tfrac{1}{2}N) \sum_{R_1 R_2} \langle R_1 R_2 | v_{12} | R_1 R_2 \rangle \tag{61}$$

since the exchange term $\langle R_1 R_2 | v_{12} | R_2 R_1 \rangle$ vanishes identically due to the non-overlaping character of the orbitals (for repulsive enough cores, overlap can only *increase* the energy). A very useful result of Bernardes[25], as well as indistinguishability of sites, allows eqs. (60) and (61) to become

$$\epsilon^0_{per}(\rho) = \frac{2\pi\hbar^2}{mK^{2/3}} [\rho^{-1/3} - \rho_0^{-1/3}]^{-2}$$

$$- \tfrac{1}{2}\beta v_0 [1 + \sum_{m=1}^{\infty} A_m (\mu d/2)^{2m}] \left\{ \sum_{n=1}^{N-1} C_n \frac{e^{-\mu s_n}}{\mu s_n} \right\},$$

$$A_m \equiv [(2m+1)(2m+1)!]^{-1} \left\{ 1 - \sum_{t=0}^{m-1} \frac{(-)^t (2m+1)!}{(2\pi)^{2t+2}(2m-2t-1)!} \right\}$$

$$s_1 \equiv a + d = a_0 + d_0 \tag{62}$$

where $C_n$ is the number of $n$th nearest-neighbors and $s_n$ the distance between them. The trivial solution energy for bosons, from eqs. (9) and (60), becomes

$$\epsilon^{HF}_{hom} = 2\pi v_0 [\frac{a_0^3}{3} - \frac{\beta}{\mu^3}] \rho \qquad \text{(bosons)} \tag{63}$$

but must be positive as otherwise the system will (rigorously) collapse. Comparing eqs. (62) and (63) shows that for $\beta v_0$ sufficiently large one *may* obtain

$$\epsilon^{HF}_{hom} > \epsilon^0_{per} < 0 \ , \tag{64}$$

for some range of density, i. e., a self-bound, crystalline-like, non-trivial HF solution.

We now briefly indicate that non-trivial *aperiodic*-probability-density HF solutions exist for both bosons and fermions, these may be relevant in consideration of the *liquid* phase. Consider that in the determinant (or permanent) of localized orbitals (53) we separate one or more spheres from each other such that the average of the 12 nearest-neighbor $a$ values for *all* $N$ particles is $\tilde{a} > a_0$: we then have an imperfect lattice (or aperiodic distribution) and the density is given by

$$\rho = \frac{\tilde{K}}{(\tilde{a} + d)^3} < \frac{K}{(a_0 + d)^3} \tag{65}$$

since $\tilde{K} < \sqrt{2}$ (the maximum value of $K$ for closest packing). Thus, for fixed $d$, $\rho$ is *decreased* somewhat relative to the periodic configuration with $K = \sqrt{2}$. There are then a whole family of curves $\epsilon_{\text{aper}}(\rho)$ lying *above* $\epsilon^0_{\text{per}}$ but certainly *below* $\epsilon^{HF}_{\text{hom}}(\rho)$ Q.E.D.

Finally, stability will be guaranteed if *all*[26] compressional wave modes, longitudinal and transverse, have real velocities but the question has not, to our knowledge, been investigated within the single-determinantal (or permanental) picture.

## IV. REMAINING PROBLEMS

Three general questions remain: 1) once *existence* is established, how can one derive the *self-consistent* single-particle orbitals? 2) is the solution in question unique, i. e., is it the lowest energy one? 3) what are the most important perturbation-theoretic Feynman diagrams to be considered in calculating "correlation" effects, and can they be summed?.

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## RESUMEN

Se hace una revisión del trabajo relacionado con las pruebas sobre la existencia de soluciones no triviales (sobre todo en el caso de densidad periódica), energéticamente preferentes, de las ecuaciones de Hartree-Fock. Se consideran sistemas de $N$ bosones o fermiones ($N \gg 1$) interactuando tanto a largo como a corto alcance y se discuten criterios de estabilidad. También, se discuten algunos resultados exactos asociados con soluciones triviales (de onda plana). La principal conclusión es que, para cualquier densidad fí-

sica fija, un acoplamiento entre las partículas suficientemente fuerte, puede inducir la aparición de estados HF no triviales. Estas soluciones proporcionan un primer paso en el estudio de las propiedades de sistemas de muchos cuerpos, desde plasmas astrofísicos y cristales cuánticos, hasta la materia nuclear y el helio a muy baja temperatura.