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LETTER TO THE EDITOR

Long-range order HF states in the deformable jellium model†

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Abstract. We display three different kinds of HF-type orbitals with spatial long-range order which, at low densities and/or strong coupling, are stabler than the well-known HF self-consistent plane-wave homogeneous density solutions in the deformable jellium model of the electron gas.

The appearance of long-range order in the electron gas has been a topic of fruitful discussions (Edwards and Hillel 1968, Shuster and Kozinshaya 1971, Isihara 1972, Crandall 1973, Care and March 1975) since the suggestion of Wigner (Wigner 1934, 1938) about the existence of an electronic crystalline phase in the jellium model. On the other hand, the role played by the exchange interaction in the onset of *charge density* waves in free-electron-like metals has been discussed by Overhauser in a series of papers (Overhauser 1962, 1967, 1968, 1971a, 1971b, 1976, 1978, Bishop and Overhauser 1977, 1978). These calculations, as well as others (Yoshimori 1961, Barrera *et al* 1979), have been based on a Hartree–Fock (HF) scheme assuming a delta function potential between electrons. In this Letter we use the true Coulomb interaction between electrons in the calculation of the HF energy with orbitals displaying long-range order in the one-particle density.

We use three different kinds of orbitals of simple analytical form which have been shown (Aguilera-Navarro *et al* 1977, de Llano and Plastino 1976) to belong to a wider class of orbitals which satisfy the HF matrix equations for occupied states and also give spatial long-range order. With the chosen orbitals the calculation is fairly simple, and we show that for the deformable jellium model (with Fermi sphere occupation) these orbitals are stabler than the well-known self-consistent plane-wave solutions in the low-density regime.

The jellium model consists of a system of N electrons imbedded in a homogeneous background of equal positive charge so as to preserve charge neutrality. It is given by the Hamiltonian

$$H = -(\hbar^2/2m)\sum_{i=1}^{N}\nabla_i^2 + \sum_{i<j}^{N} e^2/r_{ij} + V_{bb} + V_{eb} \tag{1}$$

where V_{bb} and V_{eb} describe the electrostatic interaction of the positive background with itself and with the electrons respectively.

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The HF Hamiltonian associated with equation (1) can then be written as

$$H_{HF} = -(\hbar^2/2m)\nabla^2 + V_D + V_{EX} + V_{bb} + V_{eb} \tag{2}$$

where V_D and V_{EX} are the direct and exchange parts of the interparticle interaction. The *deformable* jellium model is then defined through the following condition:

$$V_D + V_{bb} + V_{eb} = 0 \tag{3}$$

which means that the positive background 'deforms' itself in order to provide *local* neutrality, a feature resembling the polarisation of the ionic lattice in a real metal. In this model the HF energy is therefore given simply by

$$E_{HF} = \sum_{k(occ)} \langle k|-(\hbar^2/2m)\nabla^2|k\rangle - \tfrac{1}{2}\sum_{k_1,k_2(occ)} \langle k_1 k_2|e^2/r_{12}|k_2 k_1\rangle \tag{4}$$

where the sum runs over occupied HF orbitals labelled by $k \equiv (\boldsymbol{k}, \sigma)$. We now consider the following three families of N orthonormal orbitals:

$$\phi_k(\boldsymbol{r}) = \begin{cases} C_1 \exp(i\boldsymbol{k}\cdot\boldsymbol{r})[1 + \alpha\exp(-i\boldsymbol{q}\cdot\boldsymbol{r})] & \boldsymbol{k}\cdot\boldsymbol{q} > 0 \quad (5a) \\ C_2 \exp(i\boldsymbol{k}\cdot\boldsymbol{r})[1 + \alpha\exp(-i\boldsymbol{q}\cdot\boldsymbol{r})]^2 & \boldsymbol{k}\cdot\boldsymbol{q} > 0 \quad (5b) \\ C_3 \exp(i\boldsymbol{k}\cdot\boldsymbol{r})(1 + \alpha\cos\boldsymbol{q}\cdot\boldsymbol{r}) & (5c) \end{cases}$$

with

$$C_1 \equiv [V(1 + \alpha^2)]^{-1/2} \tag{5d}$$

$$C_2 \equiv [V(1 + 4\alpha^2 + \alpha^4)]^{-1/2} \tag{5e}$$

$$C_3 \equiv [V(1 + \alpha^2/2)]^{-1/2} \tag{5f}$$

where V is the volume upon which one imposes periodic boundary conditions. These orbitals have been shown (Aguilera-Navarro *et al* 1977, de Llano and Plastino 1976) to satisfy the matrix HF equations for occupied states for $q > 2k_F$, where $k_F = (3\pi^2\rho_0)^{1/3} = (3\pi^2 N/V)^{1/3}$ is the Fermi sphere radius and q and α are variational parameters.

These orbitals give rise to long-range order in the one-particle density, since

$$\rho(\boldsymbol{r})/\rho_0 = \begin{cases} 1 + [2\alpha/(1 + \alpha^2)]\cos\boldsymbol{q}\cdot\boldsymbol{r} & (6a) \\ 1 + [4\alpha(1 + \alpha^2)/(1 + 4\alpha^2 + \alpha^4)]\cos\boldsymbol{q}\cdot\boldsymbol{r} + [2\alpha^2/(1 + 4\alpha^2 + \alpha^4)]\cos 2\boldsymbol{q}\cdot\boldsymbol{r} & (6b) \\ 1 + [2\alpha/(1 + \alpha^2/2)]\cos\boldsymbol{q}\cdot\boldsymbol{r} + [(\alpha^2/2)/(1 + \alpha^2/2)]\cos 2\boldsymbol{q}\cdot\boldsymbol{r} & (6c) \end{cases}$$

which represent density oscillations along the direction of $\boldsymbol{q}$ ('corrugated-sheet' type density).

We then calculate the HF energy of the system by introducing the following dimensionless variables:

$$r_s \equiv (3/4\pi\rho_0)^{1/3}/a_0 \qquad (a_0 \equiv \hbar^2/me^2) \tag{7a}$$

$$\epsilon \equiv (E/N)/(e^2/2a_0) \tag{7b}$$

and

$$\beta \equiv \alpha^2. \tag{7c}$$

Defining the HF energy difference

$$\Delta\epsilon = \epsilon_{HF} - \epsilon_{HF-PW} \tag{8}$$

we obtain for the three different orbitals of equations (5*a*). (5*b*) and (5*c*) respectively

$$\Delta\epsilon_1 = \frac{\beta}{1+\beta}\frac{Q(14{\cdot}72Q - 11{\cdot}04)}{r^2} - \frac{1{\cdot}22}{r_s}\frac{\beta}{(1+\beta)^2}f(Q). \tag{8a}$$

$$\Delta\epsilon_2 = [7{\cdot}36/r_s^2][\beta Q/(1+4\beta+\beta^2)][8(1+\beta)Q - 3(2+\beta)] - [1{\cdot}22/r_s][\beta/(1+4\beta+\beta^2)^2][\beta f(2Q) + 4(1+\beta)^2 f(Q)] \tag{8b}$$

$$\Delta\epsilon_3 = \frac{14{\cdot}72}{r_s^2}\frac{(\beta/2)}{(1+\beta/2)}Q^2 - \frac{1{\cdot}22}{r_s}\frac{(\beta/2)}{(1+\beta/2)^2}[2f(Q) - (\beta/8)f(2Q)] \tag{8c}$$

where $Q = q/2 \geqslant 1$, all of which clearly vanish for $\beta = 0$, and

$$f(Q) = \tfrac{11}{10} + Q^2/5 + (1/5Q - Q)\ln\left|\frac{Q+1}{Q-1}\right| + Q^2\left(1 - \frac{Q^2}{5}\right)\ln\left|\frac{Q^2}{Q^2-1}\right| \tag{8d}$$

is a monotonic decreasing function. It has the special values

$$f(Q=0) = 4{\cdot}5$$
$$f(Q=1) = 0{\cdot}190$$
$$f(Q=2) = 0{\cdot}043$$
$$f(Q\to\infty) = 0{\cdot}699/Q^2.$$

Now we extremise $\Delta\epsilon$ with respect to the variational parameters. We find, by inspection,

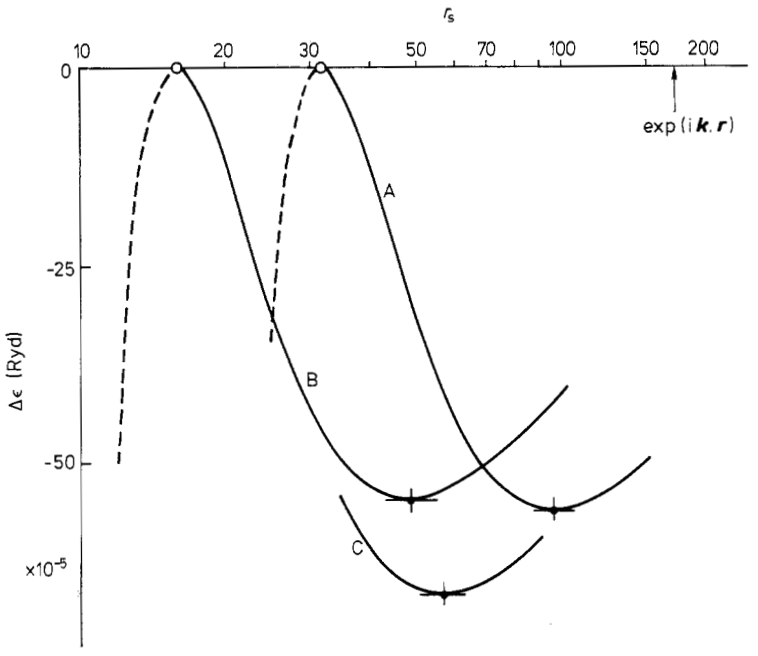

Figure 1. Energy difference in Rydbergs (equation (8)) between three non-trivial HF states, as a function of the dimensionless variable r_s (equation (7*a*)), which resulted from minimising the HF energy as discussed in the text: A $\exp\{i\boldsymbol{k}.\boldsymbol{r}[1 + \alpha\cos(\boldsymbol{q}.\boldsymbol{r})]\}$; B $\exp\{i\boldsymbol{k}.\boldsymbol{r}[1 + \alpha\exp(-i\boldsymbol{q}.\boldsymbol{r})]\}$; C $\exp\{i\boldsymbol{k}.\boldsymbol{r}[1 + \alpha\exp(-i\boldsymbol{q}.\boldsymbol{r})]\}$.

that for given β, the minimum in Q occurs for $Q = 1$; thus we require only to solve

$$(\partial/\partial\beta)\Delta\epsilon(Q = 1, \beta; r_s)|_{\beta=\beta_0} = 0 \tag{9}$$

and to determine the sign of

$$(\partial^2/\partial\beta^2)\Delta\epsilon(Q = 1, \beta; r_s)|_{\beta=\beta_0} \gtrless 0. \tag{10}$$

For orbitals (5*a*) and (5*c*), equation (9) can be solved analytically, yielding respectively

$$\beta_{01} = (0{\cdot}232r_s - 3{\cdot}68)/(0{\cdot}232r_s + 3{\cdot}68) \tag{11a}$$

$$\beta_{03} = 2(0{\cdot}463r_s - 14{\cdot}72)/(0{\cdot}201r_s + 14{\cdot}72) \tag{11b}$$

which must then be substituted back into equation (8) in order to find the extreme values of $\Delta\epsilon$ as a function of r_s. Since $\beta_0 \geqslant 0$, equations (11) impose minimum values for r_s which in both cases turned out to give *maxima* in $\Delta\epsilon$. The calculation of $\Delta\epsilon$ for orbitals of equation (5*b*) had to be done numerically. Our results are shown in figure 1 in which we plot the energy gain $\Delta\epsilon$ against r_s. It can be seen that for values of r_s greater than a critical value (low-density regime) there is always an energy gain. Although the energy gain is small, it is significant to show explicitly the role that the exchange interaction is able to play in the appearance of long-range order in the condensation of the electronic system. In figure 2 we show the values β_0 which minimise $\Delta\epsilon$ as a function of r_s.

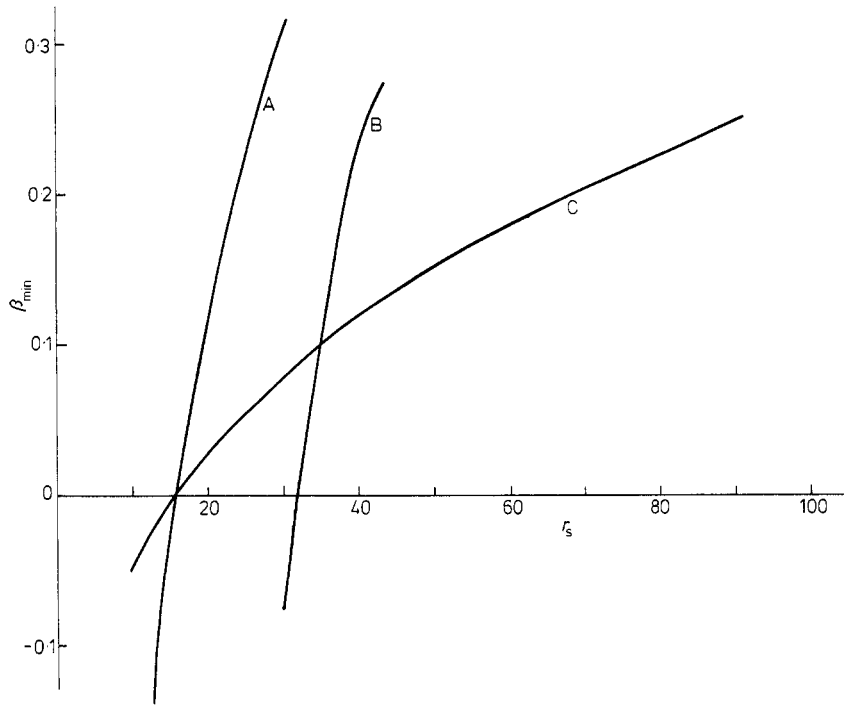

Figure 2. The order parameter $\beta_0 = (\alpha_0^2)$ corresponding to the three different orbitals (equation (5)), which minimises the HF energy for each value of r_s: A $\exp\{i\boldsymbol{k}.\boldsymbol{r}[1 + \alpha\exp(-i\boldsymbol{q}.\boldsymbol{r})]\}$; B $\exp\{i\boldsymbol{k}.\boldsymbol{r}[1 + \alpha\cos(\boldsymbol{q}.\boldsymbol{r})]\}$; C $\exp\{i\boldsymbol{k}.\boldsymbol{r}[1 + \alpha\exp(-i\boldsymbol{q}.\boldsymbol{r})]\}$.

Since to our knowledge there are no true self-consistent eigensolutions in the low-density regime (strong coupling), we believe it has been worthwhile showing that it is possible to find in a variational calculation HF-type orbitals which are stabler than the homogeneous solution, because this in itself proves the existence of such eigensolutions.

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