

## Excited states of the deformable jellium

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The excited states and the one-particle energy spectra are evaluated for the electron gas in the deformable jellium model. A screened Coulombic interaction is used. The Hartree-Fock approximation is carried out with linear combinations of periodic functions as the trial wave functions. The behavior of the energy spectra with the density of the system is discussed. The existence of overlapping bands is established. This result suggests that finite conductivity at low densities can be obtained within the Hartree-Fock approximation.

### I. INTRODUCTION

The calculation of excited states in a quantum system is a problem of fundamental interest. Many properties of the quantum system depend on an adequate understanding of the system's energy spectrum and thus on the energy of the excited states.

The basic conceptual tool of the many-body problem is to use a set of single-particle states, the orbitals. The Hartree-Fock (HF) method gives a general procedure that defines the best orbitals. Therefore it can be taken as the starting point for many approximation schemes.<sup>1-4</sup> The self-consistent HF method has been systematically used for such purposes in atoms and molecules<sup>5</sup> and nuclei.<sup>6-8</sup> The self-consistent approach for excited states requires a careful treatment for systems with large (infinite) number of degrees of freedom, such as is the case of the solids.

In the HF method the orbitals for the ground state are the solutions of the HF equations. The determination of the unoccupied states is less obvious; this point is emphasized in Refs. 2 and 4. The problem stems from the question of the potential to be used for the excited states. In the HF spirit, a natural choice is to determine these orbitals with a self-consistent potential for the excited state, with the additional constraint that they should be orthogonal to the occupied ground-state orbitals. Instead, the usual procedure—which we will use—is to take the excited orbitals as solutions of the HF equations for the *same* ground-state potential and different eigenvalues. Because the HF operator is Hermitian the orthogonality of the occupied and unoccupied states is guaranteed.

A well-studied and useful many-fermion system is the electron gas<sup>9,10</sup> for which ground-state energies have been obtained in the jellium model with several methods; among them are the integral approximant,<sup>11</sup> with Monte Carlo variational calculations for a large number of particles<sup>12</sup> and with stochastic simulations of the Schrödinger equation.<sup>13</sup> The essential approximation of the jellium model is to assume an inert uniform background.

A different model is the deformable jellium<sup>14,15</sup> in which the background is allowed to deform in order to

locally neutralize the electron-gas charge density. This fact guarantees a lower energy per particle and therefore a more stable system.<sup>15,16</sup> Using trial functions with different crystallographic symmetries, the HF method has been successful in the evaluation of the ground-state function and the energy per particle in the deformable jellium. One remarkable achievement of the deformable jellium has been the description of the electron-gas transition from the homogeneous phase at metal-like densities, with Wigner-Seitz parameter  $1 < r_s < 10$ , into localized states at lower densities,  $r_s \approx 25$ . This leads at very low densities to Wigner crystallization.<sup>15,17</sup> More recently, the convergence of this algebraic HF procedure for the ground state has been studied using an improved expansion in terms of cosine functions.<sup>16</sup> However, the detailed reasons of the transition to the localized state have remained obscure; after all, localization implies a mixing of the orbitals with states of very large kinetic energy.

Our purpose in this work is the evaluation of the one-particle energy spectra  $E(\mathbf{k})$  for the ground and the first excited states for an interacting fermion gas in the deformable jellium model. Because we are mainly interested in the mechanism that causes the transition to the corrugated state we will only allow for the most simple of all corrugations: those along a single direction. Certainly, charge-density waves (CDW's) of the Overhauser type are described.

### II. MODEL

For the particle-particle interaction a screened Coulombic (Yukawa) interaction  $V(r_{ij}) = \exp(-\mu r_{ij})/r_{ij}$  is used in order to cut the long range of the Coulomb potential. When the screening parameter  $\mu$  is equal to zero, the Coulomb interaction is recovered. This screening could, in principle, take into account the zero frequency, static, correlations.

For the state functions in the Slater determinant we use the usual plane-wave functions multiplied by modulating functions. The modulating frequency is not arbitrary, but it is constrained by the orthonormality condition of the orbitals. The generic form of the orbitals is

$$\varphi_{\mathbf{k}}(\mathbf{r}) = \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{V}} \sum_{n=0}^N \mathcal{C}_n \cos(n\mathbf{q}_0\cdot\mathbf{r}) \quad (1)$$

$$= \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{V}} \sum_{n=-N}^N C_n \exp(in\mathbf{q}_0\cdot\mathbf{r}). \quad (2)$$

$V$  is the volume in which periodic boundary conditions are imposed. The vector  $\mathbf{q}_0 = q_0 \hat{\mathbf{e}}_{q_0}$  is along the corrugation direction. The orthonormalization conditions require  $q_0 \geq 2k_F$  (Ref. 18) and the  $\mathcal{C}_n$  are simply related to the  $C_n$  by the usual factors. As usual, we assume that these coefficients are independent of  $k$ . We have imposed the orthonormality condition of the spin-orbitals as well as double occupancy of each orbital. The expansion in terms of exponentials is more general than the one of cosines, but for the lower energy bands they turn out to be equivalent.<sup>19</sup> It was shown in Ref. 16 that the dimension of the HF operator matrix is considerably reduced with the equivalent cosine expansion.

The coefficients in the expansions of the ground and the excited states are self-consistently determined for each  $r_s$  and, independently, for the physically different systems characterized by a given value of  $\mu$ . If a nonho-

mogeneous orbital is selected by the self-consistent procedure a symmetry breaking will be generated.<sup>14</sup> Otherwise, if the ground state is a plane-wave (PW) solution then the excited states will be modulated by a cosine function. Two general types of solutions are expected. First, the ground state is a PW, which turns out to be the case for the region of the metal densities,  $r_s \leq 10$ . Then, the excited states are the terms corresponding to  $n=1$ ,  $n=2$ , and so on in Eq. (1). Second, beginning with a certain value of the interparticle distance, which depends on the value of the screening parameter in the potential, the HF self-consistent solutions can be of the type of the CDW. In this case the solutions present a periodic density along the  $\mathbf{q}_0$  direction. The excited states are the solutions corresponding to the next eigenvalues of the HF operator.

An important feature of the deformable jellium model is that the terms of the background energy are identically canceled with the direct term that stems from the fermion-fermion interaction. Then the only contribution to the potential energy comes from the exchange term.

The equation for the one-particle energy spectrum, obtained with the HF approximation for a fermion system in the deformable jellium, is given by

$$E(\mathbf{k}) = \left[ \frac{9\pi}{4} \right]^{2/3} \frac{1}{r_s^2} \left[ k^2 + \sum_{n=-N}^N |C_n|^2 4n^2 \right] - \frac{1}{\pi r_s} \left[ \frac{9\pi}{4} \right]^{1/3} \sum_{n_1, n_2, n_3, n_4 = -N}^N C_{n_1}^* C_{n_2}^* C_{n_3} C_{n_4} \delta_{n_1 - n_4, n_3 - n_2} F(Q, \mu), \quad (3)$$

where atomic units a.u. are used in this equation and throughout this work. In the last equation the Wigner-Seitz parameter  $r_s$  is the interparticle distance in Bohr radii,  $\mathbf{Q} = \mathbf{k} + 2\hat{\mathbf{e}}_{q_0}(n_4 - n_1)$ , and

$$F(Q, \mu) = \frac{1 - Q^2 + 4\mu^2}{2Q} \ln \left[ \left| \frac{(1+Q)^2 + 4\mu^2}{(1-Q)^2 + 4\mu^2} \right| \right] + 2 - 4\mu \left[ \arctan \left[ \frac{1+Q}{2\mu} \right] + \arctan \left[ \frac{1-Q}{2\mu} \right] \right]. \quad (4)$$

This expression reduces to the well-known result<sup>20</sup>

TABLE I. First four coefficients  $\mathcal{C}_n$  in the orbital expansion of Eq. (1) for the unscreened,  $\mu=0$ , system. Three values of the density parameter are considered:  $r_s = 29, 30, 40$ . For densities below the transition point,  $r_s \leq 28.8$ , the expansion reduces to the trivial combinations of one and zeros.

Coefficient	Ground state	First excited state	Second excited state
$r_s = 29$			
$\mathcal{C}_0$	0.993	0.120	0.001
$\mathcal{C}_1$	0.120	-0.993	0.014
$\mathcal{C}_2$	0.003	-0.001	-0.999
$\mathcal{C}_3$	0.000	0.000	-0.002
$r_s = 30$			
$\mathcal{C}_0$	0.983	0.183	0.003
$\mathcal{C}_1$	0.183	-0.983	0.022
$\mathcal{C}_2$	0.007	-0.021	-0.999
$\mathcal{C}_3$	0.000	0.000	-0.004
$r_s = 40$			
$\mathcal{C}_0$	0.906	0.423	0.018
$\mathcal{C}_1$	0.421	-0.905	0.062
$\mathcal{C}_2$	0.043	-0.049	-0.998
$\mathcal{C}_3$	0.003	-0.003	-0.011

$$F(k,0) = \frac{1-k^2}{k} \ln \left| \left| \frac{(1+k)}{(1-k)} \right| \right| + 2, \quad (5)$$

in the  $\mu=0$ , plane-wave limit. The form of Eq. (4) implies anisotropic surfaces of constant energy in  $\mathbf{k}$  space whenever  $Q \neq \mathbf{k}$ .

From the one-particle energy spectrum it is possible to compute several properties of the electron gas, for example, the electronic density of states, which depends on the inverse of  $|\nabla_{\mathbf{k}} E(\mathbf{k})|$ . Using Eq. (3), we obtain in spherical coordinates

$$\nabla_{\mathbf{k}} E(\mathbf{k}) = (18\pi)^{1/3} \frac{k}{r_s} \hat{\mathbf{e}}_k - \frac{1}{\pi} \sum_{n_1, n_2, n_3, n_4 = -N}^N c_{n_1}^* c_{n_2}^* c_{n_3} c_{n_4} \delta_{n_1 - n_4, n_3 - n_2} D(Q, \mu) [\hat{\mathbf{e}}_k (k + 2N \cos\theta) - \hat{\mathbf{e}}_\theta 2N \sin\theta], \quad (6)$$

with  $N = n_1 - n_4$  and

$$D(Q, \mu) = -\frac{1+Q^2+4\mu^2}{2Q^3} \ln \left| \left| \frac{(1+Q)^2+4\mu^2}{(1-Q)^2+4\mu^2} \right| \right| + \frac{2}{Q^2} \frac{1+Q^4+16\mu^4-2Q^2+8\mu^2+8Q^2\mu^2}{[4\mu^2+(1+Q)^2][4\mu^2+(1-Q)^2]}. \quad (7)$$

The electronic density of states for the ground state has been obtained in Ref. 21 for several values of  $r_s$ .

The numerical calculations have been performed with  $N=6$ ; larger values of  $N$  result in negligible changes in the spectra for the first two energy bands. We will not be concerned here with the precision of the other bands because in the density range considered by this work they turn out to be very much separated from the first two bands. The results presented in this work have been obtained with a new code written mainly in a VAX C implementation of the C language. Some subroutines, including the one used for the diagonalization of the HF operator,<sup>22</sup> are in FORTRAN. The values of the self-consistent coefficients have been checked with those obtained before using ALGOL; unimportant differences in the coefficients mostly due to differences in floating point arithmetic precision were detected.

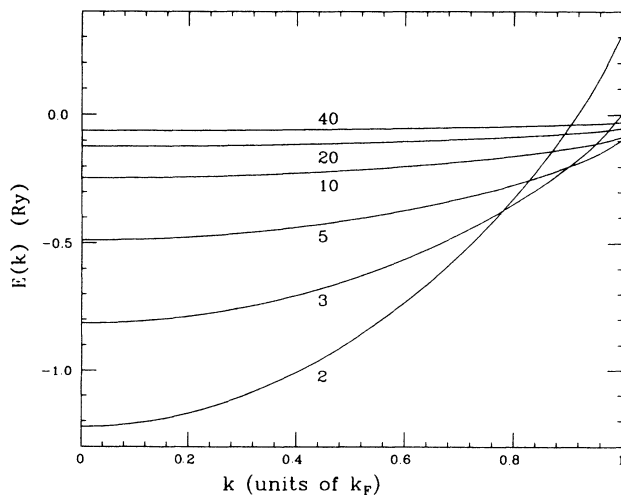


FIG. 1. The one-particle energy spectra for the ground state of the electron gas in the jellium model for various  $r_s$  values. The numbers in the curves label the values of  $r_s$ .

### III. RESULTS AND DISCUSSION

As can be seen from Eqs. (4) and (5) the screening parameter avoids the divergence that otherwise appears in  $\nabla E(\mathbf{k})$  at the Fermi level for the Coulomb potential. The use of a screened Coulombic interaction is one of the ways used to avoid the divergence at the Fermi level. Alternative methods, such as the self-interaction correction to the local-spin-density approximation, which introduces a Fourier cutoff of the interparticle interaction, have also been used in the literature.<sup>23</sup>

In Fig. 1, the behavior of the  $n=0$  energy spectra for several values of  $r_s$  is shown. Clearly this is the simple case of a pure plane-wave orbital. Because the background in this case is uniform the deformable jellium and the usual jellium coincide. Only the case  $\mu=0$  is considered. We are excluding the point  $k/k_f=1$ , where the curve has an infinite slope for the Coulomb potential. We see that the lowest values of the energy are obtained for densities in the region  $r_s \gtrsim 5$ ; for high densities, i.e.,  $r_s < 5$ , the total energy again increases. This is, of course, the well-known behavior of the jellium model.<sup>1</sup> From the

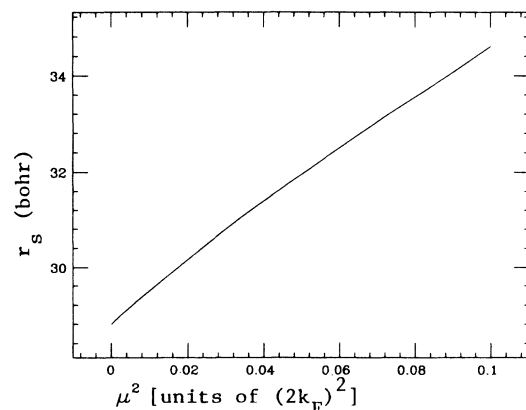


FIG. 2. The Wigner-Seitz parameter  $r_s$  for which the transition from the plane-wave to the charge-density wave solution occurs as a function of the screening parameter  $\mu$ .

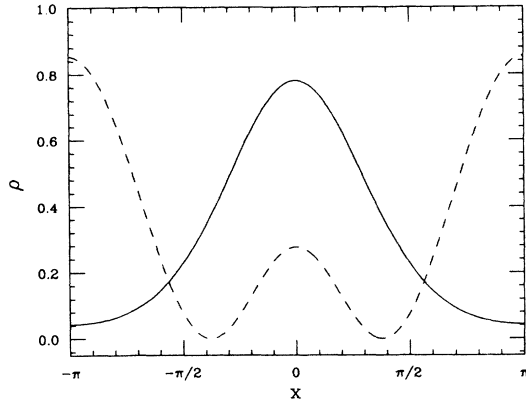


FIG. 3. Behavior of the charge density  $\rho$  along the direction of corrugation for the ground state (solid curve) and the first excited state (dashed curve). Curves have been normalized to density 1 for one period of corrugation. The charge densities correspond to the zero screening  $\mu=0$ , Coulomb, solution at  $r_s=40$ . The density curves are periodic along the corrugation direction, the period of corrugation being  $\pi/k_F$ .

plots in Fig. 1 we also learn that the region in  $k$  space responsible for the rise in the total energy per particle in the high-density limit is the one near the Fermi level.

We show the  $r_s$  values for the transition from the PW to CDW-type solution as a function of the screening parameter in Fig. 2;  $\mu$  is given in units of  $2k_F$ . The transition point for the potential with  $\mu=0$  is near the result obtained in the calculations for the electron gas in Ref. 16, where the state function used gave a particle's density centered around a simple cubic lattice. From Fig. 2 one

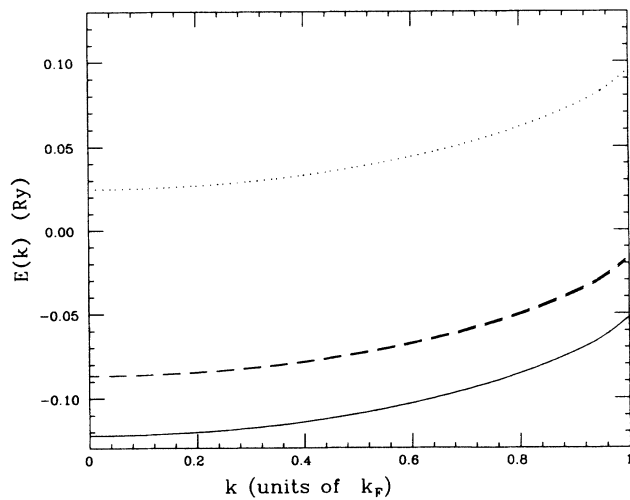


FIG. 4. The first three energy bands of the electron gas with Coulomb interaction at  $r_s=20$ . The widening of the first excited band (dashed curve) results from the anisotropy of the energy spectra contained in Eq. (3). The same effect is also present for the second excited band but is too small to be plotted at the scale of this figure.

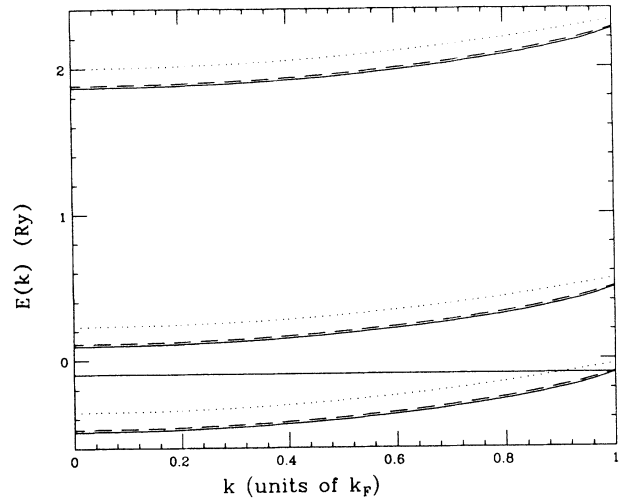


FIG. 5. Energy spectra for the Coulomb and screened interactions at  $r_s=5$  in the metal density region. The solid curves are for the spectra for  $\mu=0$ , dashed lines correspond to  $\mu=0.01$ , and dotted ones to  $\mu=0.1$ . A horizontal axis has been drawn at the upper end of the first band for the unscreened potential.

concludes that the transition for values of  $\mu \neq 0$  occurs at lower densities and that the transition  $r_s$  is an almost linear function of  $\mu^2$ . In Table I the behavior of the first four coefficients  $\mathcal{C}_n$  with the density is shown for the unscreened system. The main effect is to change the admixture of the two first orbitals, from almost zero at the transition point to about 20% at  $r_s=40$ . The density of the two first states is illustrated in Fig. 3 at  $r_s=40$  and  $\mu=0$ .

In Fig. 4, the spectra for the PW state function and the two first excited states, at  $r_s=20$ , are presented. The spectra are for the Coulomb potential. A small splitting for different angles for the first excited band can be ob-

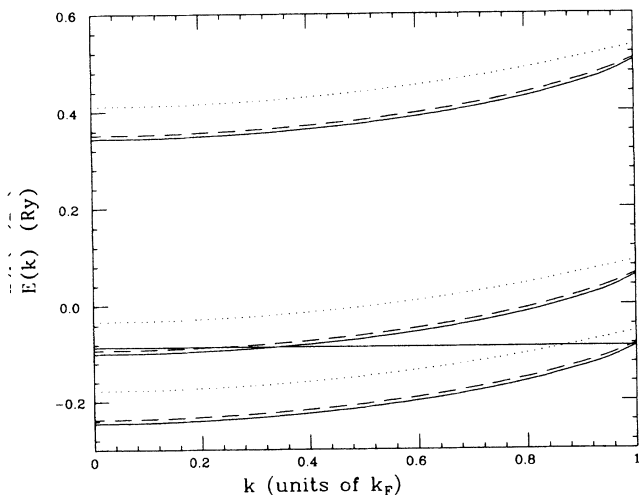


FIG. 6. The same as in Fig. 5 for  $r_s=10$ . The first two bands begin to overlap.

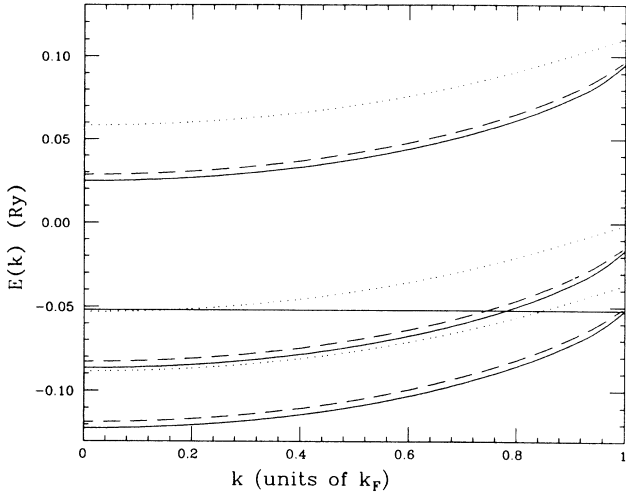


FIG. 7. The same as in Fig. 5 for  $r_s=20$ . Before the transition to CDW.

served. This is a result of the anisotropic conduct mentioned after Eq. (4). This behavior is most likely due to the hypothesis of a spherical  $\mathbf{k}$  Fermi surface which does not represent adequately the symmetry of the  $n \neq 0$  orbitals. We will neglect this effect in this work and following Ref. 23 will take here a representative value; in this work the spectra at  $\theta=90^\circ$  will be taken. More relevant for our purposes is the observation that the first two bands show an overlap at this  $r_s$ . This overlap begins for densities with  $r_s \approx 10$ .

The spectra of the three first bands are plotted in Figs. 5–8, the figures correspond to four values of  $r_s$ : 5, 10, 20, and 40, respectively. In each figure, the spectra of three different systems is depicted; the systems are characterized by a different screening parameter  $\mu$ ; the values

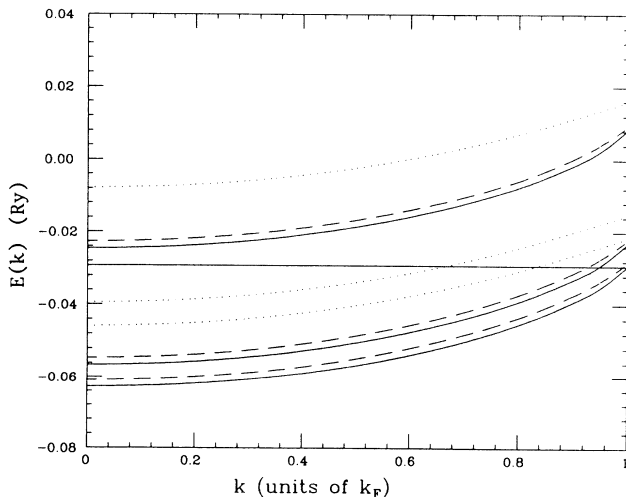


FIG. 8. The same as in Fig. 5 for  $r_s=40$ . After the transition to CDW.

selected for this parameter are  $\mu=0,0.01,0.1$ . In all the figures a value  $\theta=90^\circ$  has been taken.

The spectra in Fig. 5 show three well-separated bands in the metal density region:  $r_s=5$ . For lower densities at  $r_s \approx 10$  in Fig. 6, the two first bands begin to overlap for the unscreened potential of  $\mu=0$ . The crossover occurs for the solid curves in a small region near  $k=k_F$  in the first band and the low  $k$  region in the second band. The system with  $\mu=0.01$ , coded in dashed curves in the figures, shows a smaller overlap at this density. For this  $r_s$ , the  $\mu=0.1$  still has a gap between all the bands, as can be observed in Fig. 6.

Before the transition to the CDW's, at  $r_s=20$ , Fig. 7 shows a larger crossover of the two first bands. Figure 8 shows the important overlap in the CDW region at  $r_s=40$ ; at these densities even the third band is beginning to overlap with the second one. Not shown by the figures is the enhancing effect that the CDW's have on the band overlapping.

Within the spherical approximation that is used in this work, the density of states depends solely on the radial component of  $k$ . As can be seen from Figs. 4–8, the form of the one-particle energy spectra and consequently the form of the density of states do not show an important variation in changing from one band to the next. The most interesting behavior of the density of states is near the Fermi sphere, where the unscreened potential induces the well-known logarithmic singularity; it is clear from Eq. (6) that this singularity is removed for a nonzero  $\mu$ .

#### IV. CONCLUSIONS

The main motivation of this work was the study of the mechanism that allows the CDW to become the ground state of the deformable jellium model of the electron gas. We conclude that the transition from PW to CDW is preceded by an overlapping of the energy bands. This overlapping continues to grow until the admixture of orbitals required for the CDW's is energetically favorable. Therefore a reasonable mechanism for the generation of the CDW's has been found.

The most interesting feature in our results is precisely the overlap in the energy bands. The overlap itself is, within the deformable jellium model, a consequence of the attractive exchange interaction; which, after the cancellation of the direct term with the background energy, is the only interaction left in the deformable jellium model. The most important consequence of the band mixing is clearly to change the nature of the Hartree-Fock ground state. In order to minimize the total energy the system will first fill the orbitals of small  $k$  in the second band. If, as it is done in band theory, the nature and the energy of the single-particle orbitals is not severely affected by the new occupation, then many states are available for conduction at densities lower than  $r_s \approx 10$ .

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