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Variational approach to inhomogeneous electron liquids: Application to metallic hydrogen

V. T. Rajan and Chia-Wei Woo

Materials Research Center, and Department of Physics and Astronomy, Northwestern University, Evanston, Illinois 60201

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A variational approach is developed to treat inhomogeneous electron liquids at metallic densities using a correlated wave function. The single-particle part of the wave function is obtained by band calculation with the aid of a suitable effective one-particle potential. Many-body correlations are accounted for by a correlation factor of the Jastrow form. The Chakravarty-Woo hierarchy of integral equations is derived and solved for the one-particle distribution (density function) and pair correlation function. The results are used to evaluate the energy. The method is applied to a static lattice model of metallic hydrogen. Calculations are performed for different densities using the variational formalism and density-functional methods. Comparison is also made to calculations performed with different techniques.

I. INTRODUCTION

The homogeneous electron gas imbedded in a neutralizing-positive-charge background is one of the most extensively studied quantum many-body systems. In the earliest days, Wigner[1] calculated the energy of the system in the low-density limit, where the electron-electron interaction dominates. In the 1950s, at the advent of quantum many-body theory, Gell-Mann and Brueckner[2,3] treated the electron-electron interaction as a perturbation, and performed a selected summation of the perturbation series, using a method similar to Feynman's field-theoretic technique. The resulting ground-state energy and excitation spectrum are valid for high densities. Their work was supplemented by the efforts of many, in particular Pines and Nozières,[4-6] who devised an interpolation scheme for calculating correlation energies in the regime of intermediate densities: the metallic region. More recently, we have seen work by Singwi and collaborators[7,8] for homogeneous electron liquids at metallic densities using an equation-of-motion method. The latter is generally regarded as reliable and widely applicable.

Real metals are, of course, inhomogeneous. There have been several attempts to extend the formalisms developed for homogeneous systems to take into account the inhomogeneities. In perturbation methods, one starts with a homogeneous electron liquid and considers the effect of the external potential due to the ion lattice as a perturbation.[9-11] In the density-functional formalism,[12] one exploits the fact that the energy is a functional of the density. In the local-density approximation,[13,14] it is conjectured that the electron cloud is so weakly nonuniform that each volume element of the electron cloud can be treated as locally uniform. Its energy can thus be calculated from the known energy density for a homogeneous electron liquid. The total energy of the inhomogeneous system is then obtained by integration.[15]

Over the years, researchers in our group have sought to treat Coulomb problems by means of a variational approach based on the use of correlated wave functions. The work carried out by Lee and Feenberg[16] in the 1960s on the ground state of the charged Bose gas was given a firm perturbation-theoretic foundation by Brueckner,[17] and was followed up by analyses on both the ground-state[18] and low-lying excited states.[19] Results obtained with all methods were proven consistent, and gave credence to the variational approach. The application of the method to Fermi systems, however, told a totally different story. Despite its success in the field of liquid ^{3}He and nuclear matter, references to which are much too numerous to quote here, attempts to apply it to Coulomb liquids[20-27] always seemed to fall short of agreement with results of proven techniques. The fault lay almost invariably in its inability to properly deal with the statistical (or exchange) correlations. The difficulty was finally overcome in 1976, when an integral equation was derived and solved by Chakravarty and Woo[28] for a properly antisymmetrized correlated wave function, and correlation energies and pair-correlation functions were calculated. Their results were found to be in rather good agreement with those of Singwi *et al.* throughout the range of metallic densities. In this paper, we generalize that method, and apply it to the case of an inhomogeneous electron liquid.

Section II briefly describes essentials of the variational approach. Section III formulates the inhomogeneous-electron-liquid problem in terms of a metallic-hydrogen model. In Sec. IV, the energy of the system is expressed in terms of multiple-density correlation functions. These correlation functions are defined for each choice of the variational wave function. In the convolution approximation they can be related to the density function and the pair distribution function. The expressions were calculated in an earlier paper, and are summarized in Sec. V. Section VI gives integral equations for the density function and the pair-distribution function, and concludes the presentation of our formalism. In Sec. VII, we solve the equation for the density function for metallic hydrogen, working out in the process the Hartree-Fock or band-theoretic part of the problem. It ends up with the correlation energy as a function of the mean density. In Sec. VIII the same calculation is carried out using a density-functional approach, both with and without the density gradient correction. Numerical results obtained with the variational approach are then compared with those obtained with the density-functional approach, and with results obtained by other authors using the density-functional method and perturbation theory.

II. VARIATIONAL APPROACH

For the inhomogeneous electron liquid, there are several advantages in using a variational approach. It is these advantages which have motivated us in the prolonged search for a successful variational formalism. First, it does not require as input the solution for a homogeneous liquid. The latter emerges as a limiting case, and thus provides an independent check on the general formalism. Second, the variational approach offers upper bounds, which in turn provide guidance on whether attempts to introduce improvements are moving in the right direction. Third, from the variational result one can construct a set of correlated basis functions, upon which low-order perturbation corrections can be evaluated. It thus offers opportunities for systematic improvements. Finally, and perhaps most importantly, such a theory gives us many-body *wave functions*, not just the density function or some other macroscopic description of the system. It is then possible to define and to calculate matrix elements arising from the introduction of external perturbation, e.g., impurities in the bulk, or atoms and molecules adsorbed on a surface. Canonical transformations designed to eliminate these nondiagonal matrix elements lead then to self-consistent distribution of the positive charges, electrons, and impurities or adatoms.

The first step in any quantum-mechanical variational procedure is to select a trial wave function. The trial wave function should be of a form that takes into account the essential physics of the system. In addition, it is customary for the trial function to contain one or more parameters which can be varied to minimize the energy expectation value. A prudent choice of the form of the trial function is crucial to the success of the method.

For strongly correlated systems, we construct a variational wave function of the form

$$\Psi = F\|\varphi_\alpha(\vec{r}_i)\|. \tag{1}$$

Here $\|\varphi_\alpha(\vec{r}_i)\|$ denotes a properly symmetrized product of single-particle wave functions. For Fermi systems, it will be a determinant. $\varphi_\alpha(\vec{r}_i)$, the elements of the determinant, should be those which give rise to the best possible independent-particle description of the system. There should also be spin variables. In the case of an infinite homogeneous system, they are plane waves multiplied to spin functions. For an inhomogeneous system such as a realistic model of metals, $\varphi_\alpha(\vec{r}_i)$ are Bloch states obtained by solving a band-theoretic problem with a suitable effective potential. In the absence of the correlation operator F, the trial wave function defines a Hartree-Fock theory. The adjustable parameters imbedded in the effective potential serve as variational parameters. The minimization of the energy expectation value with respect to these parameters, and with respect to the form of the effective potential, brings the independent-particle description to its optimum. This outlines the variational approach toward formulating a self-consistent theory.

In the presence of strong correlations, be it of the short-range repulsive type as found in condensed phases of helium and nuclear matter, or of the weak long-range type as found in Coulomb systems, a Hartree-Fock description is no longer adequate. A most obvious improvement can be brought about by introducing a correlation operator into the wave functions in the form of a two-particle product known as a Jastrow function:

$$F=\prod_{i<j} f(i,j) \approx \exp\left(\frac{1}{2}\sum_{i<j} u(r_{ij})\right). \tag{2}$$

This brings the wave function Ψ into what is known as the Slater-Jastrow form. Here $u(r)$ is as yet undetermined. The specific form of F seeks to build up all the relevant many-particle correlations from two-particle correlation factors $u(r)$. In the high-density limit, Gaskell,[24] Pines,[29] and Feynmen[30] had all noted that the ground-state wave function in the random-phase approximation reduces to the Slater-Jastrow form. Furthermore, a recent t-matrix calculation by Lowy and Brown[31] argues convincingly that two-particle correlations play a dominant role in electron liquids. One would expect that such a correlation operator could adequately describe long- and short-range behavior alike. The success of the Chakravarty-Woo calculation for homogeneous electron liquids supports this conclusion.

It does not follow that the Jastrow correlation factor can be regarded as general. $u(r_{ij})$, for example, should probably depend on the spins. This can be true even if the pairwise interaction is spin independent. Also, the inclusion of three and more particle factors could certainly improve the wave function, as was shown in the case of liquid helium.[32-34] The three-particle factor $w(r_{ij}, r_{jk}, r_{ki})$ in

$$F_3 = \exp\left(\frac{1}{2}\sum_{i<j} u(r_{ij}) + \frac{1}{2}\sum_{i<j<k} w(r_{ij}, r_{jk}, r_{ki})\right), \tag{3}$$

at least in the boson case, corresponds to taking into account three-phonon perturbation corrections.[32] Moreover, it cannot be expected that an antisymmetrized single-particle product, namely, a Slater determinant, can be factored out of the true wave function. No amount of multiple correlation added to u and w can compenstate for this approximation. In spite of all this, the Slater-Jastrow form remains the simplest, and thus the most appealing.

Once the form of the trial wave function is determined, we calculate the expectation value of the Hamiltonian;

$$E[\Psi] \equiv \langle \Psi | H | \Psi \rangle / \langle \Psi | \Psi \rangle, \tag{4}$$

and minimize it with respect to Ψ to obtain an upper bound to the ground-state energy and an approximate ground-state wave function. In principle, one should solve the Euler-Lagrange equation

$$\delta E[\Psi]/\delta\Psi = 0. \tag{5}$$

With the present choice of the wave function, $\Psi \equiv F \| \varphi_\alpha(\vec{r}_i) \|$, Eq. (5) reduces to the set

$$\delta E/\delta[\varphi_\alpha(\vec{r})] = 0, \tag{6}$$

$$\delta E/\delta u(r) = 0. \tag{7}$$

In a way, we have described the variational approach toward formulating a twofold self-consistent theory. The solution of coupled Euler-Lagrange equations (6) and (7) represents an approximate treatment of pairs of particles moving in the mean two-particle field due to the remaining $N-2$ particles, which conspire to form the medium.

In practice we do less. $u(r)$ can be taken with reasonable confidence as only slightly varied from that determined for the homogeneous electron liquid. For a first calculation, one can even lift $u(r)$ right out of the latter calculation. The single-particle functions $\varphi_\alpha(\vec{r})$, as stated earlier, can be regarded as band-theoretic solutions of a suitably chosen effective potential $V_{\text{eff}}(\vec{r})$. One then minimizes $E(V_{\text{eff}}(\vec{r}))$ with respect to $V_{\text{eff}}(\vec{r})$, most conveniently by parameterizing $V_{\text{eff}}(\vec{r})$ and varying E with respect to the parameters.

III. MODEL FOR METALLIC HYDROGEN

Consider the motion of N electrons through a static lattice of N positive ions. The Hamiltonian of the system is given by

$$H = \sum_{i=1}^{N} \frac{-\hbar^2}{2m} \nabla_i^2 + \sum_{i=1}^{N} V_{eI}(\vec{r}_i) + \sum_{\substack{i<j \\ i=1}}^{N} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + U_I, \tag{8}$$

where $\vec{r}_i$ denotes the position of the ith electron. $V_{eI}(\vec{r})$ denotes the electron-ion interaction potential, often taken in the form of a pseudopotential. For metallic hydrogen, since the ions are simply protons,

$$V_{eI}(\vec{r}_i) = \sum_{j=1}^{N} \frac{-e^2}{|\vec{r}_i - \vec{R}_j|}, \tag{9}$$

where $\vec{R}_j$ represents the position of the jth ion, treated in the present case as a c number. (In reality, of course, a static lattice model is not appropriate for metallic hydrogen since the zero point motion of these light ions makes a significant contribution to the total energy of the system.) U_I represents the lattice potential energy, which will be regarded in the static approximation as an additive constant. For metallic hydrogen,

$$U_I = \sum_{\substack{i<j \\ i=1}}^{N} \frac{e^2}{|\vec{R}_i - \vec{R}_j|}. \tag{10}$$

In this paper, we shall always be referring to metallic hydrogen. It is the easiest model to deal with, since there is no question about the form of $V_{eI}(\vec{r})$. There are many other calculations to which we can compare our results. It should be pointed out that metallic hydrogen has a special place in solid-state physics. All theories predict that molecular solid hydrogen transforms to a metallic phase at very high pressures. The zero-temperature transition pressure is estimated to be of the order of megabars, but so far an exact value is unavailable, on account of uncertainties in the calculation of energies in both phases. There has been one unsubstantiated claim[35] of experimental observation of the metallic phase. Other speculations refer to a metastable metallic phase, and argue for the possibility of hydrogen remaining in this metastable phase at terrestrial temperatures and pressures. Some talk hopefully of the metastable phase going superconducting. Also, astrophysicists have placed metallic hydrogen in the interior of Jupiter and Saturn. For our purposes, it suffices as to say that metallic hydrogen is the simplest prototype of inhomogeneous electron liquids. A thorough treatment of it will serve to make our formalism concrete.

The Hamiltonian can be separated into two parts:

$$H=\sum_{i=1}^{N} h(\vec{r}_i)+H' , \tag{11}$$

$$h(\vec{r}_i)=(-\hbar^2/2m)\nabla_i^2+V_{el}(\vec{r}_i)+W(\vec{r}_i) , \tag{12}$$

$$H'=-\sum_{i=1}^{N} W(\vec{r}_i)+\sum_{\substack{i<j\\ i=1}}^{N} \frac{e^2}{|\vec{r}_i-\vec{r}_j|}+\sum_{\substack{i<j\\ i=1}}^{N} \frac{e^2}{|\vec{R}_i-\vec{R}_j|} . \tag{13}$$

The function $W(\vec{r})$ is an as yet unspecified decoupling function. Physically it can be considered as an average potential imposed on the ith electron by all the other electrons. We shall consider only the case where $W(\vec{r}_i)$ is local, although in general (as in the Hartree-Fock theory) it can be nonlocal.

All the many-body effects in H' come from the electron-electron interaction, i.e., the second term. The last term is not affected (in the present approximation) by the electron distribution, and the first term compensates for the effect already accounted for by the single-particle Hamiltonian $h(\vec{r}_i)$. The traditional approach of choosing $W(\vec{r}_i)$ might be interpreted as requiring the effect of H' be as small as possible. In that case, then, H' can be treated as a perturbation. For example, let us ignore exchange and write the first-order correction $\langle\Psi|H'|\Psi\rangle$, where Ψ denotes the ground-state solution of $\sum_{i=1}^{N} h(\vec{r}_i)$, in the form

$$\langle\Psi|H'|\Psi\rangle=-N\int W(\vec{r})n(\vec{r})\,d\vec{r}+\frac{Ne^2}{2}\int\int\frac{n(\vec{r})n(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}\,d\vec{r}\,d\vec{r}\,'+\sum_{\substack{i<j\\ i=1}}^{N}\frac{e^2}{|\vec{R}_i-\vec{R}_j|} . \tag{14}$$

$n(\vec{r})$ represents the single-particle density function. One can then minimize the correction term by solving

$$\delta\langle\Psi|H'|\Psi\rangle/\delta n(\vec{r})=0 . \tag{15}$$

A single step leads to an optimum choice of $W(\vec{r})$:

$$W(\vec{r})=e^2\int\frac{n(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}\,d\vec{r}\,' . \tag{16}$$

Thus the single-particle Schrödinger equation becomes

$$\left(\frac{-\hbar^2}{2m}\nabla_i^2+V_{el}(\vec{r}_i)+e^2\int\frac{n(\vec{r}\,')}{|\vec{r}_i-\vec{r}\,'|}\,d\vec{r}\,'\right)\varphi_{\alpha_i}(\vec{r}_i)=\epsilon_{\alpha_i}\varphi_{\alpha_i}(\vec{r}_i) , \tag{17}$$

and the energy of the sytem (to first order) becomes

$$E=\sum_{i=1}^{N}\epsilon_{\alpha_i}-\frac{Ne^2}{2}\int\int\frac{n(\vec{r})n(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}\,d\vec{r}\,d\vec{r}\,'+\sum_{\substack{i<j\\ i=1}}^{N}\frac{e^2}{|\vec{R}_i-\vec{R}_j|} . \tag{18}$$

The single-particle density function is given by

$$n(\vec{r})=\sum_{\alpha}|\varphi_\alpha(\vec{r})|^2 . \tag{19}$$

Thus, to complete the problem Eqs. (17) and (19) should be solved self-consistently. In a more sophisticated form, effects of exchange and correlation can be included in Eq. (14).

Such an approach is quite appealing. One can talk about an electron occupying a particular orbital—an eigenstate of $h(\vec{r})$. In reality, the electrons move collectively. The independent-particle description lacks clarity. Furthermore, errors in $W(\vec{r})$ enter E both directly and indirectly. Though they can be removed by including second- and higher-order perturbation corrections, there is no guarantee that such a perturbation series converges rapidly.

In our approach, even though $W(\vec{r})$ is used to decouple the Hamiltonian, its role is not given lasting significance. We use it only as a way of motivating the single-particle part of our trial wave function. Once the latter is chosen, the decoupling scheme is abandoned, and the variational calculation with a *many-body* wave function takes over. Our total energy should not be too sensitively dependent on the particular choice of $W(\vec{r})$. This point will be substantiated later in this paper.

The choice of the wave function, both the single-particle part embodied in $W(\vec{r}_i)$ and the correlation factor $u(r_{ij})$, will be discussed in Secs. VII and VIII together with numerical results.

IV. ENERGY

Equations (1) and (2) define our trial wave function. For convenience, we shall often use the symbol D to represent the determinant with single-particle elements.

$$D\equiv\|\varphi_\alpha(\vec{r}_i)\| . \tag{20}$$

Spin variables and summations will be understood, but not explicitly displayed, in accordance with usual custom.

For Coulomb systems, our formalism takes on a cleaner look when expressed in the Fourier space. Thus, with Ω denoting the normalization volume and the prime indicating omission of $\vec{k}=0$ from the sum, we write

$$\frac{1}{2}\sum_{i<j}u(r_{ij})=\frac{1}{4\Omega}\sum_{\vec{k}}{}' u(k)(\rho_{\vec{k}}\rho_{-\vec{k}}-N) , \tag{21}$$

$$u(k)=\int e^{i\vec{k}\cdot\vec{r}}u(r)\,d\vec{r}\,, \tag{22}$$

$$\rho_{\vec{k}}=\sum_i e^{i\vec{k}\cdot\vec{r}_i}\,, \tag{23}$$

$$\sum_{i<j}\frac{e^2}{|\vec{r}_i-\vec{r}_j|}=\frac{e^2}{2\Omega}\sum_{\vec{k}}v(k)(\rho_{\vec{k}}\rho_{-\vec{k}}-N)\,, \tag{24}$$

and

$$v(k)=\int e^{i\vec{k}\cdot\vec{r}}\left(\frac{e^2}{r}\right)d\vec{r}=\frac{4\pi e^2}{k^2}\,. \tag{25}$$

The wave function Ψ now appears, aside from a normalizing constant, as

$$\Psi=D\exp\left(\frac{1}{4\Omega}\sum_{\vec{k}}{}'\,u(k)\rho_{\vec{k}}\rho_{-\vec{k}}\right). \tag{26}$$

Using the notation

$$\begin{aligned}\langle 0\rangle &\equiv\langle\Psi|0|\Psi\rangle/\langle\Psi|\Psi\rangle\\ &=\int\Psi^*0\Psi\,d\vec{r}_1\cdots d\vec{r}_N\bigg/\int\Psi^*\Psi\,d\vec{r}_1\cdots d\vec{r}_N\,,\end{aligned} \tag{27}$$

we now calculate $\langle H\rangle$, or $\langle\sum_i h(\vec{r}_i)\rangle$ and $\langle H'\rangle$.

First, we find

$$\begin{aligned}\langle-\nabla_i^2\rangle &=-\left(\frac{1}{2}\int\Psi^*\nabla_i^2\Psi\,d\vec{r}_1\cdots d\vec{r}_N+\frac{1}{2}\int(\nabla_i^2\Psi^*)\Psi\,d\vec{r}_1\cdots d\vec{r}_N\right)\bigg/\int\Psi^*\Psi\,d\vec{r}_1\cdots d\vec{r}_N\\ &=\left(-\tfrac{1}{2}\int F^2(D\nabla_i^2D^*+D^*\nabla_i^2D)\,d\vec{r}_1\cdots d\vec{r}_N+\int D^*D(\nabla_iF\cdot\nabla_iF)d\vec{r}_1\cdots d\vec{r}_N\right.\\ &\qquad\left.-\int\nabla_i\cdot(D^*DF\nabla_iF)d\vec{r}_1\cdots d\vec{r}_N\right)\bigg/\int F^2D^*D\,d\vec{r}_1\cdots d\vec{r}_N\,.\end{aligned}$$

The first line relied on ∇_i^2 being a Hermitian operator. The second line was obtained with the aid of the identity

$$\tfrac{1}{2}[\nabla_i^2(FD^*)]FD+\tfrac{1}{2}FD^*[\nabla_i^2(FD)]=\tfrac{1}{2}F^2(D\nabla_i^2D^*+D^*\nabla_i^2D)-D^*D(\nabla_iF\cdot\nabla_iF)+\nabla_i\cdot(D^*DF\nabla_iF)\,.$$

The last integral in the second line can be converted into a surface integral, which vanishes for periodic boundary conditions. Hence,

$$\begin{aligned}\left\langle\sum_i h(\vec{r}_i)\right\rangle &=\left(\frac{1}{2}\int F^2\left[D\sum_i h(\vec{r}_i)D^*+D^*\sum_i h(\vec{r}_i)D\right]d\vec{r}_1\cdots d\vec{r}_N\right.\\ &\qquad\left.+\frac{\hbar^2}{2m}\sum_i\int D^*D(\nabla_iF\cdot\nabla_iF)\,d\vec{r}_1\cdots d\vec{r}_N\right)\bigg/\int F^2D^*D\,d\vec{r}_1\cdots d\vec{r}_N\\ &=\sum_i\epsilon_{\alpha_i}+\frac{\hbar^2}{2m}\sum_i\int D^*D(\nabla_iF\cdot\nabla_iF)\,d\vec{r}_1\cdots d\vec{r}_N\bigg/\int F^2D^*D\,d\vec{r}_1\cdots d\vec{r}_N\,.\end{aligned}$$

Now,

$$\sum_i\nabla_iF\cdot\nabla_iF=-F^2\frac{1}{4\Omega^2}\sum_{\vec{k},\vec{l}}{}'\,\vec{k}\cdot\vec{l}\,u(k)u(l)\rho_{\vec{k}}\rho_{-\vec{l}}\rho_{-\vec{k}-\vec{l}}\,;$$

so finally

$$\left\langle\sum_i h(\vec{r}_i)\right\rangle=\sum_i\epsilon_{\alpha_i}-\frac{\hbar^2}{2m}\,\frac{1}{4\Omega^2}\sum_{\vec{k},\vec{l}}{}'\,\vec{k}\cdot\vec{l}\,u(k)u(l)\langle\rho_{\vec{k}}\rho_{\vec{l}}\rho_{-\vec{k}-\vec{l}}\rangle\,. \tag{28}$$

Next, we define the μ-particle distribution function:

$$P_\mu(\vec{r}_1,\ldots,\vec{r}_\mu)=\frac{N!}{(N-\mu)!}\int\Psi^*\Psi\,d\vec{r}_{\mu+1}\cdots d\vec{r}_N\bigg/\int\Psi^*\Psi\,d\vec{r}_1\cdots d\vec{r}_N\,, \tag{29}$$

and express $\langle H'\rangle$ in terms of these distribution functions:

$$\begin{aligned}\langle H'\rangle = &-\int P_1(\vec{r})W(\vec{r})\,d\vec{r}\\ &+\frac{e^2}{2}\int\int\frac{P_1(\vec{r}_1)P_1(\vec{r}_2)}{|\vec{r}_1-\vec{r}_2|}\,d\vec{r}_1\,d\vec{r}_2\\ &+\sum_{i<j}\frac{e^2}{|\vec{R}_i-\vec{R}_j|}\\ &+\frac{e^2}{2}\int\int\frac{P_2(\vec{r}_1,\vec{r}_2)-P_1(\vec{r}_1)P_1(\vec{r}_2)}{|\vec{r}_1-\vec{r}_2|}\,d\vec{r}_1\,d\vec{r}_2\,.\end{aligned} \tag{30}$$

The integrals are over all space. They can be reduced to integrals over just one unit cell:

$$\int d\vec{r}=\sum_i\int_{(i)}d\vec{r}\,,$$

where the notation (i) underneath the integral sign implies integration over the ith unit cell. Writing

$$W(\vec{r})=\sum_j\omega(\vec{r}-\vec{R}_j)\,, \tag{31}$$

we find

$$\begin{aligned}\langle H'\rangle = &\sum_{i\neq j}\left(-\int_{(i)}\omega(\vec{r}-\vec{R}_j)P_1(\vec{r})\,d\vec{r}+\frac{e^2}{2}\int_{(i)}d\vec{r}_1\int_{(j)}d\vec{r}_2\,\frac{P_1(\vec{r}_1)P_1(\vec{r}_2)}{|\vec{r}_1-\vec{r}_2|}+\frac{1}{2}\,\frac{e^2}{|\vec{R}_i-\vec{R}_j|}\right)\\ &-\sum_i\int_{(i)}\omega(\vec{r}-\vec{R}_i)P_1(\vec{r})\,d\vec{r}+\sum_i\frac{e^2}{2}\int_{(i)}d\vec{r}_1\int_{(i)}d\vec{r}_2\,\frac{P_1(\vec{r}_1)P_1(\vec{r}_2)}{|\vec{r}_1-\vec{r}_2|}+\frac{e^2}{2}\int\int\frac{P_2(\vec{r}_1,\vec{r}_2)-P_1(\vec{r}_1)P_1(\vec{r}_2)}{|\vec{r}_1-\vec{r}_2|}\,d\vec{r}_1\,d\vec{r}_2\,.\end{aligned} \tag{32}$$

There is a good reason for grouping the three terms inside the large parentheses in the first line. We intend to pursue our calculation using a spherical unit-cell approximation—one in which the electron distribution in a unit cell will be regarded as spherically symmetric about the center of the cell. $W(\vec{r})$ will be chosen such that outside the jth unit cell the contribution $\omega(\vec{r}-\vec{R}_j)$ from electrons in the jth cell will simply be $e^2/|\vec{r}-\vec{R}_j|$. The first line will thus vanish, as shown immediately below.

The second term in the first line can be written as

$$\begin{aligned}\sum_{i\neq j}\frac{1}{2}\int_{(i)}d\vec{r}_1\,P_1(\vec{r}_1)\left(\int_{(j)}d\vec{r}_2\,\frac{P_1(\vec{r}_2)e^2}{|\vec{r}_1-\vec{r}_2|}\right)\\ =\sum_{i\neq j}\frac{1}{2}\int_{(i)}d\vec{r}\,P_1(\vec{r})\,\frac{e^2}{|\vec{r}-\vec{R}_j|}\,,\end{aligned}$$

since $\vec{r}_1$, being in the ith unit cell, is outside the jth unit cell, and sees the spherically symmetric distribution charges in the jth unit cell as if they were concentrated at $\vec{R}_j$. The last term in the large parentheses can be put in the same form, since for the same reason,

$$\sum_{i\neq j}\frac{1}{2}\left(\int_{(i)}d\vec{r}\,\frac{P_1(r)e^2}{|\vec{r}-\vec{R}_j|}\right)=\sum_{i\neq j}\frac{1}{2}\,\frac{e^2}{|\vec{R}_i-\vec{R}_j|}\,.$$

Thus the sum of the three terms gives

$$\begin{aligned}\sum_{i\neq j}\int_{(i)}d\vec{r}\left(-\omega(\vec{r}-\vec{R}_j)+\frac{e^2}{|\vec{r}-\vec{R}_j|}\right)P_1(\vec{r})\,d\vec{r}\\ =\sum_i\int_{(i)}\sum_{j(\neq i)}\left(-\omega(\vec{r}-\vec{R}_j)+\frac{e^2}{|\vec{r}-\vec{R}_j|}\right)P_1(\vec{r})\,d\vec{r}=0\,.\end{aligned} \tag{33}$$

Finally, the last term in Eq. (32) can be written as

$$\frac{1}{2\Omega}\sum_{\vec{k}}v(k)\left(\langle\rho_{\vec{k}}\rho_{-\vec{k}}\rangle-\langle\rho_{\vec{k}}\rangle\langle\rho_{-\vec{k}}\rangle-N\right)\,. \tag{34}$$

Combining all terms from Eqs. (28) and (32), using the results (33) and (34), we find

$$E\equiv\langle H\rangle\equiv\left\langle\sum_i h(\vec{r}_i)\right\rangle+\langle H'\rangle\equiv E_{\text{dir}}+E_{xc}\,, \tag{35}$$

$$\begin{aligned}E_{\text{dir}}=&\sum_i\epsilon_{\alpha_i}-\int_{\text{unit cell}}W(\vec{r})P_1(\vec{r})\,d\vec{r}\\ &+\frac{Ne^2}{2}\int\int_{\text{unit cell}}\frac{P_1(\vec{r}_1)P_1(\vec{r}_2)}{|\vec{r}_1-\vec{r}_2|}\,d\vec{r}_1\,d\vec{r}_2\,,\end{aligned} \tag{36}$$

$$\begin{aligned}E_{xc}=&\frac{2\pi e^2}{\Omega}\sum_{\vec{k}}\frac{1}{k^2}\left(\langle\rho_{\vec{k}}\rho_{-\vec{k}}\rangle-\langle\rho_{\vec{k}}\rangle\langle\rho_{-\vec{k}}\rangle-N\right)\\ &-\frac{1}{4\Omega^2}\,\frac{\hbar^2}{2m}\sum_{\vec{k},\vec{l}}{}'\,\vec{k}\cdot\vec{l}\,u(k)u(l)\langle\rho_{\vec{k}}\rho_{\vec{l}}\rho_{-\vec{k}-\vec{l}}\rangle\,.\end{aligned} \tag{37}$$

The next task consists of evaluating the multiple-density fluctuation matrix elements, or the "multiple-density correlation functions" $\langle \rho_{\vec{k}}\rho_{\vec{l}}\cdots\rangle$.

V. MULTIPLE-DENSITY CORRELATION FUNCTIONS

In anticipation of present need, some time ago we evaluated[36] the matrix elements

$$\langle \rho_{\vec{k}_1}\rho_{\vec{k}_2}\cdots\rho_{\vec{k}_n}\rangle = \int \Psi^*\rho_{\vec{k}_1}\rho_{\vec{k}_2}\cdots\rho_{\vec{k}_n}\Psi\, d\vec{r}_1\cdots d\vec{r}_N \Big/ \int \Psi^*\Psi\, d\vec{r}_1\cdots d\vec{r}_N \tag{38}$$

for wave functions appropriate for inhomogeneous systems. It was accomplished by generalizing a method developed for the homogeneous electron liquid. The method first expresses these correlation functions in terms of the Fourier transforms of the distribution functions (29):

$$\langle \rho_{\vec{k}}\rangle = P_1(\vec{k}), \tag{39}$$

$$\langle \rho_{\vec{k}_1}\rho_{\vec{k}_2}\rangle = P_1(\vec{k}_1+\vec{k}_2) + P_2(\vec{k}_1,\vec{k}_2), \tag{40}$$

$$\begin{aligned}\langle \rho_{\vec{k}_1}\rho_{\vec{k}_2}\rho_{\vec{k}_3}\rangle = {} & P_1(\vec{k}_1+\vec{k}_2+\vec{k}_3) + P_2(\vec{k}_1,\vec{k}_2+\vec{k}_3) \\ & + P_2(\vec{k}_2,\vec{k}_3+\vec{k}_1) + P_2(\vec{k}_3,\vec{k}_1+\vec{k}_2) \\ & + P_3(\vec{k}_1,\vec{k}_2,\vec{k}_3), \text{ etc.}\end{aligned} \tag{41}$$

For high-order distribution functions ($\mu \geq 3$), a "convolution approximation" is used to express them in terms of P_1 and P_2. The approximation is designed to preserve the sequential relations required by the definition of P_μ:

$$\int P_\mu(\vec{r}_1,\ldots,\vec{r}_\mu)\, d\vec{r}_\mu = (N-\mu+1)P_{\mu-1}(\vec{r}_1,\ldots,\vec{r}_{\mu-1}). \tag{42}$$

For example, in that approximation,

$$\begin{aligned}P_3(\vec{r}_1,\vec{r}_2,\vec{r}_3) \approx P_1(\vec{r}_1)P_1(\vec{r}_2)P_1(\vec{r}_3)\Big(&1 + h(\vec{r}_1,\vec{r}_2) + h(\vec{r}_2,\vec{r}_3) + h(\vec{r}_3,\vec{r}_1) + h(\vec{r}_1,\vec{r}_2)h(\vec{r}_2,\vec{r}_3) + h(\vec{r}_2,\vec{r}_3)h(\vec{r}_3,\vec{r}_1) \\ & + h(\vec{r}_3,\vec{r}_1)h(\vec{r}_1,\vec{r}_2) + \int P_1(\vec{r}_4)h(\vec{r}_1,\vec{r}_4)h(\vec{r}_2,\vec{r}_4)h(\vec{r}_3,\vec{r}_4)\, d\vec{r}_4\Big),\end{aligned} \tag{43}$$

where

$$h(\vec{r}_1,\vec{r}_2) \equiv g(\vec{r}_1,\vec{r}_2) - 1 = h(\vec{r}_2,\vec{r}_1), \tag{44}$$

and

$$g(\vec{r}_1,\vec{r}_2) \equiv P_2(\vec{r}_1,\vec{r}_2)/P_1(\vec{r}_1)P_1(\vec{r}_2). \tag{45}$$

For general formulas, the reader is referred to Ref. 36. We shall display in this section only those results which are needed for the present calculation.

In the convolution approximation, we find

$$\langle \rho_{\vec{k}}\rangle = u_1(\vec{k}), \tag{46}$$

$$\langle \rho_{\vec{k}_1}\rho_{\vec{k}_2}\rangle = u_1(\vec{k}_1)u_1(\vec{k}_2) + u_2(\vec{k}_1,\vec{k}_2), \tag{47}$$

$$\langle \rho_{\vec{k}_1}\rho_{\vec{k}_2}\rho_{\vec{k}_3}\rangle = u_1(\vec{k}_1)u_1(\vec{k}_2)u_1(\vec{k}_3) + u_1(\vec{k}_1)u_2(\vec{k}_2,\vec{k}_3) + u_1(\vec{k}_2)u_2(\vec{k}_3,\vec{k}_1) + u_1(\vec{k}_3)u_2(\vec{k}_1,\vec{k}_2) + u_3(\vec{k}_1,\vec{k}_2,\vec{k}_3), \ldots, \tag{48}$$

where

$$u_1(\vec{k}) = P_1(\vec{k}), \tag{49}$$

$$u_2(\vec{k}_1,\vec{k}_2) = \sum_{\vec{K}_1,\vec{K}_2} P_1(\vec{K}_1+\vec{k}_1)P_1(\vec{K}_2+\vec{k}_2)\,[g(\vec{K}_1,\vec{K}_2) - g(\vec{K}_1-\vec{k}_2,\vec{K}_2+\vec{k}_2)], \tag{50}$$

$$u_3(\vec{k}_1,\vec{k}_2,\vec{k}_3) = \sum_{\vec{K}_i,\vec{K}'_i} P_1(\vec{K}'_1+\vec{K}'_2+\vec{K}'_3) \prod_{i=1}^{3} P_1(\mathrm{K}_i+\vec{k}_i)[g(\vec{K}'_i,\vec{K}_i) - g(\vec{K}'_i-\vec{k}_i,\vec{K}_i+\vec{k}_i)], \ldots, \tag{51}$$

and

$$g(\vec{K}_1, \vec{K}_2) - 1 = \frac{1}{\Omega^2} \int\int e^{i\vec{K}_1\cdot\vec{r}_1} e^{i\vec{K}_2\cdot\vec{r}_2} \times [g(\vec{r}_1, \vec{r}_2) - 1]\, d\vec{r}_1\, d\vec{r}_2 \,. \tag{52}$$

For a periodic system,

$$P_1(\vec{k}) = N \sum_{\{\vec{G}\}} n_{\vec{G}}\, \delta_{\vec{k},\vec{G}} \,, \tag{53}$$

where $\{\vec{G}\}$ denotes the set of reciprocal-lattice vectors. From normalization,

$$n_{000} = 1.0 \,. \tag{54}$$

The other $n_{\vec{G}}$'s are to be determined.

The pair function $g(\vec{r}_1, \vec{r}_2)$ describes the deviation of $P_2(\vec{r}_1, \vec{r}_2)$ from $P_1(\vec{r}_1)P_1(\vec{r}_2)$ as a result of exchange and correlations. If we assume that the inhomgeneity and anisotropy in the system are well accounted for by the $P_1(\vec{r}_1)$ factors, $g(\vec{r}_1, \vec{r}_2)$ can be approximated thus:

$$g(\vec{r}_1, \vec{r}_2) \approx g(|\vec{r}_1 - \vec{r}_2|)$$

to be taken from the homogeneous electron liquid calculation. In that case,

$$g(\vec{k}_1, \vec{k}_2) = [S(k_1)/N]\, \delta_{\vec{k}_1+\vec{k}_2,0} \,, \tag{55}$$

with $S(k)$ given by Chakravarty and Woo in Ref. 28. Then,

$$u_1(\vec{k}) = N \sum_{\vec{G}} n_{\vec{G}}\, \delta_{\vec{k},\vec{G}} \tag{56}$$

$$u_2(\vec{k}_1, \vec{k}_2) = N \sum_{\vec{G}_1,\vec{G}_2} n_{\vec{G}_1} n_{\vec{G}_2} [S(|\vec{G}_1 - \vec{k}_1|) - S(G_2)] \times \delta_{\vec{k}_1+\vec{k}_2,\vec{G}_1+\vec{G}_2} \tag{57}$$

$$u_3(\vec{k}_1, \vec{k}_2, \vec{k}_3) = N \sum_{\vec{G}_1,\vec{G}_2,\vec{G}_3\vec{G}_4} n_{\vec{G}_1} n_{\vec{G}_2} n_{\vec{G}_3} n_{\vec{G}_4} [S(|\vec{G}_1 - \vec{k}_1|) - S(G_1)]\, [S(|\vec{G}_2 - \vec{k}_2|) - S(G_2)]\, [S(|\vec{G}_3 - \vec{k}_3|) - S(G_3)] \times \delta_{\vec{k}_1+\vec{k}_2+\vec{k}_3,\vec{G}_1+\vec{G}_2+\vec{G}_3+\vec{G}_4}, \ldots , \tag{58}$$

The entire problem reduces to the determination of $n_{\vec{G}}$ and $S(k)$.

VI. INTEGRAL EQUATIONS FOR $n_{\vec{G}}$ AND $S(k)$

From Eq. (53),

$$n_{\vec{G}} = (1/N)\langle \rho_{\vec{G}} \rangle \,. \tag{59}$$

To obtain $\langle \rho_{\vec{G}} \rangle$, we define as in Ref. 28 a generalized wave function

$$\Psi(\mu) = F(\mu) D \,, \tag{60}$$

where

$$F(\mu) = \exp\left(\frac{\mu}{4\Omega} \sum_{\vec{k}}{}' u(k) \rho_{\vec{k}} \rho_{-\vec{k}} \right) . \tag{61}$$

In the limit $\mu \to 0$, $\Psi(\mu)$ reduces to the Hartree-Fock wave function, Hence,

$$P_1(\vec{r}, \mu = 0) = \sum_{\alpha} |\varphi_\alpha(\vec{r})|^2 \equiv n^0(\vec{r}) \,, \tag{62}$$

which we can obtain from a band-theoretic calculation.

$$n_{\vec{G}}(\mu = 0) \equiv n^0_{\vec{G}} = \int_{\text{unit cell}} P_1(\vec{r}, \mu = 0) e^{i\vec{G}\cdot\vec{r}}\, d\vec{r} \,. \tag{63}$$

In the limit $\mu \to 1$, $\Psi(\mu)$ returns to the fully correlated form, which we need for calculating averages such as $\langle \rho_{\vec{G}} \rangle$.

The quantity

$$\langle \rho_{\vec{G}} \rangle_\mu \equiv \langle \Psi(\mu) | \rho_{\vec{G}} | \Psi(\mu) \rangle / \langle \Psi(\mu) | \Psi(\mu) \rangle = \int \Psi^*(\mu) \rho_{\vec{G}} \Psi(\mu)\, d\vec{r}_1 \cdots d\vec{r}_N \Big/ \int \Psi^*(\mu) \Psi(\mu)\, d\vec{r}_1 \cdots d\vec{r}_N \tag{64}$$

obeys a differential equation which can be derived easily from its definition:

$$\frac{d\langle \rho_{\vec{G}} \rangle_\mu}{d\mu} = \frac{1}{2\Omega} \sum_{\vec{k}}{}' u(k) \left(\langle \rho_{\vec{G}} \rho_{\vec{k}} \rho_{-\vec{k}} \rangle_\mu - \langle \rho_{\vec{G}} \rangle_\mu \langle \rho_{\vec{k}} \rho_{-\vec{k}} \rangle_\mu \right) . \tag{65}$$

By applying the convolution approximation to $\langle \rho_{\vec{G}}\rho_{\vec{k}}\rho_{-\vec{k}}\rangle_\mu$ and using the matrix elements given in the last section, Eq. (65) can be decomposed to read

$$\begin{aligned}\frac{dn_{\vec{G}}(\mu)}{d\mu} &= \frac{1}{2\Omega}\sum_{\vec{k}}{}' u(k)[u_1(\vec{k})_\mu u_2(\vec{G},-\vec{k})_\mu + u_1(-\vec{k})_\mu u_2(\vec{G},\vec{k})_\mu + u_3(\vec{G},\vec{k},-\vec{k})_\mu]\\ &= \frac{N}{\Omega}\sum_{\vec{G}_1,\vec{G}_2}{}'\sum u(G_1)n_{\vec{G}_1}(\mu)n_{\vec{G}_2}(\mu)n_{\vec{G}-\vec{G}_1-\vec{G}_2}(\mu)[S(|\vec{G}_1+\vec{G}_2|,\mu)-S(|\vec{G}-\vec{G}_1-\vec{G}_2|,\mu)]\\ &\quad+\frac{1}{2\Omega}\sum_{\vec{k}}{}'\sum_{\vec{G}_1,\vec{G}_2,\vec{G}_3} u(k)n_{\vec{G}_1}(\mu)n_{\vec{G}_2}(\mu)n_{\vec{G}_3}(\mu)n_{\vec{G}-\vec{G}_1-\vec{G}_2-\vec{G}_3}(\mu)\\ &\qquad\times[S(|\vec{G}_1-\vec{G}|,\mu)-S(G_1,\mu)][S(|\vec{G}_2-\vec{k}|,\mu)-S(G_2,\mu)][S(|\vec{G}_3+\vec{k}|,\mu)-S(G_3,\mu)].\end{aligned} \tag{66}$$

The solution of Eq. (66) together with the boundary condition (63) yields $n_{\vec{G}}(\mu)$, and in particular $n_{\vec{G}}$ $(\mu=1)$. This can be done provided that $S(k,\mu)$ is known.

As mentioned in Sec. V, $S(k)$, and in fact $S(k,\mu)$, will be taken from the homogeneous electron liquid calculation. In Ref. 28, using the same $\Psi(\mu)$ as defined in Eqs. (60) and (61) and plane waves in D, Chakravarty and Woo derived an equation for $\langle\rho_{\vec{k}}\rho_{-\vec{k}}\rangle_\mu$:

$$\frac{d\langle\rho_{\vec{k}}\rho_{-\vec{k}}\rangle_\mu}{d\mu} = \frac{1}{2\Omega}\sum_{\vec{l}}{}' u(l)(\langle\rho_{\vec{k}}\rho_{-\vec{k}}\rho_{\vec{l}}\rho_{-\vec{l}}\rangle_\mu - \langle\rho_{\vec{k}}\rho_{-\vec{k}}\rangle_\mu\langle\rho_{\vec{l}}\rho_{-\vec{l}}\rangle_\mu). \tag{67}$$

The convolution approximation in that simple, homogeneous case gives

$$\langle\rho_{\vec{k}}\rho_{-\vec{k}}\rangle_\mu = NS(k,\mu), \tag{68}$$

$$\langle\rho_{\vec{k}}\rho_{\vec{k}}\rho_{\vec{l}}\rho_{-\vec{l}}\rangle_\mu = \begin{cases} N^2S(k,\mu)S(l,\mu)\\ +NS(k,\mu)S(l,\mu)[S(|\vec{k}+\vec{l}|,\mu)\\ +S(|\vec{k}-\vec{l}|,\mu)-2] \quad \text{for } \vec{k},\vec{l},\vec{k}\pm\vec{l}\neq 0\\ 2N^2S^2(k,\mu) \quad \text{for } \vec{k}\pm\vec{l}=0 \end{cases}. \tag{69}$$

Consequently,

$$\frac{dS(k,\mu)}{d\mu} = \frac{N}{\Omega}u(k)S^2(k,\mu) + S^2(k,\mu)\sum_{\vec{q}}{}' u(q)S^2(q,\mu)\times[S(|\vec{k}+\vec{q}|,\mu)-1]. \tag{70}$$

Since in the $\mu\to 0$ limit, $S(k,\mu)$ reduces to the Hartree-Fock structure function, which is well known for an electron gas, Eq. (70) can be solved together with this limiting boundary condition to yield $S(k,\mu)$. In particular, the $\mu\to 1$ limit of $S(k,\mu)$ gives us $S(k)$.

VII. RESULTS-VARIATIONAL CORRELATION ENERGIES

We begin with a band-theoretic calculation for the one-electron problem. This is to select the Slater determinant part of the trial wave function and determine $n^0_{\vec{G}}$.

For metallic hydrogen, we consider a bcc lattice. The unit cell is a regular octahedron. Since there is only one electron per hydrogen atom, the band is only half filled. Hence we would expect the Fermi surface to be close to a sphere. To a good approximation, the octahedral unit cell can therefore be replaced by a sphere of the same volume. The radius r_s of the sphere is related to the density ρ of the ions (and in this case the electrons)

$$\tfrac{4}{3}\pi r_s^3 = 1/\rho. \tag{71}$$

The error incurred in this approximation is of the order of the energy difference between different crystal structures, since we change the unit cell as the crystal structure is varied. If the energy of the crystal is expressed as

$$E = E_0(\rho) + E_1(\rho, \text{structure}), \tag{72}$$

the structure-dependent term E_1 can be shown to be small compared to E_0. Previous calculations and general considerations show that E_1 is of the order of a millirydberg.

Having chosen the unit cell as a sphere of radius r_s, we proceed to construct the electron mean field $W(\vec{r})$, or its components $\omega(\vec{r}-\vec{R}_j)$ as defined in Eq. (31). The argument of $\omega(\vec{r}-\vec{R}_j)$ is measured from each unit cell j. In the spherical unit-cell approximation, the electron sees no contribution from a cell when it is outside that cell; i.e., when $|\vec{r}-\vec{R}_j| > r_s$. In other words, when $|\vec{r}-\vec{R}_j|>r_s$, $\omega(\vec{r}-\vec{R}_j)$ cancels the ion contribution from that cell exactly:

$$\omega(r-\vec{R}_j) = e^2/|\vec{r}-\vec{R}_j|, \quad |\vec{r}-\vec{R}_j|>r_s. \tag{73}$$

This result was already used in Eq. (33).

For $|\vec{r}-\vec{R}_j|\leq r_s$, we shall consider two possibilities. Let us for convenience put the origin at $\vec{R}_j$. In the first case, we take $\omega_1(\vec{r})$ to totally ignore the electron cloud:

$$\omega_1(\vec{r})=0, \quad r\leq r_s . \tag{74}$$

This is not meant to be a sensible choice—merely one to demonstrate that our variational calculation will at the end not be terribly sensitive to the choice of $W(\vec{r})$. The second choice is given by

$$\omega_2(\vec{r})=e^2\int_{\text{unit cell}}\frac{n^0(r')}{|\vec{r}-\vec{r}'|}\,dr'-\frac{2}{3}\,\frac{e^2}{2}\left(\frac{81}{\pi}\,n^0(r)\right)^{1/3}, \tag{75}$$

with

$$n^0(r)=\sum_\alpha|\varphi_\alpha(\vec{r})|^2 . \tag{76}$$

This potential takes into account both the electron cloud inside the unit cell and the Slater exchange term. It depends on the Hartree-Fock charge density $n^0(r)$, thus requiring a self-consistent solution of Eqs. (75), (76), and the single-particle equation to be given below shortly. For an electron in an arbitrary cell i, i.e., $|\vec{r}-\vec{R}_i|\leq r_s$, the total effective single-particle potential is then

$$\begin{aligned}V_{\text{eff}}(\vec{r})&=V_{eI}(\vec{r})+W(\vec{r})\\&=\sum_j\frac{-e^2}{|\vec{r}-\vec{R}_j|}+\sum_j\omega(\vec{r}-\vec{R}_j)\\&=\frac{-e^2}{|\vec{r}-\vec{R}_i|}+\omega(\vec{r}-\vec{R}_i)\\&\quad+\sum_{j(\neq i)}\left(\frac{-e^2}{|\vec{r}-\vec{R}_j|}+\omega(\vec{r}-\vec{R}_j)\right)\\&=\frac{-e^2}{|\vec{r}-\vec{R}_i|}+e^2\int_{\text{unit cell}}\frac{n^0(|\vec{r}'-\vec{R}_i|)}{|\vec{r}-\vec{r}'|}\,d\vec{r}'\\&\quad-\frac{2}{3}\,\frac{e^2}{2}\left(\frac{81}{\pi}\,n^0(|\vec{r}-\vec{R}_i|)\right)^{1/3} .\end{aligned} \tag{77}$$

Note that, about $\vec{R}_i$ as the origin, V_{eff} is spherically symmetric as expected if n^0 is spherically symmetric. Since $\vec{R}_i$ is arranged periodically on a bcc lattice $V_{\text{eff}}(\vec{r})$ is periodic in the same way. It has the same translational symmetry as $V_{eI}(\vec{r})$. The single-particle Schrödinger equation

$$\begin{aligned}h(\vec{r})\varphi_\alpha(\vec{r})&=\left(-\frac{\hbar^2}{2m}\,\nabla^2+V_{\text{eff}}(\vec{r})\right)\varphi_\alpha(\vec{r})\\&=\epsilon_\alpha\varphi_\alpha(\vec{r})\end{aligned} \tag{78}$$

poses a band-theoretic problem.

In our case, the band calculation is performed using Kohn's variational method (see Appendix). The energy band is nearly parabolical. We calculate ϵ_k at six points in the range $0<k<k_F$ and fit the results to a Legendre polynomial series:

$$\epsilon_k=\epsilon_0P_0\left(\frac{k}{k_F}\right)+5\epsilon_2P_2\left(\frac{k}{k_F}\right)+9\epsilon_4P_4\left(\frac{k}{k_F}\right)+\cdots . \tag{79}$$

Thus,

$$\begin{aligned}\sum_{\vec{k}}1&=\frac{\Omega}{(2\pi)^3}\,\frac{4\pi}{3}\,k_F^3=N ,\\\sum_{\vec{k}}\epsilon_k\Big/\sum_{\vec{k}}1&=\left(\frac{4\pi}{3}\,k_F^3\right)^{-1}4\pi\int_0^{k_F}\epsilon_k k^2\,dk\\&=\epsilon_0+2\epsilon_2 ,\end{aligned} \tag{80}$$

and the charge density is given by

$$\begin{aligned}n^0(r)&=\left(1\Big/\sum_{\vec{k}}1\right)\sum_{\vec{k}}|\varphi_{\vec{k}}(\vec{r})|^2\\&=\frac{1}{\frac{4}{3}\pi k_F^3}\,4\pi\int_0^{k_F}|\varphi_{\vec{k}}(r)|^2k^2\,dk .\end{aligned} \tag{81}$$

Even though the band-theoretic problem can be solved in the spherical unit-cell approximation, for $n^0_{\vec{G}}$ we need to return to the bcc unit cell in order to define the reciprocal-lattice vectors $\{\vec{G}\}$. To accomplish this, we take

$$n^0_{\vec{G}}=A\int n^0(r)e^{i\vec{G}\cdot\vec{r}}\,d\vec{r}, \tag{82}$$

where A is a normalizing constant which normalizes n^0_{000} to unity.

The Hartree energy of the system is given by

$$\begin{aligned}E^0&=\sum_{\vec{k}}\epsilon_k-N\int_{\text{unit cell}}W(\vec{r})n^0(r)\,d\vec{r} ,\\\frac{E^0}{N}&=\epsilon_0+2\epsilon_2-\int_{\text{unit cell}}W(\vec{r})n^0(r)\,d\vec{r}\end{aligned} \tag{83}$$

and

$$E^0_{\text{dir}}=E^0+\frac{Ne^2}{2}\int\int_{\text{unit cell}}\frac{n^0(r)n^0(r')}{|\vec{r}-\vec{r}'|}\,d\vec{r}\,d\vec{r}' . \tag{84}$$

Next we introduce effects of the correlation factor by integrating Eq. (66). Here, the choice of $u(r)$, or its Fourier transform $u(k)$, must be made. In Ref. 28, $u(r)$ was chosen for a homogeneous electron liquid to keep electrons apart at short range, though not completely, and to reduce to the RPA form at long range.

$$u(r)=-(a/r)(1-e^{-br}) , \tag{85}$$

where

$$a=(\pi\rho a_B)^{-1/2} , \tag{86}$$

a_B is the Bohr radius, and b was varied to minimize the energy at each density characterized by

r_s. We shall adopt the same $u(r)$. Thus,

$$u(k) = -4\pi a b^2 / k^2 (k^2 + b^2)\,, \tag{87}$$

with a and b dependent on r_s. Values of b were obtained from Ref. 28.

Normalization requires

$$n_{000} = n^0_{000} = 1.0\,. \tag{88}$$

It turns out that even though the correlation factor contributes significantly to the energy its effect on the charge density is relatively small:

$$|(n_{\vec{G}} - n^0_{\vec{G}})/n^0_{\vec{G}}| \leq 1\%, \quad \vec{G} \neq (0,0,0)\,. \tag{89}$$

For example, let us look at $\vec{G} = (0,0,0)$, or $|\vec{G}| = 0$ and $\vec{G}' = (1,1,0)$, or $|\vec{G}'| = 2.2797 k_F$. Note that for $\vec{G}'' = (2,0,0)$, $|\vec{G}''| = 3.2230 k_F$, and other $\vec{G}$'s correspond to still higher magnitudes. In

$$\begin{aligned}\frac{dn_{\vec{G}}(\mu)}{d\mu} = {}& \rho \sum_{\vec{G}_1}{}' \sum_{\vec{G}_2} u(G_1)\, n_{\vec{G}_1}(\mu)\, n_{\vec{G}_2}(\mu) [S(|\vec{G}_1 + \vec{G}_2|, \mu) - S(|\vec{G} - \vec{G}_1 - \vec{G}_2|, \mu)] \\ & + \frac{1}{2} \frac{1}{(2\pi)^3} \sum_{\vec{G}_1, \vec{G}_2, \vec{G}_3} n_{\vec{G}_1}(\mu)\, n_{\vec{G}_2}(\mu)\, n_{\vec{G}_3}(\mu)\, n_{\vec{G}-\vec{G}_1-\vec{G}_2-\vec{G}_3}(\mu) [S(|\vec{G}_1 - \vec{G}|, \mu) - S(G_1, \mu)] \\ & \times \int [S(|\vec{G}_2 - \vec{k}|, \mu) - S(G_2, \mu)][S(|\vec{G}_3 + \vec{k}|, \mu) - S(G_3, \mu)]\, u(k)\, d\vec{k}\,, \end{aligned} \tag{90}$$

then, since

$$S(k) \approx 1, \quad k > 2k_F\,,$$

and thus

$$S(|\vec{G}_A|) - S(|\vec{G}_B|) \approx \begin{cases} \pm 1, & \text{if } \vec{G}_A \text{ or } \vec{G}_B = (0,0,0)\,, \\ 0 & \text{otherwise}\,, \end{cases}$$

only a few terms in the above sum contribute significantly. At $r_s = 1.45$, using $b/k_F = 0.7066$ from Ref. 28 we get

$$\int [S(|\vec{G}' - \vec{k}|) - S(G')] \times [S(|\vec{G} + \vec{k}|) - S(G)] \frac{1}{k^2 (k^2 + b^2)}\, d\vec{k} = -0.259 k_F^{-1}\,. \tag{91}$$

Substituting this and values of n_G from Table I in Eq. (90), we obtain

$$\frac{1}{n_{110}} \frac{dn_{110}}{d\mu} \approx -0.0035\,. \tag{92}$$

Upon integration with respect to μ this yields $(n_{110} - n^0_{110})/n^0_{110} \sim 0.0035$.

The very small difference between $n^0_{\vec{G}}$ and $n_{\vec{G}}$ means that the correction on E^0_{dir} to give E_{dir} is also very small. For the example above

$$E_{\text{dir}/N} = E^0_{\text{dir}/N} - 0.000\,04 \text{ Ry}. \tag{93}$$

Table I lists all the relevant quantities in the single-particle calculation for the case $r_s = 1.45 a_B$. The first column of numbers are for $\omega(\vec{r}) = \omega_1(\vec{r})$, and the second column for $\omega(\vec{r}) = \omega_2(\vec{r})$.

TABLE I. Coefficients of energy-band expansion [Eq. (79)], Fourier components of the Hartree-Fock electron density $n^0_{\vec{G}}$, and the components of the total energy (in rydbergs per atom), for two different effective potentials.

	$\omega_1(\vec{r})$	$\omega_2(\vec{r})$
ϵ_0	−1.6460	−0.7309
ϵ_2	0.2217	0.2254
ϵ_4	−0.0021	−0.0014
ϵ_6	−0.0004	−0.0003
n^0_{000}	1.0000	1.0000
n^0_{110}	0.1157	0.0945
n^0_{200}	0.0479	0.0402
n^0_{211}	0.0204	0.0177
n^0_{220}	0.0103	0.0092
n^0_{310}	0.0072	0.0064
n^0_{222}	0.0061	0.0052
$-\int \omega(r) n^0(r)\, d\vec{r}$	0.0	−0.9172
$\frac{e^2}{2}\int \frac{n(\vec{r})\, n(\vec{r}')}{\lvert\vec{r} - \vec{r}'\rvert} d\vec{r}\, d\vec{r}'$	0.9070	0.8894
E^0	−1.2026	−1.1973
E^0_{dir}	−0.2956	−0.3079
E^{h}_{xc}	−0.7355	−0.7355
E^{inh}_{xc}	−0.0152	−0.0106
E	−1.0463	−1.0540

As for the exchange and correlation contributions to the total energy, Eq. (37), we observe that when the multiple-density correlation functions are expanded in terms of $n_{\vec{G}}$, the leading terms with n_{000} lead to terms identical to those in the homogeneous-electron-liquid calculation. It is possible, then, to separate E_{xc} thus:

$$E_{xc} = E_{xc}^{\mathrm{h}} + E_{xc}^{\mathrm{inh}} , \tag{94}$$

with

$$E_{xc}^{\mathrm{h}} = \frac{1}{4}\,\frac{\hbar^2}{2m}\,\frac{\rho}{(2\pi)^3}\int S(k)\,u^2(k)k^2\,d\vec{k} - \frac{1}{4}\,\frac{\hbar^2}{2m}\,\frac{1}{(2\pi)^6}\int\!\!\int S(k)S(l)[S(|\vec{k}+\vec{l}|)-1]\,u(k)\,u(l)\,\vec{k}\cdot\vec{l}\,d\vec{k}\,d\vec{l},$$

and

$$\begin{aligned}E_{xc}^{\mathrm{inh}} = -\frac{1}{4}\,\frac{\hbar^2}{2m}\Bigg(&\rho^2 \sum_{\vec{G}_1}{}' \sum_{\vec{G}_2}{}' n_{\vec{G}_1} n_{\vec{G}_2} n_{-\vec{G}_1-\vec{G}_2} \vec{G}_1\cdot\vec{G}_2\, u(G_1)\,u(G_2) \\ &+ \frac{2\rho}{(2\pi)^3} \sum_{\vec{G}_1}{}' \sum_{\vec{G}_2} n_{G_1} n_{G_2} n_{-G_1-G_2} \int [S(|\vec{G}_2-\vec{k}|) - S(|\vec{G}_1+\vec{G}_2|)]\vec{G}_1\cdot\vec{k}\,u(G_1)\,u(k)\,d\vec{k} \\ &+ \frac{\rho}{(2\pi)^3} \sum_{\vec{G}_1}{}' \sum_{\vec{G}_2} n_{\vec{G}_1} n_{\vec{G}_2} n_{-\vec{G}_1-\vec{G}_2} \int [S(|\vec{G}_2-\vec{k}|) - S(|\vec{G}_1+\vec{G}_2|)]\,u(|\vec{k}+\vec{G}_1|)\,u(k)[\vec{k}\cdot(-\vec{k}-\vec{G}_1)]\,d\vec{k} \\ &+ \frac{1}{(2\pi)^6} \sum_{\vec{G}_1,\vec{G}_2,\vec{G}_3} n_{\vec{G}_1} n_{\vec{G}_2} n_{\vec{G}_3} n_{-\vec{G}_1-\vec{G}_2-\vec{G}_3} \int\!\!\int [S(|\vec{G}_1-\vec{k}|) - S(G_1)][S(|\vec{G}_2-\vec{l}|) - S(G_2)] \\ &\qquad \times [S(|\vec{G}_3+\vec{k}+\vec{l}|)-1]\,u(k)u(l)\,\vec{k}\cdot\vec{l}\,d\vec{k}\,d\vec{l}\Bigg) \\ &+ \frac{1}{2}\,\frac{1}{(2\pi)^3} \sum_{\vec{G}}{}' n_{\vec{G}} n_{-\vec{G}} \int \frac{4\pi e^2}{k^2}\,[S(\vec{k}+\vec{G}|)-1]\,d\vec{k} .\end{aligned} \tag{95}$$

Their contributions in the $\omega_1(\vec{r})$ and $\omega_2(\vec{r})$ cases, as well as the total energies E, are also shown in Table I for $r_s = 1.45a_B$. We use atomic rydberg units, $e^2 = 2$, $m = \frac{1}{2}$, $\hbar = 1$, and measure length in Bohr radii and energy in units of Rydberg.

Note that E is lower for $\omega_2(\vec{r})$. Since $\omega_2(\vec{r})$ is more realistic, we expected this result on the basis of variational principle. Note however, that the results for $\omega_1(\vec{r})$ and $\omega_2(\vec{r})$ are not significantly different. The rather large discrepancy in the band calculation is to a large extent compensated by the $-\int \omega(r)\,n(\vec{r})\,d\vec{r}$ term.

In Table II, we summarize energy contributions obtained with $\omega_2(\vec{r})$ for a range of densities: r_s

TABLE II. Contributions to energy in rydbergs per atom for five densities.

r_s (a_{B})	1.13	1.29	1.45	1.61	1.77
E_{band}	0.0483	−0.1454	−0.2801	−0.3665	−0.4040
$-\int \omega(r)n(r)\,d\vec{r}$	−1.1351	−1.0229	−0.9172	−0.8330	−0.7843
$\frac{e^2}{2}\int\!\!\int \frac{n(r)n(r')}{\lvert\vec{r}-\vec{r}'\rvert}d\vec{r}\,d\vec{r}'$	1.1142	0.9870	0.8894	0.8129	0.7519
E_{dir}^{0}	0.0274	−0.1813	−0.3079	−0.3866	−0.4364
E_{xc}^{h}	−0.9239	−0.8183	−0.7355	−0.6684	−0.6133
E_{xc}^{inh}	−0.0060	−0.0080	−0.0106	−0.0138	−0.0178
E	−0.9025	−1.0076	−1.0540	−1.0688	−1.0675

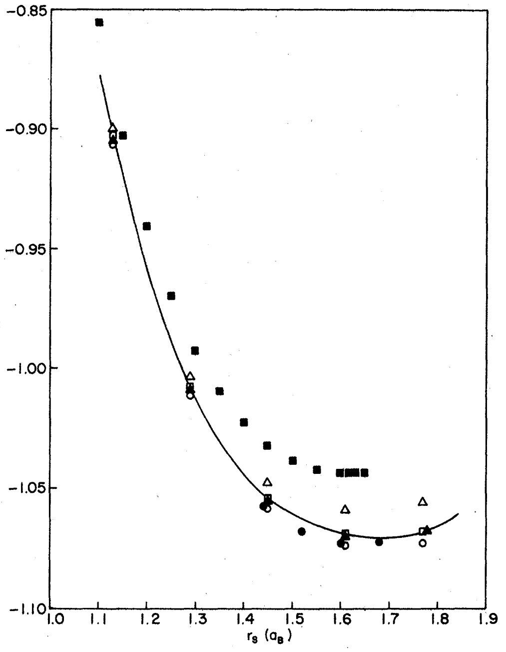

FIG. 1. Static energy of metallic hydrogen. □ : Our variational result; ○ : Our local-density-functional calculation; △ : Our density-functional calculation with gradient term; ▲ : Perturbation calculation by Caron (Ref. 9); ■ : Perturbation calculation by Hammerberg *et al.* (Ref. 10); ● : Local-density-functional calculation by Neece *et al.* (Ref. 13).

from 1.13 to 1.77. The total energy is plotted against r_s in Fig. 1, where it is seen that a minimum of -1.0697 Ry/electron appears at $r_s = 1.67 a_B$.

VIII. RESULTS-DENSITY-FUNCTIONAL CALCULATIONS

In the density functional formalism of Kohn and Sham,[37] as applied to metallic hydrogen by Neece *et al.*,[13] the energy density functional

$$E(n(\vec{r})) = T(n(\vec{r})) + \int V_{eI}(\vec{r})\, n(\vec{r})\, d\vec{r} + \frac{e^2}{2} \int\!\!\int \frac{n(\vec{r})\, n(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|}\, d\vec{r}\, d\vec{r}\,' + \int \epsilon_{xc}(n(\vec{r}))\, n(\vec{r})\, d\vec{r} + \sum_{i<j} \frac{e^2}{|\vec{R}_i - \vec{R}_j|} \tag{96}$$

is minimized with respect to the density function $n(\vec{r})$. In the local-density approximation, the exchange and correlation energy per particle ϵ_{xc} is taken to be that for a homogeneous electron liquid at the local density n. To solve this problem, one considers an auxiliary problem of N-independent particles moving in an effective single-particle field $V_e(\vec{r})$. As before, the energy-density functional

$$E'(n(\vec{r})) = T(n(\vec{r})) + \int V_e(\vec{r})\, n(\vec{r})\, d\vec{r} \tag{97}$$

should be minimized with respect to $n(\vec{r})$. The two problems can be identified by taking functional derivatives of $E(n(\vec{r})) - T(n(\vec{r}))$:

$$V_e(\vec{r}) = V_{eI}(\vec{r}) + e^2 \int \frac{n(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|}\, d\vec{r}\,' + \left.\frac{d[n\epsilon(n)]}{dn}\right|_{n = n(\vec{r})} . \tag{98}$$

Now, since the latter problem can be solved by solving the Schrödinger equation

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + V_e(\vec{r})\right) \varphi_\alpha(\vec{r}) = \epsilon_\alpha \varphi_\alpha(\vec{r}) , \tag{99}$$

one obtains the solution of the first problem by using the relations

$$n(\vec{r}) = \sum_\alpha |\varphi_\alpha(\vec{r})|^2 . \tag{100}$$

$$\begin{aligned} T(n(\vec{r})) &= E'(n(\vec{r})) - \int V_e(\vec{r})\, n(\vec{r})\, d\vec{r} \\ &= \sum_\alpha \epsilon_\alpha - \int V_e(\vec{r})\, n(\vec{r})\, d\vec{r} ; \end{aligned} \tag{101}$$

and thus,

$$\begin{aligned} E(n(\vec{r})) &= \sum_\alpha \epsilon_\alpha - \int V_e(\vec{r})\, n(\vec{r})\, d\vec{r} + \int V_{eI}(\vec{r})\, n(\vec{r})\, d\vec{r} \\ &\quad + \frac{e^2}{2} \int\!\!\int \frac{n(\vec{r})\, n(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|}\, d\vec{r}\, d\vec{r}\,' \\ &\quad + \int \epsilon_{xc}(n(\vec{r}))\, n(\vec{r})\, d\vec{r} + \sum_{i<j} \frac{e^2}{|R_i - R_j|} \\ &= \sum_\alpha \epsilon_\alpha - \frac{e^2}{2} \int\!\!\int_{\text{unit cell}} \frac{n(\vec{r})\, n(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|}\, d\vec{r}\, d\vec{r}\,' \\ &\quad + \int_{\text{unit cell}} \left(\epsilon_{xc}(n(\vec{r})) - \frac{d}{dn}\,[n\epsilon_{xc}(n)]\right) n(\vec{r})\, d\vec{r} . \end{aligned} \tag{102}$$

Here we have used the spherical unit-cell approximation referred to in Eqs. (31)–(33). We use

$$\epsilon_{xc} = \epsilon_x + \epsilon_c , \tag{103}$$

with

$$\epsilon_x = -\frac{(3/2\pi)(9\pi/4)^{1/3}}{r_s^L}\, R_y \tag{104}$$

and

$$\epsilon_c = -0.117,65 + 0.038 \ln r_s^L \text{ Ry} , \tag{105}$$

TABLE III. Results of present work for different densities: (i) variational calculation, (ii) density-functional calculation using local-density approximation (LDF), (iii) density-functional calculation including gradient terms (DF). Results of other authors: (i) perturbation calculation by Caron,[a] (ii) perturbation calculation by Hammerberg *et. al.*,[b] (iii) local-density-functional calculation by Neece *et. al.*[c]

r_s (a_B)		1.13	1.29	1.45	1.61	1.77
Present work	E_{variat}	−0.9025	−1.0076	−1.0540	−1.0688	−1.0675
	E_{LDF}	−0.9060	−1.0117	−1.0585	−1.0742	−1.0731
	E_{DF}	−0.8995	−1.0032	−1.0476	−1.0592	−1.0553
E_{perturb}[a]		−0.9049	−1.0096	−1.0554	−1.0697	−1.0673
E_{perturb}[b]		−0.8824	−0.9866	−1.0307	−1.0423	
E_{LDF}[c]				−1.0589	−1.0727	

[a] Caron, Ref. 9.

[b] Hammerberg *et al.*, Ref. 10.

[c] Neece *et al.*, Ref. 13.

the latter from Ref. 28, in Eq. (102) for our density-functional calculation. r_s^L denotes the *local* r_s, and is related to the *local* density $n(r)$ by $\frac{4}{3}\pi(r_s^L)^3 = 1/n(r)$. The results are shown in Table III for $1.13 \leqslant r_s \leqslant 1.77$ as $E_{\text{LDF}}(r_s)$.

It appears that our density-functional results are *lower* than our variational results. This may have resulted from the local-density approximation. To correct for this approximation, one can add a gradient contribution to the energy:

$$E_{\text{DF}}(r_s) = E_{\text{LDF}}(r_s) + \Delta E(r_s)\,, \tag{106}$$

where

$$\Delta E(r_s) = \int B(n(\vec{r}))\,|\nabla n(\vec{r})|^2\, d\vec{r}\,. \tag{107}$$

The coefficient $B(n(\mathbf{r}))$ can be approximated by its value at the mean density ρ.

$$\begin{aligned}\Delta E(r_s) &\approx \int B(\rho)|\nabla n(\vec{r})|^2\, d\vec{r}\\ &= B(\rho)\rho^2\Omega \sum_{\vec{G}}{}' n_{\vec{G}}^2 G^2\\ &= N\Big(\rho B(\rho)\sum_{\vec{G}}{}' n_{\vec{G}}^2 G^2\Big)\,.\end{aligned} \tag{108}$$

By taking $B(\rho) = 3.3\times10^{-3}\rho^{-4/3}$ Ry from a recent calculation by Gupta and Singwi,[38] we obtained $\Delta E(r_s)$, and thus $E_{\text{DF}}(r_s)$ as shown in Table III.

In Table III we compare our three sets of results: (i) E from the variational approach, (ii) E_{LDF} from the density functional approach using the local-density approximation and ϵ_{xc} from Chakravarty and Woo, and (iii) E_{DF} from adding to E_{LDF} a density-gradient contribution, to results obtained for metallic hydrogen by other authors. Note that $E_{\text{DF}}(r_s)$ are above $E(r_s)$ for all r_s. A few words on each of the other calculations are in order.

Neece *et al.*[13] did the same calculation using a local-density-functional approach. They used Pines-Nozières' interpolation formula for the correlation energy, which differs from the correlation energy used by us. However, their band calculation was also slightly different, and the differences approximately cancelled to give results close to ours.

Caron[9] calculated the energy of metallic hydrogen using perturbation theory. He started with a homogeneous electron gas and treated the screened electron-proton and proton-proton interaction with a perturbation theory to fourth order. The dielectric function employed to do the screening is a variant of that developed by Singwi. The ground-state energy (in rydbergs per particle) was found to be

$$\begin{aligned}E = {}&2.21r_s^{-2} - 2.70722r_s^{-1}\\ &+ (0.0622 + 0.012r_s - 0.004r_s^2)\ln r_s\\ &- 0.1874 - 0.0555r_s + 0.0024r_s^2 - 0.001r_s^3\,.\end{aligned} \tag{109}$$

The energies for different values of r_s are given in Table III.

Hammerberg and Ashcroft[10] used a method similar to that of Caron, with the exception that the dielectric function was from random-phase approximation. Interpolated results are included in Table III. Brovman *et al.*[11] also used the perturbation theory. Their aim was to calculate and compare energies for several unusual lattice structures. The results are not quoted here. The results of Refs. 9 and 10 are also shown in Fig. 1. We note in conclusion that there is rather good agreement between our (variational) results and those of Caron.[9] There is also reasonably good agreement between our results and those of Neece *et al.*[13]

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APPENDIX

The method that we used for band calculation was developed by Kohn.[39] As shown by him[40] it is especially convenient for a spherical approximation (spherical unit cell and spherical potential). It was used by Tong[41,42] for a similar problem.

The band problem can be stated as

$$\left(-\frac{\hbar^2}{2m}\nabla^2+V_{\mathrm{eff}}(r)\right)\varphi_k(\vec{r})=\epsilon(k)\varphi_k(\vec{r}), \tag{A1}$$

with

$$\varphi_k(\vec{r})=e^{2ikr_s\cos\theta}\varphi_k(-\vec{r}),\quad r=r_s, \tag{A2}$$

and

$$\frac{\partial\varphi_k(\vec{r})}{\partial\vec{r}}=-e^{2ikr_s\cos\theta}\frac{\partial\varphi_k(-\vec{r})}{\partial\vec{r}},\quad r=r_s, \tag{A3}$$

where r_s is the radius of the Wigner-Seitz sphere and $\cos\theta=\vec{k}\cdot\vec{r}/kr$.

Expanding $\varphi_k(\vec{r})$:

$$\varphi_k(\vec{r})=\sum_l\frac{\eta_l C_l P_l(\cos\theta)R_{k,l}(r)}{r}, \tag{A4}$$

where $R_{k,l}$'s are the solution of the radial Schrödinger equation with angular momentum l. $\eta_l=1$ for even l, and $\eta_l=i$ for odd l.

Kohn showed that Eqs. (A2) and (A3) are equivalent to requiring that the integral

$$K=\int_{\text{unit cell surface}}[\nabla\varphi_k(\vec{r})]\varphi_k^*(-\vec{r})e^{2ikr\cos\theta}\,d\vec{S} \tag{A5}$$

is extremum, i.e., $\delta K=0$.

Thus the C_l's are determined by the equations

$$\int|\varphi_k(\vec{r})|^2\,d\vec{r}=1 \tag{A6}$$

and

$$\sum_l\Delta_{ml}C_l=0, \tag{A7}$$

where

$$\Delta_{ml}=\eta_m\eta_l(L_l+L_m)I_{lm}, \tag{A8}$$

$$L_l=\left(\frac{1}{R_{k,l}}\frac{dR_{k,l}(r)}{dr}-\frac{1}{r}\right)_{r=r_s} \tag{A9}$$

and

$$I_{lm}=\int_{-1}^{1}e^{-2ikr_s\mu}P_l(\mu)P_m(\mu)\,d\mu. \tag{A10}$$

The system of equations (A7) has a nontrivial solution only if

$$\|\Delta_{ml}\|=0.$$

This gives us the energy spectrum $\epsilon(k)$. Once the C_l's are determined from Eqs. (A6) and (A7) we can use Eq. (A4) to find the charge density,

$$n^0(\vec{r})=\sum_k|\varphi_k(\vec{r})|^2\Big/\sum_k 1. \tag{A11}$$

In practice we use only 7–8 terms in Eq. (A4). To see if this is sufficient, we check if Kohn's condition[40-42]:

$$\frac{C_1P_1(\cos\theta)+C_3P_3(\cos\theta)+\cdots}{C_0P_0(\cos\theta)+C_2P_2(\cos\theta)+\cdots}=\tan(kr_s\cos\theta) \tag{A12}$$

it satisfied for six different values of θ.

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