

Equation of state of the metallic phase of hydrogen

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The equation of state and thermodynamic potential of the metallic phase of hydrogen are analyzed in a wide range of megabar pressures. The previously described perturbation-theory procedure with the electron-ion interaction as the perturbation parameter is used. The terms of the series are considered in their explicit form up to the fourth order inclusively. A correlation is established between the perturbation series and the series in r_s found in the Wigner-Seitz approximation, and the sum of the remaining terms of the perturbation series is estimated. A direct computation of the phonon spectrum in the entire Brillouin zone is carried out at all densities in the course of the determination of the dynamic part of the total energy. As a result, the thermodynamic potential and the equation of state of the metallic phase are found with a high accuracy, and the scale of the error that can be introduced by the assumptions made in the theory is established at the same time. The obtained results are compared with the experimental data given by F. V. Grigor'ev *et al.*, [JETP Lett. 16, 201 (1972); Sov. Phys. JETP 42, 378 (1975)] for the equation of state of hydrogen and with the thermodynamic potential of the molecular phase found on the basis of these data. The phase transition region is analyzed in detail.

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1. INTRODUCTION

Great interest has of late been aroused by the problem of the metallic state of hydrogen. The uniqueness of the predicted properties, the feasibility of realizing the transition into this state under laboratory conditions (see Refs. 1 and 2, where the first experiments are described), the transparency at first glance of the basic physical picture, all this stimulated to a considerable degree theoretical and experimental investigations in this field. It should be said that, from the standpoint of theory, the range of problems under investigation interlocks with the more general problems of the metallic state, and here metallic hydrogen is of special interest, since it is the only substance in which the ions do not possess an electron shell and the form factor of the electron-ion interaction is exactly known beforehand.

Beginning with Wigner and Huntington's pioneering work,^[3] the theoretical investigations of the metallic state of hydrogen have been concentrated largely on three problems: the analysis of the possibility of the existence, and the properties, of a metastable state of metallic hydrogen, the determination of the critical pressure of the transition from the molecular to the metallic phase, and the study of the properties of metallic hydrogen at ultrahigh pressures.

The problem of the metastable state is, apparently, most fully considered in Ref. 4 (see also Ref. 5) in the framework of the many-particle theory of metals (for references to earlier papers, see Caron's review note^[6]). In the indicated paper the authors used perturbation theory in terms of the electron-ion interaction with allowance for terms up to the third order inclusively (thereby taking into account not only the pair interaction, but also the leading term in the nonpair, conduction-electron-mediated, indirect ion-ion interaction) in a scheme with possibly complete allowance for the electron-electron interaction in all the terms of the series.

The results of the analysis confirmed the fact that metallic hydrogen possesses a metastable phase which is dynamically stable, and to which corresponds a pressure P close to zero a structure with a strongly pronounced anisotropy. As P is increased to the transition pressure P_* , the crystal lattice becomes more and more symmetrical.^[7]

In this problem there still remains open the important question of the lifetime of the metastable metallic state and its dependence on pressure in the range $0 \leq P \leq P_*$. As is well known (see Ref. 8), this lifetime is finite even at the temperature $T = 0$ because the formation of the nucleus of the more stable phase (molecular hydrogen) is a purely quantum subbarrier process.

The question of the value of the critical pressure for the transition from the molecular into the metallic phase has been considered in a large number of papers (see, for example, Refs. 3, 7, 9, 10). The range of the results turned out to be extremely wide: from 250 kbar to 15 Mbar. Such an enormous spread was primarily a consequence of the difficulty of the theoretical prediction of the equation of state and the thermodynamic potential $\Phi(P)$ of the molecular phase at high pressures, when the distances between the hydrogen molecules are already relatively small, and of the virtually complete uncertainty in the estimation of the accuracy of the assumptions made. Moreover, the error in the determination of the equation of state of the metallic phase also has quite a considerable effect on the estimate for P_* , especially if we take into account the relatively small difference in the slopes of the $\Phi(P)$ curves for the two phases in the megabar pressure region.

The possibility of theoretically determining the equation of state of the molecular phase from "first principles" with a verifiable evaluation of the approximations is at present quite problematical. Therefore, it is natural to aim at providing an approximate description with free parameters, and to use the available experi-

mental data for finite pressures to determine these parameters.^[10-17] However, the extrapolation of these data into the megabar region has to a considerable degree an uncontrollable character (see Sec. 9).

A new situation arose in connection with the publication by Grigor'ev, Kormer *et al.*^[11] of results of experiments on the determination of the equation of state of hydrogen in the pressure range from ~0.4 to ~8 Mbar in explosion experiments performed under quasiadiabatic conditions. There arose for the first time the possibility of determining the experimental equation of state of the molecular phase in the entire pressure range of interest to us, including the megabar region. The obtained data allows us to also find directly the thermodynamic potential of the molecular phase as a function of the pressure (see below). Thus, there arises the possibility in principle of determining the phase-transition pressure on the basis of the experimental data for the molecular phase and the theoretical results for the metallic phase. For this purpose it is necessary to determine the equation of state and the thermodynamic potential of the metallic phase of hydrogen in the megabar pressure range with a sufficiently high and, above all, estimable accuracy. The solution of this problem is the object of this paper.

The most adequate procedure for finding the equation of state in the pressure region under consideration is a many-particle formalism similar to the one used in Refs. 4 and 7, which is especially effective exactly at high pressures, since for pure Coulomb systems an increase in the density leads to a more rapid convergence of the perturbation series and the high-density limit is directly determinable. Moreover, this formalism is very convenient in that it enables us to find within the framework of the approximations alone not only the static, but also the dynamic (the phonon spectrum) characteristics of the metal (for greater details, see Ref. 18).

In the present paper, which is actually a development of the work published in Ref. 7, we go outside the limits of third-order perturbation theory, compute in their explicit form the fourth-order terms, including those connected with the distortion of the Fermi surface (the earliest estimates of the fourth-order terms were made by Hammerberg and Ashcroft^[19]; an estimate of the role of the distortion of the Fermi surface was first made in Carr's paper^[20]), as well as estimate the sum of the entire remaining "tail" of the perturbation series. This allows us, in particular, to establish the nature of the convergence and the accuracy of the obtained results in one or another truncation of the series. Special attention is given to the *accuracy of the determination of the zero-point vibration energy*. For this purpose we undertake a direct determination of the phonon spectrum in the entire Brillouin zone for all density values. The equation of state and the thermodynamic potential are determined for all the competing—in terms of energy—structures (see Ref. 7). This allows us to establish the scale of the sensitivity of the two equations to structure.

The results of the analysis carried out allow us to determine the band within whose limits the equation of state and the thermodynamic potential of metallic hydrogen clearly lie. It is interesting that the relatively high accuracy achieved in the determination of the individual contributions leads to a situation in which the main uncertainty in the megabar region turns out to be connected with the error in the determination of the correlation energy of the homogeneous electron gas. As a result, there arises here the possibility of carrying out a controlled—with respect to accuracy—comparison of the experimental data obtained by Grigor'ev, Kormer *et al.*^[11] with the theory and of performing an analysis of the phase-transition region. The pertinent analysis is carried out in Sec. 9.

2. THE ENERGY OF THE METALLIC PHASE

The energy of the metallic phase of hydrogen at the temperature $T=0$ depends on the density (or the standard characteristic, r_s , of the electron liquid) and the parameters, γ_j , determining the structure of the unit cell:

$$E = E_s(r_s, \gamma_j) + E_{el}(r_s, \gamma_j), \quad E_s = E_i + E_e. \quad (2.1)$$

Here E_i is the energy of the ion lattice, which is imbedded in a homogeneous negative background, E_e is the energy of the electron liquid perturbed by the interaction with the ion lattice.

The electron energy of a normal crystal can be represented in the form of a series in powers of the electron-ion interaction (for greater details, see Ref. 18):

$$E_e = E^{(0)} + E^{(2)} + E^{(4)} + \dots, \quad (2.2)$$

$$E^{(n)} = \Omega \sum_{\mathbf{K}_1, \dots, \mathbf{K}_n} \Gamma^{(n)}(\mathbf{K}_1, \dots, \mathbf{K}_n) V_{\mathbf{K}_1} \dots V_{\mathbf{K}_n} \Delta(\mathbf{K}_1 + \dots + \mathbf{K}_n) \quad (n \geq 1), \quad (2.3)$$

where in the case of hydrogen

$$V_{\mathbf{K}} = - (4\pi e^2 / K^2 \Omega_0) S(\mathbf{K}). \quad (2.4)$$

In the expressions \mathbf{K}_i is a reciprocal-lattice vector, $S(\mathbf{K})$ is the structure factor, Ω is the total volume of the crystal, and Ω_0 is the volume per ion (in the sum (2.3) there are no terms with $\mathbf{K}_i = 0$). The multipolar function figuring in (2.3) is a universal characteristic of the electron liquid.

The first term of the expansion (2.2), $E^{(0)}$, is the energy of the homogeneous electron gas. In the absence of an ion core, which is characteristic of only hydrogen, the structure-dependent terms in (2.2) begin with $E^{(2)}$. The two-pole function $\Gamma^{(2)}$ corresponding to this term is uniquely connected with the static polarization operator, $\Pi(\mathbf{q})$, for the electron gas:

$$\Gamma^{(2)}(\mathbf{q}, -\mathbf{q}) = -\frac{1}{2} \frac{\Pi(\mathbf{q})}{\varepsilon(\mathbf{q})}, \quad \varepsilon(\mathbf{q}) = 1 + \frac{4\pi e^2}{q^2} \Pi(\mathbf{q}). \quad (2.5)$$

Starting from $n=3$ the multipolar functions entering into (2.3) can be transformed into the form (see Ref. 18)

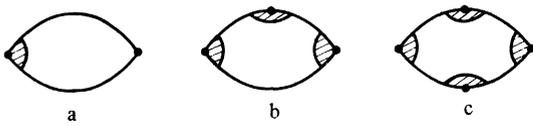


FIG. 1. n -Pole diagrams: a) for $n=2$, b) for $n=3$, and c) for $n=4$.

$$\Gamma^{(n)}(q_1, \dots, q_n) = \frac{\Lambda^{(n)}(q_1, \dots, q_n)}{\varepsilon(q_1) \dots \varepsilon(q_n)}, \quad (2.6)$$

where $\Lambda^{(n)}$ is a multipolar function not possessing polarization parts, which could have been transferred to the external-field lines.

At the densities of interest to us, to determine the $\Lambda^{(n)}$, we can use the approximation corresponding to allowance at each external vertex for the exchange and correlation of the electron with the cloud screening the ion (see Refs. 18 and 21). Then

$$\Lambda^{(n)}(q_1, \dots, q_n) = T(q_1) \dots T(q_n) \Lambda_0^{(n)}(q_1, \dots, q_n). \quad (2.7)$$

Here $\Lambda_0^{(n)}$ is a simple ring diagram with n external-field vertices. The adopted approximation corresponds to the replacement of all the simple vertices in a ring diagram by effective $T(q_i)$ (the heavy vertices in Fig. 1, b and c).

All the modern results on the successive allowance for the electron-electron interaction in the determination of $\varepsilon(\mathbf{q})$ ^[22-26] use approximations that are practically equivalent to the replacement of the exact—for $\Pi(\mathbf{q})$ —diagram in Fig. 1a with the true heavy vertex by an approximate diagram that depends only on the transferred momentum (and the replacement of the Green functions by free ones). In this case

$$\Pi(\mathbf{q}) = \Pi_0(\mathbf{q}) T(\mathbf{q}), \quad (2.8)$$

where $\Pi_0(\mathbf{q})$ is the polarization operator for the free electron gas. The expressions obtained for $T(\mathbf{q})$ in all the analyses have the form^[27]

$$T(\mathbf{q}) = \left[1 - \frac{4\pi e^2}{q^2} G(\mathbf{q}) \Pi_0(\mathbf{q}) \right]^{-1}, \quad (2.9)$$

and the various approaches differ only in the form of the function $G(\mathbf{q})$.

Thus, by choosing the appropriate form of the function $G(\mathbf{q})$, we can uniquely determine within the framework of the adopted approximation $\Gamma^{(2)}$ and $\varepsilon(\mathbf{q})$, (2.5), and $\Lambda^{(n)}$, (2.7). The expression for $\Lambda_0^{(3)}$ is well known (see, for example, Refs. 4 and 18), and $E^{(3)}$ can be determined directly.

In determining the terms of fourth and higher orders in the electron-ion interaction, it is necessary to take into account the resulting distortion of the Fermi surface.^[18] The use at $T=0$ of ordinary perturbation theory tacitly presupposes a situation in which the Fermi surface is fixed, and its application requires additional variation of the energy with respect to the shape of the Fermi surface. The determination of the extre-

mal value of the energy of the system simultaneously leads to the determination of this surface. In this case the corrections, ΔE_{FS} , to the energy due to the nonsphericity begin precisely with the terms of fourth order in V_K/ε_F . As a result, we obtain

$$\tilde{E}^{(4)} = E_n^{(4)} + \Delta E_{FS}^{(4)}, \quad (2.10)$$

where $E_n^{(4)}$ is the value corresponding to the spherical Fermi surface. It is evident that

$$\Delta E_{FS}^{(4)} < 0.$$

The most direct way of determining $E^{(n)}$ for $n \geq 4$ is to use the thermodynamic theory of perturbations,^[28] which selects the lowest energy states and thereby automatically ensures the variation with respect to the shape of the Fermi surface. We find the thermodynamic potential $\tilde{\Omega}$ (the chemical potential, μ , is fixed) within the framework of this method, the diagram technique for which coincides at $T=0$ with the perturbation-theory technique for $T=0$ if the free-electron Green function is taken in the form

$$G_0(\mathbf{p}, \omega) = [\omega - \varepsilon_0(\mathbf{p}) + i\delta \operatorname{sign}(\omega - \mu)]^{-1}. \quad (2.11)$$

The fourth-order diagrams computed with the aid of the two methods differ, in the case when the poles of the Green functions coincide, in the so-called anomalous contributions.^[29] Together with the additional contribution from the renormalization of the chemical potential they constitute ΔE_{FS} .

As a direct analysis shows, the contribution from the renormalization of μ to $E^{(4)}$ is determined by an expression of the type (2.6) with

$$\Lambda_n^{(4)}(q_1, \dots, q_n) = \frac{1}{8} \left(\frac{d\mu}{dn} \right) \left(\frac{\partial \Pi(q_i)}{\partial \mu} \right) \left(\frac{\partial \Pi(q_n)}{\partial \mu} \right) \delta(q_3, -q_2) \delta(q_4, -q_1) \quad (2.12)$$

(n is the electron density). Here and everywhere below $\delta(q_i, q_j)$ is the Kronecker symbol. If we adopt the approximation used in going over to (2.7) and (2.8), then the determination of $\tilde{\Omega}^{(4)}$ practically amounts to the determination of the ring diagram with four external-field tails, $\Lambda_0^{(4)}$, a technique, based precisely on the form (2.11), for computing which was developed in Ref. 30. The separation of the anomalous contributions is carried out directly (see Refs. 18 and 30), and for $\Delta E_{FS}^{(4)}$ we obtain an expression of the form (2.3), (2.6), (2.7) with

$$\Lambda_{FS}^{(4)}(q_1, \dots, q_n) = \Lambda_{0n}^{(4)} + \Lambda_a^{(4)}, \quad (2.13)$$

where $\Lambda_{0n}^{(4)}$ is obtained from (2.12) by making the substitution $\Pi(\mathbf{q}) \rightarrow \Pi_0(\mathbf{q})$. The values of the anomalous contribution $\Lambda_a^{(4)}$ and the normal contribution $\Lambda_n^{(4)}$ corresponding to $E_n^{(4)}$ in (2.10) will be considered in detail in Sec. 6.

Below, in determining the equation of state of the metallic phase of hydrogen in the megabar region, we shall, by directly estimating the sum of the entire remaining tail of the series (2.2), demonstrate the possibility of limiting ourselves to the explicit considera-

tion of only the first four terms of the expansion.

Finally, for the energy of the ion lattice we have¹⁾

$$E_i = \alpha_M / r_s, \quad (2.14)$$

where α_M is the Madelung constant.

3. THE CORRELATION ENERGY

In analyzing the accuracy of the determination of the total energy of the metallic phase, we encounter from the very beginning the classical problem of the correct determination of ε_c , the correlation contribution to the energy, $E^{(0)}$, of the homogeneous electron gas.

Substantial progress has been made in recent years in the study of the properties of the electron liquid at intermediate densities. Quite different approaches, based on the selection and summation of a definite class of diagrams (Geldart and Taylor (GT)^[23]), the use of the technique of uncoupling the equations of motion for the Green functions (Toigo and Woodruff (TW)^[24]), and the self-consistent allowance for the corrections to the local field (Singwi *et al.* (STLS)^[26], Vashishta and Singwi (VS)^[22]), led to comparatively close results for the static permittivity and the correlation energy in the density range of interest to us.

It is natural to assume that the spread in the ε_c values that arises in these essentially different analyses precisely reflects the scale of uncertainty characteristic of the approximate determination of this quantity in the density region in question. In Fig. 2 we have constructed in the interval $1 < r_s < 4$ the dependence $\varepsilon_c(r_s)$ obtained in the above-cited papers, as well as the curve corresponding to the well-known Nozières-Pines (NP) interpolation relation.^[32] We show in the same figure the asymptotic dependence for $\varepsilon_c(r_s)$ at small r_s ,

$$\varepsilon_c(r_s) = 0.0622 \ln r_s - 0.096 + 0.018 r_s \ln r_s - 0.036 r_s, \quad (3.1)$$

first obtained by Carr and Maradudin,^[31] who found the next two terms of the series in the well-known Gell-Mann-Brueckner asymptotic form.^[33]

Of greatest interest to us is the pressure range from 1 to 10 Mbar, to which corresponds the density range²⁾

$$1.05 \leq r_s \leq 1.45. \quad (3.2)$$

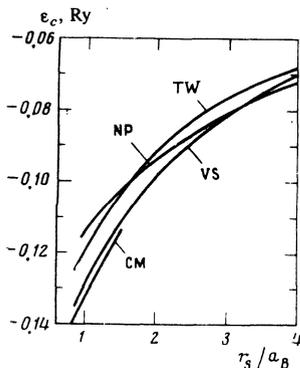


FIG. 2. The correlation energy $\varepsilon_c(r_s)$ of a homogeneous electron gas, found in various approximations: CM—Carr and Maradudin,^[31] VS—Vashishta and Singwi,^[22] TW—Toigo and Woodruff,^[24] and NP—Nozières and Pines.^[32]

The results presented force us to presume that in the interval (3.2) the error in the determination of ε_c has the order of magnitude

$$\delta \varepsilon_c \sim 10^{-2} \text{ Ry}. \quad (3.3)$$

It should be noted that, judging from the value of the first terms of the series (3.1), the error made when the next terms of the series are discarded has, in the interval (3.2), the same order of magnitude (3.3).

It is noteworthy that the curve $\varepsilon_c(r_s)$ found by Vashishta and Singwi is extremely close to the asymptotic curve (3.1) for $r_s < 1.5$. This circumstance is quite important, and we used precisely this dependence for the correlation energy in the final computations of the total energy and the thermodynamic potential. The uncertainty in the value of the correlation part of the pressure in the r_s range under consideration is

$$\delta P_c(r_s = 1.45) \approx 0.02 \text{ Mbar}, \quad \delta P_c(r_s = 1.05) \approx 0.09 \text{ Mbar}. \quad (3.4)$$

This is roughly 10% of the correlation pressure, which has at the ends of the interval (3.2) the values $P_c \approx -0.17$ and -0.50 Mbar respectively. The estimate (3.3) is very important for the subsequent analysis, since it gives the starting error, which cannot be eliminated without a fundamental advance in the theory of the electron liquid.

In the just published article by Ross and McMahan^[34] the assertion is made with reference to atomic computations that the correlation energy of an electron gas is determined up to a factor of 2 or 3. However, this assertion by the authors is based simply on a misunderstanding. It has long been found (see, for example, Ref. 35) that the cause of the discrepancy in the value of ε_c lies in the discreteness of the energy spectrum of the atom and, consequently, in the inadmissibility of the application of the results obtained for a homogeneous electron gas to a finite atomic system.

4. THE ROLE OF THE STRUCTURE AND THE SCREENING IN THE INDIRECT INTER-ION INTERACTION

The real parameter of the energy expansion at high densities is not r_s , but a much smaller quantity: $\sim r_s/4$ (see Sec. 7). Therefore, considering the range of densities (3.2) (and of higher densities), we can establish the character of the behavior of the energy and the individual contributions to it by analyzing the asymptotic relations, which can be found exactly. The corresponding expansions for $E^{(n)}$ have the form ($n \geq 2$)

$$E^{(n)} = r_s^{-(n-2)} [\xi^{(n)}(\gamma_i) + \eta^{(n)}(\gamma_i) r_s + \zeta^{(n)}(\gamma_i) r_s^2 + \dots]. \quad (4.1)$$

The $E^{(2)}$ expansion begins with the constant $\xi^{(2)}$, to which corresponds the substitutions $\Pi(\mathbf{q}) \rightarrow \Pi_0(\mathbf{q})$ and $\varepsilon(\mathbf{q}) = 1$ in (2.5). The dependence on r_s appears only when the electron-electron interaction is taken into account, but this interaction turns out to be quite weak because of the fact that all the quantities enter into (2.3) with $\mathbf{q} = \mathbf{K}$. This can clearly be seen from Table I, where

TABLE I.

Lattice	Energy in Ry/atom			
	$\xi^{(2)}$	$\eta^{(2)}$	$\xi^{(3)}$	α_M
FCC	-0.0913	0.00113	-0.02076	-1.79175
BCC	-0.0904	0.00152	-0.02078	-1.79186
HCP ($c/a=1.633$)	-0.0917	0.00080	-0.02078	-1.79168

values of $\xi^{(2)}$ and $\eta^{(2)}$ are given for three symmetrical structures that are energetically the most favorable at the high-density limit (see Ref. 7). In computing the coefficient $\eta^{(2)}$ we used the results obtained in Ref. 23, where corrections, represented by diagrams of the type shown in Fig. 3, to the simple polarization loop were found.

The $E^{(3)}$ expansion begins with a term linear in r_s , the coefficient $\xi^{(3)}$ (see Table I) exceeding $\eta^{(3)}$ by more than an order of magnitude.

Among the structure-dependent terms in E_{st} the leading role is played by the ion-lattice energy (2.14). For the symmetrical structures the difference in α_M turns out to be so small (see Table I) that the differences in the ionic energy is negligibly small in comparison with (3.3). This applies also to E_s , as can clearly be seen from the results given in Table I.

However, as was shown in Ref. 7, the more favorable—from the standpoint of E_{st} —and the more dynamically stable turn out to be the anisotropic lattices, at least at lower densities. On going over to the interval (3.2) and to higher densities, we find the energy difference between the various structures to decrease significantly. This tendency can be clearly seen from the illustrative results given in Table II for the optimal anisotropic lattices^[7]: for the primitive hexagonal (PH) and rhombohedral (RH) and concurrently for the FCC lattice, the first of the symmetrical structures to become dynamically stable under pressure (see Ref. 7). In the calculations we found for each r_s the extremal—with respect to energy—value of the parameter (c/a) and correspondingly determined the value $\alpha_M(c/a)$, which turned out to be equal at the ends of the interval (3.2) to: for $r_s = 1.45$

$$\alpha_M^{SH}(c/a=1.1385) = -1.7499, \quad \alpha_M^{RH}(c/a=1.9721) = -1.7525; \quad (4.2a)$$

and for $r_s = 1.05$

$$\alpha_M^{SH}(c/a=1.0309) = -1.7682, \quad \alpha_M^{RH}(c/a=1.7487) = -1.7775. \quad (4.2b)$$

The function $G(\mathbf{q})$ in (2.9) was chosen in the approximation used in Ref. 22.

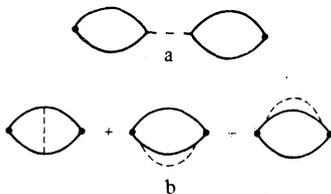


FIG. 3. Diagrams of the corrections of first order in the electron-electron interaction to $E^{(2)}$.

TABLE II.

Lattice	E_i		$E^{(2)}$		$E^{(3)}$		$E_i + E^{(2)} + E^{(3)}$	
	$r_s/a_B = 1.45$	1.05	1.45	1.05	1.45	1.05	1.45	1.05
PH	-1.1986 *	-1.6681	-0.1217	-0.1114	-0.0336	-0.0245	-1.3566	-1.8040
RH	-1.2003	-1.6769	-0.1201	-0.1053	-0.0333	-0.0237	-1.3664	-1.8059
FCC	-1.2272	-1.6903	-0.0896	-0.0894	-0.0284	-0.0213	-1.3460	-1.8020

*The energies are given in Ry/atom.

As can be seen from the results presented, as n increases, the change in energy, $\delta E^{(n)}$, as we go from one structure to another decreases, and even $\delta E^{(3)}$ turns out to be substantially smaller than (3.3). The estimate for the magnitude of the term with $n=4$ (see the following section) lets us think that $\delta E^{(4)}$ does not exceed $\sim 10^{-3}$ Ry. Therefore, the scale of the difference in the total static energy should be determined by the values given in the last two columns of Table II.

It follows from these data that the difference in E_{st} for $r_s = 1.45$ can yet have a value of the order of (3.3) in favor of the anisotropic structures, becoming significantly smaller even at $r_s = 1.05$. It should, however, be noted that this difference decreases considerably in the total energy (2.1) since to the anisotropic structures corresponds a zero-point vibration energy that is greater precisely to the same extent. However, in this case, as is quite evident from Table II, an accuracy equivalent to, or better than, (3.3) can be attained only when we take into account the next terms of the series (2.2), terms which in all the cases need to be computed only for the cases of the symmetrical structures.

A similar conclusion can be drawn on analyzing the corresponding contributions to the pressure, the only difference being that now $P^{(2)}$ is very small because of the nondependence of the leading term in $E^{(2)}$ on r_s , so that the structure-dependent terms in the perturbation series (equivalent to (2.2)) for P , which make a substantial contribution to the total pressure, practically begin with $P^{(3)}$. In this case the neglect of the actual structure for terms with $n \geq 4$ introduces an error δP certainly not exceeding (3.4).

Furthermore, we can conclude on the basis of the values of the coefficient $\eta^{(2)}$ for the symmetrical structures (Table I) that the entire contribution of the electron-electron interaction to the structure-dependent (via $\Pi(\mathbf{q})$, $\varepsilon(\mathbf{q})$, and $\Lambda^{(n)}$; see Sec. 2) terms in the energy is small compared to (3.3). This applies all the more to the difference between the energy values obtained in the various schemes of analysis of the elec-

TABLE III.

Lattice	$E^{(2)}$, Ry/atom			$E^{(3)}$, Ry/atom		
	GT	VS	TW	GT	VS	TW
PH ($c/a=1.1385$)	-0.1217 *	-0.1233	-0.1237	-0.0336	-0.0338	-0.0343
RH ($c/a=1.9721$)	-0.1201	-0.1218	-0.1221	-0.0333	-0.0336	-0.0340
FCC	-0.0896	-0.0897	-0.0900	-0.0284	-0.0284	-0.0288

*The $E^{(2)}$ and $E^{(3)}$ values are given for $r_s = 1.45$.

tron liquid (i. e., obtained with different $G(\mathbf{q})$ in (2. 7), (2. 8), and (2. 9)). This assertion is also valid for the anisotropic structures, as can easily be verified from the results of the computation of $E^{(2)}$ and $E^{(3)}$ for the for the three different types of screening (VS, [22] GT, [22] and TW[24]) given in Table III. The difference in screening leads to fluctuations in the energy not exceeding 10^{-3} Ry. Notice that the contribution to $E^{(3)}$ from the electron-electron interaction is at least an order of magnitude smaller than the $E^{(3)}$ value itself, which value is dictated by the first asymptotic term, $\xi^{(3)}r_0$, in (4. 1).

5. DETERMINATION OF $E^{(4)}$

As follows from the relations given in Sec. 2, the determination of $E^{(4)}$, (2. 10), can be reduced to the determination of the normal, $\Lambda_n^{(4)}$, and anomalous, $\Lambda_a^{(4)}$, parts of the four-point ring diagram by the technique developed in Refs. 36, 18, and 30 for computing ring diagrams.

The analysis of $E^{(4)}$ was first undertaken in Hammerberg and Ashcroft's paper. [19] Unfortunately, it is impossible to use the results of this paper, since the overcrude approximations made in the computation of some of the contributions and the insufficiently justified neglect of others led to incorrect quantitative estimates (see below).

For the anomalous contributions we can derive explicit analytic expressions. [30] Thus, upon the coincidence of the poles of the two Green functions,

$$\Lambda_a^{(4)}(\mathbf{K}_1, \mathbf{K}_2, \mathbf{K}_3, \mathbf{K}_4) = -\frac{m_0^3}{8\pi^2 k_F^3} \frac{1}{x_1^2 x_2^2 (A^2 - B^2)^{3/2}} \ln \left(\frac{A + (A^2 - B^2)^{1/2}}{B} \right) \times \delta(\mathbf{K}_3, -\mathbf{K}_2) \delta(\mathbf{K}_4, -\mathbf{K}_1) [1 - \delta(\mathbf{K}_2, -\mathbf{K}_1)], \quad (5. 1)$$

where

$$A = 1 + \frac{\mathbf{x}_1 \mathbf{x}_2}{x_1^2 x_2^2}, \quad B = \left[\left(1 - \frac{1}{x_1^2} \right) \left(1 - \frac{1}{x_2^2} \right) \right]^{1/2}, \quad x_i = \frac{K_i}{2k_F}.$$

(Here allowance has been made in the coefficient for the fact that the conditions for the coincidence of the poles are fulfilled in the summation of the general expression for two sets of arguments: $(\mathbf{K}_1, \mathbf{K}_2, -\mathbf{K}_1)$ and $(-\mathbf{K}_2, -\mathbf{K}_2, \mathbf{K}_3, -\mathbf{K}_3)$.) Upon the coincidence of the two pairs of poles, there remains in the expression for the energy a sum over a single reciprocal-lattice vector:

$$\Lambda_a^{(4)}(\mathbf{K}_1, \mathbf{K}_2, \mathbf{K}_3, \mathbf{K}_4) = \frac{m_0^3}{8\pi^2 k_F^3} \frac{1}{x_1^2 (1 - x_1^2)} \delta(\mathbf{K}_2, -\mathbf{K}_1) \delta(\mathbf{K}_3, -\mathbf{K}_2) \delta(\mathbf{K}_4, -\mathbf{K}_1) \quad (5. 2)$$

The sum of the contributions (5. 1) and (5. 2) determines the value of $\Lambda_a^{(4)}$ in (2. 13). The explicit form of $\Lambda_n^{(4)}$ in the approximation in question is as follows:

$$\Lambda_n^{(4)}(\mathbf{K}_1, \mathbf{K}_2, \mathbf{K}_3, \mathbf{K}_4) = \frac{m_0^3}{32\pi^2 k_F^3} \left(\frac{1}{x_1} \ln \left| \frac{x_1 + 1}{x_1 - 1} \right| \right) \left(\frac{1}{x_2} \ln \left| \frac{x_2 + 1}{x_2 - 1} \right| \right) \delta(\mathbf{K}_3, -\mathbf{K}_2) \delta(\mathbf{K}_4, -\mathbf{K}_1). \quad (5. 3)$$

Using these expressions and relations of the type (2. 7) and (2. 6), we can find the contribution, $\Delta E_{FS}^{(4)}$, to the energy connected with the distortion of the Fermi sur-

TABLE IV.

Lattice	$\xi_a^{(4)}$	$\xi_n^{(4)}$	$\xi_{FS}^{(4)}$
	10 ⁻³ RY		
FCC	-2.576	2.561	-0.015
BCC	-2.453	2.449	-0.004

face. Direct calculations indicated very strong cancellation of the contributions from $\Lambda_n^{(4)}$ and $\Lambda_a^{(4)}$, a process which can, generally speaking, be followed analytically.

If we neglect the screening, then the expression for $E^{(4)}$ can be written in the form (4. 1), with

$$\xi^{(4)} = \xi_n^{(4)} + \xi_{FS}^{(4)}. \quad (5. 4)$$

In Table IV we give for the FCC and BCC lattices the values of the individual contributions to $\xi_{FS}^{(4)}$, values which demonstrate the extent of the cancellation.

The total value of $\Delta E_{FS}^{(4)}$ turns out to be very small (and negative), and the obtained results allow us to come to the important conclusion that the deformation of the Fermi surface does not play a role and that, to determine the fourth-order contribution, we need to know only the value of $E^{(4)}$, or, which is the same thing, the normal part of the four-pole function $\Lambda_n^{(4)}$.

Let us note that the first estimate of the role of the nonsphericity of the Fermi surface was made as far back as 1962 by Carr, [20] using a variational approach, and led to a result that is in qualitative agreement with the result obtained above.

We begin the determination of $\Lambda_n^{(4)}$ with particular cases corresponding to the same values of the arguments as in (5. 1) and (5. 2). Using the results of Ref. 30, we have for the total (the normal and anomalous together) multipolar function, which can be computed directly, the expression

$$\Lambda_n^{(4)}(\mathbf{K}_1, \mathbf{K}_2, \mathbf{K}_3, \mathbf{K}_4) = \frac{m_0^3}{16\pi^2 k_F^3} \frac{1}{S} \left\{ \frac{(\mathbf{x}_1 \mathbf{x}_2)}{x_1} \ln \left| \frac{x_1 + 1}{x_1 - 1} \right| + \frac{(\mathbf{x}_2 \mathbf{x}_3)}{x_2} \ln \left| \frac{x_2 + 1}{x_2 - 1} \right| + x_3 \ln \left| \frac{x_3 + 1}{x_3 - 1} \right| + \frac{(\mathbf{x}_1 \mathbf{x}_2) x_3^2}{D} \ln \left| \frac{z + 1}{z - 1} \right| \right\} \times \delta(\mathbf{K}_3, -\mathbf{K}_2) \delta(\mathbf{K}_4, -\mathbf{K}_1) [1 - \delta(\mathbf{K}_2, -\mathbf{K}_1)]; \quad (5. 5)$$

here

$$S = x_1^2 x_2^2 - (\mathbf{x}_1 \mathbf{x}_2)^2, \quad D = (x_1^2 x_2^2 x_3^2 - S)$$

$$\mathbf{K}_3 = -\mathbf{K}_1 - \mathbf{K}_2, \quad z = \frac{2D}{x_1^2 + x_2^2 + x_3^2 - 2}.$$

This result is valid for $S \neq 0$, i. e., for $\mathbf{K}_1 \neq \mathbf{K}_2$. In the $S = 0$ case we have

$$\Lambda_n^{(4)}(\mathbf{K}_1, \mathbf{K}_2, \mathbf{K}_3, \mathbf{K}_4) = \frac{m_0^3}{32\pi^2 k_F^3} \frac{1}{x_1^2 x_2^2} \left\{ \frac{(x_3^2 - 1)}{x_3} \ln \left| \frac{x_3 + 1}{x_3 - 1} \right| + \frac{2x_1^2 x_2^2 + (x_1^2 - 1)(\mathbf{x}_1 \mathbf{x}_2)}{x_1 (\mathbf{x}_2 \mathbf{x}_3)} \ln \left| \frac{x_1 + 1}{x_1 - 1} \right| + \frac{2x_1^2 x_3^2 + (x_2^2 - 1)(\mathbf{x}_1 \mathbf{x}_2)}{x_2 (\mathbf{x}_1 \mathbf{x}_3)} \ln \left| \frac{x_2 + 1}{x_2 - 1} \right| \right\} \times \delta(\mathbf{K}_3, -\mathbf{K}_2) \delta(\mathbf{K}_4, -\mathbf{K}_1) [1 - \delta(\mathbf{K}_2, -\mathbf{K}_1)]. \quad (5. 6)$$

The expression for $\Lambda_n^{(4)}$ corresponding to the coincidence of the two pairs of poles of the Green functions on the ring was first obtained (together with (5. 2)) by Hammerberg and Ashcroft. [19] In the notation adopted

here (in the expression for the energy there is one summation over \mathbf{K})

$$\Lambda_n^{(4)}(\mathbf{K}_1, \mathbf{K}_2, \mathbf{K}_3, \mathbf{K}_i) = \frac{m_0^3}{16\pi^2 k_F^3} \frac{1}{x_i^2(1-x_i^2)} \left[1 - \frac{1-x_i^2}{2x_i} \ln \left| \frac{x_i+1}{x_i-1} \right| \right] \times \delta(\mathbf{K}_3, -\mathbf{K}_1) \delta(\mathbf{K}_3, -\mathbf{K}_2) \delta(\mathbf{K}_1, -\mathbf{K}_i). \quad (5.7)$$

The normal part can be found in both cases as

$$\Lambda_n^{(4)} = \Lambda_0^{(4)} - \Lambda_a^{(4)}, \quad (5.8)$$

where $\Lambda_a^{(4)}$ is determined by the relations (5.1) and (5.2).

The computation of the contribution to the energy from arbitrary combinations of the wave vectors (i. e., without coincidence of the poles) meets with great difficulties. This is primarily connected with the fact that now it is not possible to express the four-pole function in terms of elementary functions. In view of this, in computing $\Lambda_0^{(4)}$ in the general case, we used an approximate "splitting" scheme, which, as can be established, is of sufficiently high accuracy. In this case we shall restrict ourselves to the lattices of cubic symmetry (see Sec. 4).

For this scheme, it is convenient to use the representation for $\Lambda_0^{(4)}$ obtained after integrating the ring diagram over the frequency:

$$\Lambda_0^{(4)}(\mathbf{K}_1, \mathbf{K}_2, \mathbf{K}_3, \mathbf{K}_i) = \gamma_3(\mathbf{K}_1, \mathbf{K}_1 + \mathbf{K}_2, \mathbf{K}_1 + \mathbf{K}_2 + \mathbf{K}_3) \times [1 - \delta(\mathbf{K}_1, -\mathbf{K}_i)] [1 - \delta(\mathbf{K}_3, -\mathbf{K}_2)] \delta(\mathbf{K}_i, -(\mathbf{K}_1 + \mathbf{K}_2 + \mathbf{K}_3)), \quad (5.9)$$

$$\gamma_m(\kappa_1, \dots, \kappa_m) = 2 \int \frac{d^3 p}{(2\pi)^3} \frac{\theta(\mu_0 - \varepsilon_p)}{(\varepsilon_p - \varepsilon_{p+\kappa_1}) \dots (\varepsilon_p - \varepsilon_{p+\kappa_m})}. \quad (5.9a)$$

Simple transformations allow us to reduce γ_m to the form

$$\gamma_m(\kappa_1, \dots, \kappa_m) = \frac{(-1)^m \gamma_0}{\varepsilon_{\kappa_1} \varepsilon_{\kappa_2} \dots \varepsilon_{\kappa_m}} \beta_m \left(\frac{\kappa_1}{2k_F}, \dots, \frac{\kappa_m}{2k_F} \right), \quad (5.10)$$

where $\gamma_0 = k_F^3 / 3\pi^2$, $\varepsilon = (\kappa)^2 / 2m_0$, and the dimensionless function β_m is

$$\beta_m(y_1, \dots, y_m) = \frac{3}{4\pi} \int_{|z| \leq 1} \frac{dz}{(1+(y_1 z)/y_1^2) \dots (1+(y_m z)/y_m^2)}. \quad (5.11)$$

For the \mathbf{K}_i configurations occurring in (5.9), the conditions $\kappa_i \neq 0$ and $\kappa_i \neq \kappa_j$ are fulfilled. In this case $|y_i| > 1$ in a crystal of cubic symmetry (which was tacitly assumed in writing γ_m in the form (5.9a)).

The "splitting" approximation consists in the replacement of the mean—over a unit sphere—value of the product figuring under the integral sign in (5.11) by a product of mean values of the form

$$\beta_m(y_1, \dots, y_m) \approx \beta_{m-1}(y_1, \dots, y_{m-1}) \beta_1(y_m). \quad (5.12)$$

In the concrete calculations of β_3 , we optimized this procedure by choosing for each $\{\kappa_i\}$ set the appropriate "splitting" vector \mathbf{y}_j , for which we determined the i value at which the quantity

$$\Delta \beta_3(y_i) = \frac{1}{5} \frac{y_i}{y_i^2} \left(\frac{y_j}{y_j^2} + \frac{y_k}{y_k^2} \right), \quad (i, j, k) = (1, 2, 3),$$

which is the difference, computed up to the terms $\sim y^{-2}$, between β_3 and the product (β_2, β_1) , assumed its minimum value.

The resulting approximation is quite exact. This can be verified directly if we compute the contribution to $E^{(4)}$ of the degenerate $\{\mathbf{K}_i\}$ configurations, i. e., of those for which the condition $\det|\mathbf{K}_1, \mathbf{K}_2, \mathbf{K}_3| = 0$, which leads to a situation in which all the \mathbf{K}_i vectors lie in one plane, is valid. The explicit form of $\Lambda_0^{(4)}$ for this case was found in Ref. 30. Computing this contribution exactly, and using the approximation (5.12), we find that the difference does not exceed 2%. The error made in the computation of the entire energy $E^{(4)}$ can only be smaller, since the contribution of the random $\{\mathbf{K}_i\}$ configurations predominates and the approximation (5.12) for such configurations is better. In this case the degenerate configurations were, of course, taken into account by exact formulas.

In Table V we give the results of the computation of the contributions to $E_n^{(4)}$ (more exactly, to $\xi_n^{(4)}$ —see (5.4)) coming from the normal parts of $\Lambda_0^{(4)}$ that correspond to the coincidence of the two poles of $\xi_n^{(4)}$ (see (5.5) and (5.6)), or of the two pairs of poles of $\xi_n^{(4)}$ (see (5.7)), as well as the results for the general case when $\xi_n^{(4)}$ does not possess multiple poles (the approximation (5.12) for the nondegenerate configurations). Again, we give only the dominant term in $E^{(4)}$, which corresponds to the neglect of the electron-electron interaction.

As follows from these results, the quantity $E^{(4)}$ turned out to be quite substantial and comparable in magnitude to (3.3), although it is appreciably smaller than $E^{(3)}$ (see Sec. 4)—smaller precisely by a factor equal to the parameter (V_K/ε_F) of the theory. The value of $E^{(4)}$ is determined virtually entirely by the contributions from the random $\{\mathbf{K}_i\}$ configurations in the triple sum, configurations which do not give rise to coincident poles in $\Lambda_0^{(4)}$. Notice that the contribution from the distortion of the Fermi surface turned out to be almost three orders of magnitude smaller.

Let us note that Hammerberg and Ashcroft's result^[19] which leads to a much smaller estimate for $E^{(4)}$ is a consequence of the extremely crude computations of the individual contributions and the neglect of the anomalous contribution (5.1), which led to the accidental mutual canceling out of the quantities.

It is not difficult to compute $E^{(4)}$ with allowance for the electron-electron interaction, using the relations (2.6), (2.7), and (2.9). Let us give here only an interpolation expression for $E^{(4)}(r_s)$ that is valid for $r_s \leq 2$:

$$E^{(4)}(r_s) \approx -4.2r_s^2 + 0.2r_s^3 [10^{-3} \text{ Ry}]. \quad (5.13)$$

TABLE V.

Lattice	$\xi_n^{(4)}$	$\xi_{n'}^{(4)}$	$\xi_{n_0}^{(4)}$	$\xi^{(4)}$
	10^{-3} Ry			
FCC	0.134	0.118	-4.48	-4.23
BCC	0.125	0.090	-4.47	-4.25

6. DETERMINATION OF THE TAIL OF THE PERTURBATION SERIES. CONVERGENCE OF THE SERIES

An analysis of the results obtained above for $E^{(2)}$, $E^{(3)}$, and $E^{(4)}$ indicates that the first terms of the series (2.2) decrease with increasing n roughly like a power of the dimensionless parameter $4\pi e^2/K_{\text{min}}^2 \Omega_0 \epsilon_F \approx 0.11(2k_F/K_{\text{min}})^2 r_s$. This allows us *a priori* to estimate that $E^{(5)} \sim 10^{-3} r_s^3$ [Ry], and this quantity in the interval (3.2) is already smaller than (3.1). However, since we are interested in the result for $r_s \gtrsim 1$, there arises the question of the convergence of the series (2.2) and of the total estimate for its tail:

$$\mathcal{E}^{(3-\infty)} = \sum_{n=5}^{\infty} E^{(n)}.$$

As follows from the result of the preceding sections, the terms of the series with $n \geq 5$ can be considered in the approximation in which they are considered to be structure independent and with the neglect of the screening role of the electron-electron interaction. But in this case the use of the Wigner-Seitz method^[37] becomes adequate. The accuracy of this method, which was used to analyze metallic hydrogen in earlier papers (see Wigner and Huntington,^[3] Kronig,^[38] and March^[39]), is not sufficient for finding the total energy of metallic hydrogen, but it is quite reasonable for the purpose of estimating the behavior of the tail of the series (2.2). We used the Wigner-Seitz (W-S) method within the framework of Bardeen's improved scheme,^[40] which allows the determination of not only the value of the bottom, ϵ_0 , of the band, but also the effective electron mass, m^* , near $k=0$, and thereby the electron-gas energy in the parabolic-band approximation. The problem then reduces to that of solving the radial Schrödinger equation with a Coulomb potential for s and p waves.

A relatively simple procedure, developed for the solution of this problem, enabled us to determine ϵ_0 , m^* , and the total energy $E_{\text{W-S}}$ as a function of r_s for the entire domain of variation of this parameter. Leaving out the details of the calculation (they will be published separately), let us give here only the results essential to the analysis carried out in the present paper.

1. If we expand $E_{\text{W-S}}(r_s)$ in powers of r_s , then in the region $r_s < 2$ of interest to us the series converges well. The radius of convergence of the series is roughly equal to $r_s \sim 4.2$.

2. If we compare the coefficients attached to r_s^m for $m=0, 1, 2$ in this series with the corresponding coefficients $\xi^{(2)}$, $\xi^{(3)}$, and $\xi^{(4)}$ found respectively for $E^{(2)}$, $E^{(3)}$, and $E^{(4)}$ in the absence of screening (see Tables I and V), we can establish the fact that these quantities clearly correlate with each other. For a quantitative agreement it is necessary to decrease the coefficients of the series for $E_{\text{W-S}}$ by factors of 0.80–0.87.

3. For $r_s < 2$, the total value of all the terms of the series with $n \geq 5$ ($m \geq 3$) can be approximated with a relative error smaller than 1% (this also applies to the

pressure) by the expression

$$\mathcal{E}_{\text{W-S}}^{(3-\infty)} [\text{Ry}] \approx -0.98 \cdot 10^{-3} r_s^3 \left[1 + \frac{r_s (1+r_s/2.0)}{6.2 (1+r_s/4.2)} \right]. \quad (6.1)$$

The transition to the tail of the series (2.2) corresponds approximately to

$$\mathcal{E}^{(3-\infty)} \approx 0.84 \mathcal{E}_{\text{W-S}}^{(3-\infty)}, \quad (6.2)$$

where the numerical factor corresponds to the relation between the coefficients for $n=4$ ($m=2$) in the two series. From (6.1) and (6.2) we can infer that the sum of the entire tail of the series (2.2) with $n \geq 5$ in the interval (3.2) is less than (3.3), although it is comparable in magnitude.

7. THE VIBRATIONAL PART OF THE ENERGY

We have thus far considered only the static part (E_{st}) of the total energy (2.1). However, for such light particles as hydrogen the role of the vibrational contribution is quite important, and therefore a sufficient accuracy in the determination of E_{vib} should be secured. The magnitude of the vibrational energy in the density range (3.2) exceeds (3.3), and is ~ 0.015 – 0.035 Ry. It is significant here that in this density region the conduction-electron-mediated indirect interaction between the ions very drastically decreases E_{vib} (roughly by a factor of two), and any estimates of this quantity based on the computation of the energy of the zero-point vibrations of the ion lattice imbedded in a homogeneous electron gas lead to large errors in the determination of the total energy.

An especially large correction to the pressure is needed to allow for the vibrations. For $r_s = 1.45$, the quantity P_{vib} can constitute $\sim 20\%$ of the static part, P_{st} , of the pressure, decreasing to $\sim 6\%$ by the time $r_s = 1.05$. This is connected with the critical dependence of E_{vib} on r_s . It is, however, important that this dependence is dictated to a considerable degree by the contribution of the ion lattice and that this immediately reduces appreciably the possible errors in the determination of E_{vib} .

In Ref. 7, in the course of the determination of the vibrational energy in the harmonic approximation

$$E_{\text{vib}} = \frac{1}{2} \sum_{q,\alpha} \hbar \omega_\alpha(q) \quad (7.1)$$

the phonon spectrum was determined in a comparatively crude approximation based on the use of the elastic moduli. This led to an overestimation of the contribution from the longitudinal branch, and, hence, of $E_{\text{vib}}(r_s)$, as r_s was decreased.

In the present paper, bearing in mind the need to obtain results with a sufficiently high degree of accuracy, we undertook a direct determination of the phonon spectrum in the entire phase volume for all values of r_s . The integration over the Brillouin zone was performed, using a scheme developed in Ref. 41. In the dynamical matrix we took into account the indirect inter-ion inter-

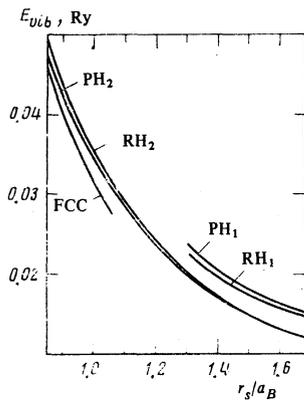


FIG. 4. The zero-point vibration energy, $E_{vib}(r_s)$, for different structures.

action corresponding not only to $E^{(2)}$, but also to $E^{(3)}$; The latter turned out to be quite important for the hydrogen problem.

In Fig. 4 we show the r_s dependence of E_{vib} found for the three optimal—for $r_s \gtrsim 1$ —lattices: RH_2 , PH_2 , FCC, as well as for the PH_1 and RH_1 lattices (the designations are the same as in Ref. 7). The curve for the FCC lattice has been drawn only in the r_s region where this lattice is stable in the harmonic approximation. The results presented correspond to choosing the function $G(\mathbf{q})$ in (2.9) in the VS form.^[22]

In the case of the phonon spectrum the sensitivity to the choice of the screening is much higher than in the determination of the static indirect interaction, since now the behavior of $\epsilon(\mathbf{q})$ and $T(\mathbf{q})$ is important at small \mathbf{q} , and not only at $\mathbf{q}=\mathbf{K}$. However, consideration of the various types of screening leads to oscillations in the energy of the zero-point vibrations within limits not exceeding 2×10^{-3} Ry. In the interval (3.2), E_{vib} has practically the same value for the optimal anisotropic structures and can be described with a high degree of accuracy by the following interpolation relation:

$$E_{vib}(r_s) \approx \frac{0.060}{r_s^2} - \frac{0.021}{r_s^3} - 0.001r_s^{1/2}. \quad (7.2)$$

For the FCC lattice the results for $r_s \lesssim 1$ can be represented by the following interpolation formula with asymptotically exact first two terms:

$$E_{vib}(r_s) = \frac{0.062}{r_s^2} - \frac{0.046}{r_s^3} + 0.027 - 0.011r_s^{1/2}. \quad (7.3)$$

Notice the closeness of the coefficients in the first terms of the representations (7.2) and (7.3), which, apparently, is not accidental, for the RH lattice goes over into the FCC lattice as $r_s \rightarrow 0$. Let us note that the obtained dependence $E_{vib}(r_s)$, (7.3), turned out to be relatively close to the dependence that was found by Caron.^[42]

Because of the large magnitude of P_{vib} , the difference in character of the screening introduces an appreciable uncertainty into the value of the total pressure P . Thus, as a fraction of the vibrational pressure obtained from (7.2) for the same family of $G(\mathbf{q})$ functions, this uncertainty is

$$\delta P_{vib}/P_{vib} \approx 0.12 \text{ for } r_s = 1.45, \quad \delta P_{vib}/P_{vib} \approx 0.03 \text{ for } r_s = 1.05. \quad (7.4)$$

8. THE THERMODYNAMIC POTENTIAL AND THE EQUATION OF STATE OF THE METALLIC PHASE OF HYDROGEN

The results obtained in the preceding sections allow us to determine the total energy E , (2.1), of the metallic phase, find the equation of state, and compute the thermodynamic potential at $T=0$

$$\Phi(P) = E + P\Omega \quad (8.1)$$

for the various crystal structures. If we analyze the density region $r_s \lesssim 1.05$, where the FCC lattice is stable in the harmonic approximation, then it turns out that the optimal anisotropic structures and the FCC structure have very close thermodynamic potentials, the uncertainty here being much smaller than (3.3). (It should be noted that the uncertainty, $\delta\Phi$, in the thermodynamic potential for fixed P is equal to the uncertainty, δE , in the energy for fixed Ω .) Caron^[42] and Straus and Ashcroft in a just published note^[43] assert that the allowance for the anharmonicity in the simplest self-consistent phonon model leads to the re-establishment of stability in the FCC lattice in the density range (3.2). If, not discussing the authenticity of this assertion as applied to the case when full allowance is made for the anharmonicity, we use Caron's result for E_{vib} in the FCC lattice^[42] or extrapolate (7.3) into the region (3.2) (this gives nearly the same result, for allowance for the anharmonicity can activate the low-frequency modes, but will change the energy of the stable phonons in the main part of phase space very little),^[44] then again the difference between the thermodynamic potentials for the various structures (FCC and others) turns out to be smaller than (3.3). A similar result is contained in Ref. 43, where the FCC- and the anisotropic-FCT-lattice energies with allowance for only $E^{(2)}$, but with the anharmonicity taken into account,³⁾ are compared at the point $r_s = 1.36$.

Thus, bearing in mind the uncertainty (3.3), we cannot, in the interval (3.2), distinguish between the thermodynamic potentials pertaining to the minimal—in energy terms—competing structures.

In Fig. 5 we have plotted the found dependence $\Phi(P)$ (the curve 1) and have specified the corridor (the cross-hatched region) in which the true $\Phi(P)$ curve may lie. As is clear from the above-performed analysis, this corridor is dictated by the uncertainty, (3.3), in the value of the correlation energy, an uncertainty which is clearly greater than all the errors connected with the determination of the individual contributions to the energy. In determining the energy, for $E^{(0)}$ we used the value of ϵ_c found by Vashishta and Singwi,^[22] the terms E_i , $E^{(2)}$, $E^{(3)}$, and E_{vib} were found for one and the same structure (for definiteness, the RH_2 structure), using everywhere the function $G(\mathbf{q})$ given in Ref. 22, $E^{(4)}$ was found in accordance with (5.13), while the tail of the series was computed in accordance with (6.1) and (6.2). An analysis of the results shows that, for the structure-

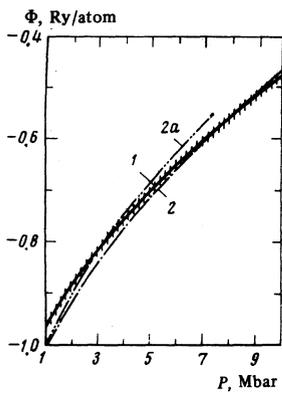


FIG. 5. The thermodynamic potential, $\Phi(P)$, of hydrogen: curve 1) result of the present investigation for the metallic phase (the vertical strokes indicate the scale of the uncertainty in the $\Phi(P)$ values), 2) the thermodynamic potential of the molecular phase, reconstructed from the zero isotherm of Ref. 1 with the use of the formula (9.1); the curve 2a is a plot of $\Phi(P)$ also reconstructed with the aid of (9.1), but from the experimental zero isotherm^[11] drawn through the upper limits of the density-measurement errors (on the side of lower densities (see Fig. 6)) at the points of the isentrope with the thermal contribution subtracted.

dependent part of $E_{s,2}$, we can write, with an error certainly smaller than (3.3), the following approximate representation ($0 < r_s \leq 1.5$):

$$E_s + E^{(2)} + E^{(3)} + E^{(4)} = -1.792r_s^{-1} - 0.091 - 0.020r_s - 0.008r_s^2. \quad (8.2)$$

The first two terms in this expression give the correct asymptotic form for $r_s \rightarrow 0$ (see Table I). For E_{vib} we have the formula (7.2).

It should be especially noted that, since the value of the phase transition pressure is very sensitive to the shape of the $\Phi(P)$ curve (see the following section), the contribution to the thermodynamic potential from $E^{(4)}$ and the tail of the series with $n \geq 5$ turns out to be important.

Notice that the uncertainty in the determination of the total energy without ϵ_c is several times smaller than (3.3), and therefore if Vashishta and Singwi's result for $\epsilon_c(r_s)$ ^[22] differs from the true dependence by a quantity appreciably less than (3.3), which is quite possible (see Sec. 3), then the found value of Φ actually possesses a greater accuracy than is indicated in Fig. 5.

In Fig. 6 we have plotted the equation of state of metallic hydrogen, $P(\Omega_0)$, or, more exactly, the inverse dependence $\Omega_0(P)$ (the curve 1).

On the basis of an analysis of the results obtained in the preceding sections, we can come to the conclusion that the main error in the determination of the total pressure is connected with the limited accuracy attained in the determination of P_{vib} and P_c . It follows from (3.4), (7.2), and (7.4) that, for $r_s \sim 1.45$, when the total pressure $P \sim 1$ Mbar, this error may constitute $\sim 4\%$. As the pressure increases, the relative error decreases and, at $r_s \sim 1.05$ ($P \sim 10$ Mbar), constitutes just 0.5%. The absolute error in this interval varies little, and does not exceed 50 kbar.

Notice that the $\Phi(P)$ and $\Omega_0(P)$ curves can be easily continued into the region of higher pressures if we use the above-obtained relations, whose accuracy increases with increasing pressure.

It must be emphasized that the thermodynamic potential and the equation of state of metallic hydrogen in the megabar region have thus been established with quite a high degree of accuracy. *To actually raise the accuracy in the determination of $\Phi(P)$ will be possible only after significant progress, guaranteeing the determination of the correlation energy with a high and estimable accuracy, has been made in the theory of electron liquid with intermediate r_s values.*

9. THE MOLECULAR PHASE. THE PHASE TRANSITION AND THE EXPERIMENTAL RESULTS

As has already been noted in the Introduction, in contrast to the metallic phase, the equation of state and the thermodynamic potential of molecular hydrogen at high densities cannot be reliably established at present on the basis of purely theoretical considerations. The only judicious course is to use, even if partially, the experimental data.

The first such attempt was made by Trubitsyn,^[11] who introduced a simple analytic representation for the short-range and long-range parts of the intermolecular interaction and determined the free coefficients in this representation by comparing with Stewart's data^[14] on $\Omega_0(P)$ measurement for solid molecular hydrogen. The dashed curve (the curve 3) in Fig. 6 is the $\Omega_0(P)$ curve obtained by Trubitsyn for $T = 0$. However, the megabar-pressure region where the phase transition occurs is too remote for Trubitsyn's curves to be extrapolated there, since Stewart's results are restricted to an in-

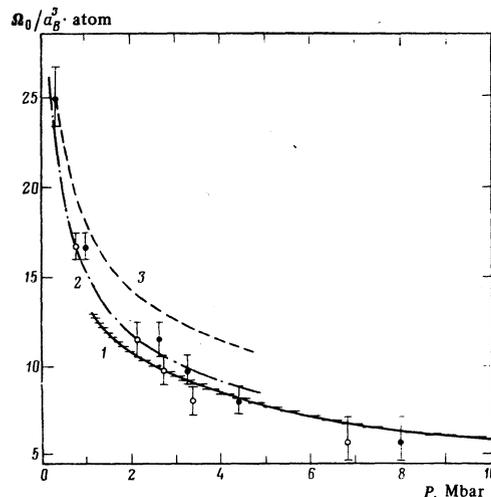


FIG. 6. Equation of state of hydrogen $P(\Omega_0)$: 1) the metallic phase's zero isotherm found in the present work (the horizontal strokes indicate the scale of the uncertainty in the theoretical equation of state), 2) the zero isotherm of the molecular phase from the experiment by Grigor'ev, Kormer, *et al.*,^[11] 3) the zero isotherm of the molecular phase, computed by Trubitsyn.^[11] The dark circles are points, taken from Ref. 1, of the isentrope of hydrogen; the light circles are points of the isentrope^[11] with the thermal contribution subtracted.

terval of only 20 kbar (the measurement region was recently extended to 25 kbar^[15]), and the very nature of the intermolecular interaction may change appreciably when the density is substantially increased further.

Attempts were later made to go outside the pressure range investigated by Stewart, using the methods of shock compression. Van Thiel and Alder^[12] have experimentally obtained a solitary density value corresponding to a pressure ~ 40 kbar, while results have comparatively recently been published^[16] of molecular-deuterium density measurements performed at two pressures: ~ 200 and ~ 800 – 900 kbar.

On the basis of these experimental data, including Stewart's results, Ross^[10] made an attempt to determine more accurately the equation of state of molecular hydrogen right up to pressures of 1 Mbar. In doing this he used the same functional representation for the pair potential of the intermolecular interaction used by Trubitsyn, considering the equation of state of the molecular phase within the framework of some liquid model (for greater details, see Ref. 10).

To describe simultaneously both the results of the shock experiments, which contain quite large errors, and those of Stewart's experiments, Ross was forced to consider a certain family of pair intermolecular potentials. The equations of state determined with the aid of these potentials reproduce with varying degrees of accuracy the low- and high-pressure experimental results. Some of these equations of state are quite close to Trubitsyn's curve. Others depict an appreciably "softer" behavior of the zero isotherms, so that the use of these equations in the megabar pressure region should lead to significantly higher values for the critical pressure of the transition of molecular hydrogen into the metallic phase. As the lower bound of the magnitude of the transition pressure, Ross gives the value 2.2 Mbar, whereas one of the family of equations of state obtained by him gives a transition pressure ~ 20 Mbar. Thus, the analysis based on the use of the results of the shock experiments did not, in fact, lead to any significant progress in the determination of the equation of state of molecular hydrogen and in the estimation of the transition pressure.

The first direct measurement of the equation of state of hydrogen in the megabar pressure region was carried out by Grigor'ev, Kormer, *et al.*,^[1] at pressures ranging up to 8 Mbar. This was accomplished in an explosion experiment in the quasi-adiabatic regime, which ensured relatively minimal warming up of the material. In Fig. 6 we show a plot of the experimentally obtained points (designated by dark circles) and the same points after recalculating the pressure to correspond to $T=0$ (light circles) in accordance with the data given in Ref. 1. It can be seen that the points for $P > 3$ Mbar lie on a curve with an appreciably smaller slope, and this allowed the authors to suggest that there occurs a phase transition into the metallic state at $P_t \sim 3$ Mbar. Using the data for $P \leq 3$ Mbar, the authors found the equation of hydrogen at $T=0$. The dot-dash curve (the curve 2) in Fig. 6 is a plot of this equation of state.

The availability of an experimentally determined zero isotherm allows the direct determination of the thermodynamic potential of the molecular phase of hydrogen with the aid of the usual relation

$$\Phi_{T=0}(P) = \Phi_{T=0}(0) + \int_0^P \Omega_0(P) dP. \quad (9.1)$$

The thus-found thermodynamic potential has been plotted in Fig. 5 (the dot-dash curve, i. e., the curve 2) with allowance for the fact that $\Phi_{T=0}(0) = -1.1645$.^[45]

As can be seen from Fig. 6, the experimental equation of state for the molecular phase turned out to be appreciably "softer" than Trubitsyn's extrapolation curve (the curve 3). A consequence of this is a shift in the transition pressure toward the region of higher P in Fig. 5. Taking into consideration the above-found accuracy in the determination of the thermodynamic potential, $\Phi(P)$, of the metallic phase, we find for the transition pressure the value $P_t \sim 8 \pm 2$ Mbar. The inclusion of the experimental points for $P > 3$ Mbar in the determination of the equation of state of the molecular phase would only further increase the transition pressure. On the face of it, this result indicates an inherent inconsistency in the experimental data, since the experimentally determined equation of state of the molecular phase leads to a value for P_t significantly exceeding the value of 3 Mbar, in the vicinity of which an anomaly was found in the $\Omega_0(P)$ curve.

If, however, we direct our attention to Fig. 6, then it is easy to observe that the experimental points for $P > 3$ Mbar lie below, though on a curve parallel to, the theoretical curve. Since it is difficult to imagine the existence of a phase denser than the metallic phase, this compels us to suppose that some systematic overestimation of the density occurred in the experiment. And, indeed, it is sufficient to shift all the experimental points to the upper error boundary (see Fig. 6) to get the points for $P > 3$ Mbar to lie on the theoretical curve for the metallic phase and the resulting thermodynamic potential of the molecular phase (the curve 2a in Fig. 5) to intersect Φ_{met} at $P_t \sim 3$ Mbar (the corridor boundaries contribute ± 1 Mbar). In consequence, we can, in so doing, re-establish the intrinsic consistency of the experimental data.

The independent agreement between the theory and experiment for the behavior of the equation of state in the metallic-phase region on the one hand, and the value of the transition pressure on the other, compels us to think that the anomaly recorded in Ref. 1 apparently corresponds to a transition into the metallic state, with the transition pressure lying near $P_t \sim 3$ Mbar. However, a more reliable judgment can be made only after an experimental verification of the suggestion that some systematic overestimation of the density exists in the published data.

¹Here and below energies are given in rydbergs per atom.

²Or the volume range per atom: $5a_B^3 \leq \Omega_0 \leq 13a_B^3$ (a_B is the Bohr radius).

- ³The assertion made in Ref. 43 that the conventional self-consistent procedure for taking the ion vibrations into account when we go outside the limits of the harmonic approximation leads to the result that E^3 does not play a role is erroneous. We can easily convince ourselves of this right away if we remember that the zero-point vibration energy, which, for $\nu_s = 1.36$, is equal to 0.017 Ry, is determined more accurately within the framework of this procedure ($\langle u^2 \rangle / a^2 \sim 0.03$, according to the estimate in Ref. 43, whereas $|E^{(3)}| \sim 0.03$ Ry (see Table I)).
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