Atomic crystalline phase of hydrogen

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The "first principles" approach is used to calculate the energy of the ground state of a hypothetic phase of solid atomic hydrogen as a function of its density in fcc and bcc lattices, ignoring the zero-point vibrations. The Wannier function representation is used. A combination of a variational procedure with perturbation theory based on a small overlap integral of the wave functions is employed in direct calculations. The ground-state energy is composed of the Hartree energy, direct exchange energy, indirect exchange energy associated with virtual transitions, and van der Waals-type energy. It is found that: 1) the hypothetic phase has the antiferromagnetic order; 2) it is an insulator stable against evaporation of atomic hydrogen; 3) at higher densities the insulator undergoes a transition to a state with metallic conduction.

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1. INTRODUCTION

We shall use the "first principles" approach to analyse a hypothetic phase of solid atomic hydrogen. Our prime task will be to determine the ground-state energy of the system as a function of the density within the framework of the exact microscopic Hamiltonian of the problem. This approach seems to be very attractive for several reasons. Firstly, it makes it possible to analyze the existence of a metastable crystalline phase of atomic hydrogen. Secondly, it provides a unique opportunity to use the same Hamiltonian in following phase transitions from an atomic crystal to an ionic one, and from an insulator to a metal. Thirdly, and this is the important point, an analysis of the atomic phase makes it possible to approach the problem of metallic hydrogen from the limit of narrow energy bands. We recall that until now the furthest advance in analysis of the metallic phase of hydrogen has been made by an approach corresponding effectively to the opposite limit of wide energy bands (see, for example, Refs. 1–3). It follows that the solution of the problem in question will make it possible to obtain a series of qualitative and sometimes quantitative results. The present paper is the first step in this direction.

We shall confine our treatment to relatively low densities, when the overlap of the electron wave functions of neighboring atoms is small. In this case the Hamiltonian of electrons in the static field of protons can be conveniently subjected to second quantization in the Wannier function representation. In the zeroth approximation, the ground state of our crystal is a state with one electron per atom. As the atomic separation decreases, the ground-state energy becomes the result of competition between reduction in the energy due to virtual transitions of electrons to excited atomic states or to neighboring sites and the obvious increase in the local part of the energy because of the reduction in the atomic volume. The net result depends on the spin configuration and this makes it possible to solve simultaneously the nature of spin ordering corresponding to minimum energy.

It should be noted that in the intermediate state the problem reduces essentially to an effective Hubbard-type Hamiltonian with very definite quantitative values of the relevant matrix elements. This makes it possible to use, in particular, the methods developed earlier for the Hubbard model.

Allowance for virtual transitions leads in a natural manner to the appearance of states with two electrons per site. The energy of such states is equal to the difference between the energy of the virtual repulsion and the energy of the attraction between an extra electron and a hole at a neighboring site. As the atomic distance decreases, the probability of such transitions increases and this eventually favors a phase transition from an atomic crystal either to a metallic state or to an ionic crystal, formed by the H^- ions and protons. This leads in a natural manner to the interesting problem of the relationship between two dielectric and one metallic phases and the hierarchy of phase transitions.

The problem under discussion is of general importance. In particular, the analysis developed in the present paper for crystalline hydrogen can easily be extended to hydride systems of the LiH type.

We shall determine the ground-state energy by a variational procedure within the framework of second quantization in the Wannier function representation. This makes it possible to go effectively beyond the limits of the Hartree–Fock approximation, which is usually employed in applications of the variational method to many-particle problems.

2. VARIATIONAL METHOD

The Hamiltonian of the system for an atomic phase considered in the Wannier function representation is

$$\begin{aligned}\hat{H}= & \sum \hat{a}^{+}_{\mathbf{R}_1\alpha_1}\hat{a}_{\mathbf{R}_2\alpha_2}\langle \mathbf{R}_1\alpha_1|\hat{h}|\mathbf{R}_2\alpha_2\rangle \\ & +\frac{1}{2}\sum \hat{a}^{+}_{\mathbf{R}_1\alpha_1}\hat{a}^{+}_{\mathbf{R}_2\alpha_2}\hat{a}_{\mathbf{R}_3\alpha_3}\hat{a}_{\mathbf{R}_4\alpha_4}\left\langle \mathbf{R}_1\alpha_1, \mathbf{R}_2\alpha_2 \left|\frac{1}{r_{12}}\right| \mathbf{R}_3\alpha_3, \mathbf{R}_4\alpha_4\right\rangle \\ & -\frac{1}{2}\sum{}' \frac{1}{|\mathbf{R}_1-\mathbf{R}_2|};\end{aligned} \tag{2.1}$$

$$\hat{h}=\frac{\hat{p}^2}{2m}-\sum\frac{1}{|\mathbf{r}-\mathbf{R}|}+\sum{}'\frac{1}{|\mathbf{R}|},$$

$$\left\langle a, b\left|\frac{1}{r_{12}}\right| c, d\right\rangle=\int d\mathbf{r}_1\, d\mathbf{r}_2\,\Psi_a{}^{+}(\mathbf{r}_1)\,\Psi_b{}^{+}(\mathbf{r}_2)\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}\Psi_c(\mathbf{r}_2)\,\Psi_d(\mathbf{r}_1).$$

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In this expression R is the coordinate of a site; α denotes the number of a given level (band) and also the spin index of an electron. We shall use atomic units ($e = m = \hbar = 1$) throughout. It should be pointed out that, strictly speaking, we are using the site (Wannier) representation and the functions $|\mathbf{R}\alpha\rangle$ can be any completely orthonormalized system of functions localized near crystal lattice sites.

The Hamiltonian (2.1) is supplemented explicitly by terms describing the Coulomb interaction between protons in the lattice. This makes it possible, on the one hand, to remove the usual Coulomb divergences and, on the other, to ensure that the eigenvalues of the Hamiltonian (2.1) represent the total energy of a crystal with a rigid ionic lattice.

It is convenient to rewrite the Hamiltonian (2.1) in the form

$$\hat{H}=\hat{H}_0+\hat{V},$$

separating clearly the part which is diagonal in respect of the occupation numbers $n_{\mathbf{R}\alpha}$ and to find the Hartree–Fock energy:

$$\begin{aligned}\hat{H}_0=&\sum_{\mathbf{R}\alpha}\hat{n}_{\mathbf{R}\alpha}\langle\mathbf{R}\alpha|\hat{h}|\mathbf{R}\alpha\rangle\\&+\frac{1}{2}\sum_{\alpha_1\neq\alpha_2}\hat{n}_{\mathbf{R}\alpha_1}\hat{n}_{\mathbf{R}\alpha_2}\left(\left\langle\mathbf{R}\alpha_1,\mathbf{R}\alpha_2\left|\frac{1}{r_{12}}\right|\mathbf{R}\alpha_2,\mathbf{R}\alpha_1\right\rangle\right.\\&\left.-\left\langle\mathbf{R}\alpha_1,\mathbf{R}\alpha_2\left|\frac{1}{r_{12}}\right|\mathbf{R}\alpha_1,\mathbf{R}\alpha_2\right\rangle\right)\\&+\frac{1}{2}\sum_{\mathbf{R}_1\neq\mathbf{R}_2}\hat{n}_{\mathbf{R}_1\alpha_1}\hat{n}_{\mathbf{R}_2\alpha_2}\left(\left\langle\mathbf{R}_1\alpha_1,\mathbf{R}_2\alpha_2\left|\frac{1}{r}\right|\mathbf{R}_2\alpha_2,\mathbf{R}_1\alpha_1\right\rangle\right.\\&\left.-\left\langle\mathbf{R}_1\alpha_1,\mathbf{R}_2\alpha_2\left|\frac{1}{r_{12}}\right|\mathbf{R}_1\alpha_1,\mathbf{R}_2\alpha_2\right\rangle\right)-\frac{1}{2}\sum_{\mathbf{R}_1\neq\mathbf{R}_2}{}'\frac{1}{|\mathbf{R}_1-\mathbf{R}_2|}\,.\end{aligned}\tag{2.2}$$

The variational method seems to be the most suitable for finding the ground-state energy of an insulating low-density phase. A certain minimum precision is needed in applications of the variational procedure to a many-particle problem because otherwise macroscopically diverging terms may appear. Bearing this point in mind, we shall write down the variational function in the form

$$\Psi=\exp(-i\tilde{A})\Psi_0,\quad \tilde{A}=\hat{P}\hat{A}\hat{P}.\tag{2.3}$$

Here, Ψ_0 is one of the eigenfunctions of the operator (2.2) which has to be selected from physical considerations as the closest to the expected ground state of the total Hamiltonian (2.1).

The Hermitian operator $\hat{A}$ and the projection operator $\hat{P}$ identify a class of functions which are included in the variational procedure. Both the type of the operator $\hat{A}$ and the function Ψ_0 are varied. In particular, variation of the function Ψ_0 in respect of the spin configuration determines the optimal magnetic structure. The approximate ground-state energy is defined as the minimum of the functional

$$E=\frac{\langle\Psi|\hat{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle}=\frac{\langle\Psi_0|\exp(i\tilde{A})\tilde{H}\exp(-i\tilde{A})|\Psi_0\rangle}{\langle\Psi_0|\Psi_0\rangle}.\tag{2.4}$$

In the case of the reduced Hamiltonian

$$\tilde{H}=\hat{P}\hat{H}\hat{P}=\tilde{H}_0+\tilde{V}\tag{2.5}$$

the subspace $\{\hat{P}\Psi\}$ of the total space $\{\Psi\}$ forms a complete system of functions. Therefore, an extremal value of the functional (2.4) corresponds to a selection of the operator $\exp(-i\hat{A})$ in the form of an S matrix defined relative to the Hamiltonian (2.5). Then, determination of the minimum of the functional (2.4) reduces effectively to calculation of the ground-state energy of a system described by the reduced Hamiltonian (2.5). This energy can be calculated employing familiar methods in the theory of many-particle systems.

Retaining the Wannier (site) representation, we can represent the operator $\tilde{V}$ as a sum of two operators:

$$\tilde{V}=\hat{K}+\hat{L}\tag{2.6}$$

The operator $\hat{K}$ is responsible only for intrasite transitions in which only atomic states are excited, whereas the operator $\hat{L}$ determines nonzero matrix elements if at least one of the electrons jumps from one site to another. Then, if we seek the eigenvalues of the reduced Hamiltonian (2.5) corresponding to a fixed spin configuration (for $\tilde{V}=0$) in the form of a perturbation theory series

$$E=E_0+\sum_n\frac{\langle\Psi_0|\tilde{V}|\Psi_n\rangle\langle\Psi_n|\tilde{V}|\Psi_0\rangle}{E_0-E_n}+\ldots,\tag{2.7}$$

we find that the series converges rapidly. In fact, the matrix elements of the operator $\hat{L}$ contain at least one small overlap integral between the site wave functions. On the other hand, for long distances between the atoms the matrix elements of the operator $\hat{K}$ responsible for the multipole interaction are, as usual, small. A direct quantitative analysis shows that the net result in the $r_s \gtrsim 2$ case is that only terms up to the second order need be retained in the expansion (2.7) and that in all the calculations, including determination of E_0, terms up to the second order in the overlap integral have to be retained.

Naturally, the rigorous variational procedure demands variation of the total expression (2.7). However, we can easily show that inclusion of higher terms of the series (2.7) results in just small corrections to the energy and to the values of the variational parameters: these corrections are of the order of the cube of the overlap integral and of the third order in $\hat{K}$. Naturally, the self-consistency of the whole calculation procedure requires a lower limit on the permissible values of r_s.

3. COVALENT PHASE

The most obvious quasiequilibrium state of crystalline atomic hydrogen is the covalent phase formed by a lattice of neutral atoms. We shall investigate this phase selecting Ψ_0 in Eq. (2.3) as the wave function in which unity is assigned to all the occupation numbers corresponding to lower electron states of atoms at all sites with some fixed spin configuration. This function is the eigenfunction of the Hamiltonian (2.2) with the eigenvalue

$$E_0=N\mathscr{E}_0-\sum_{\mathbf{R}_1\neq\mathbf{R}_2}A(\mathbf{R}_1-\mathbf{R}_2)\left\langle\Psi_0\left|\hat{\mathbf{S}}_{\mathbf{R}_1}\hat{\mathbf{S}}_{\mathbf{R}_2}+\frac{1}{4}\right|\Psi_0\right\rangle,\tag{3.1}$$

$$\mathscr{E}_0=\langle 0|\hat{h}|0\rangle+\frac{1}{2}\sum{}'\left(U_R-\frac{1}{|\mathbf{R}|}\right),\tag{3.1a}$$

$$A(\mathbf{R}_1-\mathbf{R}_2)=\left\langle \mathbf{R}_1,\mathbf{R}_2\left|\frac{1}{r_{12}}\right|\mathbf{R}_1,\mathbf{R}_2\right\rangle,\quad U_R=\left\langle 0,\mathbf{R}\left|\frac{1}{r_{12}}\right|\mathbf{R},0\right\rangle. \tag{3.1b}$$

Here and later, we shall simplify the notation by adopting $|\mathbf{R}\rangle$ for the orbital part of the Wannier function in a lower 1*s*-type state; N is the number of sites which is naturally identical with the total number of electrons; the exchange interaction energy is expressed in a standard way in terms of the spin operators at the sites $\hat{\mathbf{S}}_{\mathbf{R}}$.

The subspace of the functions selected by the projection operator $\hat{P}$ will be taken to be the set of functions obtained from Ψ_0 if at some sites an atom with one electron and a wave function $|\mathbf{R}\rangle$ is replaced either with: 1) an atom with one electron in the first odd state (of the 2*p* type) or 2) a negative ion with two electrons of opposite spins in the state $|\mathbf{R}\rangle$ or 3) a negative ion with one electron in the state $|\mathbf{R}\rangle$ and the other in $|\mathbf{R}m\rangle$ or, finally, 4) a positive ion without electrons. We do not include in the subspace the variable functions of the state which differs from Ψ_0 only by spin configuration.

The operator $\hat{K}$ of Eq. (2.6) contains all the terms of (2.1) which are nondiagonal in respect of the occupation numbers and for which there is no change of electrons at energy site:

$$\begin{aligned}\hat{K}=&\sum{}' \hat{a}^{+}_{\mathbf{R}\alpha_1}\hat{a}_{\mathbf{R}\alpha_2}\langle \mathbf{R}\alpha_1|\hat{h}|\mathbf{R}\alpha_2\rangle\\ &+\frac{1}{2}\sum{}' \hat{a}^{+}_{\mathbf{R}\alpha_1}\hat{a}^{+}_{\mathbf{R}\alpha_2}\hat{a}_{\mathbf{R}\alpha_3}\hat{a}_{\mathbf{R}\alpha_4}\left\langle \mathbf{R}\alpha_1,\mathbf{R}\alpha_2\left|\frac{1}{r_{12}}\right|\mathbf{R}\alpha_3,\mathbf{R}\alpha_4\right\rangle\\ &+\frac{1}{2}\sum_{\mathbf{R}_1\neq\mathbf{R}_2}{}' \hat{a}^{\pm}_{\mathbf{R}_1\alpha_1}\hat{a}^{+}_{\mathbf{R}_2\alpha_2}\hat{a}_{\mathbf{R}_2\alpha_3}\hat{a}_{\mathbf{R}_1\alpha_4}\left[\left\langle \mathbf{R}_1\alpha_1,\mathbf{R}_2\alpha_2\left|\frac{1}{r_{12}}\right|\mathbf{R}_2\alpha_3,\mathbf{R}_1\alpha_4\right\rangle\right.\\ &\left.-\left\langle \mathbf{R}_1\alpha_1,\mathbf{R}_2\alpha_2\left|\frac{1}{r_{12}}\right|\mathbf{R}_1\alpha_4,\mathbf{R}_2\alpha_3\right\rangle\right].\end{aligned} \tag{3.2}$$

The primed sums denote exclusion of the diagonal terms. If the Wannier functions are deduced from the Bloch eigenfunctions of the single-particle Hamiltonain $\hat{h}$ [see Eq. (2.1)], the first term in Eq. (3.2) vanishes. When the Wannier functions are selected with variable parameters, this term is in principle different from zero. However, if only the states of the opposite parity relative to the ground state are included in the excited state, then the first term in Eq. (3.2) again vanishes.

The second term in Eq. (3.2) makes no contribution to the energy (2.6) in the second order in $\tilde{V}$. The third term in Eq. (3.2) determines the van der Waals energy contribution to Eq. (2.6):

$$\left.\begin{aligned}&E_{\mathrm{vdW}}=N\mathscr{E}_{\mathrm{vdW}};\\ &\mathscr{E}_{\mathrm{vdW}}=-\frac{1}{2}\sum{}'\frac{1}{\Delta E(0m_1,\mathbf{R}m_2)}\left\langle 0m_1,\mathbf{R}m_2\left|\frac{1}{r_{12}}\right|\mathbf{R},\mathrm{C}\right\rangle^2.\end{aligned}\right\} \tag{3.3}$$

Here, $|\mathbf{R}m\rangle$ is the odd Wannier function at a site R, which goes over to the hydrogenic 2*p* function ($L=1$, $L_2=m$) in the atomic limit. The denominator of Eq. (3.3) includes the change in the energy (2.2) due to excitation of two atoms and this energy consists of the energy of excitation of atoms and of the change in the Coulomb interaction of excited atoms with unexcited atoms and with one another.

The operator $\hat{L}$ in Eq. (2.6) represents transitions accompanied by a change in the electron number, i.e., those involving electron jumps from one site to another:

$$\hat{L}=\sum_{\mathbf{R}_1\neq\mathbf{R}_2}\hat{a}^{+}_{\mathbf{R}_2\sigma}\hat{a}_{\mathbf{R}_1\sigma}T_1(\mathbf{R}_2,\mathbf{R}_1)+\sum_{\mathbf{R}_1\neq\mathbf{R}_2}\hat{a}^{+}_{\mathbf{R}_2m\sigma}\hat{a}_{\mathbf{R}_1\sigma}T_{2,m}(\mathbf{R}_2,\mathbf{R}_1), \tag{3.4}$$

$$\begin{aligned}T_1(\mathbf{R}_2,\mathbf{R}_1)=&\langle \mathbf{R}_2|\hat{h}|\mathbf{R}_1\rangle+\sum_{\sigma';\mathbf{R}_3\neq\mathbf{R}_1,\mathbf{R}_2}\hat{n}_{\mathbf{R}_3\sigma'}\left\langle \mathbf{R}_2,\mathbf{R}_3\left|\frac{1}{r_{12}}\right|\mathbf{R}_3,\mathbf{R}_1\right\rangle\\ &+(\hat{n}_{\mathbf{R}_1-\sigma}+\hat{n}_{\mathbf{R}_2-\sigma})\left\langle \mathbf{R}_2,\mathbf{R}_1\left|\frac{1}{r_{12}}\right|\mathbf{R}_1,\mathbf{R}_1\right\rangle,\end{aligned} \tag{3.5}$$

$$\begin{aligned}T_{2,m}(\mathbf{R}_2,\mathbf{R}_1)=&\langle \mathbf{R}_2m|\hat{h}|\mathbf{R}_1\rangle+\sum_{\sigma';\mathbf{R}_3\neq\mathbf{R}_1,\mathbf{R}_2}\hat{n}_{\mathbf{R}_3\sigma'}\left\langle \mathbf{R}_2m,\mathbf{R}_3\left|\frac{1}{r}\right|\mathbf{R}_3,\mathbf{R}_1\right\rangle\\ &+\hat{n}_{\mathbf{R}_1-\sigma}\left\langle \mathbf{R}_2m,\mathbf{R}_1\left|\frac{1}{r_{12}}\right|\mathbf{R}_1,\mathbf{R}_1\right\rangle\\ &+\sum_{\sigma}\hat{n}_{\mathbf{R}_2\sigma}\left\langle \mathbf{R}_2m,\mathbf{R}_2\left|\frac{1}{r_{12}}\right|\mathbf{R}_2,\mathbf{R}_1\right\rangle\\ &+\sum_{m_1,\sigma}\hat{n}_{\mathbf{R}_1m_1\sigma}\left\langle \mathbf{R}_2m,\mathbf{R}_1m_1\left|\frac{1}{r_{12}}\right|\mathbf{R}_1m_1,\mathbf{R}_1\right\rangle\\ &+\sum_{m_2\neq m_1,\sigma}\hat{n}_{\mathbf{R}_2m_2\sigma}\left\langle \mathbf{R}_2m,\mathbf{R}_2m_2\left|\frac{1}{r_{12}}\right|\mathbf{R}_2m_2,\mathbf{R}_1\right\rangle\\ &+\sum_{\sigma_3;m_3;\mathbf{R}_3\neq\mathbf{R}_1,\mathbf{R}_2}\hat{n}_{\mathbf{R}_3m_3\sigma_3}\left\langle \mathbf{R}_2m,\mathbf{R}_3m_3\left|\frac{1}{r_{12}}\right|\mathbf{R}_3m_3,\mathbf{R}_1\right\rangle.\end{aligned} \tag{3.6}$$

Here, σ is the spin index of an electron. In the above expressions we have omitted the terms proportional to the matrix elements of the second order in respect of the overlap integral:

$$\left\langle 0,0\left|\frac{1}{r_{12}}\right|\mathbf{R}_1,\mathbf{R}_2\right\rangle,\quad\left\langle 0,\mathbf{R}_1\left|\frac{1}{r_{12}}\right|0,\mathbf{R}_2\right\rangle,\quad\left\langle 0,\mathbf{R}_1\left|\frac{1}{r_{12}}\right|\mathbf{R}_2,\mathbf{R}_3\right\rangle \tag{3.7}$$

(not all $\mathbf{R}_i$ are equal).

The contribution of electron jumps (3.4) to the energy (2.7) can be represented in the form

$$\begin{aligned}&E_L=N(\mathscr{E}_{j1}+\mathscr{E}_{j2}),\\ &\mathscr{E}_{j1}=\frac{2}{N}\sum_{\mathbf{R}_1\neq\mathbf{R}_2}\left\langle\Psi_0\left|\hat{\mathbf{S}}_{\mathbf{R}_1}\hat{\mathbf{S}}_{\mathbf{R}_2}-\frac{1}{4}\right|\Psi_0\right\rangle\frac{(T_i(\mathbf{R}_1,\mathbf{R}_2))^2}{\Delta E_1(\mathbf{R}_1-\mathbf{R}_2)}\\ &\mathscr{E}_{j2}=-\sum_{m,\mathbf{R}_1\neq\mathbf{R}_2}\frac{(T_{2,m}(\mathbf{R}_1,\mathbf{R}_2))^2}{\Delta E_{2,m}(\mathbf{R}_1-\mathbf{R}_2)}.\end{aligned} \tag{3.8}$$

The effective amplitudes of virtual jumps T_1 and T_2 in Eq. (3.5) can be calculated by assuming that

$$\sum_{\sigma'}n_{\mathbf{R}_3\sigma'}=1,\quad n_{\mathbf{R}_1-\sigma}+n_{\mathbf{R}_2-\sigma}=1, \tag{3.9}$$

and the corresponding assumption in Eq. (3.7) is

$$\left.\begin{aligned}&\sum_{\sigma'}n_{\mathbf{R}_3\sigma'}=1,\quad n_{\mathbf{R}_1-\sigma}=0,\quad\sum_{\sigma}n_{\mathbf{R}_2\sigma}=1,\\ &\sum_{m}n_{\mathbf{R}_1m\sigma}=\sum_{\sigma,m_2\neq m_1}n_{\mathbf{R}_2m_2\sigma}=\sum_{\sigma_3,m_3}n_{\mathbf{R}_3m_3\sigma_3}=0.\end{aligned}\right\} \tag{3.10}$$

The denominator of Eq. (3.8) contains the excitation energy of the polar states

$$\left.\begin{aligned}&\Delta E_1(\mathbf{R})=U_0-U_R,\\ &\Delta E_{2,m}(\mathbf{R})=\langle 0m|\hat{h}|0m\rangle-\langle 0|\hat{h}|0\rangle+U_0'-U_R'+\sum_{R_1}(U_{R_1}'-U_{R_1}),\end{aligned}\right\} \tag{3.11}$$

where

$$U_R=\left\langle 0,\mathbf{R}\left|\frac{1}{r_{12}}\right|\mathbf{R},0\right\rangle,\quad U_R'=\left\langle 0m,\mathbf{R}\left|\frac{1}{r_{12}}\right|\mathbf{R},0m\right\rangle.$$

We thus find that the energy of a crystal in the covalent phase is described approximately by the sum of Eqs.

(3.1), (3.3), and (3.8):

$$E=E_0+E_L+E_{\mathrm{vdW}}. \tag{3.12}$$

4. IONIC PHASE

Another possible metastable phase of atomic crystalline hydrogen is an ionic state which, in the zeroth approximation, consists of two sublattices, one of which is formed by the H^- ions (two electrons in the lower state of $|\mathbf{R}\rangle$ per site) and the second sublattice is formed by protons. The wave function Ψ_p characterized by such occupation numbers now behaves as Ψ_0 in the variational function (2.3). This function corresponds to the energy

$$\left.\begin{aligned} E_{0p}&=N\mathscr{E}_p,\\ \mathscr{E}_p&=\langle 0|\hat{h}|0\rangle+\frac{U_0}{2}-\frac{\alpha'}{2|\mathbf{g}|}+\sum_{\mathbf{R}_2}{}'\left(U_{\mathbf{R}_2}-\frac{1}{|\mathbf{R}_2|}\right).\end{aligned}\right\} \tag{4.1}$$

To be specific, we shall assume that the $\mathbf{R}=0$ site belongs to the H^- ion sublattice. Here, the second term is due to virtual repulsion of electrons. The third term is the standard electrostatic energy of an ionic crystal, where $\mathbf{g}$ is the distance between the nearest neighbors and α' is the Madelung constant. The last term in Eq. (4.1) is the correction for the extended nature of the Wannier electron functions. The summation in this term is carried out over a sublattice with two electrons per site, except at $\mathbf{R}_2=0$.

The operator $\hat{A}$, which defines a class of variable functions (2.3), is taken to be a jump operator of the type given by Eq. (3.4). Against the background of the Coulomb interactions in an ionic crystal we can ignore the van der Waals forces and ignore transitions described by Eq. (3.2).

As a result, the energy of an ionic crystal considered in the approximation adopted above is (per one site)

$$E_p=\mathscr{E}_p-\sum_{\mathbf{R}_1}{}'\frac{T_1(\mathbf{R}_1,0)^2}{\Delta E_{1,p}}-\sum_{m,\mathbf{R}_1}{}'\frac{(T_{2,m}(\mathbf{R}_1,0))^2}{\Delta E_{2,m,p}}, \tag{4.2}$$

where the summation is carried out over the positive ion sublattice. Here, the jump amplitudes T_1 and $T_{2,m}$ are given by Eqs. (3.5) and (3.6) where we have to assume, respectively,

$$n_{\mathbf{R}_2-\sigma}=0,\quad n_{\mathbf{R}_1-\sigma}=1,\quad \sum_{\sigma'}n_{\mathbf{R}_3\sigma'}=2 \quad\text{or}\quad 0 \tag{4.3}$$

and

$$\left.\begin{aligned}&\sum_{\sigma'}n_{\mathbf{R}_3\sigma'}=2\quad\text{or}\quad 0,\quad n_{\mathbf{R}_1-\sigma}=1,\quad \sum_{\sigma}n_{\mathbf{R}_2\sigma}=2\quad\text{or}\quad 0,\\ &\sum_{m_1}n_{\mathbf{R}_1m_1\sigma}=\sum_{\sigma,m_2\neq m_1}n_{\mathbf{R}_2m_2\sigma}=\sum_{\sigma_2,m_3}n_{\mathbf{R}_2m_3\sigma_2}=0.\end{aligned}\right\} \tag{4.4}$$

The value 2 clearly corresponds to the negative ion sublattice.

The denominators of the sum (4.2) over the coordinates of the positive ions closest to the origin include the excitation energy due to a jump of an electron from the origin to one of the sites $\mathbf{R}=\mathbf{g}$:

$$\left.\begin{aligned}\Delta E_{1,p}&=-U_0-U_g+\frac{2\alpha'}{|\mathbf{g}|}+2\sum_{\mathbf{R}_2}{}'(n_{\mathbf{R}_2}-1)\left(U_{\mathbf{R}_2}-\frac{1}{|\mathbf{R}_2|}\right),\\ \Delta E_{2,m,p}&=\langle 0m|\hat{h}|0m\rangle-\langle 0|\hat{h}|0\rangle-U_0-U_g'+\sum_{\mathbf{R}_2}{}'n_{\mathbf{R}_2}U_{\mathbf{R}_2}'-\sum_{\mathbf{R}_1}{}'n_{\mathbf{R}_1}U_{\mathbf{R}_1}.\end{aligned}\right\} \tag{4.5}$$

It is assumed here that the site $\mathbf{R}=0$ in the sum over $\mathbf{R}_2$ belongs to the proton lattice and the sum over $\mathbf{R}_1$ to the H^- ion lattice.

It is worth noting the following important point. In applying of the variational procedure to the ionic phase it is desirable to select different Wannier functions for the sites in the different sublattices. This makes it possible to allow more accurately for the electron energy of the negative ions, which is of fundamental importance in any quantitative comparisons of the energies of different phases.

We shall not give the results of calculations of the ionic phase energy. We shall simply note that in the range $g>3$ ($r_s>1.7$) the Hartree energy (4.1) of the ionic phase lies above the corresponding energy of the covalent phase. Attempts to allow for the second-order perturbation theory terms in Eq. (4.2) show that the range of validity of this formula is very limited, whereas for $r_s<1.7$ the amplitudes of T_1 and $T_{2,m}$ are large but for $r_s>1.7$ the excitation energy (4.5) begins to fall rapidly.

5. CALCULATION PROCEDURE

Explicit calculation of the energy of atomic crystalline hydrogen in the covalent or ionic phases must begin with writing down the Wannier function system. The most rigorous way of obtaining the system is to apply the Fourier transformation to the Bloch functions, which are the eigenfunctions of the single-particle Hamiltonian $\hat{h}$ [see Eq. (2.2)]. However, in the case of low densities and the correspondingly small overlap integrals it is simplest to construct a system of mutually orthogonal spatially localized functions directly from functions of the type

$$|\mathbf{R})=\frac{Z^{3/2}}{\sqrt{\pi}}\exp\{-Z|\mathbf{r}-\mathbf{R}|\},\quad |\mathbf{R}m)=Y_{1,m}(\theta,\varphi)\frac{(2Z')^{5/2}}{2\sqrt{6}}r\exp\{-Z'|\mathbf{r}-\mathbf{R}|\}. \tag{5.1}$$

We shall not include the remaining quasihydrogenic functions in the variational scheme. The effective charges Z and Z' are the best regarded as independent variational parameters. However, for simplicity, we shall assume the following dependence of Z' on Z and g:

$$Z'=g^{-1}(6+6Zg+Z^2g^2)^{1/2}. \tag{5.2}$$

For this selection of Z' the matrix element $(\mathbf{O}|\mathbf{g},m=0)$ has the simplest form.

In the ionic phase case we have, instead of Eq. (5.1), a double set of such functions for sites in both sublattices and, consequently, instead of Z, we have two variational parameters Z_+ and Z_-. It should be noted that for limited densities the value of Z_- should be close to $Z_-=11/16$, which is known[4] to be an extremal value in the problem of an isolated negative ion.

An approximate orthonormalized set composed of the functions (5.1) is

$$\left.\begin{aligned}|\mathbf{R}\rangle&=\left[1+\frac{3}{8}\nu(\mathbf{g}|0)^2\right]|\mathbf{R})-\frac{1}{2}\sum_{\mathbf{g}}(\mathbf{g}|0)\,|\mathbf{R}+\mathbf{g}),\\ |\mathbf{R}m\rangle&=\left[1+\frac{3}{8}\sum_{\mathbf{g}m_1}(\mathbf{g}m_1|0m)^2+\sum_{\mathbf{g}}(\mathbf{g}|0m)^2\right]|\mathbf{R}m)\\ &\quad-\frac{1}{2}\sum_{\mathbf{g}m_1}(\mathbf{g}m_1|0m)\,|(\mathbf{R}+\mathbf{g})m_1)-\sum_{\mathbf{g}}(\mathbf{g}|0m)\,|\mathbf{R}+\mathbf{g}),\end{aligned}\right\} \tag{5.3}$$

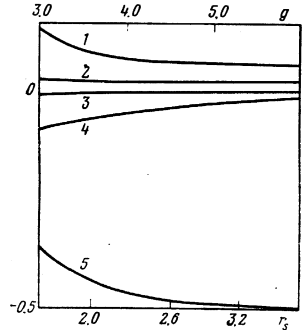

FIG. 1. Dependences of $\Delta E_{2,0}$(curve 1), ΔE_1(curve 2), $T_{2,0}$(curve 3), T_1(curve 4), and $\mathscr{E}_0$(curve 5) on the atomic distance in the bcc structure with $Z=1$ (atomic units).

where ν is the number of the nearest neighbors. The orthonormalization conditions for the nearest-neighbor functions are satisfied with an accuracy to $(\mathrm{O}|\mathrm{g})^2$ inclusive, whereas the orthogonality of the Wannier functions for the more distant neighbors is satisfied with an accuracy in excess of $(\mathrm{O}|\mathrm{g})$. This accuracy allows us to sum only over the nearest neighbors in the calculation of the energy contributions represented by Eqs. (3.1), (3.8), and (4.2).

It is worth noting that in the bcc phase the distance to the second coordination sphere g_2 is quite similar to the distance g to the nearest neighbors ($g_2=2g/\sqrt{3}$). The precision of the calculations of the total energy can be increased by including explicitly the contribution of the second coordination sphere retaining in all the calculations not only terms of the order of $(\mathrm{O}|\mathrm{g})^2$ but also of the order of $(\mathrm{O}|\mathrm{g}_2)^2$, inclusive. For example, for $r_s=2$ and the optimal value of Z we have the following for the bcc phase:

$$(0|\mathbf{g})^2=0.048,\quad (0|\mathbf{g}_2)^2=0.026,\quad (0|\mathbf{g}_3)^2=0.0016,$$

whereas for the fcc phase, we have

$$(0|\mathbf{g})^2=0.037,\quad (0|\mathbf{g}_2)^2=0.004,\quad (0|\mathbf{g}_3)^2=0.0006.$$

Hence, it follows that in the range of densities defined by $r_s\gtrsim 2$ the contribution of the first two coordination spheres is decisive.

Figure 1 shows the results of calculations of $\mathscr{E}_0$, ΔE_1, $\Delta E_{2,0}$, T_1, and $T_{2,0}$ as a function of the atomic distance in the bcc lattice with $Z=1$. Figure 2 gives the contributions to the total energy due to the direct exchange $\mathscr{E}_{\text{exch}}=-\nu A/2$ given by Eq. (3.1b), due to jumps $\mathscr{E}_{j1}=-\nu T_1^2/\Delta E_1$ and $\mathscr{E}_{j2}=-\nu T_{2,0}^2/\Delta E_{2,0}$ given by Eq. (3.8), and van der Waals interactions $\mathscr{E}_{\text{vdW}}$given by Eq. (3.3). The results show how the total energy of the atomic phase forms as a function of density. The results for the fcc lattice differ little from those for the bcc structure and, therefore, they are not given. It should be noted that the adopted approximations are less accurate for $r_s<2$. Therefore, the dependences in Figs. 1 and 2 can be regarded simply as estimates in the range $1.7<r_s<2$.

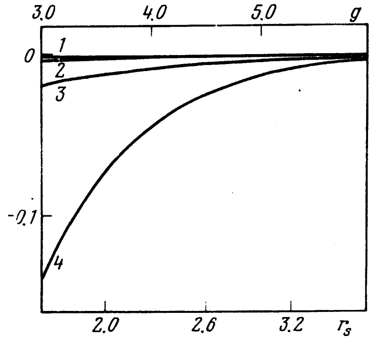

FIG. 2. Dependences of the contributions made to the total enerby by $\mathscr{E}_{j2}$ (curve 1), $\mathscr{E}_{\text{vdW}}$ (curve 2), $\mathscr{E}_{\text{exch}}$(curve 3), and $\mathscr{E}_{j1}$ (curve 4) on the atomic distance in the bcc structure with $Z=1$ (atomic units).

In the range of densities of interest to us an extremal value of the variational parameter Z does not differ greatly from unity and the behavior of the various quantities remains basically the same as shown in Figs. 1 and 2. Independent variation of Z' also has little effect on the final results.

6. ANALYSIS OF RESULTS

It is clear from Fig. 1 that the zeroth-approximation energy $\mathscr{E}_0$ of Eq. (3.1) decreases monotonically on increase in the atomic distance and, as expected, in the atomic limit it approaches the binding energy of a free hydrogen atom in the ground state $\mathscr{E}_0=-0.5$. The direct exchange energy A of Eq. (3.1) and the contribution of virtual jumps E_L of Eq. (3.8) are second-order quantities in the overlap integral $(\mathrm{O}|\mathrm{g})$ and they should be considered together. The contributions of these two quantities to the total energy depends on the spin ordering. We can easily see that

$$\sum_{\mathbf{g}}\langle\Psi_0|\hat{\mathrm{S}}_{\mathrm{R}}\hat{\mathrm{S}}_{\mathrm{R+g}}|\Psi_0\rangle={}^1/_4(\nu_+-\nu_-), \tag{6.1}$$

where ν_+ (ν_-) is the number of the nearest neighbors of the R site, which have the same (opposite) spin directions relative to R. The energy per site then becomes simply

$$\frac{E}{N}=\mathscr{E}_0-\frac{1}{2}\nu_+A(g)-\nu_-\frac{T_1^2(g)}{\Delta E_1(g)}-\nu\frac{T_{2.0}^2(g)}{\Delta E_{2.0}(g)}+\mathscr{E}_{\text{vdW}}\,. \tag{6.2}$$

It follows from the symmetry considerations that $T_{2,m=\pm1}\equiv0$ (the last term representing the contribution of the van der Waals energy will be discussed later).

It is clear from Eq. (6.2) that the direct exchange energy stimulates the ferromagnetic ordering, whereas the jump exchange energy of amplitude T_1 favors the antiferromagnetic order. It should be stressed that the separation of the exchange energy into direct and jump is quite arbitrary and it is determined by the selection of the Wannier representation. As pointed out already, the variational procedure used in the present study implies above all variation over the spin configuration. The results of our calculations show that throughout the investigated range of densities, when the distance between the nearest neighbors varies from 3 to infinity, the contribution of the jump exchange mechanism is considerably greater than the direct exchange in the bcc and fcc structures. Therefore, the energy minimum of the covalent phase corresponds to the antiferromagnetic spin order. This is true also when the optimal value of the variational parameter Z_{opt} is used. The bcc structure in the antiferromagnetic state is characterized by $\nu_+=0$ and $\nu_-=8$. The antiferromagnetic state in the fcc phase corresponds[5] to three spin configurations. In the

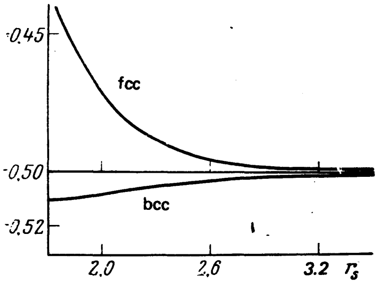

FIG. 3. Dependences of the total energy of covalent antiferromagnetic bcc and fcc structures on r_s (atomic units).

nearest-neighbor approximation two of these configurations have the same energy because for each of them we have $\nu_+ = 4$ and $\nu_- = 8$. The third structure is less favored by the energy considerations because it is characterized by $\nu_+ = \nu_1 = 6$. The contribution to (6.2) made by the jumps to excited states ($\mathcal{E}_{j2}$) is numerically very small (see Fig. 2).

The van der Waals energy of Eq. (3.3) is of the zeroth order in respect of the overlap integral and at very low densities of a crystal ($r_s > 4.5$) it decreases as β/g^6, where β is approximately half its nominal value $\beta_0 \approx 6.5$ (Ref. 6). In this limit the van der Waals energy predominates over the exchange terms which decrease as $(O|g)^2$. However, in the most interesting case of moderately low densities ($r_s < 4.5$) the numerical smallness of the matrix element of the dipole transition makes $\mathcal{E}_{vdW}$ much smaller than the direct exchange energy or the energy of jumps of amplitude T_1 (Fig. 2). Moreover, at these densities the law $1/g^6$ practically disappears because the dipole approximation is no longer valid. Consequently, a reduction in g results in a relatively slow rise of the van der Waals energy so that its contribution to the total energy (compared with the other mechanisms) decreases.

The values of the total energy given by Eq. (6.2) for the bcc and fcc covalent antiferromagnetic structures are plotted in Fig. 3. The curves given there allow for the contribution of the second coordination sphere and they are found retaining terms of the order $(O|g_2)^2$ inclusive and ignoring terms beginning from $(O|g)^3$. For each fixed atomic distance we varied the effective reciprocal radius of the atomic functions Z. These calculations show that Z_{opt} increases monotonically on reduction of r_s reaching, for example, $Z_{\text{opt}} \approx 1.07$ for $r_s = 2$ in the bcc phase. It follows from the results in Fig. 3 that throughout the range of densities of interest to us the bcc phase is energetically more favored and we shall concentrate on this phase alone.

We must particularly draw attention to the relatively weak variation of the total energy right down to relatively high densities in the range $r_s \sim 1.7$. A strong rise of the Hartree energy $\mathcal{E}_0$ (Fig. 1) on increase of the density is practically completely compensated by the energy of the virtual jumps $\mathcal{E}_{j1}$ (see Fig. 2). Since $\Delta E_1 = U_0 - U_g$ is practically constant in the range $r_s > 1.7$ (Fig. 1), the rise of $\mathcal{E}_{j1}$ is entirely due to an increase in the jump amplitude T_1. However, the rise of the same amplitude represents an increase in the degree of delocalization of electrons and the appearance of a "premetallic" situation. At high densities the electron–hole interaction U_g rises so as to overtake the interaction between electrons at one site U_0; this enhances the tendency to form the metallic phase. At high densities in the bcc and fcc structures the covalent phases are absolutely unstable, which is a consequence of vanishing of ΔE_1. In this range of densities the adopted approximations are known to be poor representations so that a reliable estimate of the critical density at which this happens is impossible.

However, the appearance of metallic conduction should really occur at much lower densities r_s. This can be demonstrated by noting that the problem is formally the same as that of the Hubbard Hamiltonian but with the antiferromagnetic spin order. Consequently, we can find the critical density r_s^c by methods used to detect the insulator–metal transition is systems described by the Hubbard Hamiltonian.

The simplest way of estimating the range where this transition occurs is to find the value of r_s^c at which the electron and hole bands of single-particle excitations begin to overlap. At high values of $g(r_s)$ these bands are separated by a gap which in our notation is denoted by U_0. On increase of the density the electron and hole energy bands become wider and their widths approach a value close to $2\nu_+ T_1(g)$, where ν_+ is the number of the nearest neighbors with the same spin direction and $T_1(g)$ is the amplitude of a jump given by Eq. (3.5) (see Fig. 1). We recall that in antiferromagnetic systems the translational transfer of excitations is due to jumps between a sublattice of sites with the same spin direction. Applying the Cyrot method,[7] we obtain the following criterion for the appearance of the overlap of the electron and hole bands in the fcc phase:

$$T_1(g)/U_0 \geqslant 0.1. \tag{6.3}$$

It follows directly from the above results that metallic conduction should appear in the fcc phase for

$$r_s^c \approx 1.7. \tag{6.4}$$

In the bcc case the appearance of metallic conduction may be associated with jumps to the second coordination sphere because we have $\nu_+ = 0$ for the nearest coordination sphere. Then, instead of Eq. (6.3), we have

$$T_1(g_2)/U_0 \geqslant 0.12. \tag{6.5}$$

The critical density r_s^c is now

$$r_s^c \approx 1.8. \tag{6.6}$$

It is interesting to note that the critical densities r_s^c of Eqs. (6.4) and (6.6) are close to the values corresponding to the minimum of the static energy of the metallic phase of hydrogen with structures of the same symmetry.[1,2] These values have been found earlier[1,2] by direct analysis of the metallic state within the framework of the many-particle formalism applying perturbation theory to the electron–ion interaction.

It is clear from Fig. 3 that the total energy of the covalent bcc phase is less than $E_\infty = -0.5$ throughout the range of densities under consideration and for $r_s \sim 1.7$

the total energy lies practically on the plateau. The precision of our calculations is too low to reveal a minimum at these values of r_s. In the fcc case the total energy is higher than -0.5 throughout the investigated range of densities.

Thus, ignoring the problem of the dynamic stability, we can see that—in principle—we can expect a metastable crystalline phase of atomic hydrogen. It is characterized by a considerable sublimation energy of ≈ 0.01, which is in fact comparable with the static zero-pressure binding energy of metallic hydrogen amounting to ≈ 0.03 for the bcc and fcc lattices (see Ref. 1). However, this quantity should not be regarded as the final value of the sublimation energy of the static lattice because our calculations are variational and, in this sense, they represent an upper limit; moreover, the calculations are characterized by limited accuracy which decreases on increase in the density.

An estimate of the scale of the zero-point vibration energy $\mathcal{E}_{zv}$ characteristic of the densities under discussion[3] easily shows that $\mathcal{E}_{zv}$ is considerably less than our sublimation energy for the static lattice.

It is clear from the above discussion that at low densities the optimal atomic phase of hydrogen is an antiferromagnetic insulator (at $T=0$).

The fact that the minimum of the static energy of the metallic bcc phase[1,2] lies in the region of the plateau and the binding energies are in both cases relatively close, as well as the fact that metallic conduction appears in the atomic phase in the same range of densities, suggests that the transition between the atomic and metastable metallic phases is close to a second order transition.

We shall conclude with two comments. The results obtained in the limit r_s do give the energy of a gas of free hydrogen atoms but the asymptotic behavior of the energy as a function of r_s, found by us, is not accurate. The point is that to obtain the best results at intermediate densities we calculated the van der Waals energy allowing only for one excited state in each atom. The correct asymptote of $E(r_s)$ would have required the use of a method developed for the interaction of two hydrogen atoms over long distances (see Refs. 9 and 10). Finally, it should be noted that in comparison of our results with those obtained in the usual Bloch representation (see, for example, Ref. 8) one should recall that the designations of the individual energy terms are not identical in the two representations. In the Bloch representation the Hartree–Fock approximation allows exactly for the kinetic energy of electrons and for the self-consistent part of the Coulomb interaction between electrons, whereas the correlation Coulomb energy is regarded as a small correction. Conversely, in the site approximation the Hartree–Fock energy [see Eq. (2.2)] includes almost all the Coulomb energy of the interaction between electrons and a considerably part of the kinetic energy of electrons, namely the part that corresponds to the motion of electrons in quasihydrogenic atoms. The "correlation" energy in the site representation allows for the van der Waals energy (intrasite excitation of electrons) and for the small part of the kinetic energy associated with the motion of electrons in a crystal by jumps (see Sec. 3). Moreover, a careful examination of the structure of the matrix elements describing electron jumps between the sites [see, for example, Eq. (3.5)] shows that the "correlation" energy E_L [see Eq. (3.8)] allows simultaneously for the one-electron motion [$\langle \mathbf{R}_2|h|\mathbf{R}_1\rangle$ term in Eq. (3.5)] and for the "Coulomb correlational" motion of electrons [remaining terms in Eq. (3.5)].

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