

Term splitting and binding energy of the hydrogen molecule in an ultrahigh magnetic field

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(Submitted 29 January 1991)

Zh. Eksp. Teor. Fiz. **100**, 407–414 (August 1991)

The exchange splitting of the singlet and triplet terms is calculated for a hydrogen molecule in an ultrahigh magnetic field, such that the distance between Landau levels, $e\hbar H/mc$, in the hydrogen atom is greater than the Coulomb energy (the Rydberg). The expressions derived here for the exchange splitting and the binding energy of the hydrogen molecule are asymptotically exact at interatomic distances R large in comparison with the characteristic sizes of the atoms in an ultrahigh magnetic field $H \gg 1$ (in atomic units). The triplet state of the hydrogen molecule is the ground state in an ultrahigh magnetic field. For the singlet state, which lies considerably higher, there may be metastable states for $R \ll 1$.

1. INTRODUCTION

In an ultrahigh magnetic field H , higher than the characteristic atomic value $H_c = m^2 e^3 c / \hbar^3 = 2.35 \cdot 10^9$ Oe, the atoms are stretched out to a great extent parallel to the magnetic field. Such atoms should have a large electric quadrupole moment, and they may bind into stable molecules. This problem was discussed in Refs. 1 and 2 in the self-consistent-field approximation. With the exchange interaction and the long-range interaction ignored, it was shown there that the formation of "dense" molecules, in which the distance between atoms is small in comparison with the size of the atoms themselves, becomes favored from the energy standpoint in an ultrahigh magnetic field.

A more accurate analysis, however, shows that for hydrogen-like atoms there exists a certain interval of magnetic fields, above the characteristic atomic value, in which the atoms may bind into molecules over distances much greater than the characteristic linear atomic dimension along the magnetic field direction. Direct numerical calculations from the formulas given in Ref. 1 for the interaction energy of a hydrogen molecule show that the results of Ref. 1 are valid only for fields ~ 1000 and above (here and below, the magnetic fields are given in atomic units; $H_c = 1$). For weaker fields, which satisfy the inequality (1) below, a numerical calculation shows that the binding energy of the molecule is small and that the size of the molecule is substantially greater than the atomic size. These results contradict the initial assumptions of Ref. 1.

We know that the Heitler-London approximation for the exchange interaction in the hydrogen molecule is not valid when the distance between the atoms is large. The first calculation of an asymptotically exact expression for the energy of the exchange interaction of the hydrogen molecule in the absence of a magnetic field was carried out in Refs. 3 and 4.

In the present paper we derive an asymptotically exact solution for the splitting of the singlet and triplet terms. We calculate the binding energies for the singlet and triplet terms of a hydrogen molecule in a high magnetic field.

2. SCHRÖDINGER EQUATION AND WAVE FUNCTIONS

We consider a hydrogen molecule in a high magnetic field, by which we mean one satisfying the inequality

$$m^2 e^3 c / \hbar^3 H \ll 1, \quad (1)$$

where m is the electron mass, H is the magnetic field strength, and the notation is otherwise standard.

Since the atoms have a large quadrupole moment in a high magnetic field, the direction of the magnetic field does not necessarily coincide with the symmetry axis of the molecule. We chose a coordinate system with x axis parallel to the field H . We put atoms 1 and 2 of the hydrogen molecule in the xz plane. The coordinates of their nuclei are

$$x_{1,2} = \mp a = \mp \frac{R}{2} \cos \theta, \quad z_{1,2} = \mp b = \mp \frac{R}{2} \sin \theta,$$

where R is the distance between the nuclei of atoms 1 and 2, and θ is the angle between the axis of the molecule and the direction of the magnetic field.

We write the Schrödinger equation in atomic units:

$$\left\{ \frac{1}{2} (P_1 + A)^2 + \frac{1}{2} (P_2 + A)^2 - \sum_i \frac{1}{R_{1i}} - \sum_i \frac{1}{R_{2i}} + \frac{1}{r_{12}} + \frac{1}{R} + \frac{1}{2} \hat{\sigma}_1 H + \frac{1}{2} \hat{\sigma}_2 H \right\} \Psi = E \Psi, \quad (2)$$

where R_{1i} and R_{2i} are the distances from electron i to the first and second nuclei, respectively, r_{12} is the distance between the electrons, and $\hat{\sigma}_1, \hat{\sigma}_2$ are Pauli matrices.

Choosing the vector potential $A = \frac{1}{2} [Hr]$, we rewrite Eq. (2) as

$$\{ \mathcal{H}(1, 2) + \frac{1}{2} \hat{\sigma}_1 H + \frac{1}{2} \hat{\sigma}_2 H \} \Psi = E \Psi, \quad (3)$$

where

$$\mathcal{H}(1, 2) = \left\{ -\frac{1}{2} \Delta_1 - \frac{1}{2} \Delta_2 - \sum_i \frac{1}{R_{1i}} - \sum_i \frac{1}{R_{2i}} + \frac{1}{r_{12}} + \frac{1}{R} + \frac{\rho_1^2 + \rho_2^2}{8\lambda^4} \right\}.$$

Here $\rho_1^2 = y_1^2 + (b + z_1)^2$ and $\rho_2^2 = y_2^2 + (b - z_2)^2$ are the coordinates of the first and second electrons as they move in a plane perpendicular to the magnetic field, and $\lambda = (c\hbar/eH)^{1/2}$ is the characteristic size of the atom in the

plane perpendicular to the magnetic field. In atomic units ($\hbar = m = c = e = 1$) we would have $\lambda = (1/H)^{1/2}$. We will be using this notation below.

We are interested in two terms: the singlet and the triplet. Corresponding to the singlet term is a total electron spin $S = 0$, and for this term we have a symmetric coordinate wave function Ψ_s . When we apply the Hamiltonian to the spin part of the wave function, we get zero, and the terms containing the Pauli matrices disappear from the Hamiltonian. The Schrödinger equation for the singlet term Ψ_s is thus written

$$\mathcal{H}(1, 2) \Psi_s = E_s \Psi_s. \quad (4)$$

Corresponding to the triplet term is a total electron spin $S = 1$, and there are three spin projections: $+1, 0, -1$. The coordinate part of the wave function, Ψ_a , is antisymmetric. The spin projection -1 corresponds to the lowest-lying energy state. The Schrödinger equation for the triplet term can be rewritten as

$$\left\{ \mathcal{H}(1, 2) - \frac{1}{2\lambda^2} - \frac{1}{2\lambda^2} \right\} \Psi_a = E_a \Psi_a. \quad (5)$$

The substitution $E_{S1} = E_s - 1/\lambda^2$ puts Eq. (4) in the form (5):

$$\left\{ \mathcal{H}(1, 2) - \frac{1}{2\lambda^2} - \frac{1}{2\lambda^2} \right\} \Psi_{s,a} = E_{s1,a} \Psi_{s,a}. \quad (6)$$

Following Ref. 3, we introduce the functions $\Psi_1 = (\Psi_s + \Psi_a)/2$ and $\Psi_2 = (\Psi_s - \Psi_a)/2$, which correspond to states in which each electron is localized for the most part near its own atom at large values of R . We choose Ψ_1 and Ψ_2 such that $\Psi_1(r_1, r_2)$ in the limit $r_1 \rightarrow -R/2$, $r_2 \rightarrow R/2$ and $\Psi_2(r_1, r_2)$ in the limit $r_1 \rightarrow R/2$, $r_2 \rightarrow -R/2$ become the product of normalized functions of hydrogen atoms in a high magnetic field.

To find the wave function of the ground state of the hydrogen atom in a high magnetic field, we can, as a first approximation, treat the motion of the electron parallel to the x axis as one-dimensional motion in a Coulomb potential, while considering only the motion in the magnetic field in the yz plane. This approximation is legitimate since the motion of the electron parallel to the x axis occurs in a region on the order of α in size, while in the perpendicular plane the motion is bounded by a cylindrical surface with a radius on the order of $\lambda \ll \alpha$. In accordance with the results of Refs. 5 and 6, we write the wave function of the ground state of the hydrogen atom in a high magnetic field as

$$\Psi(r) = \varphi(\rho) \psi(x),$$

where

$$\varphi(\rho) = \frac{1}{(2\pi)^{1/2} \lambda} \exp\left\{-\frac{\rho^2}{4\lambda^2}\right\}$$

is the wave function of the zeroth Landau level, which corresponds to motion in the plane perpendicular to the magnetic field ($\rho^2 = y^2 + z^2$). The expression for $\psi(x)$ is

$$\psi(x) = \frac{1}{\alpha^{1/2}} W_{\alpha, 1/2} \left\{ \frac{2}{\alpha} (x + \lambda) \right\},$$

where $W_{\alpha, 1/2}$ is the Whittaker function. The distinction

from the usual wave function for motion in a Coulomb field stems from the quasi-one-dimensional motion of the electron along the magnetic field direction. The expression which relates the parameter α to the ground-state energy can be written with logarithmic accuracy as follows:⁵⁻⁷

$$\xi = -\frac{1}{2\alpha^2} \approx -1/2 \ln^2 H. \quad (7)$$

Since we are interested in distances much greater than the characteristic atomic dimension along the magnetic field direction, which is of order α , the asymptotic expression for the longitudinal part $\psi(x)$ of the wave function is

$$\psi(x) \approx \frac{1}{\alpha^{1/2}} \exp\left\{-\frac{|x|}{\alpha}\right\}. \quad (8)$$

The wave function of the ground state of the hydrogen atom in a high magnetic field can thus be written

$$\Psi(r) = \frac{1}{\alpha^{1/2}} \frac{1}{(2\pi)^{1/2} \lambda} \exp\left\{-\frac{\rho^2}{4\lambda^2}\right\} W_{\alpha, 1/2} \left\{ \frac{2}{\alpha} (x + \lambda) \right\}. \quad (9)$$

We seek the wave function Ψ_1 in the form

$$\Psi_1 = B^2 \chi_1 \exp\left\{-\frac{\rho_1^2 + \rho_2^2}{4\lambda^2}\right\} W_{\alpha, 1/2} \left\{ \frac{2}{\alpha} (a + x_1 + \lambda) \right\} W_{\alpha, 1/2} \left\{ \frac{2}{\alpha} (a - x_2 + \lambda) \right\}, \quad (10)$$

where

$$B^2 = \frac{1}{\alpha} \frac{1}{2\pi\lambda^2},$$

and the function χ_1 varies slowly in comparison with the exponentially varying functions. Expression (10) is the product of the hydrogen wave functions of electron 1 near nucleus 1 and of electron 2 near nucleus 2.

Substituting (10) into (6), and retaining terms of zeroth order in α in the course of the differentiation, we find an equation for χ_1 :

$$\left\{ \frac{1}{\alpha} \frac{\partial}{\partial x_1} - \frac{1}{\alpha} \frac{\partial}{\partial x_2} - \frac{1}{R_{12}} - \frac{1}{R_{12}} + \frac{1}{r_{12}} + \frac{1}{R} \right\} \chi_1 = 0. \quad (11)$$

In deriving (11) we ignored terms containing derivatives of χ_1 with respect to $z_1, z_2, y_1,$ and y_2 . The reason is that after we substitute expression (12a) for χ_1 (written below) into Eq. (11) we easily see that incorporating the derivatives of χ_1 with respect to z_1 and z_2 gives rise to terms of order α , which are small in comparison with the terms which contain the derivatives of χ_1 with respect to x_1 and x_2 and which are on the order of unity.

Introducing the new variables $\xi = (x_1 + x_2)/2$ and $\eta = x_1 - x_2$, and going through some simple manipulations, we can write the solution of Eq. (11) as

$$\chi_1 = \left[C(\xi, z_1, z_2, y_1, y_2) \exp\left\{-\frac{(x_1 - x_2)}{R}\right\} \right]^\alpha G, \quad (12a)$$

or

$$G = \left[\frac{x_2 - x_1 + ((x_2 - x_1)^2 + (z_2 - z_1)^2 + (y_2 - y_1)^2)^{1/2}}{(a + x_2 + ((a + x_2)^2 + (b + z_2)^2)^{1/2})^2} \times \frac{1}{(a - x_1 + ((a - x_1)^2 + (b - z_1)^2)^{1/2})^2} \right]^{\alpha/2}. \quad (12b)$$

Here $C(\xi, z_1, z_2, y_1, y_2)$ is an arbitrary function of the variables $\xi, z_1, z_2, y_1,$ and y_2 . To determine this function, we make use of the obvious condition that χ_1 approaches unity when either $x_1 \rightarrow -a, z_1 \rightarrow -b$ or $x_2 \rightarrow a, z_2 \rightarrow b$. After some straightforward calculations, we find our final expression for the wave function:

$$\Psi_1(r_1, r_2) = \Gamma \exp\left\{-\frac{\rho_1^2 + \rho_2^2}{4\lambda^2}\right\} W_{\alpha, 1/2}\left\{\frac{2}{\alpha}(a+x_1+\lambda)\right\} \times W_{\alpha, 1/2}\left\{\frac{2}{\alpha}(a-x_2+\lambda)\right\} FG, \quad (13a)$$

where

$$F = \left\{ \frac{[2a+x_1+x_2 + ((2a+x_1+x_2)^2 + (2b+z_1+z_2)^2)^{1/2}]^2}{2a+x_1+x_2 + ((2a+x_1+x_2)^2 + (2b+z_1+z_2)^2 + y_{21}^2)^{1/2}} \right\}^{\alpha/2} \times \exp\left\{-\frac{\alpha(a+x_1)}{(a^2+b^2)^{1/2}}\right\}, \quad x_1+x_2 < 0, \quad z_1+z_2 < 0, \quad (13b)$$

$$F = \left\{ \frac{[2a-x_1-x_2 + ((2a-x_1-x_2)^2 + (2b-z_1-z_2)^2)^{1/2}]^2}{2a-x_1-x_2 + ((2a-x_1-x_2)^2 + (2b-z_1-z_2)^2 + y_{21}^2)^{1/2}} \right\}^{\alpha/2} \times \exp\left\{-\frac{\alpha(a-x_2)}{(a^2+b^2)^{1/2}}\right\}, \quad x_1+x_2 > 0, \quad z_1+z_2 > 0, \quad (13c)$$

$$\Gamma = B^2 \{2[a + (a^2+b^2)^{1/2}]\}^\alpha, \quad y_{21} = y_2 - y_1.$$

The function Ψ_2 is found from Ψ_1 through the interchange $1 \leftrightarrow 2$.

3. TERM SPLITTING AND BINDING ENERGY OF THE HYDROGEN MOLECULE IN A HIGH MAGNETIC FIELD

To calculate the splitting energy of the terms, it is convenient to rotate the coordinate system through an angle θ , so that we obtain

$$x = x' \cos \theta - z' \sin \theta, \quad z = x' \sin \theta + z' \cos \theta.$$

All the expressions below are written in the primed coordinate system, so we will omit the primes.

To calculate the difference between the energies of the singlet and triplet terms as a result of the exchange interaction, we use an expression derived in Ref. 3 for the term splitting of the hydrogen molecule. The corresponding expression is, with exponential accuracy,

$$E_{S1} - E_a = 2 \oint_S (\Psi_2 \nabla_1 \Psi_1 - \Psi_1 \nabla_1 \Psi_2) dS, \quad (14)$$

where S is a hyperplane ($x_1 = x_2$) in the six-dimensional space $\{r_1, r_2\}$. The scalar product in (14) reduces to differentiation of the expressions in (14) with respect to x_1 alone, since the gradients of the wave functions in the integrand are projected onto the direction of the surface dS .

Assuming that the distance between the nuclei of the hydrogen molecule is much greater than the linear dimension of a hydrogen atom ($\sim \alpha$) in the magnetic field direction, we use the asymptotic expression (8) for $\psi(x)$. Differentiating the exponential factors in (10) with respect to x_1 (after rotating the coordinate system), we put expression (14) in the form

$$E_{S1} - E_a = -4 \left[\frac{2 \cos \theta}{\alpha} + \frac{b \sin \theta}{\lambda^2} \right] \times \int_0^{R/2} dx \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} dy_1 dy_2 dz_1 dz_2 [\Psi_1 \Psi_2]_{x_1=x_2, x_1+x_2>0}. \quad (15)$$

Substituting Ψ_1 and Ψ_2 into (15), imposing the condition $0 < \alpha \ll 1$, and going through some calculations, we find the following expression for the exchange splitting for angles θ in the interval $0 \leq \theta < \pi/2 - \varepsilon$ (where $\varepsilon \propto \alpha$):

$$E_{S1} - E_a = - \frac{2R}{\alpha^2 \cos^2 \theta} \left[\frac{\Gamma \cos \theta}{\alpha} + \frac{R \sin^2 \theta}{2\lambda^2} \right] \times \exp\left\{-R \left[\frac{2 \cos \theta}{\alpha} + \frac{R \sin^2 \theta}{4\lambda^2} \right]\right\}. \quad (16)$$

Finally, we find the following expression for the exchange part of the term splitting energy, in atomic units:

$$\Delta E = (E_S - H) - E_a = - \frac{2R \ln^2 H}{\cos^2 \theta} [2 \ln H \cos \theta + 1/2 R H \sin^2 \theta] \times \exp\{-R[2 \ln H \cos \theta + 1/4 R H \sin^2 \theta]\}. \quad (17)$$

The corresponding calculations for value $\theta = \pi/2$ yield

$$E_{S1} - E_a = - \frac{R}{2\pi^{1/2} \lambda^3} \exp\left\{-\frac{R^2}{4\lambda^2}\right\}.$$

At large distances R , two hydrogen atoms in a high magnetic field interact as two quadrupoles. Since the electron density has a $\Psi^2(x)$ distribution [see (9)], the quadrupole moment of the atom is $Q = 2\langle x^2 \rangle = \alpha^2/2$. The energy of the interaction of the two quadrupoles when they are far apart is therefore given by

$$U_{qq} = \frac{9}{8} \frac{1}{\ln^4 H} \frac{1}{R^5} P_4(\cos \theta), \quad (18)$$

where

$$P_4(\cos \theta) = 1/8 (35 \cos^4 \theta - 30 \cos^2 \theta + 3)$$

is the Legendre polynomial.

Taking account of the quadrupole interaction along with the exchange correction, which leads to splitting of the terms, we find our final expression for the interaction energy of the hydrogen molecule in a high magnetic field (under the condition $R \gg \langle x^2 \rangle^{1/2} \propto \alpha$).

For the singlet term we find

$$U_S = E_S - E_0 = -1/2 \Delta E + H + U_{qq}. \quad (19)$$

For the triplet term we find

$$U_a = E_a - E_0 = +1/2 \Delta E + U_{qq}, \quad (20)$$

where E_0 is twice the energy of the isolated hydrogen atoms.

Since the energy of the quadrupole interaction has a negative minimum as a function of angle at $\theta \approx 49^\circ$ [it was for this reason that we used expression (17) in (19) and (20)], it is clear that bound states are possible for both the singlet and the triplet, but for $H \gg 1$ the triplet state lies well below the singlet state and is the ground state of the hydrogen molecule in a high magnetic field.

Figure 1 shows the interaction energy for the triplet and singlet terms as a function of R for various values of the magnetic field for the angle $\theta \approx 49^\circ$. Lines 1-3 in this figure correspond to magnetic fields of 20, 50, and 100, respectively. At small values $R \ll \alpha$, the quadrupole-quadrupole attraction gives way to a Coulomb repulsion of the nuclei, and for $\alpha \ll R < 2$ the interaction energy has a deep minimum, for

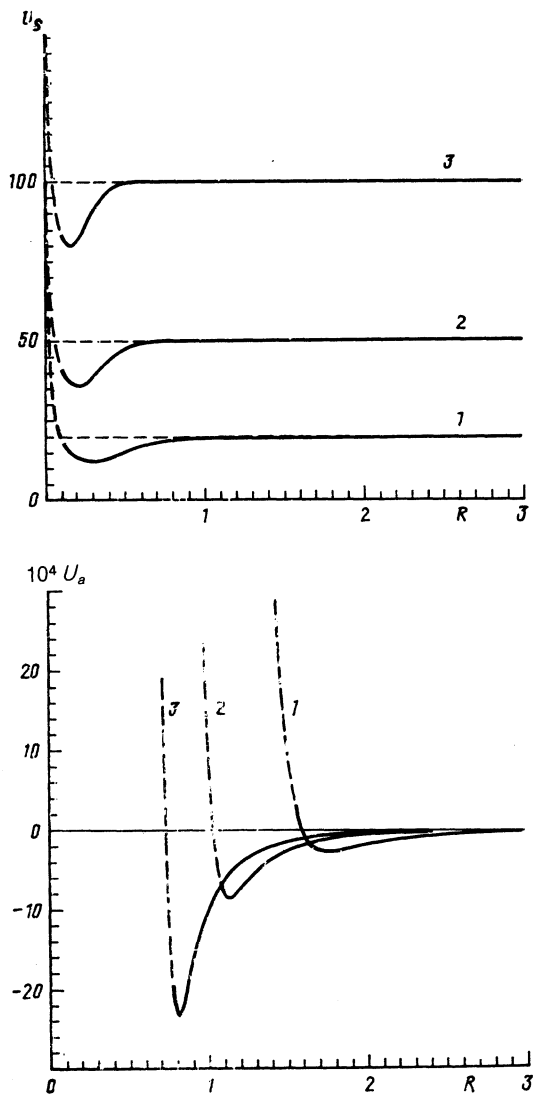


FIG. 1.

both the singlet and the triplet. This minimum corresponds to possible bound states of the hydrogen molecule. In any case, the triplet term lies well below the singlet term; i.e., the ground state of the hydrogen molecule in an ultrahigh magnetic field is the triplet term. As can be seen from the curves in this figure, the depth of the potential well increases rapidly with increasing magnetic field, for both the singlet and triplet terms. The binding energy for the triplet term, for example, changes from $\varepsilon_t = 2.86 \cdot 10^{-4}$ (2 Ry) at $H = 20$ to $\varepsilon_t = 4.4 \cdot 10^{-2}$ (2 Ry) at $H = 500$, while the depth of the potential well for the singlet term changes from $\Delta\varepsilon_s = 7$ (2 Ry) at $H = 20$ to $\Delta\varepsilon_s = 40$ (2 Ry) at $H = 500$.

As the magnetic field is strengthened, the hydrogen molecule decreases in size. For example, the minimum of the energy $U_a(R)$ at $H = 300$ occurs at $R = 0.46$, but since this is much larger than the size of the hydrogen atom ($\approx 9 \cdot 10^{-2}$ at $H = 300$) in a high magnetic field, the solution found above remains asymptotically exact. The situation remains unchanged up to fields on the order of 1000, at which the size of the molecule (the position of the minima of the interaction energy) becomes comparable to the size of an atom.

4. CONCLUSION

This analysis shows that the physical properties of a substance change substantially in a high magnetic field. In particular, hydrogen atoms may bind into molecules whose ground state is a triplet, rather than the triplet which we find in the H_2 molecule in the absence of a magnetic field. As the magnetic field is strengthened, the depth of the well in the atomic interaction energy increases rapidly.

The hydrogen molecule in a high magnetic field thus has an interesting characteristic: The binding energy of the molecule in its triplet ground state is relatively low (it reaches 1–2 eV in ultrahigh fields), while the depth of the potential well for the higher-lying singlet term, which is in this case metastable, may be more than two orders of magnitude greater than the binding energy of the ordinary hydrogen molecule, reaching values of several hundred electron volts in high fields.

The behavior of a system of spin-oriented atoms, which are very elongated parallel to the magnetic field, is of interest for astrophysics, as is the formation of anisotropic structures reminiscent of liquid crystals or molecular chains. Magnetic fields at the scale of interest here, on the order of 10^{10} – 10^{12} Oe, would be possible at the surfaces of neutron stars and pulsars.

Another topic of interest might be the behavior of a hydrogen-like system of excitons in a semiconductor or an insulator. The characteristic "atomic" magnetic field for such a system would be determined by the condition $H \gg \mu^2 e^3 c / \kappa^2 \hbar^3$, where μ is the reduced mass of the electron and the hole, and κ is the dielectric constant. Such fields are attainable in the laboratory. For InSb, for example, a magnetic field becomes "ultrahigh" at values as low as a few kiloersteds. Then at low temperatures and under certain other conditions there is the possibility in principle that spin-oriented structures (possibly metastable) would arise, forming in the course of an interaction of excitons in an ultrahigh magnetic field.

We wish to thank L. P. Pitaevskii for numerous discussions and valuable advice in the course of this study and S. M. Gol'berg for assistance in the numerical calculations.

¹ B. B. Kadomtsev and V. S. Kudryavtsev, Pis'ma Zh. Eksp. Teor. Fiz. **13**, 15 (1971) [JETP Lett. **13**, 9 (1971)].

² B. B. Kadomtsev and V. S. Kudryavtsev, Zh. Eksp. Teor. Fiz. **62**, 144 (1972) [Sov. Phys. JETP **35**, 76 (1972)].

³ L. P. Gor'kov and L. P. Pitaevskii, Dokl. Akad. Nauk SSSR **151**, 822 (1963) [Sov. Phys. Dokl. **8**, 788 (1964)].

⁴ C. Herring and M. Flicker, Phys. Rev. A **134**, 362 (1964).

⁵ R. J. Elliott and R. London, J. Phys. Chem. Solids **15**, 196 (1960).

⁶ H. Hasegawa and R. E. Howard, J. Phys. Chem. Solids **21**, 179 (1961).

⁷ L. D. Landau and E. M. Lifshitz, *Quantum Mechanics: Non-Relativistic Theory*, Nauka, Moscow, 1989 (previous editions of this book have been published in English translation by Pergamon, New York).

Translated by D. Parsons