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CORRELATION EFFECTS OF THE SUPERCONDUCTING TYPE IN A π-ELECTRON SYSTEM

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Pair correlation effects of collectivized π electrons in complex molecules are investigated. Various attraction mechanisms as well as the dependence of the electron spectrum on the parity of the number of electrons are investigated. The behavior of a π-electron system in external electric and magnetic fields (i.e., anomalous diamagnetism, polarizability, and so on) are investigated. Collective excitations and the multiplet structure of the spectrum are considered.

It is well known that pair correlation effects play a very important role in systems consisting of a large number of Fermi particles. These effects are due to the presence of attraction mechanisms between the fermions, and have very varied consequences. Pair correlation in an electron system in a metal or a degenerate semiconductor leads to the appearance of superconductivity. Nucleon pair correlation effects can be used to explain, for example, the observed moments of inertia.

The present paper is concerned with pair correlation effects in a π electron system. It is well known that many complex molecules (for example, polycyclic molecules, phthalocyanines, the molecules of biologically active media, and so on) are characterized by the presence of collectivized π electrons whose number can be quite high. The electrons move in the field of the σ core formed by the ion system and the set of uncollectivized electrons. Interactions between the π electrons, which lead to the correlation effects, are largely due to the polarization of this σ core (see below). Pair correlation in a π-electron system was briefly reviewed in our previous paper.[1] In the present paper we discuss this problem in greater detail and, in addition, report a number of new results.

The π electrons form a finite Fermi system.[2-4] It is not, therefore, accidental that, as will be seen below, the effect which we are considering is, in many ways, analogous to the nucleon-nucleon pair correlation effect in the atomic nucleus.

A universal feature of pair correlation is the appearance of an energy gap Δ in the spectrum of the multiparticle system, which separates the ground state from the first excited state. Finite Fermi systems have discrete energy levels, and the presence of pair correlation is responsible for the fact that the energy gap between the ground state and the first excited state (0-0′) is much greater than the 0′-0″ and other level separations. The gap Δ can be measured directly by optical methods.

To begin with, we consider the various mechanisms which can lead to pair correlation in a π-electron system. We next discuss the properties of the electron spectrum of complex molecules (the 0-0′ transition and the effect upon it of a transition to systems with an odd number of π electrons). The magnetic properties of complex molecules and their behavior in electric fields are discussed next. An expression is obtained for the polarizability of a π-electron system. Collective (exciton) excitations and the associated multiplet structure of the electron spectrum are also discussed.

1. ATTRACTION MECHANISMS

The complex molecules which we shall discuss are, in many ways, analogous to metals. The σ core plays the role of the crystal lattice. Usually, the number of π electrons is such that the π band is half-filled and this means that it is analogous with the conduction band of metals, and governs the great sensitivity of π electrons to external fields.

Pair correlation mechanisms in π-electron systems are completely analogous to the well-known superconducting mechanisms. Let us begin by considering the interaction between the π electrons and the σ core. The most important transitions are the virtual transitions in the σ-electron system due to Coulomb interactions between the π and σ electrons. We note that, experimentally, one observes various σ-electron excitations (σ-π transitions) corresponding, for example, to frequencies $\nu \sim 4 \times 10^4\ \mathrm{cm}^{-1}$ (the electron-level difference is usually $\sim 10^3$–$10^4\ \mathrm{cm}^{-1}$).

The effective Hamiltonian which governs the interaction between the π electrons through the σ core is

$$\hat{H}^{\mathrm{eff}}_{\pi\pi} = \sum_{\lambda_i} g^{\pi\pi}_{\lambda_1\lambda_2;\lambda_3\lambda_4} a_{\lambda_1}{}^{+} a_{\lambda_2}{}^{+} a_{\lambda_3} a_{\lambda_4}, \tag{1}$$

where

$$g^{\pi\pi}_{\lambda_1\lambda_2;\,\lambda_3\lambda_4} = \sum_{\mu\mu'} \frac{A^{\pi\sigma}_{\lambda_1\mu_1;\lambda_3\mu'}\ A^{\pi\sigma}_{\mu',\,\lambda_2;\,\mu\lambda_4} n_{\mu'}(1-n_\mu)}{(\varepsilon_{\lambda_3}-\varepsilon_{\lambda_1}-\Delta\varepsilon^{\sigma}_{\mu\mu'})(\varepsilon_{\lambda_4}-\varepsilon_{\lambda_2}-\Delta\varepsilon^{\sigma}_{\mu\mu'})} \tag{1′}$$

[$\epsilon_{\lambda i}$ are the single-particle levels of the π-electron system, $\Delta\epsilon^{\sigma}_{\mu\mu'} = \epsilon_\mu - \epsilon_{\mu'}$ is the change in the σ-electron energy during a virtual transition, and the factors $n_{\mu'}(1-n_\mu)$ are connected with restrictions imposed by Pauli's principle]. It is clear that $\Delta\epsilon^{\sigma}_{\mu\mu'} > 0$. For the sake of simplicity, we shall restrict our attention to second-order perturbation theory. It is clear from Eq. (1) that for transitions in the π-electron system corresponding to changes in energy which are small in comparison with $\Delta\epsilon^{\sigma}_{\mu\mu'}$, we have $g < 0$, i.e., we have an effective attraction in the π-electron system. This mechanism is completely analogous to the electronic mechanism in superconductivity (see [5,6]; $g \sim g_{\text{Coul}}$).

In a more accurate calculation based on the use of the diagram technique one must calculate the four-terminal quantity $\Gamma_{\pi\pi,\pi\pi}$, which describes the effective interaction between the π electrons. Knowledge of this quantity enables us to determine the proper-energy part Σ and then the energy gap with the aid of

$$\Sigma_{\lambda\lambda'} = \sum_{\lambda_1\lambda_2} (\lambda\lambda'|\Gamma|\lambda_1\lambda_2) F^{+}_{\lambda_1\lambda_2}$$

The precise determination of Γ depends on the form of the single-particle wave functions and is, therefore, possible only in special models. We shall not calculate Γ and the energy gap in the present paper, and will confine our attention to a review of the attraction mechanisms. This approach is fully justified because the energy gap can be measured directly (see below) and we shall, therefore, consider it as a parameter of the theory.

We note that attractions in the π-electron system need not be exclusively due to σ-π electron transitions, but can be due to the existence of different groups of π electrons. For example, virtual transitions of π electrons belonging to the phenyl groups in the tetraphenylporphin molecule lead to an effective attraction in the main π-electron system (see Fig. 1; it is shown in [7] that these groups exhibit weak conjugation with the main part of the tetraphenylporphin molecule and can, therefore, be regarded as independent).

In some cases, vibrational degrees of freedom of the σ core may play a significant role which is quite analogous to the usual BCS superconducting mechanism. It is clear that the contribution of this mechanism in the complex molecules which we are considering is connected either with the presence of groups having high vibrational frequency, or with a deviation from the simple adiabatic picture which is possible in complex molecules (see, for example, [8]) because, as the molecules become more complicated, the electron-level separation becomes smaller.

Pair correlation leads to the appearance of a gap in the energy spectrum. This gap can be obtained directly by optical measurements which are capable of yielding with sufficient accuracy the difference between the ground and the first excited states (0-0′ transition). The size of the energy gap will be considered as the main parameter of the theory, by analogy with the theory of superconductivity. We note also that since the two-dimensional systems we are considering are finite, the correlation effects are stable against fluctuations in electron density.

Virtual electron transitions are thus the leading attraction mechanisms. Vibrational degrees of freedom of the σ core may, under certain conditions, be also significant.

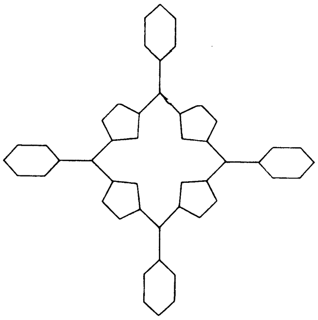

FIG. 1. Tetraphenylporphin molecule.

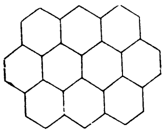

FIG. 2. Ovalene molecule.

2. ENERGY GAP. THE 0-0′ TRANSITION

As noted above, the energy gap can be measured directly by optical methods (0-0′ transition). The pair correlation effects which we are investigating are, of course, important when at least a few single-particle levels, which are simply connected with the finite nature of the system, are fitted into the gap 2Δ. This is why, for example, these effects play no appreciable role in simple molecules such as benzene. On the other hand, in molecules of materials such as, for example, ovalene (Fig. 2), coronene, phthalocyanine, and so on, there is a sufficiently high number of π electrons, and pair correlation must be taken into account.

It is clear from the above discussion that the main consequence of the above effect is that the 0-0′ energy separation between the ground state and the first excited state is much greater than the 0′-0″, 0″-0‴, and so on, separations. This is confirmed by experiment (see, for example, [9]). Thus, in the ovalene molecule ($C_{32}H_{14}$) the first electronic excited state corresponds to the frequency $\omega_{01} = 21\,000\ \text{cm}^{-1}$ and the 0′-0″ separation corresponds to $\omega_{12} \approx 5000\ \text{cm}^{-1}$. Coronene is characterized by $\omega_{01} \approx 22\,500\ \text{cm}^{-1}$, $\omega_{12} \approx 5500\ \text{cm}^{-1}$.

This relationship between the energy separations is not, of course, an obvious fact. Thus, the properties of the complex molecules which we are discussing can be described by quasiclassical means because most of the electrons are characterized by high principal quantum numbers (for example, according to [10] this approximation adequately describes the properties of π electrons for $\nu \gtrsim 10$, where ν is the number of π electrons). At the same time, it is well known that the energy levels should be approximately equally spaced (see, for example, [11], p. 202). When the validity of the quasiclassical approximation is discussed, one must, of course, consider the total number of electrons, including the σ electrons. The presence of pair correlation, on the other hand, explains the appreciable excess of the value of ω_{01} because, in this case, the 0-0′ transition is equivalent to the energy gap which contains a number of single-particle levels. We note that an analogous situation is observed in the case of even-even atomic nuclei.

The presence of pair correlation should lead to an appreciable difference between the spectra of molecules containing even and odd numbers of π electrons, respectively, and this is, in fact, observed experimentally.[12] The addition or removal of one π electron in the system, which makes the number of electrons either even or odd, is known to lead to the appearance of a lower frequency in the radiation absorbed by the molecule, i.e., in other words, to an essential reduction in the 0-0′ separation. For example, the spectrum of the perylene molecule is characterized by the following frequencies: $\omega_{01} \approx 22\,000\ \mathrm{cm}^{-1}$, $\omega_{12} \approx 8000\ \mathrm{cm}^{-1}$. On the other hand, when the compound $C_{20}H_{18}-$ is considered, which differs from perylene by the addition of a single π electron, it is found that $\omega_{01} \approx 10\,000\ \mathrm{cm}^{-1}$, $\omega_{12} \approx 8000\ \mathrm{cm}^{-1}$. Again, the addition of two π electrons again leads to the appearance of the gap in the spectrum.[12] A similar reduction in the 0-0′ separation is noted in coronene, $C_{24}H_{18}$. Whereas coronene itself is characterized by $\omega_{01} \approx 22\,500\ \mathrm{cm}^{-1}$, $\omega_{12} \approx 5500\ \mathrm{cm}^{-1}$, the compound $C_{24}H_{18}-$ is found to have $\omega_{01} \approx 8000\ \mathrm{cm}^{-1}$, $\omega_{12} \approx 10\,000\ \mathrm{cm}^{-1}$. The observed reduction in the 0-0′ separation can naturally be related to the presence of the unpaired electron.

The change in the color, which is associated with transition to cation-radicals and anion-radicals (see, for example, [13]), is also a manifestation of the above effects.

3. MAGNETIC PROPERTIES

Pair correlation has also an important effect on the magnetic properties of molecules since it governs the observed anomalous diamagnetism of the electron system.

The interaction between π electrons and the magnetic field is described by the paramagnetic ($\hat{H}_P$) and diamagnetic ($\hat{H}_D$) parts of the π-electron Hamiltonian

$$\hat{H}_P = \frac{ie}{2m}\int \Psi^+ (\nabla \mathbf{A} + \mathbf{A}\nabla)\Psi\, dr, \tag{2}$$

$$\hat{H}_D = -\frac{e^2}{2m}\int \Psi^+\Psi A^2\, dr. \tag{3}$$

The operators Ψ and Ψ^+ describe the state of the π electrons with allowance for the pair correlation effect.

The expression for $\langle H_P \rangle$ can be written in the form

$$\langle \hat{H}_P \rangle = \frac{ie}{m}\int \mathbf{A}\nabla_{\mathbf{r}} G'(x, x')\Big|_{\substack{x=x'\\ t=t'+0}} d\mathbf{r}, \tag{2′}$$

where G is the Green function for the system and $\mathbf{A} = \frac{1}{2}\mathbf{H} \times \mathbf{r}$.

Equation (2′) can readily be transformed to read

$$\langle \hat{H}_P \rangle = \frac{ie}{2m} H_i \sum_{\lambda,\lambda'} \rho'_{\lambda\lambda'} \hat{M}_{i\lambda'\lambda}.$$

In this expression ρ' is the addition to the density matrix of the quasiparticles due to the field, H_i is the magnetic field component, and $\hat{M}_i = -i(\mathbf{r} \times \nabla)_i$.

The addition to the density matrix $\rho'_{\lambda\lambda'}$ is connected with the presence of an arbitrarily small perturbation V and, according to [14,3], it is of the form

$$\rho'_{\lambda\lambda'} = \frac{(\xi_\lambda\xi_{\lambda'} - \varepsilon_\lambda\varepsilon_{\lambda'} - \Delta_\lambda\Delta_{\lambda'}\hat{T})\, V^0_{\lambda\lambda'}}{2\varepsilon_\lambda\varepsilon_{\lambda'}(\varepsilon_\lambda + \varepsilon_{\lambda'})}. \tag{4}$$

The eigenvalues of the operator $\hat{T}$ are ±1, where the positive sign corresponds to external fields which do not change sign on time reversal, whereas the minus sign corresponds to odd fields. In the case we are considering, we have the negative sign. Henceforth we shall neglect the dependence of Δ on λ, which is valid for sufficiently homogeneous distribution in the π-electron system. On this case, the perturbation operator is

$$\hat{V} = \frac{ie\hbar}{4mc}\mathbf{H}\hat{\mathbf{M}}. \tag{5}$$

We shall use Eq. (4) to find $\langle \hat{H}_P \rangle$ and then, using the well-known relationship $\chi = -\partial^2(\Delta E)/\partial H^2$, we shall calculate the paramagnetic susceptibility in the direction perpendicular to the plane of the molecule:

$$\chi_{\perp P} = \frac{e^2}{8m^2}\sum_{\lambda,\lambda'} \frac{\varepsilon_\lambda\varepsilon_{\lambda'} - \xi_\lambda\xi_{\lambda'} - \Delta^2}{2\varepsilon_\lambda\varepsilon_{\lambda'}(\varepsilon_\lambda + \varepsilon_{\lambda'})} |M_{z\lambda\lambda'}|^2. \tag{6}$$

In the absence of pair correlation

$$\chi_{\perp P,\Delta=0} = \frac{e^2}{8m^2}\sum_{\lambda,\lambda'} \frac{1}{|\xi_\lambda| + |\xi_{\lambda'}|} |\hat{M}_{z\lambda\lambda'}|^2, \quad \xi_\lambda\xi_\lambda' < 0. \tag{7}$$

Equation (7), which is a consequence of the general relation given by Eq. (6) for $\Delta = 0$, is well known in the theory of molecules, and is often referred to as the Van Vleck paramagnetism[15] (it is occasionally called the polarization paramagnetism).

The operator V^0 in Eq. (5) describes the direct interaction between the π-electron quasiparticles and the external field. In a more rigorous approach, Eqs. (4) and (5) should involve the effective field[3,4]

$$V^{\mathrm{eff}}_{\lambda_1\lambda_2} = V^0_{\lambda_1\lambda_2} + \sum_{\lambda\lambda'} (\lambda_1\lambda_2|\Gamma|\lambda, \lambda')\rho'_{\lambda'\lambda} \tag{8}$$

where Γ is the four-terminal quantity describing the interaction between the quasiparticles, since allowance for the interaction between the quasiparticles ensures that the field acting on the quasiparticle is different from the external field. This difference is due to the modification of the π-electron system, and is described by the second term in the expression for V^{eff}. It is clear that, when the interaction between the quasiparticles is taken into account, this ensures that Eqs. (4)–(6) involve $V^{\mathrm{eff}} = \mathbf{H}\cdot\mathbf{M}^p$ ($\mathbf{M}^p = \mathbf{M} + \mathbf{M}'$; $\mathbf{M}'$ is determined by the second term in Eq. (8) which is the integral equation for the effective field). Replacement of $M_{z\lambda\lambda'}$ by $M^p_{z\lambda\lambda'}$ in Eqs. (6) and (7) leads to different qualitative values of $\chi_\perp$. However, the main conclusion (see below), that pair correlation is suppressed because of pair correlation, is connected with the estimate of the function

$$F(\lambda, \lambda') = (\varepsilon_\lambda\varepsilon_{\lambda'} - \xi_\lambda\xi_{\lambda'} - \Delta^2) / 2\varepsilon_\lambda\varepsilon_{\lambda'}(\varepsilon_\lambda + \varepsilon_{\lambda'})$$

and does not change when V^0 is replaced by V^p.

We note also that, according to Eqs. (4), (5), and (8), in the case of axial symmetry (see below), the effective field becomes identical with V^0 in calculations of $\chi_\perp$.

Therefore, the resultant orbital susceptibility consists of the paramagnetic part given by Eq. (6) and the diamagnetic term determined in the usual way from Eq. (3). In ordinary metals it is well known that χ_P and χ_D eventually cancel out (and there is only minor Landau diamagnetism). In superconductors, the "rigidity" of the wave function leads to the suppression of the paramagnetic contribution. When the magnetic properties of the molecules are investigated, there is no compensation, and we must take into account both the Van

Vleck paramagnetism and χ_D. The semi-empirical method of solving this problem is developed in [16].

Experiment shows, however, that the electron system exhibits anomalous diamagnetic properties. The magnetic properties of, for example, the polycyclic compounds are described with high accuracy by including only χ_D. The problem then arises as to what are the reasons leading to the reduction in the paramagnetic contribution in Eq. (2).

We note, first of all, that χ_P vanishes for molecules with axial symmetry because, in this case, the operator $\hat{M}_z$ is diagonal. When $\lambda = \lambda'$, on the other hand, it is clear from Eqs. (6) and (7) that χ_P is zero independently of the pair correlation effect. The magnetic susceptibility of the molecule and, consequently, the π-electron current, are then determined exclusively by the diamagnetic part of the Hamiltonian. This occurs in particular for the benzene molecule, whose symmetry is frequently assumed to correspond to the $D_{\infty h}$ group. The current state of benzene is therefore described by the London equation $\mathbf{j} = -(ne/mc)\mathbf{A}$,[17] which is the usual quantum-mechanical expression for the current without the paramagnetic term. This anomalous mechanism is connected, as we shall see, not with pair correlation, but with the axial symmetry of the molecule.

In the complex molecules of aromatic compounds which have no axial symmetry there are, at first sight, no reasons which would allow us to neglect the paramagnetic contribution of Eq. (6). Their anomalous diamagnetism therefore requires special analysis.

The paramagnetic susceptibility of ordinary molecules is given by Eq. (7) which describes with sufficient accuracy the experimental data. The quantities $\chi_{\perp P,\Delta=0}$ and χ_D are quantities of the same order of magnitude. In the polycyclic molecules which we are considering, we must take into account pair correlation effects, in which case $\chi_{\perp P}$ is calculated not from Eq. (7) but from Eq. (6). It can be shown that, under certain definite conditions (see below), the value of $\chi_{\perp P}$ calculated from Eq. (6) is much less than $\chi_{\perp P,\Delta=0}$ and this means suppression of the paramagnetic contribution.

Let us consider Eq. (6) which gives the expression for $\chi_{\perp P}$ in greater detail. We shall first investigate the values of ξ_λ and $\xi_{\lambda'}$ which provide the main contribution to the sum in Eq. (6). This will be done by evaluating the matrix element $M_{z\lambda\lambda'}$ on the basis of the quasiclassical method (see [2,3]). The separation between levels with neighboring values of the principal quantum number in the two-dimensional case corresponding to the plane molecule is

$$\partial\varepsilon / \partial n \approx v / r_0 N^{1/2} \approx \varepsilon_F / N^{1/2}$$

(this equation is obtained by term-by-term differentiation with respect to n of the Bohr condition $\int p_\rho d\rho = n$, where N is the number of electrons, ϵ_F is the Fermi energy which, in this case, is given by $\epsilon_F = 4\pi\hbar^2 N/g2mS$, S is the area, and g = 2). It is clear that the values $M_{z\lambda\lambda'}$ will be appreciably different from zero if $|\xi_\lambda - \xi_{\lambda'}| \sim \epsilon_F/N^{1/2}$. In the opposite case, the wave functions will have a very different number of nodes and this will lead to a low value of the corresponding matrix element.

Let us now consider the function

$$F = \frac{\varepsilon_\lambda\varepsilon_{\lambda'} - \xi_\lambda\xi_{\lambda'} - \Delta^2}{2\varepsilon_\lambda\varepsilon_{\lambda'}(\varepsilon_\lambda + \varepsilon_{\lambda'})},$$

in Eq. (6). Since $\epsilon_\lambda = \sqrt{\xi_\lambda^2 + \Delta^2}$, this can be written in the form

$$F = \frac{[(\xi_\lambda\xi_{\lambda'} + \Delta^2)^2 + \Delta^2(\xi_\lambda - \xi_{\lambda'})^2]^{1/2} - (\xi_\lambda\xi_{\lambda'} + \Delta^2)}{2\varepsilon_\lambda\varepsilon_{\lambda'}(\varepsilon_\lambda + \varepsilon_{\lambda'})}.$$

Next, we find that

$$F(\lambda, \lambda', \Delta) < \frac{|\xi_\lambda - \xi_{\lambda'}|}{2\Delta} \frac{\Delta^2}{\varepsilon_\lambda\varepsilon_{\lambda'}(\varepsilon_\lambda + \varepsilon_{\lambda'})}.$$

If $|\xi_\lambda - \xi_{\lambda'}| \lesssim 2\Delta$, then $F \ll (|\xi_\lambda| + |\xi_{\lambda'}|)^{-1} = F(\lambda, \lambda', \Delta = 0)$. The last function determines the usual Van Vleck paramagnetism in accordance with Eq. (8). The inclusion of terms corresponding to $\xi_\lambda\xi_{\lambda'} > 0$ in Eq. (6) does not modify this estimate.

In view of the foregoing discussion, we obtain

$$\varepsilon_F / N^{1/2} \lesssim 2\Delta. \tag{9}$$

When this is satisfied, the paramagnetic contribution due to pair correlation is suppressed, and we have anomalous diamagnetic susceptibility. This condition is practically always satisfied in the complex molecules which we are considering because, as noted above, several single-particle levels can be fitted into the interval 2Δ. Moreover, the increase in the density of states and the associated reduction in the level separation near the edge of the gap play an appreciable role. In molecules such as, for example, ovalene or hexabenzocoronene, we have $\epsilon_F \approx 10^5$ cm^{-1}. On the other hand, $2\Delta \sim 2 \times 10^4$ cm^{-1}, i.e., this quantity is of the same order of magnitude as $\epsilon_F/N^{1/2}$. As the molecules become more complicated the above inequality is more readily satisfied because ϵ_F and Δ become practically independent of N (see, for example, [18]). It is clear that in different cases there may be different manifestations of the presence of the superconducting state, and a different degree of reduction in the paramagnetic contribution. A similar situation is found in the case of nuclear moments of inertia.[14] The moment of inertia is found to depend on the extent to which pair correlation effects are important. We note that the case $|\xi_\lambda - \xi_{\lambda'}| \ll 2\Delta$ is analogous to the London limit in the usual theory of superconductivity.

More precise numerical calculations require a knowledge of the wave functions for the π electrons. In the "metal" model of the ovalene molecule[19] calculations of $\hat{M}_{z\lambda\lambda'}$ have shown that this quantity is a maximum for $|\xi_\lambda - \xi_{\lambda'}| \sim 3 \times 10^3$ cm^{-1} which, in view of the fact that the inequality $|\xi_\lambda - \xi_{\lambda'}| \ll 2\Delta$ is satisfied, again confirms the conclusion about the presence of anomalous diamagnetism.

The above pair correlation effects should vanish in sufficiently strong magnetic fields. This is analogous to the disappearance of superconductivity in metals when the external magnetic field assumes its critical value. An analogous effect was investigated in [20] in the case of rotating nuclei.

The behavior of molecules in strong magnetic fields will be considered in detail elsewhere. The disappearance of correlation effects takes place only in very strong magnetic fields. Nevertheless, some reduction in Δ for the transition from the ground to the first excited state can probably be observed in fields that can be produced by existing superconducting magnets. In view of this, it would be interesting to have the results of experiments on the effect of a strong field on the electronic spectrum of a complex molecule.

We may thus conclude that the inclusion of pair correlation in the π-electron system enables us to use the London equation for the diamagnetic current, and the associated anomalous diamagnetic susceptibility described by Eq. (3), because the paramagnetic contribution turns out to be highly suppressed.

4. POLARIZABILITY

Pair correlation has an important effect on the polarizability of complex molecules. Let us begin by considering the static polarizability. We shall start with the general formula given by Eq. (4) for the single-particle density matrix. In this case, the perturbation operator is $V_0 = -\mathbf{d}\cdot\mathbf{E}$ where d is the dipole moment. The positive eigenvalue then corresponds to the operator $\hat{T}$. The change in energy of the system due to the external electric field is

$$\langle\hat{H}\rangle = \sum_{\lambda,\lambda'}\rho'_{\lambda\lambda'}(\mathbf{dE})_{\lambda'\lambda} = \sum_{\lambda,\lambda'}\frac{\xi_\lambda\xi_{\lambda'} - \varepsilon_\lambda\varepsilon_{\lambda'} - \Delta^2}{2\varepsilon_\lambda\varepsilon_{\lambda'}(\varepsilon_\lambda + \varepsilon_{\lambda'})}(\mathbf{dE})_{\lambda\lambda'}(\mathbf{dE})_{\lambda'\lambda}.$$

From the general formula $\langle H\rangle = \alpha_{ik}E_iE_k$ we obtain the following expression for the polarizability tensor:

$$\alpha_{ik} = -\sum_{\lambda,\lambda'}\frac{\xi_\lambda\xi_{\lambda'} - \Delta^2 - \varepsilon_\lambda\varepsilon_{\lambda'}}{2\varepsilon_\lambda\varepsilon_{\lambda'}(\varepsilon_\lambda + \varepsilon_{\lambda'})}d_{i\lambda\lambda'}\,d_{k\lambda'\lambda}. \tag{10}$$

The diagonal component of this tensor is of the form

$$\alpha_{ii} = \sum_{\lambda,\lambda'}\frac{\varepsilon_\lambda\varepsilon_{\lambda'} - \xi_\lambda\xi_{\lambda'} + \Delta^2}{2\varepsilon_\lambda\varepsilon_{\lambda'}(\varepsilon_\lambda + \varepsilon_{\lambda'})}|\hat{d}_{i\lambda\lambda'}|^2. \tag{11}$$

Substituting $\Delta = 0$, we obtain

$$\alpha_{ii} = \sum_{\lambda,\lambda'}\frac{1}{|\xi_\lambda| + |\xi_{\lambda'}|}|\hat{d}_{i\lambda\lambda'}|^2, \quad \xi_\lambda, \xi_{\lambda'} < 0 \tag{12}$$

This gives the polarizability tensor which is well known in the theory of molecules (see, for example, [11,21]) and which is usually established from the usual perturbation theory. The inclusion of pair correlation in the analysis of the above molecules is thus seen to lead to Eq. (11) which is different from the usual formula. Inclusion of the interaction between the quasiparticles will lead, as above (see Sec. 3), to the replacement of d by the value d_p which is renormalized on account of the interaction.

Let us consider Eq. (11) in greater detail. By analogy with the foregoing discussion (see Section 3), we shall use the quasiclassical estimates for the matrix elements, and will then be able to show that the main contribution to Eq. (11) is due to terms satisfying the condition $|\xi_\lambda - \xi_{\lambda'}| \lesssim \epsilon_F/N^{1/2}$. The values which are important in the sum in Eq. (11) are those satisfying the condition $|\xi_\lambda|$, $|\xi_{\lambda'}| \lesssim \Delta$. In point of fact, when we consider the terms corresponding to $|\xi_\lambda|$, $|\xi_{\lambda'}| \gg \Delta$, the effects of pair correlation become unimportant and Δ can be neglected. We then obtain Eq. (12), again with the values of ξ_λ, $\xi_{\lambda'}$ satisfying the condition $\xi_\lambda\xi_{\lambda'} > 0$ providing the only important contributions. Because of the presence of the gap, these values are well separated and are very different in the number of nodes. As noted above, this leads to small values for the matrix element.

Next, we shall assume that $\epsilon_F/N^{1/2} \ll \Delta$. In that case, $|\xi_\lambda| \ll \Delta$ and Eq. (11) will assume the form (we shall confine our attention to diagonal components $\alpha_{ii} \equiv \alpha_i$)

$$\alpha_i \approx \frac{1}{2\Delta}\sum_{\lambda,\lambda'}|\hat{d}_{i\lambda\lambda'}|^2 \approx \frac{1}{2\Delta}\sum_{\lambda}d_{i\lambda\lambda} \quad (|\xi_\lambda| \leqslant \Delta).$$

The component of the susceptibility α_ρ in the direction lying in the plane of the molecule is

$$\alpha_\rho = \frac{e^2}{2\Delta}\sum_{\lambda}\rho_{\lambda\lambda}{}^2 \quad (|\xi_\lambda| \leqslant \Delta). \tag{13}$$

It is readily seen that the susceptibility α_ρ which is determined by the sum on the right-hand side of Eq. (13) is uniquely related to the diamagnetic susceptibility $\chi_{\perp D}$ of π electrons given by Eq. (3) and referring to the corresponding energy interval. The relation between α_ρ and χ_D turns out to be linear ($\alpha_\rho \sim \chi_D$). It is substantially different from the Kirkwood formula $\chi = -e^2a_0(Z\alpha)^{1/2}/4me^2$ (a_0 is the Bohr radius) obtained for the centrally-symmetric electron system which is unsuitable for the description of the complex systems of collectivized electrons which we are considering (see, for example, [21], p. 204).

In the case of a uniform distribution of π electrons, when the density $n(\rho)$ is not very dependent on ρ, which is possible when Eq. (9) is satisfied, the susceptibility α_ρ and the total diamagnetic susceptibility $\chi_{\perp D}$ of the electron system are related by

$$\chi_{\perp D} = \gamma\alpha_\rho, \quad \gamma \approx -\varepsilon_F/4mc^2. \tag{14}$$

This can be verified experimentally. Consider, for example, the ovalene molecule $C_{32}H_{14}$. We shall use the susceptibility and polarizability data given in [16]: $\chi_{\perp D} \approx 6 \times 10^{-28}\ \text{cm}^3$, $\alpha \approx 9 \times 10^{-23}\ \text{cm}^3$. Moreover, $\epsilon_F \approx \pi h^2 n/m \approx 3 \times 10^{-11}$ erg. Substitution of this in Eq. (14) will show that this equation is satisfied with sufficient accuracy.

Let us now calculate a polarizability of the molecule in an external alternating electric field. The perturbation is now given by

$$V = {}^1/_2\mathbf{dE}e^{i\omega t} + \text{c.c.}$$

The addition to the single-particle density matrix turns out to be

$$\rho'_{\lambda\lambda'} = \frac{(\varepsilon_\lambda + \varepsilon_{\lambda'})(\varepsilon_\lambda\varepsilon_{\lambda'} - \xi_\lambda\xi_{\lambda'} + \Delta^2)}{2\varepsilon_\lambda\varepsilon_{\lambda'}[(\varepsilon_\lambda + \varepsilon_{\lambda'})^2 - \omega^2]}d_{k\lambda\lambda'}E_k.$$

We shall use the relation

$$P_i = \sum_{\lambda,\lambda'}\rho'_{\lambda\lambda'}\,d_{i\lambda'\lambda}$$

to calculate the polarizability of the molecule in the external field. The polarizability α_{ik} is obtained from the well known relation $P_i = \alpha_{ik}E_k$. It turns out to be

$$\alpha_{ik}(\omega) = \sum_{\lambda,\lambda'}\frac{(\varepsilon_\lambda + \varepsilon_{\lambda'})(\varepsilon_\lambda\varepsilon_{\lambda'} - \xi_\lambda\xi_{\lambda'} + \Delta^2)}{2\varepsilon_\lambda\varepsilon_{\lambda'}[(\varepsilon_\lambda + \varepsilon_{\lambda'})^2 - \omega^2]}d_{i\lambda'\lambda}\,d_{k\lambda'\lambda}. \tag{15}$$

The diagonal component of the tensor $\alpha_{ii}(\omega)$ is

$$\alpha_{ii}(\omega)=\sum_{\lambda,\lambda'}\frac{(\varepsilon_\lambda+\varepsilon_{\lambda'})(\varepsilon_\lambda\varepsilon_{\lambda'}-\xi_\lambda\xi_{\lambda'}+\Delta^2)}{2\varepsilon_\lambda\varepsilon_{\lambda'}[(\varepsilon_\lambda+\varepsilon_{\lambda'})^2-\omega^2]}|d_{i\lambda\lambda'}|^2. \qquad (15')$$

If we set $\Delta = 0$, we obtain

$$\alpha_{ii,\,\Delta=0}=\sum_{\lambda,\lambda'}\frac{|\xi_\lambda|+|\xi_{\lambda'}|}{(|\xi_\lambda|+|\xi_{\lambda'}|)^2-\omega^2}|d_{i\lambda\lambda'}|^2, \quad \xi_\lambda\xi_{\lambda'}<0,$$

which is well known in the theory of molecules. The sum $|\xi_\lambda| + |\xi_\lambda{}'|$ is the change in the energy of the molecule for a single-particle electronic excitation. Substituting $|\xi_\lambda| + |\xi_\lambda{}'| = \omega_{0,n}$, we obtain the more usual expression:

$$\alpha_{ii,\,\Delta=0}=\sum_{\xi_\lambda\xi_\lambda{}'<0}[\omega_{0n}/(\omega_{0n}{}^2-\omega^2)]\,|d_{i\lambda\lambda'}|^2.$$

Equation (15) is therefore a generalization of the usual expression for the polarizability tensor to the case when pair correlation effects must be taken into account.

5. COLLECTIVE (EXCITON) EXCITATIONS

The presence of the gap in the energy spectrum of the π-electron system leads to the possible existence of exciton-type collective levels within the energy gap. These do not decay to single-particle levels. The spectrum of these excitations, whose existence is due to the electron-hole interaction, may be obtained by considering the properties of the two-particle Green function.

1. Let us introduce the matrix

$$G_{\alpha;\beta}(\lambda,\omega)=\begin{pmatrix} G(\lambda,\omega) & iF(\lambda,\omega) \\ iF(\tilde\lambda,\omega) & G(\tilde\lambda,-\omega)\end{pmatrix},$$

where

$$G=\frac{u_\lambda{}^2}{\omega-\varepsilon_\lambda+i\delta}+\frac{v_\lambda{}^2}{\omega+\varepsilon_\lambda-i\delta}$$

is the corresponding component of the usual Green function

$$F^+(\lambda,\omega)=u_\lambda v_\lambda[(\omega-\varepsilon_\lambda+i\delta)^{-1}-(\omega-\varepsilon_\lambda-i\delta)^{-1}],$$

$$\varepsilon_\lambda=(\xi_\lambda{}^2+\Delta^2)^{1/2}, \quad u_\lambda{}^2=\frac{1}{2}\left(1+\frac{\xi_\lambda}{\varepsilon_\lambda}\right), \quad v_\lambda{}^2=\frac{1}{2}\left(1-\frac{\xi_\lambda}{\varepsilon_\lambda}\right),$$

and $F^+ = \langle T(\psi^+\psi^+)\rangle$ is the anomalous Green function.[21]

Next, let us introduce the matrix $K_{\alpha\beta;\gamma\delta}$ containing the various two-particle Green functions:

$$K_{\alpha\beta;\,\gamma\delta}(12;34)=$$
$$=\begin{pmatrix} \langle 12;3^+4^+\rangle & i\langle 12;3^+\tilde4\rangle & i\langle 12;\widetilde{34}^+\rangle & -\langle 12;\tilde3\tilde4\rangle \\ i\langle \widetilde{12}^+;3^+4^+\rangle & -\langle \widetilde{12}^+;3^+\tilde4\rangle & -\langle \widetilde{12}^+;\widetilde{34}^+\rangle & -i\langle 12^+;\tilde3\tilde4\rangle \\ i\langle \tilde1^+2;3^+4^+\rangle & -\langle \tilde1^+2;3^+\tilde4\rangle & -i\langle \tilde1^+2;\widetilde{34}^+\rangle & -i\langle \tilde1^+2;\tilde3\tilde4\rangle \\ -\langle \tilde1^+\tilde2^+;3^+4^+\rangle & -i\langle \tilde1^+\tilde2^+;3^+\tilde4\rangle & -i\langle \tilde1^+\tilde2^+;\widetilde{34}^+\rangle & \langle \tilde1^+\tilde2^+;34\rangle \end{pmatrix}.$$

We now shall write down the Bethe-Salpeter equation for the two-particle Green function (an analogous calculation in the case of collective excitations of the nucleus is given in [22]; for the sake of simplicity, we shall confine our attention to the axially symmetric case):

$$K^{i;\,k}(12;34;m)=K_0^{i;\,k}(12;34;m)$$
$$+\,{}^1/{}_2K_0^{i;\,l}(12;56;m)\,\Gamma_l(65;87;m)\,K^{l;\,k}(78;34;m), \qquad (16)$$

where

$$K_0^{i;\,k}=\frac{2}{4\varepsilon^2-\omega^2}\begin{pmatrix} 2\varepsilon & i\omega(u^2-v^2) & i\omega 2uv \\ i\omega(u^2-v^2) & -2\varepsilon(u^2-v^2) & -4\varepsilon uv(u^2-v^2) \\ i\omega 2uv & -4\varepsilon uv(u^2-v^2) & -8\varepsilon u^2v^2 \end{pmatrix} \qquad (16')$$

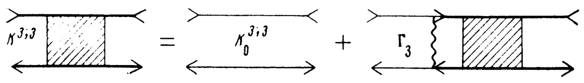

FIG. 3

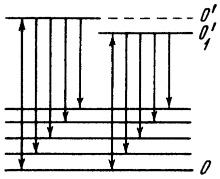

FIG. 4

describes the noninteracting quasiparticles, and Γ_l is the corresponding component of the four-terminal graph describing their interaction. Equation (16) with $i = 1, 2$ describes the propagation of two particles and two holes, respectively. The value $i = 3$, on the other hand, corresponds to the propagation of a particle and a hole.

Let us substitute $\Gamma_1 = \Gamma_2 = 0$, i.e., we shall investigate only the interaction in the particle-hole channel, which leads to the collective (exciton) excitations in which we are interested. We then find from Eq. (16) (see Fig. 3)

$$K^{3;\,3}=K_0^{3;\,3}+{}^1/{}_2K_0^{3;\,3}\Gamma_3K^{3;\,3}$$

and in view of Eq. (16′), this enables us to obtain the following expression for the pole of the two-particle Green function which determines the spectrum of the collective excitations:

$$\omega=2\varepsilon\left(1-\frac{\Delta^2}{2\varepsilon^3}\Gamma_3\right)^{1/2}.$$

The number of these can be quite high because of the multicomponent nature of Γ_3. Next, we find that

$$\omega_{min}=2\Delta(1-\Gamma_3/2\Delta)^{1/2}. \qquad (17)$$

It is clear from this expression that there may be levels lying within the gap.

2. The electron-hole interaction therefore leads to the appearance of exciton-type collective levels if there is pair correlation.

Experiments concerned with the spectra of the complex molecules which we are considering have established the presence of multiplet structure. Groups of lines with constant frequency separation are observed, and this corresponds to the presence of electron levels (for example, $0_1'$ in Fig. 4; vibrational levels are shown near 0) lying below the 0′ level. This multiplet structure is a characteristic feature of the quasiline spectrum.[23] It was supposed earlier that the appearance of this structure was connected with the presence in the crystal matrix of different types of radiating center.[24] However, this hypothesis is incapable of explaining the observed reproducibility of this structure and its complexity. Direct experimental studies of the spectra of phthalocyanines[25] have shown that at least some of the lines in the complex multiplets are not due to different centers, but to a single molecule.

It may be concluded from the foregoing that at least one of the reasons for the appearance of the multiplet structure is connected with pair correlation in the π-electron system and the presence of intramolecular collective (exciton) levels lying within the energy gap.

3. We have so far discussed the properties of polycyclic molecules contining a few tens of π electrons. It is clear, however,(see Sec. 1), that the pair correlation effect and the associated appearance of the energy gap are due to the presence of the π-electron system and the attraction mechanisms within it. This effect is, of course, possible in more complex molecules as well, including biologically active molecules. All the most important biochemical materials contain conjugated systems (see, for example, [26], p. 546). The presence of pair correlation within the collectivized electron system, which leads to the appearance of the gap in the spectrum, ensures a stability which is analogous to that observed in superconducting metals. Long-range order due to electron correlation is important for the understanding of the mechanism responsible for the coupling and transfer of excitations in biochemical materials.

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100