PAIR CORRELATION IN POLYCYCLIC MOLECULES

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PAIR CORRELATION IN POLYCYCLIC MOLECULES

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As is known, the molecules of aromatic compounds are characterized by the presence of a system of collectivized π-electrons situated in the field created by the σ-skeleton of the molecule. These π-electrons, whose number in complex molecules may be rather large, form a system whose properties can be studied with the aid of the theory of finite Fermi systems (^{1}).

Below we consider the question of the possibility of pair correlation of the superconducting type in such molecules, and certain physical properties caused by the presence of such correlation.

1. A necessary condition for the occurrence of pair correlation is the presence of attractive forces in the system under consideration. In a π-electron system the existence of such forces may be due to a number of causes. Let us first consider the interaction of the π-electrons with the vibrational degrees of freedom of the molecule.

The Hamiltonian of the molecule may be written in the form:

$$\hat{H} = \hat{H}_0 + \hat{H}_1,$$

where

$$\hat{H}_1 = \sum_{i,a} v(\mathbf{r}_i - \mathbf{R}_a)$$

($\mathbf{r}_i$ describes the position of the π-electron, and $\mathbf{R}_a$ that of the ion) corresponds to the electron-ion interaction.

Expanding $\hat{H}_1$ in powers of $\delta\mathbf{R}_a$ ($\delta\mathbf{R}_a$ is a small displacement of the ions) and then representing $\delta\mathbf{R}_a$ in the form of a superposition of normal vibrations, we obtain, for the interelectronic interaction, which for simplicity we assume to be weak, the following Hamiltonian in the second-quantization representation:

Fig. 1. Hexabenzocoronene molecule

Figure 1: Fig. 1. Hexabenzocoronene molecule

$$H_{int} = \sum_{\lambda,\lambda';\,\lambda_1,\lambda_1'} g_{\lambda,\lambda';\lambda_1,\lambda_1'}\, a^+_{\lambda} a^+_{\lambda_1} a_{\lambda_1'} a_{\lambda'}, \tag{1}$$

where

$$g_{\lambda,\lambda';\lambda_1,\lambda_1'} = \sum_{l} M^l_{\lambda\lambda'} M^l_{\lambda_1\lambda_1'} \frac{\omega_l}{(\varepsilon_\lambda - \varepsilon_{\lambda'})^2 - \omega_l^2}$$

($M^l_{\lambda\lambda'}$ are matrix elements describing the corresponding transitions in the electron-ion system).

It is clear that the values $\varepsilon_\lambda - \varepsilon_{\lambda'} < \omega_l$, for which the change in the electronic energy is less than the excitation energy of a virtual vibrational quantum, correspond to interelectronic attraction. The mechanism considered is entirely analogous to the usual one determining superconductivity in metals, associated with the interaction of conduction electrons with vibrations of the crystal lattice (see, for example, (^{2})).

Interelectronic attraction may also arise through the interaction of π-electrons with σ-electrons. Experimentally, excitation of σ-electrons corresponding to frequencies $\nu \sim 4 \cdot 10^4$ cm^{-1} is observed. The Coulomb interaction of π- and σ-electrons, accompanied by virtual transitions in the σ-electron system, leads to an effective interaction of the π-electrons, analogous to the electronic mechanism of superconductivity (^{3}).

The σ skeleton of the molecules under consideration is planar (see, for example, Fig. 1; for a detailed description of the properties of the complex molecules considered, see, for example, in (4)). Pair correlation in them is analogous to the effect of surface, two-dimensional superconductivity (5). Let us note, incidentally, that the finite character of the system under consideration ensures its stability with respect to fluctuations of the electron density.

It is significant that experimental data (see, for example, (4)) show that the first excited electronic level corresponds to an energy interval 1—0 that considerably exceeds the interval 2—1, etc.

Fig. 1. Hexabenzocoronene molecule

In the presence of pair correlation, the energy gap should disappear on passing to systems with an odd number of π electrons. This regularity is in fact observed experimentally (15).

2. Let us dwell on the question of the influence of pair correlation on the magnetic properties of the molecules considered. In the presence of a magnetic field the π-electron Hamiltonian can be written in the form

$$\hat{H} = \hat{H}_0 + \hat{H}_1 + \hat{H}_2,$$

where

$$\hat{H}_0 = \int \{\psi^+ \Delta\psi + g\psi^+(\psi^+\psi)\psi\}\, d\mathbf{r}; \tag{2}$$

$$\hat{H}_1 = \frac{ie}{2m}\int \psi^+(\nabla\mathbf{A} + \mathbf{A}\nabla)\psi\, d\mathbf{r}; \tag{3}$$

$$\hat{H}_2 = -\frac{e^2}{2m}\int \psi^+\psi A^2\, d\mathbf{r}. \tag{4}$$

The expression for

$$\hat{H}_1 = \frac{ie}{m}\int \mathbf{A}\nabla_r G'(x,x')\Big|_{\substack{x=x'\\ t=t'+0}} d\mathbf{r}$$

(G' is the addition to the Green function due to the field; we choose $\mathbf{A} = \frac{1}{2}[\mathbf{Hr}]$) can be reduced to the form:

$$\hat{H}_1 = \frac{ie}{m}\sum_{\lambda,\lambda'} \rho'_{\lambda\lambda'}\hat{M}_{i\lambda'\lambda}$$

($\hat{M}_i = -i[\mathbf{r}\nabla]_i$; H_i is a component of the magnetic-field strength, which in what follows we shall regard as weak).

The addition to the density matrix $\rho_{\lambda\lambda'}$, connected with the presence of an arbitrary small perturbation V, according to (6), has the form

$$\rho'_{\lambda\lambda'} = \frac{(\xi_\lambda\xi_{\lambda'} - \varepsilon_\lambda\varepsilon_{\lambda'})V_{\lambda\lambda'} - \Delta^2 V^*_{\lambda\lambda'} + \Delta(\xi_\lambda\Delta'_{\lambda\lambda'} + \xi_{\lambda'}\Delta'^*_{\lambda\lambda'})}{2\varepsilon_\lambda\varepsilon_{\lambda'}(\varepsilon_\lambda + \varepsilon_{\lambda'})} \tag{5}$$

(ξ_λ is the energy of an ordinary electron, measured from the Fermi level, $\varepsilon_\lambda = \sqrt{\xi_\lambda^2 + \Delta^2}$).

Taking (5) into account, we find $\hat{H}_1$ and then, with the aid of the known relation $\chi = -c^2(\Delta E)/\partial H^2$, calculate the paramagnetic susceptibility $\chi_{\perp p}$ in the direction perpendicular to the plane of the molecule:

$$\chi_{\perp p} = \frac{e^2}{8m^2} \sum_{\lambda,\lambda'} \frac{\varepsilon_\lambda \varepsilon_{\lambda'} - \xi_\lambda \xi_{\lambda'} - \Delta^2}{2\varepsilon_\lambda \varepsilon_{\lambda'}(\varepsilon_\lambda + \varepsilon_{\lambda'})} \left|\hat{M}_{i\lambda\lambda'}\right|^2 . \tag{6}$$

A contribution to $\chi_{\perp P}$ is also made by the term associated with the change of the gap Δ in a magnetic field, to which the estimates made below are likewise applicable.

In the absence of pair correlation,

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

The expression for $\chi_{\perp P}$ vanishes for molecules possessing axial symmetry, since in this case $\hat{M}_z$ is diagonal. In this case the molecule exhibits an anomalous diamagnetism $\chi_{\perp D}$, determined with the aid of (4) and not connected with pair correlation. In particular, this is the case for benzene ([7]), whose symmetry in the calculations is assumed to be $D_{\infty h}$.

In calculating the susceptibility of more complicated molecules it is necessary to take into account both $\chi_{\perp P}$ and $\chi_{\perp D}$ (see, for example, ([8])). In ([8]) it is noted that, for complex aromatic molecules, $\chi_{\perp P} = 0$ is observed experimentally. This circumstance, in our opinion, may be explained by pair correlation in such compounds and by the "rigidity" of the wave functions associated with it, which weakens the paramagnetic contribution.

In expression (6), in the case of interest to us, when at least several one-particle levels fit within the interval 2Δ, the main role is played by ξ_λ and $\xi_{\lambda'}$ such that $|\xi_\lambda - \xi_{\lambda'}| \lesssim 2\Delta$ (this relation usually describes a superconductor of the "London" type). This relation can be obtained with the aid of quasiclassical estimates of the matrix elements ([1,9]), and also by using the numerical calculations of molecules presented in ([10]).

At the same time, as is readily seen from (6), (7), $\chi_{\perp P} \ll \chi_{\perp P,\Delta=0}$, i.e., the paramagnetic contribution turns out to be suppressed to a considerable degree by pair correlation, and the molecule exhibits anomalous diamagnetism. It is clear that in different cases the manifestation of the superconducting state may be different, as may the degree of reduction of the paramagnetic contribution. An analogous situation arises in calculating the moments of inertia of nuclei ([6]): the magnitude of the moment of inertia proves to depend on the degree to which pair-correlation effects are manifested in them.

The excess of the observed total susceptibility χ_D over the calculated value in complex molecules ([8]) is apparently connected with pair correlation.

3. Pair correlation in the π-electron system leads to the possibility of the existence of exciton, collective levels lying inside the energy gap and there-

Fig. 2

Figure 2: Fig. 2

fore not decaying into one-particle levels. In ordinary superconductors such levels were investigated in (^{11}), and in the nucleus in (^{1},^{12},^{13}). The spectrum of these exciton excitations may be obtained by considering the singularities of the two-particle Green' s function.

The one-particle Green' s function in the case under consideration may be represented in the following matrix form:

$$G_{\alpha;\beta}(\lambda,\omega)=\frac{A_{\alpha;\beta}(\lambda)}{\omega-\varepsilon_\lambda}+\frac{B_{\alpha;\beta}(\lambda)}{\omega+\varepsilon_\lambda};$$

$$A_{\alpha;\beta}(\lambda)=\begin{pmatrix} u_\lambda^2 & iu_\lambda v_\lambda \\ -iu_\lambda v_\lambda & -v_\lambda^2 \end{pmatrix}; \qquad B_{\alpha;\beta}(\lambda)=\begin{pmatrix} v_\lambda^2 & iu_\lambda v_\lambda \\ iu_\lambda v_\lambda & -u_\lambda^2 \end{pmatrix},$$

$$u_\lambda^2=\frac{1}{2}\left(1+\xi_\lambda/\varepsilon_\lambda\right); \qquad v_\lambda^2=\frac{1}{2}\left(1-\xi_\lambda/\varepsilon_\lambda\right).$$

By the states λ and $\bar{\lambda}$ entering into the wave function of the pair, one should, as usual, understand states conjugate with respect to the transformation $t\to -t$. Introducing in analogous fashion a matrix representation $K_{\alpha\beta;\gamma\delta}$ (12; 34) for the two-particle Green' s function (an analogous calculation

in the case of a nucleus, see (12)), we obtain the equation:

$$K^{i;k}(12;34,M)=K_0^{i;k}(12;34,M)+$$

$$+\frac{1}{2}K_0^{i;l}(12;56,M)\Gamma_l(65;87,M)K^{l;k}(78;34,M). \tag{8}$$

Here the values of the indices $i=1,2$ and $i=3,0$ correspond to the propagation of two particles (or two holes) and of a particle and a hole; Γ_l is a four-pole quantity describing the interaction of quasiparticles.

For exciton levels caused by the electron-hole interaction Γ_3, from (8) one can obtain the formula

$$\omega=2\varepsilon\sqrt{1-\frac{\Delta^2}{\varepsilon^3}\Gamma_3}, \tag{9}$$

i.e., the existence of levels lying inside the gap proves possible.

Fig. 2

In experiment, in the study of the spectra of the complex molecules under consideration (see, for example, (14)), groups of lines with an unchanged spacing in frequencies are observed (see Fig. 2). This corresponds to the presence of electron levels lying below the level $0'$. Since, in the presence of pairing, the interval $0'$—$0''$ turns out to be connected with the energy gap, it is apparently the case that the appearance of such groups of lines is due to the exciton excitations considered above.

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