Superconductivity — a new insight offered by a nonadiabatic molecular electron-vibrational theory

P. BAŇACKÝ, M. SVRČEK, and A. ZAJAC

Institute of Chemistry, Division of Chemistry and Physics of Biomolecules, Comenius University, CS-832 32 Bratislava

Received 4 January 1991

Discovery of high-T_c superconductors has also renewed an interest in the theoretical aspects of superconductivity phenomenon. The most successful microscopic theory of superconductivity — BCS theory [1] has been unable to interpret some new facts characteristic of high-T_c materials.

Besides the standard electron-phonon mechanism which is the basis of BCS theory, a wide variety of physical phenomena, *e.g.* excitons, plasmons, d-mons, resonance valence bonds, has become the basis of different microscopic theories of superconductivity [2]. The common feature of all these theories is some kind of pairing mechanism which yields the energy gap, ground state energy lowering connected with the charge-carrier formation characterized by a high degree of coherence. However, recently it has been proved that off-diagonal long-range order (ODLRO) can be reached even by the repulsive coulombic electron—electron interaction without necessity of pairing, *i.e.* without any effective attractive electron—electron interaction mechanism [3].

Nonadiabatic molecular electron-vibrational theory which we have recently formulated [4] offers substantially different microscopic interpretation of the superconductivity mechanism comparing to the existing ideas. We have shown that pairing, particularly Cooper's pairs formation is irrelevant to the energy gap formation, and superconductivity itself is the consequence of one-particle fermionic term in nonadiabatic systems. The theory is based on the *ab initio* solution of electron-vibrational problem characterized by the most general form of nonrelativistic Hamiltonian which treats the motion of the electrons to be dependent not only on the coordinates of nuclei but also on the nuclei momenta. The solution of the problem after quasiparticle transformation yields "new" fermions with the Hamiltonian of the following form

$$\hat{H}_F = (H^0 + \Delta E^0) + (\hat{H}' + \Delta\hat{H}') + (\hat{H}'' + \Delta\hat{H}'') \qquad (1)$$

The electronic Hamiltonian of a molecular system with "frozen" position of nuclei (*e.g.* equilibrium geometry) which we term "crude" electronic system reads

$$\hat{\mathscr{H}} = H^0 + \hat{H}' + \hat{H}'' \tag{2}$$

where

$$H^0 = E^0_{\mathrm{NN}} + E^0_{\mathrm{SCF}} \tag{3}$$

while

$$E^0_{\mathrm{SCF}} = \sum_{\mathrm{I}}^{\mathrm{occ}} h^0_{\mathrm{II}} + 0.5 \sum_{\mathrm{IJ}}^{\mathrm{occ}} (V^0_{\mathrm{IJIJ}} - V^0_{\mathrm{IJJI}}) \tag{4}$$

is the SCF energy of "crude" electronic system, and $\hat{H}'$ $\hat{H}''$ are one- and two-particle terms

$$\hat{H}' = \sum_{\mathrm{P}} \varepsilon^0_{\mathrm{P}} N[a^+_{\mathrm{P}} a_{\mathrm{P}}]; \quad \hat{H}'' = 0.5 \sum_{\mathrm{PQRS}} V^0_{\mathrm{PQRS}} N[a^+_{\mathrm{P}} a^+_{\mathrm{Q}} a_{\mathrm{S}} a_{\mathrm{R}}] \tag{5}$$

Due to the electron-vibrational (phonon) interaction there are corrections to the ground state energy (ΔE^0), to the one-particle term ($\Delta \hat{H}'$) and two-particle term ($\Delta \hat{H}''$) which have been derived for a nonadiabatic system in the form

$$\Delta E^0 = \sum_{\mathrm{A}}^{\mathrm{unocc}} \sum_{\mathrm{I}}^{\mathrm{occ}} \sum_{\mathrm{v}} \hbar\omega_{\mathrm{v}} [|c^{\mathrm{v}}_{\mathrm{AI}}|^2 - |\tilde{c}^{\mathrm{v}}_{\mathrm{AI}}|^2] \tag{6}$$

$$\Delta \hat{H}' = \sum_{\mathrm{P}} \sum_{\mathrm{v}} \hbar\omega_{\mathrm{v}} \left[\sum_{\mathrm{A}}^{\mathrm{unocc}} (|c^{\mathrm{v}}_{\mathrm{PA}}|^2 - |\tilde{c}^{\mathrm{v}}_{\mathrm{PA}}|^2) - \sum_{\mathrm{I}}^{\mathrm{occ}} (|c^{\mathrm{v}}_{\mathrm{PI}}|^2 - |\tilde{c}^{\mathrm{v}}_{\mathrm{PI}}|^2) \right] N[a^+_{\mathrm{P}} a_{\mathrm{P}}] \tag{7}$$

$$\Delta \hat{H}'' = \sum_{\mathrm{PQRS}} \sum_{\mathrm{v}} \hbar\omega_{\mathrm{v}} (c^{\mathrm{v}}_{\mathrm{PR}} c^{\mathrm{v}*}_{\mathrm{SQ}} - \tilde{c}^{\mathrm{v}}_{\mathrm{PR}} \tilde{c}^{\mathrm{v}}_{\mathrm{SQ}}) N[a^+_{\mathrm{P}} a^+_{\mathrm{Q}} a_{\mathrm{S}} a_{\mathrm{R}}] \tag{8}$$

while

$$c^{\mathrm{v}}_{\mathrm{PQ}} = u^{\mathrm{v}}_{\mathrm{PQ}} \frac{\varepsilon^0_{\mathrm{P}} - \varepsilon^0_{\mathrm{Q}}}{(\hbar\omega_{\mathrm{v}})^2 - (\varepsilon^0_{\mathrm{P}} - \varepsilon^0_{\mathrm{Q}})^2}; \quad \tilde{c}^{\mathrm{v}}_{\mathrm{PQ}} = u^{\mathrm{v}}_{\mathrm{PQ}} \frac{\hbar\omega_{\mathrm{v}}}{(\hbar\omega_{\mathrm{v}})^2 - (\varepsilon^0_{\mathrm{P}} - \varepsilon^0_{\mathrm{Q}})^2}; \quad \mathrm{P} \neq \mathrm{Q} \tag{9}$$

with $u^{\mathrm{v}}_{\mathrm{PQ}}$ being electron—phonon coupling constant. The eigenenergy of the Hartree—Fock operator of "crude" electronic system is equal to

$$\varepsilon^0_{\mathrm{P}} = h^0_{\mathrm{PP}} + \sum_{\mathrm{I}} (V^0_{\mathrm{PIPI}} - V^0_{\mathrm{PIIP}}) \tag{10}$$

In the complex quasimomentum ($\boldsymbol{k}$, $\boldsymbol{q}$) space representation, the corrections (*6—8*) are of the following forms

$$\Delta E^0 = 2 \sum_{k,k'} |u^{k-k'}|^2 f_k (1 - f_{k'}) \frac{\hbar\omega_{k'-k}}{(\varepsilon^0_{k'} - \varepsilon^0_k)^2 - (\hbar\omega_{k'-k})^2} \tag{11}$$

$$\Delta\hat{H}' = \sum_{kq\sigma} \frac{|u^q|^2}{(\varepsilon^0_k - \varepsilon^0_{k-q}) - \hbar\omega_q} N[a^+_{k\sigma} a_{k\sigma}] -$$

$$- 2 \sum_{kq\sigma} f_{k-q} \frac{|u^q|^2 \hbar\omega_q}{(\varepsilon^0_k - \varepsilon^0_{k-q})^2 - (\hbar\omega_q)^2} N[a^+_{k\sigma} a_{k\sigma}] \tag{12}$$

and the reduced (attractive) form of the two-particle correction is

$$\Delta\hat{H}''_{\text{red}} = -2 \sum_{k\,k'} |u^{k'-k}|^2 \frac{\hbar\omega_{k'-k}[(\varepsilon^0_{k'} - \varepsilon^0_k)^2 + (\hbar\omega_{k'-k})^2]}{[(\varepsilon^0_{k'} - \varepsilon^0_k)^2 - (\hbar\omega_{k'-k})^2]^2} \; N[a^+_{k\uparrow} a^+_{-k'\downarrow} a_{-k\downarrow} a_{k\uparrow}] \tag{13}$$

It is evident that the ground state energy correction (*11*) is of the same form as the one derived for the electron—phonon interaction by *Fröhlich* [5]. The two-particle term is different from the form derived by *Fröhlich* [6] but it also yields Cooper's pairs formation, and moreover the derived nonadiabatic reduced form is absolutely attractive.

The one-particle correction (*12*) is of crucial importance. The first part of it represents the well-known expression for polaron [7], while the second part stands for correction to the polaron energy due to its interaction with the SCF field produced by all other polarons. From the one-particle term in its orbital representation (*7*) information can be derived which is, in our opinion, crucial for microscopic mechanism of superconductivity:

1. Under the conditions when electron-vibrational interaction yields ground state energy lowering, *i.e.* $\Delta E^0 < 0$ in (*6*), from the one-particle correction (*7*) it directly follows that electron-vibrational interaction results in the increase of the orbital energies of unoccupied states {A} and decrease of the orbital energies of occupied states {I}. For systems with quasidegenerate states near to FS (quasicontinuum) this mechanism yields the gap formation with the following relation between T_c and zero-temperature gap $\Delta(0)$

$$\frac{\Delta(0)}{k_B T_c} = 4 \tag{14}$$

Derived temperature dependences of the gap and electronic specific heat match correctly experimental dependences.

2. From the expression for the ground state energy correction (*6*), when $\Delta E^0 < 0$, the requirement on electronic structure of a molecular system characteristic of low-T_c, high-T_c, and gapless superconductors can be derived. Results

also yield correct isotopic dependences of $T_c \approx m^{-0.5}$ and $T_c \approx m^0$ for low-T_c/ /high-T_c superconductors.

3. High coherence of electronic motion and the mechanism of superconductivity itself is due to the Jahn—Teller effect. It is related to the mechanism of avoiding of the singularity in the ground state energy correction (eqns (*6, 11*)). To be specific, whenever "crude" electronic structure and the corresponding electron-vibrational interaction were to result in the singularity of ΔE^0, which would mean destabilization of a system, a new stable nuclear geometry is established. In principle there are possible several different equilibrium geometries which all correspond to the same "stabilized" ground state (it is evident from eqns (*6, 11*)). That means, there is possible an existence of "nuclear microflows" around the forbidden "crude" electronic nuclear positions, and what is extremely important, this new kind of motion represents nondissipative degree of freedom (all geometries are equivalent and correspond to the same "stabilized" ground state). On the level of crystal lattice it yields symmetry lowering and formation of sublattices — nested lattices, which is connected with formation of a new optical phonon band. Flowing nuclei pull an electronic cloud and when the system is given an initial momentum the electrons keep in motion without dissipation in a direction of an initial external field. Over T_c the unique property of a system due to nonadiabaticity is destroyed and the system becomes of plain metal character of conductivity. The Meissner effect can also be interpreted within the derived theory as well as a charge-carrier formation of the value $2e$.

The manuscripts dealing with the problem in more detail are in preparation.

References

1. Bardeen, J., Cooper, L. N., and Schrieffer, J. R., *Phys. Rev. 108*,1175 (1957).
2. Cohen, M. L., in *Novel Superconductivity*. (Volf, S. A. and Kresin, V., Editors.) P. 1095. Plenum Press, New York, 1987, and theoretical papers therein.
3. Dunne, L. J., Murrell, J. N., and Brandas, E. J., *Physica C169*, 501 (1990).
4. Svrček, M., Baňacký, P., and Zajac, A., to be published.
5. Fröhlich, H., *Phys. Rev. 79*, 845 (1950).
6. Fröhlich, J., *Proc. R. Soc. London, A 215*, 291 (1952).
7. Lee, T. D., Low, F. E., and Pines, D., *Phys. Rev. 90*, 192 (1953).

Translated by P Baňacký