CORRELATION EFFECTS IN HOPPING CONDUCTION IN SEMICONDUCTORS

P. GOSAR

Physics Department and J.Stefan Institute, E.Kardelj University of Ljubljana, Ljubljana, Yugoslavia

Recent experiments[1] strongly support the idea of correlated hopping as a new mechanism of the electron transport in moderately compensated semiconductors. The basic model of the correlated hopping which uses the concept of two–electron single–phonon transitions has been developed by Knotek and Pollak[2–4]. Recently Gosar[5] improved the theory by using approximations which go beyond the Hartree method. In this communication we discuss the importance of the electron–electron correlation which must be taken into account in all steps of the calculation.

First, a short presentation of the model is given. The two–electron hopping model considers the hopping of two electrons between four impurity sites. The first electron can occupy the localized states $|1\rangle$ or $|2\rangle$ at sites 1 or 2 and the second one the states $|3\rangle$ and $|4\rangle$ at sites 3 or 4. The energy E_{ij} of the particular two–electron localized state $|i = 1,2\rangle$ $|j = 3,4\rangle$ is equal to the sum of local energies E_i, E_j and the Coulomb repulsion energy between electrons. A small transfer matrix element W_{12} in the hamiltonian of this system makes possible the motion of the first electron from the site 1 to the site 2 and vice versa. Similarly, W_{34} determines the rate of the transfer of the second electron between sites 3 and 4. The spacing of energy levels $E_{ks} - E_{ij}$ is considered to be large as compared with W_{12} and W_{34}. Next, the two–electron system is coupled to acoustic phonons via a local deformation potential type interaction

$$\hat{H}' = \sum_{i=1}^{4'} \hat{H}(i)\, |i\rangle\langle i| \qquad (1)$$

where $\hat{H}(i)$ is linear in creation and annihilation operators for longitudinal phonons.

Knotek and Pollak assumed that only one of two electrons carries the current. We drop this restriction. According to the linear response Kubo

theory[6] the d.c. conductivity tensor $\underline{\sigma}$ is given by

$$\underline{\sigma} = \pi\beta V \sum_{\alpha\beta} \langle\alpha|\hat{\rho}|\alpha\rangle\langle\alpha|\hat{j}|\beta\rangle\langle\beta|\hat{j}|\alpha\rangle \delta(E_\beta - E_\alpha); \quad \beta = 1/kT \qquad (2)$$

where V is the volume, $\hat{\rho}$ the density matrix, and $\hat{j}$ the current density operator. $|\alpha\rangle$, $|\beta\rangle$ are states of the system with the corresponding energies E_α, E_β.

The contribution of two electrons in the four-site cluster to the current density operator is

$$-i(e/V)[uW_{12}(\hat{T}_{21} - \hat{T}_{12}) + vW_{34}(\hat{T}_{43} - \hat{T}_{34})] \qquad (3)$$

where $u = r_2 - r_1$, $v = r_4 - r_3$, r_i being the position vector of the site i, and $\hat{T}_{ji} = |j\rangle\langle i|$ is the operator for the transfer of the electron from the site i to the site j.

The terms in (2) which give correlation effects describe two-electron transitions, for instance (1,3) → (2,4). States $|\alpha\rangle$ which correspond to a particular configuration (i = 1,2; j = 3,4) of electrons will be denoted by $|i,j;\{n_q\}\rangle$ where $\{n_q\}$ represents a set of occupation numbers of the lattice modes. q is the wave vector of the longitudinal acoustic mode. More precisely, the leading term in the expansion of $|\alpha\rangle$ in terms of the orthonormal set of localized states $|i\rangle$ and states of the free phonon field $|\{n_q\}\rangle$ is $|i\rangle|j\rangle|\{n_q\}\rangle$. A good approximation to the energy of the state $|i,j;\{n_q\}\rangle$ is the sum of E_{ij} and the energy of the phonon field $E(\{n_q\})$.

Let (1,3) be a ground state and (2,4) the first excited state configuration of the two-electron system. Then at low enough temperatures only the states $|1,3;\{n_q\}\rangle$ and $|2,4;\{n_q\}\rangle$ are important in the expression (2). The transition $|\alpha\rangle \rightarrow |\beta\rangle$ is assumed to be a single-phonon and therefore the occupation of the particular mode q in $|\beta\rangle$ is increased or decreased by 1. The transfer rate W_{ij} being small, the matrix elements of $\hat{T}_{ji}$ in (3) may be readily calculated by using the perturbation expansion of $|i,j;\{n_q\}\rangle$. For instance,

$$\begin{aligned}
|1,3;\{n_q\}\rangle &= |1\rangle|3\rangle|\{n_q\}\rangle + \frac{W_{12}}{E_{13}-E_{23}}|2\rangle|3\rangle|\{n_q\}\rangle \\
&+ \frac{W_{34}}{E_{13}-E_{14}}|1\rangle|4\rangle|\{n_q\}\rangle + \sum_{\{n_{q'}\}}\langle\{n_{q'}\}|\left\{\frac{\hat{H}(1)+\hat{H}(3)}{E(\{n_q\})-E(\{n_{q'}\})}|1\rangle|3\rangle\right. \\
&+ \frac{W_{12}}{E_{13}-E_{23}+E(\{n_q\})-E(\{n_{q'}\})}\left[\frac{\hat{H}(2)+\hat{H}(3)}{E_{13}-E_{23}} + \frac{\hat{H}(1)+\hat{H}(3)}{E(\{n_q\})-E(\{n_{q'}\})}\right]|2\rangle|3\rangle \\
&+ \left.\frac{W_{34}}{E_{13}-E_{14}+E(\{n_q\})-E(\{n_{q'}\})}\left[\frac{\hat{H}(1)+\hat{H}(4)}{E_{13}-E_{14}} + \frac{\hat{H}(1)+\hat{H}(3)}{E(\{n_q\})-E(\{n_{q'}\})}\right]|1\rangle|4\rangle\right\}|\{n_q\}\rangle|\{n_{q'}\}\rangle.
\end{aligned} \qquad (4)$$

In this approximation the contribution of the correlated motion of two electrons in the four-site cluster to $\underline{\sigma}$ is given by

$$\underline{\sigma}_{corr} = \beta e^2 V^{-1} f_{13} C W_{12}^2 W_{34}^2 (u+v)(u+v)$$

$$\times (E_{13} + E_{24} - E_{14} - E_{23})^2 \left[\frac{1}{(E_{24} - E_{14})^2 (E_{23} - E_{13})^2} \right. \qquad (5)$$

$$\left. + \frac{1}{(E_{14} - E_{13})^2 (E_{24} - E_{23})^2} \right] \Delta [\exp(\beta \Delta) - 1]^{-1}$$

where f_{13} is the probability of the occupation of the ground state which corresponds to the configuration (1,3) and $C = E_1^2/\pi \rho_0 s^5$, E_1 being the deformation potential constant, ρ_0 the density, and s the sound velocity. Further, $\Delta = E_{24} - E_{13}$.

Some important conclusions can be derived from (5). Note that $\underline{\sigma}_{corr} = 0$ if electrons do not interact. Further, the expression (5) reveals an interference effect between the contributions of the first and the second electron to the current. The total current is not a simple sum of the currents carried by two electrons separately. In fact, it is proportional to $(u+v)(u+v)$. This interference effect may strongly enhance the current as the constructive interferences are more likely.

It follows from the derivation of (5) that the electron–electron correlation has been taken into account already in the perturbation expansion of states $|\alpha>$. Also, if we neglect the coupling to phonons, the states $|\alpha>$, for instance (4), describe the correlative motion of two electrons and the corresponding wave function is not a product wave function. Hartree product wave functions are obtained only in case of the vanishing Coulomb interaction. The approximations which go beyond the Hartree method are therefore required.

Correlative motions of particles are important in many fields of the solid state physics. In this respect are most interesting protonic semiconductors in which the correlation between the proton jumps in neighboring hydrogen bonds plays a dominant role in the charge transport mechanism.

REFERENCES

1. J.Chroboczek, H.Fritzsche, C.L.Jiang, M.Pollak, and R.L.Wild, Physics of Semiconductors 1978 (Inst.Phys.Conf.Ser. No. 43), The Institute of Physics, Bristol (1979), p. 935;
2. M.L.Knotek and M.Pollak, Phys. Rev. B9 (1974) 664;
3. M.L.Knotek and M.Pollak, Phil. Mag. 35 (1977) 1133;
4. M.Pollak, Impurity Bands in Semiconductors, Würtzburg (1979), p. 16;
5. P.Gosar, J. Phys. C 13 (1980) L111;
6. R.Kubo, J. Phys. Soc. Japan 12 (1957) 570.