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One-Electron Hamiltonian Matrix Elements in Conducting Polymers

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The Wannier function method used in a stable lattice is extended to calculate one-electron Hamiltonian matrix elements in polyacetylene. In this technique only a $2P_z$ orbital of the electrons is taken into account and the matrix elements are given analytically, to show the electronic contribution to the nonneighbor hopping.

The one-dimensional treatment of conjugated polymers has had some notable successes, including accounting for trans-polyacetylene being a semiconductor rather than a metal, and predicting the existence and properties of solitons in the trans-polyacetylene chain, Heeger *et al.* (1988). Since polyacetylene has the four carbon valence electrons, three of them are in sp^2 hybridized orbitals. The remaining electron has the symmetry of a $2p_z$ orbital with its charge-density lobes perpendicular to the plane defined by the other three. In this note the Wannier function method (Kohn, 1973) used in the stable lattice is extended to calculate one-electron Hamiltonian matrix elements in polyacetylene. Our aim is to show the electronic contribution to the nonneighbor hopping and not to give the exact value of hopping integrals. So only the $2p_z$ orbital of electrons is taken into account in the following calculation. All of the elements are given analytically. The results show that the nonneighbor terms are of great importance. From the quantum chemical angle this calculation is too simple. But from the viewpoint of the SSH model (Su *et al.*, 1979) the calculation of the nonneighbor hopping shows the approximative degree of this model.

For trans-polyacetylene the bond between the nth site and $(n + 1)$th sites is short and that between the $(n + 1)$th and $(n + 2)$th sites is long.

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According to Kohn's (1973) method, the basic function of the nth site can be written

$$W_n = \sum_m b_m \psi_{n+m}, \qquad m = 0, \pm 1, \pm 2, \ldots \tag{1}$$

which is called the extended Wannier function, and ψ is the site-atom wave function, taken to be the form of a $2p_z$ orbital of hydrogenlike atoms

$$\psi = \left(\frac{\lambda^5}{\pi}\right)^{1/2} r \cos\theta \exp(-\lambda r) \tag{2}$$

where λ is an adjustable parameter. Because ψ is a real function, the coefficient b_m is real and dependent on the dimerized amplitude u, which can be determined from the following relation:

$$\delta_{nl} = \langle W_n | W_l \rangle = \sum_m \sum_k b_m b_k S(n+m, l+k) \tag{3}$$

where

$$S(i,j) = \langle \psi_i | \psi_j \rangle = (1 + \rho_{ij} + \tfrac{2}{5}\rho_{ij}^2 + \tfrac{1}{15}\rho_{ij}^3) \exp(-\rho_{ij}) \tag{4}$$

and

$$\rho_{ij} = \lambda |R_i - R_j|$$

$$R_i = ia + [(-1)^i - 1]u, \qquad i = 0, \pm 1, \pm 2, \ldots$$

Here S is the overlap integral, R_i the lattice position, and a the lattice constant of a uniform chain. The one-electron Hamiltonian can be written in atomic units as

$$H = -\tfrac{1}{2}\nabla^2 + \sum_i V(r - R_i) \tag{5}$$

where

$$V(r - R_i) = -Z/|r - R_i| \tag{6}$$

Z is the effective kernel charge number of a carbon atom, and V represents the crystal Coulomb potential. In the W_n representation the Hamiltonian matrix elements are then

$$t_{nl} = \langle W_n | H | W_l \rangle = \sum_m \sum_k b_m b_k H(n+m, l+k) \tag{7}$$

where

$$H(i,j) = \langle \psi_i | H | \psi_j \rangle \tag{8}$$

For $i = j$,

$$H(i, i) = \tfrac{1}{2}(\lambda - Z)\lambda - Z \sum_{k \neq i} V_{iik} \tag{9}$$

and

$$V_{iik} = \lambda\rho_{ik}^{-1}[1 - \tfrac{3}{2}\rho_{ik}^{-2} + (\tfrac{1}{2}\rho_{ik} + 2 + 3\rho_{ik}^{-1} + \tfrac{3}{2}\rho_{ik}^{-2}) \exp(-2\rho_{ik})]$$

For $i \neq j$,

$$H(i, j) = -\tfrac{1}{2}\lambda^2 S(i, j) + (2\lambda - Z)U_{ij} - Z \sum_{k \neq j} K_{ikj} \tag{10}$$

$$U_{ij} = \lambda(\tfrac{1}{2}\rho_{ij} + \rho_{ij}^2 - \tfrac{5}{6}) \exp(-\rho_{ij}) \tag{11}$$

$$K_{ikj} = \langle \psi_i | 1/|r - R_k| \cdot | \psi_j \rangle$$

For $k = i$,

$$K_{iij} = \lambda(\tfrac{1}{2} + \tfrac{1}{6}\rho_{ij}^2) \exp(-\rho_{ij})$$

For $k \neq i, j$ and $R_k < R_j$,

$$K_{ikj} = \lambda\rho_{ik}^{-1}\rho_{ij}^{-3} \exp(-\rho_{ij})\, A(\rho_{ik}, \rho_{ij}) + \lambda\rho_{ik}^{-2}\rho_{ij}^{-4} \exp(-\rho_{ij}) B(\rho_{ik}, \rho_{ij})$$
$$+ \lambda\rho_{ik}\rho_{ij}^{-4} \exp(-\rho_{ij}) \sum_{m=1}^{5} C_m J_m + \lambda\rho_{ik}\rho_{ij}^{-4} \sum_{m=1}^{4} d_m q_m + \cdots$$

where

$$A = \sum_{m=0}^{5} I_m \rho_{ik}^m - \exp(-2\rho_{ik}) \sum_{m=0}^{3} L_m \rho_{ik}^m$$

$$B = \sum_{m=1}^{5} [C_m \rho_{ik}^{m+1}/(m + 1) + C_m g_m \exp(-2\rho_{ik})]$$
$$- \tfrac{1}{4}(2C_2 + \tfrac{3}{2}C_3 + 3C_4 + \tfrac{15}{2}C_5)$$

$$I_5 = -\tfrac{1}{10}(\rho_{ij} + 1)$$

$$I_4 = \tfrac{1}{3}(\rho_{ij}^2 + 3\rho_{ij} + 3)$$

$$I_3 = -\tfrac{1}{3}I_2 = -\tfrac{1}{3}(\rho_{ij}^3 + 6\rho_{ij}^2 + 15\rho_{ij} + 15)$$

$$I_2 = -3I_3$$

$$I_1 = \tfrac{1}{6}(I_2 - 9I_4 + 60I_5)\rho_{ij}^2 - (I_2 + 12I_4 + \tfrac{15}{2}I_5)$$

$$I_0 = I_2 + \tfrac{9}{2}I_4 - 15I_5$$

$$L_0 = I_0$$

$$
\begin{aligned}
L_1 &= \tfrac{1}{2}(I_2 + 12I_4 - 45I_5)\\
L_2 &= 3I_4 - 15I_5\\
L_3 &= -5I_5\\
C_5 &= 6I_4\\
C_4 &= 4I_2\\
C_3 &= 6I_4\rho_{ij}^2 + 18I_2\\
C_2 &= 3C_3 - 12I_2 = C_1\\
g_1 &= \tfrac{1}{2}(\rho_{ik} + 1)\\
g_2 &= \tfrac{1}{2}(\rho_{ik}^2 + 2g_1)\\
g_3 &= \tfrac{1}{2}(\rho_{ik}^3 + 3g_2)\\
g_4 &= \tfrac{1}{2}(\rho_{ik}^4 + 4g_3)\\
g_5 &= \tfrac{1}{2}(\rho_{ik}^5 + 5g_4)\\
q_1 &= \tfrac{1}{2}(\rho_{ij}^2 + \rho_{ij} + \tfrac{1}{2})\exp(-2\rho_{ij})\\
q_2 &= \tfrac{1}{2}(\rho_{ij} + \tfrac{1}{2})\exp(-2\rho_{ij})\\
q_3 &= \tfrac{1}{2}\exp(-2\rho_{ij})\\
q_4 &= \int_{\rho_{ij}}^{\infty} \tfrac{1}{\rho}(1 + \tfrac{1}{\rho})\exp(-2\rho)\,d\rho\\
J_1 &= \ln(\rho_{ik}/\rho_{ij}) - \int_{\rho_{ik}}^{\rho_{ij}} \tfrac{1}{\rho^2}\exp(-2\rho)\,d\rho\\
J_2 &= \rho_{ik}^{-1} - \rho_{ij}^{-1} - \int_{\rho_{ik}}^{\rho_{ij}} \tfrac{1}{\rho}\exp(-2\rho)\,d\rho\\
J_3 &= \rho_{ij} - \rho_{ik} + \tfrac{1}{2}[\exp(-2\rho_{ij}) - \exp(-2\rho_{ik})]\\
J_4 &= q_2 - g_1\exp(-2\rho_{ik}) - \tfrac{1}{2}(\rho_{ij}^2 - \rho_{ik}^2)\\
J_5 &= \tfrac{1}{3}(\rho_{ij}^3 - \rho_{ik}^3) - g_2\exp(-2\rho_{ik}) + q_1\\
d_1 &= (4\rho_{ij}^2 + 12)\sinh\rho_{ij} - 12\rho_{ij}\cosh\rho_{ij}\\
d_2 &= (48\rho_{ij}^2 + 120)\sinh\rho_{ij} - (8\rho_{ij}^3 + 120\rho_{ij})\cosh\rho_{ij}\\
d_3 &= (4\rho_{ij}^4 + 228\rho_{ij}^2 + 540)\sinh\rho_{ij} - (48\rho_{ij}^3 + 540\rho_{ij})\cosh\rho_{ij}\\
d_4 &= (12\rho_{ij}^4 + 540\rho_{ij}^2 + 1260)\sinh\rho_{ij} - (120\rho_{ij}^3 + 1260\rho_{ij})\cosh\rho_{ij}
\end{aligned}
$$

For $k \neq i, j$ and $R_k > R_j$, K_{ikj} has been given in Tong (1994).

The summation over k in (9) leads to divergences for this partial electron nuclear interaction. This part is compensated by the Coulomb interaction of the electrons, which is not included in the Hamiltonian.

Taking $Z = 3.21$, $\lambda = 2.4$, $u = 0.03$ Å, and $l = n + 1, n - 1, n \pm 2, n + 3, n - 3$ in equation (7), we find the corresponding values of the elements 3.011, 2.169, 0.301, 0.173, and 0.123 eV, respectively. It is evident that the nonneighbor hopping of the electrons is important and that the SSH model is too simple.

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REFERENCES

Heeger, A. J., Kivelson, S., Schrieffer, J. R., and Su, W. P. (1988). *Reviews of Modern Physics*, **60**, 781.
Kohn, W. (1973). *Physical Review B*, **7**, 4388.
Su, W. P., Schrieffer, J. R., and Heeger, A. J. (1979). *Physical Review Letters*, **42**, 1698.
Tong Guo-Ping (1994). *Acta Physica Sinica*, **43**(8), 1362.