Asymmetric propagation of electronic wave function through molecular bonding and anti-bonding states.

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Abstract

Electron transport through molecular bridge shows novel quantum features. Propagation of electronic wave function through molecular bridge is completely different than individual atomic bridge employed between two contacts. In case of molecular bridge electronic wave propagators interfere and effect conduction through molecular bonding and anti-bonding states. In the present work i showed through simple calculation that interference of electronic wave propagators cause asymmetric propagation of electronic wave through bonding and anti-bonding state. While for hydrogenic molecule these propagators interfere completely destructively for bonding state and constructively for anti-bonding state, giving rise to only one peak in spectral function for anti-bonding state.
Aptitude of semiconductor technology towards miniaturization of electronic devices has lead to emergence of nano and molecular electronics. Now the work of nano scientists is to control electron transport at such minute scale. As the size of the nano devices are comparable to the wavelength of current carriers so quantum features are playing dominant role in nano devices. A theoretical model of electron transport through a molecule was first presented by A.Aviram and Mark.A.Ratner[1,2]. Since then there has been great interest both in experimental and theoretical sides for progress of molecular electronics[13–17]. A single molecule could be used as electronic mixers[10], switches[11,12], and rectifiers[13]. Along with progress of molecular electronics a lot of problems are appearing both from experimental and theoretical sides. For instance, from experimental side its very difficult to place a molecule between unambiguous contacts[14]. Electron transport through molecule has very non-intuitive characteristics. Many experimentalists and theoreticians of nano science refers to hydrogenic molecular transport to be explained by transport through a single channel[3–6]. K. S. Thygesen et.al[7] presented that transmission through molecular anti-bonding state becomes nearly equal to one, where as they utilize density function theory with wannier function. They predicted that a hydrogen molecule contacted by platinum contacts will provide only one resonant robust channel for conduction which is anti-bonding state of molecule. Apart from hydrogenic molecule, even more complex molecules shows asymmetry in conduction through Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO)[9]. In the present work I explain a possible physical mechanism which could cause this asymmetry in conduction through a diatomic molecular bonding and anti-bonding states.

In modeling Hamiltonian for the diatomic molecule employed between contacts I considered contacts as charge carriers bath and electron on diatomic molecule loss energy with it. Therefore I take complex energy for electron on each atom.

\[
H = \sum_{i=1}^{2} \tilde{\epsilon}_i d_i^\dagger d_i + \sum_{i,j=1; i\neq j}^{2} \tau d_i^\dagger d_j
\]  \hspace{1cm} (1)

The present Hamiltonian is written under approximation of linear combination of atomic orbitals and in second quantized form[8]. Here \(d_i^\dagger(d_i)\) represents creation(annihilation) of electron on ith atom, where as second term refers to inter-atomic coupling and \(\tau\) shows inter-atomic coupling energy. Where as “ \(\tilde{\epsilon}_i = \epsilon_i - i\Gamma\) ” \(\epsilon_i\) gives electronic energy of the ith
atom electron and Γ shows dissipation of electron energy with contacts.

Now time evolution of operator is given by Heisenberg’s equation of motion, (I assume for simplicity $\hbar = 1$ )

\[ i \frac{\partial}{\partial t} \left[ \exp(i\tilde{\epsilon}_1 t) d_1(t) \right] = \tau \exp(i\tilde{\epsilon}_1 t) d_2(t) \]  
\( (2) \)

\[ i \frac{\partial}{\partial t} \left[ \exp(i\tilde{\epsilon}_2 t) d_2(t) \right] = \tau \exp(i\tilde{\epsilon}_2 t) d_1(t) \]  
\( (3) \)

\[ F_1(t) \equiv \exp(i\tilde{\epsilon}_1 t) d_1(t) \]  
\( (4) \)

\[ F_2(t) \equiv \exp(i\tilde{\epsilon}_2 t) d_2(t) \]  
\( (5) \)

\[ \frac{i}{\tau} \exp(i\Delta t) \frac{\partial}{\partial t} F_1(t) = F_2(t) \]  
\( (6) \)

\[ \frac{i}{\tau} \exp(-i\Delta t) \frac{\partial}{\partial t} F_2(t) = F_1(t) \]  
\( (7) \)

Here “$\Delta = (\epsilon_2 - \epsilon_1)$”. For decoupling equations (6 & 7) I operate $i \frac{\partial}{\partial t}$ on above two equations,

\[ \ddot{F}_1 + i\Delta \dot{F}_1 + \tau^2 F_1 = 0 \]  
\( (8) \)

\[ \ddot{F}_2 - i\Delta \dot{F}_2 + \tau^2 F_2 = 0 \]  
\( (9) \)

Here $\bullet$ & (●●) represents $\frac{\partial}{\partial t}$ & $\left( \frac{\partial^2}{\partial t^2} \right)$ ,

By solving above two differential equations,

\[ d_1(t) = \frac{1}{2\gamma} \left\{ \left[ (\gamma + \Delta) d_1(0) - 2\tau d_2(0) \right] \exp(-i(\epsilon_b - i\Gamma)t) + \left[ (\gamma - \Delta) d_1(0) + 2\tau d_2(0) \right] \exp(-i(\epsilon_a - i\Gamma)t) \right\} \]  
\( (10) \)

\[ d_2(t) = \frac{1}{2\gamma} \left\{ \left[ (\gamma - \Delta) d_2(0) - 2\tau d_1(0) \right] \exp(-i(\epsilon_b - i\Gamma)t) + \left[ (\gamma + \Delta) d_2(0) + 2\tau d_1(0) \right] \exp(-i(\epsilon_a - i\Gamma)t) \right\} \]  
\( (11) \)
Here \( \gamma = \sqrt{\Delta^2 + 4\tau^2} \), \( \epsilon_b = \frac{(\epsilon_1 + \epsilon_2 - \gamma)}{2} \) and \( \epsilon_a = \frac{(\epsilon_1 + \epsilon_2 + \gamma)}{2} \), Where as \( \epsilon_b(\epsilon_a) \) represents molecular bonding (molecular anti-bonding) energy.

Similarly,

\[
d_1^d(t) = \frac{1}{2\gamma} \left\{ \left[ (\gamma + \Delta) d_2^d(0) - 2\tau d_2^s(0) \right] \text{Exp}(i(\epsilon_b - i\Gamma)t) + \left[ (\gamma - \Delta) d_2^d(0) + 2\tau d_2^s(0) \right] \text{Exp}(i(\epsilon_a - i\Gamma)t) \right\}
\]

\[
d_2^d(t) = \frac{1}{2\gamma} \left\{ \left[ (\gamma - \Delta) d_1^d(0) - 2\tau d_1^s(0) \right] \text{Exp}(i(\epsilon_b - i\Gamma)t) + \left[ (\gamma + \Delta) d_1^d(0) + 2\tau d_1^s(0) \right] \text{Exp}(i(\epsilon_a - i\Gamma)t) \right\}
\]

Finally, propagator for diatomic molecular system will be,

\[
G^R(t, t') = \sum_{i,j=1}^2 G^R_{ij}(t, t')
\]

Here “ \( G^R(t, t') \) ” represents retarded Green’s function,

\[
G^R_{ij}(t, t') \equiv -i\theta(t - t') \left\langle d_i(t) \ d_j^\dagger(t') \right\rangle
\]

Where as, in frequency space,

\[
G^R_{ij}(\epsilon) = \int d(t - t') \text{Exp}(i\epsilon(t - t')) G^R_{ij}(t, t')
\]

By utilizing eqs (10-13),

\[
G^R_{11}(\epsilon) = \frac{1}{2\gamma} \left[ \frac{(\gamma + \Delta)}{(\epsilon - \epsilon_b + i\Gamma)} + \frac{(\gamma - \Delta)}{(\epsilon - \epsilon_a + i\Gamma)} \right]
\]

\[
G^R_{12}(\epsilon) = \frac{\tau}{\gamma} \left[ \frac{1}{(\epsilon - \epsilon_a + i\Gamma)} - \frac{1}{(\epsilon - \epsilon_b + i\Gamma)} \right]
\]

\[
G^R_{21}(\epsilon) = \frac{\tau}{\gamma} \left[ \frac{1}{(\epsilon - \epsilon_a + i\Gamma)} - \frac{1}{(\epsilon - \epsilon_b + i\Gamma)} \right]
\]

\[
G^R_{22}(\epsilon) = \frac{1}{2\gamma} \left[ \frac{(\gamma - \Delta)}{(\epsilon - \epsilon_b + i\Gamma)} + \frac{(\gamma + \Delta)}{(\epsilon - \epsilon_a + i\Gamma)} \right]
\]
FIG. 1: Energy difference between bonding and anti-bonding energies increase linearly for two atoms of same energy level $\epsilon_1 = \epsilon_2 = 8$, while it increases in terms of square root for two atoms of different energy level $\epsilon_1 = 4, \epsilon_2 = 12$.

Now the spectral function for the system will be,

$$A(\epsilon) = -2 \sum_{ij} \text{Im}[G_{ij}^R(\epsilon)]$$ (21)

The difference in bonding and anti-bonding energies for diatomic molecule (with both atoms of same energy) increase linearly with increase in inter-atomic coupling “$\epsilon_b = \epsilon_0 - \tau$ & $\epsilon_a = \epsilon_0 + \tau$”. While for diatomic molecule (with both atoms of different energy) the difference in bonding and anti-bonding energy increases in terms of square roots “$\epsilon_b = \frac{(\epsilon + \epsilon_1 - \sqrt{\Delta^2 + 4\tau^2})}{2}$ & $\epsilon_a = \frac{(\epsilon + \epsilon_2 + \sqrt{\Delta^2 + 4\tau^2})}{2}$” In Fig(1) it is shown that difference in energy with increase in inter-atomic coupling for bonding and anti-bonding energy changes differently for two atoms of same energy level and two atoms of different energy level.

In Fig(2) spectral function solid black peak refers to two atoms of same energy levels with no inter-atomic coupling “$A(\epsilon) = \frac{4\Gamma}{(\epsilon - \epsilon_0)^2 + \Gamma^2}$”, which gets peak value at “$\epsilon = \epsilon_0$”. With finite value of inter-atomic coupling only single peak appears in spectral function which is shifted to right by amount “$\epsilon_0 + \tau$”. This peak correspond to anti-bonding state “$A(\epsilon) = \frac{4\Gamma}{(\epsilon - \epsilon_0)^2 + \Gamma^2}$”.
FIG. 2: Spectral function for a diatomic molecule consisting of two atoms of the same energy level $\epsilon_1 = \epsilon_2 = 11$ and dissipation of electron energy with contacts $\Gamma = 0.25$.

$$\frac{4\Gamma}{(\epsilon - \epsilon_a)^2 + \Gamma^2}$$ while no peak of bonding state appears as propagators destructively interfere to cancel bonding state peak. With increase in inter-atomic coupling the anti-bonding state peak shifts right by amount “$\tau$”. This provides a good physical explanation for hydrogenic molecular conduction through a single channel of anti-bonding state, as predicted by K. S. Thygesen et al. [7], although I have not included contacts and molecular coupling geometry in our model.

A diatomic molecule is completely different than two atoms laterally placed between contacts without any inter-atomic coupling. As in former case electronic wave function get hybridized and collectively two atoms propagator amplitudes interfere. In spectral function two symmetric peaks will be seen in case of two atoms with no inter atomic coupling “

$$A (\epsilon) = \frac{2\Gamma}{(\epsilon - \epsilon_1)^2 + \Gamma^2} + \frac{2\Gamma}{(\epsilon - \epsilon_2)^2 + \Gamma^2}$$” which gets peak value at “$\epsilon = \epsilon_1$ & $\epsilon = \epsilon_2$” while in a diatomic molecule rather than two symmetric peaks we get two asymmetric peaks for bonding and anti-bonding states and its amplitude is also different than two atoms with no inter-atomic coupling peaks.

In Fig(3) spectral function for a diatomic molecule consisting of two atoms of different energy level is shown. Here two symmetric peaks in spectral function refers to no inter-
atomic coupling, while with finite value of inter-atomic coupling two peaks start shifting with asymmetric amplitude. Here bonding state peak amplitude is smaller than two atoms with no inter atomic coupling because of destructive interference between propagators, while anti bonding state peak amplitude is larger than two atoms with no inter atomic coupling peaks in spectral function by the amount the propagators interfere constructively. With increase in inter-atomic coupling separation between bonding and anti-bonding states peaks start increasing and asymmetry in their peaks amplitude also increase.

Molecular bonding state is symmetric state and it tends to localize charge carriers while molecular anti-bonding state is anti-symmetric state it tends to delocalize charge carriers. This effects electronic wave propagators in a way that electronic wave propagation amplitude interferes constructively for anti-bonding state which gives large amplitude peak in spectral function while electronic wave propagation amplitudes interfere destructively for bonding state and gives smaller peak amplitude in spectral function for bonding state.
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