Quantum transport through single molecules is very sensitive to the strength of the molecule-electrode contact. When a molecular junction weakly coupled to external electrodes, charging effects do play an important role (Coulomb blockade regime). In this regime, the non-equilibrium Green function is usually substituted with master equation approaches, which prevents the density functional theory from describing Coulomb blockade in non-equilibrium case. Last year, we proposed an Ansatz to combine the non-equilibrium Green function technique with the equation of motion method. With help of it, Coulomb blockade was obtained by non-equilibrium Green function, and completely agrees with the master equation results [Phys. Rev. B 76, 045408 (2007)]. Here, by the Ansatz, we show a new way to introduce Coulomb blockade correction to DFT calculation in non-equilibrium case. And the characteristics of Coulomb blockade are obtained in the calculation of a toy molecule correctly.

I. INTRODUCTION

Single molecule electronics\cite{1,2,3} has been mostly investigated in the high temperature and strong contact to the electrode regime. The opposite limit of low temperature and weakly coupled molecular junctions poses a challenge to the currently available experimental techniques. Still the possibility to probe the spectroscopy of single molecule junctions via a lateral gate could offer new insights to the peculiar coupling of the electrical and mechanical degrees of freedom at the nanoscale. In order to be able to establish the transport mechanisms governing such molecular junctions, a technique which could tackle on one hand single electron charging effects and, on the other hand, the inclusion of the electron-vibron coupling is of extreme importance.

In the last ten years, the nonequilibrium Green function (NEGF) formalism has been successfully employed to describe transport observables on the base of a density functional theory (DFT) description of the electronic structure\cite{1,2,3,4,5,6,7,8,9,10,11,12} and model Hamiltonian approaches\cite{13,14,15} Recently it is applied for the influence of the vibron dynamics onto a molecular transistor, and lots of excellent results are obtained.\cite{16,17,18} However, when coming to the CB regime, the NEGF method has been usually substituted with master equation approaches (ME), which prevents DFT from describing CB effects. Last year, we proposed an Ansatz to combine NEGF with equation of motion (EOM) method.\cite{19} With help of the Ansatz above, in non-equilibrium case, the Coulomb blockade can be completely described just within single-particle space simply, and the result fully agrees with the one from ME which is performed in many-particle space.

For DFT to describe Coulomb blockade,\cite{12,20} the double subspace (spin-up and spin-down) is usually employed. However, it is hard to obtain the Coulomb blockade effects correctly in non-equilibrium case. Our purpose is to introduce Coulomb blockade effect to non-equilibrium DFT calculation by this Ansatz.

In this paper, with the help of the Ansatz in Ref.\cite{19}, by the model Hamiltonian and EOM approach, we propose a self energy to describe CB effects in non-equilibrium case. Electronic occupation number, electronic current and differential conductance are calculated. The charging-induced steps and the ratio of 2/3 : 1/3 in the step heights of the occupation number and the current, which are the important characteristics of CB by ME,\cite{21} is obtained correctly. The comparison with the complete CB results also is done. For the occupation number and the current, the difference is very small. For the conductance, only in the peak height, the difference is very clear, while there is no difference in the peak position. The CB stability diagram is also shown in the paper. We can see that the self energy can describe CB characteristics. The more important is that it is very convenient to introduce this self energy to DFT code even in non-equilibrium case. A scheme to perform CB correction in DFT calculation is suggested with double counting correction (DCC). Then it is realized in gDFTB.\cite{8,9,10} A toy molecule is taken for testing, and the CB characteristics are shown in the results correctly.

The paper is organized as follows: firstly a self energy for CB is proposed by the model Hamiltonian and EOM approach (Sec. II); secondly, based on the self energy above, a scheme with DCC is proposed to introduce

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig1.png}
\caption{(Color online) The molecule for Coulomb blockade calculation. See text for details.}
\end{figure}
CB correction to DFT code (Sec. IIIA); finally, the calculation on a toy molecule is performed in weak coupling regime, and the CB characteristics are shown in the results correctly (Sec. IIIB).

II. METHOD AND FORMULA

In non-equilibrium DFT calculation here, the CB correction will be introduced to each level of the molecular fragment D (see Fig. 1)\textsuperscript{22} Therefore, the multi-level Anderson impurity model is read as follows,

\[ H = H_D + \sum_\alpha (H_\alpha + H_{\alpha D}), \]

with

\[ H_D = \sum_{m,\sigma} \epsilon_{m,\sigma}^0 d_{m,\sigma}^\dagger d_{m,\sigma} + \frac{1}{2} \sum_{m,\sigma} U_{mn,m',\sigma} n_{m',\sigma}, \]

\[ H_\alpha = \sum_{k,\sigma} \epsilon_{k,\sigma}^\alpha c_{k,\sigma,\alpha}^\dagger c_{k,\sigma,\alpha}, \]

\[ H_{\alpha D} = \sum_{k,m,\sigma} (V_{\alpha,k,m,\sigma} c_{k,\sigma,\alpha}^\dagger d_{m,\sigma} + h.c.), \]

where \( d \) and \( c \) are the operators for electrons on the dot and on the left (\( \alpha = L \)) and the right (\( \alpha = R \)) lead, \( U_m \) is the charging energy of level \( m, \epsilon_{m,\sigma} \) is the \((m, \sigma)\) level of the quantum dot, while \( \epsilon_{k,\sigma}^\alpha \) is the spin \( \sigma \) level of lead \( \alpha \) in \( k \) space, \( \sigma = \uparrow, \downarrow \). With the help of the EOM and the truncation approximation, we can obtain a closed set of equations for the retarded and advanced GFs \( G_{m,\sigma,n,\tau}^{r/a} \),

\[ (\omega - \epsilon_{m,\sigma} - \Sigma_m^{(a)r/a} G_{m,\sigma,n,\tau}^{r/a}) = \delta_{mn} \delta_{\sigma,\tau}, \]

\[ + U_m G_{m,\sigma,n,\tau}^{(2)r/a}, \]

\[ (\omega - \epsilon_{m,\sigma}^0 - U_m \pm i\eta) G_{m,\sigma,n,\tau}^{(2)r/a} = (n_{m,\sigma}) \delta_{mn} \delta_{\sigma,\tau}, \]

\[ + \Sigma_m^{(a)r/a} (n_{m,\sigma}) G_{m,\sigma,n,\tau}^{r/a}, \]

where

\[ G_{m,\sigma,n,\tau}^{r/a} = (\langle d_{m,\sigma} d_{m,n,\tau}^{\dagger} \rangle)^{r/a}, \]

\[ G_{m,\sigma,n,\tau}^{(2)r/a} = (\langle n_{m,\sigma} d_{m,n,\tau} \rangle)^{r/a}, \]

and

\[ \Sigma_m^{(a)r/a}(\omega) = \Sigma_m^{L,r/a} + \Sigma_m^{R,r/a} = \sum_{\alpha,k} \frac{|V_{\alpha,k,m,\sigma}|^2}{\omega - \epsilon_{k,\sigma}^\alpha \pm i\eta}, \]

are the electron self-energies from leads with \( \eta = 0^+ \).

Re-arranging Eqs. (5) and (6), we can obtain the retarded GF as follows,

\[ G^r = G^{(U)r} + G^{(U)r} \Sigma^{(r)a} G^{(U)r}, \]

with

\[ G^{(U)r} = G^{(0)r} + G^{(0)r} \Sigma_{H}^{(1)r}, \]

\[ G^{(0)r} = \{\omega - H_0 + i\eta\}^{-1}, \]

\[ G^{(1)r} = \{\omega - H_0 + U + i\eta\}^{-1}, \]

\[ H_0 \] is a diagonal matrix composed of \( \epsilon_{m,\sigma}^0 \), \( \Sigma_{H}^{r} = \Sigma_{H}^{(r)a} \) is the one of \( \langle n_{m,\sigma} \rangle U_m \), and \( U \) is of \( U_m \), while \( \Sigma^{(a)r} \) is the self-energy matrix from Eq. (9).

From Eq. (10), we can see that the Coulomb interaction is just included in \( G^{(U)r} \). Therefore, with the help of Eq. (11), the retarded CB self energy \( \Sigma^{(CB)r} \) can be
obtained by the relation
\[
[G^{(U)r}(\omega)]^{-1} = \left\{ \frac{1}{\omega - H_0 + i\eta} + \frac{1}{\omega - H_0 - i\eta} - \Sigma^{H}_r \cdot \frac{1}{\omega - H_0 - U + i\eta} \right\}^{-1}
\equiv \left\{ \omega - H_0 - \Sigma^{(CB)r} \right\}^{-1}.
\]
(14)
The result is as follows,
\[
\Sigma^{(CB)r} = \omega - H_0 - [G^{(U)r}]^{-1}.
\]
(15)

By the Ansatz in Ref.\cite{19}, the lesser GF can be written out directly,
\[
G^{<} = G^{(U)<} + G^{(U)<} \Sigma^{(a)\alpha} G^{a} + G^{(U)r} \Sigma^{(a)r} G^{<},
\]
(16)
with \(\Sigma^{(a)<} = \sum_{\alpha} \Gamma_{\alpha} f_{\alpha}(\omega)\), and \(\Gamma_{\alpha} = i(\Sigma^{a}_{\alpha} - \Sigma^{a}_{\alpha})\), \(f_{\alpha}(\omega) = f(\omega - \mu_{\alpha})\), while \(\Sigma^{a}_{\alpha}\) are the diagonal matrix composed of \(\Sigma^{a}_{m,a}\), and \(f\) is the equilibrium Fermi function. After the re-arrangement by the way in Ref.\cite{21}, we can obtain,
\[
G^{<} = G^{r} \Sigma^{<} G^{a},
\]
(17)
\[
\Sigma^{<} = \Sigma^{(a)<} + \Sigma^{(CB)<}.
\]
(18)

By the helps of \(\Sigma^{(CB)<} \to 0\) (see appendix A), we could get \(\Sigma^{<} = \Sigma^{(a)<}\) if \(\Sigma^{(a)<} \neq 0\).

Therefore, here, the current \(I\) can be calculated simply by the Landau formula\cite{22,23,24,25},
\[
I = \frac{2e}{h} \int d\omega \operatorname{Tr} \left\{ \Gamma_L G^r \Gamma_R G^a \right\} \cdot \left[ f_L(\omega) - f_R(\omega) \right],
\]
(19)

FIG. 3: (Color online) The comparison on conductance with the same parameters in Fig. 1. The red dash curve is from approximation in Eq.\cite{19} while the black solid curve from the truncation in Ref.\cite{19} which fully agrees with the one from ME.\cite{19}

FIG. 4: (Color online) The CB stability diagram (the contour plot of the differential conductance) calculated by approximation in Eq.\cite{19} with \(\epsilon_{v,\uparrow} = -0.65\ eV, \epsilon_{v,\downarrow} = -0.45\ eV, U = 1.0\ eV, \Gamma = 0.02\ eV\).

III. SCHEME FOR DFT

A. scheme

For CB calculation, the system is partitioned as follows (shown in Fig. 1): the molecular fragment \(\mathbb{D}\) is the CB part, the fragments \(\mathbb{C}_1\) and \(\mathbb{C}_2\) are contacting area, and the L1 and L2 are the leads. Then we just instead of the complicated formula in Ref.\cite{19,26}.

In the case of double levels (\(m \equiv 1\) and \(\epsilon_{v,\uparrow}^{0} = \epsilon_{v,\downarrow}^{0}\)), the numerical calculation is performed, which contributes the direct comparison between the truncation in Eq.\cite{6} and the one in Ref.\cite{19} by which CB results fully in agreement with the ones from ME can be obtained.\cite{19} The comparisons of the electronic occupation number \(\langle n \rangle\) and the current \(I\) as a function of the bias voltage \(V_{bias}\) at fixed gate voltage \(V_g\) are shown in Fig. 2. Firstly, the difference of the results by the two methods is very small. Secondly, the CB characteristics are very clear in them: the steps appear for charging-induced level-split, and the step heights are in the ratio of 2/3 : 1/3, which are also obtained by ME as the important CB characteristics.\cite{26} Only in the comparison of differential conductance \(\langle G = \partial I / \partial V_{bias} \rangle\) (see Fig. 3), the difference in the heights of the peaks \((G\text{-axis})\) is very clear, while no difference appears in the positions of the peaks \((V_{bias}\text{-axis})\). From the CB stability diagram in the case of \(m \equiv 1\) and \(\epsilon_{v,\uparrow}^{0} = \epsilon_{v,\downarrow}^{0}\) (Fig. 4), it can be seen that in this case, the approximation in Eq.\cite{19} almost includes all CB characteristics the complete CB stability diagram by NEGF is shown in Ref.\cite{19}.

It should be noted that although the approximation above can just include some CB characteristics correctly,\cite{22} it is very convenient to be introduced to DFT calculation (which will be shown in the next chapter).
introduce CB correction in fragment $\mathbb{D}$, while the non-equilibrium calculation should be performed within the fragment $C_1 - \mathbb{D} - C_2$.

In DFT, the KS equation $H^{KS}\Psi = SE\Psi$ can be rewritten as,

$$S^{-1}H^{KS}\Psi = E\Psi,$$  \hspace{1cm} (20)

with $S$ is the overlap matrix. Then an effective Hamiltonian matrix\textsuperscript{27,28} for model-Hamiltonian calculation can be obtained from KS one,

$$H^{eff} = S^{-1}H^{KS}. \hspace{1cm} (21)$$

After performing the transformation on $H^{eff}_{C_1 - \mathbb{D} - C_2}$ from atomic basis to the fragment basis (which are from the eigenvectors of molecular fragment $C_1 - \mathbb{D} - C_2$ and are orthonormal), we take,

$$h^\text{CB}_{\text{C}_1 - \mathbb{D} - C_2, m,n} = \begin{cases} h^{\text{eff}}_{\text{C}_1 - \mathbb{D} - C_2, m,m}, & (m = n), \\ 0, & (m \neq n), \end{cases} \hspace{1cm} (22)$$

with $m, n$ are the index for the eigenvectors of the fragment $C_1 - \mathbb{D} - C_2$, and $h^{\text{eff}}_{\text{C}_1 - \mathbb{D} - C_2}$ are the the element of effective Hamiltonian matrix $H^{eff}$.

Within the fragment basis, from equation (15), we can obtain the self energy for CB correction in DFT as follows,

$$\Sigma^\text{(CB)}_{m,m,\sigma} = (\bar{\omega} - \epsilon^0_{m,\sigma}) - \frac{\omega - \epsilon^0_{m,\sigma}}{\omega - \epsilon^0_{m,\sigma} - (1 - \langle n_{m,\sigma}\rangle) U_m},$$

where $\bar{\omega} = \omega + i\eta$, $U_m$ is the Hubbard energy of the fragment orbital $m$, and $\Sigma_{m,n,\sigma} = 0$ if $m \neq n$. The occupation number of electrons $\langle n_{m,\sigma} \rangle = \rho_{m,n,\sigma}$ can be obtained by the transformation on the density matrix from atomic basis $\rho_{\mu,\nu,\sigma}$ to fragment basis $\rho_{m,n,\sigma}$. Considering DCC along the idea similar to the case in LDA+U\textsuperscript{29,30}, we can get $\epsilon^0_{m,\sigma} = h^\text{CB}_{\text{C}_1 - \mathbb{D} - C_2, m,m,\sigma} - \langle n_{m,\sigma}\rangle U_m$. The way to calculate $U_m$ within DFTB/gDFTB is shown in appendix\textsuperscript{21}.

Finally the CB-correction self energy $\Sigma^\text{(CB)}_{m,m,\sigma}$ will be transformed back to the atomic basis $\Sigma_{\mu,\nu,\sigma}$ from the fragment basis $\Sigma_{m,m,\sigma}$. By the help of Eqs. (14), (17) and (18), introducing the self energy $\Sigma^{(a),r/a}_\mu$, from leads, we can calculate the GFs as follows,

$$G^{r/a}_{\text{C}_1 - \mathbb{D} - C_2} = (\omega S - H^{KS}_{\text{C}_1 - \mathbb{D} - C_2} - \Sigma^{(a),r/a} - \Sigma^{(CB),r/a})^{-1},$$

and

$$G^{<}_{\text{C}_1 - \mathbb{D} - C_2} = G^{r}_{\text{C}_1 - \mathbb{D} - C_2} \Sigma^{(a),<}_{\text{C}_1 - \mathbb{D} - C_2} G^{a}_{\text{C}_1 - \mathbb{D} - C_2}. \hspace{1cm} (25)$$

It should be noted that the eigenvectors of the fragment $C_1 - \mathbb{D} - C_2$ is updated in every cycle according to the updated KS Hamiltonian.

B. Calculation on a toy molecule

The scheme above is realized within gDFTB\textsuperscript{8,9,10}. A toy molecule (C$_2$S$_2$) is taken for the calculation (see Fig. 1). The C$_2$ is the CB part, while S is the linker. The bond length of C-C is 1.2 Å, and the one of S-C is 3.0 Å.

In the testing calculation of this chapter, for clarity within the level structure and the CB characteristics, the contribution from fragments C1 and C2 is ignored, and $U_m \equiv 1.0$ eV is taken instead of the $U_m$ calculated by the method in appendix\textsuperscript{21} (which are about 9.0 eV). Also for simplicity in the calculation, the fictitious golden leads are used\textsuperscript{21} and the minimal basis is taken.

The transmission function in spectral space is shown in Fig. 5. In the case without CB correction, we can see that there are seven levels close to the Fermi energy, while the HOMO and the LUMO+1 are double-degenerate, respectively. When CB correction is introduced, for charging effect, the LUMO and the HOMO-2 will split, respectively. See text for details.

![FIG. 5: (Color online) The transmission function $T(\omega)$ in spectral space $\omega$. The black solid curve is for the transmission function in the case without CB correction, and the red dash is with CB correction and $U_m \equiv 1.0$ eV, while the black dot-dash line is the Fermi level $E_F = -8.5$ eV. In the case without CB correction, we can see that there are seven levels close to the Fermi energy, the HOMO and the LUMO+1 are double-degenerate, respectively. When CB correction is introduced, for charging effect, the LUMO and the HOMO-2 will split, respectively. See text for details.](image-url)
FIG. 6: (Color online) (a) the electronic occupation number $n_{\text{LUMO}}$ of LUMO as a function of the bias voltage. (b) the current $I$ as a function of the bias voltage. In them, the CB characteristics (the charging-induced steps and the ratio of $2/3 : 1/3$ in the heights of the steps) are very clear.

The physics under it can be understood with the help of the charging-induced level-split, which is shown in the following. 1) When $V_{\text{bias}} = 0$, the LUMO level $\epsilon_{\text{LUMO}}$ is almost empty. 2) Then the positive bias voltage is added, and when the LUMO level $\epsilon_{\text{LUMO}}$ is coming into the Fermi windows ($\mu_F^R - \mu_F^L$), there are two channels ($\epsilon_{\text{LUMO},\uparrow} = \epsilon_{\text{LUMO},\downarrow} + U_{\text{LUMO}}$) to be opened for current. As this leads to the ‘2/3’ in the ratio. 3) After that, the electronic occupation number of LUMO comes to be 0.66 (see Fig. 6(a) and Fig. 2(a)), and for the charging effect, the degenerate levels ($\epsilon_{\text{LUMO},\uparrow}, \epsilon_{\text{LUMO},\downarrow}$) will split into two ($\epsilon_{\text{LUMO},\uparrow}$ and $\epsilon_{\text{LUMO},\downarrow} = \epsilon_{\text{LUMO},\uparrow} + U_{\text{LUMO}}$). 4) At the time that the level $\epsilon_{\text{LUMO},\downarrow}(= \epsilon_{\text{LUMO},\uparrow} + U_{\text{LUMO}})$ enters the Fermi windows, there will be only one channel to be opened, which is the reason of the ‘1/3’ in the ratio.

IV. CONCLUSION

In this paper, we have shown a new way to introduce CB correction to DFT calculation for the non-equilibrium case. The main elements of the approach are the following.

1) With the help of the Ansatz in Ref. 19, a self-energy is proposed for the (non-equilibrium) CB by the model Hamiltonian and EOM approach. From the comparison with the complete CB results, we can see that it can include the characteristics of CB correctly. Further, the more important is that, from the view of DFT-based quantum transport calculation in non-equilibrium case, this self-energy is very convenient for programming more than the truncation in Ref. 19 and ME approaches.

2) Based on this self energy, a scheme with DCC is proposed to introduce CB correction to non-equilibrium DFT calculation. As is then realized within gDFTB 8,9,10.

By the new code above, the quantum-transport properties of a toy molecule is calculated in CB regime. In the results of the electronic occupation number and the current as a function of bias voltage, the CB characteristics (the charging-induced steps and the ratio of $2/3 : 1/3$ in the step heights) appear correctly.

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APPENDIX A: WAY TO CALCULATE $\Sigma^{(CB)}$

For simplicity, here, only a double-level ($m \equiv 1$ with spin-up and spin-down) case is taken to describe the quantum dot. Then the index $m$ is ignored in this part, and from Eq. 2, the Hamiltonian of the dot can be re-written as,

$$H_D = \sum_{\sigma} \epsilon_\sigma^0 d_\sigma^\dagger d_\sigma + \frac{1}{2} \sum_{\sigma} U n_\sigma n_{\bar{\sigma}}.$$  (A1)
By Eq. (11), with the help of the Ansatz in Ref. 19, we can directly write out $G^{(U)}_\sigma$ as follows,

$$G^{(U)}_\sigma = G^{(0)}_\sigma + G^{(0)}_\sigma \sum_{i=0}^{n} G^{(1)}_\sigma + G^{(0)}_\sigma \sum_{i=0}^{n} G^{(1)}_\sigma$$

where

$$\bar{f}(\omega) = \int f(\omega) \Gamma^{(CB)}(\omega) \, d\omega$$

Comparing Eqs. (A2) and (A4), we can get

$$G^{(U)}_\sigma = G^{(0)}_\sigma \sum_{i=0}^{n} G^{(1)}_\sigma$$

Then with the help of Eq. (11), we will obtain

$$G^{(U)}_\sigma(\omega) = i\bar{f}(\omega) \Gamma^{(CB)}(\omega) \left\{ \frac{1 - \langle n_\sigma \rangle}{(\omega - \varepsilon^0_\sigma)^2 + \eta^2} + \frac{\langle n_\sigma \rangle}{(\omega - \varepsilon^0_\sigma - U)^2 + \eta^2} \right\}.$$ (A5)

with

$$D(\omega) = \frac{1 - \langle n_\sigma \rangle}{(\omega - \varepsilon^0_\sigma)^2 + \eta^2} + \frac{\langle n_\sigma \rangle}{(\omega - \varepsilon^0_\sigma - U)^2 + \eta^2}.$$ (A6)

Therefore, it is clear that $\Sigma^{(CB)}(\omega) = i\bar{f}(\omega) \Gamma^{(CB)}(\omega) \rightarrow 0$, since $\eta \rightarrow 0^+$ and $D(\omega)$ never comes to be infinite.

**APPENDIX B: WAY TO CALCULATE HUBBARD ENERGY U BY DFTB/GDFTB**

In DFTB/gDFTB, the tight-binding Hamiltonian is written as follows,

$$H_{\mu,\nu} = H^{0}_{\mu,\nu} + H^{SCC}_{\mu,\nu}.$$ (B1)

$$H^{SCC}_{\mu,\nu} = \frac{1}{2} S_{\mu,\nu} \sum_{\xi}^{N} (\gamma_{\alpha,\xi} + \gamma_{\beta,\xi}) \Delta q_\xi$$ (B2)

with

$$q_\xi = \frac{1}{2} \sum_{\nu}^{N} n_\xi \sum_{\mu}^{N} (c^*_{\mu,i} c_{\nu,j} + c_{\mu,i} c^*_{\nu,j}) S_{\mu,\nu},$$ (B3)

where $\mu \in \alpha$ and $\nu \in \beta$. $i$ is the index for the eigenstate of molecule (or molecular fragment), $\mu, \nu$ are the index of atomic basis, while $\alpha, \beta, \xi$ indicates atoms. $q_\alpha$ is the charge of atom $\alpha$, and $n_\xi$ is the electron occupation number of eigenstate $i$. $\gamma_{\alpha,\beta}$ is a function of $U_\alpha, U_\beta$ and $|R_\alpha - R_\beta|$ with $U_\alpha (U_\beta)$ is the Hubbard $U$ of atom $\alpha$ (atom $\beta$), and $|R_\alpha - R_\beta|$ is the distance between the two atoms. $c_{\mu,i}$ is the project of the eigenvector $i$ on the atomic basis $\mu$, while $S_{\mu,\nu}$ are the elements of overlap matrix in atomic basis.

With the help of linear combination of atomic orbitals (LCAO) ansatz, we can transform the Hamiltonian matrix from atomic basis to molecular basis, and get the eigenvalue of the eigenstate $i$ as follows,

$$\epsilon_i = H_{i,i} = \sum_{\mu,\nu} c^*_{\mu,i} H_{\mu,\nu} c_{\nu,i}.$$ (B4)

Then, according to the definition of Hubbard $U^{35,36,37}$ we will obtain,

$$U_{i,j} = \frac{\partial \epsilon_i}{\partial n_j} = \frac{\partial H^{0}_{i,i}}{\partial n_j} + \frac{\partial H^{SCC}_{i,i}}{\partial n_j}$$

$$= \frac{\partial H^{0}_{i,i}}{\partial n_j} + \sum_{\mu,\nu} \left\{ \frac{\partial c^*_{\mu,i} S_{\mu,\nu} c_{\nu,j}}{\partial n_j} + c_{\mu,i} H^{SCC}_{\mu,\nu} \frac{\partial c_{\nu,j}}{\partial n_j} \right\}$$

$$+ \sum_{\mu,\nu} c^*_{\mu,i} \frac{\partial H^{SCC}_{\mu,\nu}}{\partial n_j} c_{\nu,j}.$$ (B5)

Ignoring the contribution from $\partial c/\partial n$ and $\partial H^{0}/\partial n$, with the condition $\partial n_i/\partial n_j = \delta_{i,j}$, we can get

$$U_{i,j} \approx \sum_{\mu,\nu} c^*_{\mu,i} \frac{\partial H^{SCC}_{\mu,\nu}}{\partial n_j} c_{\nu,i}$$

$$\approx \frac{1}{4} \sum_{\mu,\nu} c^*_{\mu,i} S_{\mu,\nu} c_{\nu,j} \cdot \sum_{\xi}^{N} (\gamma_{\alpha,\xi} + \gamma_{\beta,\xi})$$

$$\cdot \sum_{\nu,\nu}^{N} (c_{\mu,j} S_{\nu,\nu} c_{\nu,j} + c_{\nu,j} S_{\nu,\nu} c_{\mu,j}),$$ (B6)

with $\mu \in \alpha, \nu \in \beta$.

The calculation of Hubbard $U$ by the approximations is performed in four examples: 1) guanine-cytosine base pair (GC), 2) adenine-thymine base pair (AT), 3) benzene ($C_6H_6$), 4) double carbon ($C_2$) in the case that the bond length is 1.2 Å. The results are shown in the table I. The error from the approximations is less than 12%, which is acceptable within DFTB/gDFTB.
TABLE I: The calculation of Hubbard $U$ by approximation \[ B6 \]

|                | GC | AT | $C_6H_6$ | $C_2$ |
|----------------|----|----|----------|------|
| $U_{HOMO}$ (eV) | 6.170 | 6.235 | 7.157 | 9.040 |
| $\partial n_{HOMO}/\partial HOMO$ (eV) | 5.556 | 5.645 | 6.451 | 9.022 |
| $\Delta_1$ (eV) | 0.614 | 0.590 | 0.706 | 0.018 |
| $\Delta_2$ (%) | 11.05 | 10.45 | 10.94 | 0.20 |

\( a \) results of HOMO by approximation \[ B6 \].

\( b \) $\Delta_1 = U_{HOMO} - \partial n_{HOMO}/\partial HOMO$.

\( c \) $\Delta_2 = \Delta_1 / (\partial n_{HOMO}/\partial HOMO)$.