

Aligning Fermi Levels for the Tutorial "Hands on Simulations of Interfacial Electron Transfer"

Wendu Ding, Benjamin Rudshteyn, Adam Matula, and Victor S. Batista*

Department of Chemistry, Yale University, P.O. Box 208107, New Haven, CT, USA 06520-8107

Energy Sciences Institute, Yale University, P.O. Box 27394, West Haven, CT, USA 06516-7394

Created December 8th, 2015

In this extension of the main IET tutorial, we will deal with the mis-alignment issue that is inherent in Extended Hückel (EH) theory. In such method, the energies of states in different materials are parametrized differently. As a result, the position of the Fermi levels (E_F) of different materials are not referenced to the same vacuum energy. [1] This causes an issue in that a supercell containing different materials will have mis-aligned molecular states. Here we describe a patch fix for this problem, based on the original code of YAEHMOP. Because the IET code also uses YAEHMOP to perform electronic structure calculations, this implementation works for the IET code as well.

We will first look at the theory behind this E_F alignment. Then, the implementation in the YAEHMOP code will be introduced together with the explanation and usage of new keyword options. Finally an example will be discussed to show how this implementation helps us in electronic structure calculations with Extended Hückel theory. As in the main IET tutorial, colored text indicates links that can be clicked on.

1 Theory

The idea of E_F alignment is to modify the EH Hamiltonian such that the E_F is aligned to a more reliable value, such as an experimental measurement or a density functional theory (DFT) result. These other values have the same reference vacuum within the same framework. Here we adopt the method presented by Kienle and co-workers. [1]

We start from the time-independent Schrödinger equation:

$$\hat{H} |\psi_k\rangle = E_k \hat{S} |\psi_k\rangle \quad (1)$$

where \hat{H} is the Hamiltonian matrix, \hat{S} is the overlap matrix, E_k is the k th eigenvalue, and $|\psi_k\rangle$ is the k th eigenvector. We can use rewrite Equation 1 in a all-matrix form:

$$\hat{H} \hat{\Psi} = \hat{S} \hat{\Psi} \hat{\Lambda} \quad (2)$$

by using a square matrix $\hat{\Psi}$ with each column of $\hat{\Psi}$ being one eigenvector, and a diagonal matrix $\hat{\Lambda}$ such that $\hat{\Lambda}_{kk}$ is the eigenvalue associated with the column k of $\hat{\Psi}$. Since the columns of $\hat{\Psi}$ are linearly independent, it is invertible. Hence, the Hamiltonian can be expressed by right multiplying $\hat{\Psi}^{-1}$ on both side of Equation 2:

$$\hat{H} \hat{\Psi} \hat{\Psi}^{-1} = \hat{S} \hat{\Psi} \hat{\Lambda} \hat{\Psi}^{-1} \Rightarrow \hat{H} = \hat{S} \hat{\Psi} \hat{\Lambda} \hat{\Psi}^{-1}. \quad (3)$$

The only modification we want to implement is to shift all the molecular states so that the calculated EH Fermi level is aligned to a certain value. The *relative* values for the states will not be changed. Therefore, we need to write a new Hamiltonian, \hat{H}' , whose eigenvalues are systematically shifted from the original Hamiltonian (\hat{H}^0):

$$\begin{aligned} \hat{H}' &= \hat{S} \hat{\Psi} \hat{\Lambda}' \hat{\Psi}^{-1} \\ &= \hat{S} \hat{\Psi} (\hat{\Lambda} + V \hat{I}) \hat{\Psi}^{-1} \\ &= \hat{S} \hat{\Psi} \hat{\Lambda} \hat{\Psi}^{-1} + V \hat{S} \\ &= \hat{H}^0 + V \hat{S} \end{aligned} \quad (4)$$

where V is the amount of the shift, and \hat{I} is a unitary matrix with appropriate dimensions.

In EH theory, the Hamiltonian and overlap matrix elements are expressed as the following:

$$\begin{aligned} H_{kk} &= E_{kk} \\ H_{kl} &= \frac{1}{2} K S_{kl} (H_{kk} + H_{ll}) \\ S_{kl} &= \int d^3\mathbf{r} \psi_k^*(\mathbf{r}) \psi_l(\mathbf{r}) \end{aligned} \quad (5)$$

where k and l indicate specific atomic orbitals, E_{kk} is the onsite energy for atomic orbital k , K is the EH fitting parameter which usually equals to 1.75, and \mathbf{r} is the spatial vector. If we assume that the system contains only one type of material, then the Hamiltonian will be changed into the following when applying the shift described as above:

$$\begin{aligned} H'_{kk} &= H_{kk}^0 + V S_{kk} = E_{kk} + V \\ H'_{kl} &= \frac{1}{2} S_{kl} (K H_{kk}^0 + K H_{ll}^0 + 2V) \end{aligned} \quad (6)$$

where $S_{kk} = 1$ in EH theory.

If the system contains two different materials, A and B, then we have to treat the Hamiltonian differently. First, let us write the total Hamiltonian in block form:

$$\hat{H}_T = \begin{pmatrix} \hat{H}_A & \hat{H}_{AB} \\ \hat{H}_{BA} & \hat{H}_B \end{pmatrix} \quad (7)$$

For all matrix elements associated with the same material (i.e. elements in $\hat{H}_{A/B}$), [Equation 6](#) can be used, where k and l are atomic orbitals from the same material. As for the elements in $\hat{H}_{AB/BA}$, a more complicated form should be used:

$$H'_{k_A l_B} = \frac{1}{2} S_{k_A l_B} [(K H_{k_A k_A}^0 + V_A) + (K H_{l_B l_B}^0 + V_B)] \quad (8)$$

where V_A and V_B are the corresponding shift for each different material in the system. A further modification can be made for the fitting parameter K , so that different materials can use different parameters:

$$H'_{k_A l_B} = \frac{1}{2} S_{k_A l_B} [(K_A H_{k_A k_A}^0 + V_A) + (K_B H_{l_B l_B}^0 + V_B)]. \quad (9)$$

2 Keywords

The E_F alignment is only implemented for calculations with the non-weighted Hamiltonian. According to the YAEHMOP Version 3.0 [manual](#), the non-weighted Hamiltonian [2] is not corrected to "reduce problems arising from counter-intuitive orbital mixing" as opposed to the weighted Hamiltonian. [3, 4] To do such a non-weighted calculation, the YAEHMOP keyword

```
Nonweighted
```

should be added in the input file. Only when this keyword is used do the additional keywords implemented for the alignment have effect. They are

```
EAlignment1
VA(0.0) KA(1.75)
```

```
EAlignment2
VA(0.0) VB(0.0) KA(1.75) KB(1.75) OrbNum(10000)
```

where the first two lines are used for the alignment of systems containing only one material, and the last two lines are for those with two different materials. The variables VA and VB represent the amount of shift used for E_F alignment in material A and B, while the variables KA and KB represent the corresponding fitting parameter for different materials (1.75 should be used for most cases). The variable $OrbNum$ is the number of atomic orbitals in material A, and it is only required when using keyword *EAlignment2*. It indicates that for

the first 10,000 orbitals, the VA and KA values will be used. Starting from the 10,001th orbital, the VB and KB values will be used. Note that in order to use *EAlignment2*, the system coordinates must be in order such that all atoms in material A are listed first followed by the atoms in material B. Note that these are the valence orbitals available to the atom and do not necessarily have to be occupied by electrons. The default value for each variable is shown in parenthesis.

If the value for the band gap is significantly off from an experimental value, one may need to change EHT parameters, as described in the original IET tutorial. For example (this might be useful in the Section 3), swapping out the original eht_parms.dat file for eht_parms.dat.pm6 may improve the description of Se atoms specifically. Example commands to use before launching calculations are given as follows :

```
$ cd dynamics2
$ cp eht_parms.dat eht_parms.dat.old
$ cp eht_parms.dat.pm6 eht_parms.dat
```

3 Example

In this section, an example is shown to illustrate the use of the E_F alignment. The system of interest is a small CdSe quantum dot (QD) (acting as the adsorbate) attached to one single-walled carbon nanotube (SWNT) (see Figure 1(A)). The QD is approximately 1.3 nm in diameter with 29 Cd atoms and equal number of Se atoms, while the SWNT is a 2.5 nm long (12,0) nanotube. Without using the implementation, the QD and SWNT are misaligned, referencing to different vacuum. Figure 1(B) shows that the edge of the conduction band of the QD is lower in energy than the Fermi level of the SWNT. However, experimental data suggests that the E_F of SWNT should be positioned in between the valence and conduction bands of QD. Therefore, this is a perfect case to apply the E_F alignment procedure. The three structures (QD, SWNT, and bound together) discussed in this tutorial are available as .gjf files (Gaussian input format) as part of a zip file at this [link](#).

To open this .zip file, double click on it in the Finder or a similar application or do the following command in the terminal:

```
$ unzip iet_EF_structures.zip
```

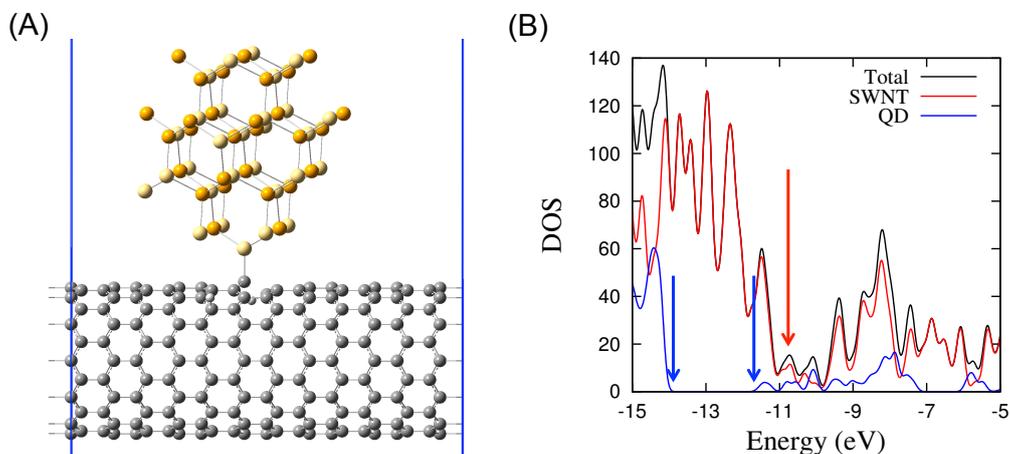


Figure 1: (A) The system of interest, a CdSe quantum dot attached to one single-walled carbon nanotube; (B) The density of states for the system shown in panel (A). The red arrow in panel (B) indicates the E_F of SWNT, while the blue arrows indicate the edges of the valence and conduction bands of QD.

The first step is to calculate the E_F and DOS for each part of the system (QD and SWNT) separately without any shifting in states. We find the E_F for the CdSe QD to be -12.9180 eV and that for SWNT to be -10.4729 eV. Experimental results suggest that these two numbers should be about -4.34 eV (Reference [5] gives -4.25 eV for the slightly bigger 1.9 nm QD) and -4.75 eV [6] for QD and SWNT, respectively. Therefore, the amounts of shifting that need to be used in place of the variables VA and VB are -4.34 eV $- (-12.9180)$ eV = 8.5780 eV and -4.75 eV $- (-10.4729)$ eV = 5.7229 eV respectively.

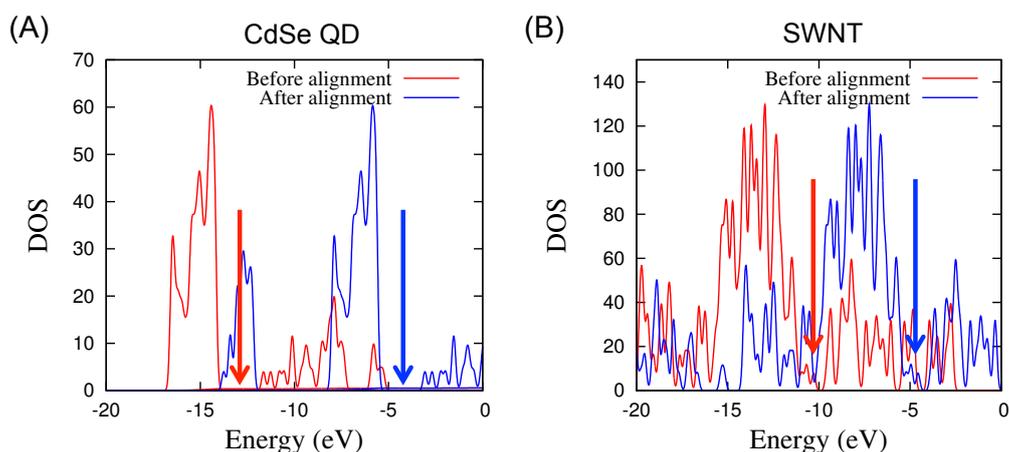


Figure 2: (A) Density of states for the QD before and after alignment; (B) Density of states for SWNT before and after alignment. Red arrows indicate E_F before alignment; blue arrows indicate E_F after alignment.

Using the values above, redo the calculations, but with the keywords:

```
EAlignment1
8.5780 1.75
```

for QD and

```
EAlignment1
5.7229 1.75
```

for SWNT, we manage to align the calculated E_F to experimental values. Figure 2 shows the comparison in DOS between before and after alignment for both materials. We can see that for both cases, the line shape of the DOS does not change after the alignment, the energetic positions of the peaks just are systematically shifted.

Now that we have found the correct shift for each material, it is time to combine them and use the keyword *EAlignment2*. The following section should be used in the input file:

```
EAlignment2
5.7229 8.5780 1.75 1.75 1154
```

with the SWNT atoms listed first and then the QD atoms. Since we have 288 C atoms and 2 H atoms in the SWNT part, the variable *OrbNum* is set to 1154 here (4 orbitals, 1 s and 3 p for each C and 1 s for each H). The 2 H atoms are present to fill the valence. Specifically, the QD is bound to the SWNT via an sp^3 defect. Then the C (number 285) to which the QD is bound carries a negative charge (and a lone pair) which is balanced out by the proton (number 290). The second hydrogen (number 289) is there to bind to the nearby sp^2 C (number 281) to prevent the consideration of radicals. Therefore, from the 288 C atoms and the 2 H atoms, we have, $4 * 288 + 1 * 2 = 1154$. This calculation yields the DOS in Figure 3, in which we can see that E_F is positioned between the valence and conduction bands of QD.

Therefore, in practice, we have to do 3 calculations: one for the adsorbate with an unaligned Fermi level, one for the second subsystem with an unaligned Fermi level, and then both together with the correct alignment for each subsystem. One may also align the LUMO's/conduction bands. It may also be useful to align to theoretical DFT calculations if possible, since they exhibit no such alignment issues.

References

- [1] D. Kienle, J. I. Cerda, and A. W. Ghosh. Extended Hückel theory for band structure, chemistry, and transport. I. carbon nanotubes. *J. Appl. Phys.*, 100(4):043714, 2006.
- [2] M. Wolfsberg and L. Helmholz. The spectra and electronic structure of the tetrahedral ions MnO_4^- , CrO_4^- , and ClO_4^- . *J. Chem. Phys.*, 20(5):837–843, 1952.

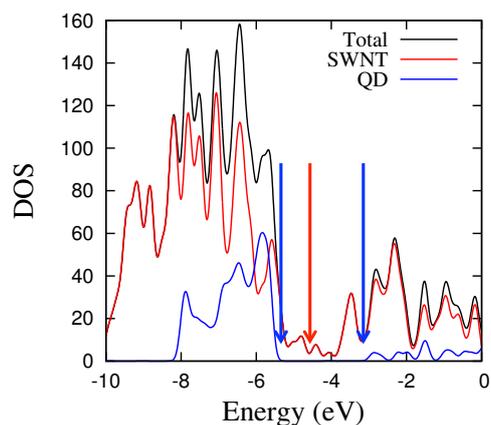


Figure 3: The density of states for the system shown in [Figure 1\(A\)](#) after alignment. The red arrow indicates the E_F of SWNT, while the blue arrows indicate the edges of the valence and conduction bands of QD.

- [3] M.-H. Whangbo and R. Hoffmann. Counterintuitive orbital mixing. *J. Chem. Phys.*, 68(12):5498–5500, 1978.
- [4] J. H. Ammeter, H. B. Buergi, J. C. Thibeault, and R. Hoffmann. Counterintuitive orbital mixing in semiempirical and ab initio molecular orbital calculations. *J. Am. Chem. Soc.*, 100(12):3686–3692, 1978.
- [5] S. N. Inamdar, P. P. Ingole, and S. K. Haram. Determination of band structure parameters and the quasi particle gap of cdse quantum dots by cyclic voltammetry. *ChemPhysChem*, 9(17):2574–2579, 2008.
- [6] J. Zhao, J. Han, and J. P. Lu. Work functions of pristine and alkali metal intercalated carbon nanotubes and bundles. *Phys. Rev. B*, 65:193401, 2002.