Supporting Information for "The Simplest Possible Approach for Simulating S_0-S_1 Conical Intersections with DFT/TDDFT — Adding *One* Doubly Excited Configuration"

Hung-Hsuan Teh* and Joseph E. Subotnik*

Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323, USA

E-mail: teh@sas.upenn.edu; subotnik@sas.upenn.edu

Minimization of the Energy of the One Doubly Excited State

In this section, we derive Eq. (2) and describe how to solve for the lone doubly excited state.

To proceed, notice that one can always apply a unitary transformation to the canonical Hartree-Fock orbitals, $\{i_0, j_0, \cdots\}$ (spatial orbitals), without changing the Hartree-Fock ground state energy E_0^{HF},

$$E_0^{\mathrm{HF}} = 2\sum_{i_0=1}^{N_{\mathrm{o}}}(i_0|h|i_0) + \sum_{i_0,j_0=1}^{N_{\mathrm{o}}}(2J_{i_0j_0} - K_{i_0j_0}). \tag{1}$$

Here h is the one-electron Hamiltonian, and two-electron terms $J_{ij} = (ii|jj)$ (Coulomb), and $K_{ij} = (ij|ji)$ (exchange). Thus, we can minimize the energy of the one doubly excited state

$|\Psi_{\hbar\bar{\hbar}}^{\ell\bar{\ell}}\rangle$ by applying two separate unitary transformations to the occupied space and the virtual space, obtaining the optimized orbitals $\{i, j, \cdots, \hbar\}$ and $\{\ell, a, b, \cdots\}$. Set $|\hbar\rangle = \sum_{i=1}^{N_o} c_i|i_0\rangle$ and $|\ell\rangle = \sum_{a=1}^{N_v} c_a|a_0\rangle$, where $\sum_{i=1}^{N_o} |c_i|^2 = 1$ and $\sum_{a=1}^{N_v} |c_a|^2 = 1$ have to be satisfied. In order to find minimal energy of the doubly excited state, we define the Lagrangian as

$$\mathscr{L}(\{c_i\}, \{c_a\}, \epsilon^{\hbar}, \epsilon^{\ell}) = \langle\Psi_{\hbar\bar{\hbar}}^{\ell\bar{\ell}}|H|\Psi_{\hbar\bar{\hbar}}^{\ell\bar{\ell}}\rangle - 2\epsilon^{\hbar}\left(\sum_{i=1}^{N_o} |c_i|^2 - 1\right) - 2\epsilon^{\ell}\left(\sum_{a=1}^{N_v} |c_a|^2 - 1\right), \tag{2}$$

where $\epsilon^{\hbar}$ and ϵ^{ℓ} represent Lagrange multipliers. Note that the optimized orbitals $\{i, j, \cdots, \hbar\}$ and $\{\ell, a, b, \cdots\}$ are automatically orthonormal to each other in Eq. (2) as one is from the occupied subspace and one is from the virtual subspace. By setting $\nabla\mathscr{L} = 0$, we find

$$\sum_{i=1}^{N_o}\Bigg\{(i_0|h|j_0) + \sum_{k=1}^{N_o}[2(i_0j_0|k_0k_0) - (i_0k_0|k_0j_0)] - \sum_{k,l=1}^{N_o}(i_0k_0|l_0j_0)c_kc_l + \sum_{a,b=1}^{N_v}[2(i_0j_0|a_0b_0) - (i_0b_0|a_0j_0)]\, c_ac_b\Bigg\}c_i = \epsilon^{\hbar} c_j, \tag{3a}$$

$$\sum_{a=1}^{N_v}\Bigg\{(a_0|h|b_0) + \sum_{i=1}^{N_o}[2(a_0b_0|i_0i_0) - (a_0i_0|i_0b_0)] - \sum_{i,j=1}^{N_o}[2(i_0j_0|a_0b_0) - (i_0b_0|a_0j_0)]\, c_ic_j + \sum_{c,d=1}^{N_v}(a_0c_0|d_0b_0)c_cc_d\Bigg\}c_a = \epsilon^{\ell} c_b, \tag{3b}$$

which can be recast as Eq. (2). Equation (2) has exactly the same form as the standard Hartree-Fock equations, except that the contributions from the HOMO $\hbar$ and the LUMO ℓ have been exchanged. In order to implement Eq. (2), we iteratively perform the following steps until convergence,

1. Solve the Hartree-Fock equations, and obtain the canonical molecular orbital (MO) coefficients $\mathbf{C}$.

2. Switch the two columns corresponding to HOMO and LUMO in $\mathbf{C}$, getting $\mathbf{C}'$.

3. With the new MO coefficient $\mathbf{C}'$, construct the new Fock matrix $\mathbf{f}'(\mathbf{C}')$ corresponding

to $\mathbf{C}'$,

$$\mathbf{f}' = \begin{bmatrix} \mathbf{f}'_{\mathrm{oo}} & \mathbf{f}'_{\mathrm{ov}} \\ \mathbf{f}'_{\mathrm{vo}} & \mathbf{f}'_{\mathrm{vv}} \end{bmatrix}, \tag{4}$$

where $\mathbf{f}'_{\mathrm{oo}}$ and $\mathbf{f}'_{\mathrm{vv}}$ have dimensionality $N_{\mathrm{o}} \times N_{\mathrm{o}}$ and $N_{\mathrm{v}} \times N_{\mathrm{v}}$ respectively.

4. Diagonalize the two blocks with unitary transformations U_{o} and U_{v} respectively.
5. Obtain the new MO coefficient $\tilde{\mathbf{C}} = \mathbf{C}[U_{\mathrm{o}}\, 0;\, 0\, U_{\mathrm{v}}]$, and compare $\tilde{\mathbf{C}}$ with $\mathbf{C}$. If the difference is smaller than the tolerance, we get the optimized orbitals; if not, set $\mathbf{C} = \tilde{\mathbf{C}}$ and go back to step 2.

In Fig. 1 (a), we show the energy change of the doubly excited state as a function of the iteration number. The optimization of the HF orbitals and KS orbitals is reported at $\pi/2$ for the case of stilbene, starting from the most obvious guess: $|\hbar\rangle$ is equal to HOMO and $|\ell\rangle$ is equal to LUMO. Notice that the optimization requires only a few iterations to converge. Interestingly, the optimization procedure lowers the energy of the HF double excitation state significantly (by up to 1.35 eV), whereas the DFT double excitation energy (E_d) barely changes. In Fig. 1 (b), we plot the energy difference for E_d as found before and after our optimization as a function angle θ for the HF case. The discontinuity near $\pi/2$ is likely due to different initial guesses for solving the SCFs, as the HF orbitals change very suddenly at 90 degrees. At present, using the simple self consistent algorithm in this paper, we are likely converging to different configurations at slightly different geometries around 90 degrees. A better solver should allow us to remove this discontinuity in Fig. 1 (b) (though the final energy will likely have a very small dip). In the end, if the HF solution does not have a smooth gradient, CIS-1D will also most likely not have a smooth gradient, but any small errors will hopefully not affect our potential to run dynamics in the future. Note that, as might be expected, a direct HOMO-LUMO transition is far from optimal double excitation around $\theta = \pi/2$, again confirming that our suspicion that HF orbitals are less meaningful than DFT orbitals.

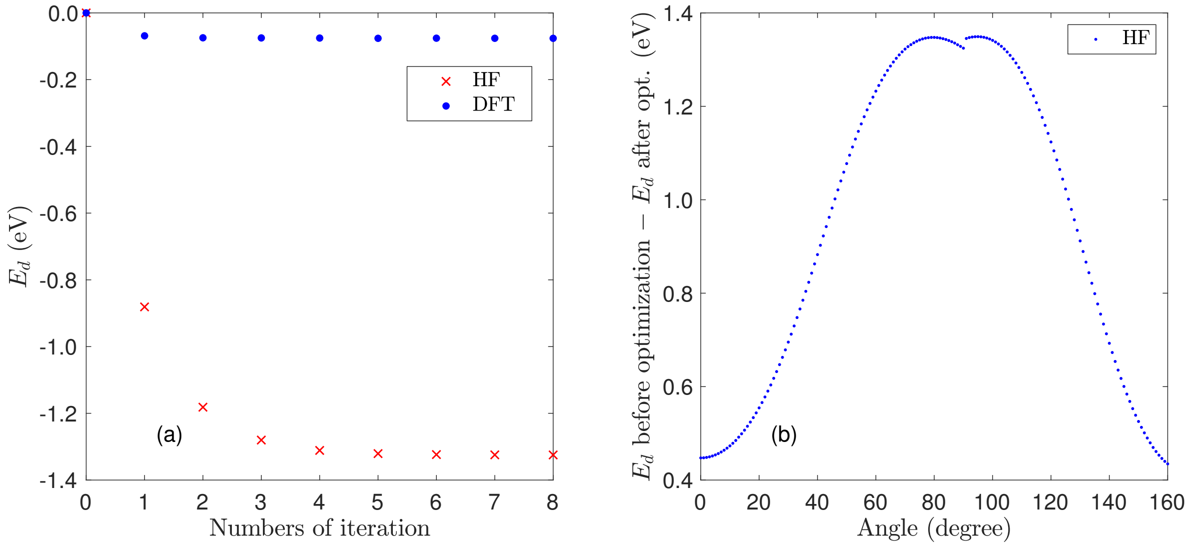

Figure 1: (a) The energy change of the lone doubly excited configuration, E_d, during the optimization as a function of the iteration number. Data are calculated at $\pi/2$ for stilbene. (b) The energy decrease for the lone doubly excited configuration as a function of angle θ as caused by the optimization of the HF orbitals for the case of stilbene.