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

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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 $E_{0}^{\text{HF}}$,

$$E_{0}^{\text{HF}} = 2 \sum_{i_0=1}^{N_0} (i_0|h|i_0) + \sum_{i_0,j_0=1}^{N_0} (2J_{i_0,j_0} - K_{i_0,j_0}).$$

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
by applying two separate unitary transformations to the occupied space and the virtual space, obtaining the optimized orbitals \( \{ i, j, \cdots, \beta \} \) and \( \{ \ell, a, b, \cdots \} \). Set \( | \beta \rangle = \sum_{i=1}^{N_o} c_i | i_0 \rangle \) 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

\[
\mathcal{L}(\{ c_i \}, \{ c_a \}, \epsilon^\beta, \epsilon^\ell) = \langle \Psi_{hh}^\ell | H | \Psi_{hh}^\ell \rangle - 2 \epsilon^\beta \left( \sum_{i=1}^{N_o} | c_i |^2 - 1 \right) - 2 \epsilon^\ell \left( \sum_{a=1}^{N_v} | c_a |^2 - 1 \right),
\]

where \( \epsilon^\beta \) and \( \epsilon^\ell \) represent Lagrange multipliers. Note that the optimized orbitals \( \{ i, j, \cdots, \beta \} \) 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 \( \nabla \mathcal{L} = 0 \), we find

\[
\sum_{i=1}^{N_o} \left\{ (i_0 | h | j_0) + \sum_{k=1}^{N_o} [2(i_0 j_0 | k_0 k_0) - (i_0 k_0 | k_0 j_0)] \\
- \sum_{k,l=1}^{N_o} (i_0 k_0 | l_0 j_0) c_k c_l + \sum_{a,b=1}^{N_v} [2(i_0 j_0 | a_0 b_0) - (i_0 b_0 | a_0 j_0)] c_a c_b \right\} c_i = \epsilon^\beta c_j,
\]

\[
\sum_{a=1}^{N_v} \left\{ (a_0 | h | b_0) + \sum_{i=1}^{N_o} [2(a_0 b_0 | i_0 i_0) - (a_0 i_0 | i_0 b_0)] \\
- \sum_{i,j=1}^{N_o} [2(i_0 j_0 | a_0 b_0) - (i_0 b_0 | a_0 j_0)] c_i c_j + \sum_{c,d=1}^{N_v} (a_0 c_0 | d_0 b_0) c_c c_d \right\} c_a = \epsilon^\ell c_b,
\]

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 \( \beta \) and the LUMO \( \ell \) 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 \( C \).
2. Switch the two columns corresponding to HOMO and LUMO in \( C \), getting \( C' \).
3. With the new MO coefficient \( C' \), construct the new Fock matrix \( f'(C') \) corresponding
to $C'$,

$$f' = \begin{bmatrix} f'_{\text{oo}} & f'_{\text{ov}} \\ f'_{\text{vo}} & f'_{\text{vv}} \end{bmatrix},$$

(4)

where $f'_{\text{oo}}$ and $f'_{\text{vv}}$ have dimensionality $N_o \times N_o$ and $N_v \times N_v$ respectively.

4. Diagonalize the two blocks with unitary transformations $U_o$ and $U_v$ respectively.

5. Obtain the new MO coefficient $\tilde{C} = C[U_o; 0; 0 U_v]$, and compare $\tilde{C}$ with $C$. If the difference is smaller than the tolerance, we get the optimized orbitals; if not, set $C = \tilde{C}$ 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: $|\kappa\rangle$ 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 $1.35\text{ eV}$), 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 $\theta$ 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 $\theta$ as caused by the optimization of the HF orbitals for the case of stilbene.