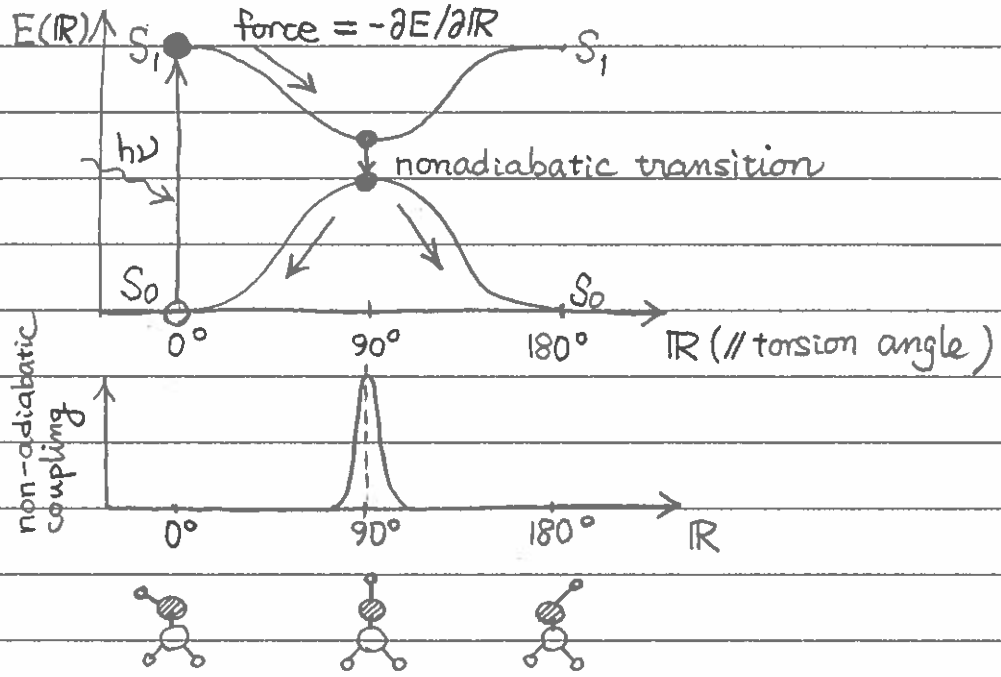
Excited-State Force Calculation Recipes

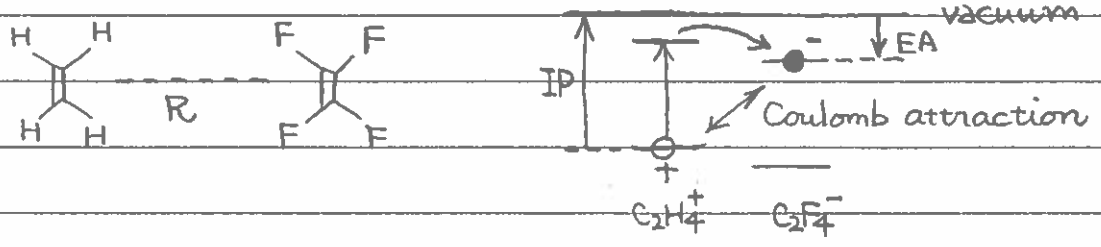
6/8/11

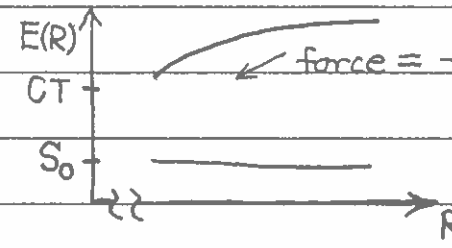
— Goal: Low-cost, non-self consistent (perturbative) calculation of forces on excited adiabatic surfaces, which captures correct physics.

(Example: Photo-isomerization of $CH_2=NH$)



(Example 2: Change-transfer (CT) excitation)





The Coulomb attraction between donor$^+$ and acceptor$^-$ requires

① Self-consistent charge density / Kohn-Sham (KS) state calculation w/ CT-excitation configuration.

OR

② Many-body (Casida) approach w/ ground-state KS basis, which eliminates self-interaction (so that the newly occupied acceptor state's energy $\epsilon_{a\sigma}$ does not include the Hartree-potential contribution from the evacuated $|\psi_{i\sigma}(\mathbb{r})|^2$ in the donor).

— Finite-difference approach

1. Obtain the I-th excited-state energy, $E_I(\mathbb{R})$, as a linear combination of ground-state KS orbitals, using asymptotically correct (long-range exact exchange) exchange-correlation functional in Casida's equation.
2. Then compute the force by finite difference,

$$\mathbb{F} = -\frac{E(\mathbb{R}+\Delta) - E(\mathbb{R})}{\Delta}$$

↓

Need 3N excited-energy calculations, which is prohibitive for large systems.

– Non-self consistent (Harris-Foulkner) force calculation

1. Obtain ground-state KS orbitals self-consistently.

2. Solve Casida equation to obtain the I-th excited state,

$$\Psi_I = \sum_{ia\sigma} \sqrt{\frac{\epsilon_{a\sigma} - \epsilon_{i\sigma}}{\omega_I}}\, F^I_{ia\sigma}\, \hat{c}^\dagger_{a\sigma} \hat{c}_{i\sigma}\, \Phi_0 \qquad (1)$$

$F^I_{ia\sigma}$ → Casida eigenvector; ω_I → Casida eigenvalue; Φ_0 → ground-state Slater determinant

OK to equate this = 1 for large band-gap materials, if keeping orthogonality is beneficial [Walter & Häkkinen, New J. Phys. 10, 043018 ('08)]

3. Compute the density perturbation

$$\delta\rho(\mathbf{r}) = \rho[\mathbf{r}; \Psi_I] - \rho[\mathbf{r}; \Phi_0] \qquad (2)$$

which contains the crucial information (e.g. electron-hole polarization for a CT excitation state).

4. Compute the excited-state force using the Harris-Foulkner perturbation approach [Torralba et al., JCTC 5, 1499 ('09)].

$$\mathbb{F}_n = \mathbb{F}_n^{\text{Hellmann-Feynman}} + \mathbb{F}_n^{\text{Non-self consistent}} \qquad (3)$$

$\mathbb{F}_n$ → force of n-th atom

where

$$F_n^{HF} = -\int dr\, \rho(r) \frac{\partial V_{loc}}{\partial(r - R_n)} \quad \text{(local pseudo-potential)}$$

$$- \sum_{ia\sigma} |F_{ia\sigma}^{I}|^2 \sum_{j\tau} f_{ia\sigma}(\epsilon_{j\tau}) \sum_{lm} \int dr \int dr' \left\{ \psi_{j\tau}^*(r) \frac{\partial \xi_{lm}^i}{\partial(r - R_n)} \xi_{lm}^{*i}(r' - R_n) \psi_{j\tau}(r') \right.$$

($|F_{ia\sigma}^{I}|^2$: weight of each of multi Slater-determinant excited state; $f_{ia\sigma}(\epsilon_{j\tau})$: occupation of each determinant)

$$\left. + \psi_{j\tau}^*(r) \xi_{lm}^i(r - R_n) \frac{\partial \xi_{lm}^{*i}}{\partial(r' - R_n)} \psi_{j\tau}(r') \right\}$$

(nonlocal pseudo-potential)

(4)

$$F_n^{NSC} = -\int dr \left\{ \delta V_{Hartree}(r) \frac{\partial \rho[r; \Phi_0]}{\partial R_n} + \delta\rho(r) \frac{\partial V_{xc}}{\partial R_n} \right\} \quad (5)$$

(Please see Torralba et al. for the implementation of F_n^{NSC}.)

- Test the NSC force calculation for the CT excitation state of $C_2H_4 - C_2F_4$ pair, and compare it with $-dE/dR$.