Chem3208 Lectures 25–28
Excited States Methods

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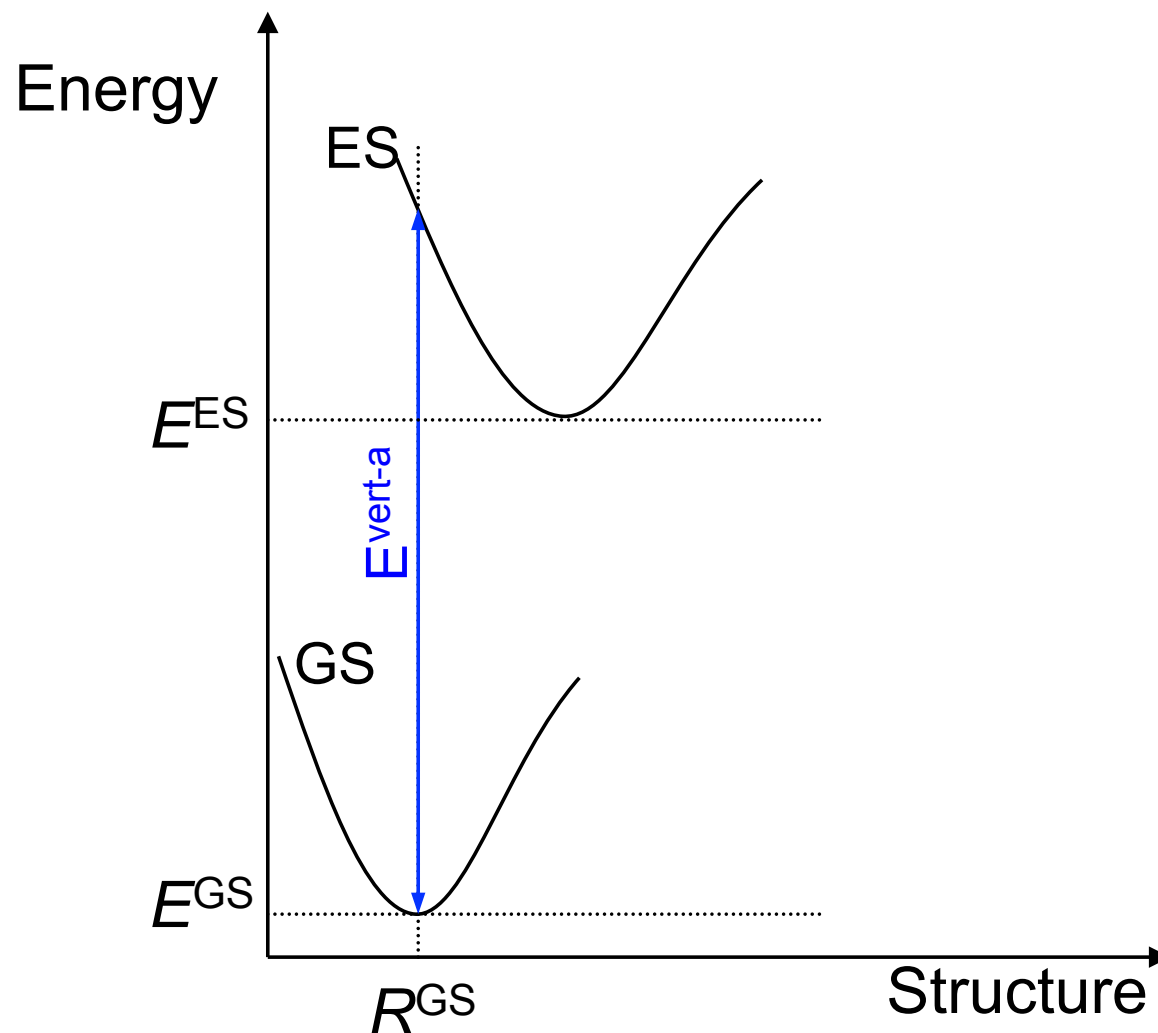
2nd Semester 2016

Excited state methods: single-reference methods

- HF- and DFT-based methods
  - Configuration interaction single (CIS)
  - Time-dependent HF (TDHF)
  - Time-dependent DFT (TDDFT)

- CC-based methods
  - Equation-of-motion CC (EOM-CCSD)
  - CC2 and CC3 (approximation of CCSD and CCSDT with linear response)

- CI-based methods
  - CIS(D): perturbative approach to CIS that approximately introduces doubles
  - Symmetry-adapted cluster CI (SAC-CI)

- Green's function-based methods
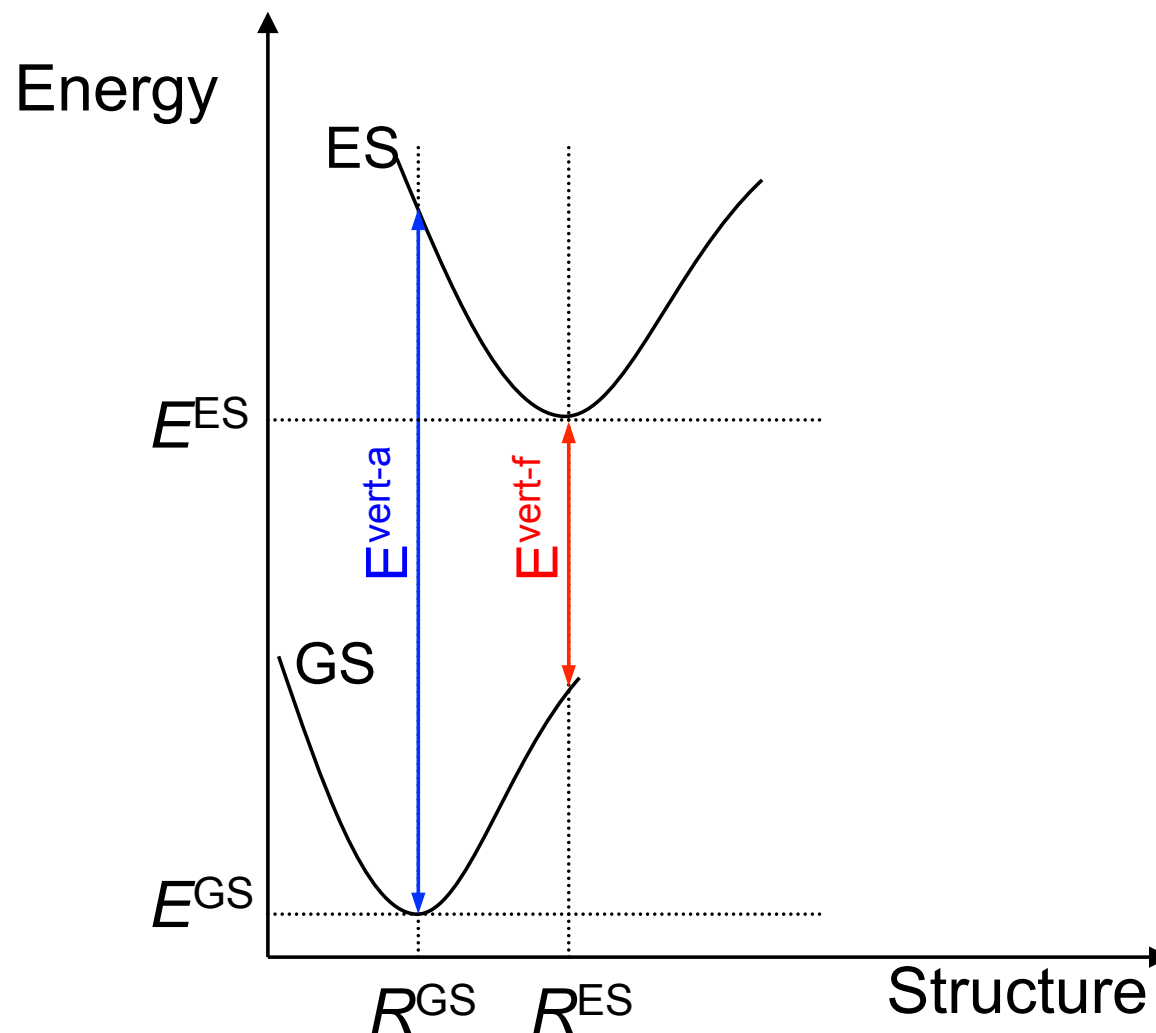 - algebraic diagrammatic construction (ADC)

Excited state methods: multi-reference methods

- Multiconfigurational self-consistent field (MCSCF)
  - Complete active space self-consistent field (CASSCF)
  - Complete active space perturbation theory 2nd order (CASPT2)
  - Restricted active space self-consistent field (RASSCF)
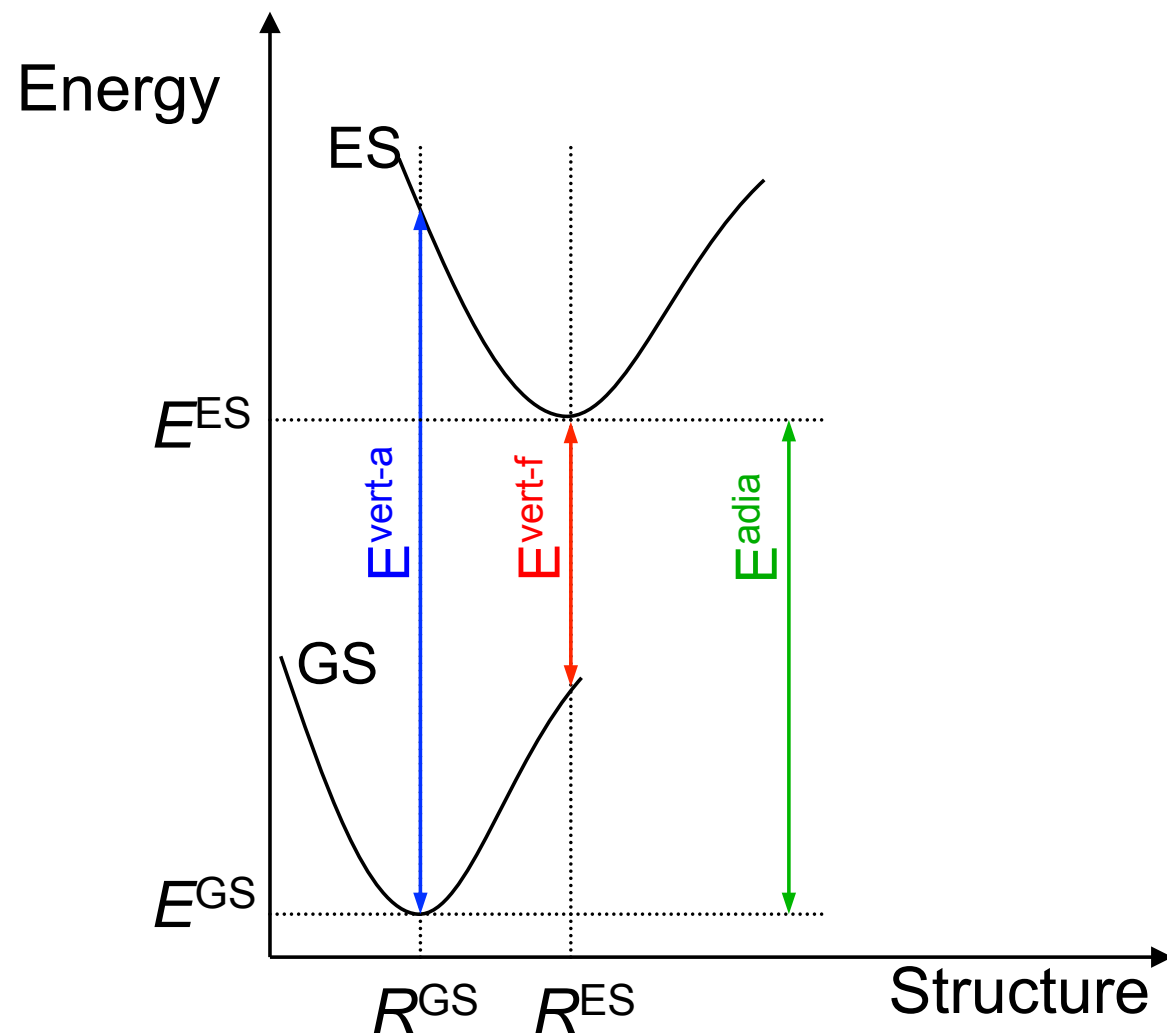
- Multireference CI (MRCI)
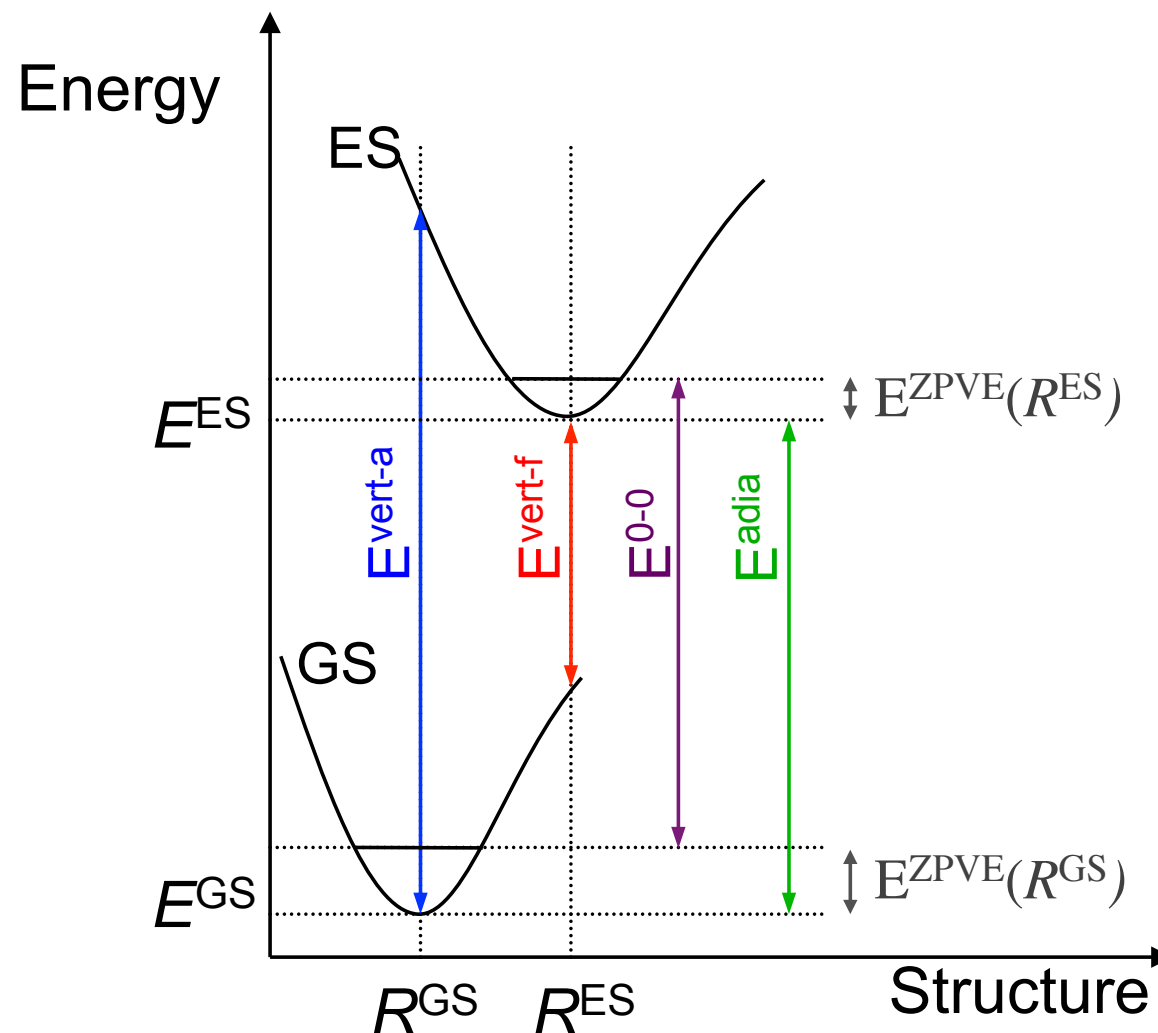
- Multireference CC (MRCC)

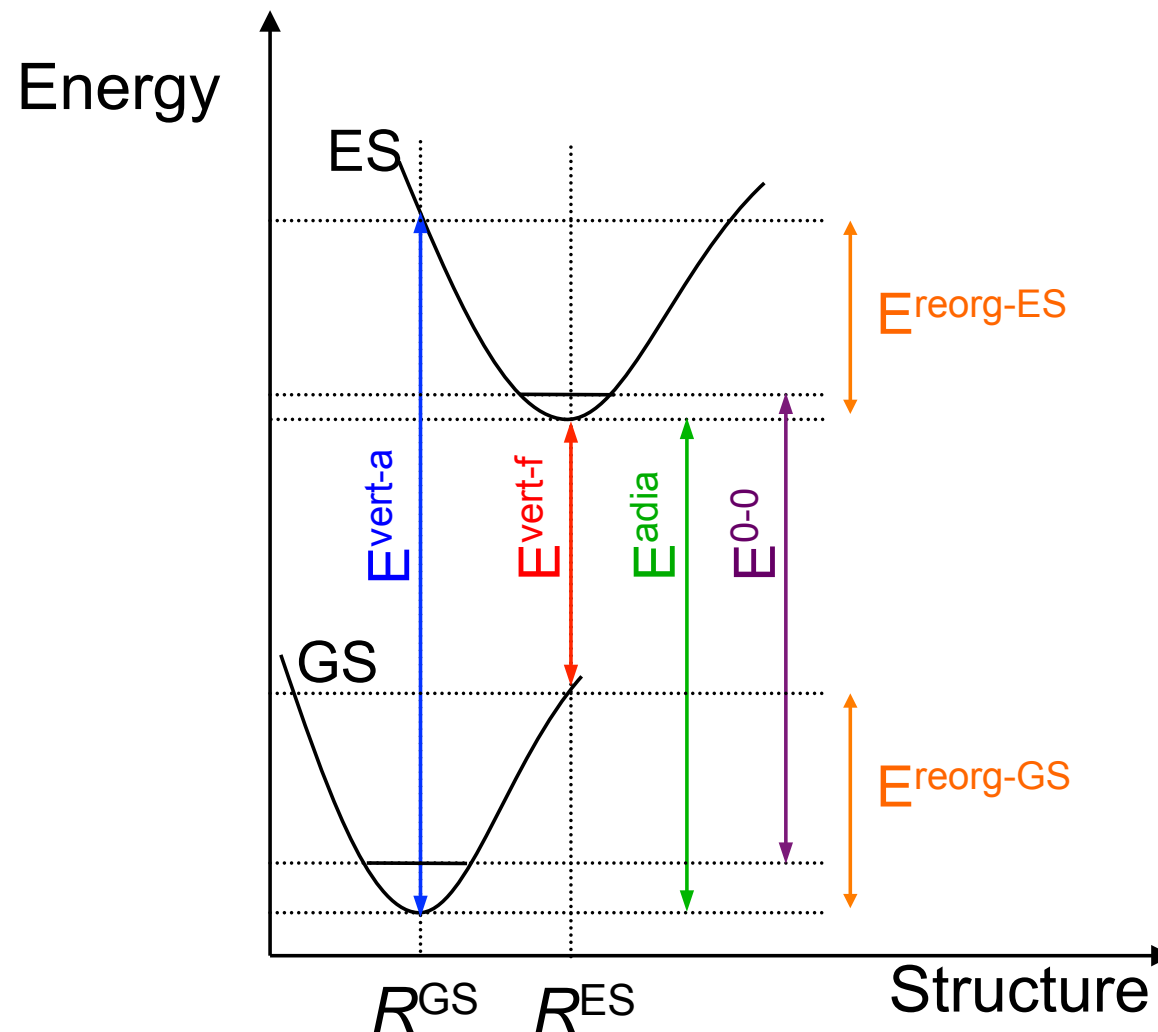# Photochemistry: fluorescence

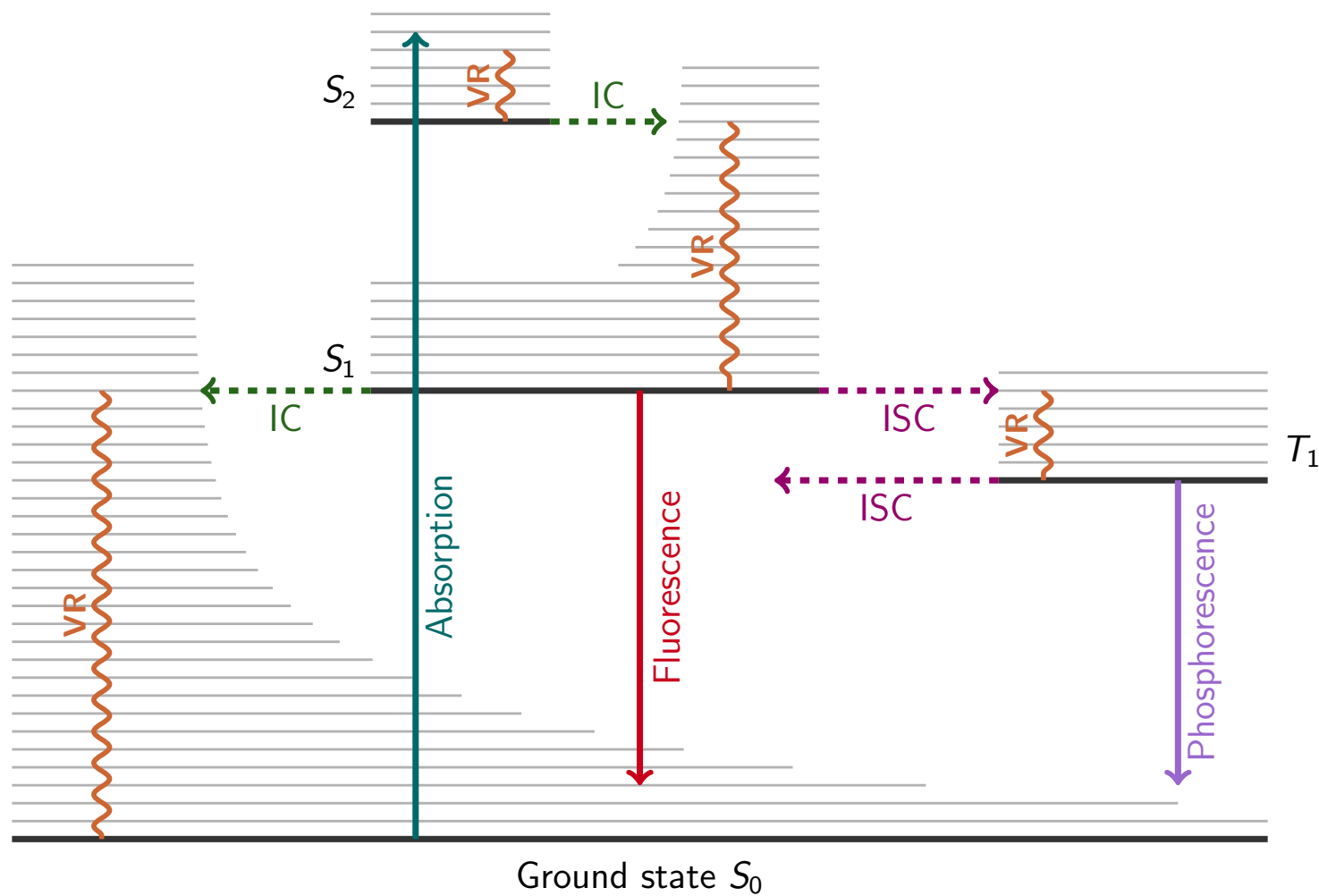# Photochemistry: fluorescence

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Equations for CIS

HF wave function

The HF ground-state wave function is taken as a reference

$$|\Psi_0(\boldsymbol{r})\rangle = |\phi_1(\boldsymbol{r})\phi_2(\boldsymbol{r})\ldots\phi_n(\boldsymbol{r})\rangle$$

CIS wave function

$$|\Psi_{\text{CIS}}\rangle = \sum_i^{\text{occ}} \sum_a^{\text{virt}} c_i^a |\Psi_i^a\rangle \quad \text{where } |\Psi_i^a\rangle \text{ are singly-excited determinants}$$

CIS energy

$$\boxed{\mathbf{H}|\Psi_{\text{CIS}}\rangle = E_{\text{CIS}}|\Psi_{\text{CIS}}\rangle} \Rightarrow \sum_{ia} c_i^a \mathbf{H}|\Psi_i^a\rangle = E_{\text{CIS}} \sum_{ia} c_i^a |\Psi_i^a\rangle$$

$$\Rightarrow \sum_{ia} c_i^a \langle\Psi_j^b|\mathbf{H}|\Psi_i^a\rangle = E_{\text{CIS}} \sum_{ia} c_i^a \delta_{ij}\delta_{ab}$$

Solving the CIS equations

The Slater-Condon rules tell us that

$$\langle \Psi_j^b | \mathbf{H} | \Psi_i^a \rangle = (E_0 + \varepsilon_a - \varepsilon_i)\delta_{ij}\delta_{ab} + (ia||jb)$$

with $(ia||jb) = (ia|jb) - (ij|ab)$, and

$$(ia|jb) = \iint \frac{\phi_i(\mathbf{r}_1)\phi_a(\mathbf{r}_1)\phi_j(\mathbf{r}_2)\phi_b(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$$

Therefore,

$$\sum_{ia} [(\varepsilon_a - \varepsilon_i)\delta_{ij}\delta_{ab} + (ia||jb)]c_i^a = \omega_{\text{CIS}} \sum_{ia} \delta_{ij}\delta_{ab}c_i^a$$

We obtain ω by diagonalising $\mathbf{A}$

$$\boxed{\mathbf{A}\,\mathbf{X} = \omega\mathbf{X} \quad \Rightarrow \quad (\mathbf{A} - \omega)\mathbf{X} = \mathbf{0}}$$

$$A_{ia,jb} = (\varepsilon_a - \varepsilon_i)\delta_{ij}\delta_{ab} + (ia||jb)$$

Comments, properties and limitations of CIS

Comments

1. $(\varepsilon_a - \varepsilon_i)\delta_{ij}\delta_{ab}$: energy difference between orbitals i and a, which are the ones from which and to which the electron is excited

2. $(ia||jb)$: linear response of the Coulomb operator to the first-order changes in the one-electron orbitals

Properties and limitations

1. All excited-state total energies are true upper bounds to their exact values

2. CIS is size-consistent

3. One can obtain pure singlet and triplet states (no spin contamination)

4. CIS excitation energies are usually overestimated
   (too large by about 0.5-2 eV compared to experimental values)

1. Introduction

2. Configuration interaction single

3. **Time-dependent Hartree-Fock**

4. Time-dependent density-functional theory

5. Multiconfigurational self-consistent field methods

6. Green's function methods

Time-dependent Hartree-Fock (TDHF)

TDHF wave function

The reference wave function is a time-dependent HF wave function:

$$|\Psi_{\mathsf{HF}}(\boldsymbol{r}, t)\rangle = |\phi_1(\boldsymbol{r}, t)\phi_2(\boldsymbol{r}, t)\dots\phi_n(\boldsymbol{r}, t)\rangle$$

TDHF equations

$$\mathbf{F}(\boldsymbol{r}, t)\,|\Psi_{\mathsf{HF}}(\boldsymbol{r}, t)\rangle = i\frac{\partial}{\partial t}\,|\Psi_{\mathsf{HF}}(\boldsymbol{r}, t)\rangle \quad \mathbf{F}(\boldsymbol{r}, t) = \mathbf{F}(\boldsymbol{r}) + \mathbf{V}(\boldsymbol{r}, t) = \mathbf{F}(\boldsymbol{r}) + \sum_{i}^{n} v_i(\boldsymbol{r}, t)$$

What physically happens?

1. At $t = 0$, the system is in a stationary state given by $|\Psi_0(\boldsymbol{r})\rangle$
2. A small TD perturbation is applied: $\phi_i(\boldsymbol{r})$'s respond only slightly
3. Linear response: we use 1st-order TD perturbation theory to find this response

Time-dependent Hartree-Fock (TDHF)

How to solve the TDHF equations?

We have a non-Hermitian problem:

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \omega \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & \mathbf{1} \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix}$$

$$A_{ia,jb} = (\varepsilon_a - \varepsilon_i)\delta_{ij}\delta_{ab} + (ia||jb) \qquad B_{ia,jb} = (ia||bj)$$

which can be reduced in a Hermitian eigenvalue equation

Tamm-Dancoff approximation

1. CIS is equivalent to TDHF with $\mathbf{B} = \mathbf{0}$

2. This is the Tamm-Dancoff approximation (TDA)!

Comments on TDHF

Comments

1. $(\varepsilon_a - \varepsilon_i)\delta_{ij}\delta_{ab}$: energy difference between orbitals i and a, which are the ones from which and to which the electron is excited

2. $(ia||jb)$: linear response of the Coulomb operator to the first-order changes in the one-electron orbitals

3. $(ia||bj)$ linear response of the exchange operator to the first-order changes in the one-electron orbitals

4. TDHF is an extension of CIS:
   It includes "singly de-excited" states as well as "singly excited" states

Properties and limitations of TDHF

Properties and limitations

1. TDHF is a size-consistent method

2. One can obtain pure singlet and triplet states for closed-shell molecules

3. TDHF has problems with triplets

4. TDHF has **not** been very successful in the quantum chemistry community

5. Excitation energies calculated with TDHF are slightly smaller than the ones obtained with CIS, but they are still overestimated

6. TDHF is **not** a significative improvement over CIS and is slightly more expensive