

TCCM Winter School LTTC 2025:

Excited-State Methods

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Here we propose to code two excited-state methods which target vertical excitation energies. We encourage the students to browse Ref. [1] where they will find additional details about each of the methods succinctly presented here.

1 Configuration Interaction With Singles

The simplest method to obtain the energy of excited states in atoms and molecules is called configuration interaction with singles (CIS). It is solely based on the Hartree-Fock (HF) molecular orbitals (MO) $\phi_p(\mathbf{r}) = \sum_{\mu} c_{\mu p} \chi_{\mu}(\mathbf{r})$ and their corresponding energies ϵ_p , where $\chi_{\mu}(\mathbf{r})$ is an atomic orbital (AO). In CIS, the m th singlet excitation energies ω_m (i.e., the energy difference between the ground state and the m th singlet excited state) is obtained by solving the following linear eigenvalue problem:

$$\mathbf{A} \cdot \mathbf{X}_m = \omega_m \mathbf{X}_m \quad (1)$$

where the elements of the matrix \mathbf{A} are given by

$$A_{ia,jb} = (\epsilon_a - \epsilon_i) \delta_{ij} \delta_{ab} + 2(\langle ia|bj \rangle - \langle ij|ba \rangle) \quad (2)$$

and

$$(pq|rs) = \iint \phi_p(\mathbf{r}_1) \phi_q(\mathbf{r}_1) \frac{1}{r_{12}} \phi_r(\mathbf{r}_2) \phi_s(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \quad (3)$$

is a two-electron integral in the MO basis. Here, i and j denote occupied orbitals, a and b are unoccupied orbitals, and p, q, r and s indicate arbitrary orbitals. Note that the matrix \mathbf{A} is built in the basis of all single excitations $i \rightarrow a$ and is therefore of size $OV \times OV$ where O and V are the number of occupied and virtual orbitals respectively. By diagonalising \mathbf{A} , one then obtains OV eigenvalues, the lowest one corresponding to the energy difference between the ground state and the first singlet excited state.

Exercise 1 (5 points): Create a subroutine to transform the two-electron integrals from the AO basis $(\mu\nu|\lambda\sigma)$ to the MO basis $(pq|rs)$:

$$(pq|rs) = \sum_{\mu\nu\lambda\sigma} c_{\mu p} c_{\nu q} c_{\lambda r} c_{\sigma s} (\mu\nu|\lambda\sigma) \quad (4)$$

Exercise 2 (5 points): Construct the CIS matrix \mathbf{A} and diagonalise it to obtain the excitation energies of helium, beryllium and neon in several basis sets.

2 Time-Dependent Hartree-Fock

A slightly more involved method to obtain excited states is time-dependent Hartree-Fock (TDHF). In this case, the singlet excitation energies are obtained via the diagonalisation of the following non-Hermitian linear eigenproblem

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ -\mathbf{A} & -\mathbf{B} \end{pmatrix} \cdot \begin{pmatrix} \mathbf{X}_m \\ \mathbf{Y}_m \end{pmatrix} = \omega_m \begin{pmatrix} \mathbf{X}_m \\ \mathbf{Y}_m \end{pmatrix} \quad (5)$$

where

$$A_{ia,jb} = (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} + 2(\text{ia}|\text{bj}) - (\text{ij}|\text{ba}) \quad (6)$$

$$B_{ia,jb} = 2(\text{ia}|\text{jb}) - (\text{ib}|\text{ja}) \quad (7)$$

In most cases, this non-Hermitian problem can be recast as a Hermitian problem of half the size

$$\mathbf{C} \cdot \mathbf{Z}_m = \omega_m^2 \mathbf{Z}_m \quad (8)$$

thanks to the following transformation:

$$\mathbf{C} = (\mathbf{A} - \mathbf{B})^{1/2} \cdot (\mathbf{A} + \mathbf{B}) \cdot (\mathbf{A} - \mathbf{B})^{1/2} \quad (9)$$

$$\mathbf{Z} = (\mathbf{A} - \mathbf{B})^{-1/2} \cdot (\mathbf{X} + \mathbf{Y}) \quad (10)$$

Exercise 3 (5 points): Construct the matrix \mathbf{A} and \mathbf{B} in the case of TDHF. Then, compute $(\mathbf{A} - \mathbf{B})^{1/2}$.

Exercise 4 (5 points): Construct and diagonalize the matrix \mathbf{C} to obtain the TDHF excitation energies for helium, beryllium and neon in several basis sets. Compare with CIS.

References

- [1] Andreas Dreuw and Martin Head-Gordon. Single-Reference ab Initio Methods for the Calculation of Excited States of Large Molecules. *Chem. Rev.*, 105:4009–4037, 2005.