

Quantum Chemistry

Lecture 19

Doubly Excited Configurations
Complete Active Space
Coupled Cluster Approximation

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The Central Role of Doubly Excited Configuration Interaction

Here we focus on the most common application of CI, which includes singles and doubles (CISD). However, by Brillouin's theorem, the singles do not contribute to the ground state energy. Therefore, the lowest order of theory that enhances the correlation energy is doubly excited CI (DCI). Focusing on the doubles determinant correction we can see how the correlation energy is calculated.

$$|\Phi_0\rangle = |\Psi_0\rangle + \sum_{\substack{a < b \\ r > s}} c_{ab}^{rs} |\Psi_{ab}^{rs}\rangle$$

The correlation energy is:

$$(H - E_0)|\Phi_0\rangle = E_{\text{corr}}|\Phi_0\rangle$$

The Correlation Energy Calculated by Doubly Excited CI

$$(H - E_0) \left(|\Psi_0\rangle + \sum_{\substack{a < b \\ r > s}} c_{ab}^{rs} |\Psi_{ab}^{rs}\rangle \right) = E_{\text{corr}} \left(|\Psi_0\rangle + \sum_{\substack{a < b \\ r > s}} c_{ab}^{rs} |\Psi_{ab}^{rs}\rangle \right)$$

Left-multiplying by $\langle \Psi_0 |$ and $\sum_{\substack{a < b \\ r > s}} c_{ab}^{rs} \langle \Psi_{ab}^{rs} |$ we obtain the terms.

$$\sum_{\substack{a < b \\ r > s}} c_{ab}^{rs} \langle \Psi_0 | H | \Psi_{ab}^{rs} \rangle = E_{\text{corr}}$$

$$\langle \Psi_{ab}^{rs} | H | \Psi_0 \rangle + \sum_{\substack{a < b \\ r > s}} c_{ab}^{rs} \langle \Psi_{ab}^{rs} | H - E_0 | \Psi_{cd}^{tu} \rangle = c_{ab}^{rs} E_{\text{corr}}$$

The Correlation Energy Calculated by Doubly Excited CI (DCI)

By defining the matrices

$$(\mathbf{B})_{\text{rasb}} = \langle \Psi_{\text{ab}}^{\text{rs}} | H | \Psi_0 \rangle$$

$$(\mathbf{D})_{\text{rasb,tcud}} = \langle \Psi_{\text{ab}}^{\text{rs}} | H - E_0 | \Psi_{\text{cd}}^{\text{tu}} \rangle$$

$$(\mathbf{c})_{\text{rasb}} = c_{\text{ab}}^{\text{rs}}$$

we can write the above terms as

$$\mathbf{B}^T \mathbf{c} = E_{\text{corr}}$$

$$\mathbf{B} + \mathbf{Dc} = \mathbf{c}E_{\text{corr}}$$

Because of the extreme increase in computational cost for CI, it is logical to use perturbation theory to decrease the computational cost while maintaining the advantage of the approaches to calculating the correlation energy. The approaches collectively are known as Rayleigh-Schrodinger perturbation theory or many-body perturbation theory (MBPT). Specifically, the approach of Moller and Plesset has gained widespread application. The development of this theory provides an interesting case in the development of mathematics, which is beyond the scope of this text. However, it is worth describing the general problem. The issue that must be confronted in perturbation theory is whether the various terms are size consistent. In these expansions there are mathematically ill-behaved terms. Using a diagrammatic approach it has been shown that all of these ill-behaved terms cancel to all orders of the perturbation expansion. Thus, the perturbation approach is on solid ground.

The Complete Active Space Concept

CASSCF

A popular approach to the CI problem is to limit the number of both occupied and unoccupied orbitals used in the calculation. Up to this point, we have implicitly assumed that all of the orbitals necessarily were included in the calculation. However, most of the important effects in bonding are in the frontier orbitals, i.e. those orbitals near the HOMO and LUMO. Thus, it is possible to use only a subset of the N occupied spin orbitals and $2K - N$ virtual or unoccupied orbitals. We can call the number of occupied orbitals N_{CAS} (starting with the HOMO and including successively lower MOs). Likewise, the number of virtual orbitals is $2K_{\text{CAS}} - N_{\text{CAS}}$.

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Multireference CASSCF

A complete active space is a type of classification of molecular orbitals. Spatial orbitals are classified as belonging to three classes:

- core, always hold two electrons

- active, partially occupied orbitals

- virtual, always hold zero electrons

This classification permits definition of the wavefunction as a linear combination of Slater determinants. Based on the freedom left for the occupation in the active orbitals, a certain number of electrons are allowed to populate all the active orbitals in appropriate combinations, developing a finite-size space of determinants. The resulting wavefunction is called a multireference wave function.

The active space is defined assuming that the electrons come from the highest occupied orbitals in the initial guess determinant and that the remaining orbitals required for the active space come from the lowest virtuals of the initial guess. Thus, for a 4-electron, 6-orbital CAS—specified as CASSCF(4,6)—on a closed-shell system, the active space would consist of

1. enough occupied orbitals from the guess to provide 4 electrons. Thus, the 2 highest occupied MOs would be included.
2. enough virtual orbitals to make a total of 6 orbitals. Since 2 occupied orbitals were included, the lowest 4 virtual orbitals would become part of the active space.

In Gaussian 09, algorithmic improvements make an active space of up to about 14 orbitals feasible

An example of CASSCF(4,6) is shown in the figure. In this case one can consider the total number of configurations even in this case is 2520. However, this is much smaller than the number we would have if we considered full-CI on the entire molecule. For example, if this were H₂O (10 electrons) and we considered full CI up to the level of quadruples for a 6-31+G(d,p) basis set we would have 12 orbitals.

Thus, $n = 4$, $N = 10$: $2K = 24$, using:

$$\binom{N}{n} \binom{2K - N}{n} = \frac{N!}{n! (N - n)!} \frac{(2K - N)!}{n! (2K - N - n)!}$$

We calculate 5×10^7 configurations for full-CI up to the level of quadruples.



The Importance of Size Consistency

A further issue that must be considered is the size consistency of the method. Size consistency refers to the idea that the energy scales with the number of electrons. While full CI is size consistent, one of the disadvantages of truncated CI methods is that they are not size consistent. To see this we consider a dimer of H_2 molecules. The energy of the dimer should be just twice the energy of a single H_2 molecule. However, under DCI the energy of each H_2 is corrected by a double excitation. In order to correct the energy of both H_2 molecules simultaneously, we would need two double excitations, which is a quadruple excitation. However, by definition DCI is truncated at double excitations and does not include quadruple excitations. Thus, it is not possible for the energy of the dimer to equal the energy of two monomers.

Independent Electron Pair Approximation

We have seen that we can write the correlation as:

$$E_{\text{corr}} = \sum_{\substack{a < b \\ r > s}} c_{ab}^{rs} \langle \Psi_0 | H | \Psi_{ab}^{rs} \rangle$$

The coefficients in this equation, c_{ab}^{rs} , are determined by variational treatment of the doubly excited determinants. These are the terms that survive because the interactions in the hamiltonian are pairwise interactions. We can write this in a shorthand as:

$$E_{\text{corr}} = \sum_{a < b} e_{ab} \quad e_{ab} = \sum_{r > s} c_{ab}^{rs} \langle \Psi_0 | H | \Psi_{ab}^{rs} \rangle$$

where the e_{ab} terms represent the interaction of a pair of electrons which occupy spin orbitals ϕ_a and ϕ_b .

Independent Electron Pair Approximation

Focusing on the doubles determinant correction we can see how the correlation energy is calculated.

$$H|\Psi_{ab}\rangle = E_{ab}|\Psi_{ab}\rangle$$

$$H\left(|\Psi_0\rangle + \sum_{t<u} c_{ab}^{tu} |\Psi_{ab}^{tu}\rangle\right) = E_{ab}\left(|\Psi_0\rangle + \sum_{t<u} c_{ab}^{tu} |\Psi_{ab}^{tu}\rangle\right)$$

Left-multiplying by $\langle\Psi_0|$ and $\langle\Psi_{ab}^{rs}|$ we obtain the terms

$$E_0 + \sum_{t<u} c_{ab}^{tu} \langle\Psi_0|H|\Psi_{ab}^{tu}\rangle = E_{ab}$$

$$\langle\Psi_{ab}^{rs}|H|\Psi_0\rangle + \sum_{t<u} c_{ab}^{tu} \langle\Psi_{ab}^{rs}|H|\Psi_{ab}^{tu}\rangle = c_{ab}^{rs} E_{ab}$$

Independent Electron Pair Approximation

$$\sum_{t < u} c_{ab}^{tu} \langle \Psi_{ab}^{rs} | H | \Psi_{cd}^{tu} \rangle = e_{ab}$$

$$\langle \Psi_{ab}^{rs} | H | \Psi_0 \rangle + \sum_{t < u} c_{ab}^{tu} \langle \Psi_{ab}^{rs} | H - E_0 | \Psi_{cd}^{tu} \rangle = c_{ab}^{rs} e_{ab}$$

By defining the matrices

$$(\mathbf{B}_{ab})_{rs} = \langle \Psi_{ab}^{rs} | H | \Psi_0 \rangle$$

$$(\mathbf{D}_{ab})_{rs,tu} = \langle \Psi_{ab}^{rs} | H - E_0 | \Psi_{cd}^{tu} \rangle$$

$$(\mathbf{c}_{ab})_{rs} = c_{ab}^{rs}$$

The matrix equation is

$$\begin{pmatrix} 0 & \mathbf{B}_{ab}^\dagger \\ \mathbf{B}_{ab} & \mathbf{D}_{ab} \end{pmatrix} \begin{pmatrix} 1 \\ \mathbf{c}_{ab} \end{pmatrix} = e_{ab} \begin{pmatrix} 1 \\ \mathbf{c}_{ab} \end{pmatrix}$$

Independent Electron Pair Approximation

This matrix eigenvalue problem is solved for the $N(N-1)/2$ pairs of electrons in occupied orbitals. The total correlation energy is obtained by adding up the pair energies,

$$E_{\text{corr}}(\text{IEPA}) = \sum_{a < b} e_{ab}$$

This approach is known as "pair-at-a-time" CI. We can make a further simplifying assumption keeping only terms where $t = r$ and $u = s$. This means that we ignore coupling between excited state determinants.

If we solve for the coefficient, c_{ab}^{rs} , we obtain the Epstein-Nesbitt pair correlation energy:

$$e_{ab}^{\text{EN}} = - \sum_{r < s} \frac{\langle \Psi_0 | H | \Psi_{ab}^{rs} \rangle^2}{\langle \Psi_{ab}^{rs} | H - E_0 | \Psi_{cd}^{rs} \rangle}$$

where we have made the assumption that

$$\langle \Psi_{ab}^{rs} | H - E_0 | \Psi_{cd}^{rs} \rangle \gg e_{ab}$$

First Order Correction to Hartree-Fock Theory: A Perturbation Method

This is really an intermediate result, which is not so useful as a method since this method can overestimate the correlation energy. To cast the result into a useful form we can further approximate the pair interaction matrix element as

$$\langle \Psi_{ab}^{rs} | H - E_0 | \Psi_{cd}^{rs} \rangle \approx \epsilon_r + \epsilon_s - \epsilon_a - \epsilon_b$$

The first order correction to the Hartree-Fock energy is therefore:

$$e_{ab}^{\text{FO}} = \sum_{a < b} \sum_{r < s} \frac{\langle \Psi_0 | H | \Psi_{ab}^{rs} \rangle^2}{\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s}$$

Note the similarity of this term with the second order correction to the energy using perturbation theory.

Individual Electron Pair Approximation: Need to Include IEPA in Comprehensive Approach

It can be shown that IEPA is scalable, while DCI is not size consistent. However, IEPA is no longer a variational method. Therefore, it is possible to overestimate the correlation energy. In fact, the problem is quite serious. Thus, the advance made in creating a size-consistent theory that includes pairwise interactions is not a good stopping point for CI theory.

The comprehensive approach that permits us to use doubles configuration interaction combined with the independent electron pair approximation is known as the coupled cluster approximation (CCA).

The Coupled Cluster Approximation

The problem up to this point can be summarized as follows. The DCI approximation is not size consistent because of the need to include matrix elements of the type $\langle \Psi_{ab}^{rs} | H | \Psi_{cd}^{tu} \rangle$. While the IEPA gives a method for including those terms, the method is not well controlled since it is no longer a variational method. In order to make progress and to keep the improvements along this path of investigation, we can return to a consideration of the full CI matrix in order to find an appropriate approximation. From Brillouin's theorem we know that the singles do not contribute to the HF reference state. It is also known that the triples make a much smaller contribution than the even numbered excitations. To obtain the variation energy of the wave function we substitute it into

$$(H - E_0)|\Phi_0 \rangle = E_{\text{corr}}|\Phi_0 \rangle$$

The Coupled Cluster Approximation

Considering the even-numbered excitations, we have

$$|\Phi_0\rangle = c_0|\Psi_0\rangle + \sum_{\substack{a<b \\ r<s}} c_{ab}^{rs} |\Psi_{ab}^{rs}\rangle + \sum_{\substack{a<b<c<d \\ r<s<t<u}} c_{abcd}^{rstu} |\Psi_{abcd}^{rstu}\rangle \dots$$

and then left multiply by $\langle\Psi_0|$, $\langle\Psi_{ab}^{rs}|$, and $\langle\Psi_{abcd}^{rstu}|$, etc. to obtain the coupled equations:

$$\sum_{t<u} c_{ab}^{tu} \langle\Psi_0|H|\Psi_{ab}^{tu}\rangle = E_{\text{corr}}$$

$$\langle\Psi_{ab}^{rs}|H|\Psi_0\rangle + \sum_{\substack{t<u \\ c<d}} c_{cd}^{tu} \langle\Psi_{ab}^{rs}|H|\Psi_{cd}^{tu}\rangle + \sum_{\substack{t<u \\ c<d}} c_{abcd}^{rstu} \langle\Psi_{ab}^{rs}|H|\Psi_{abcd}^{rstu}\rangle = c_{ab}^{rs} E_{\text{corr}}$$

The Coupled Cluster Approximation

We want an approximation that retains the contribution to the correlation energy from in the higher terms, such as the quadruples. The method used is to write the quadruples term as a product of two doubly-excited terms. Thus, our approximation will be,

$$c_{abcd}^{rstu} \approx c_{ab}^{rs} * c_{cd}^{tu}$$

However, there are 18 different ways that a single quadruple excitation can be represented by coupled pair excitations.

$$\begin{aligned} c_{abcd}^{rstu} &\approx c_{ab}^{rs} * c_{cd}^{tu} = c_{ab}^{rs} c_{cd}^{tu} - \langle c_{ab}^{rs} * c_{cd}^{tu} \rangle \\ &= c_{ab}^{rs} c_{cd}^{tu} - c_{ac}^{rs} c_{bd}^{tu} + c_{ad}^{rs} c_{bc}^{tu} - c_{ab}^{rt} c_{cd}^{su} + c_{ac}^{rt} c_{bd}^{su} - c_{ad}^{rt} c_{bc}^{su} \\ &+ c_{ab}^{ru} c_{cd}^{st} - c_{ac}^{ru} c_{bd}^{st} + c_{ad}^{ru} c_{bc}^{st} + c_{ab}^{tu} c_{cd}^{rs} - c_{ac}^{tu} c_{bd}^{rs} + c_{ad}^{tu} c_{bc}^{rs} \\ &- c_{ab}^{su} c_{cd}^{rt} + c_{ac}^{su} c_{bd}^{rt} - c_{ad}^{su} c_{bc}^{rt} + c_{ab}^{st} c_{cd}^{ru} - c_{ac}^{st} c_{bd}^{ru} + c_{ad}^{st} c_{bc}^{ru} \end{aligned}$$

$$\langle \Psi_{ab}^{rs} | H | \Psi_0 \rangle + \sum_{\substack{t < u \\ c < d}} c_{cd}^{tu} \langle \Psi_{ab}^{rs} | H - E_0 | \Psi_{cd}^{tu} \rangle + \sum_{\substack{t < u \\ c < d}} c_{cd}^{tu} \langle \Psi_{ab}^{rs} | H | \Psi_{abcd}^{rstu} \rangle (c_{ab}^{rs} * c_{cd}^{tu}) =$$

$$= \left(\sum_{\substack{t < u \\ c < d}} c_{cd}^{tu} \langle \Psi_0 | H | \Psi_{cd}^{tu} \rangle \right) c_{ab}^{rs}$$

There are two cases

1. when $ab \neq cd$ and $rs \neq tu$ we can

$$\langle \Psi_0 | H | \Psi_{cd}^{tu} \rangle = \langle \Psi_{ab}^{rs} | H | \Psi_{abcd}^{rstu} \rangle$$

2. when $ab = cd$ and $rs = tu$. Thus, we can write the equation as:

$$c_{ab}^{rs} * c_{cd}^{tu} = 0$$

We can substitute

$$\begin{aligned}
 & \langle \Psi_{ab}^{rs} | H | \Psi_0 \rangle + \sum_{\substack{t < u \\ c < d}} c_{cd}^{tu} \langle \Psi_{ab}^{rs} | H - E_0 | \Psi_{cd}^{tu} \rangle \\
 - & \sum_{\substack{t < u \\ c < d}} c_{cd}^{tu} \langle \Psi_{ab}^{rs} | H | \Psi_{cd}^{tu} \rangle \langle c_{ab}^{rs} * c_{cd}^{tu} \rangle + \sum_{\substack{t < u \\ c < d}} c_{cd}^{tu} \langle \Psi_{ab}^{rs} | H | \Psi_{cd}^{tu} \rangle c_{ab}^{rs} c_{cd}^{tu} \\
 & = \left(\sum_{\substack{t < u \\ c < d}} c_{cd}^{tu} \langle \Psi_0 | H | \Psi_{cd}^{tu} \rangle \right) c_{ab}^{rs}
 \end{aligned}$$

Therefore,

$$\langle \Psi_{ab}^{rs} | H | \Psi_0 \rangle + \sum_{\substack{t < u \\ c < d}} c_{cd}^{tu} \langle \Psi_{ab}^{rs} | H - E_0 | \Psi_{cd}^{tu} \rangle - \sum_{\substack{t < u \\ c < d}} c_{cd}^{tu} \langle \Psi_{ab}^{rs} | H | \Psi_{cd}^{tu} \rangle \langle c_{ab}^{rs} * c_{cd}^{tu} \rangle = 0$$

This is a result of coupled-pair many electron theory (CPMET), which forms the basis of the coupled cluster approximation (CCA). The transformation of these equations into code for quantum chemical calculations is quite involved, but these equations form the basis for the approximation, which is now known the CCA. The CCA can include singles as well. The CCSD keyword in Gaussian request such a calculation.