

Quantum Chemistry

Lecture 18

Configuration Interaction
Brillouin's Theorem
Full-CI Matrix

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Hartree-Fock is not well suited to calculation of excited state properties

Hartree-Fock theory works well for ground state properties because the energies of occupied orbitals are relatively accurately determined. However, the energy of unoccupied orbitals is not well determined and therefore excited state properties and transition energies are not well determined within the HF approach. To account for excited state properties one can include excited electron configurations. Such *ab initio* approaches that move beyond HF theory are collectively called configuration interaction (CI).

The Hartree-Fock Limit

The Hartree-Fock (HF) method is a single-determinant method. This means that it can be expressed as a single Slater determinant and that the electron population is entirely in the ground state orbitals. The fact that no excited state (or virtual) orbitals are present in the determinant has the consequence that ground state properties, including the structure can be quite accurate, but excited state properties and transition energies are not accurate. Stated slightly differently we can say that the HF hamiltonian includes electron exchange, but does not account for electron correlation. The HF method can be made more accurate by increasing the basis set to include higher order polarization functions. However, a larger basis will only improve the ground state properties. If one continues to increase the basis set one approaches the HF limit, which is the best calculation possible in the absence of electron correlation.

The Correlation Energy

Conceptually we can define the missing correlation energy as

$$E_{\text{corr}} = \varepsilon_0 - E_{\text{HF}}$$

where ε_0 is the exact non-relativistic energy of the system and E_{corr} is the correlation energy. E_{HF} is the energy of the Hartree-Fock limit. Since the true energy will always be lower than the calculated energy, we can conclude that $E_{\text{corr}} < 0$.

Multi-Determinant Methods

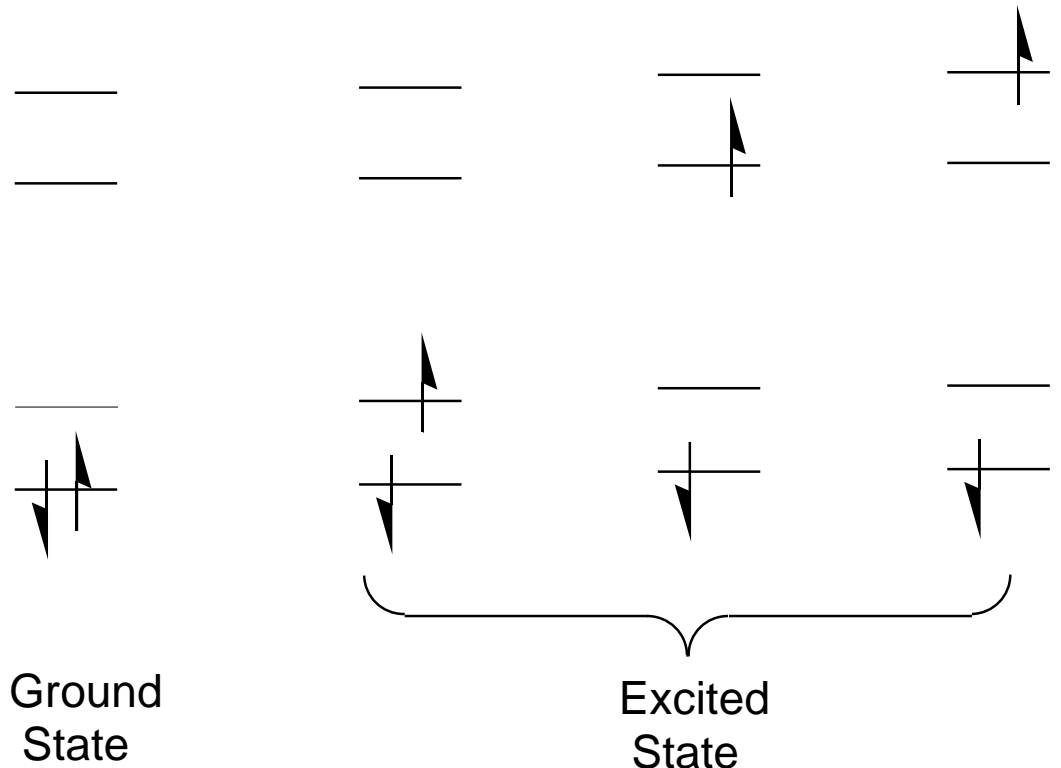
To surpass the HF limit one needs to use multi-determinant methods. In these methods one includes excited state occupancies in these additional determinants. Each determinant has the form of a Slater determinant, but the orbitals used may include excited state orbitals, i.e. which would not be included in the HF calculation. The inclusion of determinants that contain electron promotions to virtual or excited state orbitals is known as configuration interaction. An example is shown on the next slide for a single electron promotion. Such a configuration is known as "single" since it is based on the collection of single electron promotions. By including a determinant for each of these configurations, the energies of the normally unoccupied orbitals are included in the calculation. Such an approach is a first step towards the calculation of accurate excited state energies and molecular orbitals.

Configuration Interaction for Singles

If we imagine the case of H_2 we can implement CI for singles by mixing in the excited state configurations. In molecules of high symmetry only the configurations of appropriate symmetry can “mix” in this way.

CI that includes singles only is appropriate for improving transition energies, but does not help ground state properties.

This is known as Brillouin’s theorem.



Multielectron Configuration Interaction

The CI expansion is variational and, if the expansion is complete (Full CI), gives the exact correlation energy (within the basis set approximation). The number of determinants in full CI grows factorially with the system size, making the method impractical for all but the smallest systems. For this reason the CI expansion is usually truncated at some order, for example CISD, where only singly and doubly excited determinants are considered. Brillouin's Theorem states that singly excited determinants do not mix with the HF determinant. Therefore CISD is the cheapest worthwhile form of CI, yet this method scales as $O(N^6)$ where N is the size of the system.

The full CI wave function can be written as:

$$\begin{aligned}
 |\Phi_0\rangle = & c_0 |\Psi_0\rangle + \sum_{ra} c_a^r |\Psi_a^r\rangle \\
 & + \frac{1}{4} \sum_{\substack{a<b \\ r>s}} c_{ab}^{rs} |\Psi_{ab}^{rss}\rangle + \frac{1}{36} \sum_{\substack{a<b<c \\ r>s>t}} c_{abc}^{rst} |\Psi_{abc}^{rst}\rangle \dots
 \end{aligned}$$

where $|\Psi_0\rangle$ represents the HF determinant and the terms and

$$|\Psi_a^r\rangle \quad |\Psi_{ab}^{rs}\rangle$$

, etc. represent the single, double and higher electron promoted determinants. The indices a, b, c etc. and r, s, t etc. refer to the ground and excited state occupation numbers.

Each set of electron promoted determinants is multiplied by a factor of $(1/n!)^2$ where n is the promotion number. This is because terms such as

$$c_{ab}^{rs} \quad c_{ba}^{rs} \quad c_{ab}^{sr} \quad c_{ba}^{sr}$$

are all the same given the requirement that the wave function be anti-symmetric with respect to electron exchange.

Binomial coefficient used to calculate number of possible configurations

The number of total spin orbitals is $2K$. The factor of 2 arises from the fact that there are two electrons, while K indicates the number of spatial atomic orbitals in the basis set. The number of occupied orbitals is determined only by the number of electrons, N . Thus, there are N occupied and $2K - N$ virtual orbitals that must be included in the calculation. If we consider n -tuple excitation (i.e. $n = 1$ for single, $n = 2$ for double etc.), then the total number of configurations is given by:

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

where we have used the binomial coefficient to indicate the number of ways that n objects can be distributed among N locations.

Brillouin's Theorem

While CI including singly-excited states (CIS) can improve the energies of excited states (and therefore transition energies for calculation of absorption spectra), the contribution of singles to the ground state energy is zero. This is a result known as Brillouin's theorem.

Brillouin's theorem: Singly excited determinants, $|\Psi_a^r\rangle$, will not interact directly with a reference Hartree-Fock determinant, Ψ_0 , i. e. $\langle\Psi_0|H|\Psi_a^r\rangle = 0$

Proof of Brillouin's Theorem

The proof of this theorem starts with fact that a correction to the reference state by the variational method requires diagonalization of the matrix:

$$\begin{pmatrix} \langle \Psi_0 | H | \Psi_0 \rangle & \langle \Psi_0 | H | \Psi_a^r \rangle \\ \langle \Psi_a^r | H | \Psi_0 \rangle & \langle \Psi_a^r | H | \Psi_a^r \rangle \end{pmatrix} \begin{pmatrix} c_0 \\ c_a^r \end{pmatrix} = E_0 \begin{pmatrix} c_0 \\ c_a^r \end{pmatrix}$$

The mixing of the two states arises from the off-diagonal elements

$$\langle \Psi_0 | H | \Psi_a^r \rangle$$

These have the form

$$\langle \Psi_0 | H | \Psi_a^r \rangle = \langle a | h | r \rangle + \sum_b \langle ab || rb \rangle$$

Proof of Brillouin's Theorem

The matrix elements of the Fock operator are

$$\langle \phi_i | f | \phi_j \rangle = \langle i | h | j \rangle + \sum_b \langle ib || jb \rangle$$

Therefore,

$$\langle \Psi_0 | H | \Psi_a^r \rangle = \langle \phi_i | f | \phi_j \rangle$$

However, the off-diagonal elements of the Fock matrix are zero,

$$\langle \phi_i | f | \phi_j \rangle = 0$$

Thus, the solution is

$$\begin{pmatrix} E_0 & 0 \\ 0 & \langle \Psi_a^r | H | \Psi_a^r \rangle \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = E_0 \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

One can say that the HF energy is "stable", meaning that it does not mix directly with the single excitations. Note that single excitations can mix via high excitations.

Full-Configuration Interaction Matrix

To view the full-CI matrix with greater clarity we can write it symbolically as

$$|\Phi_0\rangle = c_0|\Psi_0\rangle + c_S|S\rangle + c_D|D\rangle + c_T|T\rangle + c_Q|Q\rangle + \dots$$

Where $|S\rangle$, $|D\rangle$, $|T\rangle$, and $|Q\rangle$ represent the terms involving excitation of single, double, triple and quadruple electrons. In full-CI, there will be as many such terms as electrons, but we have truncated the series at four electrons for clarity. Of course, the calculation can be carried out for any number of such promotions. Thus, we speak of singles, doubles, triples etc. as a kind of calculation beyond the HF limit. These are post-HF calculations.

Configuration Interaction Summary

1. There is no coupling between the ground state and the singles. Brillouin's theorem states that

$$\langle \Psi_0 | H | S \rangle = 0.$$

The consequence of this theorem is that a calculation of singles only can improve the energies of the virtual orbitals, but can improve the accuracy of the ground state energy or properties only indirectly.

2. All matrix elements of Hamiltonians that differ by more than two electron promotions are zero. Thus,

$$\langle \Psi_0 | H | T \rangle = \langle \Psi_0 | H | Q \rangle = 0$$

$$\langle S | H | Q \rangle = 0$$

3. The non-zero CI matrix cross terms are sparse, meaning that only terms that contain the overlap in the electron indices a, b, c... or r, s, t,... are non-zero.

The full CI matrix is shown below.

$$\begin{vmatrix}
 \langle \Psi_0 | H | \Psi_0 \rangle & 0 & \langle \Psi_0 | H | D \rangle & 0 & 0 & 0 \\
 0 & \langle S | H | S \rangle & \langle S | H | D \rangle & \langle S | H | T \rangle & 0 & 0 \\
 \langle \Psi_0 | H | D \rangle & \langle S | H | D \rangle & \langle D | H | D \rangle & \langle D | H | T \rangle & \langle D | H | Q \rangle & 0 \\
 0 & \langle S | H | T \rangle & \langle D | H | T \rangle & \langle T | H | T \rangle & \langle T | H | Q \rangle & \dots \\
 0 & 0 & \langle D | H | Q \rangle & \langle T | H | Q \rangle & \langle Q | H | Q \rangle & \dots \\
 0 & 0 & 0 & \dots & \dots & \dots
 \end{vmatrix}$$

We can conclude the most of the correlation energy relevant for improving the ground state is in the doubly-excited configurations. The next most important terms are the quadruply-excited configurations. These have an indirect effect through the doubles that is significant. However, this does not mean that one only includes the doubles or quadruples in the calculations. The singles and triples have a significant effect on the energies of the doubles and quadruples so they should be included.