

Electron Correlation

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Sources / Further reading

- Textbooks on *ab initio* quantum chemistry written by **T. Helgaker**, **P. Jørgensen**, and **J. Olsen** (unpublished).
- **B. O. Roos** (editor), *Lecture Notes in Quantum Chemistry* — *European Summer School in Quantum Chemistry*, Lecture Notes in Chemistry, Vols. 58 and 64, Springer, Berlin, 1992 and 1994.
 - ☞ Chapters by **B. O. Roos** and **P. R. Taylor**.
- **D. R. Yarkony** (editor), *Modern Electronic Structure Theory, Parts I and II*, Advanced Series in Physical Chemistry, Vol. 2, World Scientific, Singapore, 1995.
 - ☞ Chapters by **H. F. Schaefer III** (*et al.*) and **R. J. Bartlett**.

Electron-correlation effects

- If the n -electron Hamiltonian of a molecule would have the form

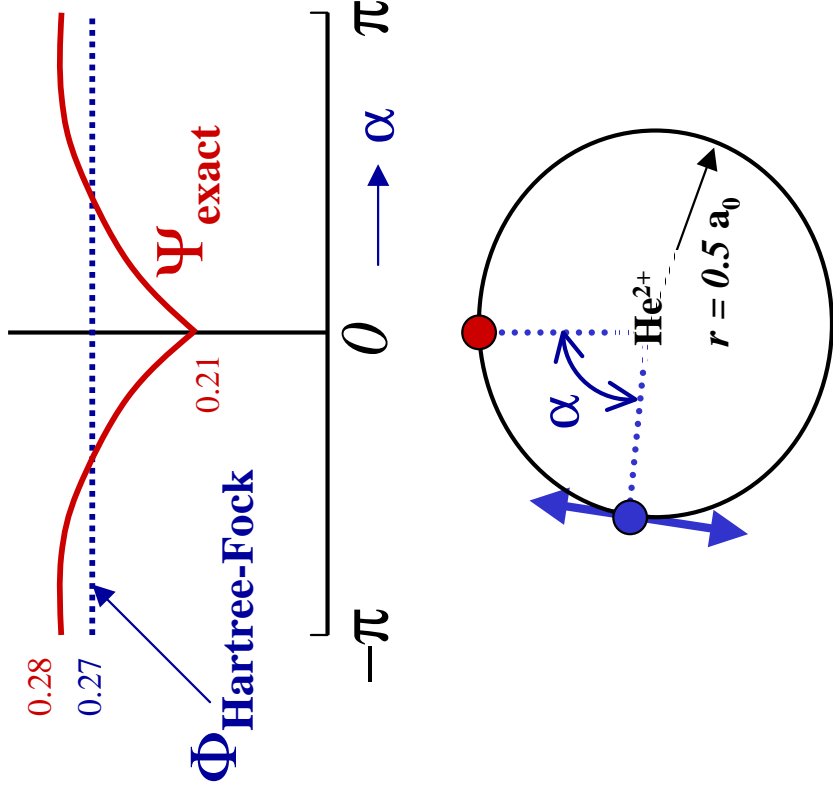
$$\hat{H}_{\text{approx.}} = \sum_{i=1}^n \hat{f}(i),$$

then a Slater-determinant built from the one-electron eigenfunctions (spin-orbitals) of the one-electron operator f would be an *exact* solution to the electronic Schrödinger equation.

- However, the true Hamiltonian has *not* this form, and a single determinant *cannot* be an eigenfunction of the Schrödinger equation.
- **The Hartree-Fock method consists of finding the best possible determinant by means of the variational principle.**
- The difference between the exact eigenvalue of the Schrödinger equation and the Hartree-Fock energy is termed the “correlation energy”. **Thus, electron-correlation effects are determined in post-Hartree-Fock calculations.**
- Note at this point that we refer to a *nonrelativistic, clamped-nuclei* Schrödinger equation.

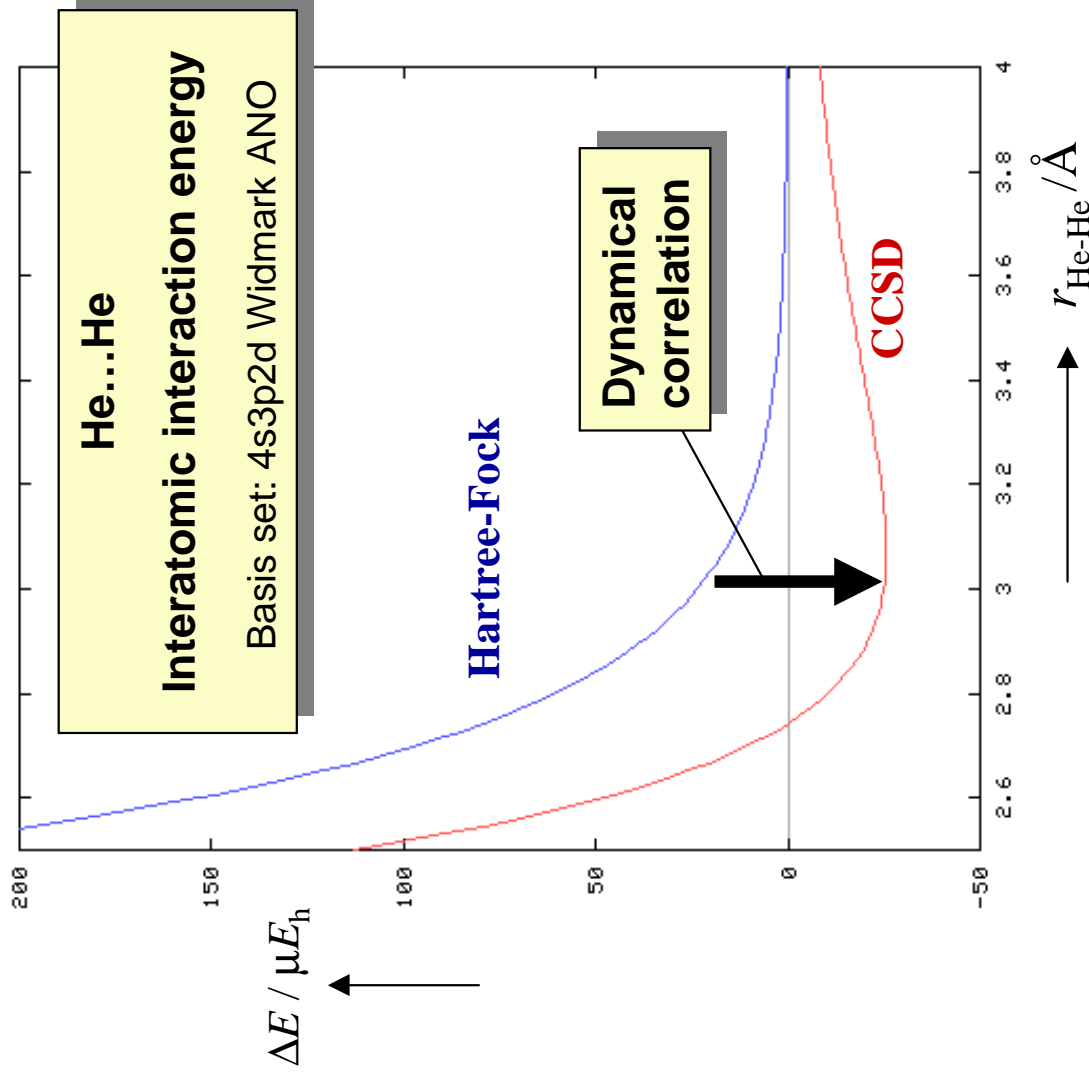
Dynamical electron correlation: The Coulomb hole

$1S$ ground state of He



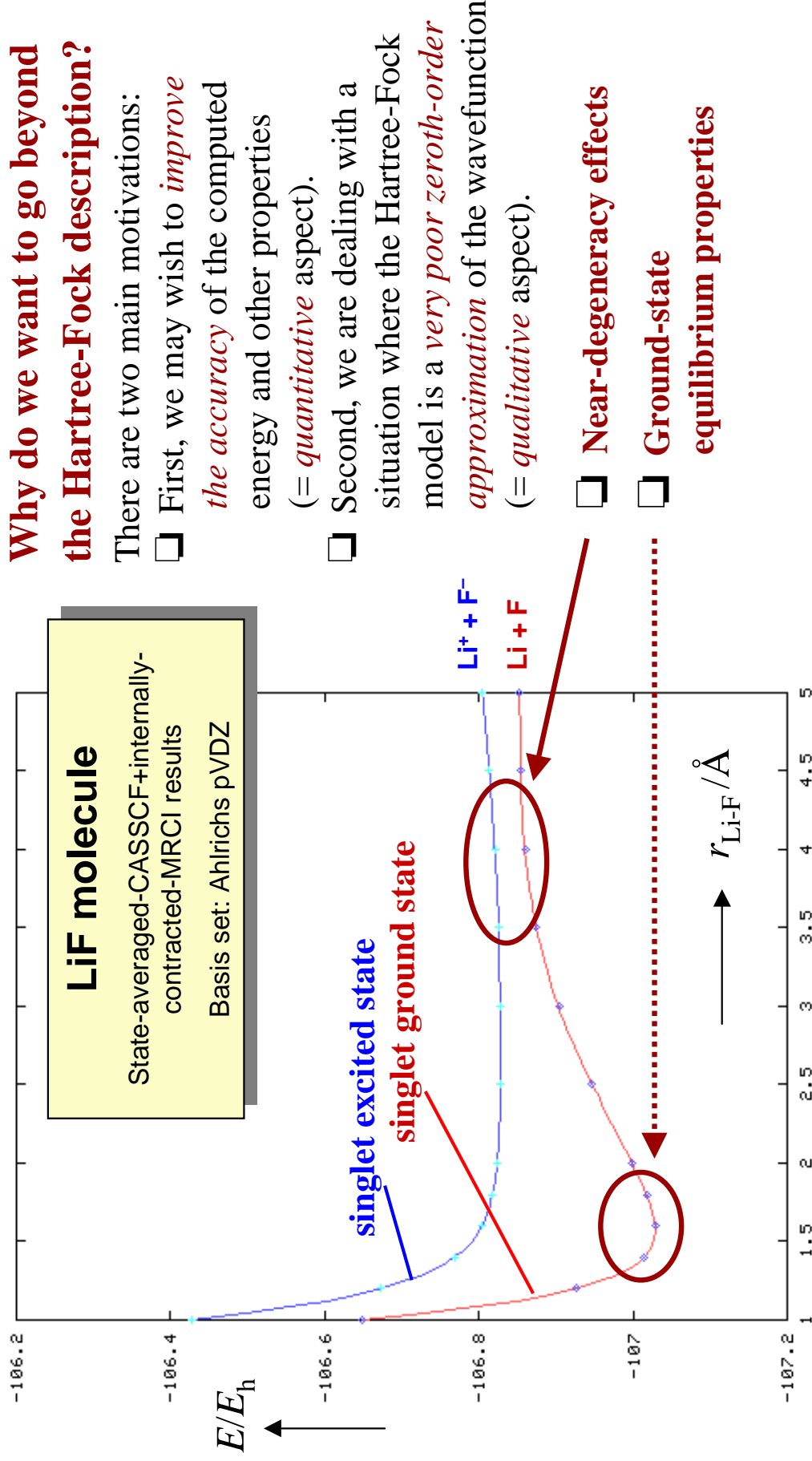
- Let us plot (the spatial part of) the electronic wavefunction $\Psi(\mathbf{r}_1, \mathbf{r}_2)$ of the helium atom as a function of the positions of the two electrons, which are chosen on a circle around the nucleus with radius $1/2$ bohr (a_0).
- **When we fix the first electron at an arbitrary position, we can move with the second electron on the circle and plot the value of the wavefunction as a function of the angle α .**
- Due to the instantaneous motion of the two electrons (= correlation) we find that the probability of finding the second electron near the first one is smaller than finding it at an opposite position on the circle.
- **Not so at the Hartree-Fock level!**
The probability for the second electron is *completely independent* of the position of the first electron (independent particles).

Dispersion interaction between closed-shell atoms



- ❑ The correlation energy is of the order of 1% of the total electronic energy. Nevertheless, correlation effects can change the Hartree-Fock results dramatically. For example, correlation effects are responsible for the attractive dispersion interaction between two closed-shell, ground-state atoms.
- ❑ The correlation energy of the nitrogen molecule amounts to only **0.5% of the total electronic energy**. However, **ca. 50% of the binding energy** of this molecule is due to electron-correlation effects.
- ❑ **Dynamical correlation is related to the Coulomb hole. It changes Hartree-Fock results mostly in a quantitative manner.**

Qualitative and quantitative aspects of electron correlation



Why do we want to go beyond the Hartree-Fock description?

There are two main motivations:

- ❑ First, we may wish to *improve the accuracy* of the computed energy and other properties (= *quantitative* aspect).
- ❑ Second, we are dealing with a situation where the Hartree-Fock model is a *very poor zeroth-order approximation* of the wavefunction (= *qualitative* aspect).

❑ **Near-degeneracy effects**

❑ **Ground-state equilibrium properties**

Dynamical and non-dynamical correlation

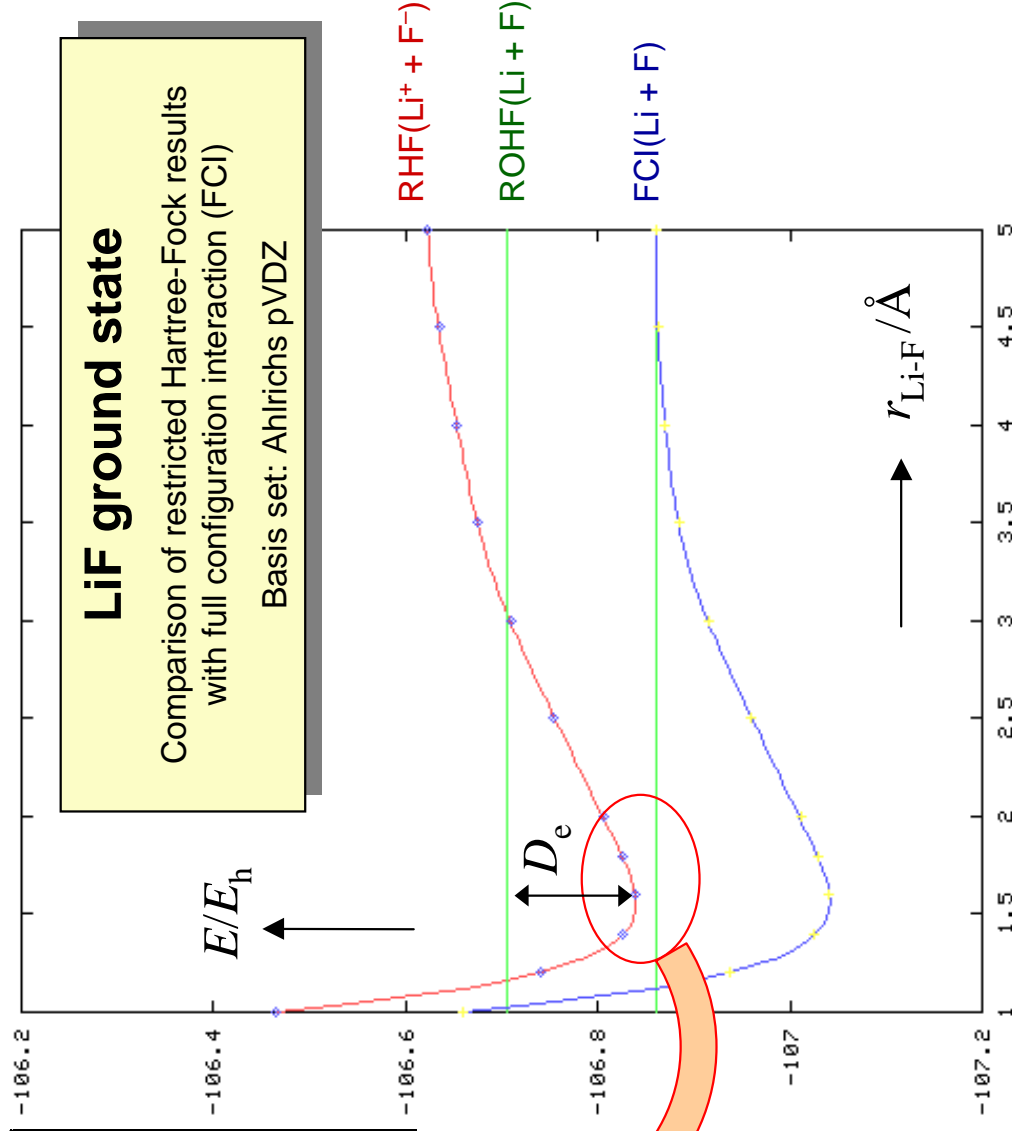
- ❑ If the Hartree-Fock determinant is a good zeroth-order approximation to the exact non-relativistic wavefunction, then the correlation effects are due to the Coulomb hole and this type of electron correlation is sometimes referred to as “**dynamical correlation**”. The computation of dynamical correlation effects requires **many determinants**.
- ❑ In other cases, the Hartree-Fock description is either a very poor zeroth-order approximation, or it is perhaps *not possible at all* to describe the electronic state of interest by a single determinant. Then, we are forced to use a few determinants to obtain a reasonable zeroth-order approximation to the exact nonrelativistic wavefunction. It is sometimes said that such an expansion in terms of a **few determinants** accounts for the “**non-dynamical**” —or “static” or “structural” — correlation effects.
- ❑ Often, non-dynamical correlation effects are related to **near-degeneracy problems**.
- ❑ The distinction between dynamical and non-dynamical correlation effects is not always clear. However, it is useful to realize that electron correlation has qualitative (non-dynamical) and quantitative (dynamical) aspects.

Restricted Hartree-Fock (RHF) results for LiF

	Hartree-Fock	Error
$r_e / \text{\AA}$	1.57	-0.6 %
$\omega_e / \text{cm}^{-1}$	991	+2.5 %
μ_e / D	6.49	+3.9 %
$\mu'_e / \text{D}\text{\AA}^{-1}$	4.14	+4.6 %
$D_e / \text{kJ mol}^{-1}$	352	-26 %

For LiF, the Hartree-Fock method is quite useful for calculations around the equilibrium, although the binding energy is too low by 26%.

For large internuclear distance, however, the RHF model *dissociates wrongly* into the ionic fragments Li^+ and F^- .



Size-consistency, size-extensivity, and size-intensivity

- A quantum-chemical calculation is said to be **size-consistent** if the energy of a compound system **AB** approaches the sum of the individual energies of the subsystems **A** and **B** when the distance R_{AB} becomes infinitely large.

$$E_{AB}(R_{AB} \rightarrow \infty) = E_A + E_B$$

- For the (spin-restricted) Hartree-Fock calculations on the LiF molecule, this is *not* so. A calculation on the compound system at large internuclear distance yields an energy that is much *higher* than the sum of the two energies that are obtained from separate calculations on the isolated atoms Li and F.
- Size-consistency problems can occur due to **improper dissociation** or due to **incorrect scaling** of the method.

- Computational methods are **size-extensive** or **size-intensive** if the calculated energies or properties *scale properly with the number of particles*.
- A *size-extensive* method ensures that a calculation on a compound system consisting of m non-interacting subsystems yields a calculated value that is the sum of the m individual subsystem results.

$$E(S_1 + S_2 + \dots + S_m) = E(S_1) + E(S_2) + \dots + E(S_m)$$

- *Size-intensively* computed properties are *independent* of the number of non-interacting subsystems. The electronic excitation energy in system S_k , for example, should be the same both in a calculation of the compound system and of the subsystem alone.

Configuration-interaction (CI) wavefunctions

- In Hartree-Fock theory, the n -electron wavefunction is approximated by one single Slater-determinant, denoted as: $|\text{HF}\rangle$
- This determinant is built from n orthonormal spin-orbitals. The spin-orbitals that form $|\text{HF}\rangle$ are said to be *occupied*. The other orthonormal spin-orbitals that follow from the Hartree-Fock calculation in a given one-electron basis set of atomic orbitals (AOs) are known as *virtual* orbitals. For simplicity, we assume that all spin-orbitals are real.

- In electron-correlation or post-Hartree-Fock methods, the wavefunction is expanded in a many-electron basis set that consists of many determinants. Sometimes, we only use a few determinants, and sometimes, we use millions of them:

$$|\text{CI}\rangle = |\text{HF}\rangle + \sum_{\mu} c_{\mu} |\mu\rangle$$

In this notation, $|\mu\rangle$ is a Slater-determinant that is obtained by replacing a certain number of occupied orbitals by virtual ones.

- Three questions:
 1. Which determinants should we include?
 2. How do we determine the expansion coefficients?
 3. How do we evaluate the energy (or other properties)?