Lecture 2: Exact and Approximate Wave Functions

Slowly but surely towards quantum chemical models. Electron correlation, isn’t it fun?
From the last session:
Things to think about

• Quantum chemistry: why bother?
  – Mere reproduction of experiments does not make too much sense
  – What is the added value from the computational approach?
Molecular orbitals (LiH)

\[ E = -2.451 \]

\[ E = -0.300 \]
From the last session:
Things to think about

• Molecular wave functions: what *are* they?
  – Can some kind of meaning be given to
    • The full N-electron wave function
    • One-electron wave functions (spin-orbitals)
  – Or are they just mathematical constructs? What is ”real” then?
    • Have a look at: Lundeen *et al*, Nature 474, 188–191 (2011)
Addressing electron correlation

- **Correlation energy** \( E_{\text{corr}} = E_{\text{exact}} - E_{\text{HF}} \)
  - This definition is most usable when speaking of molecular ground states and equilibrium geometries
- **Fermi correlation** arises from the Pauli antisymmetry of the wave function
- **Static correlation** arises from the near-degeneracy of electronic configurations
- **Dynamical correlation** is associated with the instantaneous correlation among the electrons
- Two sources: Pauli exclusion principle and repulsion
Potential energy curve (LiH)

The effect of electron correlation:
- Single SD description fails (wrong spin state)
- The effect of electron correlation

The graph shows the relationship between the potential energy ($E$) in electron units ($E_h$) and the distance ($r$) in Ångstroms (Å). The red line represents the Single SD description, which fails to accurately represent the energy curve due to the wrong spin state. The green line represents the Full CI description, which takes into account the electron correlation and provides a more accurate energy curve.
Correlation hole

**Hartree-Fock** wave function of He atom: the wave function electron 1 while keeping the another fixed at $x=0.5$

Helgaker et al (Wiley 2002)
Correlation hole

**Exact** wave function of He atom: the wave function electron 1 while keeping the another fixed at \( x=0.5 \)

Helgaker et al (Wiley 2002)
Correlation hole

Difference between the exact and HF wave functions

Helgaker et al (Wiley 2002)

Electronic cusp
Electron and nuclear cusps
Electron and nuclear cusps

Figure 5. The helium ground-state wave function with both electrons on the same circle of radius $0.5a_0$, for different maximum principal quantum number $n_{\text{max}}$. 
Requirements for many-electron wave functions

• The exact molecular wave function
  – Is **antisymmetric** with respect to the permutation of any pair of the electrons

\[
\hat{P} \Psi(x_1, \ldots, x_N) = \varepsilon_P \Psi(x_1, \ldots, x_N)
\]

(\(\varepsilon_P=+1\) or -1 for even and odd number of permutations, respectively)

– Is **square-integrable** everywhere in space

\[
\langle \Psi | \Psi \rangle = a \in \mathbb{R}
\]

– Is variational

\[
\langle \delta \Psi | \Psi \rangle = 0 \Rightarrow \langle \delta \Psi | H | \Psi \rangle = 0
\]
Requirements for many-electron wave functions

• The exact molecular wave function
  – Is **size-extensive**: for a system containing non-interacting subsystems A and B the total energy is equal to
    \[ E_{AB} = E_A + E_B \]
  – Possesses the characteristic non-differentiable behavior for spatially coinciding electrons and electrons coinciding nuclei (**electron and nuclear cusp conditions**)
Requirements for many-electron wave functions

• The exact molecular wave function
  – Is an eigenfunction of both projected and total spin operators
    \[
    \hat{S}^2 \Psi = S(S + 1) \Psi \\
    \hat{S}_z \Psi = M \Psi
    \]

• There are also other identities which are of importance only in some special cases

• Square integrability and antisymmetricity is easy to impose; the rest more challenging
Things to think about

• Take a system of fictitious “neutral” electrons. Would they be correlated in any manner?
• How about $N$ charged integer-spin particles, whose total wave function is symmetric wrt permutation?
• Is there a clear difference between static and dynamical correlation?
  – Why do we speak about them as separate phenomena?
Homework

- Study the Sections 2.1-2.3 and the Tew *et al* paper
- Have a look at the Section 2.4 and Appendix A
- Start doing the preparatory exercise assignment