Overview of Electronic Correlation

A locked box called

Schrödinger Equation

$$\hat{H}\Psi = E\Psi$$

Question:

What would be the world,

if $\frac{1}{a+b} = \frac{1}{a} + \frac{1}{b}$ **?**

Answer:

Mathematics was much more easier than it is !

In addition to Schrödinger, Ψ must be antisymmetric.

It is why, half of the computational chemistry exists!

Electron is Fermion !

Ψ for two-electron system must satisfy

$$\Psi(x_1, x_2) = -\Psi(x_2, x_1)$$ (Antisymmetricity)

There exist infinite number of antisymmetric functions, e.g.,

$$\Psi(x_1, x_2) = f(1)g(2) - g(1)f(2)$$

Determinantal wave function

There is a compact way to describe an antisymmetric wave function:

Slater determinant

$$\Psi(x_1, x_2) = \begin{vmatrix} f(1) & g(1) \\ f(2) & g(2) \end{vmatrix}$$

Sometimes we are going to take an exam, and …

what we think

(Before the exam)

what we get

(After the exam)

Determinantal wave function

Are all determinants antisymmetric?

Sure

$$\Psi(x_1, x_2) = \begin{vmatrix} f(1) & g(1) \\ f(2) & g(2) \end{vmatrix}$$

Are all antisymmetrics determinant?

Never !

Single Slater determinants are unique in many ways. They are

- **Efficient**
- **Compact**
- **Simple to manipulate**
- **Simple to store**
- **Simple to compute**

BUT

Electrons are not single determinants !

We like the electrons in real molecular systems adopt …

Single Slater determinant

But they are not

So, what they actually are?

Unknown!

$\hat{H}\Psi = E\Psi$

Antisymmetricity

Not single determinant

The poor computational chemist !

The exact solution is unknown. Are we helpless?

Chemist

No, just expand it !

Mathematician

It is a correlated wave function !

$$\Psi(x_1, x_2) = c_1\varphi_1(x_1, x_2) + c_2\varphi_2(x_1, x_2) + \cdots$$

General antisymmetric wave function for many-electron systems

Single determinants

$$\Psi = C_1 D_1 + C_2 D_2 + \cdots$$

How about the coefficients?

Correlation methods try to obtain the coefficients in different ways:

Configuration Interaction (CI)

Energy based

Multi-Configuration Self-Consistent Field (MC-SCF)

Combines SCF and CI

Coupled-Cluster (CC)

Some coefficients are guess in sensible manner

Møller-Plesset Perturbation (MP)

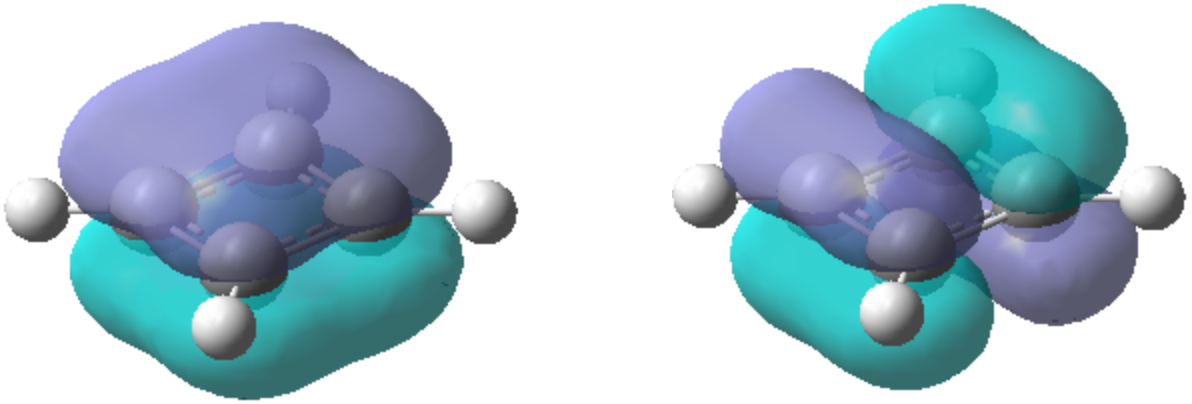
Approximate solution to Schrodinger equation

Density Functional Theory (DFT)

Estimates the correlation energy

Static vs Dynamic correlation

Planar square cyclobutadiene pi molecular orbitals:



It seems that something is wrong with respect to the molecular symmetry !

At least two equivalent configurations are required.

It is static correlation.

What is dynamic correlation?

To be continued …