The Standard Models:
Configuration Interaction

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What the electrons are doing in molecules?

- The exact solution to the Schrödinger equation cannot be obtained and we must introduce **approximation** in our solutions.

- Computational quantum chemistry has developed a few **standard models** for the construction of approximate electronic wave functions.

- At the simplest level, the wave function is represented by a **single Slater determinant**. The true wave function is represented by the variationally determined **superposition of all determinants** in the N-particle Fock space.

Hydrogen Molecule in a Minimal Basis

Electronic structure of H_2 in variational space of two orbitals.

One-electron Basis

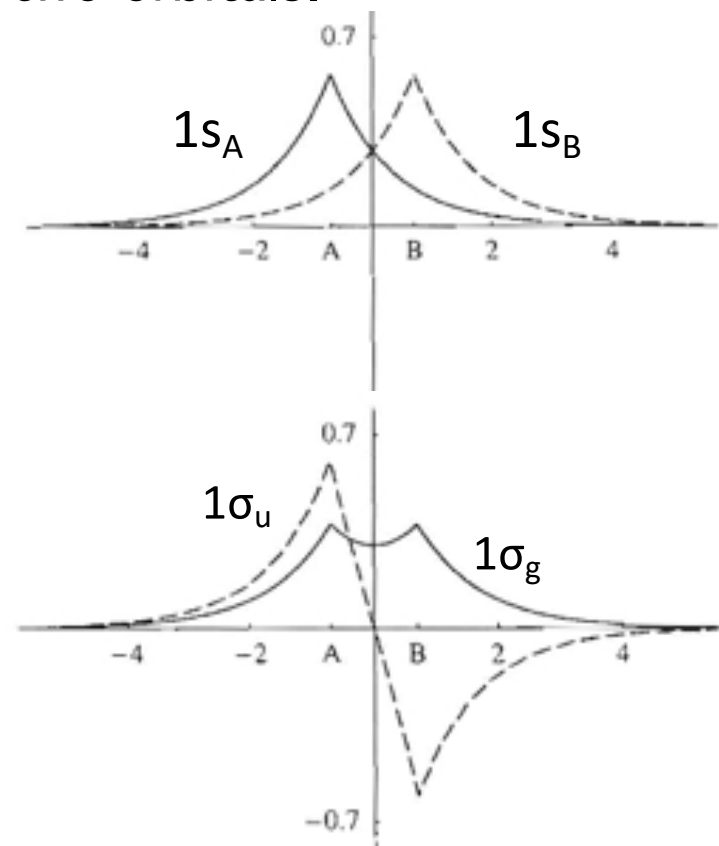$$1s_A(r) = \frac{1}{\sqrt{\pi}} e^{-r_A} \qquad 1s_B(r) = \frac{1}{\sqrt{\pi}} e^{-r_B}$$

r_A and r_B: distance between the electron and nuclei A and B.
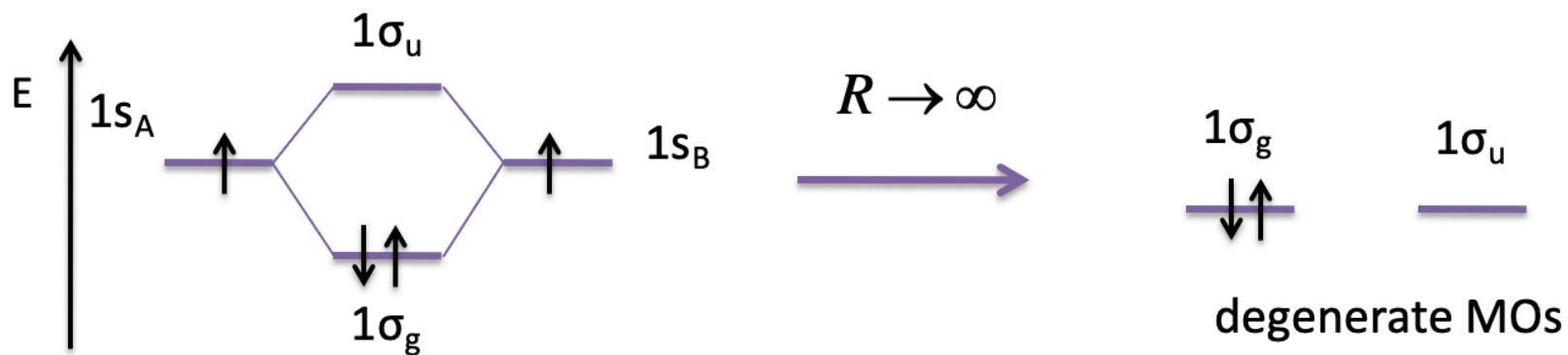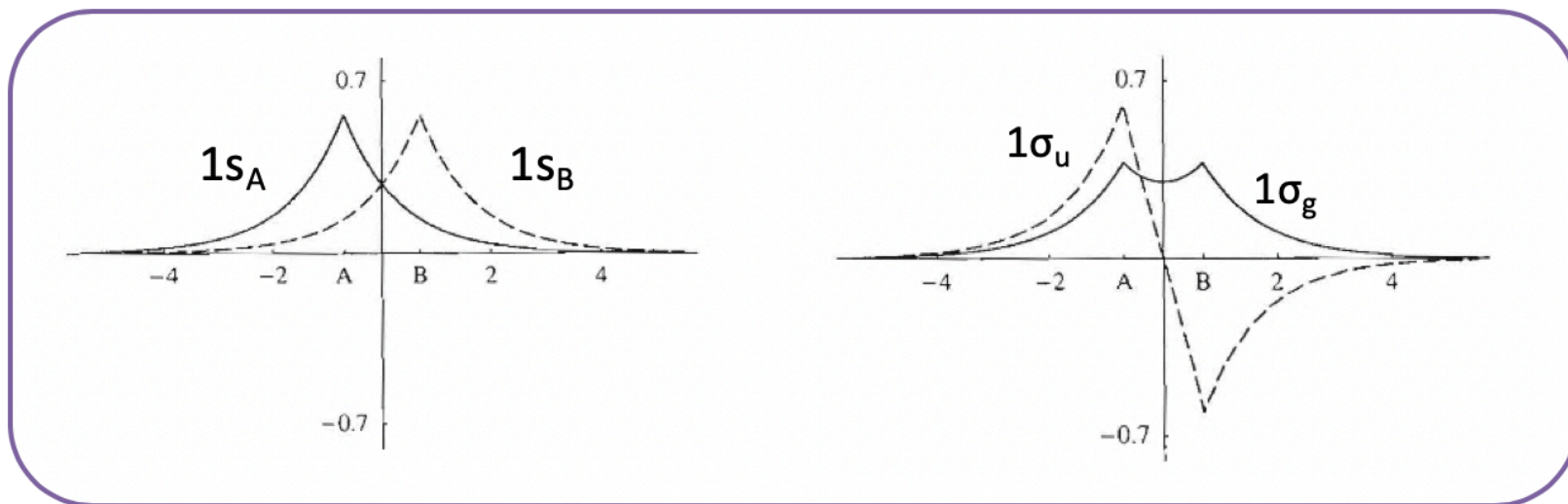
Symmetry-adapted orthonormal MOs

$$\varphi_1(r) = 1\sigma_g(r) = \frac{1}{\sqrt{2(1+S)}} \left[1s_A(r) + 1s_B(r) \right]$$

$$\varphi_2(r) = 1\sigma_u(r) = \frac{1}{\sqrt{2(1-S)}} \left[1s_A(r) - 1s_B(r) \right]$$

$$S = \int 1s_A(\mathbf{r}) 1s_B(\mathbf{r}) d\mathbf{r} = (1 + R + \frac{1}{3}R^2) e^{-R}$$
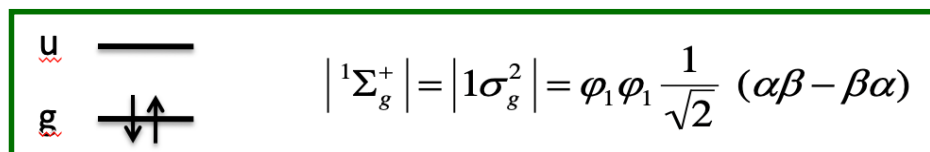

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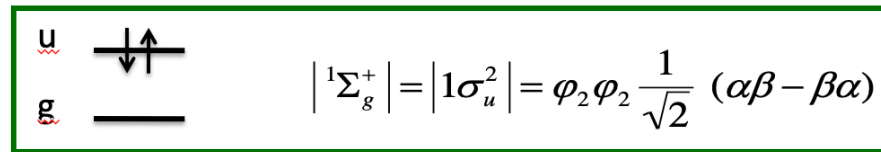# Hydrogen Molecule in a Minimal Basis

Generate **six determinates** by distributing the **two electrons** among the **four spin orbitals** in all possible ways
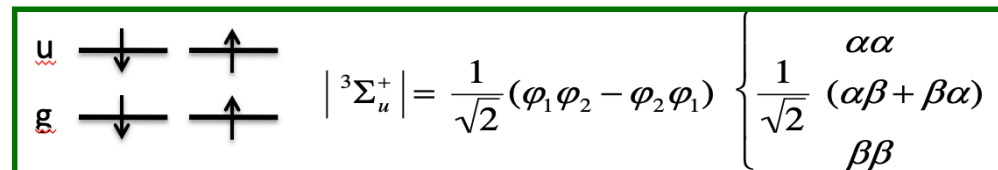
bonding orbital

$$\left|{}^{1}\Sigma_g^+\right| = \left|1\sigma_g^2\right| = \varphi_1\varphi_1 \frac{1}{\sqrt{2}} (\alpha\beta - \beta\alpha)$$

antibonding orbital

$$\left|{}^{1}\Sigma_g^+\right| = \left|1\sigma_u^2\right| = \varphi_2\varphi_2 \frac{1}{\sqrt{2}} (\alpha\beta - \beta\alpha)$$

Superposition of bonding and antibonging orbital

$$\left|{}^{1}\Sigma_u^+\right| = \frac{1}{\sqrt{2}} (\varphi_1\varphi_2 + \varphi_2\varphi_1) \frac{1}{\sqrt{2}} (\alpha\beta - \beta\alpha)$$

$$\left|{}^{3}\Sigma_u^+\right| = \frac{1}{\sqrt{2}} (\varphi_1\varphi_2 - \varphi_2\varphi_1) \begin{cases} \alpha\alpha \\ \frac{1}{\sqrt{2}} (\alpha\beta + \beta\alpha) \\ \beta\beta \end{cases}$$

Bonding orbital
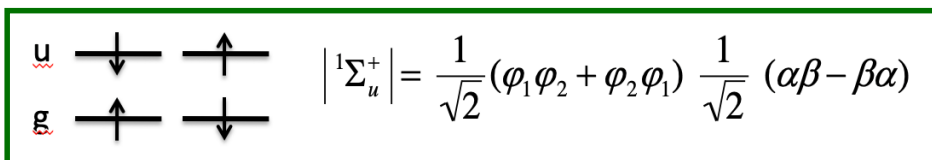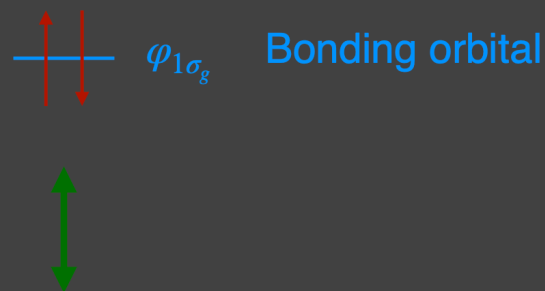
$$\varphi_{1\sigma_g}$$ Bonding orbital

$$\Phi^{RHF}(x_1, x_2) = \frac{1}{\sqrt{2}} \left(\varphi_{1\sigma_g,\alpha}(x_1)\varphi_{1\sigma_g,\beta}(x_2) - \varphi_{1\sigma_g,\alpha}(x_2)\varphi_{1\sigma_g,\beta}(x_1) \right)$$

$$= \varphi_{1\sigma_g}(r_1)\varphi_{1\sigma_g}(r_2) \times \frac{1}{\sqrt{2}} \left(\delta_{\sigma_1\alpha}\delta_{\sigma_2\beta} - \delta_{\sigma_2\alpha}\delta_{\sigma_1\beta} \right)$$

$s_A(r)$ $s_B(r)$

H .... H

Bonding orbital

$$\varphi_{1\sigma_g}(r) = \frac{1}{\sqrt{2}} \left(s_A(r) + s_B(r) \right)$$

$$= \varphi_{1\sigma_g}(r_1)\varphi_{1\sigma_g}(r_2) \times \frac{1}{\sqrt{2}} \left(\delta_{\sigma_1\alpha}\delta_{\sigma_2\beta} - \delta_{\sigma_2\alpha}\delta_{\sigma_1\beta} \right)$$

H .... H

$$\frac{1}{2} \left(s_A(r_1)s_B(r_2) + s_A(r_2)s_B(r_1) + s_A(r_1)s_A(r_2) + s_B(r_1)s_B(r_2) \right)$$

$$= \varphi_{1\sigma_g}(r_1)\varphi_{1\sigma_g}(r_2) \times \frac{1}{\sqrt{2}} \left(\delta_{\sigma_1\alpha}\delta_{\sigma_2\beta} - \delta_{\sigma_2\alpha}\delta_{\sigma_1\beta} \right)$$

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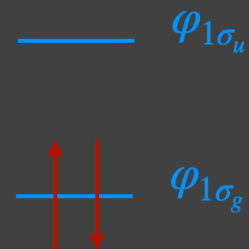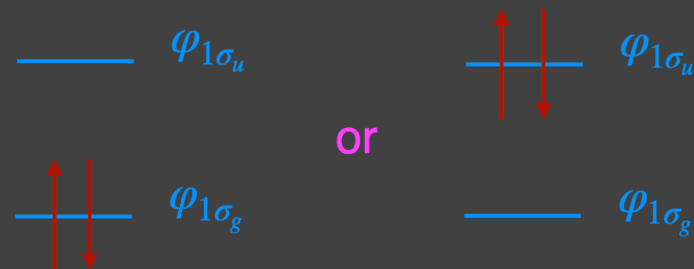$$|\Psi\rangle = \left|\left(1\sigma_g\right)^2\right\rangle$$

$$|\Psi\rangle = \frac{1}{\sqrt{2}}\left[\left|\left(1\sigma_g\right)^2\right\rangle - \left|\left(1\sigma_u\right)^2\right\rangle\right]$$

$$\equiv \frac{1}{\sqrt{2}}\left(\varphi_{1\sigma_g}(\boldsymbol{r_1})\varphi_{1\sigma_g}(\boldsymbol{r_2}) - \varphi_{1\sigma_u}(\boldsymbol{r_1})\varphi_{1\sigma_u}(\boldsymbol{r_2})\right)$$

$$|\Psi\rangle = \frac{1}{\sqrt{2}}\varphi_{1\sigma_g}(\mathbf{r_1})\varphi_{1\sigma_g}(\mathbf{r_2})$$

$$\frac{1}{2}\left(s_A(r_1)s_B(r_2) + s_A(r_2)s_B(r_1) + s_A(r_1)s_A(r_2) + s_B(r_1)s_B(r_2)\right)$$

H⁻······H⁺   H⁺······H⁻

$$|\Psi\rangle \equiv \frac{1}{\sqrt{2}}\left(\varphi_{1\sigma_g}(\boldsymbol{r_1})\varphi_{1\sigma_g}(\boldsymbol{r_2}) - \varphi_{1\sigma_u}(\boldsymbol{r_1})\varphi_{1\sigma_u}(\boldsymbol{r_2})\right)$$

$$= \frac{1}{\sqrt{2}}\left(s_A(\boldsymbol{r_1})s_B(\boldsymbol{r_2}) + s_A(\boldsymbol{r_2})s_B(\boldsymbol{r_1})\right)$$

H······H   H······H

7
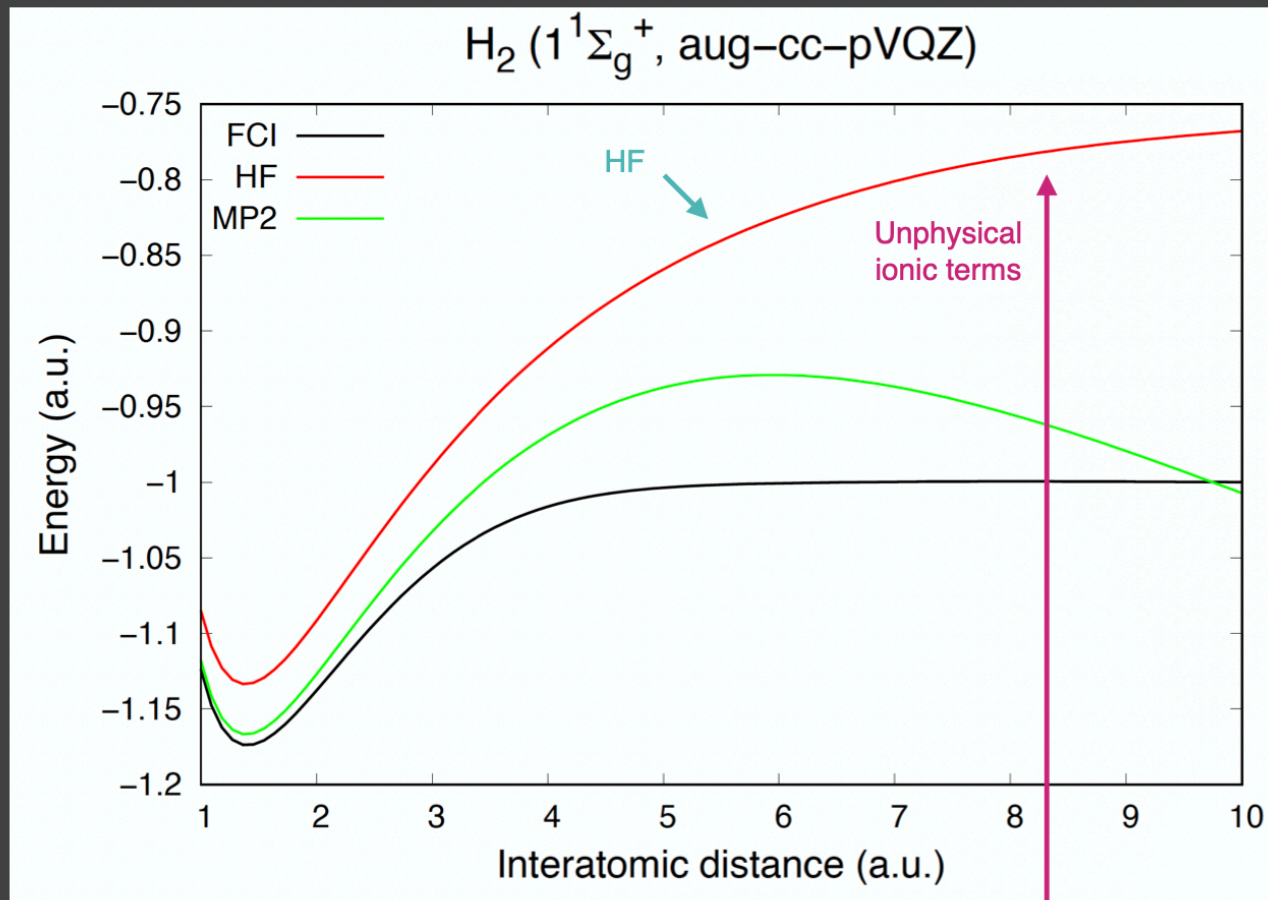
$$\frac{1}{2}\left(s_A(r_1)s_B(r_2) + s_A(r_2)s_B(r_1) + s_A(r_1)s_A(r_2) + s_B(r_1)s_B(r_2)\right)$$

H-······H+   H+······H-

Energy:

$$E = \sum_{pq} D_{pq} h_{pq} + \frac{1}{2} \sum_{pqrs} d_{pqrs} g_{pqrs} + \frac{1}{R}$$

One and two-electron density function:

$$\rho(r) = \sum_{pq} D_{pq} \varphi_p^*(r) \varphi_q(r) \qquad \rho(r_1, r_2) = \frac{1}{2} \sum_{pqrs} d_{pqrs} \varphi_p^*(r_1) \varphi_q(r_1) \varphi_r^*(r_2) \varphi_s(r_2)$$

D_{pq} and d_{pqrs} are one- and two-electron density matrix.

$$D_{pq} = \left\langle 0 \left| E_{pq} \right| 0 \right\rangle = \sum_\sigma \left\langle 0 \left| a_{p\sigma}^+ a_{q\sigma} \right| 0 \right\rangle \qquad d_{pqrs} = \left\langle 0 \left| E_{pq} E_{rs} - \delta_{rq} E_{ps} \right| 0 \right\rangle = \sum_{\sigma\tau} \left\langle 0 \left| a_{p\sigma}^+ a_{r\tau}^+ a_{s\tau} a_{q\sigma} \right| 0 \right\rangle$$

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Exercise: Show that one and two-electron density function.

$$D_{11}(1\sigma_g^2) = \langle 1\sigma_g^2 | E_{11} | 1\sigma_g^2 \rangle = 2$$

$$d_{1111}(1\sigma_g^2) = \sum_{\sigma\tau} \langle 1\sigma_g^2 | a_{1\sigma}^\dagger a_{1\tau}^\dagger a_{1\tau} a_{1\sigma} | 1\sigma_g^2 \rangle = 2$$

$$D_{22}(1\sigma_u^2) = \langle 1\sigma_u^2 | E_{22} | 1\sigma_u^2 \rangle = 2$$

$$d_{2222}(1\sigma_u^2) = \sum_{\sigma\tau} \langle 1\sigma_u^2 | a_{2\sigma}^\dagger a_{2\tau}^\dagger a_{2\tau} a_{2\sigma} | 1\sigma_u^2 \rangle = 2$$

Energy:

$$E(1\sigma_g^2) = 2h_{11} + g_{1111} + \frac{1}{R} \qquad E(1\sigma_u^2) = 2h_{22} + g_{2222} + \frac{1}{R}$$

State	Kinetic	Attraction	Electron repulsion	Nuclear repulsion	Total
$1\sigma_g^2$	0.8162	-3.1874	0.5660+0.0000	0.7143	-1.0909
$1\sigma_u^2$	2.3042	-3.4516	0.5863+0.0000	0.7143	0.1532

One and two-electron density functions

One-electron density functions:

$$\left| {}^1\Sigma_g^+ \right| = \left| 1\sigma_g^2 \right| = \varphi_1 \varphi_1 \frac{1}{\sqrt{2}} (\alpha\beta - \beta\alpha)$$

$$\rho_{1\sigma_g^2}(\mathbf{r}) = 2\varphi_1^2(\mathbf{r})$$
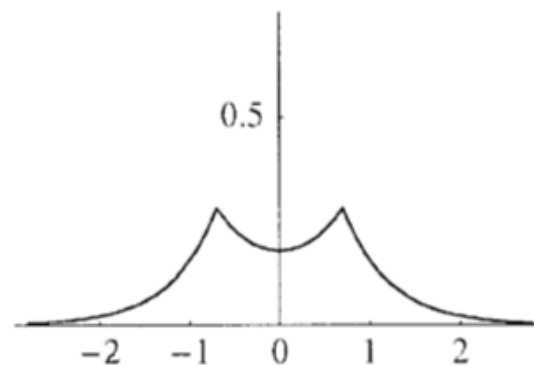
Accumulation of density in internuclear

$$\left| {}^1\Sigma_g^+ \right| = \left| 1\sigma_u^2 \right| = \varphi_2 \varphi_2 \frac{1}{\sqrt{2}} (\alpha\beta - \beta\alpha)$$
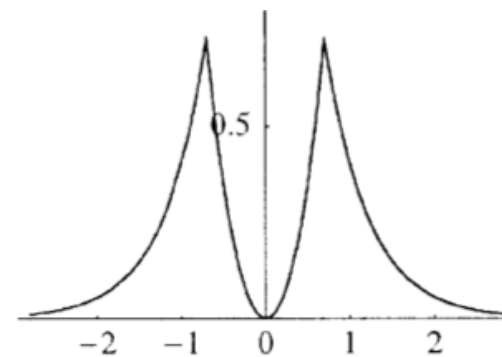
$$\rho_{1\sigma_u^2}(\mathbf{r}) = 2\varphi_2^2(\mathbf{r})$$

Depletion of density in internuclear

Two-electron density functions

$$\rho_{1\sigma_g^2}(r_1, r_2) = \varphi_1^2(r_1)\, \varphi_1^2(r_2)$$

$$\rho_{1\sigma_u^2}(r_1, r_2) = \varphi_2^2(r_1)\, \varphi_2^2(r_2)$$

$$\rho_{1\sigma_g^2}(\mathbf{r_1}, \mathbf{r_2}) = \frac{1}{4}\rho_{1\sigma_g^2}(\mathbf{r_1})\rho_{1\sigma_g^2}(\mathbf{r_2})$$

$$\rho_{1\sigma_u^2}(\mathbf{r_1}, \mathbf{r_2}) = \frac{1}{4}\rho_{1\sigma_u^2}(\mathbf{r_1})\rho_{1\sigma_u^2}(\mathbf{r_2})$$

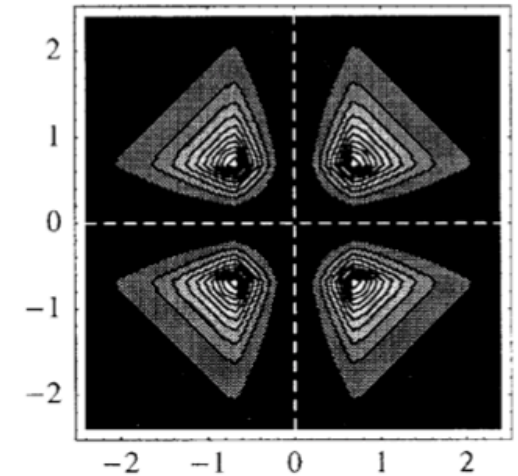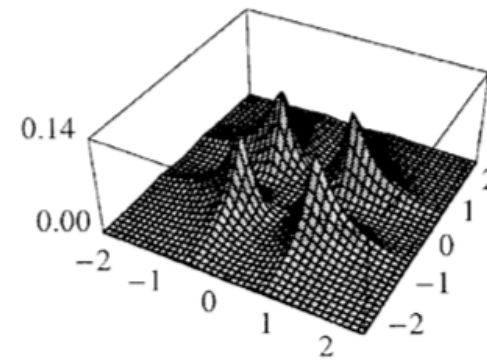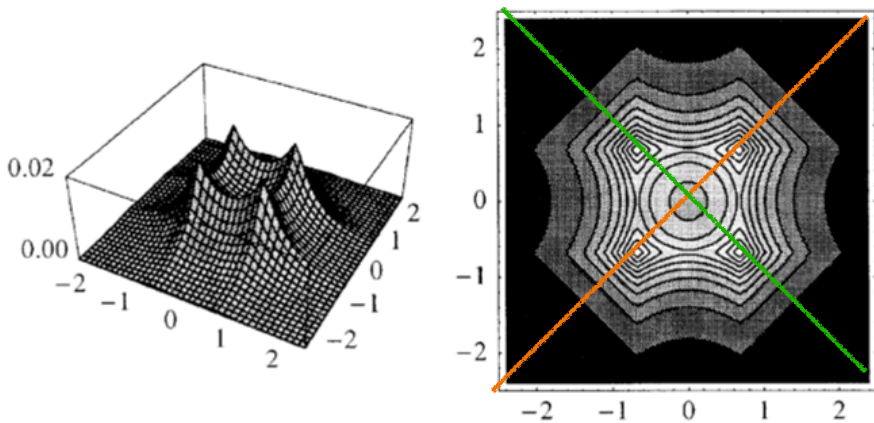The relative probabilities of locating one electron at different positions are independent of the whereabouts of the other electron, so provides **uncorrelated description.**

$z_1 = -z_2$ covalent character

$z_1 = z_2$ ionic character

Superposition of Configurations

Mixing the bonding and antibonding configurations:

$$\left| {}^{1}\Sigma_{g}^{+}(\tau) \right\rangle = \cos(\tau) \left| 1\sigma_{g}^{2} \right\rangle + \sin(\tau) \left| 1\sigma_{u}^{2} \right\rangle$$

An arbitrary normalized state, where τ is the variational parameter.

$$E_{\tau}(\Sigma_{g}^{+}) = \cos^{2}(\tau) E(g^{2}) + \sin^{2}(\tau) E(u^{2}) + \sin(2\tau) g_{2121}$$

Ground State W.F. $\left| {}^{1}\Sigma_{g}^{+}(\tau_{0}) \right\rangle_{e} = 0.9939 \left| 1\sigma_{g}^{2} \right\rangle - 0.1106 \left| 1\sigma_{u}^{2} \right\rangle$ $E_{\tau_{0}} = -1.1066$ Bonding Weight = 98.8%
Antibonding Weight = 1.2%

Exited State W.F. $\left| {}^{1}\Sigma_{g}^{+}(\tau_{1}) \right\rangle_{e} = 0.1106 \left| 1\sigma_{g}^{2} \right\rangle + 0.9939 \left| 1\sigma_{u}^{2} \right\rangle$ $E_{\tau_{1}} = 0.1688$

One and two-electron density functions

By mixing the bonding and antibonding configurations, we arrive at a more realistic description of the electronic system, where the motion of electrons is correlated.
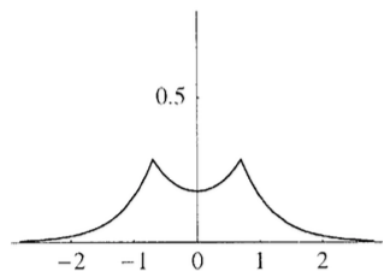
$z_1 = z_2$ ionic character

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$z_1 = -z_2$

$z_1 = z_2$
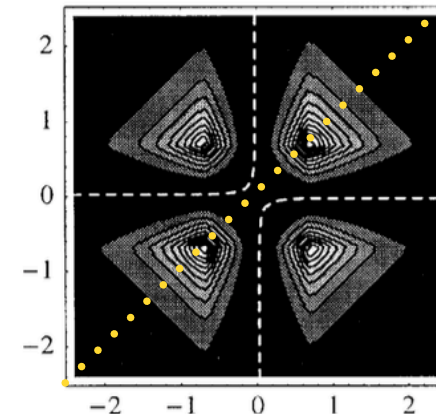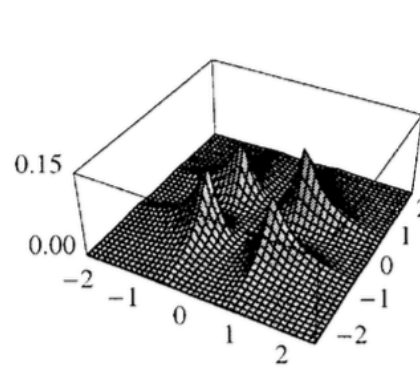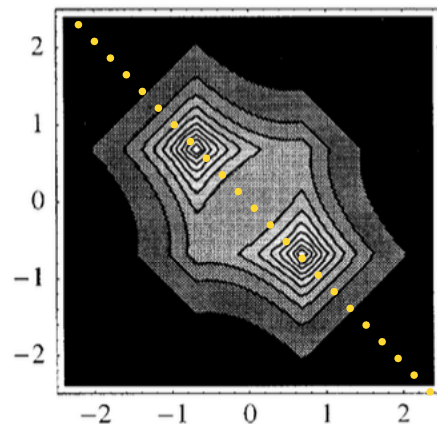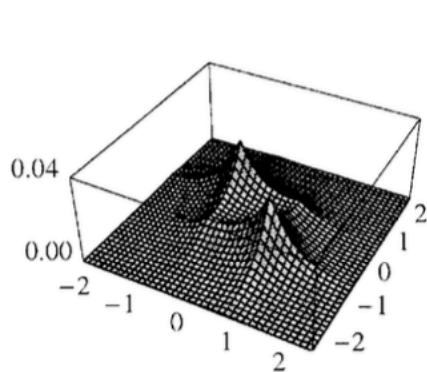
Covalent and Ionic States

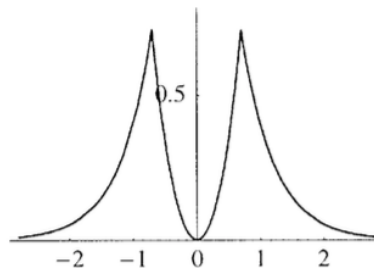$$\left|\text{cov}\right\rangle = \cos(\tau_{\text{cov}})\left|1\sigma_g^2\right\rangle + \sin(\tau_{\text{cov}})\left|1\sigma_u^2\right\rangle$$

$$\left|ion\right\rangle = \cos(\tau_{\text{cov}})\left|1\sigma_g^2\right\rangle - \sin(\tau_{\text{cov}})\left|1\sigma_u^2\right\rangle$$

$$\left|\text{cov}\right\rangle_e = 0.9902\left|1\sigma_g^2\right\rangle - 0.1396\left|1\sigma_u^2\right\rangle$$

$$\left|ion\right\rangle_e = 0.9902\left|1\sigma_g^2\right\rangle + 0.1396\left|1\sigma_u^2\right\rangle$$

At the equilibrium, the covalent and ionic states are both dominated by the bonding configuration.

Covalent
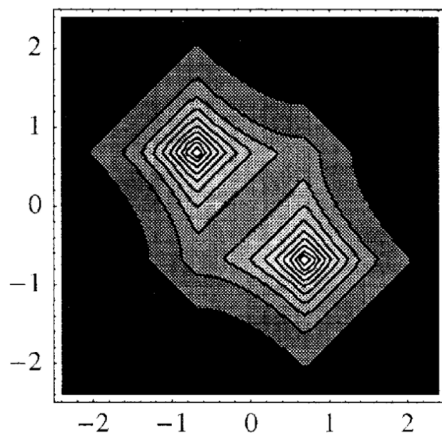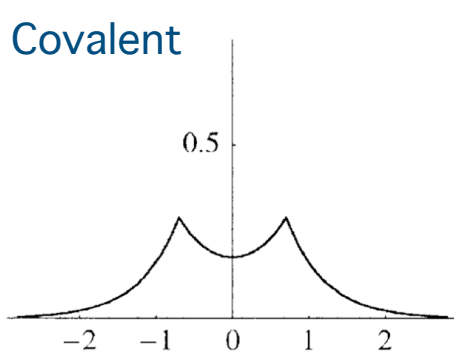
Ionic
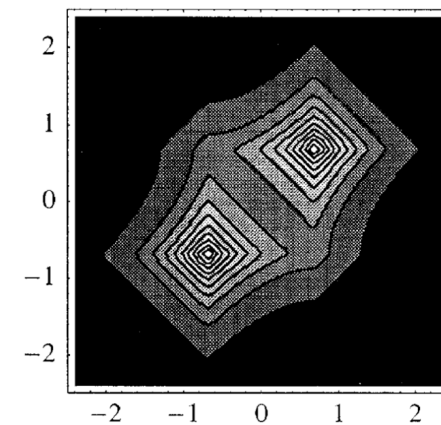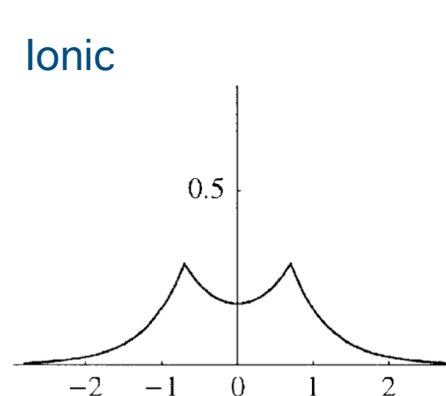
Electron Correlation

- In normal usage, the term correlation occurs upon superposition of configurations and the description provided by a single configuration is referred to as uncorrelated.

- The correlated behavior of the singlet and triplet states is instead described as an exchange effect since it arises from the Pauli principle's anti-symmetrization of the wave function.

- Generally, a truly uncorrelated many-particle state is always represented by a product of one-particle functions.

- Any superposition of such products represented a state where the motion of the particles is correlated.

Dissociation Limit
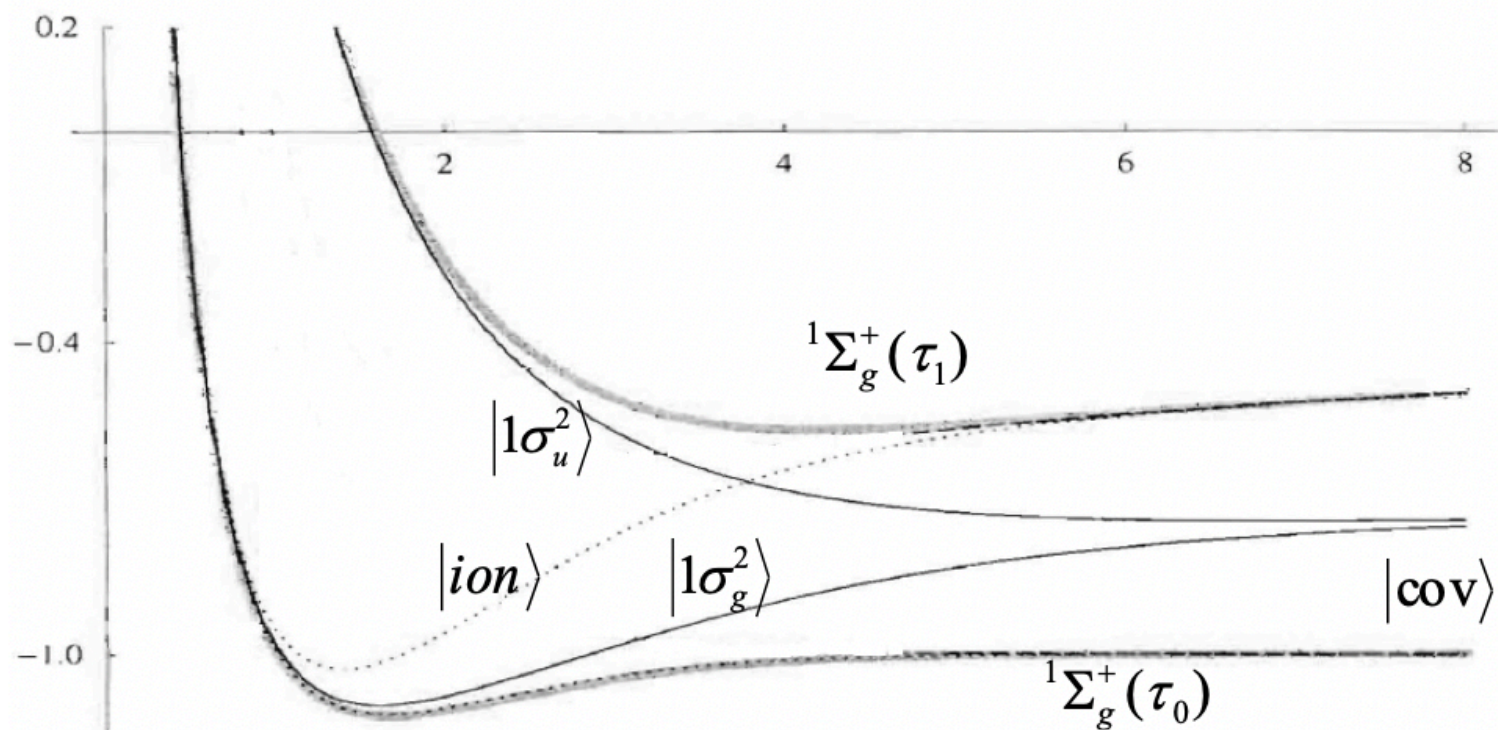
Electron Correlation

Our reasons for going beyond the single-configuration of wave function for hydrogen molecules:

In the equilibrium geometry: To describe the detailed correlated motion of the electrons as induced by their instantaneous mutual repulsion.

In the molecular dissociation limit: The reason is related to the degeneracy of the bonding and antibonding configurations and unrelated to the repulsion between the electrons.

In the intermediate region: Considering the two configurations serves the double purpose of accounting for the effects of Coulomb repulsion and near-degeneracy of the configurations.

The exact solution to the Schrödinger equation may be written as a linear combination of all determinates that can be constructed from this one-electron basis in the N-electron Fock space

$$|\text{FCI}\rangle = \sum_i C_i |i\rangle$$

The expansion coefficient may be obtained from the variation principle and the solution is called the **full configuration-interaction (FCI) wave function.**

The number of determinates in a FCI wave function

$$N_{\text{det}} = \binom{M}{N} = \frac{M!}{N!\,(M-N)!}$$

N number of electrons

M number of orbitals

The **factorial dependence** of the number of determinates makes **FCI intractable** for all but the smallest systems.

Static and Dynamical Correlation

In the design of configuration spaces smaller than that of FCI, it is important to distinguish between static and dynamical correlation.

Static Correlation is treated by considering the dominant configuration of the FCI expansion as well as those configurations that are nearly degenerate with the dominant configurations.

Dynamical Correlation is subsequently treated by adding to the wave function configurations generated by excitations, all single, double, and triple excitations, and so on.

The electronic energy and the occupation numbers of the most important natural orbitals **hydrogen molecule** at the **FCI/cc-pVQZ** level of theory and the weight of the HF determinant (W(HF)).

	R=1.4 a_0	R=4.0 a_0	R=15.0 a_0
E(FCI)	-1.173796 E_h	-1.015724 E_h	-0.999891 E_h
W(HF)	0.9820	0.7445	0.4751
$\eta(1\sigma_g)$	1.9643	1.5162	1.0000
$\eta(2\sigma_g)$	0.0061	0.0015	0.0000
$\eta(3\sigma_g)$	0.0003	0.0000	0.0000
$\eta(1\sigma_u)$	0.0199	0.4804	1.0000
$\eta(2\sigma_u)$	0.0002	0.0000	0.0000
$\eta(1\pi_u)$	0.0043	0.0000	0.0000
$\eta(1\pi_g)$	0.0001	0.0000	0.0000

At equilibrium single determinant with doubly occupied $1\sigma_g$ is enough.

Second most important orbital, with nodal plane, increases probability of locating electron around opposite nucleus "**left-right correlation**"

$1\pi_u$ has a nodal plane, increasing the probability of finding an electron on the opposite side of the molecular axis **angular correlation**.

$2\sigma_g$ with same irrep as $1\sigma_g$ but radial node, introduces **radial correlation** increasing the probability of locating electrons in different distances from molecular axis.

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At long distances as the interaction between electrons vanishes the importance of **dynamical correlation** decreases and the importance of **static correlation** increases, and orbital $1\sigma_g$ and $1\sigma_u$ becomes degenerate.

Static correlation is dominant.

Dynamical correlation is dominant.

	R=1.4 a_0	R=4.0 a_0	R=15.0 a_0
E(FCI)	-1.173796 E_h	-1.015724 E_h	-0.999891 E_h
W(HF)	0.9820	0.7445	0.4751
$\eta(1\sigma_g)$	1.9643	1.5162	1.0000
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$\eta(2\sigma_u)$	0.0002	0.0000	0.0000
$\eta(1\pi_u)$	0.0043	0.0000	0.0000
$\eta(1\pi_g)$	0.0001	0.0000	0.0000

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Configuration Interaction Theory

Configuration interaction (CI) is the most straightforward and general approach for the treatment of electron correlation in atoms and molecules.

In the early literature, one used the term "**superposition of configurations**" which as an acronym would be misleading nowadays.

The nodal properties of virtual orbitals can be exploited to improve the description of electron interactions.

For this purpose, excited configurations are generated by moving electrons from occupied to virtual orbitals.

$ns \rightarrow ks \quad k > n$ Radial correlation

$\sigma \rightarrow \pi^{*}$ Angular correlation

$\sigma \rightarrow \sigma^{*}$ Left-right correlation

The Early Days of Configuration Interaction Theory

The first CI calculation was carried out by **Hyllerass in** 1928 for the helium atom. He investigated the electron corrlation by exciting one or both electron to higher lying *ns* orbitals.
He was the ***father of the CI theory***.

In 1950**, S**. **F**. **Boys** published CI study on beryllium atom.
He concluded in his paper that CI is the only feasible method for calculating, analyzing, and predicting the electronic structure of atoms and molecules.

Boys and his students (among them Shavitt) pushed forward the algorithms and computational techniques to carry out CI.

In 1955**, Löwdin** introduced the natural spin orbitals, which helped to analyze and understand the wave function of a CI calculation.

A big step was made when **Boys** group programmed CI calculation for the **EDSAC** in 1956 ...

Configuration Interaction Theory

Wave Function: a linear combination of Slater-determinants

| HF | Singlet | Doublet | Triplet |
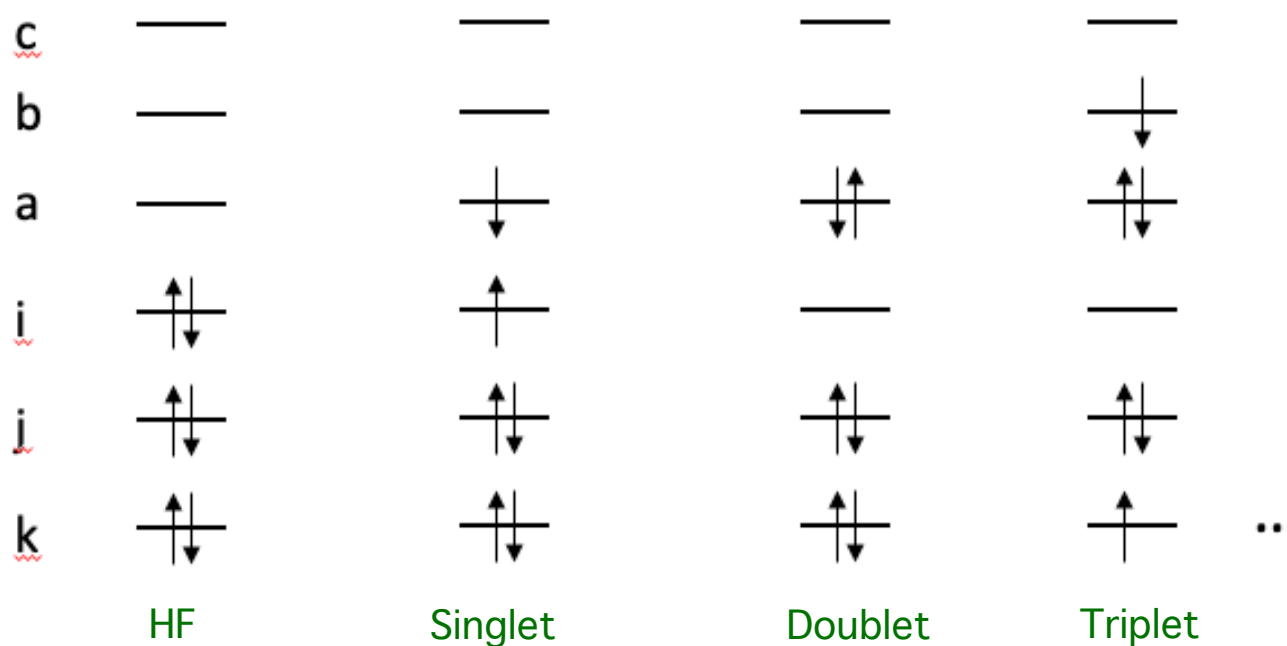
$$\Psi_{CI} = C_0\Psi_{HF} + \sum_{ia} C_i^a\Phi_i^a + \sum_{i>j,a>b} C_{ij}^{ab}\Phi_{ij}^{ab} + \sum_{i>j>k,a>b>c} C_{ijk}^{abc}\Phi_{ijk}^{abc} + \cdots$$

CI Model

In CI method, the electronic wave function is constructed as a linear combination of Slater determinants.

$$|\mathbf{C}\rangle = \sum_i C_i |i\rangle$$

C_i coefficients determined by **variational optimization**.

$$E_{CI} = \frac{\langle \mathbf{C} | \widehat{H} | \mathbf{C} \rangle}{\langle \mathbf{C} | \mathbf{C} \rangle} \qquad \frac{\partial}{\partial C_i} \frac{\langle \mathbf{C} | \widehat{H} | \mathbf{C} \rangle}{\langle \mathbf{C} | \mathbf{C} \rangle} = 0$$

$$\mathbf{HC} = E\mathbf{C}$$

This is Matrix eigenvalue equation. With element $\qquad H_{ij} = \langle i | \widehat{H} | j \rangle$

CI recipe:

1. Select the expansion space $\{|i\rangle\}$

2. Construction of the CI matrix elements $\langle \mathbf{c} | \widehat{H} | \mathbf{c} \rangle$

3. Diagonalization of the Hamiltonian or Fock matrix.

Full CI Wave Functions

Full CI (FCI) wave function generated by distributing **all electrons among all orbitals**.
In this expansion the number of Slater determinants increase very rapidly with the number of electrons and number of orbitals.

$$N_{\text{det}} = \binom{n}{N^{\alpha}}\binom{n}{N^{\beta}} = \binom{n}{N}^2$$

n number of orbital
N^{α} number of α electron
N^{β} number of β electron

2N	Ndet
2	4
4	36
6	400
8	4 900
10	63 504
12	853 776
20	34 134 779 536

CI Expansion Space

Type		Number of functions
Single–	Φ_i^a	$n_{occ} \times n_{vrt}$
Double–	Φ_{ij}^{ab}	$\begin{pmatrix} n_{occ} \\ 2 \end{pmatrix} \times \begin{pmatrix} n_{vrt} \\ 2 \end{pmatrix}$
Triple–	Φ_{ijk}^{abc}	$\begin{pmatrix} n_{occ} \\ 3 \end{pmatrix} \times \begin{pmatrix} n_{vrt} \\ 3 \end{pmatrix}$
n–tuple	FCl	

$$N_{det} = \begin{pmatrix} n \\ N^{\alpha} \end{pmatrix} \begin{pmatrix} n \\ N^{\beta} \end{pmatrix} = \begin{pmatrix} n \\ N \end{pmatrix}^2$$

Truncation is necessary

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CI Expansion Space

$$\Psi_{CI} = C_{HF}|\Psi_{HF}\rangle + C_S|S\rangle + C_D|D\rangle + C_T|T\rangle + \cdots$$

1. No coupling between the HF ground state and single excitations "**Brillouin's theorem**".

$$\left\langle \Psi_{HF} \left| \widehat{H} \right| S \right\rangle = 0$$

$$\left\langle \Psi_{HF} \left| \widehat{H} \right| \Phi_i^a \right\rangle = \left\langle i \left| \hat{h} \right| a \right\rangle + \sum_j \left(\langle ij|aj\rangle - \langle ij|ja\rangle \right) = \left\langle i \left| \hat{f} \right| a \right\rangle$$

$$\left\langle i \left| \hat{f} \right| a \right\rangle = \varepsilon_a \langle i|a\rangle = 0$$
If spin-orbitals are generated with HF method then the Brillouin theorem applied as spin-orbitals orthogonal.

Single excitations do not mix directly with HF ground state, they can be expected to have a very small effect on the ground state energy. Their effect is not zero because they do mix indirectly through doubles.

CI Expansion Space

2. There is no coupling between HF ground state and triples and higher. All matrix elements of the Hamiltonian which differ by more than 2 spin orbitals are zero.

$$
\begin{bmatrix}
\left\langle \Psi_{HF} \left| H \right| \Psi_{HF} \right\rangle & 0 & \left\langle \Psi_{HF} \left| H \right| D \right\rangle & 0 & \cdots \\
 & \left\langle S \left| H \right| S \right\rangle & \left\langle S \left| H \right| D \right\rangle & \left\langle S \left| H \right| T \right\rangle & \cdots \\
 & & \left\langle D \left| H \right| D \right\rangle & \left\langle D \left| H \right| T \right\rangle & \cdots \\
 & & & \left\langle T \left| H \right| T \right\rangle & \cdots
\end{bmatrix}
$$

It would be good to terminate it in such a way that all essential terms are retained.

The approximate order of importance is: $|D\rangle >> |S\rangle > |Q\rangle > |T\rangle$

Table 4.2 Weights of excited configurations for the Neon atom

Excitation level	Weight		Relative importance
0	0.9644945073	Ref.	
1	0.0009804929	Singles	2
2	0.0336865893	Doubles	1
3	0.0003662339	Triples	4
4	0.0004517826	Quadruples	3
5	0.0000185090		
6	0.0000017447		
7	0.0000001393		
8	0.0000000011		

$$weight = \sum_{ijk\cdots}^{abc\cdots} \left(C_{ijk\cdots}^{abc\cdots} \right)^2$$

CI Expansion Space: Truncated CI Wave Functions

$$\Psi_{CI} = C_0 \Psi_{HF} + \sum_{ia} C_i^a \Phi_i^a + \sum_{i>j,a>b} C_{ij}^{ab} \Phi_{ij}^{ab} + \sum_{i>j>k,a>b>c} C_{ijk}^{abc} \Phi_{ijk}^{abc} + \cdots$$

$$\widehat{H} \, | \Psi_{CI} \rangle = E \, | \Psi_{CI} \rangle$$

$$(\widehat{H} - E_{HF}) \, | \Psi_{CI} \rangle = (E - E_{HF}) \, | \Psi_{CI} \rangle = E_{corr} \, | \Psi_{CI} \rangle$$

Then multiply by

$$\langle \Phi_{HF} | \, , \langle \Phi_i^a | \, , \langle \Phi_{ij}^{ab} | \, , etc$$

$$\left\langle \Phi_{HF} \left| \hat{H} - E_0 \right| \Psi_{CI} \right\rangle = E_{corr} \left\langle \Phi_{HF} | \Psi_{CI} \right\rangle = E_{corr} \qquad \left\langle \Phi_{HF} | \Psi_{CI} \right\rangle = 1$$

Intermediate normalized

$$\left\langle \Phi_{HF} \left| \hat{H} \right| \Psi_{CI} \right\rangle = \left\langle \Phi_{HF} \left| \hat{H} \right(\left| \Phi_{HF} \right\rangle + \sum_{ia} c_i^a \left| \Phi_i^a \right\rangle + \sum_{i>j\,a>b} c_{ij}^{ab} \left| \Phi_{ij}^{ab} \right\rangle + \sum_{i>j>k\,a>b>c} c_{ijk}^{abc} \left| \Phi_{ijk}^{abc} \right\rangle + \cdots \right)$$

$$E = \underbrace{\left\langle \Phi_{HF} \left| \hat{H} \right| \Phi_{HF} \right\rangle}_{E_{HF}} + \sum_{ia} c_i^a \underbrace{\left\langle \Phi_{HF} \left| \hat{H} \right| \Phi_i^a \right\rangle}_{0} + \sum_{i>j\,a>b} c_{ij}^{ab} \left\langle \Phi_{HF} \left| \hat{H} \right| \Phi_{ij}^{ab} \right\rangle$$

$$+ \underbrace{\sum_{i>j>k\,a>b>c} c_{ijk}^{abc} \left\langle \Phi_{HF} \left| \hat{H} \right| \Phi_{ijk}^{abc} \right\rangle}_{0} + \cdots$$

$$E_{corr} = E - E_{HF} = \sum_{i>j,a>b} c_{ij}^{ab} \left\langle \Phi_{HF} \left| \hat{H} \right| \Phi_{ij}^{ab} \right\rangle$$

$$E_{corr} = \sum_{i>j,a>b} c_{ij}^{ab} \left\langle \Phi_{HF} \left| \widehat{H} \right| \Phi_{ij}^{ab} \right\rangle$$

Correlation energy is determined solely by the coefficients of the
double excitations !!!

Is it enough to include only double excitations in the wave function???

NO! c_{ij}^{ab} depends on the other coefficients through the CI equations!

BUT: if c_{ij}^{ab} small, this dependence can be neglected.

CID (CI with double excitations) is a good approximation.

Requirement: Φ_{HF} is a good starting wave function, i.e. $c_0 \sim 1.0$

CI Expansion Space: Truncated CI Wave Functions

$$\times \langle \Phi_i^b | \, \hat{H} | \Psi_{CI} \rangle = E | \Psi_{CI} \rangle$$

$$E \langle \Phi_i^b | \Psi_{CI} \rangle = \langle \Phi_i^b | \hat{H} | \Psi_{CI} \rangle$$

$$E \, c_i^b = \langle \Phi_i^b | \hat{H} | \Phi_{HF} \rangle + \sum_{ia} c_i^a \langle \Phi_i^b | \hat{H} | \Phi_i^a \rangle + \sum_{\substack{i>j \\ a>b}} c_{ij}^{ab} \langle \Phi_i^b | \hat{H} | \Phi_{ij}^{ab} \rangle + \sum_{\substack{i>j>k \\ a>b>c}} c_{ijk}^{abc} \langle \Phi_i^b | \hat{H} | \Phi_{ijk}^{abc} \rangle$$

$$E \, c_i^b = \sum_{ia} c_i^a \langle \Phi_i^b | \hat{H} | \Phi_i^a \rangle + \sum_{\substack{i>j \\ a>b}} c_{ij}^{ab} \langle \Phi_i^b | \hat{H} | \Phi_{ij}^{ab} \rangle + \sum_{\substack{i>j>k \\ a>b>c}} c_{ijk}^{abc} \langle \Phi_i^b | \hat{H} | \Phi_{ijk}^{abc} \rangle$$

$$\times \langle \Phi_{ij}^{cd} | \, \hat{H} | \Psi_{CI} \rangle = E | \Psi_{CI} \rangle \qquad \times \langle \Phi_{ijk}^{cde} | \, \hat{H} | \Psi_{CI} \rangle = E | \Psi_{CI} \rangle$$

The double excitation coefficients affected by the presence of other excitations. We would end of with a **hierarchy of equations** that must be solved simultaneously to obtain the correlation energy.

CI with single and double substitutions (CISD)

In practice: CISD - only single and double excitations

$$\Phi_{CISD} = C_0\Psi_{HF} + \sum_{ia} C_i^a\Phi_i^a + \sum_{i>j,a>b} C_{ij}^{ab}\Phi_{ij}^{ab}$$

We consider the singles also, because:
- Not expensive – much less than double excitations
- One electron properties such as dipole moment
- They will interact (i.e. have non-vanishing matrix elements) with the doubly-excited configurations.

This approximation is valid if: $c_0 \sim 1.0$,
i.e. the wave function is dominated by the reference (HF) determinant

Truncated CI Wave Functions

$c_0 \sim 1.0$ **is usually satisfied:**

   -At ground electronic states

    -At equilibrium geometry

Very often this is not satisfied:

  – Dissociation limit; potential energy surface

  – Low-lying virtual orbital; transition metal

  – Excited states

If $c_0 \sim 1.0$ **is not satisfied what can we do?**

- Include triple, quadruple, etc excitations – too expensive

- Use multi-reference wave function

- Use Coupled-Cluster theory

Water dissociation energy
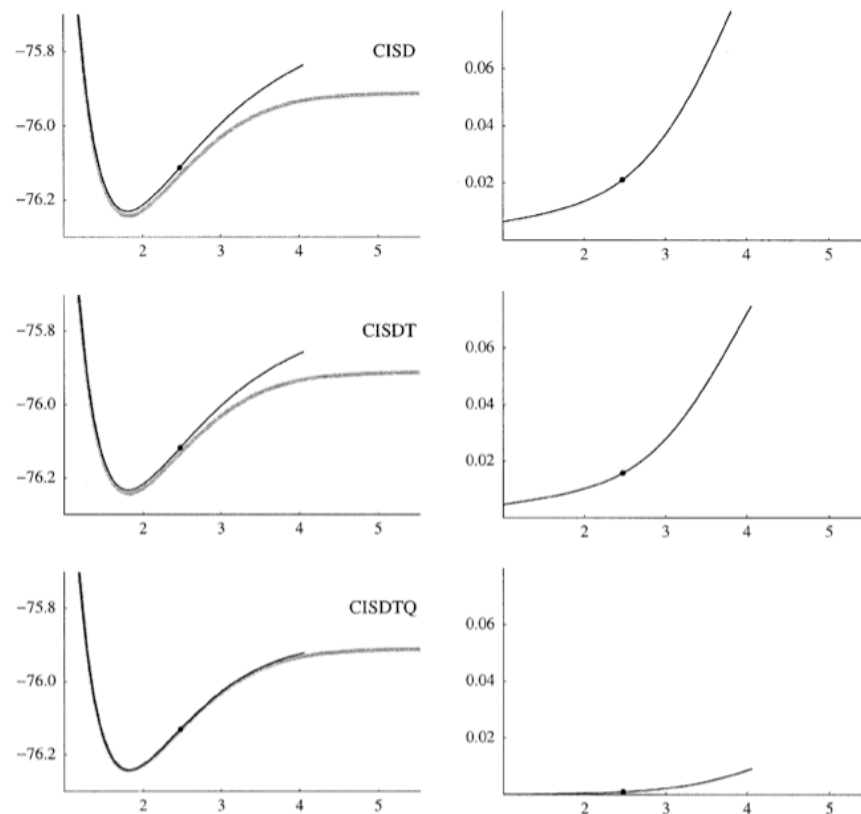
CI dissociation curves of water at fixed bond angle **(left pan**
Difference between CI and FCI energies **(right panel)**

Truncated CI Calculation for Dissociation of H2O

	$R=R_{ref}$		$R=2R_{ref}$	
	$E-E_{FCI}$	W^a	$E-E_{FCI}$	W
RHF	0.217822	0.941050	0.363954	0.589664
CISD	0.012024	0.998047	0.072015	0.948757
CISDT	0.009043	0.998548	0.056094	0.959086
CISDTQ	0.000327	0.999964	0.005817	0.998756
CISDTQ5	0.000139	0.999985	0.002234	0.999553
CISDTQ56	0.000003	1.000000	0.000074	0.999993

[a] the weights of the CI wave functions in the FCI wave function.

Main problem with CI

Energy does not scale properly with the size of the system:

-not size-consistent

-not size-extensive

Consider two subsystems at **infinite separation**. We have two choices:

- treat the two systems separately

- consider only a super-system

Provided that there is no interaction between the two systems, the two treatments should give the **same result**.

Size-consistency

CID wave function is used to describe two non-interacting system!

For the supersystem we have:

$$\Psi_{AB}^{CID} = \Phi_{AB}^{HF} + \Phi_{AB}^{D}$$

Φ_{AB}^{D} is the sum of all double excitations out of Φ_{AB}^{HF} (including coefficients).

For the subsystems, we can write:

$$\Psi_{B}^{CID} = \Phi_{B}^{HF} + \Phi_{B}^{D} \qquad \Psi_{A}^{CID} = \Phi_{A}^{HF} + \Phi_{A}^{D}$$

The product of these two wave functions gives the other choice for the wave function of the super-system:

$$\Psi_{AB}^{CID} = \Psi_{A}^{CID}\,\Psi_{B}^{CID}$$

$$= \Phi_{A}^{HF}\,\Phi_{B}^{HF} + \Phi_{A}^{HF}\,\Phi_{B}^{D} + \Phi_{A}^{D}\,\Phi_{B}^{HF} + \Phi_{A}^{D}\,\Phi_{B}^{D}$$

$$= \Phi_{AB}^{HF} + \Phi_{AB}^{D} + \Phi_{A}^{D}\,\Phi_{B}^{D}$$

Size-consistency

This simple model enables us to identify the origin of the size-consistency error.

The difference of the two super-system wave functions:

$$\Psi_A^{CID} \, \Psi_B^{CID} - \Psi_{AB}^{CID} = \Phi_A^D \, \Phi_B^D$$

i.e. simultaneous double excitations on the subsystems are missing from the CI wave function.

This error is present also if there is an interaction between A and B, but we cannot quantify it by two calculations
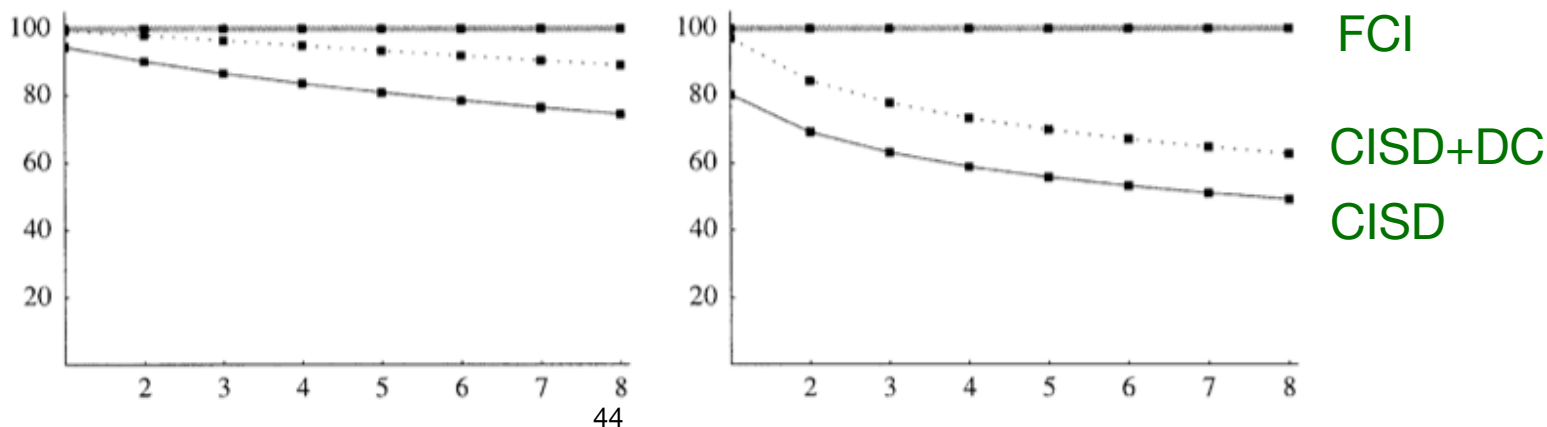
$$\Downarrow$$

Lack of Size-extensivity

Size-consistency Correction

Davidson corrections:
$$E_{DC} = (1 - c_0^2)\Delta E$$

$$\Delta E = E_{corr}(CID) = \sum_{k>l,c>d} c_{kl}^{cd} \langle \Phi_0 | H - E_0 | \Phi_{kl}^{cd} \rangle \qquad c_0^2 = 1 - \sum_{k>l,c>d} (c_{kl}^{cd})^2$$

Correlation energy per water monomer a function of non-interacting water molecules.

FCI

CISD+DC

CISD

Bottlenecks of CI Calculation

Prerequisite for any CI methods is the efficient calculation of:

$$H_{ij} = \left\langle \Phi_i \left| \widehat{H} \right| \Phi_j \right\rangle$$

1. Two-electron integrals

2. Diagonalization of large matrix H.

3. Slow convergence toward FCI limit.