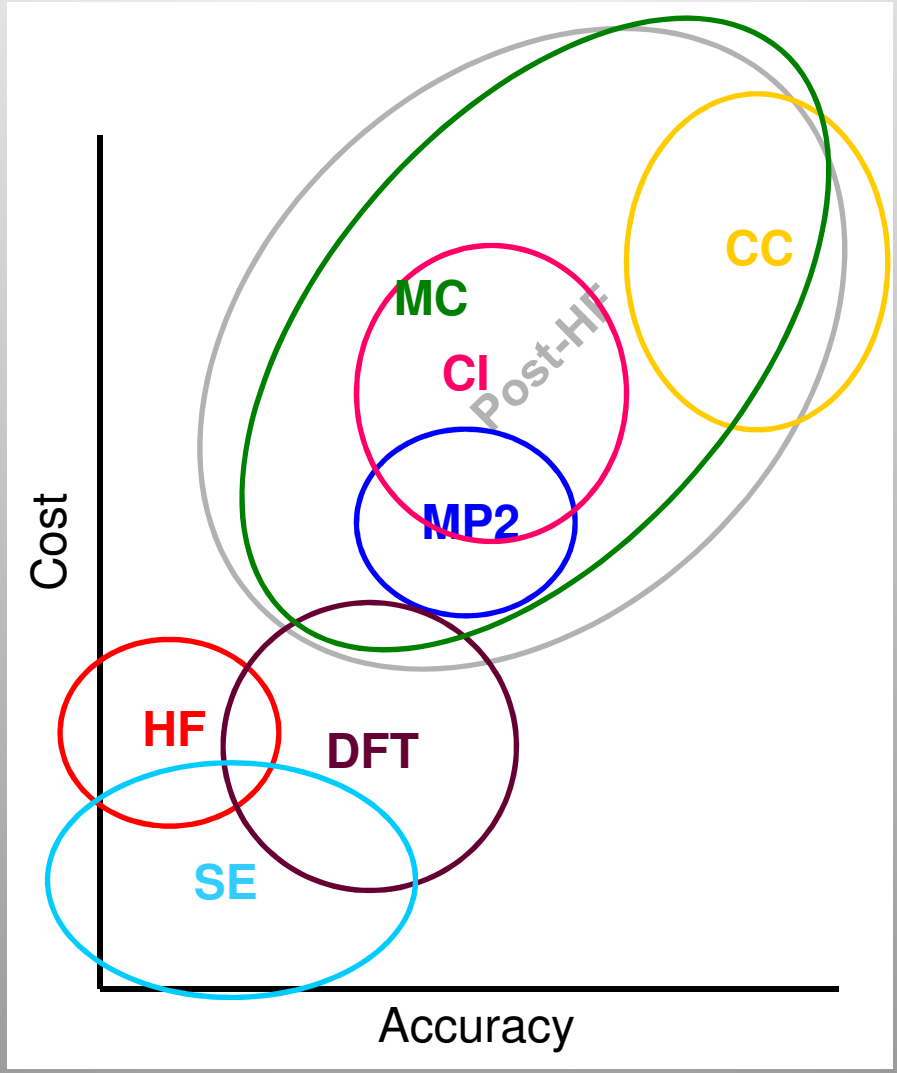
Electron Correlation in Wavefunction Based Methods

Benjamin G. Levine

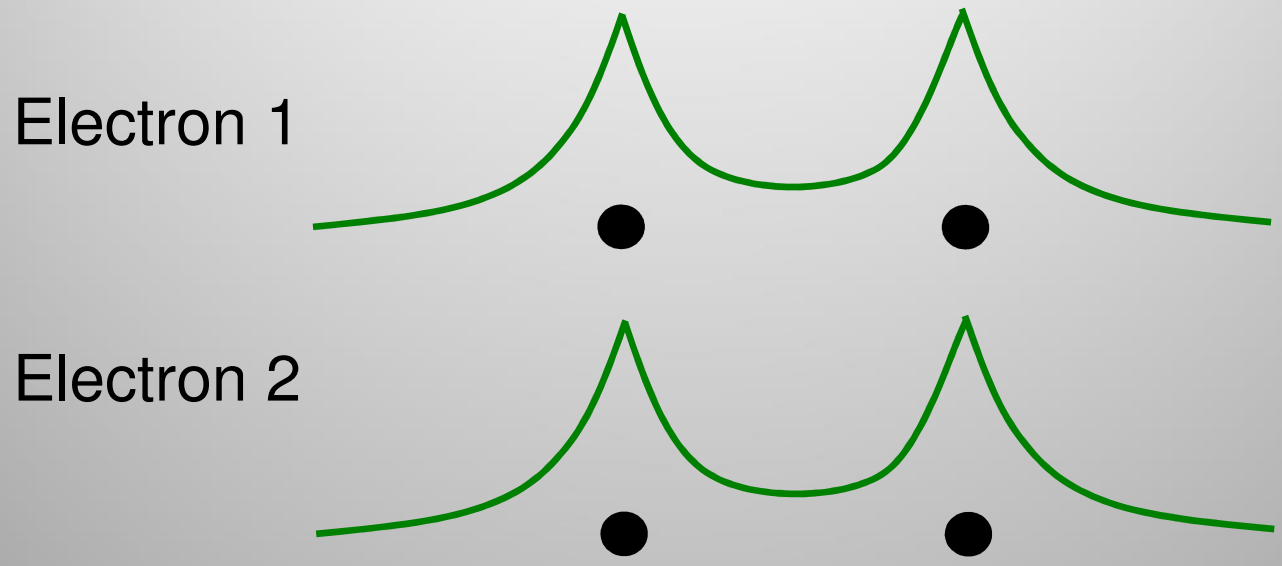
How do we improve Hartree-Fock?



What is electron correlation?

- The wavefunction describes the probability distribution of the location of the electron
- Electron correlation is best described in conditional statements: “If electron 1 is here then electron 2 is there”
- In Hartree-Fock electrons of the same spin are correlated (exchange), but electrons of different spins are not

Correlation Example 1: Dissociation Catastrophe



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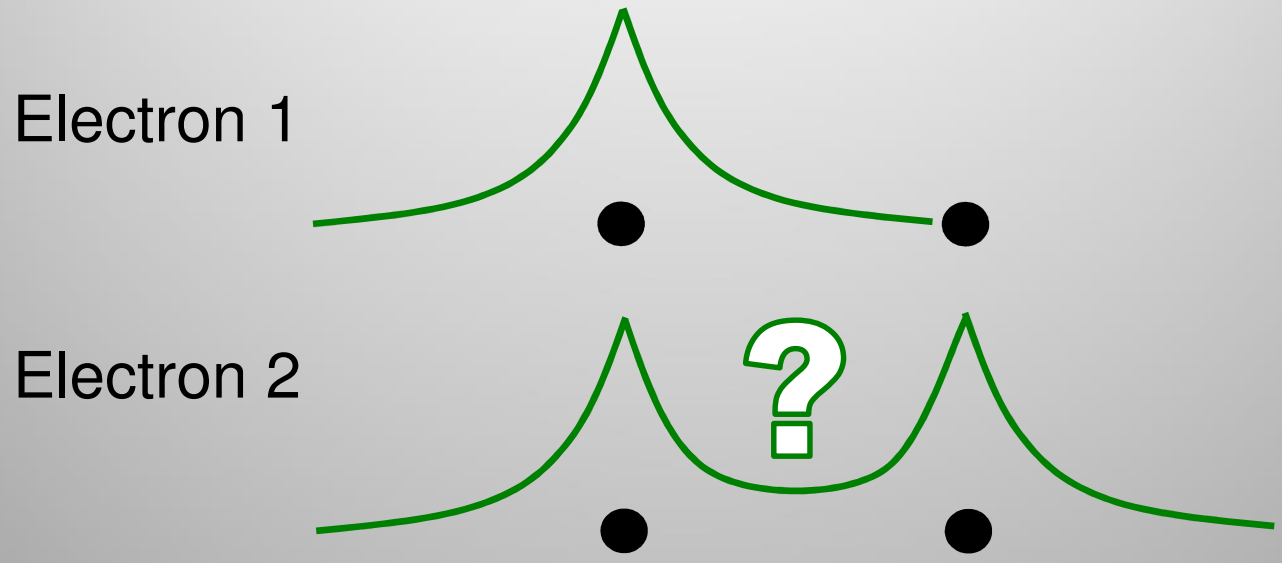

“If electron 1 is on the left…”

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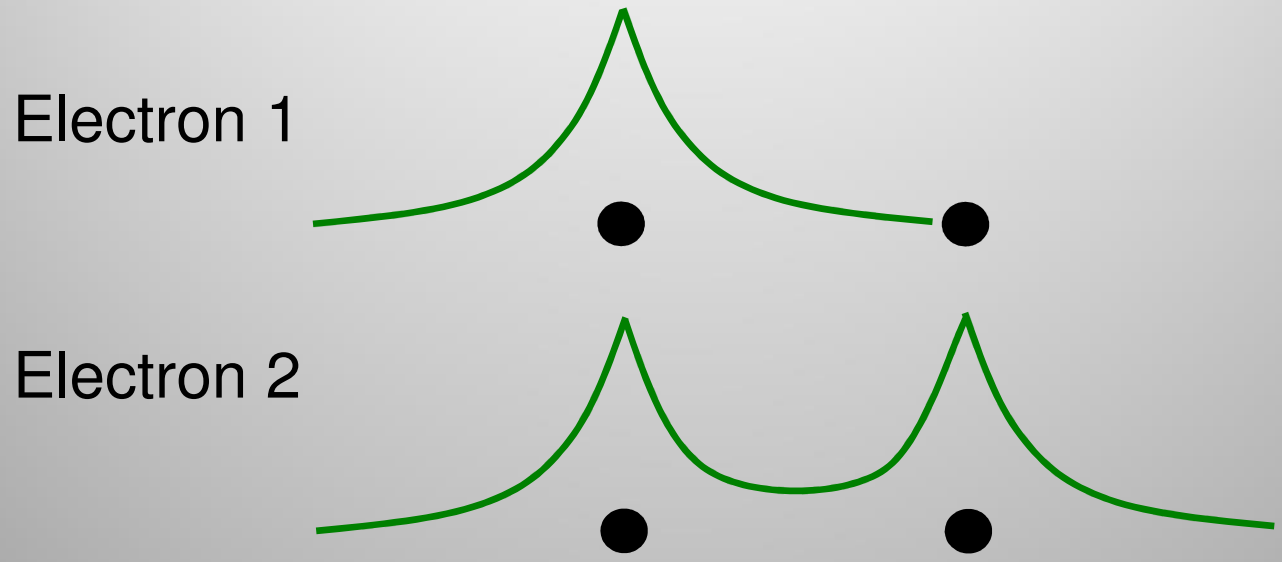

“If electron 1 is on the left…”

HF – “then electron 2 is still in the bonding orbital”

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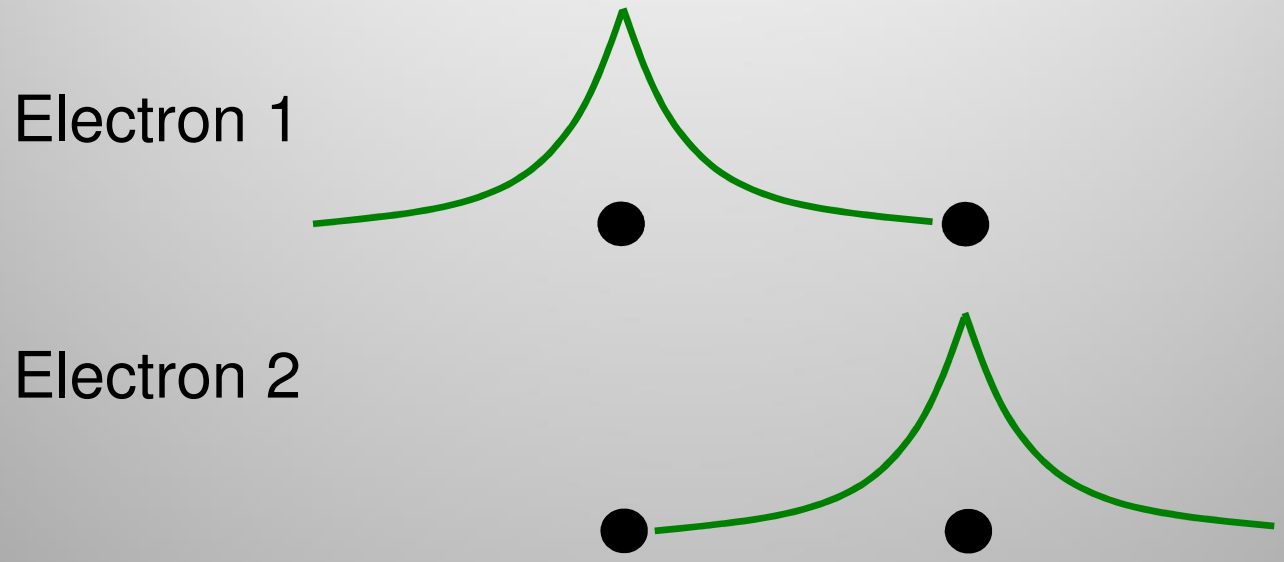


“If electron 1 is on the left…”

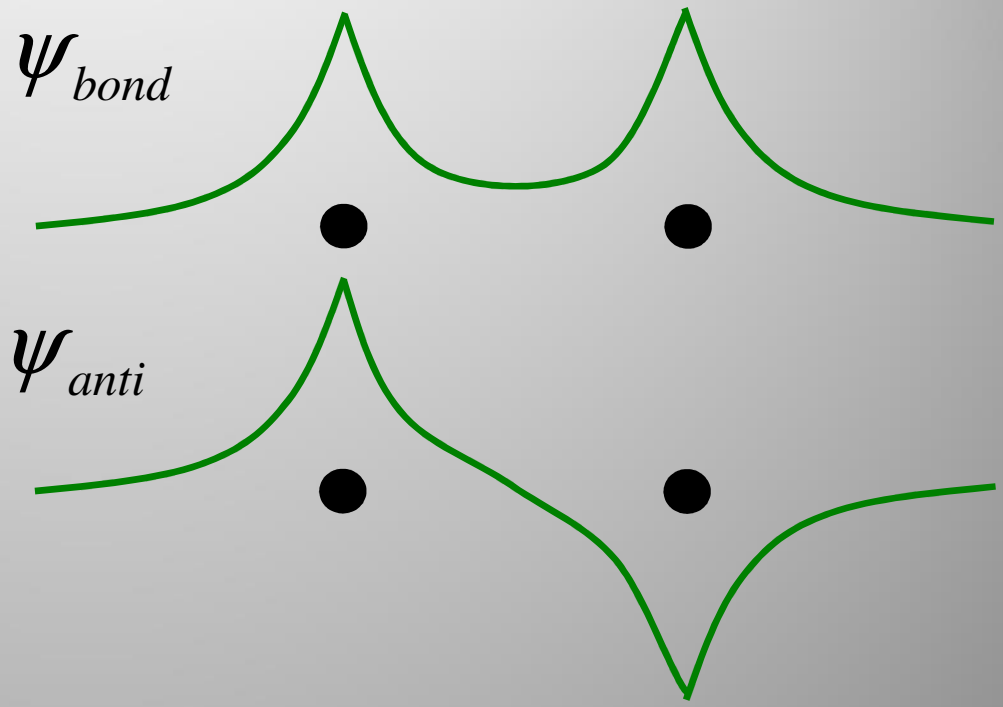
HF – “then electron 2 is still in the bonding orbital”

Post-HF – “then electron 2 is on the right”

Correlation Example 1: Dissociation Catastrophe

$$\frac{1}{\sqrt{2}}\left|\psi^{\alpha}_{bond}\psi^{\beta}_{bond}\right\rangle-\frac{1}{\sqrt{2}}\left|\psi^{\alpha}_{anti}\psi^{\beta}_{anti}\right\rangle=$$

$$\frac{1}{\sqrt{2}}\left|\varphi^{\alpha}_{left}\varphi^{\beta}_{right}\right\rangle+\frac{1}{\sqrt{2}}\left|\varphi^{\alpha}_{right}\varphi^{\beta}_{left}\right\rangle$$



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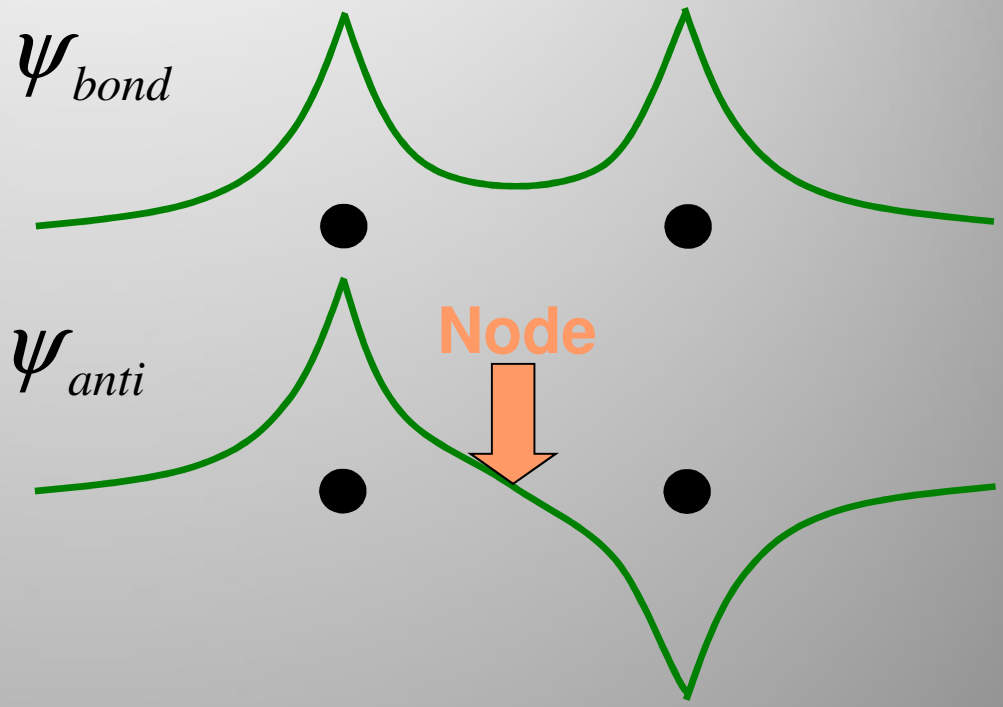

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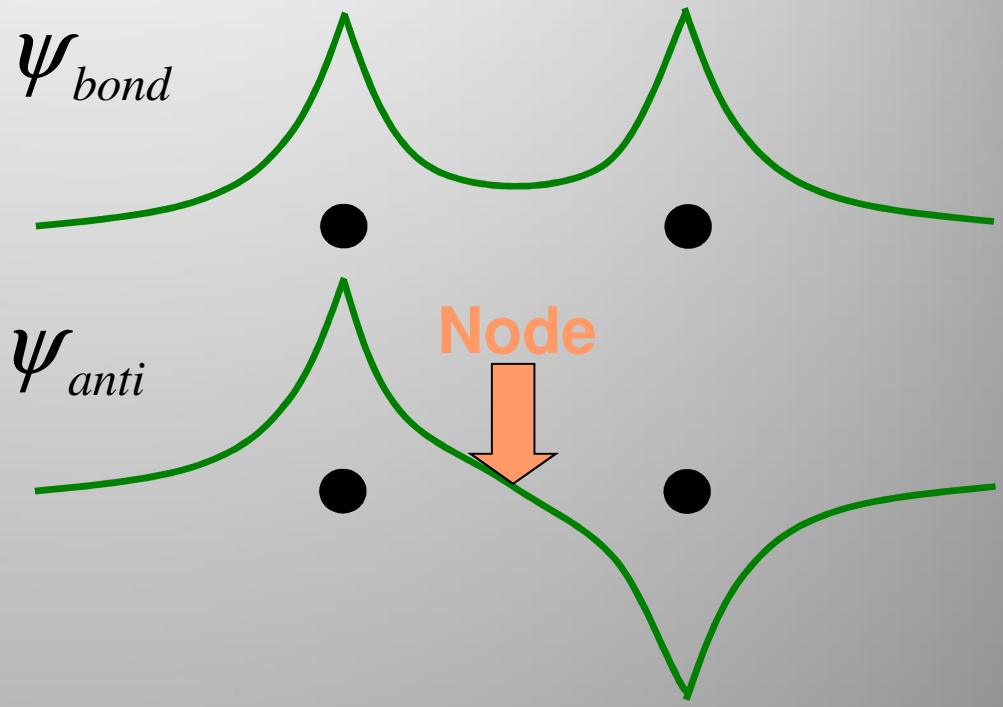

Subtracting a doubly excited configuration is like saying "**if electron 1 is on one side of the node, electron 2 is more likely on the other side**"

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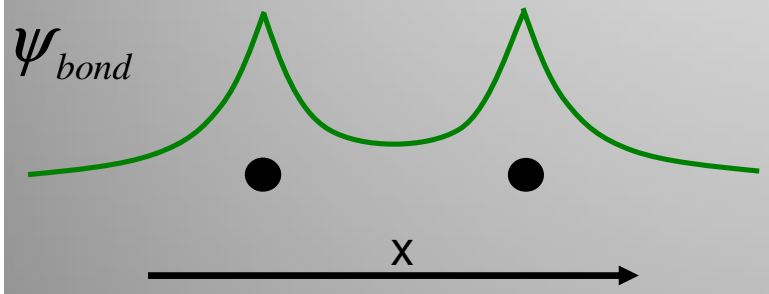

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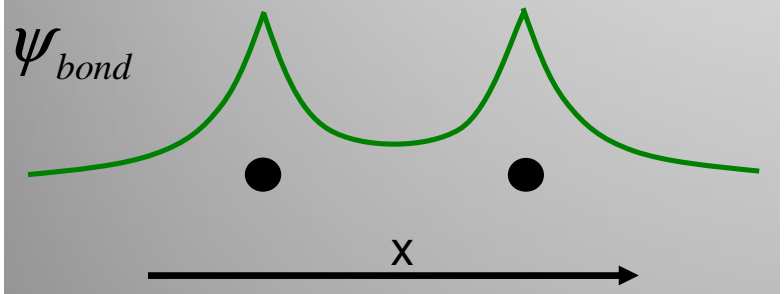

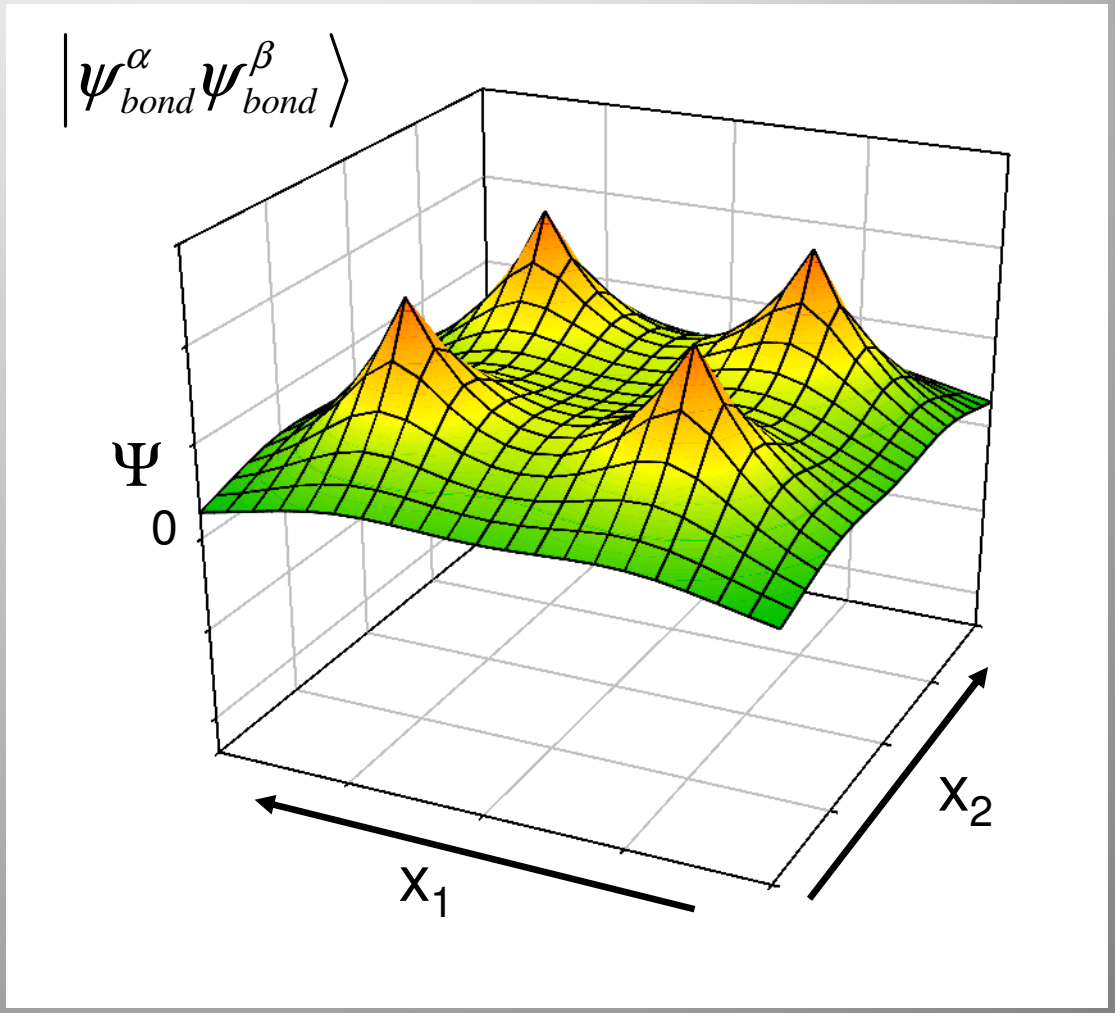

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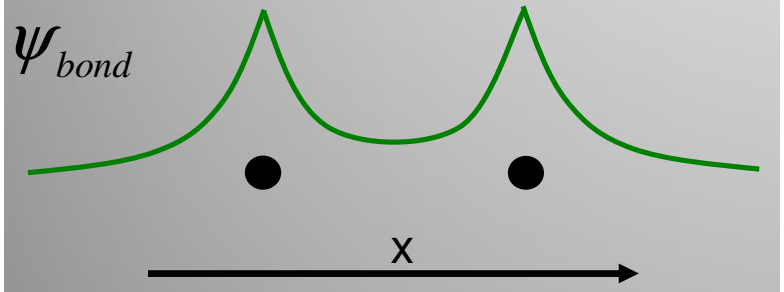

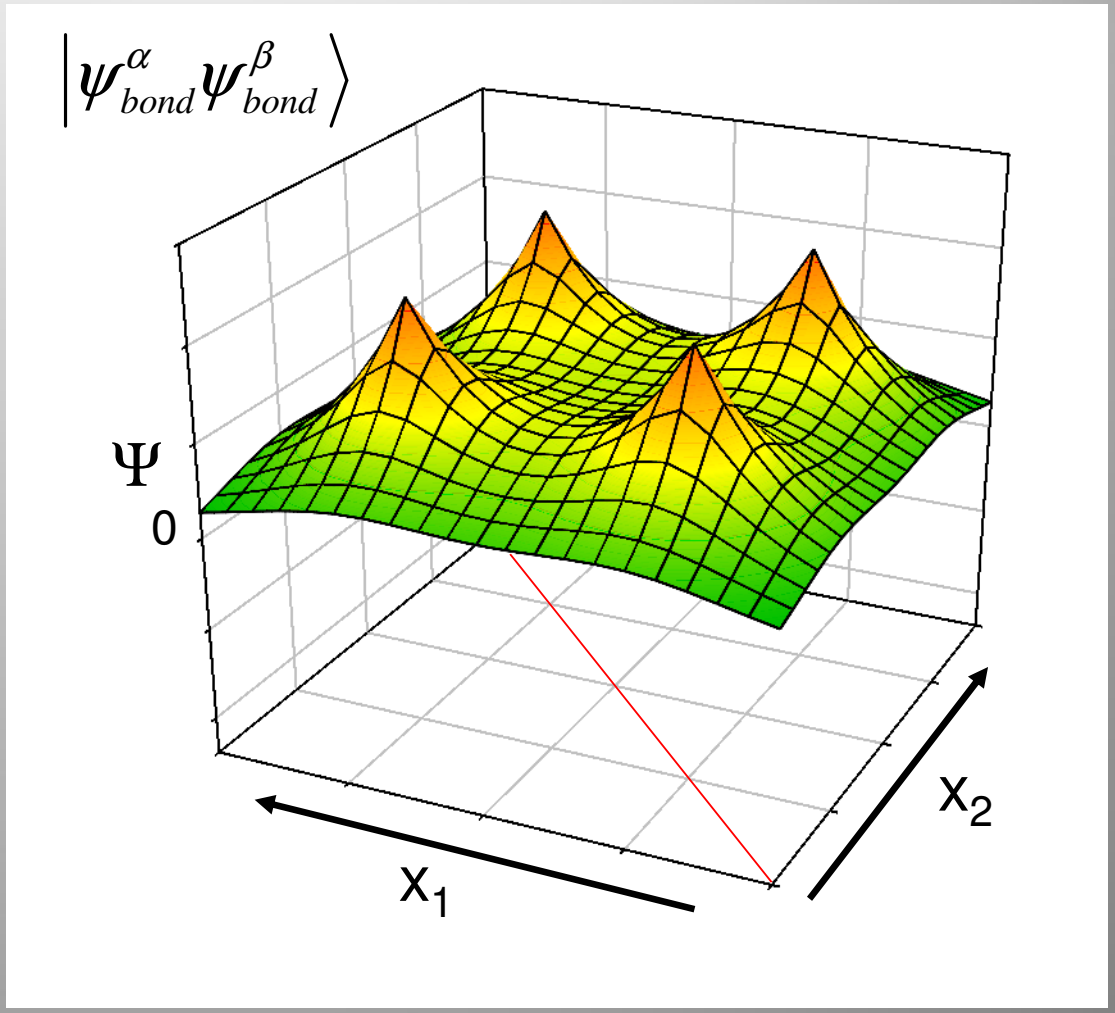

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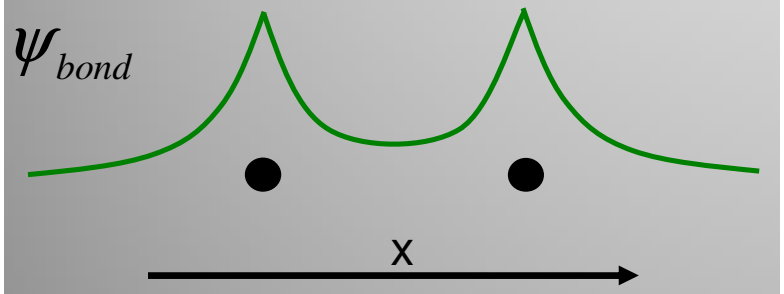

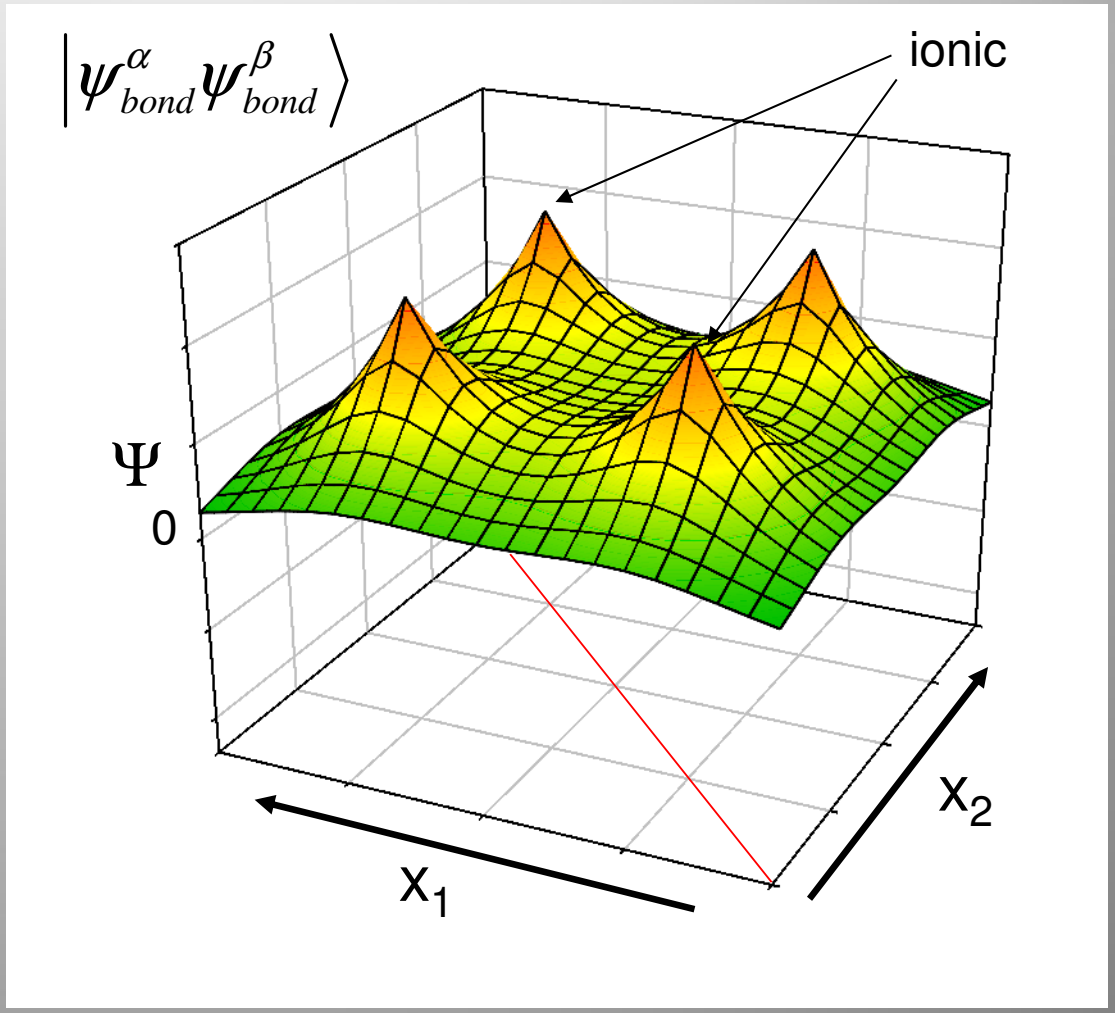

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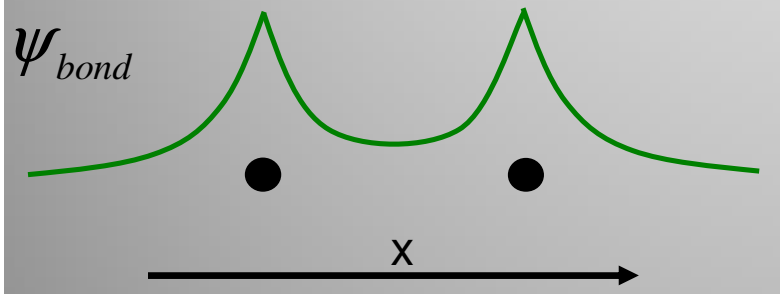

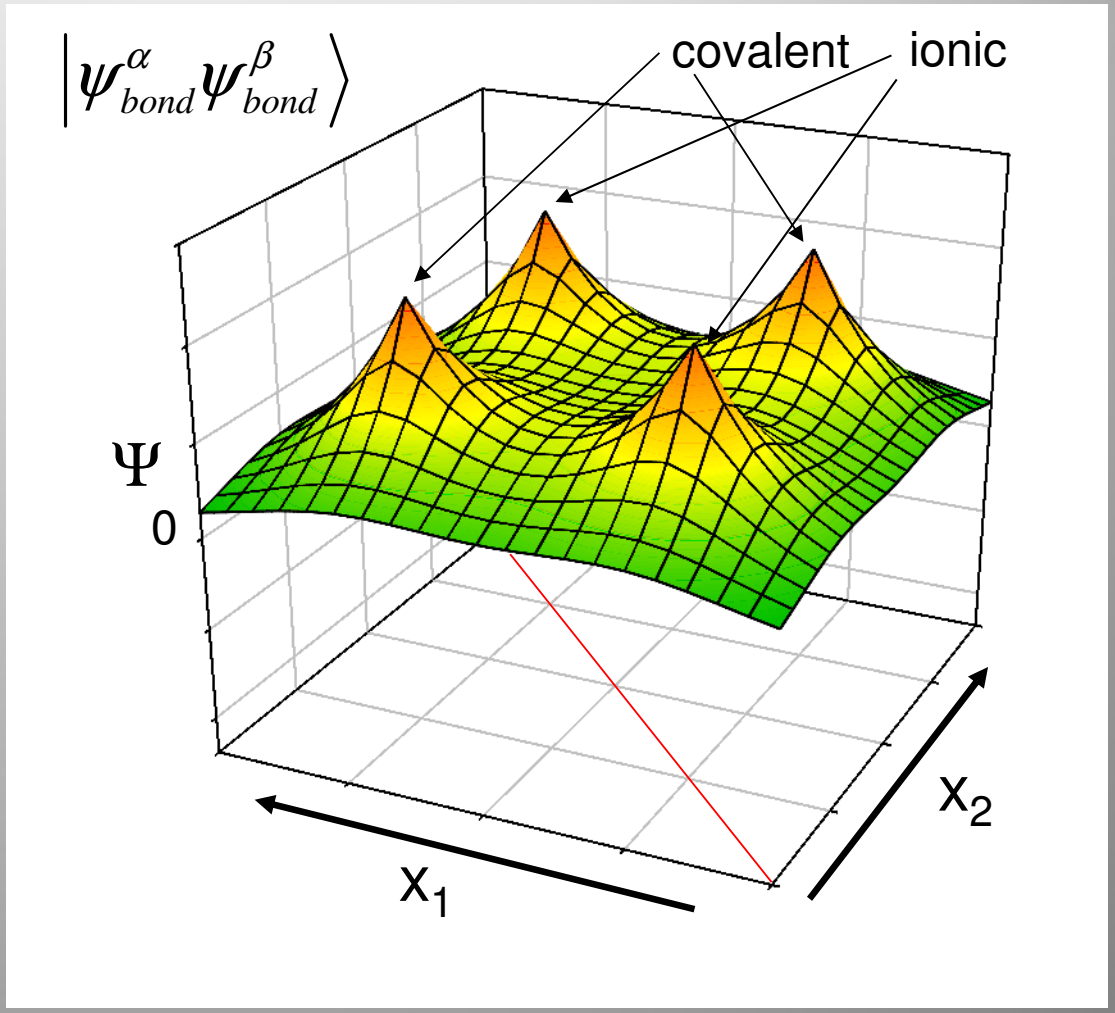

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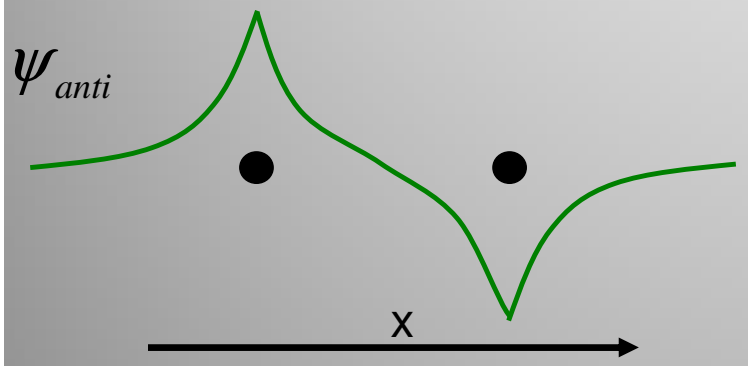

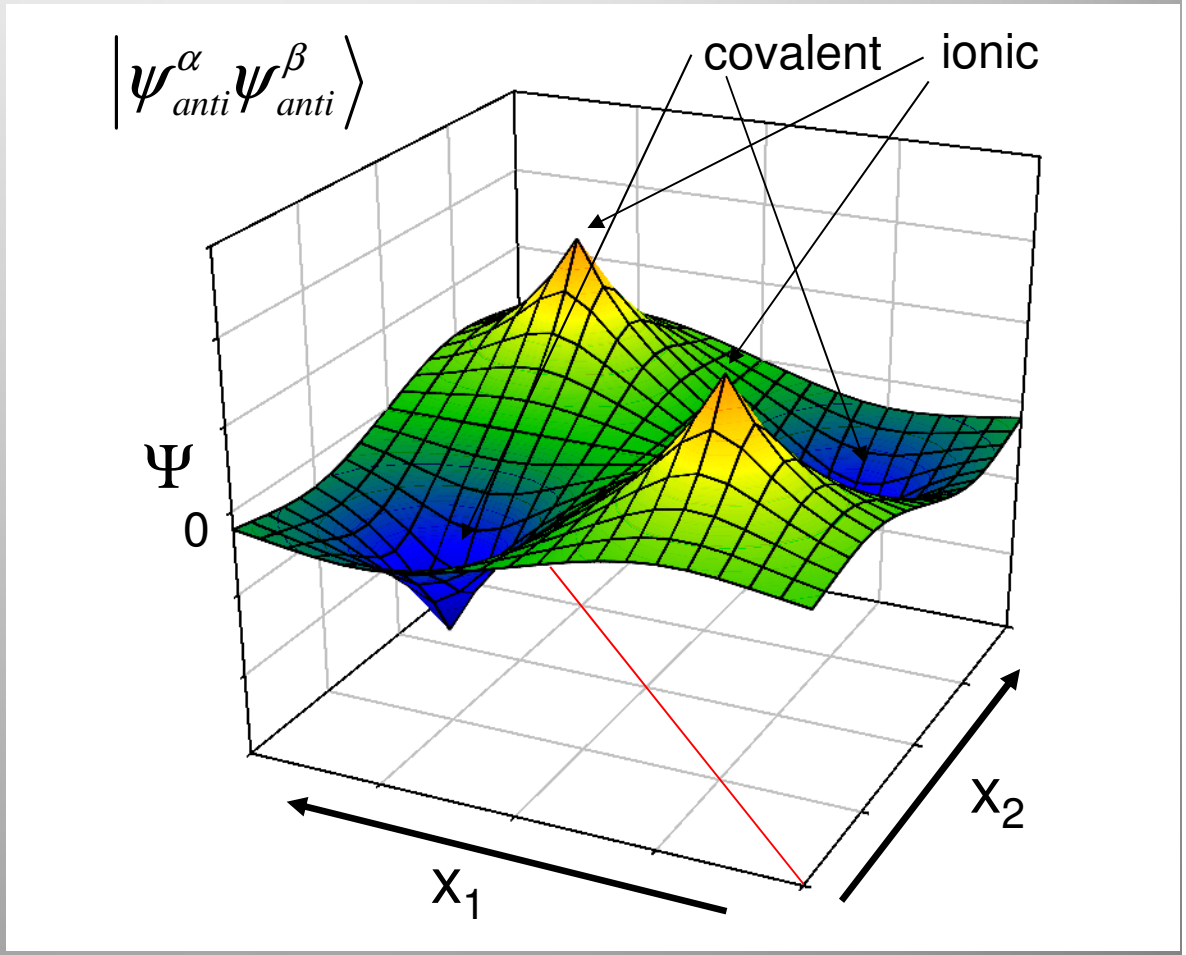

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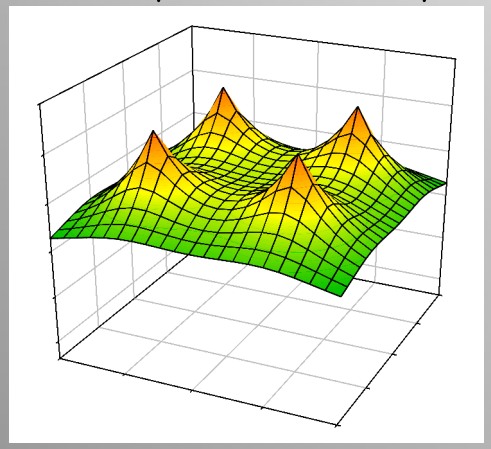

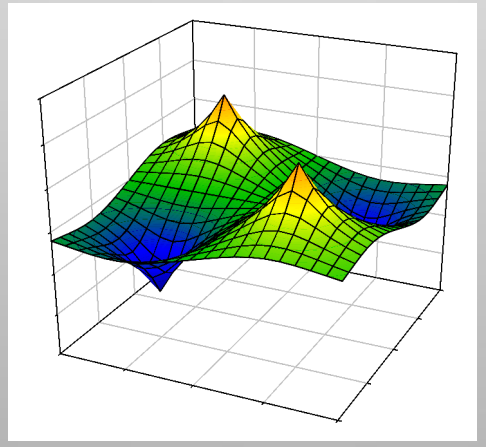

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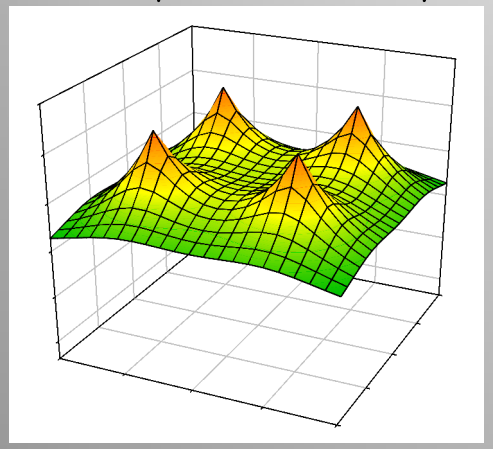

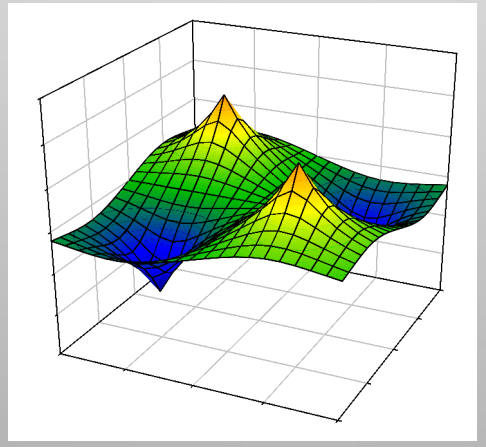

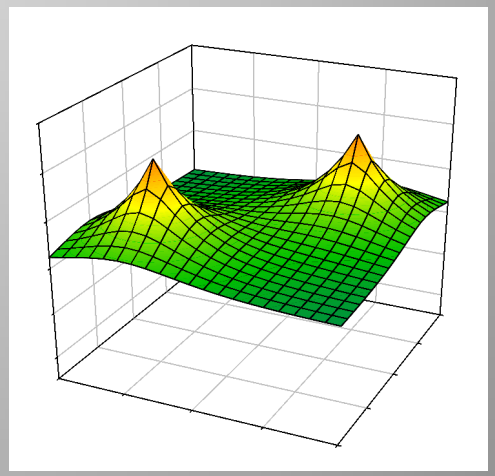

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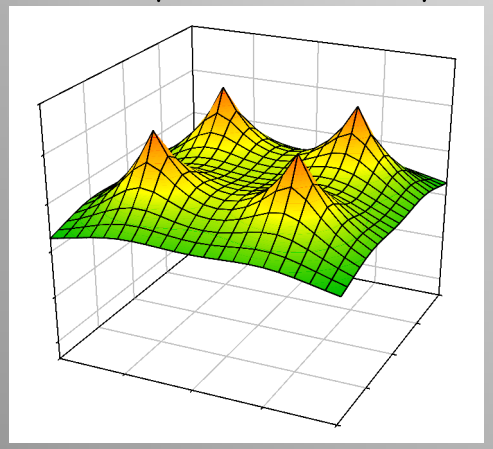

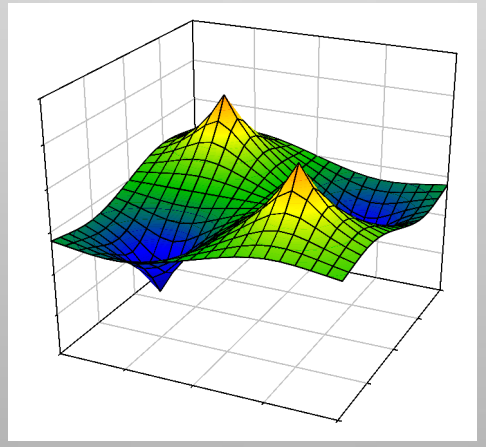

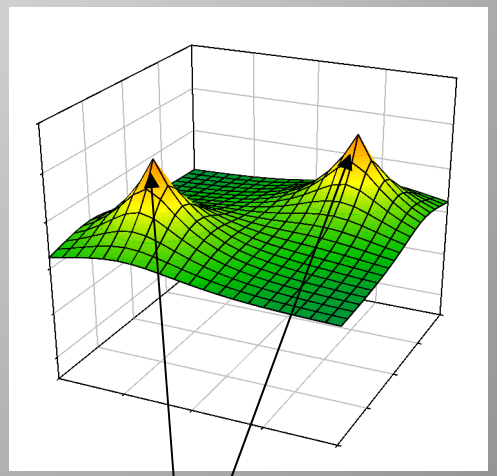

Correlation Example 1: Dissociation Catastrophe

- For long bond distances

$$\frac{\left\langle \psi^{\alpha}_{bond}\psi^{\beta}_{bond} \left| \hat{\mathbf{H}} \right| \psi^{\alpha}_{bond}\psi^{\beta}_{bond} \right\rangle}{\left\langle \psi^{\alpha}_{bond}\psi^{\beta}_{bond} \left| \psi^{\alpha}_{bond}\psi^{\beta}_{bond} \right\rangle} \approx \frac{\left\langle \psi^{\alpha}_{anti}\psi^{\beta}_{anti} \left| \hat{\mathbf{H}} \right| \psi^{\alpha}_{anti}\psi^{\beta}_{anti} \right\rangle}{\left\langle \psi^{\alpha}_{anti}\psi^{\beta}_{anti} \left| \psi^{\alpha}_{anti}\psi^{\beta}_{anti} \right\rangle}$$

- Nearly degenerate configurations mix strongly

$$\frac{1}{\sqrt{2}}\left| \psi^{\alpha}_{bond}\psi^{\beta}_{bond} \right\rangle - \frac{1}{\sqrt{2}}\left| \psi^{\alpha}_{anti}\psi^{\beta}_{anti} \right\rangle$$

- This type of correlation is called “static” or “non-dynamics” correlation

Configuration Interaction

$$\frac{1}{\sqrt{2}}\left|\psi^{\alpha}_{bond}\psi^{\beta}_{bond}\right\rangle - \frac{1}{\sqrt{2}}\left|\psi^{\alpha}_{anti}\psi^{\beta}_{anti}\right\rangle$$

Configuration Interaction

- A more general wavefunction would be:

$$c_{bond}\left|\psi_{bond}^{\alpha}\psi_{bond}^{\beta}\right\rangle - c_{anti}\left|\psi_{anti}^{\alpha}\psi_{anti}^{\beta}\right\rangle$$

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Coefficients are optimized variationally

Configuration Interaction

- A more general wavefunction would be:

$$c_{bond}\left|\psi_{bond}^{\alpha}\psi_{bond}^{\beta}\right\rangle - c_{anti}\left|\psi_{anti}^{\alpha}\psi_{anti}^{\beta}\right\rangle$$

- The ground state is found by building the H matrix between the above configurations and finding the lowest eigenvalue and eigenvector

$$\mathbf{H} = \begin{bmatrix} \left\langle \psi_{bond}^{\alpha}\psi_{bond}^{\beta}\left|\hat{\mathbf{H}}\right|\psi_{bond}^{\alpha}\psi_{bond}^{\beta}\right\rangle & \left\langle \psi_{anti}^{\alpha}\psi_{anti}^{\beta}\left|\hat{\mathbf{H}}\right|\psi_{bond}^{\alpha}\psi_{bond}^{\beta}\right\rangle \\ \left\langle \psi_{bond}^{\alpha}\psi_{bond}^{\beta}\left|\hat{\mathbf{H}}\right|\psi_{anti}^{\alpha}\psi_{anti}^{\beta}\right\rangle & \left\langle \psi_{anti}^{\alpha}\psi_{anti}^{\beta}\left|\hat{\mathbf{H}}\right|\psi_{anti}^{\alpha}\psi_{anti}^{\beta}\right\rangle \end{bmatrix}$$

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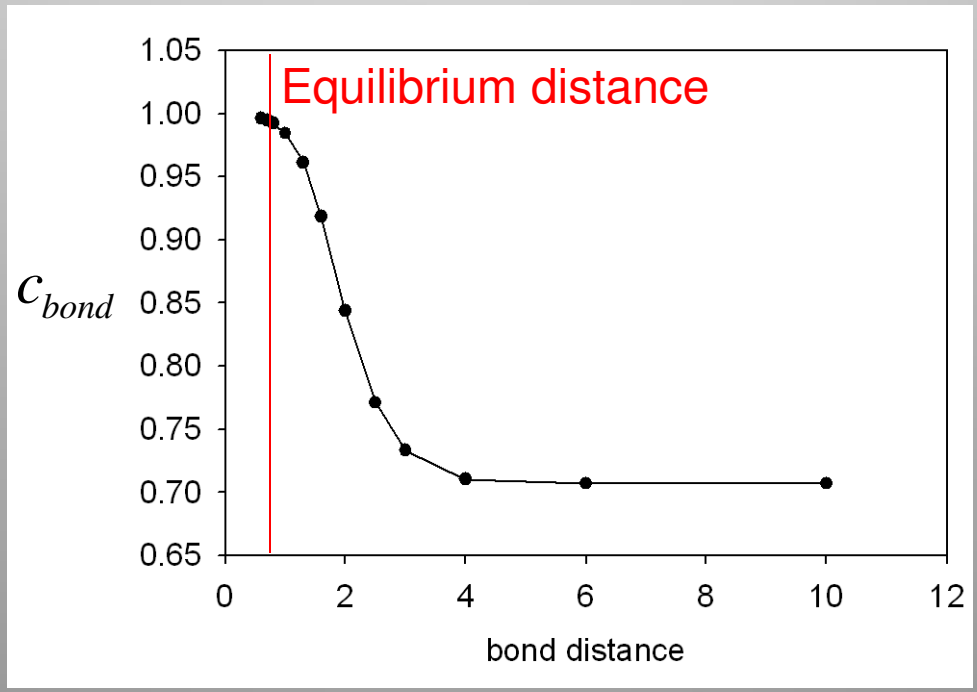

Configuration Interaction

- A more general form of the CI wavefunction:

$$\left|\Psi_{CI}\right\rangle = c_{HF}\left|\Psi_{HF}\right\rangle + \sum_i c_i \left|\Psi_i\right\rangle$$

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The HF determinant

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The HF determinant

other excited determinants of our choice

Configuration Interaction

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$$\left|\Psi_{CI}\right\rangle = c_{HF}\left|\Psi_{HF}\right\rangle + \sum_i c_i \left|\Psi_i\right\rangle$$

CI vector

The HF determinant

other excited determinants of our choice

Correlation Example 2: Beryllium

- The beryllium atom is another example of static correlation

$$\frac{\left\langle 1s^2 2s^2 \left| \hat{\mathbf{H}} \right| 1s^2 2s^2 \right\rangle}{\left\langle 1s^2 2s^2 \left| 1s^2 2s^2 \right\rangle} \approx \frac{\left\langle 1s^2 2p_x^2 \left| \hat{\mathbf{H}} \right| 1s^2 2p_x^2 \right\rangle}{\left\langle 1s^2 2p_x^2 \left| 1s^2 2p_x^2 \right\rangle} \approx$$

$$\frac{\left\langle 1s^2 2p_y^2 \left| \hat{\mathbf{H}} \right| 1s^2 2p_y^2 \right\rangle}{\left\langle 1s^2 2p_y^2 \left| 1s^2 2p_y^2 \right\rangle} \approx \frac{\left\langle 1s^2 2p_z^2 \left| \hat{\mathbf{H}} \right| 1s^2 2p_z^2 \right\rangle}{\left\langle 1s^2 2p_z^2 \left| 1s^2 2p_z^2 \right\rangle}$$

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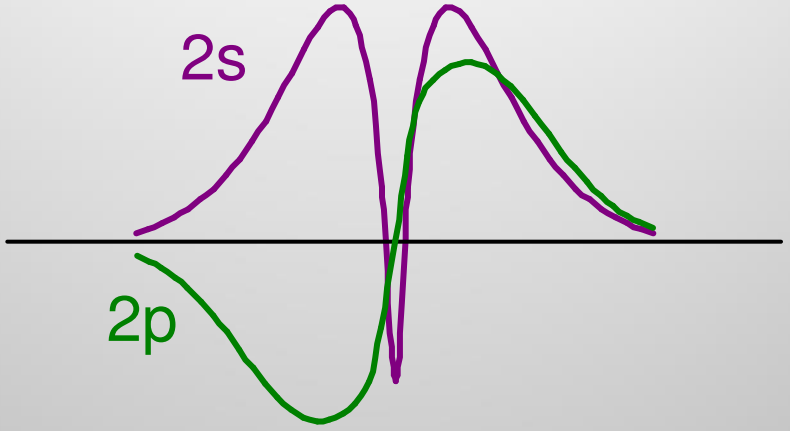

$$\frac{\left\langle 1s^2 2s^2 \left| \hat{\mathbf{H}} \right| 1s^2 2s^2 \right\rangle}{\left\langle 1s^2 2s^2 \left| 1s^2 2s^2 \right\rangle} \approx \frac{\left\langle 1s^2 2p_x^2 \left| \hat{\mathbf{H}} \right| 1s^2 2p_x^2 \right\rangle}{\left\langle 1s^2 2p_x^2 \left| 1s^2 2p_x^2 \right\rangle} \approx$$

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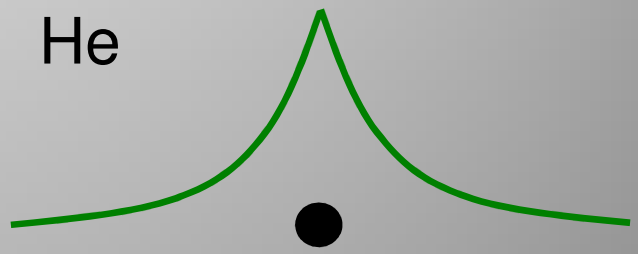
Correlation Example 3: Helium Atom



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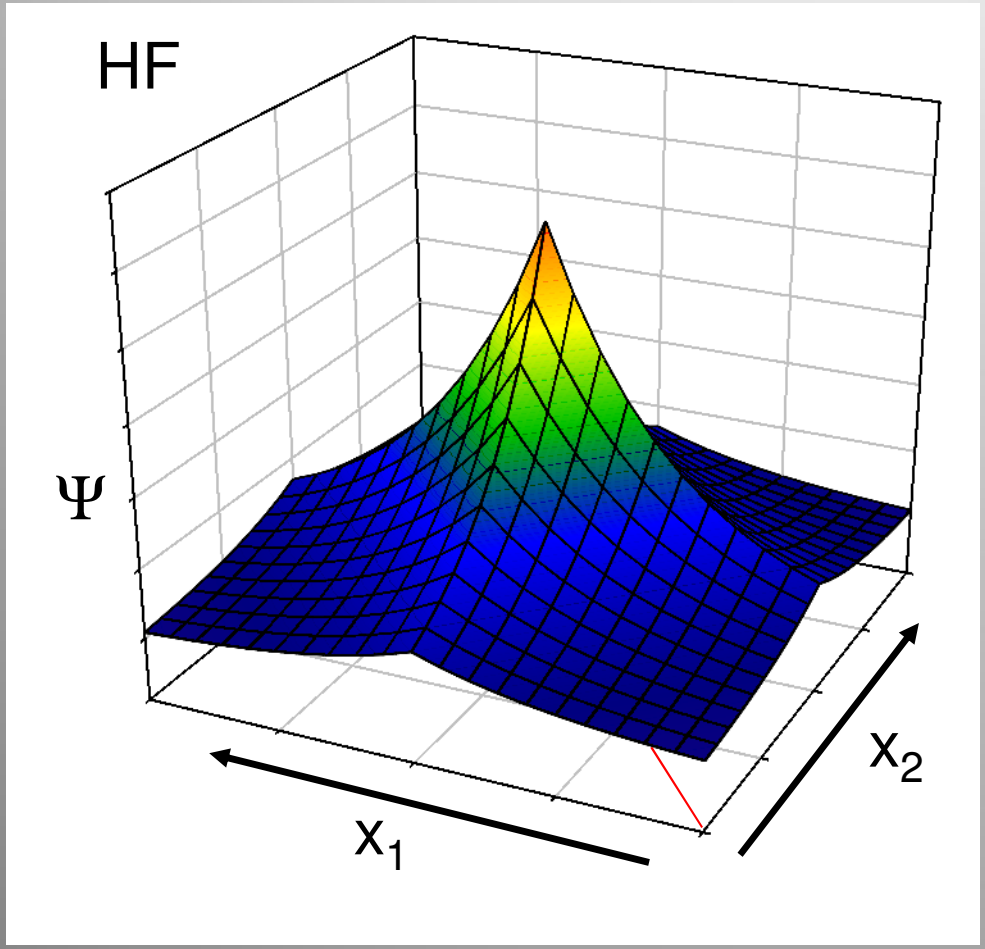

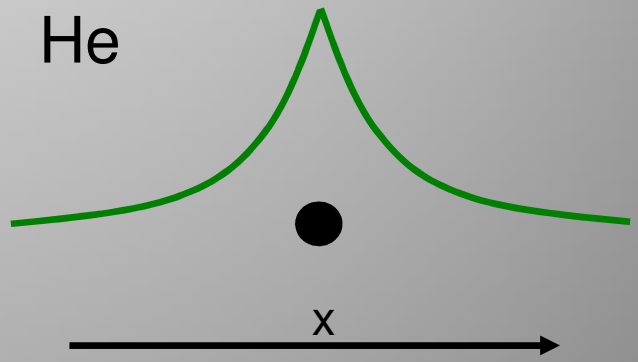

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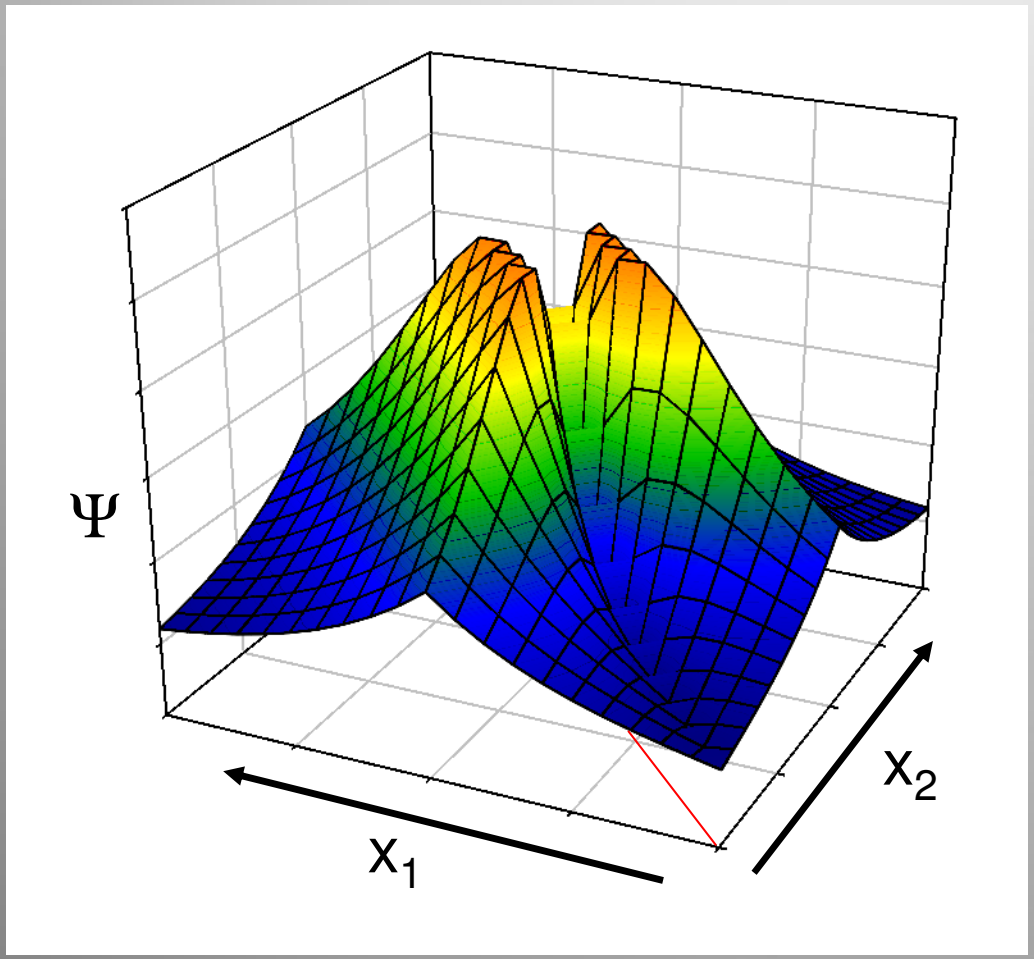

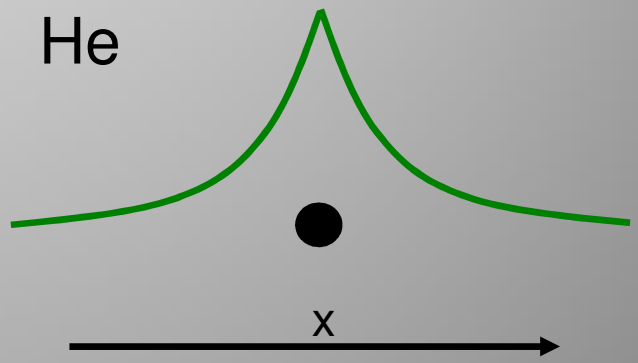

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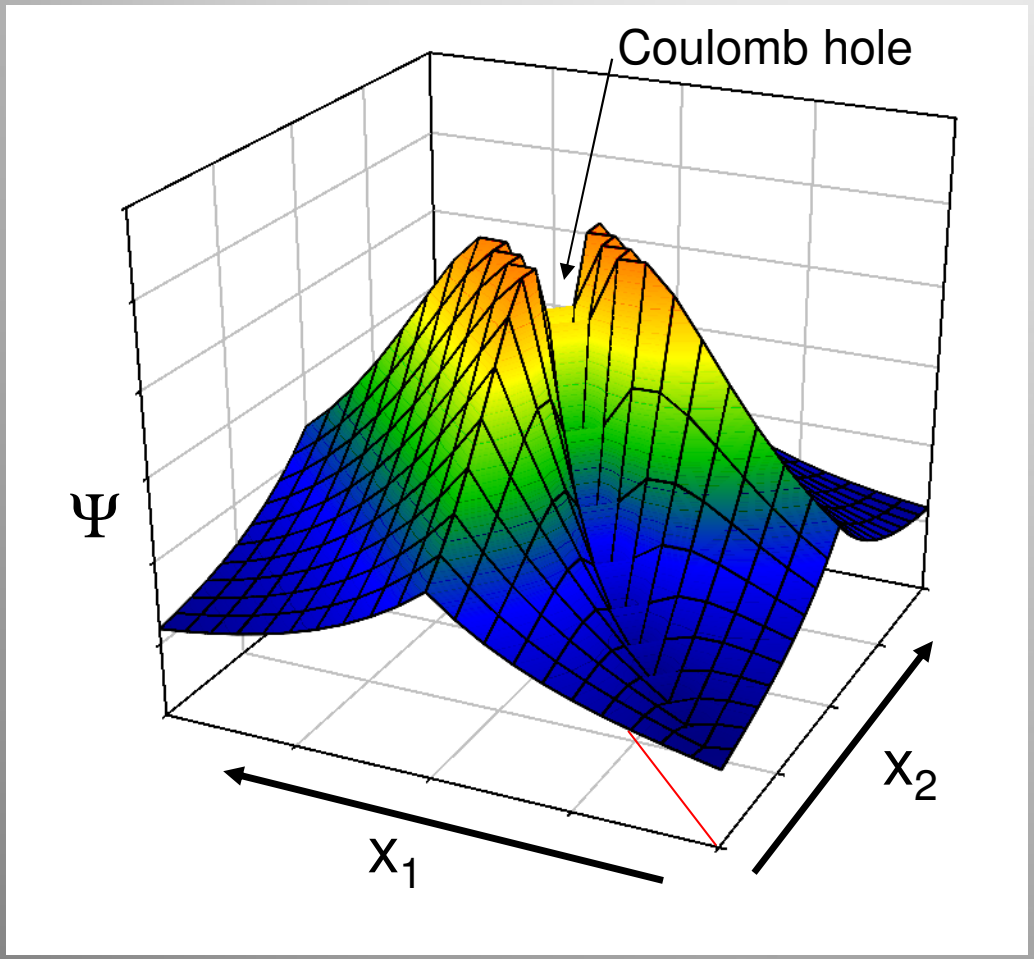

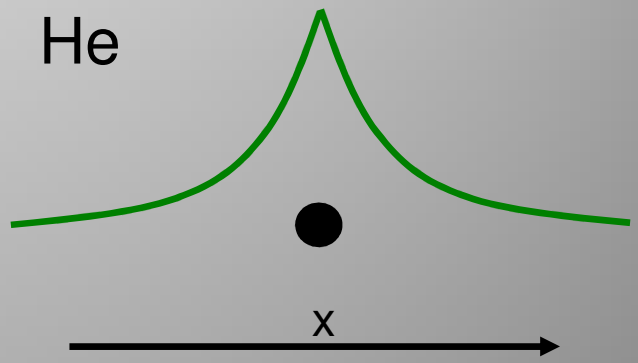

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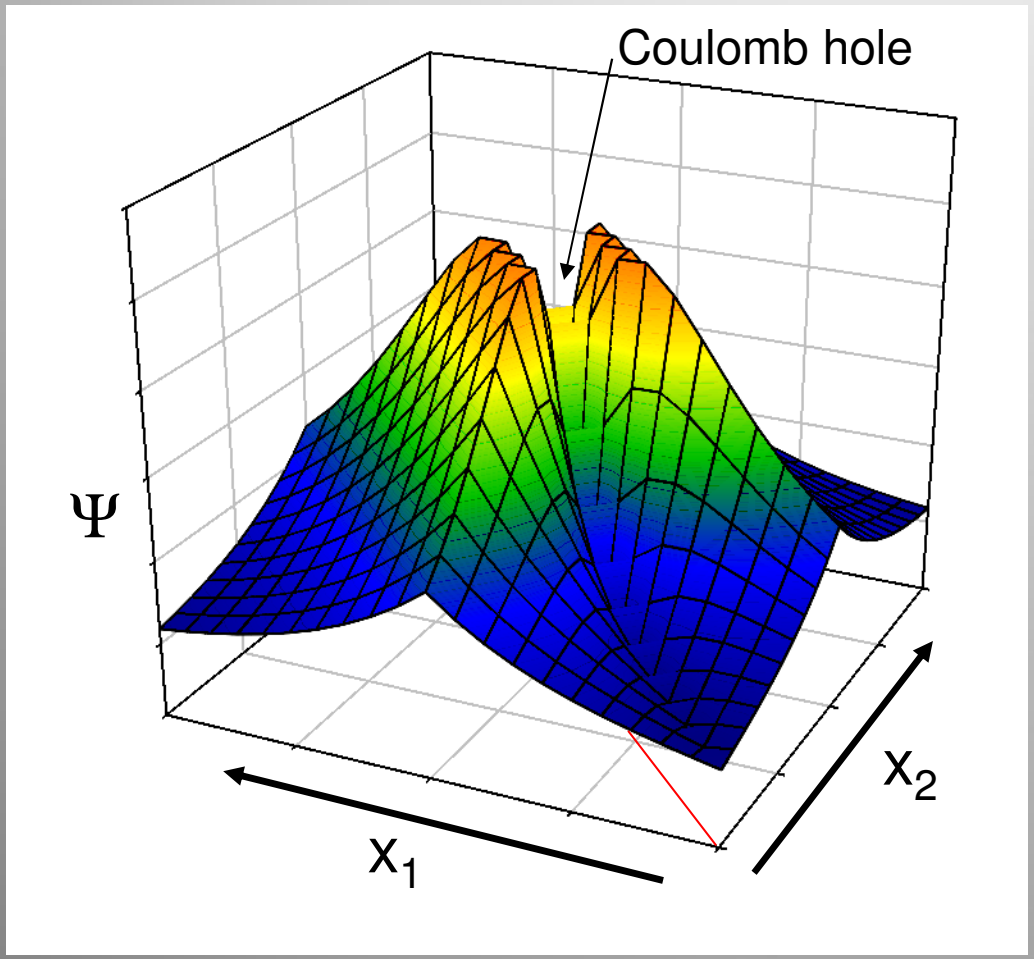

- Coulomb hole: "if electron 1 is here, electron 2 is probably somewhere else"
- We "dig" the Coulomb hole by adding small contributions from many configurations

Correlation Example 3: Helium Atom

$$|\Psi\rangle = c_{1s^2}|1s^2\rangle + c_{2s^2}|2s^2\rangle + c_{2p_x^2}|2p_x^2\rangle + c_{2p_y^2}|2p_y^2\rangle + \ldots$$

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These coefficients will likely be near 0.0

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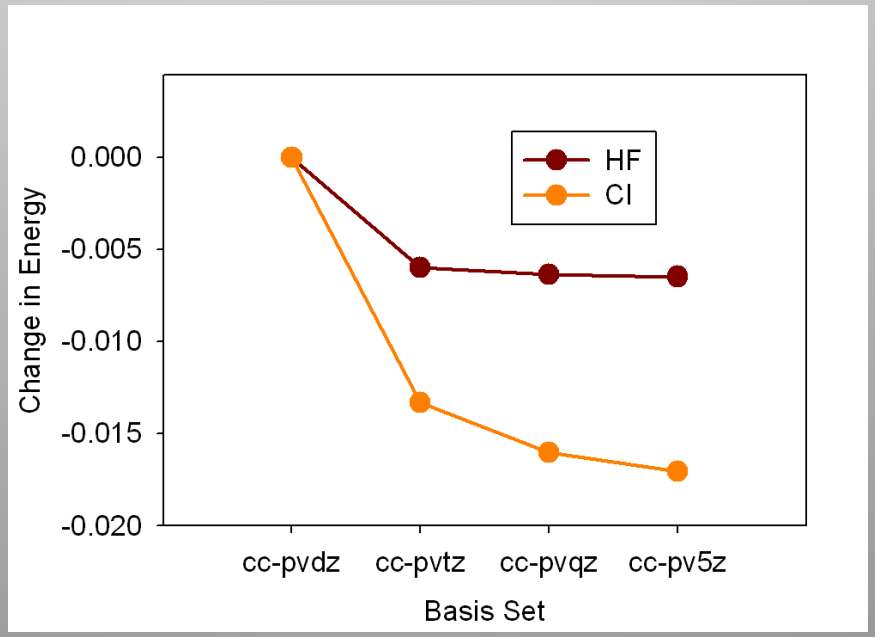
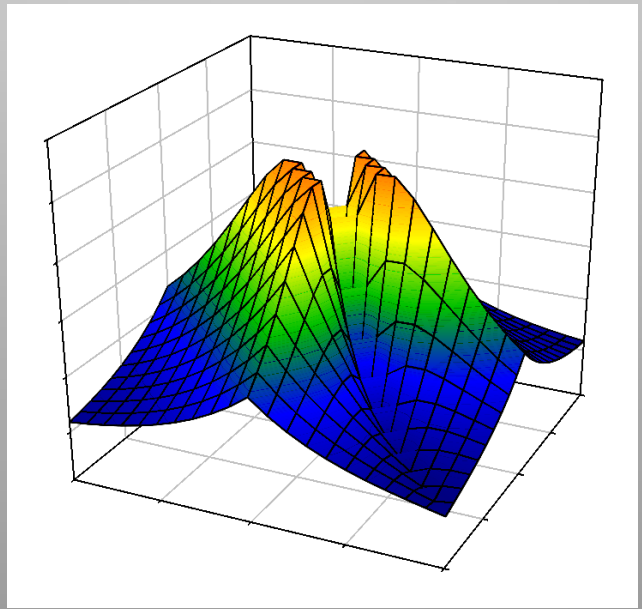


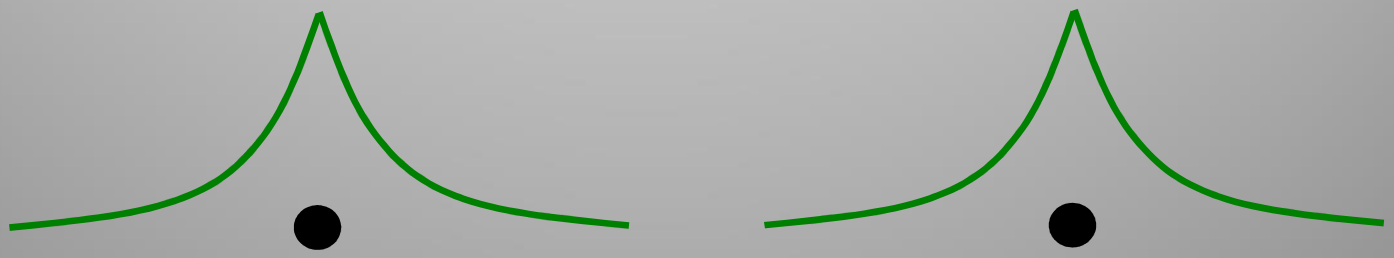
Dynamic Correlation

- Correlation that requires a lot of high energy configurations to describe accurately is called “dynamics” correlation
- The Coulomb hole is one example



Correlation Example 4: Van der Waals forces

- Van der Waals (London dispersion) forces are another common example



Correlation Example 4: Van der Waals forces

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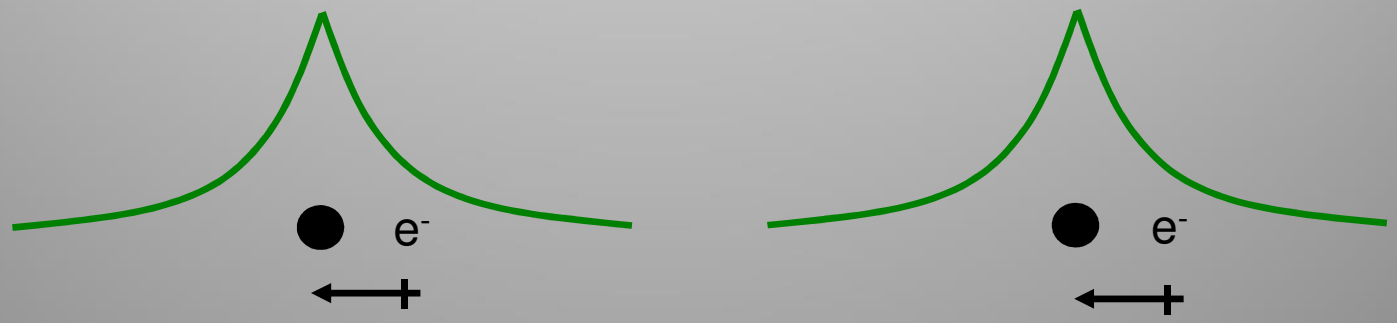
  - "If electron 1 is on the right side of atom A then electron 2 is probably on the right side of atom B"



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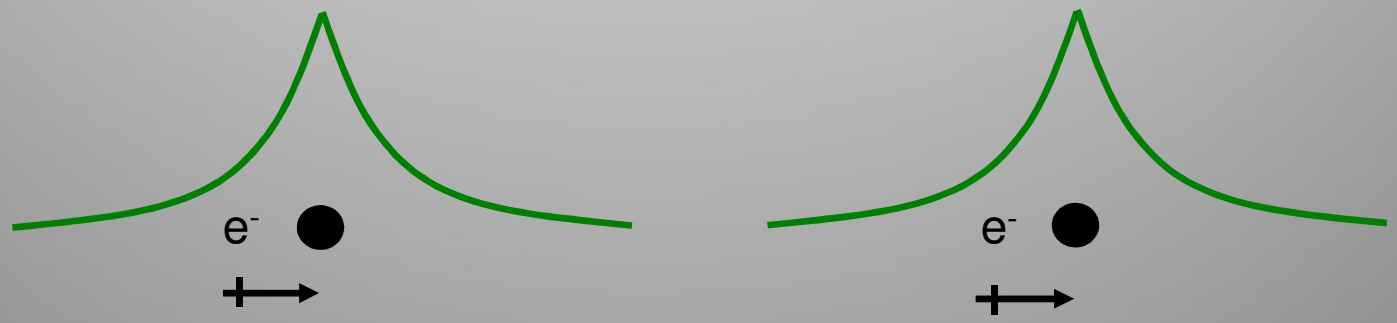
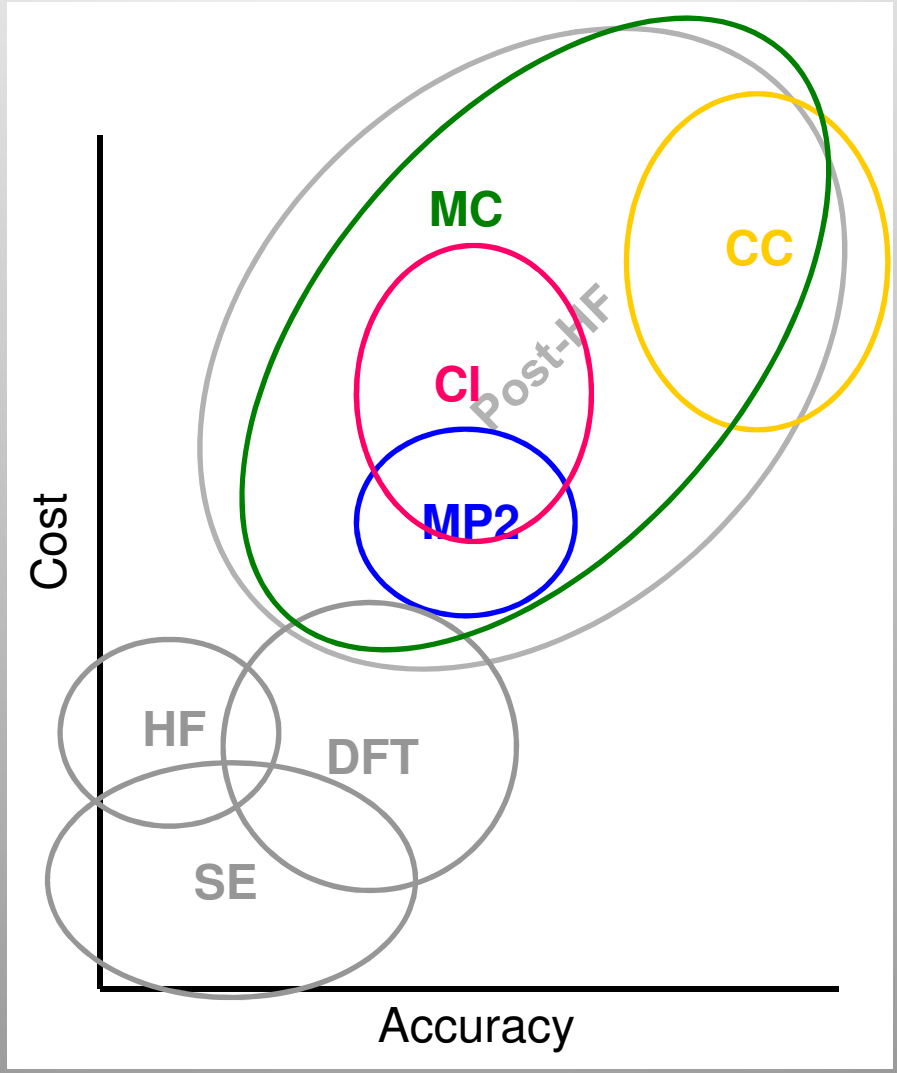


Correlation Summary

- Correlation can be described in conditional statements about the locations of electrons: “if electron 1 is here, electron 1 is probably there”
- Static correlation results when a small number of configurations are nearly degenerate
- Dynamics correlation requires a large number of high energy configurations to describe

Wavefunction based treatments of correlation



Classification of Correlated Methods

- Single Reference Methods (CI, CC, MP)
  - Start from the HF determinant and add correlation
  - Typically used when HF is already a decent approximation (no static correlation)
- Multireference (Multiconfigurational) methods (MCSCF, CASSCF, CASPT2, MRCI)
  - Include static correlation though the addition of a small number of configurations

Configuration Interaction

- Expand the wavefunction in a “many-electron” basis of configurations
- Typically, CI wavefunctions start from the HF reference configuration

$$\left|\Psi_{CI}\right\rangle = c_{HF}\left|\Psi_{HF}\right\rangle + \sum_{r,a} c_a^r \left|\Psi_a^r\right\rangle + \sum_{r<s,a<b} c_{ab}^{rs}\left|\Psi_{ab}^{rs}\right\rangle + \ldots$$

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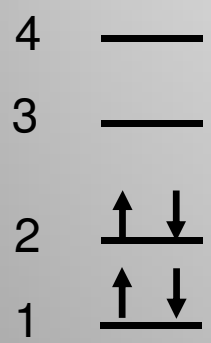
Configuration Interaction

$|\Psi_{HF}\rangle$



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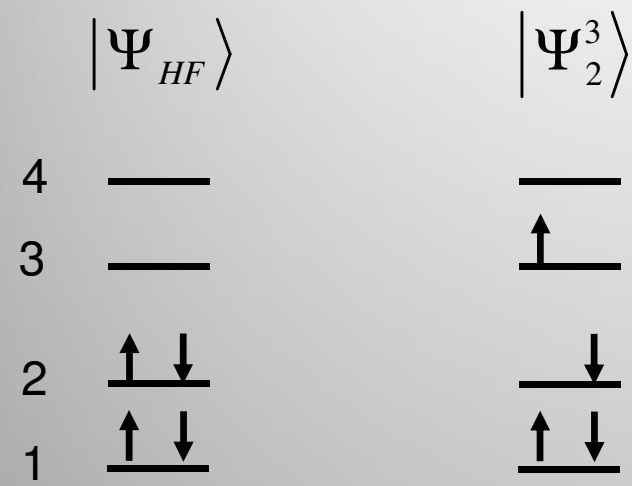

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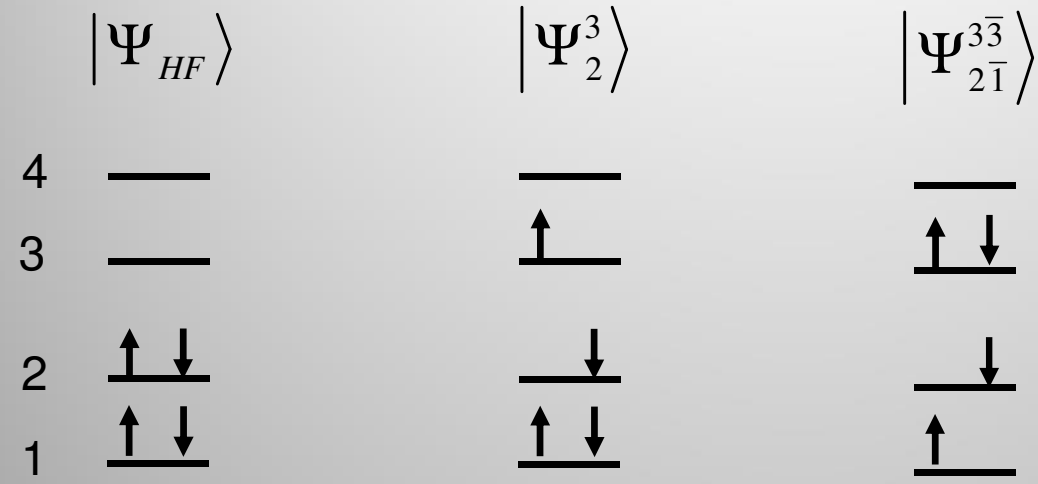

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Configuration Interactions

- The CI H matrix will look like this

$$\begin{bmatrix} \langle \Psi_{HF} | \hat{\mathbf{H}} | \Psi_{HF} \rangle & 0 & \langle \Psi_{HF} | \hat{\mathbf{H}} | D \rangle & 0 & 0 \\ & \langle S | \hat{\mathbf{H}} | S \rangle & \langle S | \hat{\mathbf{H}} | D \rangle & \langle S | \hat{\mathbf{H}} | T \rangle & 0 \\ & & \langle D | \hat{\mathbf{H}} | D \rangle & \langle D | \hat{\mathbf{H}} | T \rangle & \langle D | \hat{\mathbf{H}} | Q \rangle \\ & & & \langle T | \hat{\mathbf{H}} | T \rangle & \langle T | \hat{\mathbf{H}} | Q \rangle \\ & & & & \langle Q | \hat{\mathbf{H}} | Q \rangle \end{bmatrix}$$

Singly excited configurations

Doubly excited configurations

Triply excited configurations

Quadruply excited configurations

Configuration Interactions

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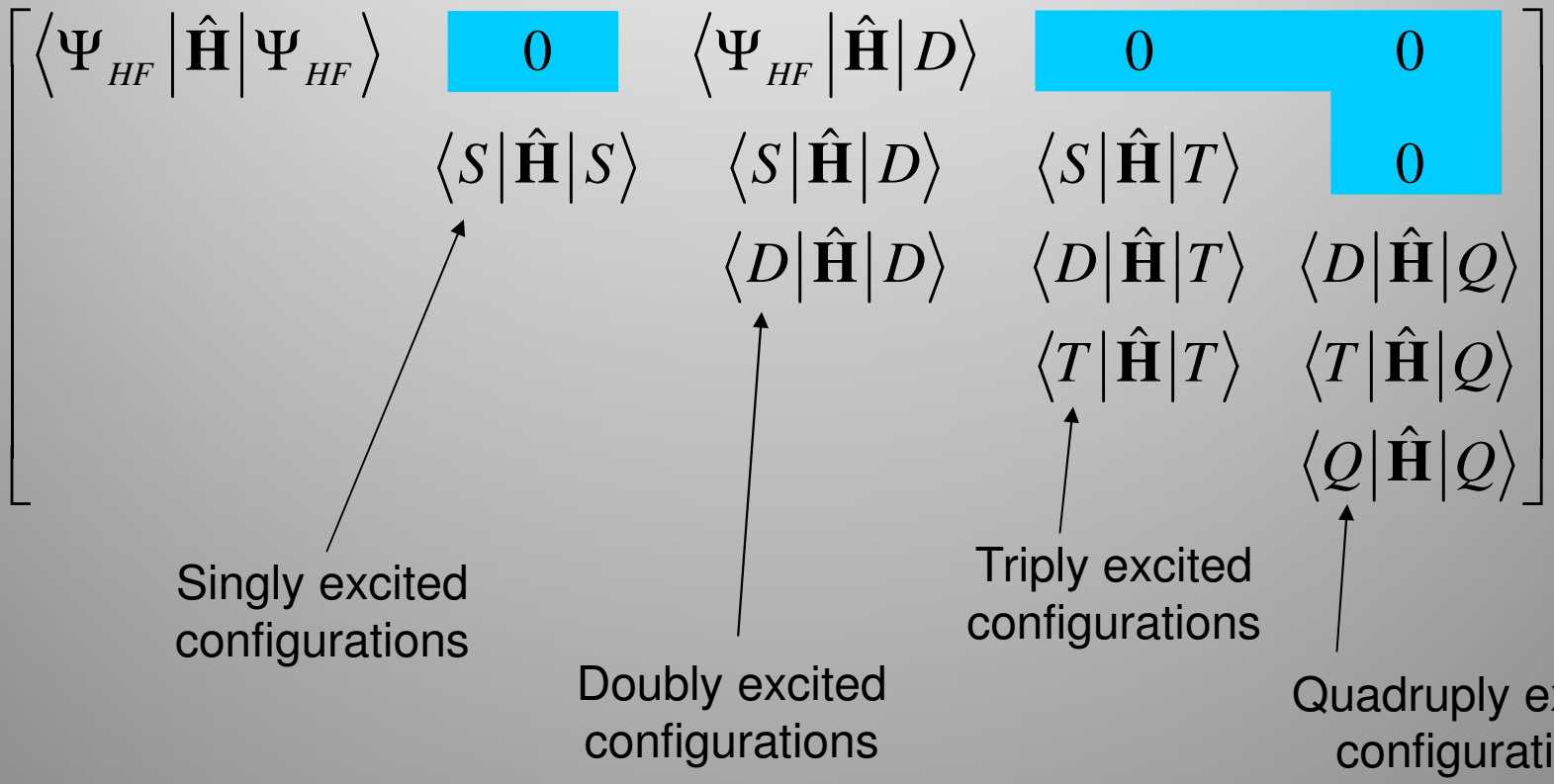

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$$\hat{H}_{elec} = -\tfrac{1}{2} \sum_{elec} \nabla^2(\mathbf{r}) + \sum_{nuc} \sum_{nuc} \frac{q_I q_J}{r_{IJ}} - \sum_{nuc} \sum_{elec} \frac{q_I}{r_{Ij}} + \sum_{elec} \sum_{elec} \frac{1}{r_{ij}}$$

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H is a 2-electron operator, therefore configurations differing by more than 2 electrons do in interact

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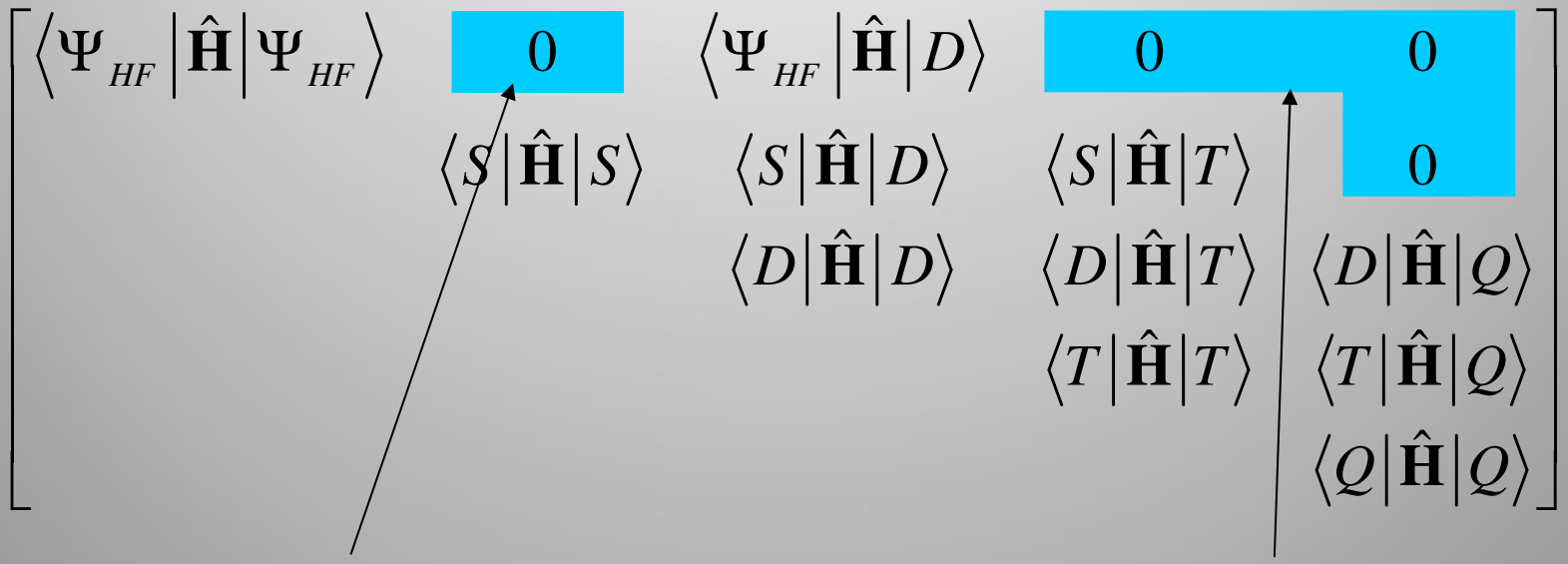

Brillouin's theorem – the HF determinant does not interact with singly excited configurations

H is a 2-electron operator, therefore configurations differing by more than 2 electrons do in interact

Configuration Interaction

- Common varieties of CI
  - CID – $\left|\Psi_{HF}\right\rangle, \left|\Psi_{ab}^{rs}\right\rangle$
  - CISD – $\left|\Psi_{HF}\right\rangle, \left|\Psi_{a}^{r}\right\rangle, \left|\Psi_{ab}^{rs}\right\rangle$
  - CISDT – $\left|\Psi_{HF}\right\rangle, \left|\Psi_{a}^{r}\right\rangle, \left|\Psi_{ab}^{rs}\right\rangle, \left|\Psi_{abc}^{rst}\right\rangle$
  - CISDTQ…
  - Full CI (FCI) – All possible configurations

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Truncated CI

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  - CISDTQ…
  - Full CI (FCI) – All possible configurations
    - In a complete basis FCI is the *exact* solution of the Schrodinger equation
    - The cost of FCI scales factorially with the size of the basis set

Truncated CI

The Problems with CI

- CI can be very computationally expensive
- Truncated CI is not size-extensive/size-consistent

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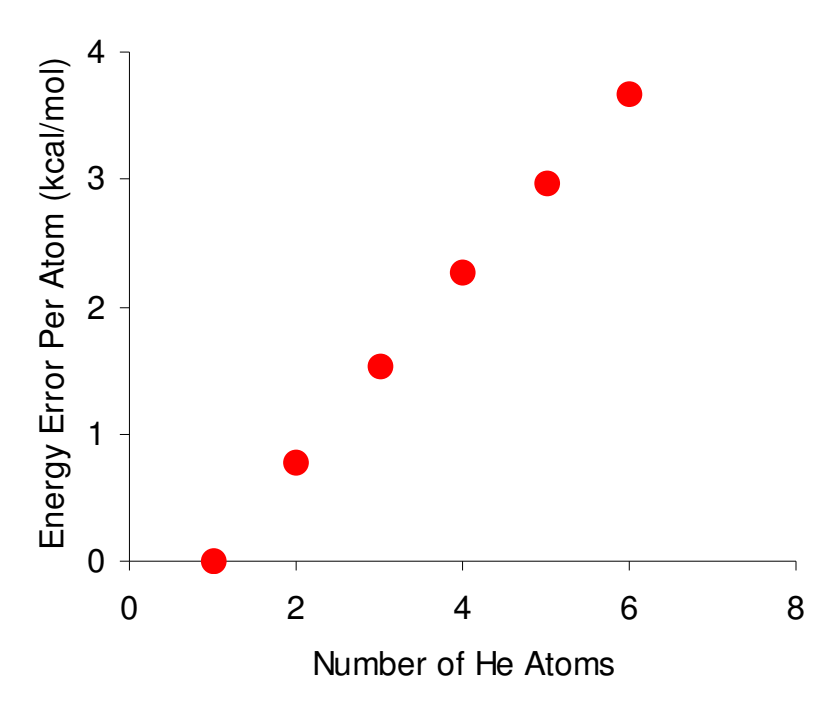

Size extensivity/Size consistency

- Size consistency: $E(A) + E(B) = E(A+B)$ in the limit that A and B do not interact
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Coupled Cluster

- Solves the size-extensivity problem
- Is more accurate that the equivalent CI
- The computational cost is slightly more than an equivalent CI

Coupled Cluster

- The wavefunction is described by an operator applied to the HF determinant

$$\left|\Psi_{CC}\right\rangle = e^{\hat{\mathbf{T}}}\left|\Psi_{HF}\right\rangle$$

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amplitudes

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Normalization constant

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e.g. CID:

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The amplitudes are the CI vector

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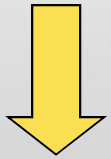

Taylor expand the exponential

$$= \left(1 + \hat{\mathbf{T}} + \frac{\hat{\mathbf{T}}^2}{2!} + \frac{\hat{\mathbf{T}}^3}{3!} + \ldots\right)\left|\Psi_{HF}\right\rangle$$

Coupled Cluster

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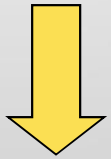

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Coupled Cluster

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Taylor expand the exponential

$$= \left(\underbrace{1+\hat{\mathbf{T}}}_{\text{CI}} + \underbrace{\frac{\hat{\mathbf{T}}^2}{2!} + \frac{\hat{\mathbf{T}}^3}{3!} + \ldots}_{\text{These terms allow simultaneous excitations}}\right)\left|\Psi_{HF}\right\rangle$$

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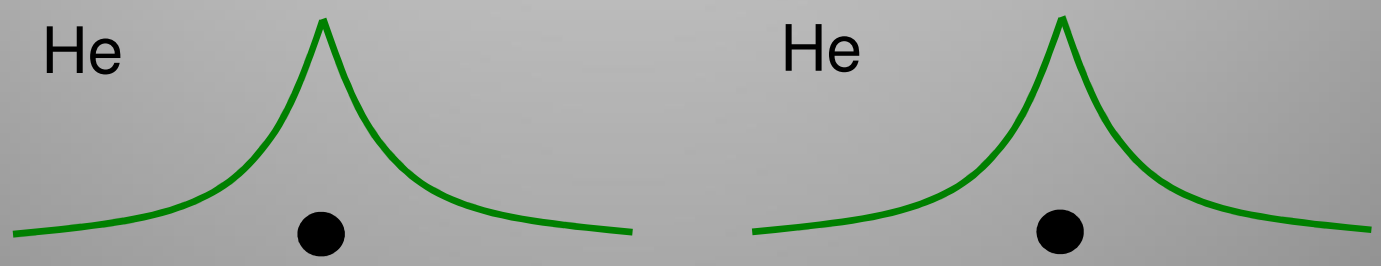
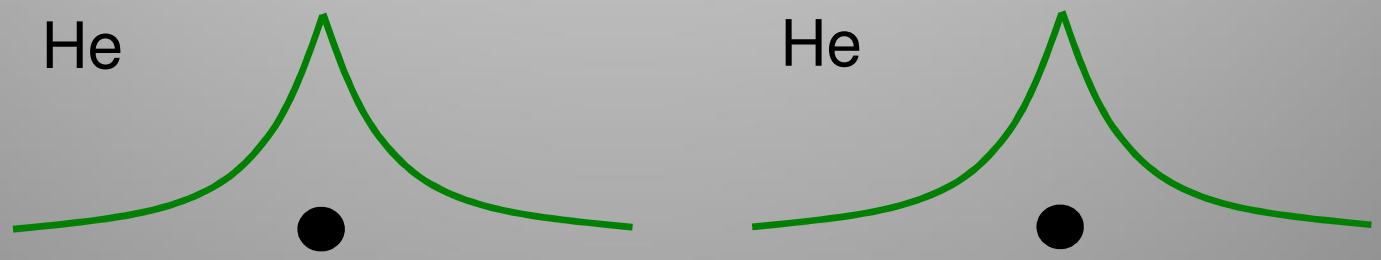


Coupled Cluster

$$\left|\Psi_{CI}\right\rangle = \left|\Psi_{HF}\right\rangle + \ldots + t_{ab}^{rs}\left|\Psi_{ab}^{rs}\right\rangle + t_{cd}^{tu}\left|\Psi_{cd}^{tu}\right\rangle + \ldots$$



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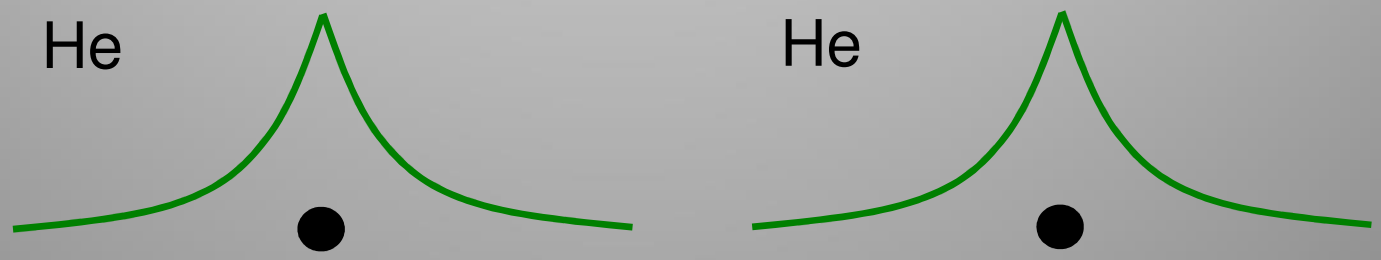


Coupled Cluster

- Intermediate normalization

$$\left\langle \Psi_{HF} \middle| e^{\hat{\mathbf{T}}} \Psi_{HF} \right\rangle = 1 \qquad \left\langle e^{\hat{\mathbf{T}}} \Psi_{HF} \middle| e^{\hat{\mathbf{T}}} \Psi_{HF} \right\rangle > 1$$

- CC energy expression:

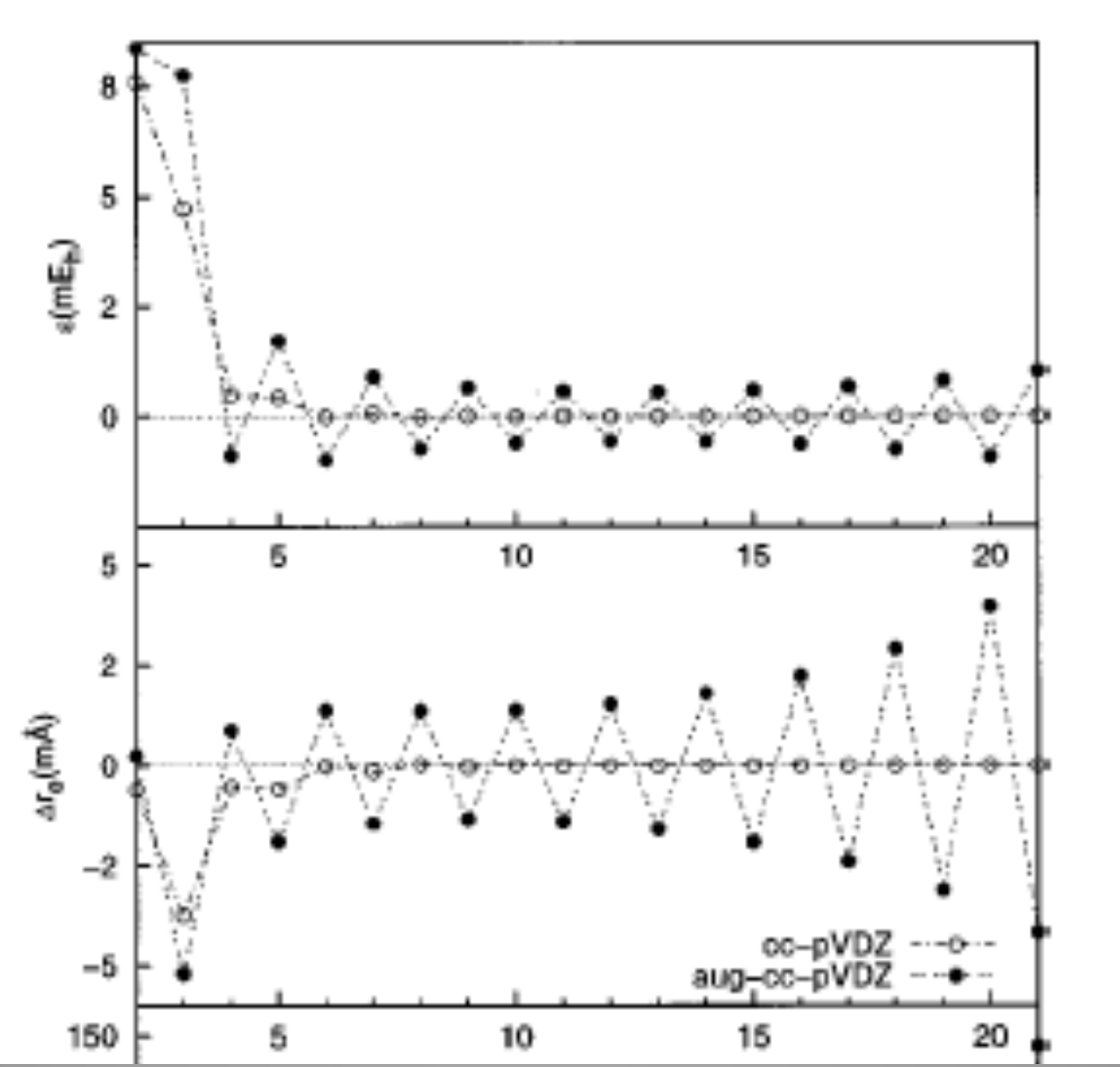
$$E = \left\langle \Psi_{HF} \middle| \hat{\mathbf{H}} \middle| e^{\hat{\mathbf{T}}} \Psi_{HF} \right\rangle \neq \left\langle e^{\hat{\mathbf{T}}} \Psi_{HF} \middle| \hat{\mathbf{H}} \middle| e^{\hat{\mathbf{T}}} \Psi_{HF} \right\rangle$$

- The CC energy is not variational

Coupled Cluster

- CCSD
- CCSDT
- CCSDTQ
- Full CC is exact
- CCSD(T), etc.
- Coupled cluster is size-extensive, but often too computationally expensive to study large systems

Perturbation Theory



from Leninger et. al., J. Chem. Phys., 2000

Perturbation Theory

- MP2 is widely used when an accurate, but reasonably inexpensive description of dynamics correlation is needed
- MP2 is size extensive
- The denominators in the MP expressions can cause problems when static correlation is important
- The MP series does not necessarily converge

Computational Scaling

Method	Cost
FCI	$O(N!)$
CCSD(T)	$O(N^7)$
CISD, CCSD	$O(N^6)$
MP2	$O(N^5)$
HF	$O(N^4)$

N is the number of basis functions

Single-Reference Summary

- Lots of configurations need to be added to correctly describe dynamic correlation
- CI is simple in concept, but is not size-extensive
- Coupled cluster achieves size-extensivity and high accuracy, but at a large computational cost
- Moller-Plesset PT is less accurate, but more efficient than coupled cluster

Multireference Methods

- If a singled determinant is insufficient to describe a system we can use a small number of determinants as our simplest description

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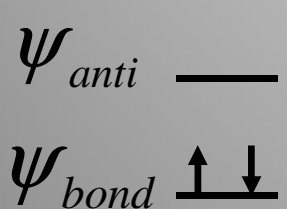

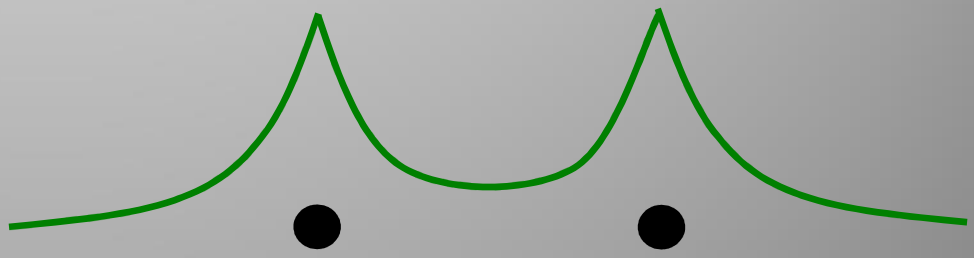

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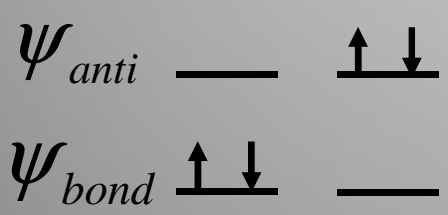
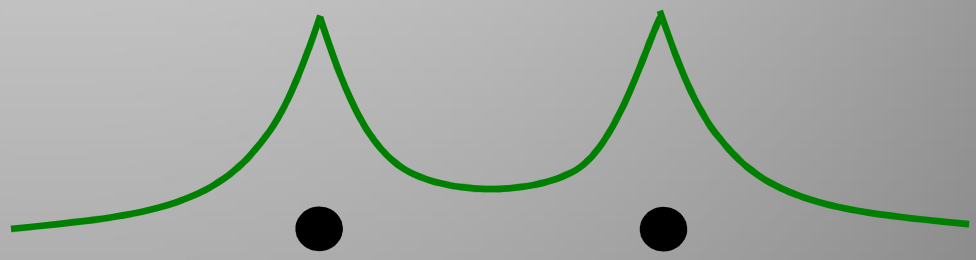
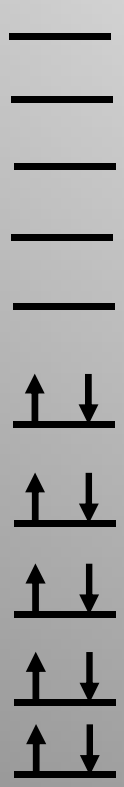




Complete Active Space Self Consistent Field (CASSCF)

$$|\Psi_{HF}\rangle$$



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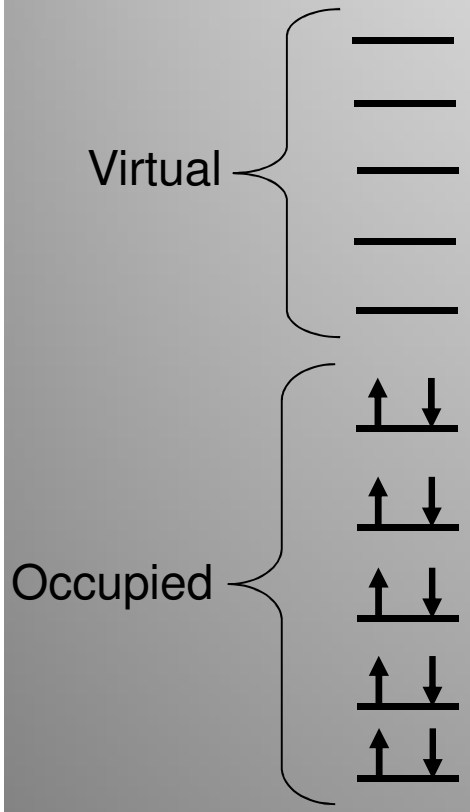

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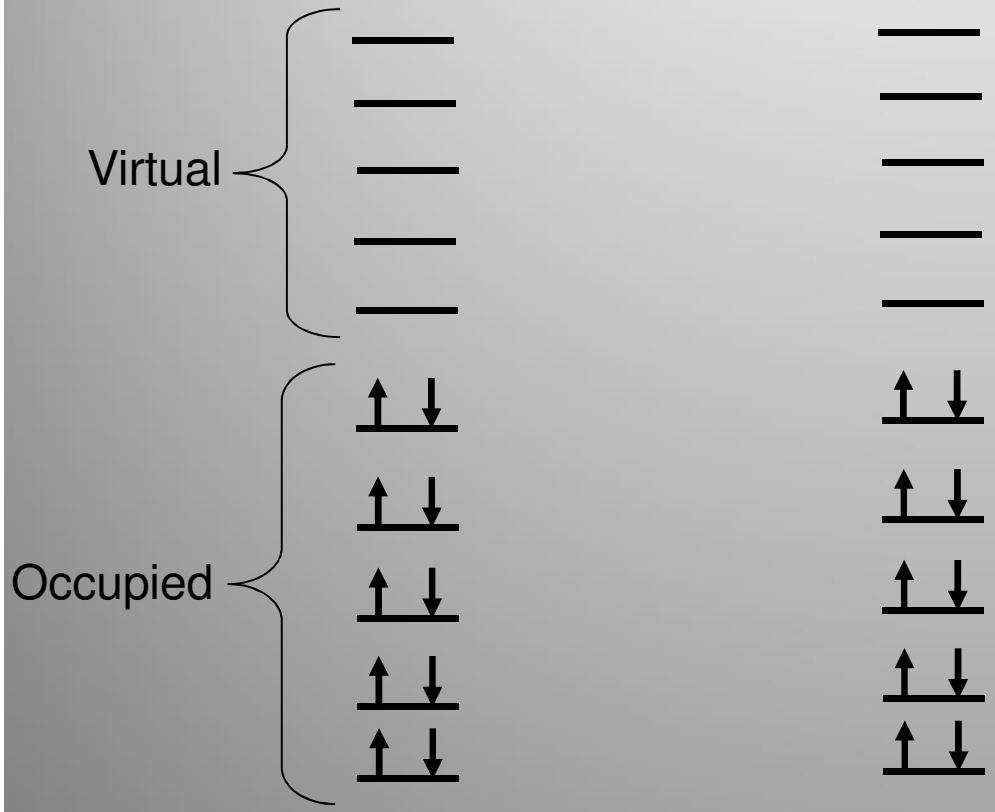

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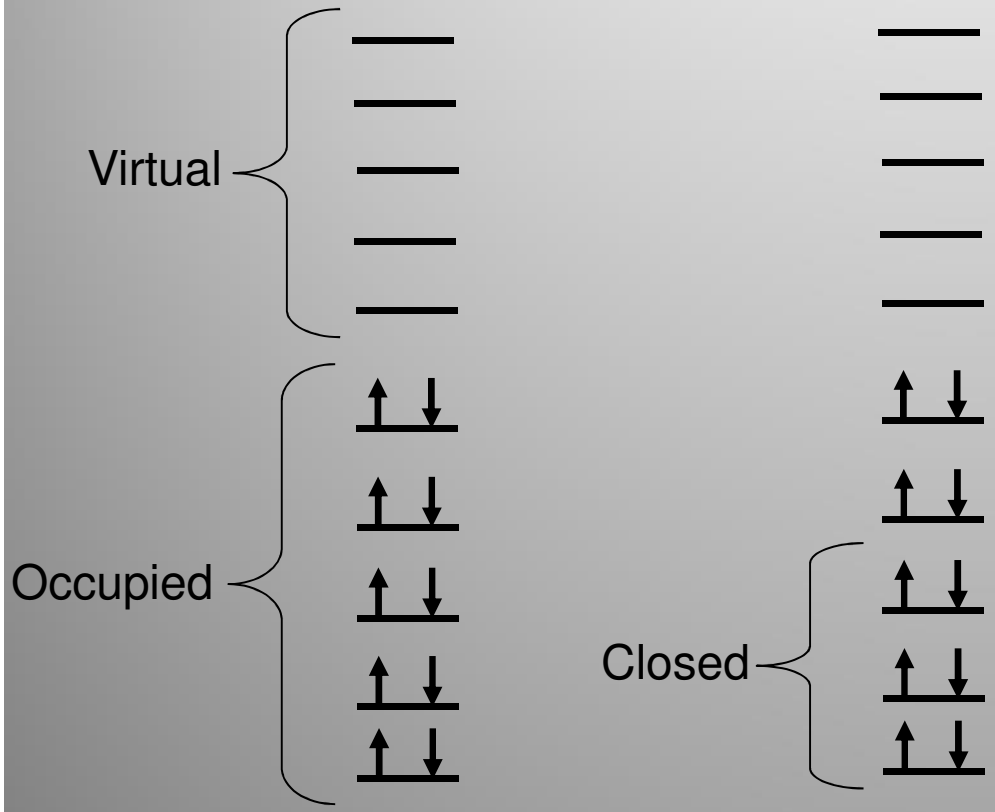

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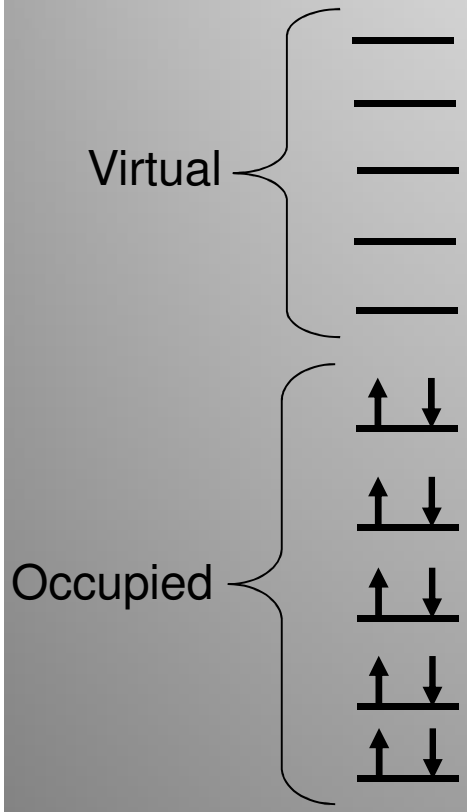

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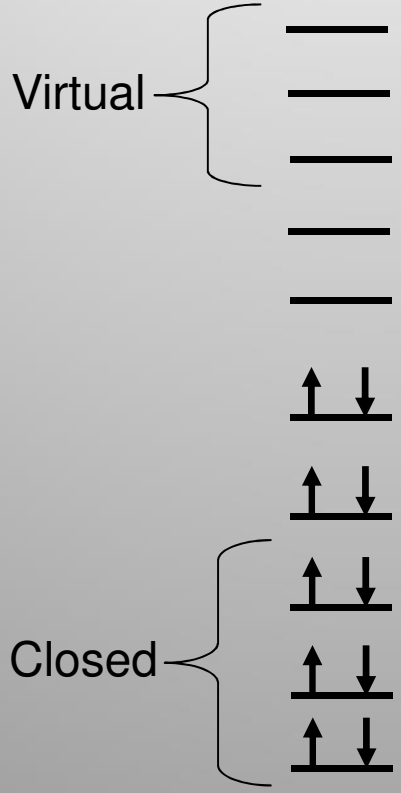

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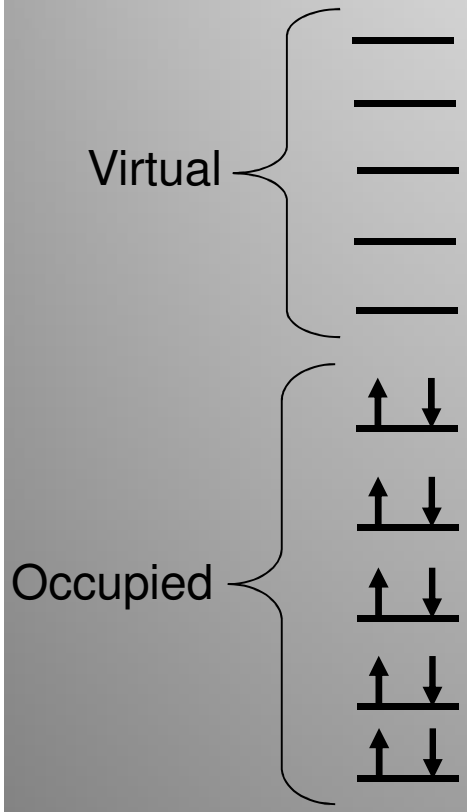

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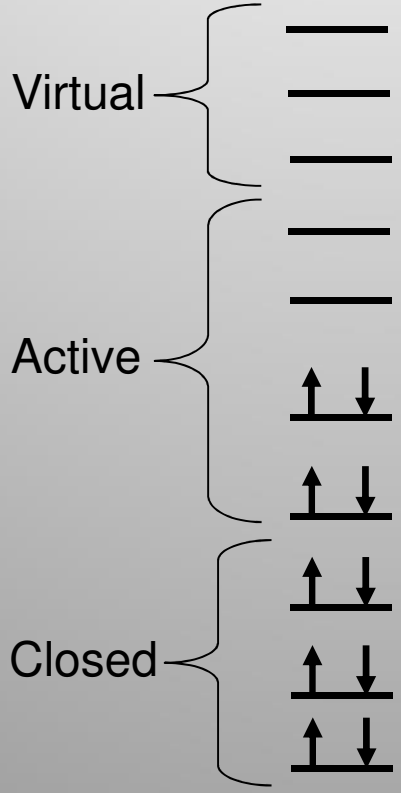

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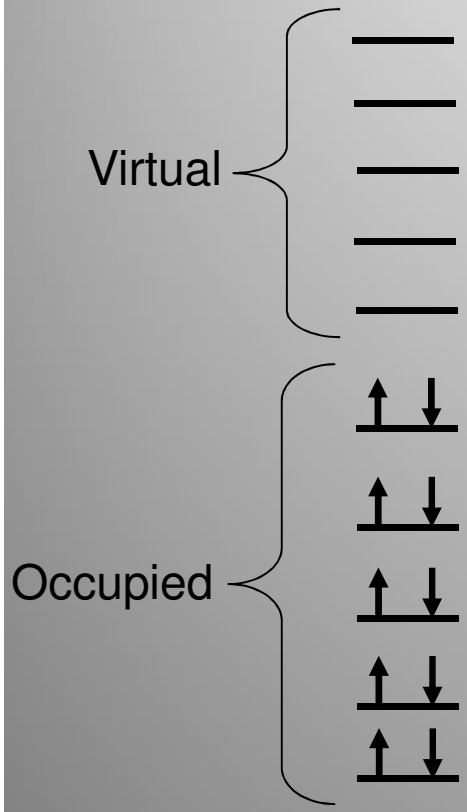

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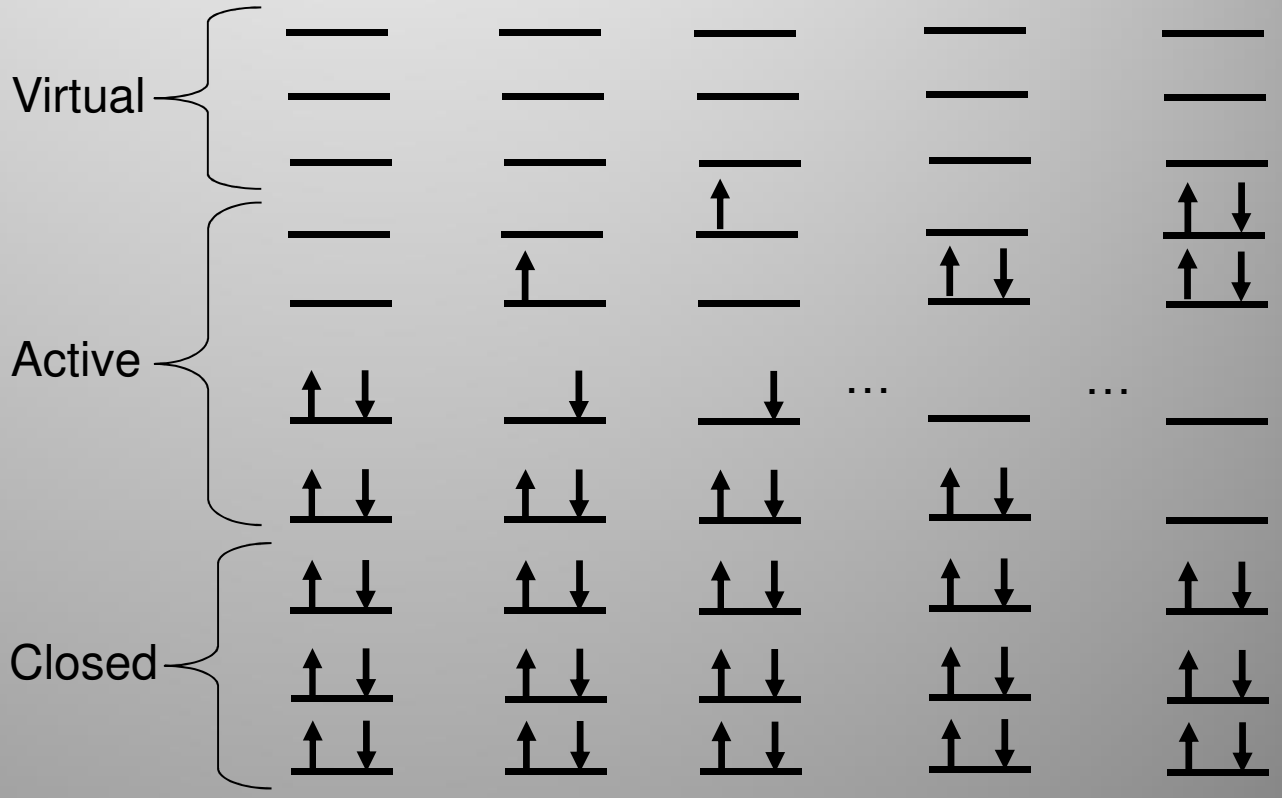

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$$\left|\Psi_{CAS}\right\rangle = \sum_{i=0}^{\binom{N}{M_\alpha}*\binom{N}{M_\beta}} c_i \left|\Psi_i\right\rangle$$

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CI vector

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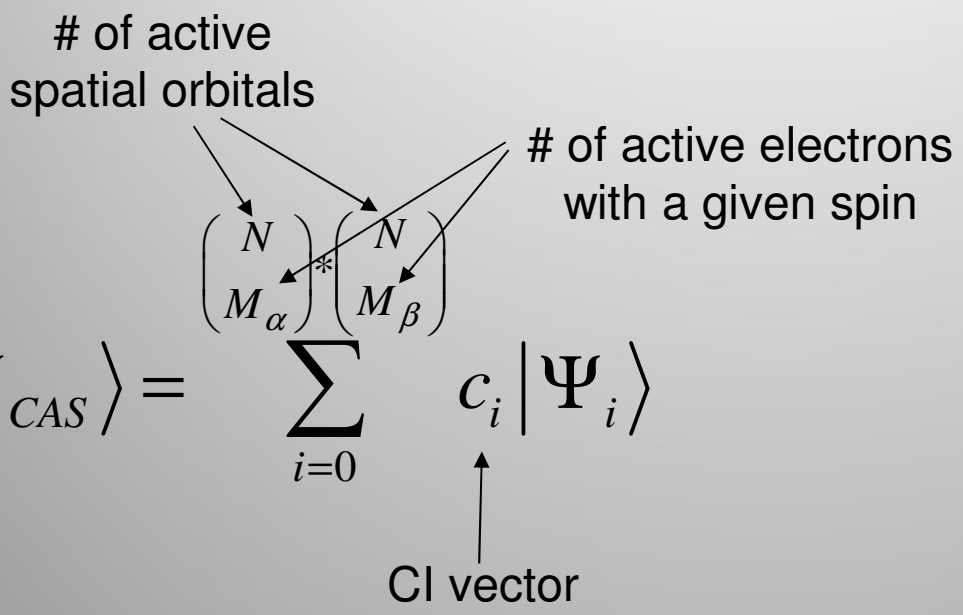

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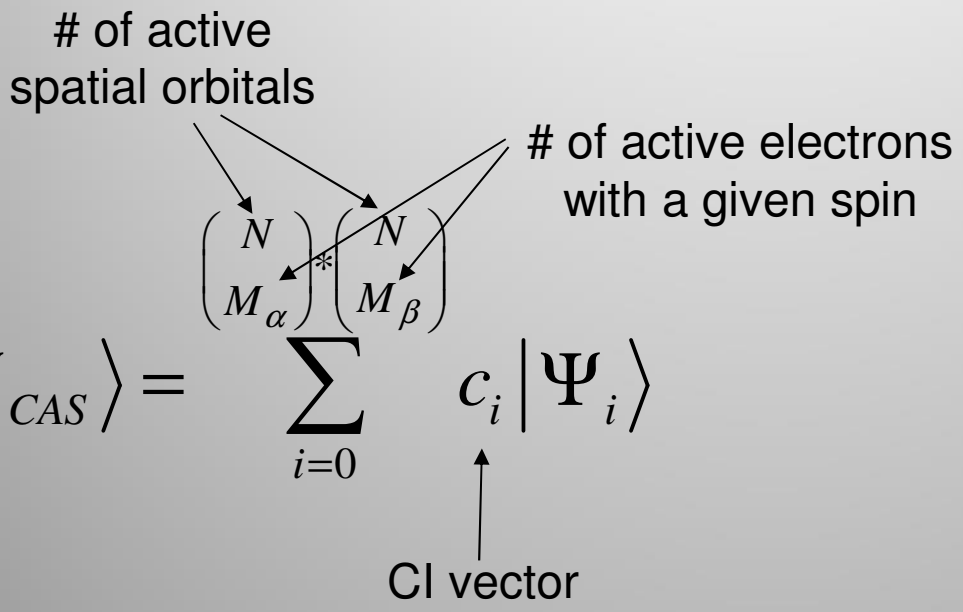

Abbreviate: CAS(*M*/*N*)

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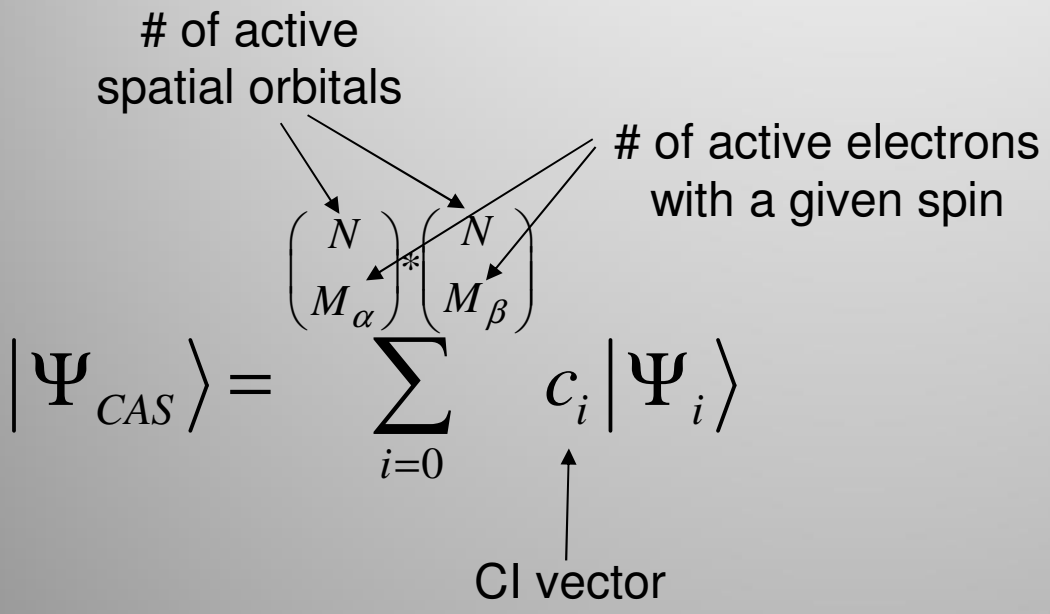

Active Space	# of determinants
CAS(2/2)	4
CAS(4/4)	36
CAS(6/6)	400
CAS(8/8)	4900
CAS(10/10)	63504
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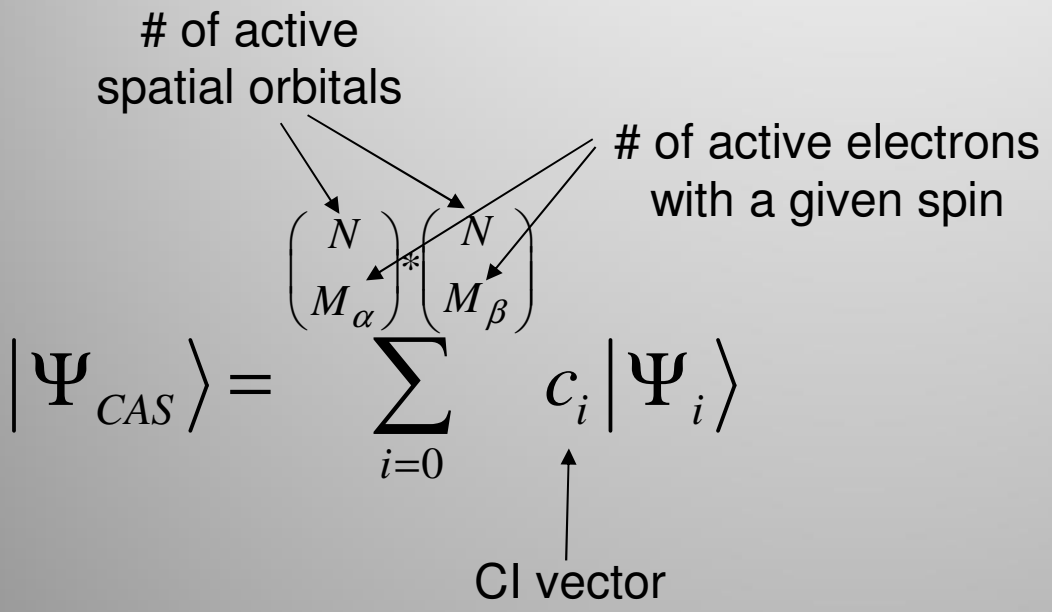

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H——H

2/2?

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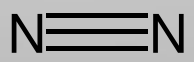

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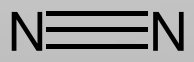

6/6?

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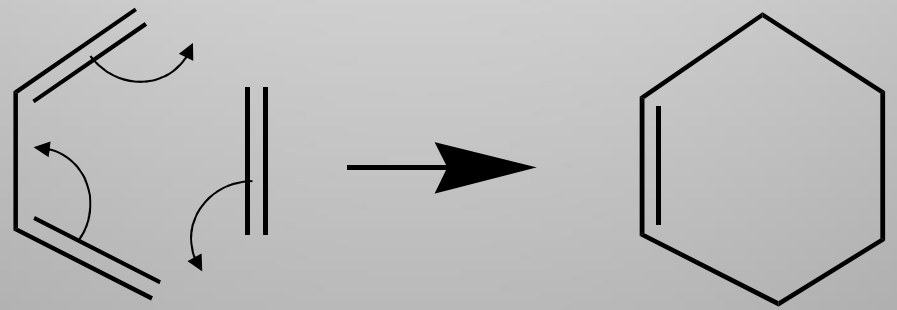

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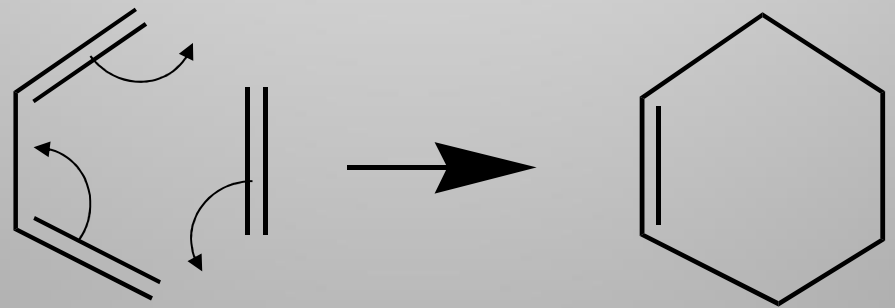

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8/8?

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		π antibonding orbitals			
π bonding orbitals		1	2	3	4
	1	-3.13 eV	-0.96	-0.95	-0.88
	2	-0.69	1.27	**0.67**	**0.69**
	3	-0.63	**0.71**	1.17	1.19
	4	-0.56	**0.80**	1.41	1.25

Target: .4-.5 eV

8/8?

Adding Dynamics Correlation

- CASPT2
  - HF:MP2::CASSCF:CASPT2
  - can be very accurate, but is very expensive
- MRCI
  - CI involving CASSCF determinants and all single and double excitations from them
  - can be more accurate, but is even more expensive

Multireference Method Summary

- Multireference methods are ideal for systems with significant static correlation
- CASSCF is not terribly accurate, but correctly describes bond breaking
- CASPT2 and MRCI allow the addition of dynamic correlation to the statically correlated CASSCF wavefunction

Correlation Summary

- Electron correlation takes many forms
  - Static correlation, resulting from near-degeneracy of configurations
    - Bond breaking
    - Transition state
  - Dynamic correlation
    - A Coulomb hole
    - Dispersion
- Dynamics correlation is well described by single reference methods
  - CI – rarely used today due to the lack of size-extensivity
  - CC – The “gold standard,” but expensive
  - MP – Less expensive, less accurate than CC

Correlation Summary

- Static correlation can be treated by multireference methods
  - CASSCF has results which depend strongly and unpredictably on the choice of active space
  - CASPT2 and MRCI allow the addition of dynamic correlation

Post-HF Methods in Context