COUPLED CLUSTER THEORY

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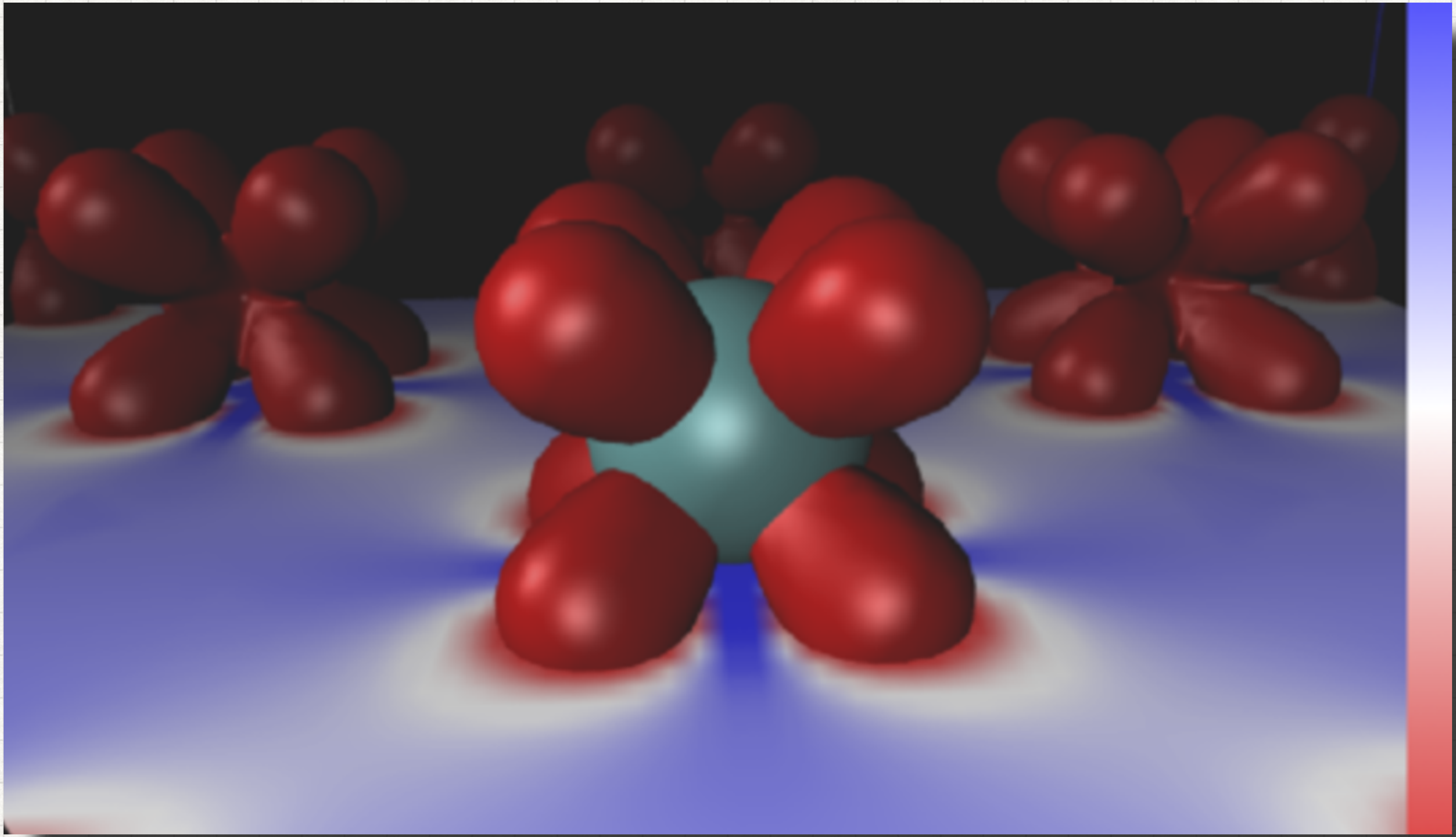


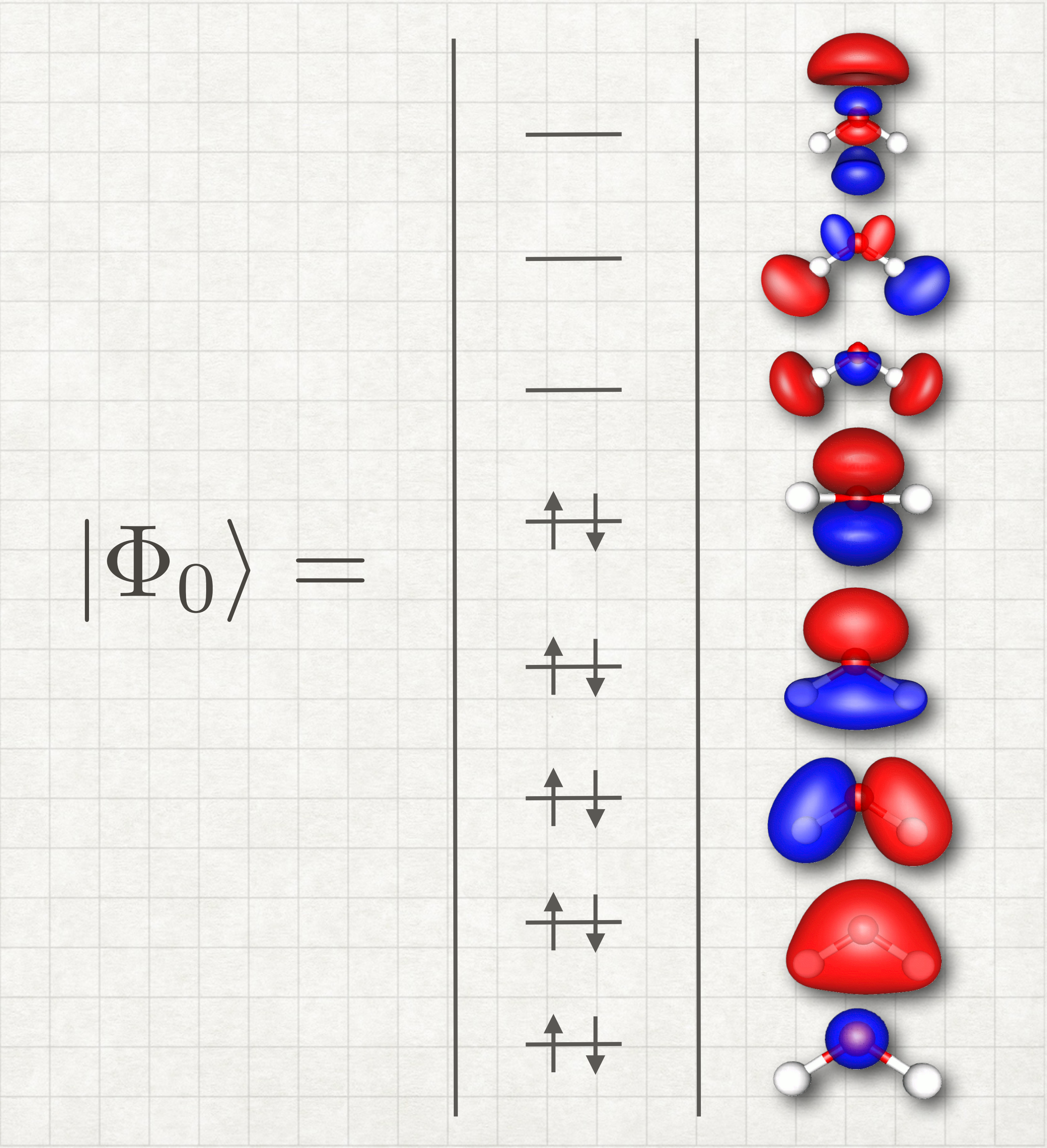
ALPHABET SOUP OF QUANTUM CHEMISTRY

WHAT METHOD SHOULD WE CHOOSE?

T. D. Crawford, S. S. Wesolowski, E. F. Valeev, R. A. King, M. L. Leininger, and H. F. Schaefer, "The Past, Present, and Future of Quantum Chemistry," in Chemistry for the 21st Century, E. Keinan and I. Schecter, eds., Wiley-VCH, Weinheim, pp. 219-246 (2001).

HARTREE-FOCK THEORY

- In Hartree-Fock theory, the many-electron wave function is written as a single Slater determinant.
- Advantages:
  - Obeys Pauli antisymmetry
  - Inexpensive to compute
  - Frequently semi-quantitatively correct
- Disadvantages:
  - Fails to correlate the motions of opposite-spin electrons
  - Cannot provide "chemical accuracy"



$$|\Phi_0\rangle =$$

HARTREE-FOCK THEORY

- A Hartree-Fock Slater determinant yields an antisymmetric wave function:

$$|\Psi\rangle \approx |\Phi_0\rangle = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\mathbf{x}_1) & \phi_2(\mathbf{x}_1) & \phi_3(\mathbf{x}_1) & \dots & \phi_N(\mathbf{x}_1) \\ \phi_1(\mathbf{x}_2) & \phi_2(\mathbf{x}_2) & \phi_3(\mathbf{x}_2) & \dots & \phi_N(\mathbf{x}_2) \\ \phi_1(\mathbf{x}_3) & \phi_2(\mathbf{x}_3) & \phi_3(\mathbf{x}_3) & \dots & \phi_N(\mathbf{x}_3) \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \phi_1(\mathbf{x}_N) & \phi_2(\mathbf{x}_N) & \phi_3(\mathbf{x}_N) & \dots & \phi_N(\mathbf{x}_N) \end{vmatrix}$$

where

$$\phi_p(\mathbf{x}) = \psi_p(\mathbf{r})\alpha \qquad \text{or} \qquad \phi_p(\mathbf{x}) = \psi_p(\mathbf{r})\beta$$

is a one-electron spin-orbital and *N* is the number of electrons/orbitals.

- The orbitals are obtained by variational optimization of the Hartree-Fock energy subject to the constraint that the orbitals remain orthonormal.
- We will abbreviate the notation for a Slater determinant using only the diagonal entries of the matrix:

$$|\Phi_0\rangle = |\phi_1(\mathbf{x}_1)\phi_2(\mathbf{x}_2)\phi_3(\mathbf{x}_3)\dots\phi_N(\mathbf{x}_N)\rangle$$

HARTREE-FOCK DENSITY

- The one- and two-electron densities are given as:

$$\rho(\mathbf{x}_1) = \int d\mathbf{x}_2 \int d\mathbf{x}_3 ... \int d\mathbf{x}_N \, |\Psi|^2$$

$$\rho(\mathbf{x}_1, \mathbf{x}_2) = \int d\mathbf{x}_3 ... \int d\mathbf{x}_N \, |\Psi|^2$$

- The one-electron density is the probability of finding an electron at a given point $\mathbf{r}_1$ in space (assuming unit normalization), whereas the two-electron density (or "pair density") is the probability of finding two electrons simultaneously with coordinates $\mathbf{x}_1$ and $\mathbf{x}_2$.
- In Hartree-Fock theory, the pair density for ***opposite-spin*** electrons is exactly separable into a product of one-electron densities:

$$\rho_{\mathrm{HF}}(\mathbf{x}_1, \mathbf{x}_2) = \rho(\mathbf{x}_1)\rho(\mathbf{x}_2)$$

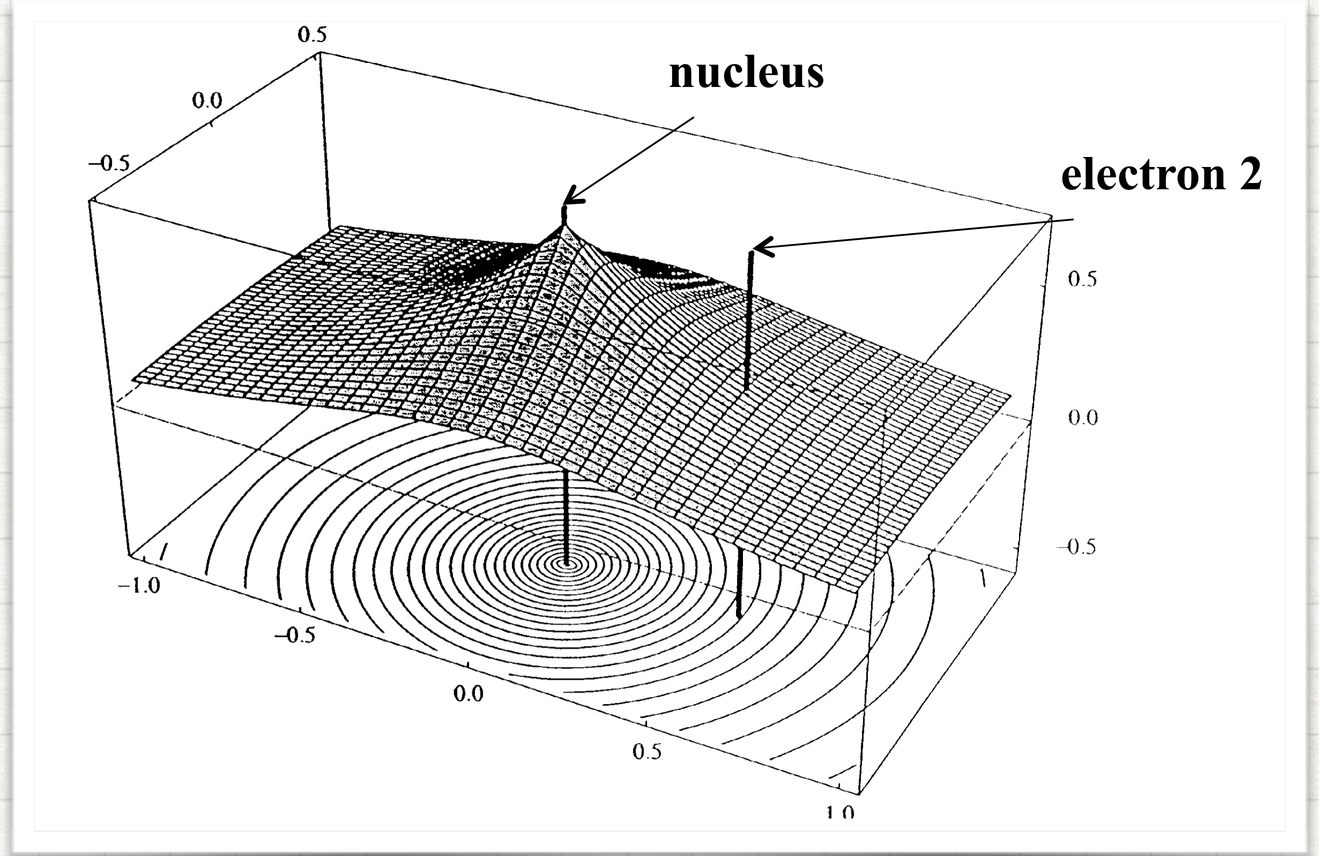
  Thus, their position probabilities are ***uncorrelated***.

- However, the Hartree-Fock pair density for ***same-spin*** electrons is correlated because of wave function antisymmetry – the "Fermi hole."

HARTREE-FOCK THEORY: HELIUM ATOM

- This figure‡ plots the Hartree-Fock wave function for the ground state of the helium atom (^1S) as a function of the coordinates of electron 1 (*i.e.* for a fixed position of electron 2).

- The motion of the electrons is completely independent of one another.



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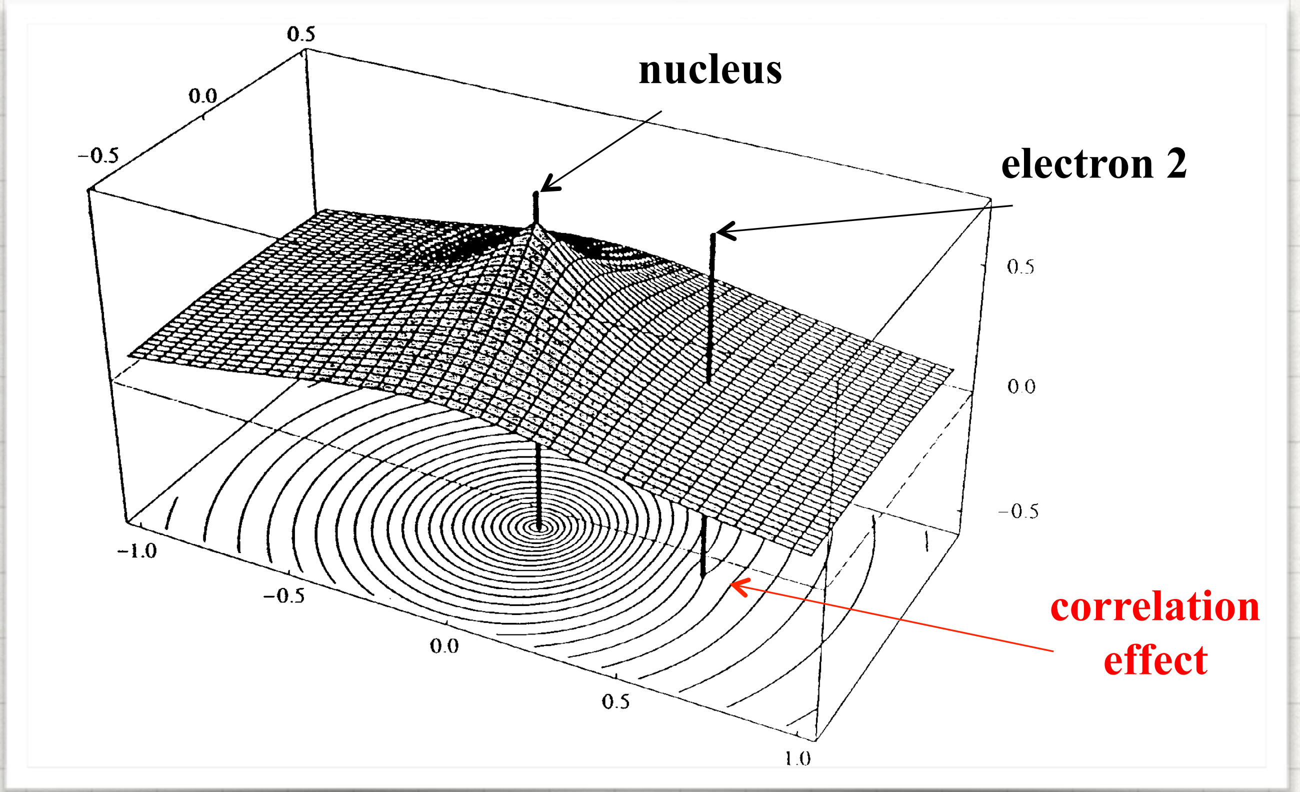
‡"Borrowed" from Prof. Jürgen Gauss

EXACT WAVE FUNCTION: HELIUM ATOM

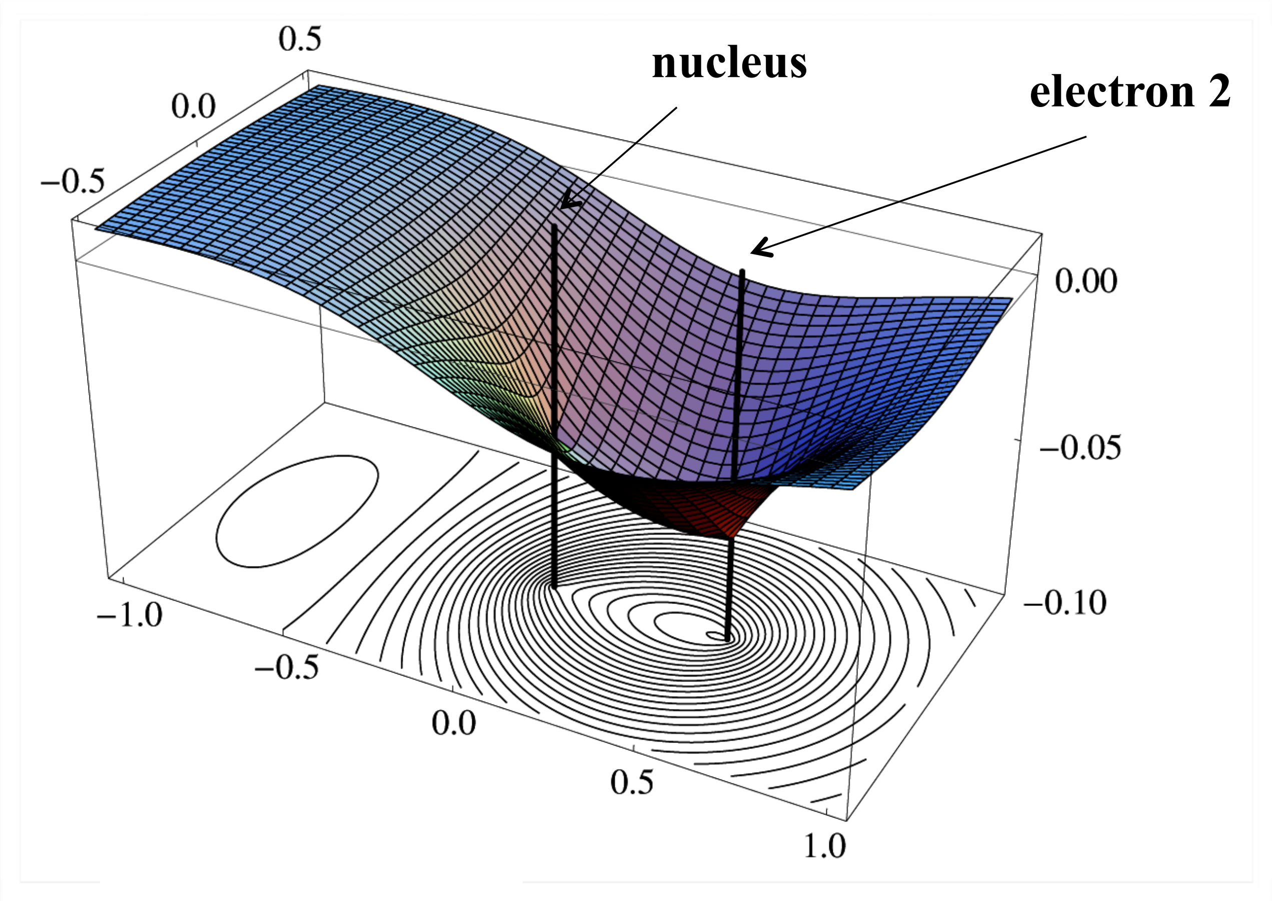
- This figure[‡] plots the exact wave function for the ground state of the helium atom (^1S) as a function of the coordinates of electron 1 (*i.e.* for a fixed position of electron 2).
- We observe a "small" deviation in the wave function as electron 1 approaches electron 2.
- This is a purely correlation effect.



[‡] Also "borrowed" from Prof. Jürgen Gauss

THE COULOMB HOLE

- This figure[‡] plots the ***difference*** between the exact and Hartree-Fock wave functions for the ground state of the helium atom (^1S), again as a function of the coordinates of electron 1 (*i.e.* for a fixed position of electron 2).
- This perspective makes the appearance of the Coulomb hole more pronounced.



[‡] Yes, another "borrowed" from Prof. Jürgen Gauss

CORRELATION ERRORS IN HARTREE-FOCK THEORY

- The first ionization energy of the helium atom ground state provides a good example of the importance of correlation energy.

- The Hartree-Fock energy of the helium atom ground state is:[a]

$$\langle \Phi_0(\mathrm{He}\ {}^1S)|\hat{H}|\Phi_0(\mathrm{He}\ {}^1S)\rangle \approx -2.861\ 679\ 995\ 612\ E_h$$

- The "exact" (non-relativistic, Born-Oppenheimer) energy of the helium atom ground state is:[b]

$$\langle \Psi(\mathrm{He}\ {}^1S)|\hat{H}|\Psi(\mathrm{He}\ {}^1S)\rangle \approx -2.903\ 724\ 377\ 034\ E_h$$

- The "exact" (non-relativistic, Born-Oppenheimer) energy of the helium cation is:[b]

$$\langle \Psi(\mathrm{He}^+\ {}^2S)|\hat{H}|\Psi(\mathrm{He}^+\ {}^2S)\rangle = -\frac{Z^2}{2} = -2\ E_h$$

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[a] K. Szalewicz and H. J. Monkhorst, J. Chem. Phys., 76, 5785-5788 (1981).

[b] H. Nakashima and H. Nakatsuji, Phys. Rev. Lett., 101, 240406 (2008).

CORRELATION ERRORS IN HARTREE-FOCK THEORY

- The Hartree-Fock model predicts that the first ionization potential of the helium atom ground state is:

$$\mathrm{IP}_{\mathrm{HF}} = E(\mathrm{He}^{+}\ {}^{2}S) - E(\mathrm{He}\ {}^{1}S) = 0.8617\ E_h = 2262.\ \mathrm{kJ/mol}$$

- This compares poorly to the exact value:

$$\mathrm{IP}_{\mathrm{exact}} = E(\mathrm{He}^{+}\ {}^{2}S) - E(\mathrm{He}\ {}^{1}S) = 0.9037\ E_h = 2372.\ \mathrm{kJ/mol}$$

- A 2001 study by Korobov and Yelkhovsky[a] determined that the effects of (non-Born-Oppenheimer) nuclear recoil, relativity, and quantum electrodynamics account for only ~0.4 kJ/mol of the total ionization energy.

- Thus bulk of the error is due to the ***lack of electron correlation*** in the Hartree-Fock prediction.

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[a] V. Korobov and A. Yelkhovsky, Phys. Rev. Lett., 87, 193001 (2001).

IMPORTANCE OF ELECTRON CORRELATION

While correlation energies are typically <1% of the total energy, errors in the correlation energy can be magnified when computing energy differences:

$$\mathrm{CO}(^1\Sigma^+) \rightarrow \mathrm{C}(^3\mathrm{P}) + \mathrm{O}(^3\mathrm{P})$$

	C (E_h)	**O (E_h)**	**CO (E_h)**	**D_e (kJ/mol)**
E_{HF}	-37.693 774	-74.819 232	-112.790 997	729.9
E_{corr}	-0.151 537	-0.248 978	-0.535 591	357.3
E_{total}	-37.845 307	-75.068 210	-113.327 588	1087.2

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[a] Even **more** data "borrowed" from Prof. Jürgen Gauss.

COMPUTING ELECTRON CORRELATION ENERGIES

What approaches are there to including electron correlation effects in our quantum chemical models?

- Density-Functional Theory (DFT)
  - LSDA, BLYP, B3LYP, CAM-B3LYP, PBE, SAOP, M06-L, …
- Configuration Interaction (CI)
  - CISD, MR-CI, RAS-CI, …
- Many-Body/Møller-Plesset Perturbation Theory (MBPT/MPn)
  - MP2, SDQ-MP4, CASPT2, GVV-PT2, …
- Coupled Cluster Theory
  - CC2, CCSD, CCSD(T), CC3, CCSDT, …

Almost all commonly used techniques in the chemical physics literature are based on these four approaches, and each has its own advantages and disadvantages.

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INTRODUCING CORRELATION EFFECTS

- Consider a four-electron Slater determinant:

$$\Phi_0 = |\phi_i(\mathbf{x}_1)\phi_j(\mathbf{x}_2)\phi_k(\mathbf{x}_3)\phi_l(\mathbf{x}_4)\rangle$$

From this point forward, we'll use *i*, *j*, *k*, *l*, … to denote orbitals that are occupied in the Hartree-Fock wave function, *a*, *b*, *c*, *d*, … to denote unoccupied/virtual orbitals, and *p*, *q*, *r*, *s*, … to denote general orbitals.

- Any function of *N* variables may be written as a linear combination of unique *N*-tuple products of the $\phi_p(\mathbf{x})$ on the same space as the full set of functions:

$$f(\mathbf{x}_1, \mathbf{x}_2) = \sum_{p>q} c_{pq}\phi_p(\mathbf{x}_1)\phi_q(\mathbf{x}_2)$$

- However, we must treat the electrons as indistinguishable, so instead we could write a pairwise "cluster function" that correlates the motion of ***any*** pair of electrons associated with two particular occupied orbitals, *e.g.*, *i* and *j:*

$$f_{ij}(\mathbf{x}_m, \mathbf{x}_n) = \sum_{a>b} t_{ij}^{ab}\phi_a(\mathbf{x}_m)\phi_b(\mathbf{x}_n)$$

INTRODUCING CORRELATION EFFECTS

- Inserting this cluster function into our Hartree-Fock wave function yields an improved function:

  $$\Psi = |\left[\phi_i(\mathbf{x}_1)\phi_j(\mathbf{x}_2) + f_{ij}(\mathbf{x}_1, \mathbf{x}_2)\right]\phi_k(\mathbf{x}_3)\phi_l(\mathbf{x}_4)\rangle$$

  where the determinant notation implies proper antisymmetry and normalization of the individual terms. Expanding the expression gives:

  $$\Psi = \Phi_0 + \sum_{a>b} t_{ij}^{ab}|\phi_a(\mathbf{x}_1)\phi_b(\mathbf{x}_2)\phi_k(\mathbf{x}_3)\phi_l(\mathbf{x}_4)\rangle$$

- We could also have chosen to correlate electrons appearing in any other pair of occupied orbitals, *e.g.*, *k* and *l*:

  $$\Psi = |\phi_i(\mathbf{x}_1)\phi_j(\mathbf{x}_2)\left[\phi_k(\mathbf{x}_3)\phi_l(\mathbf{x}_4) + f_{kl}(\mathbf{x}_3, \mathbf{x}_4)\right]\rangle$$

  which would give a similar expression:

  $$\Psi = \Phi_0 + \sum_{a>b} t_{kl}^{ab}|\phi_i(\mathbf{x}_1)\phi_j(\mathbf{x}_2)\phi_a(\mathbf{x}_3)\phi_b(\mathbf{x}_4)\rangle$$

INTRODUCING CORRELATION EFFECTS

- Perhaps a better approach would be to introduce all possible pairwise combinations of occupied orbitals in our four-electron system:

$$\Phi = |\phi_i\phi_j\phi_k\phi_l\rangle + |f_{ij}\phi_k\phi_l\rangle - |f_{ik}\phi_j\phi_l\rangle + |f_{il}\phi_j\phi_k\rangle + |\phi_i f_{jk}\phi_l\rangle - |\phi_i f_{jl}\phi_k\rangle + |\phi_i\phi_j f_{kl}\rangle + |f_{ij}f_{kl}\rangle - |f_{ik}f_{jl}\rangle + |f_{il}f_{jk}\rangle$$

  where the electron coordinates are now implied, and the negative signs arise naturally from the definition of the determinant whenever we have to permute columns to bring two occupied orbitals together.

- We could also go beyond pairs and introduce three-electron cluster functions:

$$\Phi = |\phi_i\phi_j\phi_k\phi_l\rangle + |f_{ij}\phi_k\phi_l\rangle - |f_{ik}\phi_j\phi_l\rangle + |f_{il}\phi_j\phi_k\rangle + |\phi_i f_{jk}\phi_l\rangle - |\phi_i f_{jl}\phi_k\rangle + |\phi_i\phi_j f_{kl}\rangle + |f_{ij}f_{kl}\rangle - |f_{ik}f_{jl}\rangle + |f_{il}f_{jk}\rangle + |f_{ijk}\phi_l\rangle - |f_{ijl}\phi_k\rangle + |f_{ikl}\phi_j\rangle + |\phi_i f_{jkl}\rangle$$

- If we include all possible *N*-electron cluster functions, we would obtain the ***exact wave function*** within the space spanned by the $\phi_p(\mathbf{x})$.

INTRODUCING CORRELATION EFFECTS

- Alternatively, we could assume that clusters of three or more electrons are less important than pairs, and that we should define single-orbital “clusters” to account for the fact that the orbitals should adjust for the presence of the new terms:

$$
\begin{aligned}
\Psi = {} & |\phi_i\phi_j\phi_k\phi_l\rangle + |f_i\phi_j\phi_k\phi_l\rangle + |\phi_i f_j\phi_k\phi_l\rangle + |\phi_i\phi_j f_k\phi_l\rangle + |\phi_i\phi_j\phi_k f_l\rangle + \\
& |f_i f_j\phi_k\phi_l\rangle + |f_i\phi_j f_k\phi_l\rangle + |f_i\phi_j\phi_k f_l\rangle + |\phi_i f_j f_k\phi_l\rangle + |\phi_i f_j\phi_k f_l\rangle + \\
& |\phi_i\phi_j f_k f_l\rangle + |f_i f_j f_k\phi_l\rangle + |f_i f_j\phi_k f_l\rangle + |f_i\phi_j f_k f_l\rangle + |\phi_i f_j f_k f_l\rangle + \\
& |f_{ij}\phi_k\phi_l\rangle - |f_{ik}\phi_j\phi_l\rangle + |f_{il}\phi_j\phi_k\rangle + |\phi_i f_{jk}\phi_l\rangle - |\phi_i f_{jl}\phi_k\rangle + \\
& |\phi_i\phi_j f_{kl}\rangle + |f_{ij} f_{kl}\rangle - |f_{ik} f_{jl}\rangle + |f_{il} f_{jk}\rangle + |f_i f_j f_k f_l\rangle + \\
& |f_{ij} f_k\phi_l\rangle + |f_{ij}\phi_k f_l\rangle + |f_{ij} f_k f_l\rangle - |f_{ik} f_j\phi_l\rangle - |f_{ik}\phi_j f_l\rangle - |f_{ik} f_j f_l\rangle + \\
& |f_{il} f_j\phi_l\rangle + |f_{il}\phi_j f_l\rangle + |f_{il} f_j f_l\rangle + |f_i f_{jk}\phi_l\rangle + |\phi_i f_{jk} f_l\rangle + |f_i f_{jk} f_l\rangle - \\
& |f_i f_{jl}\phi_k\rangle - |\phi_i f_{jl} f_k\rangle - |f_i f_{jl} f_k\rangle + |f_i\phi_j f_{kl}\rangle + |\phi_i f_j f_{kl}\rangle + |f_i f_j f_{kl}\rangle
\end{aligned}
$$

- Clearly we need a new notation…

CLUSTER OPERATORS

- The 27th term on the right-hand side of our complicated expression can be written more explicitly as:

$$|f_{ij}\phi_k f_l\rangle = \sum_{a>b}\sum_{c} t_{ij}^{ab} t_l^c |\phi_a\phi_b\phi_k\phi_c\rangle$$

  This is a linear combination of determinants in which orbitals *i*, *j*, and *l* have been replaced by orbitals *a*, *b*, and *c*, respectively.

- This is conveniently expressed in second quantization by defining single- and double-orbital "cluster operators":

$$\hat{t}_i \equiv \sum_a t_i^a a_a^\dagger a_i \qquad \text{and} \qquad \hat{t}_{ij} \equiv \sum_{a>b} t_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i$$

- Thus, the 27th term on the right-hand side of our complicated expression becomes very compact:

$$|f_{ij}\phi_k f_l\rangle = \hat{t}_{ij}\hat{t}_l|\Phi_0\rangle$$

CLUSTER OPERATORS

- Using these cluster operators, our complicated four-electron wave function becomes:

$$\Psi = \left(1 + \sum_i \hat{t}_i + \frac{1}{2}\sum_{ij}\hat{t}_i\hat{t}_j + \frac{1}{6}\sum_{ijk}\hat{t}_i\hat{t}_j\hat{t}_k + \frac{1}{2}\sum_{ij}\hat{t}_{ij} + \right.$$

$$\left. \frac{1}{8}\sum_{ijkl}\hat{t}_{ij}\hat{t}_{kl} + \frac{1}{24}\sum_{ijkl}\hat{t}_i\hat{t}_j\hat{t}_k\hat{t}_l + \frac{1}{2}\sum_{ijk}\hat{t}_{ij}\hat{t}_k + \frac{1}{4}\sum_{ijkl}\hat{t}_{ij}\hat{t}_k\hat{t}_l\right)\Phi_0$$

- We can make the expression even simpler, though, by introducing total cluster operators by summing over combinations of occupied orbitals:

$$\hat{T}_1 \equiv \sum_i \hat{t}_i = \sum_{ia} t_i^a a_a^\dagger a_i \quad \text{and} \quad \hat{T}_2 \equiv \frac{1}{2}\sum_{ij}\hat{t}_{ij} = \frac{1}{4}\sum_{ijab} t_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i$$

- More generally:

$$\hat{T}_n = \left(\frac{1}{n!}\right)^2 \sum_{ij\ldots ab\ldots}^{n} t_{ij\ldots}^{ab\ldots} a_a^\dagger a_b^\dagger \ldots a_j a_i$$

THE COUPLED CLUSTER WAVE FUNCTION

- Note well two key observations:
  1. Because all the creation operators act on unoccupied orbitals and all the annihilation operators act on occupied orbitals, they exactly anti-commute:
  $$a_a^\dagger a_i + a_i a_a^\dagger = \delta_{ia} = 0$$
  2. Because the total cluster operators always contain even numbers of creation and annihilation operators, they always commute, *e.g.*:
  $$\hat{T}_1\hat{T}_2 = \hat{T}_2\hat{T}_1$$
- Thus, our four-electron wave function becomes:

$$\Psi = \left(1 + \hat{T}_1 + \frac{1}{2!}\hat{T}_1^2 + \frac{1}{3!}\hat{T}_1^3 + \hat{T}_2 + \frac{1}{2!}\hat{T}_2^2 + \frac{1}{4!}\hat{T}_1^4 + \hat{T}_2\hat{T}_1 + \frac{1}{2!}\hat{T}_2\hat{T}_1^2\right)\Phi_0$$

- These terms all appear in the power-series expansion of an exponential!

$$\Psi = e^{\hat{T}_1+\hat{T}_2}\Phi_0 \equiv e^{\hat{T}}\Phi_0$$

- This is a concise expression for the ***coupled cluster*** wave function.

COUPLED CLUSTER METHODS

- A hierarchy of coupled cluster methods may be defined based on the truncation of the $\hat{T}$ operator:

Method	$\hat{T}$	Scaling/Cost
CCS	$\hat{T} = \hat{T}_1$	$\mathcal{O}(N^5)$
CCD	$\hat{T} = \hat{T}_2$	$\mathcal{O}(N^6)$
CCSD	$\hat{T} = \hat{T}_1 + \hat{T}_2$	$\mathcal{O}(N^6)$
CCSDT	$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3$	$\mathcal{O}(N^8)$
CCSDTQ	$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_4$	$\mathcal{O}(N^{10})$

- Later we will examine other coupled cluster methods that approximate higher order correlation effects using perturbational approaches.

FORMAL COUPLED CLUSTER THEORY

- We have a general structure of the coupled cluster wave function, but we need a recipe for determining the wave function amplitudes. Start from the Schrödinger equation:

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

- Insert the coupled cluster *Ansatz* (roughly: German for "approach"):

$$\hat{H}e^{\hat{T}}|\Phi_0\rangle = Ee^{\hat{T}}|\Phi_0\rangle$$

- "Project" this equation onto the Hartree-Fock determinant to obtain an expression for the energy:

$$\langle\Phi_0|\hat{H}e^{\hat{T}}|\Phi_0\rangle = E\langle\Phi_0|e^{\hat{T}}|\Phi_0\rangle = E$$

- Or onto substituted (or "excited") determinants to obtain equations for the amplitudes:

$$\langle\Phi_{ij\dots}^{ab\dots}|\hat{H}e^{\hat{T}}|\Phi_0\rangle = E\langle\Phi_{ij\dots}^{ab\dots}|e^{\hat{T}}|\Phi_0\rangle$$

NB: the "excited" determinant notation is to avoid specifying the number of electrons/orbitals:

$$|\Phi_{ij\dots}^{ab\dots}\rangle = a_a^\dagger a_b^\dagger \dots a_j a_i |\Phi_0\rangle$$

TRUNCATION OF THE EXPONENTIAL

- Start from our energy equation:

$$\langle \Phi_0 | \hat{H} e^{\hat{T}} | \Phi_0 \rangle = E \langle \Phi_0 | e^{\hat{T}} | \Phi_0 \rangle = E$$

- Insert the power-series expansion of the exponential:

$$\langle \Phi_0 | \hat{H} (1 + \hat{T} + \frac{\hat{T}^2}{2!} + \frac{\hat{T}^3}{3!} + \ldots) | \Phi_0 \rangle = E$$

- And distribute terms:

$$\langle \Phi_0 | \hat{H} | \Phi_0 \rangle + \langle \Phi_0 | \hat{H} \hat{T} | \Phi_0 \rangle + \langle \Phi_0 | \hat{H} \frac{\hat{T}^2}{2!} | \Phi_0 \rangle + \langle \Phi_0 | \hat{H} \frac{\hat{T}^3}{3!} | \Phi_0 \rangle + \ldots = E$$

- Slater's rules state that matrix elements of the Hamiltonian between determinants that differ by more than two orbitals are zero, thus the cubic and higher terms cannot contribute, and the energy expression is simply:

$$\langle \Phi_0 | \hat{H} | \Phi_0 \rangle + \langle \Phi_0 | \hat{H} \hat{T} | \Phi_0 \rangle + \langle \Phi_0 | \hat{H} \frac{\hat{T}^2}{2!} | \Phi_0 \rangle = E$$

- This expression is *exact*: it depends only on the two-electron nature of the Hamiltonian and does not depend on the particular truncation of the cluster operator.

THE SIMILARITY-TRANSFORMED HAMILTONIAN

- We can take a better approach to the coupled cluster equations by multiplying the coupled-cluster Schrödinger equation by the *inverse* of the exponential:

$$e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Phi_0\rangle = e^{-\hat{T}}Ee^{\hat{T}}|\Phi_0\rangle = E|\Phi_0\rangle$$

- Now project onto the Hartree-Fock reference to obtain the energy:

$$\boxed{\langle\Phi_0|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Phi_0\rangle = E}$$

- And onto excited determinants to obtain the equations for the amplitudes:

$$\boxed{\langle\Phi_{ij\ldots}^{ab\ldots}|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Phi_0\rangle = 0}$$

- The similarity transformation yields the Cambell-Baker-Hausdorff expansion:

$$e^{-\hat{T}}\hat{H}e^{\hat{T}} = \hat{H} + \left[\hat{H},\hat{T}\right] + \frac{1}{2!}\left[\left[\hat{H},\hat{T}\right],\hat{T}\right] + \frac{1}{3!}\left[\left[\left[\hat{H},\hat{T}\right],\hat{T}\right],\hat{T}\right] + \frac{1}{4!}\left[\left[\left[\left[\hat{H},\hat{T}\right],\hat{T}\right],\hat{T}\right],\hat{T}\right] + \ldots$$

HOW IS THIS BETTER???

- The Hamiltonian contains one- and two-electron second-quantized operators:

$$\hat{H} = \sum_{pq} h_{pq} a_p^\dagger a_q + \frac{1}{4} \sum_{pqrs} \langle pq || rs \rangle a_p^\dagger a_q^\dagger a_s a_r = \hat{h} + \hat{V}$$

- Assuming the cluster operators commute, each commutator in the Hausdorff expansion between $\hat{H}$ and $\hat{T}$ eliminates one general-orbital annihilation/creation operator. For example:

$$\begin{aligned} \left[\hat{h}, \hat{T}_1\right] &\rightarrow [a_p^\dagger a_q, a_a^\dagger a_i] \\ &= a_p^\dagger a_q a_a^\dagger a_i - a_a^\dagger a_i a_p^\dagger a_q \\ &= a_p^\dagger \delta_{qa} a_i - a_a^\dagger \delta_{ip} a_q \end{aligned}$$

- Because the the second-quantized Hamiltonian contains at most four annihilation/creation operators, the Hausdorff expansion will truncate after the ***quadruply nested commutator***. This result assumes that the $\hat{T}$ operators commute, but doesn't depend on the truncation of $\hat{T}$.

VARIATIONAL COUPLED CLUSTER THEORY

- Our "projective" formulation of the coupled cluster equations results in a non-variational energy expression. However, we could have taken a different approach by minimizing a variational expression:

$$E_{exact} \leq E = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \frac{\langle \Phi_0 | (e^{\hat{T}})^{\dagger} \hat{H} e^{\hat{T}} | \Phi_0 \rangle}{\langle \Phi_0 | (e^{\hat{T}})^{\dagger} e^{\hat{T}} | \Phi_0 \rangle}$$

- The adjoint operation changes the "excitation" operator $\hat{T}$ into a "de-excitation" operator $\hat{T}^{\dagger}$:

$$\hat{T}_n^{\dagger} = \left(\frac{1}{n!} \right)^2 \sum_{ij\ldots ab\ldots}^{n} t_{ab\ldots}^{ij\ldots} a_i^{\dagger} a_j^{\dagger} \ldots a_b a_a$$

- The $\hat{T}$ and $\hat{T}^{\dagger}$ operators do not commute: $\left[\hat{T}^{\dagger}, \hat{T} \right] \neq 0$ Thus, the variational expressions ***do not truncate naturally*** and must be cut off at some selected number of terms. The unitary coupled cluster (UCC)[a,b] and expectation value coupled cluster (XCC)[c] methods are based on this approach.

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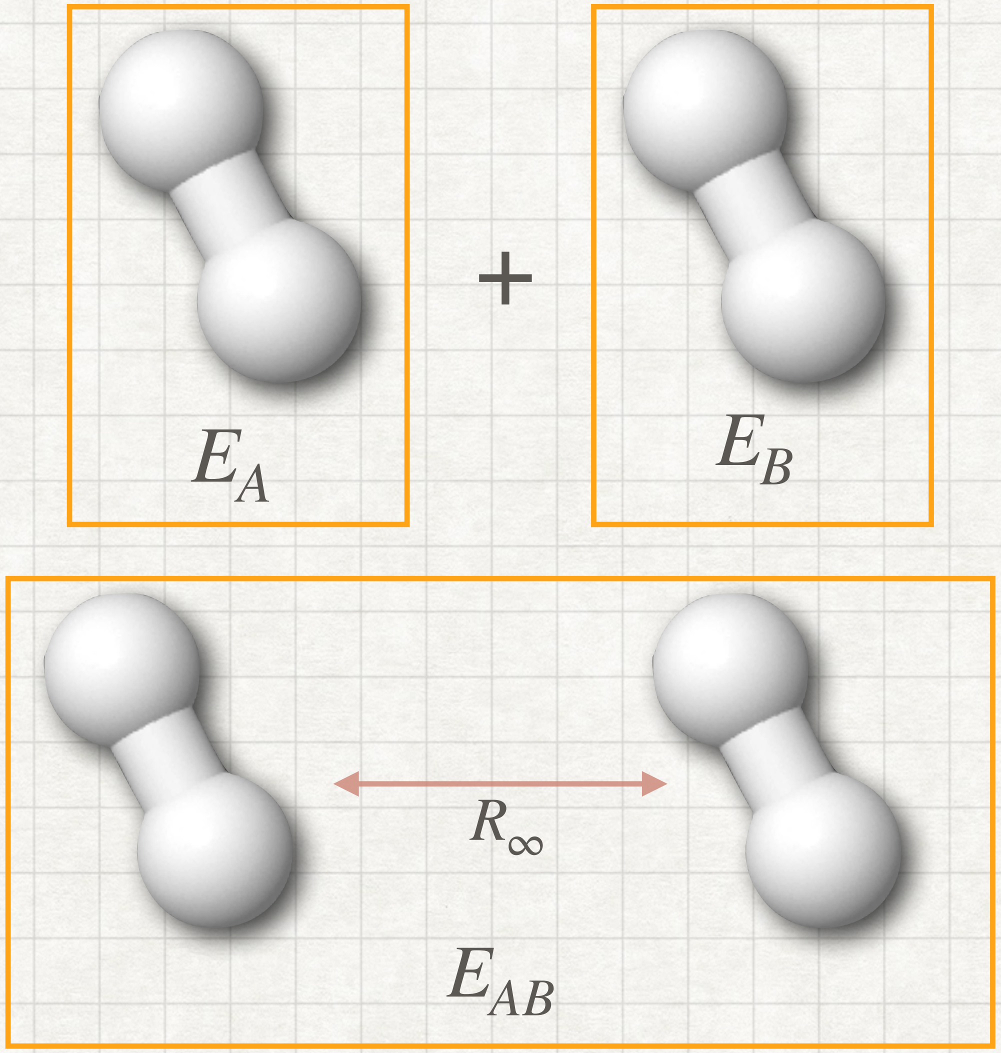
[a] M. R. Hoffmann and J. Simons,J. Chem. Phys., 88,993 (1988). [b] R. J. Bartlett, S. A. Kucharski, and J. Noga, Chem. Phys. Lett., 155, 133 (1989). [c] R. J. Bartlett and J. Noga, Chem. Phys. Lett., 150, 29 (1988).

SIZE CONSISTENCY

- A quantum chemical method is “size consistent” if the sum of the energies computed individually for two or more systems is equal to the energy computed of the supersystem containing all non-interacting systems.



Sum of separate calculations on each fragment

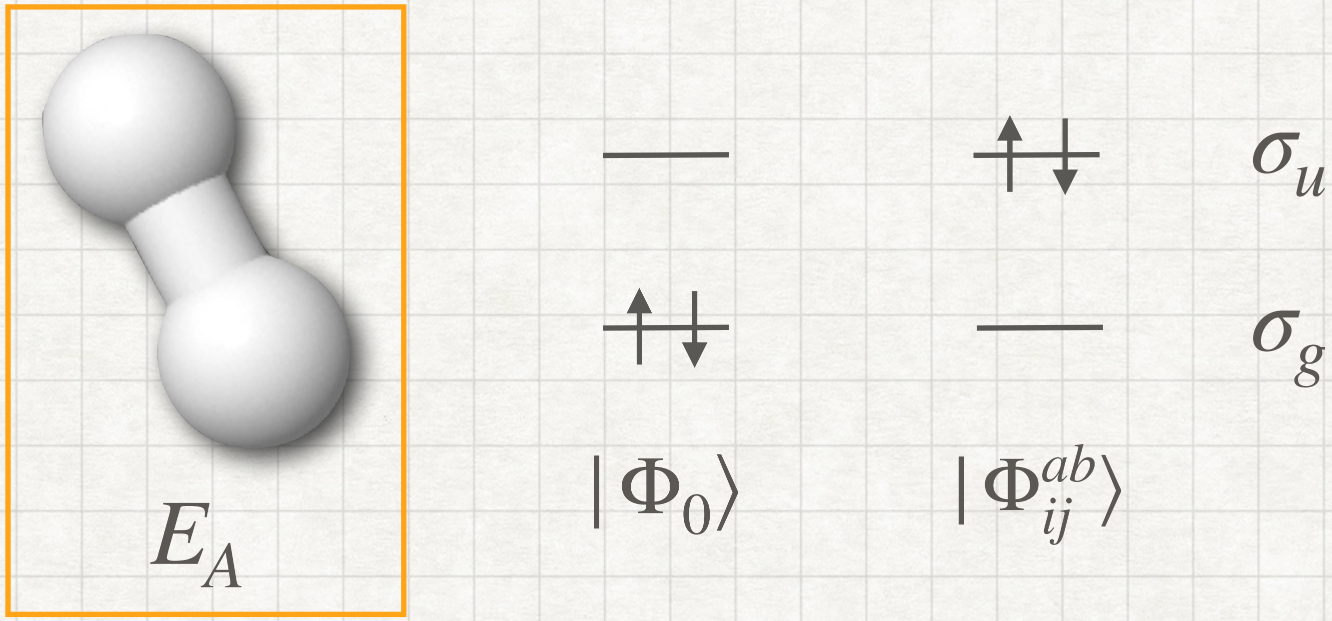
A single calculation on both fragments: “supermolecule"

- For this property to hold, the wave function must be ***multiplicatively separable***:

$$|\Psi^{AB}\rangle = \mathcal{A}|\Psi^{A}\rangle|\Psi^{B}\rangle$$

EXAMPLE: H_2 DIMER

- Consider two hydrogen molecules separated by a large distance such that they do not interact. For a single H_2 molecule in a minimal basis set (two orbitals), only two determinants are needed due to symmetry:

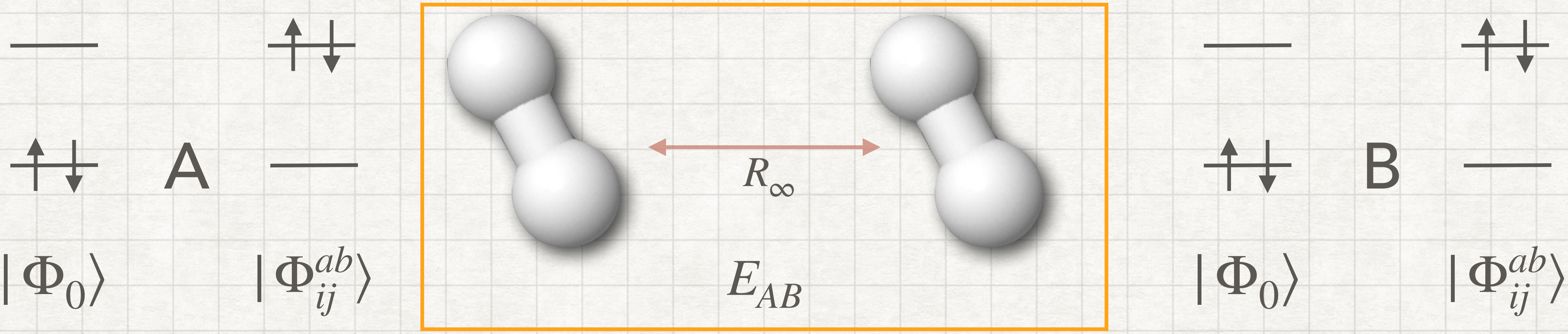


$$|\Psi\rangle_{\text{exact}} = |\Psi\rangle_{\text{CID}} = \left(1+\hat{T}_2^A\right)|\Phi_0^A\rangle$$

- The "configuration interaction doubles” (CID) wave function, in which only linear terms in the cluster expansion are retained, is exact in this case.

EXAMPLE: H_2 DIMER

- For two non-interacting hydrogen molecules, the exact wave function must include double excitations on ***both*** fragments simultaneously – a ***quadruple excitation***:

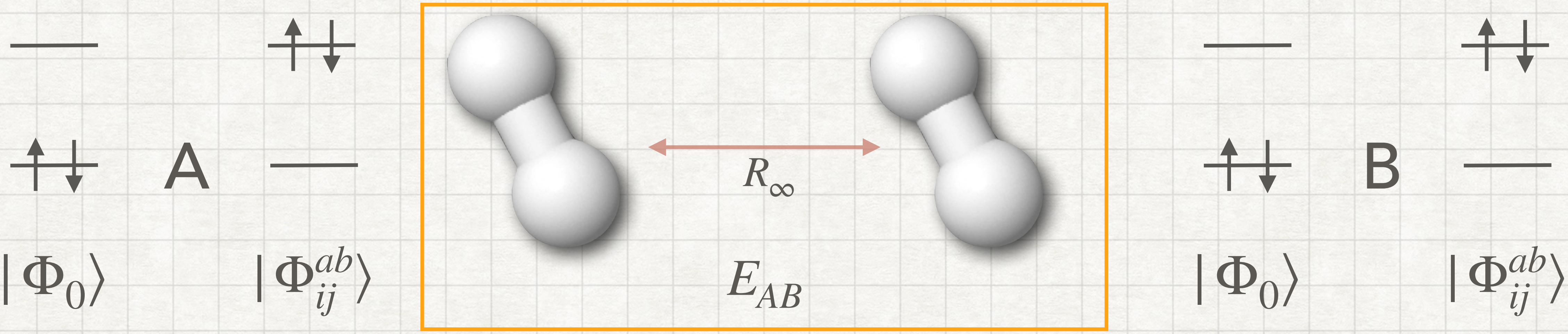


$$
\begin{aligned}
|\Psi\rangle^{AB}_{\text{exact}} &= \mathcal{A}\left\{\left(1+\hat{T}_2^A\right)|\Phi_0^A\rangle\right\} \times \left\{\left(1+\hat{T}_2^B\right)|\Phi_0^B\rangle\right\} \\
&= \left(1+\hat{T}_2^A+\hat{T}_2^B+\underline{\hat{T}_2^A\hat{T}_2^B}\right)|\Phi_0^{AB}\rangle \\
&\neq \left(1+\hat{T}_2^A+\hat{T}_2^B\right)|\Phi_0^{AB}\rangle \\
&= |\Psi\rangle^{AB}_{\text{CID}}
\end{aligned}
$$

- CID does not include this term and thus is ***not size consistent.***

EXAMPLE: H_2 DIMER

- For two non-interacting hydrogen molecules, the exact wave function must include double excitations on ***both*** fragments simultaneously – a ***quadruple excitation***:



$$
\begin{aligned}
|\Psi\rangle_{CCD}^{AB} &= \mathcal{A}\left\{e^{\hat{T}_2^A}|\Phi_0^A\rangle\right\} \times \left\{e^{\hat{T}_2^B}|\Phi_0^B\rangle\right\} \\
&= e^{\hat{T}_2^A} e^{\hat{T}_2^B} |\Phi_0^{AB}\rangle \\
&= e^{\hat{T}_2^A + \hat{T}_2^B} |\Phi_0^{AB}\rangle \\
&= |\Phi_{\mathrm{CCD}}^{AB}\rangle
\end{aligned}
$$

- CCD gives a multiplicatively separable wave function and thus is size consistent.

SIZE CONSISTENCY: DOES THIS MATTER?

- Energies and size-consistency errors (in E_h) for the H_2 dimer in an STO-3G basis set:

Method	$2 \times E_A$	E_{AB}	Δ
SCF	-2.221 701	-2.221 701	0.000 000
MP2	-2.250 907	-2.250 907	0.000 000
CCD	-2.268 295	-2.268 295	0.000 000
CID	-2.268 295	-2.267 587	-0.000 708 (-1.86 kJ/mol)

- The error will increase as the number of electrons and basis functions increase.

LOOKING AHEAD

In the upcoming lectures, we learn about:

- Two approaches to deriving explicit algebraic equations for the coupled cluster energy and wave function amplitudes that can be coded for real applications:
  - Second-quantization methods
  - Diagrammatic methods
- Size extensivity
- Perturbative approximations – CC2, CCSD(T), CC3
- Analytic energy gradients and molecular properties
- Electronic excited states