COUPLED CLUSTER THEORY

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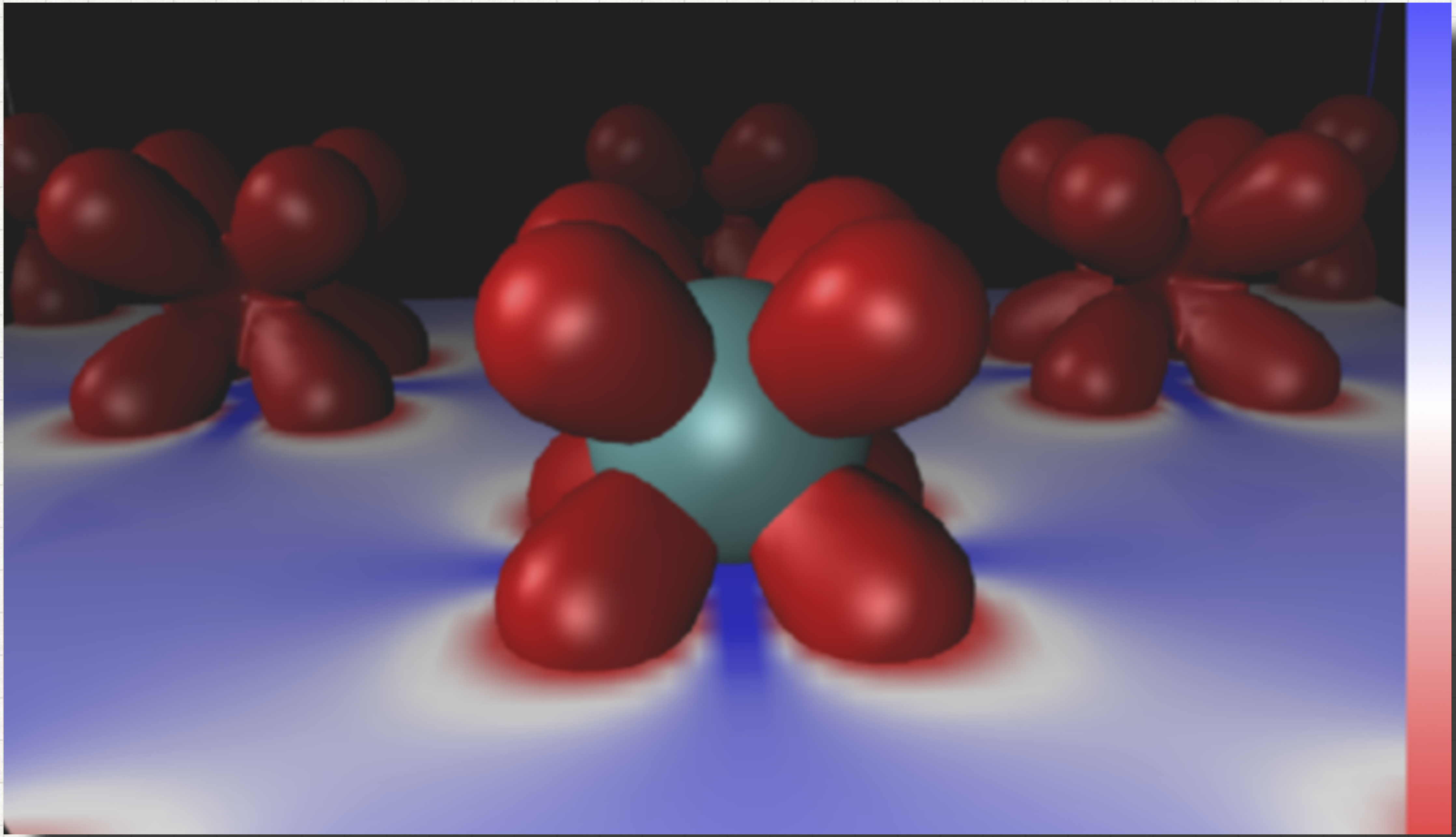


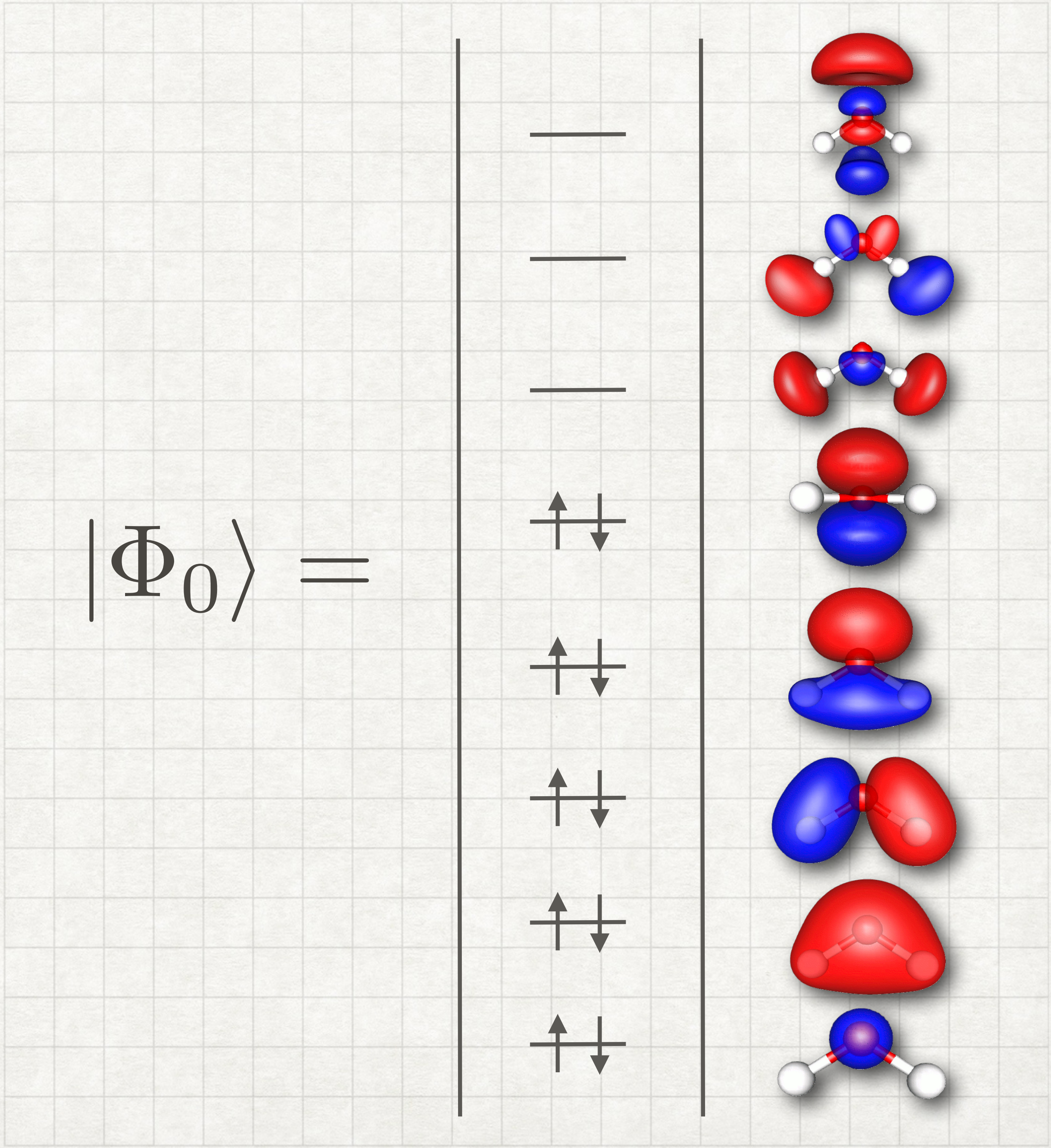
ALPHABET SOUP OF QUANTUM CHEMISTRY

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:

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

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

- 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:

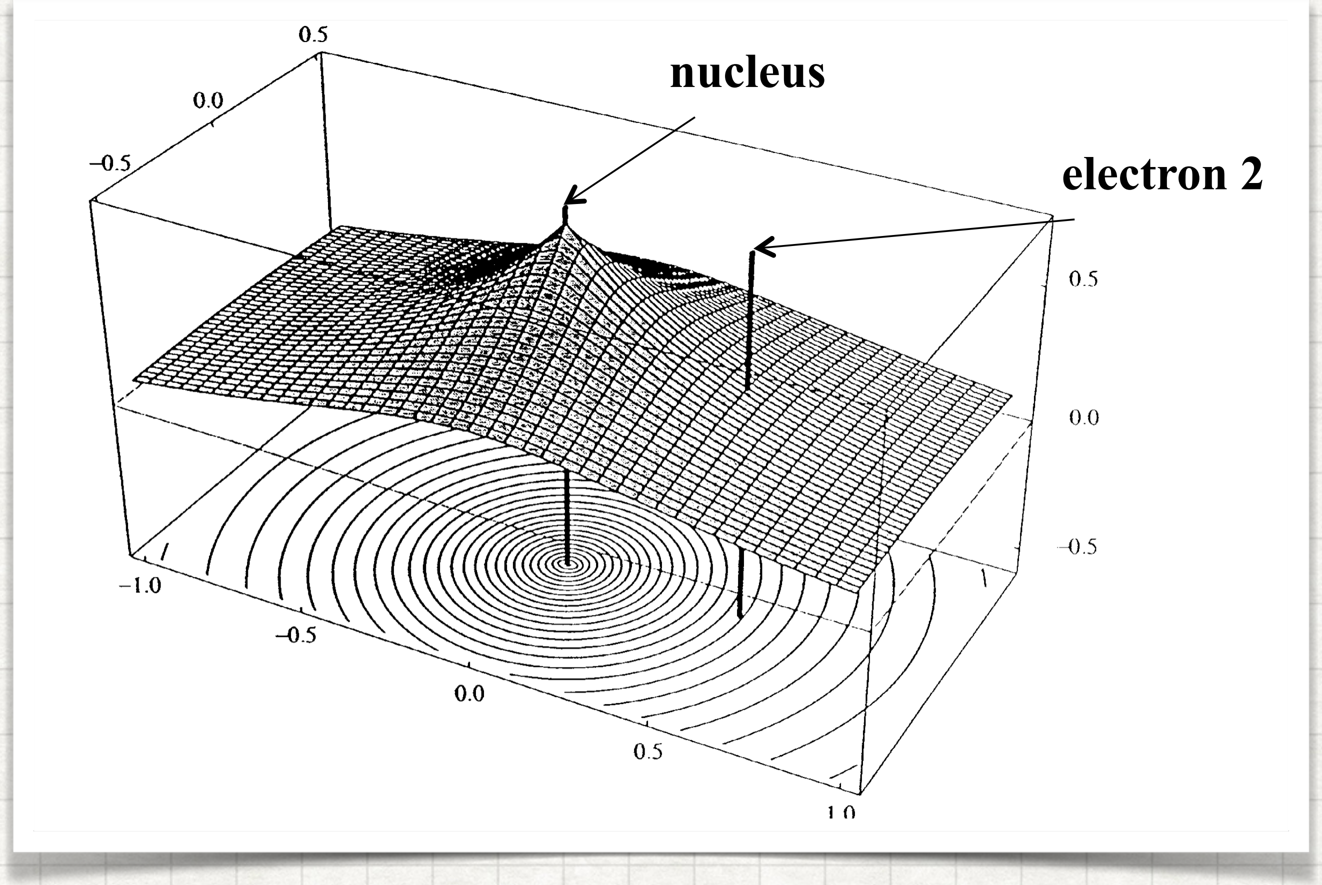
$$\rho_{\text{HF}}(\mathbf{x}_1, \mathbf{x}_2) = \rho(\mathbf{x}_1)\rho(\mathbf{x}_2)$$

  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

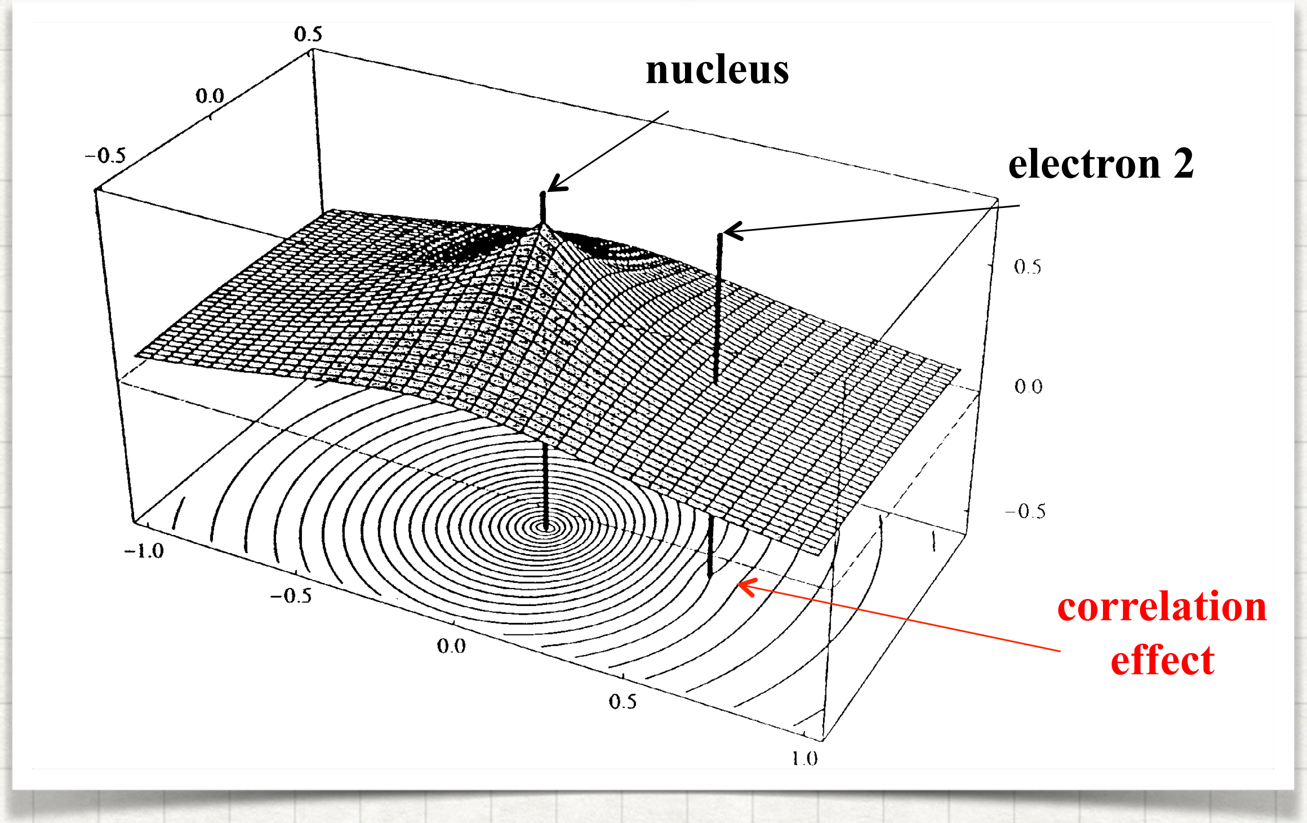
- This figure[‡] plots the Hartree-Fock wave function for the ground state of the helium atom (^1S) as a function of the coordinates of electron 1 (*i.e.* for a fixed position of electron 2).
- The motion of the electrons is completely independent of one another.



[‡] "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 (^{1}S) 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.



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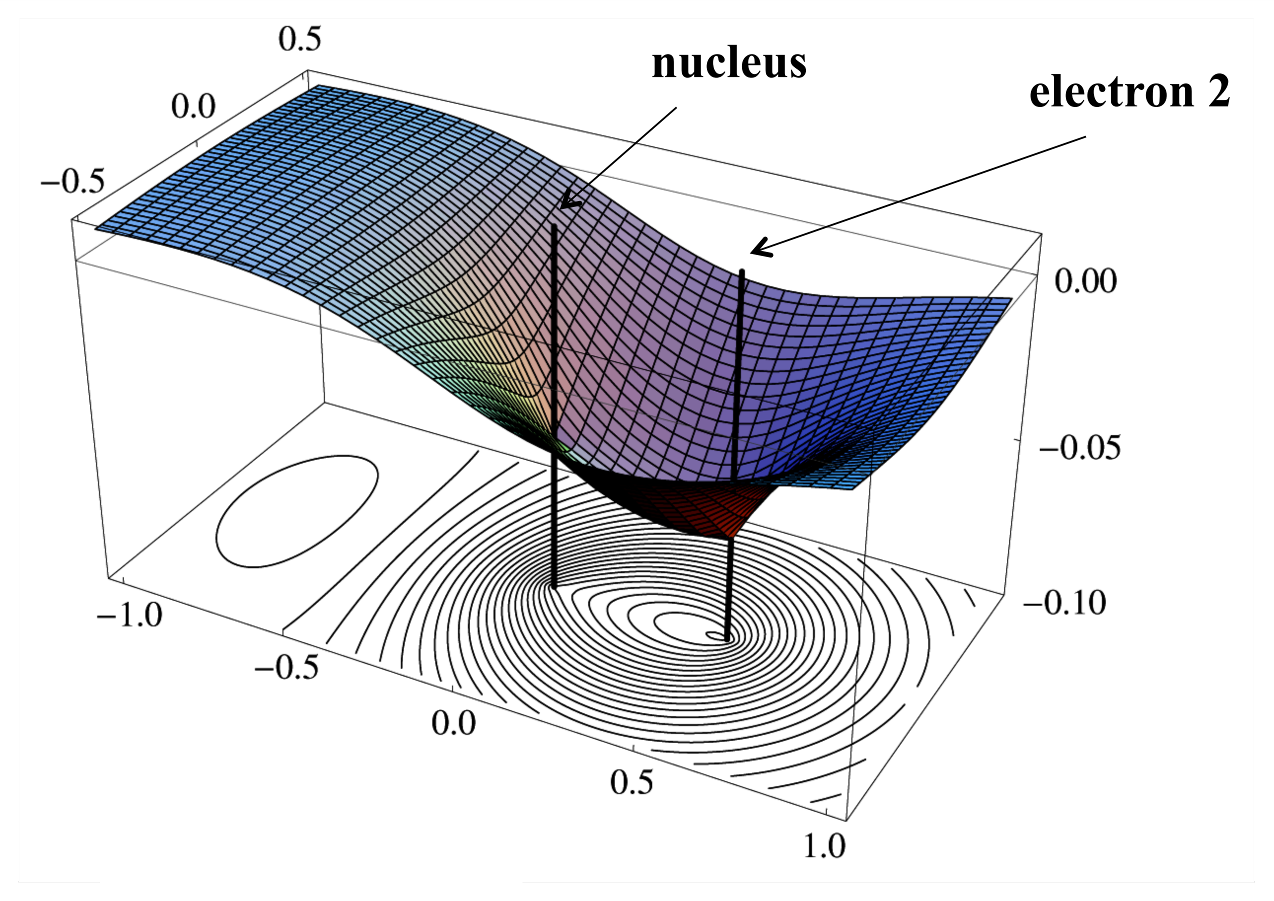
‡Also “borrowed” from Prof. Jürgen Gauss

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:

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

- 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:

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

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

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

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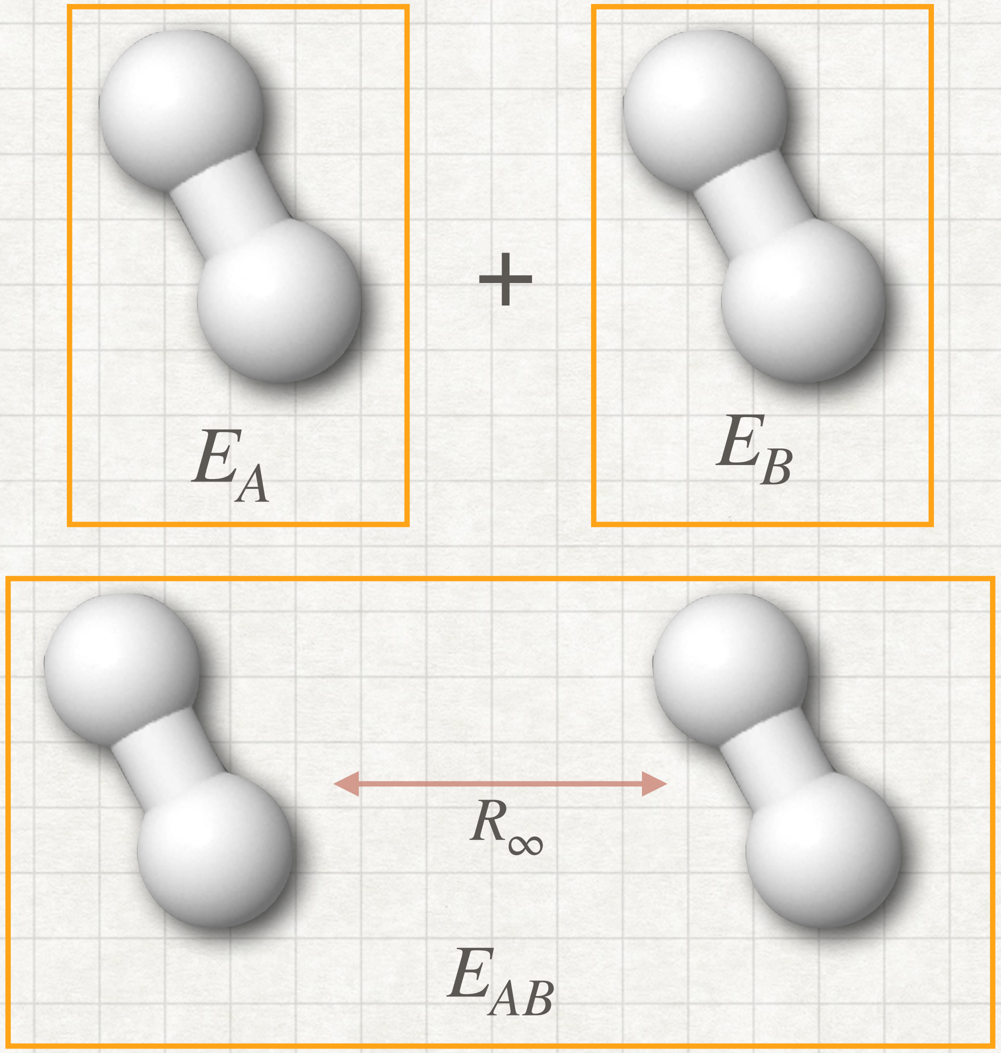
[a] M. R. Hoffmann and J. Simons,J. Chem. Phys., 88,993 (1988). [b] R. J. Bartlett, S. A. Kucharski, and J. Noga, Chem. Phys. Lett., 155, 133 (1989). [c] R. J. Bartlett and J. Noga, Chem. Phys. Lett., 150, 29 (1988).

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

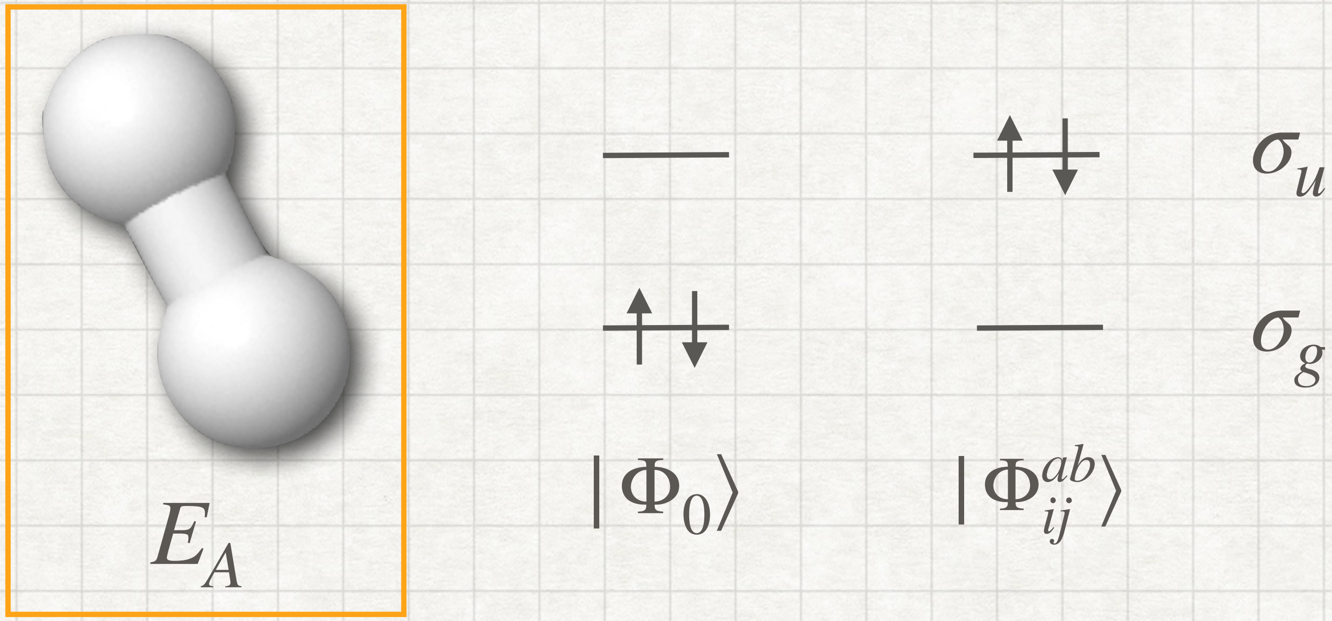
A single calculation on both fragments: "supermolecule"

- 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

- For a single H_2 molecule in a minimal basis set (two orbitals), only two determinants are needed due to symmetry:

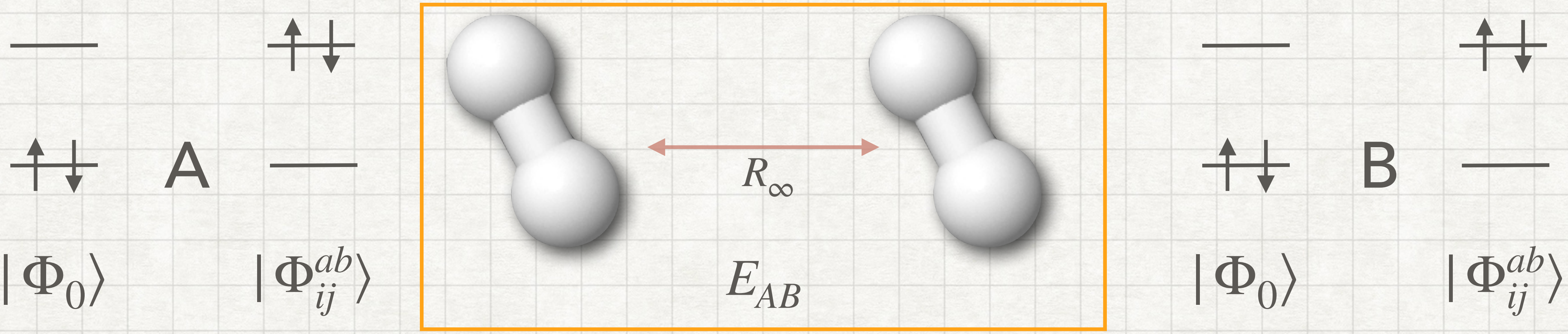


$$|\Psi\rangle_{\text{exact}} = |\Psi\rangle_{\text{CID}} = \left(1 + \hat{T}_2^A\right) |\Phi_0^A\rangle$$

- 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***:

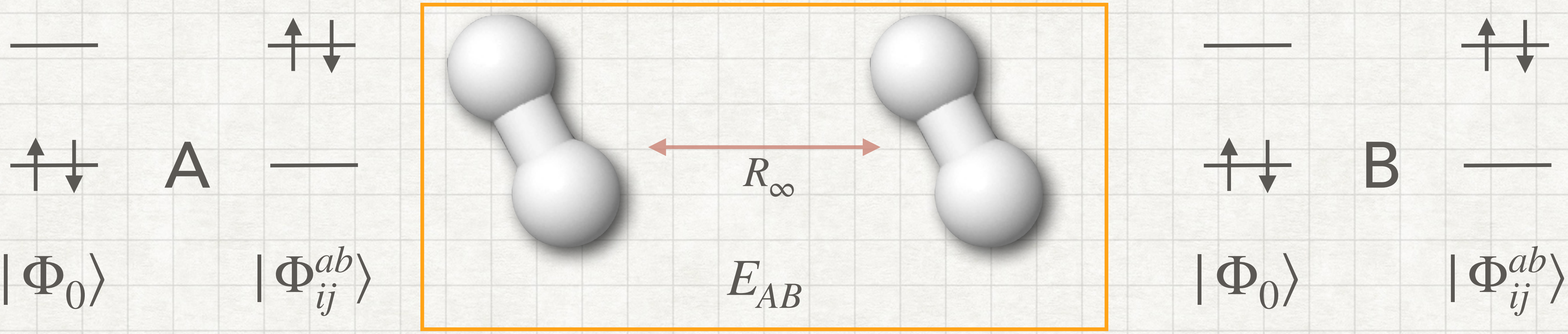


$$
\begin{aligned}
|\Psi\rangle_{\text{exact}}^{AB} &= \mathcal{A}\left\{\left(1+\hat{T}_2^A\right)|\Phi_0^A\rangle \times \left(1+\hat{T}_2^B\right)|\Phi_0^B\rangle\right\} \\
&= \left(1+\hat{T}_2^A+\hat{T}_2^B+\underline{\hat{T}_2^A\hat{T}_2^B}\right)|\Phi_0^{AB}\rangle \\
&\neq \left(1+\hat{T}_2^A+\hat{T}_2^B\right)|\Phi_0^{AB}\rangle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

- 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***:



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

- 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.

THE COUPLED CLUSTER EQUATIONS

- So far, we have derived several key expressions for coupled cluster theory:

CC Wave Function: $$|\Psi_{\text{CC}}\rangle = e^{\hat{T}}|\Phi_0\rangle$$

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

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

Similarity-transformed Hamiltonian:

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

- Our next goal is to convert these equations to algebraic form in terms of the cluster amplitudes and the one- and two-electron integrals that comprise the electronic Hamiltonian.

NORMAL ORDERING

- Evaluation of matrix elements of second-quantized operators between determinants is easier when those operators are written in "normal order." In general, this means that all annihilation or creation operators that would give zero when acting on the "vacuum state" are moved to the right in a given string.

- In quantum chemistry the "vacuum state" is conveniently chosen to be the Hartree-Fock reference state, $|\Phi_0\rangle$, which contains a set of *N* occupied orbitals (the "Fermi vacuum"):

$$a_i^\dagger|\Phi_0\rangle = 0 \qquad a_a|\Phi_0\rangle = 0$$

- Thus, our definition of normal ordering requires us to move all operators such as $a_i^\dagger$ and a_a to the right of operators such as a_i and $a_a^\dagger$.

- One way to achieve this ordering would be to use the anti-commutation relations of the annihilation and creation operators:

$$a_p^\dagger a_q + a_q a_p^\dagger = \delta_{pq} \qquad a_p^\dagger a_q^\dagger + a_q^\dagger a_p^\dagger = 0 \qquad a_p a_q + a_q a_p = 0$$

- A better way is through Wick's theorem…

OPERATOR CONTRACTIONS

- We define a “contraction” between two adjacent annihilation/creation operators as:

$$\overbracket{AB} \equiv AB - \{AB\}$$

where the { } around a string implies that the operators may be rearranged at will, while still keeping up with changes in sign.

- This leads us to four possible contractions in accord with the Fermi vacuum:

$$\overbracket{a_i^\dagger a_j} = a_i^\dagger a_j - \{a_i^\dagger a_j\} = a_i^\dagger a_j + a_j a_i^\dagger = \delta_{ij}$$

$$\overbracket{a_a a_b}^\dagger = a_a a_b^\dagger - \{a_a a_b^\dagger\} = a_a a_b^\dagger + a_b^\dagger a_a = \delta_{ab}$$

$$\overbracket{a_a^\dagger a_b} = \overbracket{a_i a_j}^\dagger = 0$$

- Contractions between operators in ***different*** orbital spaces are zero.

WICK'S THEOREM

- Wick's theorem provides a mechanism for expressing a given string of annihilation/creation operators as a linear combination of normal-ordered strings:

$$ABC\ldots XYZ = \{ABC\ldots XYZ\} + \sum_{\text{singles}} \{\contraction{}{A}{}{B}ABC\ldots XYZ\}$$

$$+ \sum_{\text{doubles}} \{\contraction{}{A}{B}{C}\contraction[2ex]{}{A}{BC\ldots XY}{Z}ABC\ldots XYZ\} + \ldots$$

- In the case of a product of normal-ordered strings (the case we'll most often encounter), Wick's theorem also helps:

$$\{ABC\ldots\}\{XYZ\ldots\} = \{ABC\ldots XYZ\ldots\} + \sum_{\text{singles}} \{\contraction{}{A}{BC\ldots}{X}ABC\ldots XYZ\ldots\}$$

$$+ \sum_{\text{doubles}} \{\contraction{}{A}{BC\ldots}{X}\contraction[2ex]{A}{B}{C\ldots X}{Y}ABC\ldots XYZ\ldots\} + \ldots$$

- A contraction takes a negative sign if an odd number of operators stand between the two under contraction, and a positive sign otherwise.

THE NORMAL-ORDERED HAMILTONIAN

- Let's apply Wick's theorem to the second-quantized Hamiltonian:

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

- The second-quantized string in the one-electron term becomes:

$$a_p^\dagger a_q = \{a_p^\dagger a_q\} + \{\overline{a_p^\dagger a_q}\} = \{a_p^\dagger a_q\} + \delta_{pq}\delta_{p\in i}$$

where the notation $p \in i$ means that p must be an occupied orbital.

- Thus, the one-electron term becomes:

$$\sum_{pq} h_{pq} a_p^\dagger a_q = \sum_{pq} h_{pq} \{a_p^\dagger a_q\} + \boxed{\sum_i h_{ii}}$$

- The last term, which contains no second-quantized operators, is the one-electron contribution to the Hartree-Fock energy.

THE NORMAL-ORDERED HAMILTONIAN

- The two-electron term involves more components:

$$a_p^\dagger a_q^\dagger a_s a_r = \{a_p^\dagger a_q^\dagger a_s a_r\} + \{\wick{\c1{a}_p^\dagger a_q^\dagger \c1{a}_s a_r}\} + \{\wick{a_p^\dagger \c1{a}_q^\dagger \c1{a}_s a_r}\} + \{\wick{\c1{a}_p^\dagger a_q^\dagger a_s \c1{a}_r}\}$$

$$+ \{\wick{a_p^\dagger \c1{a}_q^\dagger a_s \c1{a}_r}\} + \{\wick{\c1{a}_p^\dagger \c2{a}_q^\dagger \c1{a}_s \c2{a}_r}\} + \{\wick{\c1{a}_p^\dagger \c2{a}_q^\dagger \c2{a}_s \c1{a}_r}\}$$

- Now evaluate the contractions:

$$a_p^\dagger a_q^\dagger a_s a_r = \{a_p^\dagger a_q^\dagger a_s a_r\} - \delta_{p\in i}\delta_{ps}\{a_q^\dagger a_r\} + \delta_{q\in i}\delta_{qs}\{a_p^\dagger a_r\} + \delta_{p\in i}\delta_{pr}\{a_q^\dagger a_s\}$$

$$- \delta_{q\in i}\delta_{qr}\{a_p^\dagger a_s\} - \delta_{p\in i}\delta_{ps}\delta_{q\in j}\delta_{qr} + \delta_{p\in i}\delta_{pr}\delta_{q\in j}\delta_{qs}$$

- Insert this back into the expression for $\hat{V}$ and change the summations:

$$\frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle a_p^\dagger a_q^\dagger a_s a_r = \frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle\{a_p^\dagger a_q^\dagger a_s a_r\} - \frac{1}{4}\sum_{qri}\langle iq||ri\rangle\{a_q^\dagger a_r\}$$

$$+ \frac{1}{4}\sum_{pri}\langle pi||ri\rangle\{a_p^\dagger a_r\} + \frac{1}{4}\sum_{qsi}\langle iq||is\rangle\{a_q^\dagger a_s\} - \frac{1}{4}\sum_{psi}\langle pi||is\rangle\{a_p^\dagger a_s\}$$

$$\boxed{- \frac{1}{4}\sum_{ij}\langle ij||ji\rangle + \frac{1}{4}\sum_{ij}\langle ij||ij\rangle} \longleftarrow$$

Two-electron contribution
to the Hartree-Fock energy

THE NORMAL-ORDERED HAMILTONIAN

- The four terms involving only two annihilation/creation operators are identical and can be combined into one:

$$-\frac{1}{4}\sum_{qri}\langle iq||ri\rangle\{a_q^\dagger a_r\}+\frac{1}{4}\sum_{pri}\langle pi||ri\rangle\{a_p^\dagger a_r\}+\frac{1}{4}\sum_{qsi}\langle iq||is\rangle\{a_q^\dagger a_s\}-\frac{1}{4}\sum_{psi}\langle pi||is\rangle\{a_p^\dagger a_s\}=\boxed{\sum_{pqi}\langle pi||qi\rangle\{a_p^\dagger a_q\}}$$

- The two terms with no annihilation/creation operators are identical and can also be combined into one:

$$-\frac{1}{4}\sum_{ij}\langle ij||ji\rangle+\frac{1}{4}\sum_{ij}\langle ij||ij\rangle=\boxed{\frac{1}{2}\sum_{ij}\langle ij||ij\rangle}$$

- Bringing all the one- and two-electron terms together we have:

$$\hat{H}=\boxed{\sum_i h_{ii}+\frac{1}{2}\sum_{ij}\langle ij||ij\rangle}+\boxed{\sum_{pq}h_{pq}\{a_p^\dagger a_q\}+\sum_{pri}\langle pi||qi\rangle\{a_p^\dagger a_q\}}+\frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle\{a_p^\dagger a_q^\dagger a_s a_r\}$$

The Hartree-Fock energy

The Fock operator

- Final form:

$$\hat{H}=\langle\Phi_0|\hat{H}|\Phi_0\rangle+\sum_{pq}f_{pq}\{a_p^\dagger a_q\}+\frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle\{a_p^\dagger a_q^\dagger a_s a_r\}$$

THE NORMAL-ORDERED HAMILTONIAN

- We can thus define the normal-ordered Hamiltonian to be the original second-quantized Hamiltonian minus its (Fermi) vacuum expectation value:

$$\begin{aligned}\hat{H}_N &= \hat{H} - \langle\Phi_0|\hat{H}|\Phi_0\rangle \\ &= \sum_{pq} f_{pq}\{a_p^\dagger a_q\} + \frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle\{a_p^\dagger a_q^\dagger a_s a_r\} \\ &= \hat{F}_N + \hat{V}_N\end{aligned}$$

- We may therefore think of the normal-ordered Hamiltonian as a ***correlation operator*** in that the contributions to the Hartree-Fock energy have been removed. This is the form of the Hamiltonian we use from this point forward.
- This is a general result: The normal-ordered form of an operator is the operator itself minus its vacuum/reference expectation value.
- *A key corollary: The vacuum/reference expectation value of a normal-ordered operator is **zero**.*

NORMAL-ORDERED CLUSTER OPERATORS

- In the previous lecture, we defined the cluster operators as:

$$\hat{T}_1 = \sum_{ia} t_i^a a_a^\dagger a_i \qquad \text{and} \qquad \hat{T}_2 = \frac{1}{4}\sum_{ijab} t_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i$$

or, more generally:

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

- Recall that our definition of normal ordering relative to the Fermi vacuum means that all $a_i^\dagger$ and a_a must stand to the right of all $a_a^\dagger$ and a_i. This is already the case with the excitation operators, so we may trivially write:

$$\hat{T}_1 = \sum_{ia} t_i^a \{a_a^\dagger a_i\} \qquad \hat{T}_2 = \frac{1}{4}\sum_{ijab} t_{ij}^{ab} \{a_a^\dagger a_b^\dagger a_j a_i\}$$

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

- Again: the { } means that we may rearrange the operators at will, as long as we keep up with the sign.

SIMPLIFYING THINGS (A BIT)

- We can now modify the Hausdorff expansion to use only normal-ordered operators:

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

- This leads to another important property of the commutator expansion:

Only those terms from the Wick's theorem evaluation of the commutators in the Hausdorff expansion in which the Hamiltonian contracts at least once with every cluster operator on its right can make a non-zero contribution.

- We will illustrate this property using two of the simplest terms from the expansion:

$$\left[\hat{F}_N, \hat{T}_1\right] \quad \text{and} \quad \frac{1}{2}\left[\left[\hat{F}_N, \hat{T}_1\right], \hat{T}_1\right]$$

SIMPLIFYING THINGS (A BIT)

- First, write the linear commutator explicitly in terms of second-quantized operators:

$$\left[\hat{F}_N, \hat{T}_1\right] = \sum_{pq}\sum_{ia} f_{pq} t_i^a \left[\{a_p^\dagger a_q\}, \{a_a^\dagger a_i\}\right]$$

$$= \sum_{pq}\sum_{ia} f_{pq} t_i^a \left(\{a_p^\dagger a_q\}\{a_a^\dagger a_i\} - \{a_a^\dagger a_i\}\{a_p^\dagger a_q\}\right)$$

- Next, use Wick's theorem to evaluate the each of the products:

$$\{a_p^\dagger a_q\}\{a_a^\dagger a_i\} = \{a_p^\dagger a_q a_a^\dagger a_i\} + \wick{\{\c1 a_p^\dagger a_q a_a^\dagger \c1 a_i\}} + \wick{\{a_p^\dagger \c1 a_q \c1 a_a^\dagger a_i\}} + \wick{\{\c1 a_p^\dagger \c2 a_q \c2 a_a^\dagger \c1 a_i\}}$$

$$= \boxed{\{a_p^\dagger a_q a_a^\dagger a_i\}} + \delta_{pi}\{a_q a_a^\dagger\} + \delta_{qa}\{a_p^\dagger a_i\} + \delta_{pi}\delta_{qa}$$

$$\{a_a^\dagger a_i\}\{a_p^\dagger a_q\} = \boxed{\{a_a^\dagger a_i a_p^\dagger a_q\}}$$

- We can recognize that the uncontracted terms in both products are ***identical*** because we may rearrange the operators within the $\{\}$. Thus, they exactly cancel in the commutator, leaving only terms in which $\hat{F}_N$ has at least one contraction with $\hat{T}_1$ on its right.

SIMPLIFYING THINGS (A BIT)

- The quadratic commutator may be expanded into three terms:

$$\frac{1}{2}\left[\left[\hat{F}_N,\hat{T}_1\right],\hat{T}_1\right] = \frac{1}{2}\left(\hat{F}_N\hat{T}_1^2 - 2\hat{T}_1\hat{F}_N\hat{T}_1 + \hat{T}_1^2\hat{F}_N\right)$$

$$= \frac{1}{2}\sum_{pq}\sum_{ia}\sum_{jb} f_{pq}t_i^a t_j^b \left(\{a_p^\dagger a_q\}\{a_a^\dagger a_i\}\{a_b^\dagger a_j\} - 2\{a_a^\dagger a_i\}\{a_p^\dagger a_q\}\{a_b^\dagger a_j\} + \{a_a^\dagger a_i\}\{a_b^\dagger a_j\}\{a_p^\dagger a_q\}\right)$$

- Wick's theorem for each product gives:

$$\begin{aligned}
\{a_p^\dagger a_q\}\{a_a^\dagger a_i\}\{a_b^\dagger a_j\} &= \{a_p^\dagger a_q a_a^\dagger a_i a_b^\dagger a_j\} + \wick{\{\c1 a_p^\dagger a_q a_a^\dagger \c1 a_i a_b^\dagger a_j\}} + \wick{\{\c1 a_p^\dagger a_q a_a^\dagger a_i a_b^\dagger \c1 a_j\}} \\
&\quad + \wick{\{a_p^\dagger \c1 a_q \c1 a_a^\dagger a_i a_b^\dagger a_j\}} + \wick{\{a_p^\dagger \c1 a_q a_a^\dagger a_i \c1 a_b^\dagger a_j\}} + \wick{\{\c2 a_p^\dagger \c1 a_q \c1 a_a^\dagger \c2 a_i a_b^\dagger a_j\}} \\
&\quad + \wick{\{\c2 a_p^\dagger \c1 a_q \c1 a_a^\dagger a_i a_b^\dagger \c2 a_j\}} + \wick{\{\c1 a_p^\dagger \c2 a_q a_a^\dagger \c1 a_i \c2 a_b^\dagger a_j\}} + \wick{\{\c2 a_p^\dagger \c1 a_q a_a^\dagger a_i \c1 a_b^\dagger \c2 a_j\}}
\end{aligned}$$

$$\begin{aligned}
-2\{a_a^\dagger a_i\}\{a_p^\dagger a_q\}\{a_b^\dagger a_j\} &= -2\Big(\{a_a^\dagger a_i a_p^\dagger a_q a_b^\dagger a_j\} + \wick{\{a_a^\dagger a_i \c1 a_p^\dagger a_q a_b^\dagger \c1 a_j\}} + \wick{\{a_a^\dagger a_i a_p^\dagger \c1 a_q \c1 a_b^\dagger a_j\}} \\
&\quad + \wick{\{a_a^\dagger a_i \c2 a_p^\dagger \c1 a_q \c1 a_b^\dagger \c2 a_j\}}\Big)
\end{aligned}$$

$$\{a_a^\dagger a_i\}\{a_b^\dagger a_j\}\{a_p^\dagger a_q\} = \{a_a^\dagger a_i a_b^\dagger a_j a_p^\dagger a_q\}$$

- The only contributions that don't cancel are terms 7 and 8 from the first product!

SIMPLIFYING THINGS (A BIT)

- The uncontracted terms are clearly identical:

$$\{a^\dagger_p a_q a^\dagger_a a_i a^\dagger_b a_j\} - 2\{a^\dagger_a a_i a^\dagger_p a_q a^\dagger_b a_j\} + \{a^\dagger_a a_i a^\dagger_b a_j a^\dagger_p a_q\} = 0$$

- We can see that the singly contracted terms are also identical when we convert the summations to the same patterns, *e.g.*:

$$\frac{1}{2}\sum_{pq}\sum_{ia}\sum_{jb} f_{pq} t_i^a t_j^b \left(\contraction{\{}{a^\dagger_p}{a_q a^\dagger_a}{a_i} \{a^\dagger_p a_q a^\dagger_a a_i a^\dagger_b a_j\} + \contraction{\{}{a^\dagger_p}{a_q a^\dagger_a a_i a^\dagger_b}{a_j} \{a^\dagger_p a_q a^\dagger_a a_i a^\dagger_b a_j\} - 2\contraction{\{a^\dagger_a a_i}{a^\dagger_p}{a_q a^\dagger_b}{a_j} \{a^\dagger_a a_i a^\dagger_p a_q a^\dagger_b a_j\} \right)$$

$$= \frac{1}{2}\sum_{pq}\sum_{ia}\sum_{jb} f_{pq} t_i^a t_j^b \left(\delta_{pi}\{a_q a^\dagger_a a^\dagger_b a_j\} + \delta_{pj}\{a_q a^\dagger_a a_i a^\dagger_b\} - 2\delta_{pj}\{a^\dagger_a a_i a_q a^\dagger_b\} \right)$$

$$= \frac{1}{2}\sum_{ia}\sum_{jb} t_i^a t_j^b \left(\sum_q f_{iq}\{a_q a^\dagger_a a^\dagger_b a_j\} + \sum_q f_{jq}\{a_q a^\dagger_a a_i a^\dagger_b\} - 2\sum_q f_{jq}\{a^\dagger_a a_i a_q a^\dagger_b\} \right)$$

$$= \frac{1}{2}\sum_{ia}\sum_{jb} t_i^a t_j^b \left(\sum_q f_{jq}\{a_q a^\dagger_b a^\dagger_a a_i\} + \sum_q f_{jq}\{a_q a^\dagger_a a_i a^\dagger_b\} - 2\sum_q f_{jq}\{a^\dagger_a a_i a_q a^\dagger_b\} \right)$$

$$= 0$$

SIMPLIFYING THINGS (A BIT)

- The doubly contracted terms in which the Fock operator shares both of its indices with only one of the two $\hat{T}_1$ operators are also zero:

$$
\begin{aligned}
&\frac{1}{2}\sum_{pq}\sum_{ia}\sum_{jb} f_{pq} t_i^a t_j^b \left(\{\wick{\c1 a_p^\dagger \c2 a_q \c2 a_a^\dagger \c1 a_i} a_b^\dagger a_j\} + \{\wick{\c1 a_p^\dagger \c2 a_q a_a^\dagger a_i \c2 a_b^\dagger \c1 a_j}\} - 2\{a_a^\dagger a_i \wick{\c1 a_p^\dagger \c2 a_q \c2 a_b^\dagger \c1 a_j}\} \right) \\
&\qquad = \frac{1}{2}\sum_{ia}\sum_{jb} t_i^a t_j^b \sum_{pq} f_{pq} \left(\delta_{pi}\delta_{qa}\{a_b^\dagger a_j\} + \delta_{pj}\delta_{qb}\{a_a^\dagger a_i\} - 2\delta_{pj}\delta_{qb}\{a_a^\dagger a_i\} \right) \\
&\qquad = \frac{1}{2}\sum_{ia}\sum_{jb} t_i^a t_j^b \left(f_{ia}\{a_b^\dagger a_j\} + f_{jb}\{a_a^\dagger a_i\} - 2f_{jb}\{a_a^\dagger a_i\} \right) \\
&\qquad = \frac{1}{2}\sum_{ia}\sum_{jb} t_i^a t_j^b \left(f_{jb}\{a_a^\dagger a_i\} + f_{jb}\{a_a^\dagger a_i\} - 2f_{jb}\{a_a^\dagger a_i\} \right) \\
&\qquad = 0
\end{aligned}
$$

SIMPLIFYING THINGS (A BIT)

- The only non-zero contributions arise from the double contractions in which the Fock operator shares an index with each of the two $\hat{T}_1$ operators to its right, leading to a rather compact final result:

$$\begin{aligned}
\frac{1}{2}\left[\left[\hat{F}_N, \hat{T}_1\right], \hat{T}_1\right] &= \frac{1}{2}\sum_{pq}\sum_{ia}\sum_{jb} f_{pq} t_i^a t_j^b \left(\wick{\{\c1 a_p^\dagger \c2 a_q \c2 a_a^\dagger a_i a_b^\dagger \c1 a_j\}} + \wick{\{\c1 a_p^\dagger \c2 a_q a_a^\dagger \c1 a_i \c2 a_b^\dagger a_j\}} \right) \\
&= \frac{1}{2}\sum_{pq}\sum_{ia}\sum_{jb} f_{pq} t_i^a t_j^b \left(\delta_{pj}\delta_{qa}\{a_i a_b^\dagger\} - \delta_{pi}\delta_{qb}\{a_a^\dagger a_j\} \right) \\
&= \sum_{ia}\sum_{jb} f_{ja} t_i^a t_j^b \{a_i a_b^\dagger\}
\end{aligned}$$

Only those terms from the Wick's theorem evaluation of the commutators in the Hausdorff expansion in which the Hamiltonian contracts at least once with every cluster operator on its right can make a non-zero contribution.

- We can summarize this important finding using a relatively simple notation:

$$e^{-\hat{T}} \hat{H}_N e^{\hat{T}} = \left(\hat{H}_N e^{\hat{T}} \right)_c$$

THE CCSD ENERGY EQUATION

- We now have the tools necessary to derive an algebraic expression for the CCSD energy, starting from our formal equation:

$$E_{\mathrm{CC}} = \langle \Phi_0 | e^{-\hat{T}} \hat{H}_N e^{\hat{T}} | \Phi_0 \rangle = \langle \Phi_0 | \left(\hat{H}_N e^{\hat{T}} \right)_c | \Phi_0 \rangle$$

recognizing from our earlier analysis that we need only consider up to terms that are quadratic in $\hat{T}$:

$$E_{\mathrm{CC}} = \langle \Phi_0 | \left(\hat{H}_N \left[1 + \hat{T} + \frac{1}{2} \hat{T}^2 \right] \right)_c | \Phi_0 \rangle$$

- The leading term vanishes because the reference expectation value of a normal-ordered operator is zero:

$$\langle \Phi_0 | \hat{H}_N | \Phi_0 \rangle = 0$$

- The linear term contains four contributions:

$$\langle \Phi_0 | \left(\hat{H}_N \hat{T} \right)_c | \Phi_0 \rangle = \langle \Phi_0 | \left(\hat{F}_N \hat{T}_1 + \hat{V}_N \hat{T}_1 + \hat{F}_N \hat{T}_2 + \hat{V}_N \hat{T}_2 \right)_c | \Phi_0 \rangle$$

- Let’s deal with each of these in order using the techniques we’ve learned…

THE CCSD ENERGY EQUATION

- Given that the reference expectation value of a normal-ordered operator is zero, ***only fully contracted terms*** from Wick's theorem can give non-zero results:

$$\begin{aligned}
\langle\Phi_0|\left(\hat{F}_N\hat{T}_1\right)_c|\Phi_0\rangle &= \sum_{pq}\sum_{ia} f_{pq}t_i^a\langle\Phi_0|\{a_p^\dagger a_q\}\{a_a^\dagger a_i\}|\Phi_0\rangle \\
&= \sum_{pq}\sum_{ia} f_{pq}t_i^a\langle\Phi_0|\{\wick{\c1 a_p^\dagger \c2 a_q \c2 a_a^\dagger \c1 a_i}\}|\Phi_0\rangle \\
&= \sum_{pq}\sum_{ia} f_{pq}t_i^a\langle\Phi_0|\delta_{pi}\delta_{qa}|\Phi_0\rangle \\
&= \sum_{ia} f_{ia}t_i^a
\end{aligned}$$

- For the $\left(\hat{V}_N\hat{T}_1\right)_c$ term, however, it is not possible to generate fully contracted terms, and so it makes no contribution to the energy:

$$\langle\Phi_0|\left(\hat{V}_N\hat{T}_1\right)_c|\Phi_0\rangle = \frac{1}{4}\sum_{pqrs}\sum_{ia}\langle pq||rs\rangle t_i^a\langle\Phi_0|\{a_p^\dagger a_q^\dagger a_s a_r\}\{a_a^\dagger a_i\}|\Phi_0\rangle = 0$$

THE CCSD ENERGY EQUATION

- Similarly, the $\left(\hat{F}_N\hat{T}_2\right)_c$ cannot yield a fully contracted expression, and also vanishes:

$$\langle\Phi_0|\left(\hat{F}_N\hat{T}_2\right)_c|\Phi_0\rangle = \frac{1}{4}\sum_{pq}\sum_{ijab} f_{pq}t_{ij}^{ab}\langle\Phi_0|\{a_p^\dagger a_q\}\{a_a^\dagger a_b^\dagger a_j a_i\}|\Phi_0\rangle = 0$$

- The $\left(\hat{V}_N\hat{T}_2\right)_c$ term is the only remaining non-zero linear contribution:

$$\begin{aligned}
\langle\Phi_0|\left(\hat{V}_N\hat{T}_2\right)_c|\Phi_0\rangle &= \frac{1}{16}\sum_{pqrs}\sum_{ijab}\langle pq||rs\rangle t_{ij}^{ab}\langle\Phi_0|\{a_p^\dagger a_q^\dagger a_s a_r\}\{a_a^\dagger a_b^\dagger a_j a_i\}|\Phi_0\rangle \\
&= \frac{1}{16}\sum_{pqrs}\sum_{ijab}\langle pq||rs\rangle t_{ij}^{ab}\Bigg(\wick{\{\c1 a_p^\dagger \c2 a_q^\dagger \c3 a_s \c4 a_r \c4 a_a^\dagger \c3 a_b^\dagger \c2 a_j \c1 a_i\}} + \wick{\{\c1 a_p^\dagger \c2 a_q^\dagger \c3 a_s \c4 a_r \c3 a_a^\dagger \c4 a_b^\dagger \c1 a_j \c2 a_i\}} + \\
&\qquad \wick{\{\c1 a_p^\dagger \c2 a_q^\dagger \c3 a_s \c4 a_r \c4 a_a^\dagger \c3 a_b^\dagger \c1 a_j \c2 a_i\}} + \wick{\{\c1 a_p^\dagger \c2 a_q^\dagger \c3 a_s \c4 a_r \c3 a_a^\dagger \c4 a_b^\dagger \c2 a_j \c1 a_i\}}\Bigg) \\
&= \frac{1}{16}\sum_{pqrs}\sum_{ijab}\langle pq||rs\rangle t_{ij}^{ab}\left(\delta_{pi}\delta_{qj}\delta_{ra}\delta_{sb} + \delta_{pj}\delta_{qi}\delta_{rb}\delta_{sa} - \delta_{pj}\delta_{qi}\delta_{ra}\delta_{sb} - \delta_{pi}\delta_{qj}\delta_{rb}\delta_{sa}\right) \\
&= \frac{1}{4}\sum_{ijab}\langle ij||ab\rangle t_{ij}^{ab}
\end{aligned}$$

THE CCSD ENERGY EQUATION

- Among the six components of the energy expression involving $\hat{T}^2$, only one can yield fully contracted terms:

$$\frac{1}{2}\langle\Phi_0|\left(\hat{V}_N\hat{T}_1^2\right)_c|\Phi_0\rangle = \frac{1}{8}\sum_{pqrs}\sum_{ia}\sum_{jb}\langle pq||rs\rangle t_i^a t_j^b \langle\Phi_0|\{a_p^\dagger a_q^\dagger a_s a_r\}\{a_a^\dagger a_i\}\{a_b^\dagger a_j\}|\Phi_0\rangle$$

$$= \frac{1}{8}\sum_{pqrs}\sum_{ijab}\langle pq||rs\rangle t_i^a t_j^b \Big(\{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_i a_b^\dagger a_j\} + \{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_i a_b^\dagger a_j\} +$$

$$\{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_i a_b^\dagger a_j\} + \{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_i a_b^\dagger a_j\}\Big)$$

$$= \frac{1}{8}\sum_{pqrs}\sum_{ijab}\langle pq||rs\rangle t_i^a t_j^b \left(-\delta_{pj}\delta_{qi}\delta_{ra}\delta_{sb} + \delta_{pj}\delta_{qi}\delta_{rb}\delta_{sa} + \delta_{pi}\delta_{qj}\delta_{ra}\delta_{sb} - \delta_{pi}\delta_{qj}\delta_{rb}\delta_{sa}\right)$$

$$= \frac{1}{2}\sum_{aibj}\langle ij||ab\rangle t_i^a t_j^b$$

- We can now bring all of the non-zero terms together to obtain the final CCSD energy expression:

$$E_{\text{CC}} = \sum_{ia} f_{ia} t_i^a + \frac{1}{4}\sum_{ijab}\langle ij||ab\rangle t_{ij}^{ab} + \frac{1}{2}\sum_{ijab}\langle ij||ab\rangle t_i^a t_j^b$$

THE CCSD AMPLITUDE EQUATIONS

- The derivation of algebraic expressions for the cluster amplitudes is similar to that of the energy equation. In the CCSD approximation, the single-and double-excitation amplitudes are determined from, respectively:

$$0 = \langle \Phi_i^a | \left(\hat{H}_N e^{\hat{T}} \right)_c | \Phi_0 \rangle \qquad \text{and} \qquad 0 = \langle \Phi_{ij}^{ab} | \left(\hat{H}_N e^{\hat{T}} \right)_c | \Phi_0 \rangle$$

- Key concept: Although each of these expressions does not immediately appear to involve reference expectation values, they can be converted to this form by recognizing that the excited determinants on the left can be written as:

$$\langle \Phi_i^a | = \langle \Phi_0 | \{ a_i^\dagger a_a \} \qquad \text{and} \qquad \langle \Phi_{ij}^{ab} | = \langle \Phi_0 | \{ a_i^\dagger a_j^\dagger a_b a_a \}$$

- For example the leading $\hat{H}_N$ contribution to the single-excitation amplitude equations is:

$$\langle \Phi_i^a | \hat{F}_N | \Phi_0 \rangle = \sum_{pq} f_{pq} \langle \Phi_0 | \{ a_i^\dagger a_a \} \{ a_p^\dagger a_q \} | \Phi_0 \rangle = \sum_{pq} f_{pq} \{ \overbracket{a_i^\dagger \overbracket{a_a a_p^\dagger} a_q} \} = \sum_{pq} f_{pq} \delta_{iq} \delta_{ap} = f_{ai}$$

THE CCSD AMPLITUDE EQUATIONS

- Similarly, the leading $\hat{H}_N$ contribution to the double-excitation amplitude equations is:

$$\langle \Phi_{ij}^{ab} | \hat{V}_N | \Phi_0 \rangle = \frac{1}{4} \sum_{pqrs} \langle pq||rs \rangle \langle \Phi_0 | \{ a_i^\dagger a_j^\dagger a_b a_a \} \{ a_p^\dagger a_q^\dagger a_s a_r \} | \Phi_0 \rangle$$

$$= \frac{1}{4} \sum_{pqrs} \langle pq||rs \rangle \Bigg(\contraction[4ex]{\{}{a}{_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q^\dagger a_s}{a} \contraction[3ex]{\{a_i^\dagger}{a}{_j^\dagger a_b a_a a_p^\dagger a_q^\dagger}{a} \contraction[2ex]{\{a_i^\dagger a_j^\dagger}{a}{_b a_a a_p^\dagger}{a} \contraction[1ex]{\{a_i^\dagger a_j^\dagger a_b}{a}{_a}{a} \{ a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q^\dagger a_s a_r \} + \contraction[4ex]{\{}{a}{_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q^\dagger a_s}{a} \contraction[3ex]{\{a_i^\dagger}{a}{_j^\dagger a_b a_a a_p^\dagger a_q^\dagger}{a} \contraction[2ex]{\{a_i^\dagger a_j^\dagger}{a}{_b a_a}{a} \contraction[1ex]{\{a_i^\dagger a_j^\dagger a_b}{a}{_a a_p^\dagger}{a} \{ a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q^\dagger a_s a_r \} +$$

$$\contraction[4ex]{\{}{a}{_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q^\dagger}{a} \contraction[3ex]{\{a_i^\dagger}{a}{_j^\dagger a_b a_a a_p^\dagger a_q^\dagger a_s}{a} \contraction[2ex]{\{a_i^\dagger a_j^\dagger}{a}{_b a_a a_p^\dagger}{a} \contraction[1ex]{\{a_i^\dagger a_j^\dagger a_b}{a}{_a}{a} \{ a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q^\dagger a_s a_r \} + \contraction[4ex]{\{}{a}{_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q^\dagger}{a} \contraction[3ex]{\{a_i^\dagger}{a}{_j^\dagger a_b a_a a_p^\dagger a_q^\dagger a_s}{a} \contraction[2ex]{\{a_i^\dagger a_j^\dagger}{a}{_b a_a}{a} \contraction[1ex]{\{a_i^\dagger a_j^\dagger a_b}{a}{_a a_p^\dagger}{a} \{ a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q^\dagger a_s a_r \} \Bigg)$$

$$= \frac{1}{4} \sum_{pqrs} \langle pq||rs \rangle \left(\delta_{pa}\delta_{qb}\delta_{ri}\delta_{sj} - \delta_{pb}\delta_{qa}\delta_{ri}\delta_{sj} - \delta_{pa}\delta_{qb}\delta_{rj}\delta_{si} + \delta_{pb}\delta_{qa}\delta_{rj}\delta_{si} \right)$$

$$= \langle ab||ij \rangle$$

THE CCSD AMPLITUDE EQUATIONS

- And a term that I include here mainly because it looks so awesome:

$$\langle\Phi_{ij}^{ab}|\left(\hat{V}_N\hat{T}_1\right)_c|\Phi_0\rangle = \frac{1}{4}\sum_{pqrs}\sum_{kc}\langle pq||rs\rangle t_k^c\langle\Phi_0|\{a_i^\dagger a_j^\dagger a_b a_a\}\left(\{a_p^\dagger a_q^\dagger a_s a_r\}\{a_c^\dagger a_k\}\right)_c|\Phi_0\rangle$$

$$= \frac{1}{4}\sum_{pqrs}\sum_{kc}\langle pq||rs\rangle t_k^c\Big(\{a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q^\dagger a_s a_r a_c^\dagger a_k\}+$$

$$\{a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q^\dagger a_s a_r a_c^\dagger a_k\}+\{a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q^\dagger a_s a_r a_c^\dagger a_k\}+\{a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q^\dagger a_s a_r a_c^\dagger a_k\}+$$

$$\{a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q^\dagger a_s a_r a_c^\dagger a_k\}+\{a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q^\dagger a_s a_r a_c^\dagger a_k\}+\{a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q^\dagger a_s a_r a_c^\dagger a_k\}+$$

$$\{a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q^\dagger a_s a_r a_c^\dagger a_k\}+\{a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q^\dagger a_s a_r a_c^\dagger a_k\}+\{a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q^\dagger a_s a_r a_c^\dagger a_k\}+$$

$$\{a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q^\dagger a_s a_r a_c^\dagger a_k\}+\{a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q^\dagger a_s a_r a_c^\dagger a_k\}+\{a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q^\dagger a_s a_r a_c^\dagger a_k\}+$$

$$\{a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q^\dagger a_s a_r a_c^\dagger a_k\}+\{a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q^\dagger a_s a_r a_c^\dagger a_k\}+\{a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q^\dagger a_s a_r a_c^\dagger a_k\}\Big)$$

$$= \frac{1}{4}\sum_{pqrs}\sum_{kc}\langle pq||rs\rangle t_k^c\times$$

$$(\delta_{pa}\delta_{qb}\delta_{rc}\delta_{sj}\delta_{ik} - \delta_{pb}\delta_{qa}\delta_{rc}\delta_{sj}\delta_{ik} - \delta_{pa}\delta_{qb}\delta_{rc}\delta_{si}\delta_{jk} + \delta_{pb}\delta_{qa}\delta_{rc}\delta_{si}\delta_{jk}-$$

$$\delta_{pa}\delta_{qb}\delta_{rj}\delta_{sc}\delta_{ik} + \delta_{pb}\delta_{qa}\delta_{rj}\delta_{sc}\delta_{ik} + \delta_{pa}\delta_{qb}\delta_{ri}\delta_{sc}\delta_{jk} - \delta_{pb}\delta_{qa}\delta_{ri}\delta_{sc}\delta_{jk}-$$

$$\delta_{pa}\delta_{qk}\delta_{ri}\delta_{sj}\delta_{bc} + \delta_{pb}\delta_{qk}\delta_{ri}\delta_{sj}\delta_{ac} - \delta_{pb}\delta_{qk}\delta_{rj}\delta_{si}\delta_{ac} + \delta_{pa}\delta_{qk}\delta_{rj}\delta_{si}\delta_{bc}+$$

$$\delta_{pk}\delta_{qa}\delta_{ri}\delta_{sj}\delta_{bc} - \delta_{pk}\delta_{qb}\delta_{ri}\delta_{sj}\delta_{ac} - \delta_{pk}\delta_{qa}\delta_{rj}\delta_{si}\delta_{bc} + \delta_{pk}\delta_{qb}\delta_{rj}\delta_{si}\delta_{ac})$$

$$= \sum_c\left(\langle ab||cj\rangle t_i^c - \langle ab||ci\rangle t_j^c\right) + \sum_k\left(\langle ij||bk\rangle t_k^a - \langle ij||ak\rangle t_k^b\right)$$

THE $\hat{T}_1$ AMPLITUDE EQUATIONS

- Using a great deal of mental (and physical!) fortitude, one can apply Wick's theorem to all of the terms from the Hausdorff expansion and obtain the following expression for the single-excitation amplitudes:

$$\begin{aligned}
0 =& f_{ai} + \sum_{c} f_{ac} t_i^c - \sum_{k} f_{ki} t_k^a + \sum_{kc} \langle ka||ci\rangle t_k^c + \sum_{kc} f_{kc} t_{ik}^{ac} + \frac{1}{2} \sum_{kcd} \langle ka||cd\rangle t_{ki}^{cd} - \\
& \frac{1}{2} \sum_{klc} \langle kl||ci\rangle t_{kl}^{ca} - \sum_{kc} f_{kc} t_i^c t_k^a - \sum_{klc} \langle kl||ci\rangle t_k^c t_l^a + \sum_{kcd} \langle ka||cd\rangle t_k^c t_i^d - \\
& \sum_{klcd} \langle kl||cd\rangle t_k^c t_i^d t_l^a + \sum_{klcd} \langle kl||cd\rangle t_k^c t_{li}^{da} - \frac{1}{2} \sum_{klcd} \langle kl||cd\rangle t_{ki}^{cd} t_l^a - \frac{1}{2} \sum_{klcd} \langle kl||cd\rangle t_{kl}^{ca} t_i^d
\end{aligned}$$

THE $\hat{T}_2$ AMPLITUDE EQUATIONS

$$
\begin{aligned}
0 = {} & \langle ab||ij\rangle + \sum_{c}\left(f_{bc}t_{ij}^{ac} - f_{ac}t_{ij}^{bc}\right) - \sum_{k}\left(f_{kj}t_{ik}^{ab} - f_{ki}t_{jk}^{ab}\right) + \frac{1}{2}\sum_{kl}\langle kl||ij\rangle t_{kl}^{ab} + \frac{1}{2}\sum_{cd}\langle ab||cd\rangle t_{ij}^{cd} \\
& + P(ij)P(ab)\sum_{kc}\langle kb||cj\rangle t_{ik}^{ac} + P(ij)\sum_{c}\langle ab||cj\rangle t_{i}^{c} - P(ab)\sum_{k}\langle kb||ij\rangle t_{k}^{a} + \frac{1}{2}P(ij)P(ab)\sum_{klcd}\langle kl||cd\rangle t_{ik}^{ac}t_{lj}^{db} \\
& + \frac{1}{4}\sum_{klcd}\langle kl||cd\rangle t_{ij}^{cd}t_{kl}^{ab} - P(ab)\frac{1}{2}\sum_{klcd}\langle kl||cd\rangle t_{ij}^{ac}t_{kl}^{bd} - P(ij)\frac{1}{2}\sum_{klcd}\langle kl||cd\rangle t_{ik}^{ab}t_{jl}^{cd} + P(ab)\frac{1}{2}\sum_{kl}\langle kl||ij\rangle t_{k}^{a}t_{l}^{b} \\
& + P(ij)\frac{1}{2}\sum_{cd}\langle ab||cd\rangle t_{i}^{c}t_{j}^{d} - P(ij)P(ab)\sum_{kc}\langle kb||ic\rangle t_{k}^{a}t_{j}^{c} + P(ab)\sum_{kc}f_{kc}t_{k}^{a}t_{ij}^{bc} + P(ij)\sum_{kc}f_{kc}t_{i}^{c}t_{jk}^{ab} \\
& - P(ij)\sum_{klc}\langle kl||ci\rangle t_{k}^{c}t_{lj}^{ab} + P(ab)\sum_{kcd}\langle ka||cd\rangle t_{k}^{c}t_{ij}^{db} + P(ij)P(ab)\sum_{kcd}\langle ak||dc\rangle t_{i}^{d}t_{jk}^{bc} \\
& + P(ij)P(ab)\sum_{klc}\langle kl||ic\rangle t_{l}^{a}t_{jk}^{bc} + P(ij)\frac{1}{2}\sum_{klc}\langle kl||cj\rangle t_{i}^{c}t_{kl}^{ab} - P(ab)\frac{1}{2}\sum_{kcd}\langle kb||cd\rangle t_{k}^{a}t_{ij}^{cd} \\
& - P(ij)P(ab)\frac{1}{2}\sum_{kcd}\langle kb||cd\rangle t_{i}^{c}t_{k}^{a}t_{j}^{d} + P(ij)P(ab)\frac{1}{2}\sum_{klc}\langle kl||cj\rangle t_{i}^{c}t_{k}^{a}t_{l}^{b} - P(ij)\sum_{klcd}\langle kl||cd\rangle t_{k}^{c}t_{i}^{d}t_{lj}^{ab} \\
& - P(ab)\sum_{klcd}\langle kl||cd\rangle t_{k}^{c}t_{l}^{a}t_{ij}^{db} + P(ij)\frac{1}{4}\sum_{klcd}\langle kl||cd\rangle t_{i}^{c}t_{j}^{d}t_{kl}^{ab} + P(ab)\frac{1}{4}\sum_{klcd}\langle kl||cd\rangle t_{k}^{a}t_{l}^{b}t_{ij}^{cd} \\
& + P(ij)P(ab)\sum_{klcd}\langle kl||cd\rangle t_{i}^{c}t_{l}^{b}t_{kj}^{ad} + P(ij)P(ab)\frac{1}{4}\sum_{klcd}\langle kl||cd\rangle t_{i}^{c}t_{k}^{a}t_{j}^{d}t_{l}^{b}
\end{aligned}
$$

- The permutation operator maintains antisymmetry of the resulting terms:

$$P(pq)f(p,q) = f(p,q) - f(q,p)$$

A FEW OBSERVATIONS

- Wick's theorem is certainly superior to application of the raw anti-commutation relations, but it still involves substantial tedium and numerous opportunities for error.
- For most terms, the result obtained from Wick's theorem still contains many redundancies that can only be reduced by further algebraic manipulation, *e.g.* re-indexing of summations, permutation of indices, etc.
- If we were to continue this approach to higher-order excitations (*i.e.*, triples, quadruples, etc.), the number of algebraic manipulations required by Wick's theorem becomes insurmountable if completed by hand.
- Computer algorithms exist to automate this process, and they have been quite successful even for higher excitations.[a]
- However, another approach exists that streamlines the process and offers a topological perspective on the various terms in the coupled cluster equations: ***diagrams!***

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[a] See for example: S. Hirata, "Tensor contraction engine: Abstraction and automated parallel implementation of configuration-interaction, coupled-cluster, and many-body perturbation theories," J. Phys. Chem. A, 107, 9887 (2003).