A C4 Tutorial on Dynamical Electron Correlation

- Monday October 2nd

10:15	Electron correlation: The many-body problem at the heart of chemistry (D.P. Tew)
13:15	Second Quantization (W. Klopper)
15:00	Exercises

- Tuesday October 3rd

10:15	Coupled cluster theory: Fundamentals (D.P. Tew)
13:15	Coupled cluster theory: Analytic derivatives, molecular properties and response theory (W. Klopper)
15:00	Exercises

- Wednesday October 4th

10:15	Explicitly correlated wavefunctions (D.P. Tew)
13:15	R12 methods: Approximations and performance assessment (W. Klopper)
15:00	Exercises

Electron correlation: The many-body problem at the heart of chemistry

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C^4 Tutorial, Zürich, 2–4 October 2006

Outline

- Computation as an investigational tool
- Solvable one electron systems
- Lessons from helium
    - Fermi correlation
    - Coulomb correlation
    - Basis functions
    - Convergence of the CI expansion
    - Nuclear and electron cusps
    - Explicit correlation
- Lessons from molecular hydrogen
    - Dynamic and non-dynamic correlation
- Many electron systems
    - Hartree-Fock theory
    - Coupled-cluster theory

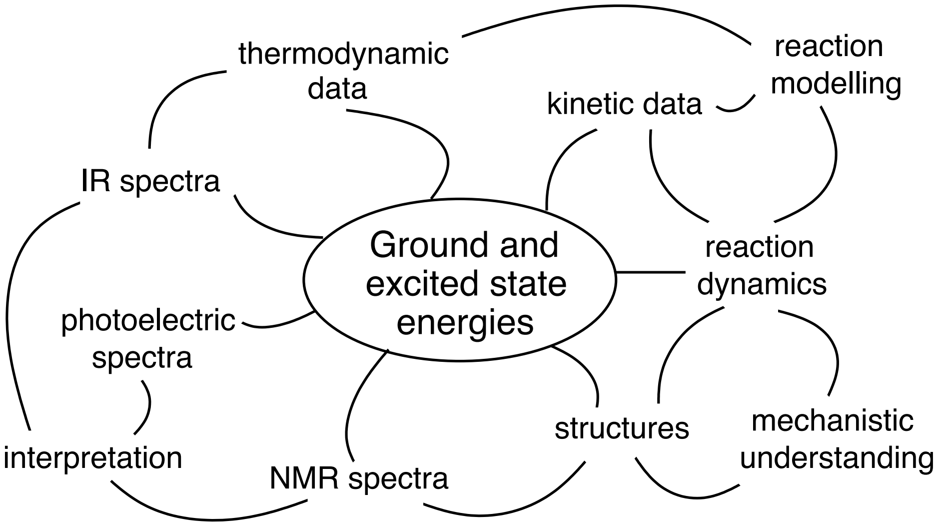
Computation as an investigative tool

- At a fundamental level, all of chemistry is determined by the physics of the composite electrons and nuclei – Quantum Mechanics.
- A chemical experiment can be reduced to finding an accurate quantum mechanical treatment of the system.

We use computers to approximately solve the Schrödinger equation, performing a "virtual experiment".

- The better our description of the system, the more reliable our conclusions. We need to compute the wave function accurately.

What can theory do?



Ground and excited state energies

thermodynamic data

reaction modelling

kinetic data

IR spectra

reaction dynamics

photoelectric spectra

structures

mechanistic understanding

interpretation

NMR spectra

- Plus much more ...
- The size of system we can treat depends critically on the accuracy we require. However, computation is now at least as reliable as experiment in many areas of chemistry.

Solvable systems

- Analytic solutions are only available for a few one-electron systems related to H and H_2^+. Much of our treatment of many electron systems is based on these solutions.
- The hydrogen atom $\psi(r,\theta,\varphi)$

$$-\frac{1}{2r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{2r^2}\hat{L}^2\psi-\frac{Z}{r}\psi \quad = \quad E\psi$$

- $\hat{L}^2$ is the total angular momentum operator whose eigenfunctions are the spherical harmonics $Y_{lm}(\theta,\varphi)$

$$\hat{L}^2 Y_{lm}(\theta,\varphi)=l(l+1)Y_{lm}(\theta,\varphi)$$

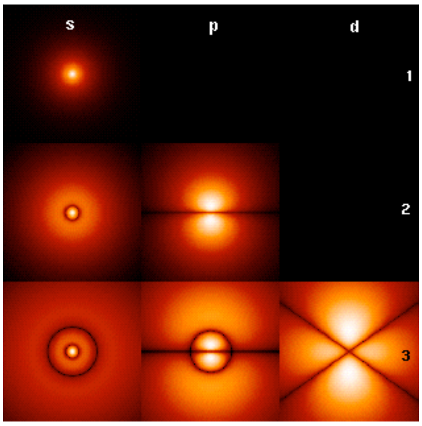
- The solutions for the radial functions are related to the associated Laguerre polynomials $L^{2l+1}_{n-l-1}(r')$

$$R_{nl}(r)=N_{nl}\left(\frac{2Zr}{n}\right)^{l}L^{2l+1}_{n-l-1}\left(\frac{2Zr}{n}\right)\exp\left(-\frac{Zr}{n}\right)$$

The hydrogen orbitals

- The solutions to the hydgrogenic Schrödinger equation are

$$\psi_{nlm}(r,\theta,\varphi) = R_{nl}(r)Y_{lm}(\theta,\varphi) \qquad E_n = -\frac{Z}{2n^2}$$



- We attach a spin function σ for the spin of the electron.

$$\hat{S}_z\sigma_{m_s} = m_s\sigma \qquad \sigma_{\frac{1}{2}} = \alpha \qquad \sigma_{-\frac{1}{2}} = \beta$$

The hydrogen molecular ion

- The Schrödinger equation is separable if we transform to elliptic coordinates $\psi(\xi,\eta,\varphi)$.

$$\left(\frac{\partial}{\partial\xi}\left((\xi^2-1)\frac{\partial}{\partial\xi}\right) + \frac{\partial}{\partial\eta}\left((\eta^2-1)\frac{\partial}{\partial\eta}\right) + \left(\frac{1}{\xi^2-1} + \frac{1}{\eta^2-1}\right)\frac{\partial^2}{\partial\varphi^2} + 2R_{AB}\xi\right)\psi = \frac{1}{4}R_{AB}^2(\xi^2-\eta^2)E\psi$$

$$\xi = \frac{r_A + r_B}{R_{AB}} \quad \eta = \frac{r_A - r_B}{R_{AB}} \quad \varphi$$

- The solutions are of the form $\psi(\xi,\eta,\varphi) = N(\xi)M(\eta)\chi(\varphi)$
  - $N(\xi)$ is an infinite sum of associated Legendre polynomials.
  - $M(\eta)$ is an infinite sum of hypergeometric functions.
  - $\chi(\varphi)$ is either $\cos m\varphi$ or $\sin m\varphi$.
- The resulting orbitals exhibit $D_{\infty h}$ symmetry. The quantum number m dictates σ, π, $\delta \cdots$ symmetry and each state is either gerade or ungerade.
- The orbitals resemble linear combinations of the hydrogen orbitals.

- Thus far, no analytic solutions to helium or H_2 have been found, or for any other system with more than one electron
- For the rest of chemistry we must approximate ψ.
- The underlying difficulty is that many particles interact simultaneously and their motion is *correlated*.

This is the *many body problem* at the heart of chemistry.

- The approximate description of electron correlation is the largest single source of error in our approximations to ψ.
- Since all interactions are pairwise, most of the physics involved is present in 2-electron systems.
- The physics of electron correlation and the methods we use to approximate ψ can be illustrated through examining He and H_2.

Helium: and uncorrelated model

- Thinking of the electrons as independent particles we may write the helium wave function as a *Hartree product* of two occupied spin orbitals.

$$\psi_H = \phi_a(\mathbf{r}_1)\sigma_a(1)\phi_b(\mathbf{r}_2)\sigma_b(2)$$

- The probability of locating electrons 1 and 2 at space-spin coordinates $\mathbf{x}_1$ and $\mathbf{x}_2$ respectively is given by $|\psi|^2$.
- For ψ_H this probability is a product of one factor for each electron.

$$\rho(\mathbf{x}_1, \mathbf{x}_2) = \phi_a^2(\mathbf{r}_1)\sigma_a^2(1)\phi_b^2(\mathbf{r}_2)\sigma_b^2(2)$$

- The motion of each electron is therefore independent of the other and the electrons are *uncorrelated*.

Pauli antisymmetry

- However, the Hartree description is fundamentally flawed. It treats the two electrons differently, assuming that they are distinguishable.
- In nature electrons are indistinguishable. Interchanging the coordinates of two electrons does not affect a physically observable quantity.
- In particular, the invariance of $|\psi|^2$ means that

$$\psi(\mathbf{x}_1, \mathbf{x}_2) = \pm\psi(\mathbf{x}_2, \mathbf{x}_1)$$

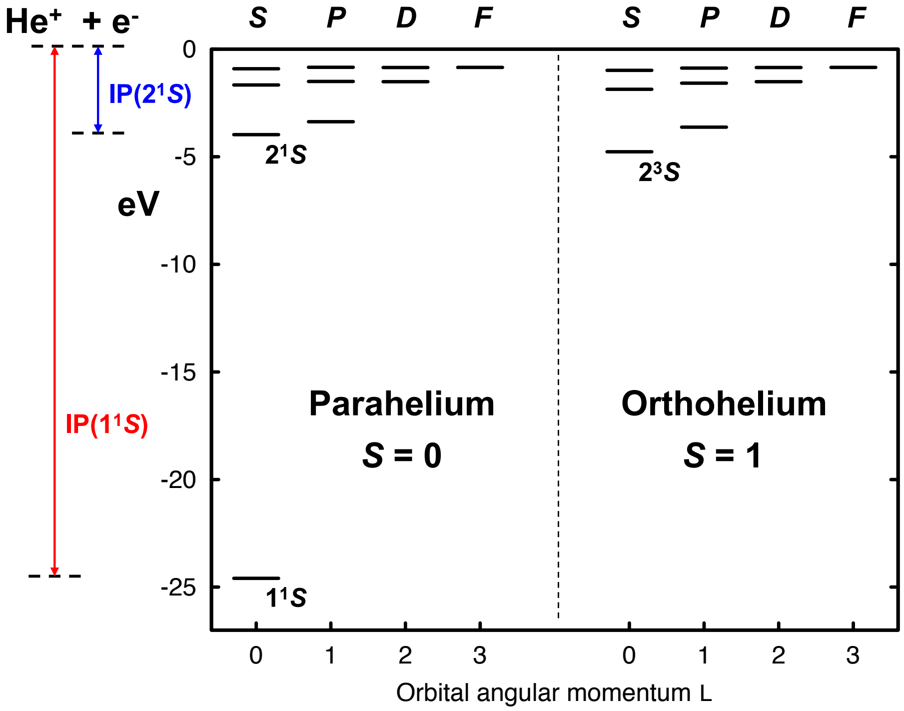
- Electrons are fermions and a sign change occurs.
- A physically acceptable wave function must satisfy this *Pauli antisymmetry*.

- The Hartree description may be corrected by separately symmetrizing or antisymmetrizing the space and spin factors of ψ_H

$$\begin{aligned}\psi_A &= [\phi_a(\mathbf{r}_1)\phi_b(\mathbf{r}_2) \pm \phi_b(\mathbf{r}_1)\phi_a(\mathbf{r}_2)]\,[\sigma_a(1)\sigma_b(2) \mp \sigma_b(1)\sigma_a(2)] \\ \psi_A &= \Phi(\mathbf{r}_1, \mathbf{r}_2)\Theta(1,2)\end{aligned}$$

- The probability is no longer a product of 1-electron factors, the motion of electron 1 in space-spin coordinates depends on that of electron 2.
- This is *Fermi correlation*. It has nothing to do with the Coulomb repulsion between the electrons. It is purely a consequence of their quantum nature.
- Let us examine the Fermi correlation present in the three lowest states of He, and its energetic consequences.

Experimental energy levels of helium



Singlet and triplet states

- For helium there is only one way to realize the antisymmetric spin factor.

$$\Theta_{0,0}(1,2) = \frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right]$$

- and three ways to realize the symmetric spin factor.

$$\begin{aligned}\Theta_{1,1}(1,2) &= \alpha(1)\alpha(2)\\ \Theta_{1,0}(1,2) &= \frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) + \beta(1)\alpha(2)\right]\\ \Theta_{1,-1}(1,2) &= \beta(1)\beta(2)\end{aligned}$$

- These spin functions are eigenfunctions of the total and z-projected spin operators with quantum numbers S and M_S respectively.

$$\begin{aligned}\hat{S}^2\Theta_{S,M_S} &= S(S+1)\Theta_{S,M_S}\\ \hat{S}_z\Theta_{S,M_S} &= M_S\Theta_{S,M_S}\end{aligned}$$

- $\Theta_{0,0}(1,2)$ is a *singlet state* with zero total spin $S = M_S = 0$.
- The three symmetric spin functions represent the three components of a *triplet state* with total spin quantum number $S = 1$ and z-projected spin $M_S = 1, 0, -1$.
- In the non-relativistic limit there are no 2-electron spin interactions and in the absence of an external magnetic field the singlet and triplet spin states would be degenerate.
- However, the space and spin descriptions are coupled.
- Singlet states must combine with a symmetric spatial function and triplet states with an antisymmetric spatial function.
- This greatly affects the relative motion of the electrons in space. To understand the energetics we must examine the spatial part of the wave function.

The He ground state 1^1S

- Both electrons occupy the $1s$ orbital and the spatial function is symmetric. $\Theta(1,2)$ must therefore be antisymmetric.

$$\psi_{1^1S}(\mathbf{x}_1, \mathbf{x}_2) = \phi_{1s}(\mathbf{r}_1)\phi_{1s}(\mathbf{r}_2)\frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right]$$

- The effect of Fermi correlation is that the spin coordinates of the two electrons are correlated. If electron 1 has spin $M_S = \frac{1}{2}$ then electron 2 has spin $M_S = -\frac{1}{2}$.
- In other words spin orbitals can be at most singly occupied.
- The 2-electron density (the 2-electron probability distribution) can be factorized into two 1-electron parts.

$$\rho(\mathbf{r}_1, \mathbf{r}_2) = \phi_{1s}^2(\mathbf{r}_1)\phi_{1s}^2(\mathbf{r}_2)$$

- The spatial motion of the electrons is *uncorrelated* in this simple orbital description.

The excited states 2^3S and 2^1S

- The first excited states of He are obtained by promoting one electron from the $1s$ to the $2s$ orbital.
- The spatial factor can be either symmetric with triplet spin or antisymmetric with singlet spin.

$$\begin{aligned}\Phi_{2^3S}(\mathbf{r}_1,\mathbf{r}_2) &= \tfrac{1}{\sqrt{2}}\left[\phi_{1s}(\mathbf{r}_1)\phi_{2s}(\mathbf{r}_2)-\phi_{2s}(\mathbf{r}_1)\phi_{1s}(\mathbf{r}_2)\right]\\ \Phi_{2^1S}(\mathbf{r}_1,\mathbf{r}_2) &= \tfrac{1}{\sqrt{2}}\left[\phi_{1s}(\mathbf{r}_1)\phi_{2s}(\mathbf{r}_2)+\phi_{2s}(\mathbf{r}_1)\phi_{1s}(\mathbf{r}_2)\right]\end{aligned}$$

- The 2-electron probability distributions are

$$\begin{aligned}{}^3\rho(\mathbf{r}_1,\mathbf{r}_2) &= \tfrac{1}{2}\phi_{1s}^2(\mathbf{r}_1)\phi_{2s}^2(\mathbf{r}_2)+\tfrac{1}{2}\phi_{2s}^2(\mathbf{r}_1)\phi_{1s}^2(\mathbf{r}_2)\\ &\quad -\phi_{1s}(\mathbf{r}_1)\phi_{2s}(\mathbf{r}_1)\phi_{1s}(\mathbf{r}_2)\phi_{2s}(\mathbf{r}_2)\\ {}^1\rho(\mathbf{r}_1,\mathbf{r}_2) &= \tfrac{1}{2}\phi_{1s}^2(\mathbf{r}_1)\phi_{2s}^2(\mathbf{r}_2)+\tfrac{1}{2}\phi_{2s}^2(\mathbf{r}_1)\phi_{1s}^2(\mathbf{r}_2)\\ &\quad +\phi_{1s}(\mathbf{r}_1)\phi_{2s}(\mathbf{r}_1)\phi_{1s}(\mathbf{r}_2)\phi_{2s}(\mathbf{r}_2)\end{aligned}$$

- The 2-electron probability distribution cannot be factorized, the spatial motion of the electrons is *Fermi correlated*.

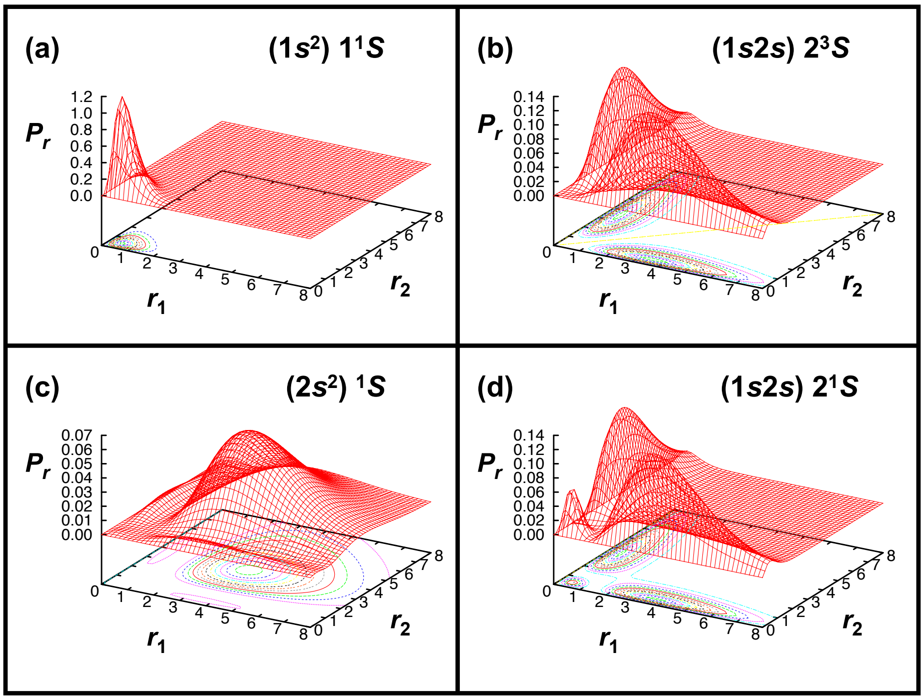
Fermi holes and Fermi heaps

- The probability distributions differ only in the last term.
- Wherever this term reduces the probability of the electrons being located at $\mathbf{r}_1, \mathbf{r}_2$ for the triplet state, it is increased by that same amount for the singlet state and vice versa.
- At $\mathbf{r}_1 = \mathbf{r}_2$ the triplet 2-electron probability vanishes, creating a *Fermi hole* (exchange hole), a reduced probability of finding the electrons close together.

$$\begin{aligned}{}^3\rho(\mathbf{r}_1,\mathbf{r}_1) &= \tfrac{1}{2}\phi_{1s}^2(\mathbf{r}_1)\phi_{2s}^2(\mathbf{r}_1)+\tfrac{1}{2}\phi_{2s}^2(\mathbf{r}_1)\phi_{1s}^2(\mathbf{r}_1)\\ &\quad -\phi_{1s}(\mathbf{r}_1)\phi_{2s}(\mathbf{r}_1)\phi_{1s}(\mathbf{r}_1)\phi_{2s}(\mathbf{r}_1) \qquad = 0\end{aligned}$$

- For the singlet state there is therefore a *Fermi heap*, an increased probability of finding the two electrons at the same point in space.
- Since electrons repel each other the triplet state is therefore lower in energy than the singlet state.

2-electron radial distribution functions $P(r) = 16\pi^2 r_1^2 r_2^2 \rho(r_1, r_2)$



Variational calculations

- Optimize the orbitals for the lowest energy singlet (1^1S) and triplet (2^3S) states separately.
- Use the orbitals of the 2^3S calculation for the 2^1S state.

Ionization potentials and energy differences in eV

	orbital	exact	experiment
IP(1^1S)	23.447	24.591	24.587
IP(2^3S)	4.742	4.768	4.767
IP(2^1S)	3.976	3.972	3.972
ΔE($2^3S - 1^1S$)	18.706	19.823	19.820
ΔE($2^1S - 2^3S$)	0.766	0.796	0.796

- Orbital occupancy and Fermi correlation give the correct qualitative picture, it captures most of the physics.
- 4%-5% error means that it is not quantitative. The instantaneous Coulomb repulsion has not been properly accounted for, only in a mean field average sense.

Coulomb Correlation in helium

- Hartree products of orbitals are uncorrelated.
- Fermi correlation is introduced into the wave function due to a symmetric linear combination of orbital products.
- Attempt to recover the remaining Coulomb correlation by taking linear combinations of many orbital products.
- Properly symmetrize each orbital product before adding it to our wave function.

$$\Phi^{\pm}(\mathbf{r}_1, \mathbf{r}_2) \quad = \quad \sum_{p \geq q} C_{pq} \left[\phi_p(\mathbf{r}_1)\phi_q(\mathbf{r}_2) \pm \phi_q(\mathbf{r}_1)\phi_p(\mathbf{r}_2)\right]$$

- Each term represents an *orbital configuration*.
- The result is the *configuration interaction wave function*
- The coefficients C_{pq} are not determined by symmetry and may be variationally optimized.

The orbital basis set

- Must choose the form of the orbitals for a CI calculation.
- Should constitute a *complete set* in the sense that we can make our error arbitrarily small by including sufficiently many orbitals in the CI expansion.
- The hydrogen orbitals are only complete if the (awkward) continuum functions are included.
- Slater-type functions form a complete set and are a much better choice

$$\phi_{nlm}(\mathbf{r}) = N_{nl}(\zeta r)^l L^{2l+2}_{n-l-1}(2\zeta r)\,\mathrm{exp}(-\zeta r) Y_{lm}(\theta, \phi)$$

- They have the same radial and angular structure as the hydrogen orbitals, but depend on ζr rather than Zr/n.
- As a result Slater orbitals are much more compact. Necessary to use various exponents to better reproduce the hydgrogenic functions.

Slater-type Gaussians

- 2-electron integrals using Slater functions are only solvable for 1-center and symmetric 2-center integrals.
- This is sufficient for He and H_2, but a general treatment for chemistry requires some approximations.
- The Gaussian product theorem says that the product of 2 Gaussians is another Gaussian.

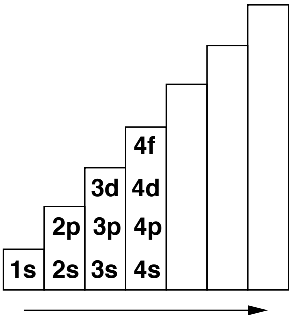
$$\exp(-a\mathbf{r}_A^2)\exp(-b\mathbf{r}_B^2) = \exp(-q\mathbf{R}_{AB}^2)\exp(-p\mathbf{r}_P^2)$$

$$q = \frac{ab}{a+b} \quad \mathbf{R}_{AB} = \mathbf{A} - \mathbf{B} \qquad p = a+b \quad \mathbf{P} = \frac{a\mathbf{A} + b\mathbf{B}}{a+b}$$

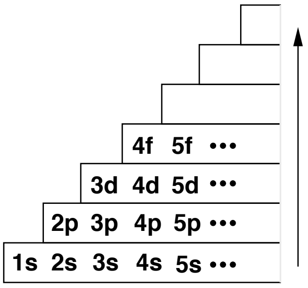
- This reduces 2-electron 4-center integrals to 2-center 2-electron integrals, which can be made to factorize.
- In most quantum chemistry programs the orbitals are linear combinations of Gaussian functions fitted to resemble Slater orbitals.

Principle *vs* partial wave expansions

- Having defined a set of functions there are two ways in which to systematically increase the basis of orbitals included in the CI expansion.



principal expansion

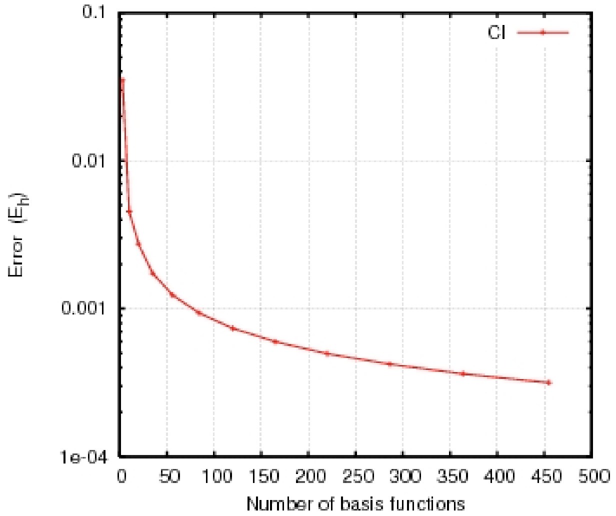


partial–wave expansion

- It is observed that the energy gain from adding the next ns function is of the same order as adding the set np, which is of the same order as adding the nd set etc.
- Orbital basis sets are thus constructed according to the principal quantum number expansion.
- The number of basis functions N is $\propto n_{\text{max}}^2$

CI calculations on the 1^1S ground state

- The error in the energy as a function of the number of orbitals in the CI expansion.



Each point is a successive maximum principle quantum number n_{max} defining the orbital basis used for configurations

$$[\phi_p(\mathbf{r}_1)\phi_q(\mathbf{r}_2) \pm \phi_q(\mathbf{r}_1)\phi_p(\mathbf{r}_2)]$$

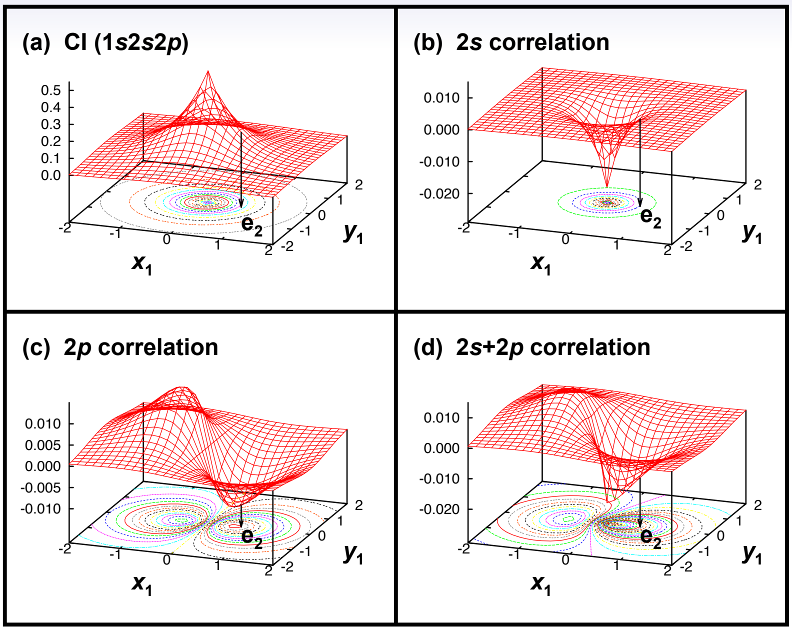
- Very difficult to reduce the error below 3 kJmol^{-1} (0.03 eV).

Angular and radial correlation

- For $n_{\mathrm{max}} = 1$ only the $1s$ orbitals enter the calculation, representing a simple uncorrelated model.
- For $n_{\mathrm{max}} = 2$, introduce $2s$, $2p_x$, $2p_y$ and $2p_z$ functions.
- The CI wavefunction then includes the extra configurations $1s2s$, $2s^2$, $2p_x^2$, $2p_y^2$ and $2p_z^2$. (Note spherical symmetry).
- Each orbital configuration introduces a certain type of correlation. The $2s$ orbital contains a radial node and introduces radial correlation, making it less likely that the electrons will be found the same side of the radial node.

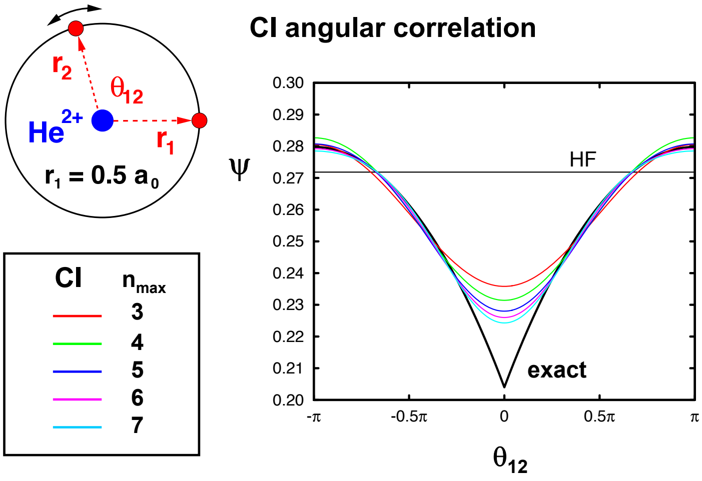
$$\phi_{2s}(r) \propto (3 - 2\zeta r)\,\mathrm{exp}(-\zeta r) \qquad \phi_{2p_z}(\mathbf{r}) \propto z\,\mathrm{exp}(-\zeta r)$$

- Likewise the $2p$ functions introduce angular correlation, making it more likely that the electrons will be located at opposite sides of nucleus.



- As functions with higher principal quantum numbers, and therefore more nodes, are introduced, the description of the correlation becomes more accurate and the energy converges towards the exact value.

Slow convergence to the exact wavefunction



- Consider the cut of the wave function where both electrons are at a radius of $0.5\ a_0$.
- The exact wave function has a cusp, which the smooth orbital functions are unable to describe.
- This is the reason for the observed slow convergence.

Cusps in the wavefunction

- The Hamiltonian for the helium atom is

$$\hat{H} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}$$

- The Hamiltonian becomes *singular* (diverges to infinity) when one of the electron coincides with the nucleus or when the two electrons coincide.
- The wave function satisfies $\hat{H}\psi = E\psi$. In order for ψ not to diverge, there must be infinities due to the kinetic energy that exactly cancel those of the potential energy.
- Infinite second derivatives occur when the first derivative is discontinuous → *cusps*.
- The requirement of exact cancellation imposes particular conditions on these cusps, general to all molecular wave functions.

Nuclear cusp conditions

- The infinity in the potential Z/r_i is exactly canceled if the partial derivative of $\psi(\mathbf{x}_1, \cdots, r_i, \theta_i, \phi_i, \sigma_i, \cdots, \mathbf{x}_n)$ satisfies

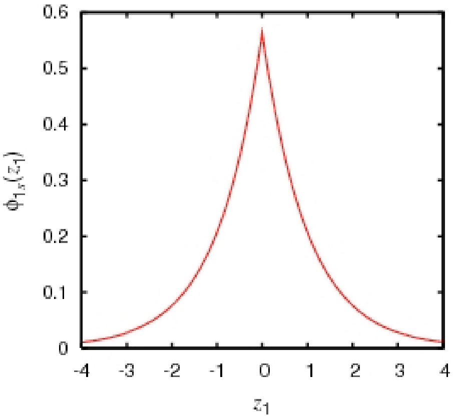
$$\left.\frac{\partial\psi}{\partial r_i}\right|_{r_i=0} = -Z\psi(r_i = 0)$$

- In the region where $r_i \approx 0$ this means that

$$\psi(r_i) = \psi(0)(1 - Zr_i) + O(r_i^2)$$

- Nuclear cusps are familiar since they occur in the hydrogen $1s$ orbital

$$\begin{aligned}\psi_{1s}(r) &= \left(\frac{Z^3}{\pi}\right)^{1/2} \exp(-Zr) \\ &= \left(\frac{Z^3}{\pi}\right)^{1/2} (1 - Zr + O(r^2))\end{aligned}$$

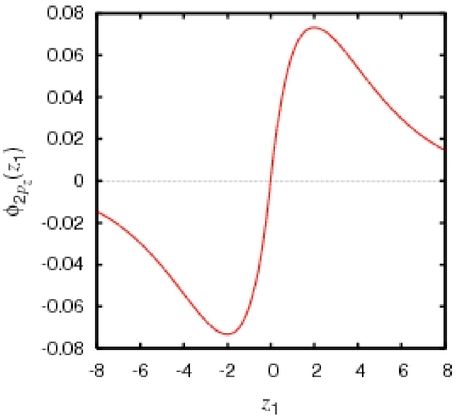


- The cusp condition for p orbitals is different to that for s orbitals. There is zero probability of locating an electron in a p orbital at the nucleus and thus no singularity.
- But, for the Schrödinger equation to be satisfied for very small r_i, the wave function must vanish in a particular way.
- This results in a condition on the second derivatives

$$\frac{\partial^2 \psi}{\partial r_i^2}\bigg|_{r_i=0} = -Z \frac{\partial \psi}{\partial r_i}\bigg|_{r_i=0}$$

- The discontinuity in the second derivative is present in the $2p_z$ hydrogen orbital

$$\begin{aligned} \psi_{2p_z}(z) &= \left(\frac{32}{\pi}\right)^{1/2} z \exp(-\tfrac{|z|}{2}) \\ &= \left(\frac{32}{\pi}\right)^{1/2} z(1 - \tfrac{|z|}{2}) + O(z^3) \end{aligned}$$



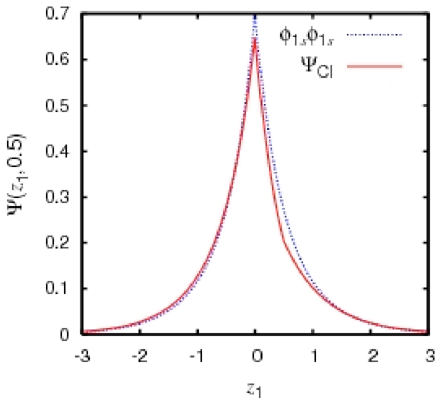
Electronic cusp conditions

- The conditions on the wave function for when two electrons coalesce are analogous to the nuclear cusp conditions.
- Two electrons with opposite spins have zero relative angular momentum ($S = 0$, singlet).
- In the region of coalescence the wave function satisfies

$$\frac{\partial \psi}{\partial r_{12}}\bigg|_{r_{12}=0} = \frac{1}{2}\psi(r_{12} = 0)$$

- Therefore there is a cusp in ψ
- Consider the He 1^1S ground state.
- Fix electron 2 at $z = 0.5\ a_0$ and move electron 1 along the z axis.

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi|_{r_{12}=0}(1 + \tfrac{1}{2}r_{12}) + O(r_{12}^2)$$



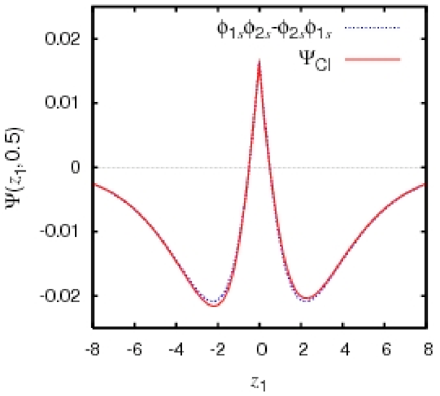
- Two electrons with the same spin have non zero relative angular momentum ($S = 1$, triplet).
- There is zero probability of locating two electrons with the same spin at the same point in space and the coalescence condition applies to the second derivative.

$$\left.\frac{\partial^2\psi}{\partial r_{12}^2}\right|_{r_{12}=0} = \frac{1}{2}\left.\frac{\partial\psi}{\partial r_{12}}\right|_{r_{12}=0}$$

- For small r_{12}

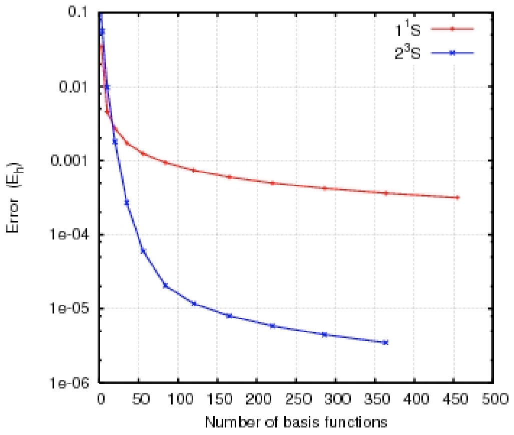
$$\psi(\mathbf{r}_1,\mathbf{r}_2) = \mathbf{r}_{12}\cdot\mathbf{w}_{12}(1+\tfrac{1}{4}r_{12}) + O(r_{12}^3)$$

$$\mathbf{w}_{12} = \frac{\partial\psi}{\partial\mathbf{r}_{12}}$$



- There is no cusp in ψ, but there is a cusp in the first derivative of ψ.
- Consider the He 2^3S ground state.

Convergence in CI type calculations

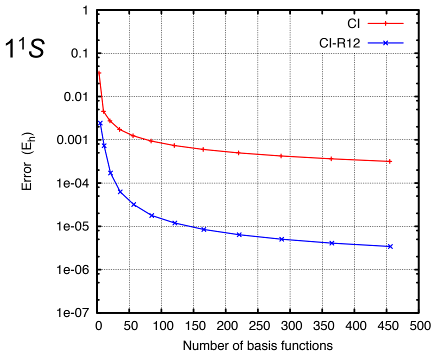


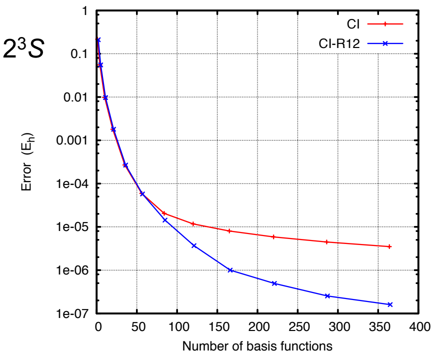
- The error in the energy for the triplet state is smaller than for the singlet, and decays faster.
- Note that every configuration in 2^3S is correct to first order in r_{12}, but none display the discontinuity in the second derivative.
- This slow energy convergence is indicative of all orbital based calculations (MP2, CC, CI, etc).
- It is observed that, for optimal orbitals, the singlet and triplet state errors decrease as n_{max}^{-3} and n_{max}^{-5} respectively.
- The error only reduces as N^{-1} with the number of basis functions. For a method which scales as N^4 each new decimal place takes 10000 times longer.

Including r_{12} explicitly

- The principal deficiency in the CI wave function is the inability to model the discontinuities in the exact ψ.
- If a single term, explicitly dependent on r_{12}, is added to the CI expansion then the convergence is much faster (n_{max}^{-7}).

$$(1 + cr_{12})\phi_{1s}(\mathbf{r}_1)\phi_{1s}(\mathbf{r}_2) \qquad (1 + cr_{12})\left[\phi_{1s}(\mathbf{r}_1)\phi_{2s}(\mathbf{r}_2) - \phi_{2s}(\mathbf{r}_1)\phi_{1s}(\mathbf{r}_2)\right]$$





- For the singlet $c \approx \frac{1}{2}$, describing the cusp. For the triplet $c \approx \frac{1}{4}$, describing the second derivative discontinuity.

Lessons from helium

- The antisymmetry requirement for electronic wave functions leads to *Fermi correlation* of the electrons.
  - Triplet states exhibit *Fermi holes*.
  - Closed shell singlet states are spatially uncorrelated.
  - Open shell singlet states exhibit *Fermi heaps*.
  - Fermi correlation accounts for the main spectral features.
- The instantaneous Coulomb interaction between electrons also correlates their motion, *Coulomb correlation*.
  - Electrons avoid each other as much as possible.
  - CI calculations correct for Coulomb correlation.
- Wave functions exhibit cusps at the nuclei and at electron coalescence.
  - The nuclear cusp is well described by atomic orbitals.
  - The electronic cusp is not, resulting in slow convergence.
  - Including r_{12} explicitly in the wave function significantly accelerates convergence → chemical accuracy.

The orbital picture for H_2

- The orbital solutions to H_2^+ resemble symmetrized combinations of the hydrogenic orbitals.
- For the H_2 molecule we construct an orbital basis in the same vein. Let us take a minimal basis of $1s$ AOs.
- The MOs must possess the $D_{\infty h}$ symmetry of the molecule.

$$\begin{aligned} \phi_{\sigma_g}(\mathbf{r}) &= N_g[\phi_{s_A}(\mathbf{r}) + \phi_{s_B}(\mathbf{r})] \\ \phi_{\sigma_u}(\mathbf{r}) &= N_u[\phi_{s_A}(\mathbf{r}) - \phi_{s_B}(\mathbf{r})] \end{aligned}$$

- The *symmetry adapted linear combinations of atomic orbitals* are normalized by N_g and N_u.
- $\phi_{\sigma_g}(\mathbf{r})$ is a nodeless bonding orbital. $\phi_{\sigma_g}(\mathbf{r})$ is an antibonding orbital with a nodal plane bisecting the two atoms A and B.

Fermi correlation in H_2

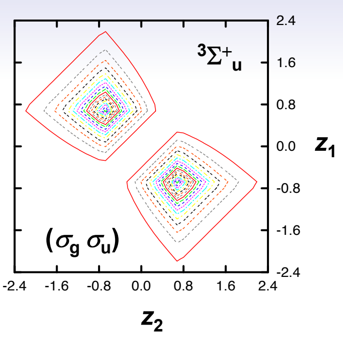
- There are 4 spin orbitals and 2 electrons. The 6 states, satisfying Pauli antisymmetry, are the doubly occupied bonding and antibonding singlet states.

$$\begin{aligned} \psi^{0,0}_{1^1\Sigma_g^+}(\mathbf{x}_1, \mathbf{x}_2) &= \phi_{\sigma_g}(\mathbf{r}_1)\phi_{\sigma_g}(\mathbf{r}_2)\Theta_{0,0}(1,2) \\ \psi^{0,0}_{2^1\Sigma_g^+}(\mathbf{x}_1, \mathbf{x}_2) &= \phi_{\sigma_u}(\mathbf{r}_1)\phi_{\sigma_u}(\mathbf{r}_2)\Theta_{0,0}(1,2) \end{aligned}$$

- and the open shell singlet and triplet states ($M_S = 1, 0, -1$)

$$\begin{aligned} \psi^{0,0}_{1^1\Sigma_u^+}(\mathbf{x}_1, \mathbf{x}_2) &= \frac{1}{\sqrt{2}}[\phi_{\sigma_g}(\mathbf{r}_1)\phi_{\sigma_u}(\mathbf{r}_2) + \phi_{\sigma_u}(\mathbf{r}_1)\phi_{\sigma_g}(\mathbf{r}_2)]\Theta_{0,0}(1,2) \\ \psi^{1,M_S}_{1^3\Sigma_u^+}(\mathbf{x}_1, \mathbf{x}_2) &= \frac{1}{\sqrt{2}}[\phi_{\sigma_g}(\mathbf{r}_1)\phi_{\sigma_u}(\mathbf{r}_2) - \phi_{\sigma_u}(\mathbf{r}_1)\phi_{\sigma_g}(\mathbf{r}_2)]\Theta_{1,M_S}(1,2) \end{aligned}$$

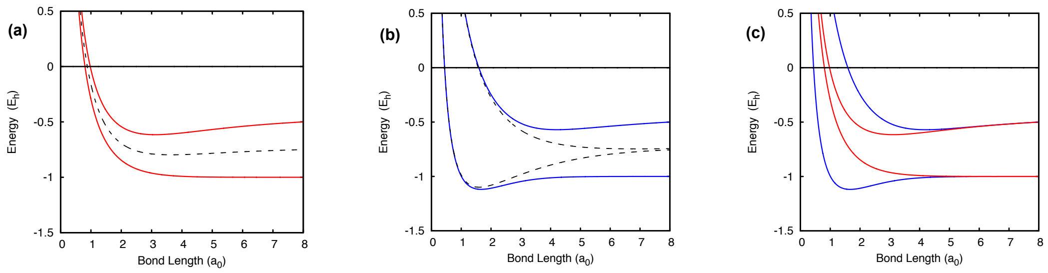
- In the same way as for He, the doubly occupied states are spatially uncorrelated. The open shell triplet and singlet states exhibit Fermi holes and Fermi heaps respectively.



- The cut of the 2-electron density functions for the open shell singlet and triplet states where both electrons are on the molecular axis.
- There is zero probability of finding both electrons at the same point on the molecular axis for the triplet (*Fermi hole*).
- There is zero probability of finding the electrons at exactly opposite ends of the molecule for the singlet (*Fermi heap*).
- Coulomb correlation will modify description, but does not remove these nodes or change the energy level ordering.

Dynamic and non-dynamic Coulomb correlation

- Coulomb correlation is introduced through taking linear combinations of orbital products. In our minimal AO basis only the two states with the same symmetry mix.
- It is instructive to examine the amount of mixing as the H_2 bond is stretched.



(a) Fermi correlation in $^3\Sigma_u^+$, $^1\Sigma_u^+$. (b) Coulomb correlation in $^1\Sigma_g^+$.

- In the absence of Coulomb correlation the bonding and antibonding $^1\Sigma_g^+$ states become degenerate as the bond length increases.

- The amount of Coulomb correlation varies significantly with bond length.
- At equilibrium it is small, amounting to less than 1% of the energy. In this situation the Coulomb correlation is referred to as *dynamic correlation*.
- At infinite separation the bonding and antibonding states mix strongly, lifting the degeneracy and creating an ionic state and a covalent state.

$$\begin{aligned}
\tfrac{1}{2}\phi_{\sigma_g}(\mathbf{r}_1)\phi_{\sigma_g}(\mathbf{r}_2) + \tfrac{1}{2}\phi_{\sigma_u}(\mathbf{r}_1)\phi_{\sigma_u}(\mathbf{r}_2) &= \phi_{s_A}(\mathbf{r}_1)\phi_{s_A}(\mathbf{r}_2) + \phi_{s_B}(\mathbf{r}_1)\phi_{s_B}(\mathbf{r}_2) \\
\tfrac{1}{2}\phi_{\sigma_g}(\mathbf{r}_1)\phi_{\sigma_g}(\mathbf{r}_2) - \tfrac{1}{2}\phi_{\sigma_u}(\mathbf{r}_1)\phi_{\sigma_u}(\mathbf{r}_2) &= \phi_{s_A}(\mathbf{r}_1)\phi_{s_B}(\mathbf{r}_2) + \phi_{s_B}(\mathbf{r}_1)\phi_{s_A}(\mathbf{r}_2)
\end{aligned}$$

- It is necessary to use more than one product of MOs to achieve a qualitatively correct description.
- Here the Coulomb correlation is referred to as *non-dynamic correlation*.

- This situation occurs when there are degeneracies in orbital products and it is common practice to include all products in the zeroth order description of the system (*Multi-reference*).
- Degeneracies can also occur in atoms and molecules, not just for stretched bonds. Typical examples are Be and transition metals, where orbital configurations are similar in energy. In these cases this Coulomb correlation is referred to as *static correlation*.
- Dynamic, non-dynamic and static correlation are not physically different, all arise from the Coulomb repulsion between the electrons.
- The distinction is an operational one, connected to the machinery we use to treat them.
- In this tutorial we are concerned with the methods used to accurately treat dynamic correlation.

Fermi correlation in many-electron systems

- Having illustrated Fermi and Coulomb correlation in the 2-electron systems He and H_2 let us move on to the methods we use to treat many electron systems.
- The first issue is how to construct an antisymmetric n-electron wave function that has a well defined total and z-projected spin.
- The n-electron spin eigenfunctions with spin quantum numbers S and M_S are known. E.g.

$$\Theta^3_{\frac{1}{2}\frac{1}{2}}(\boldsymbol{\sigma}) = \alpha\beta\alpha - \beta\alpha\alpha \qquad \text{3-electron doublet}$$

- It is always possible to construct a n-electron wave function by antisymmetrizing the product of separate space and spin functions.

$$\psi(\mathbf{r},\boldsymbol{\sigma}) \quad = \quad \hat{\mathcal{A}}_n \left(\Phi(\mathbf{r})\Theta^n_{S,M_S}(\boldsymbol{\sigma})\right) \qquad \hat{\mathcal{A}} = \frac{1}{\sqrt{n!}}\sum_u^{n!} p_u \hat{P}_u$$

Slater determinants

- An alternative method is to antisymmetrize a product of spin orbitals directly. This is equivalent to a determinant of a matrix.

$$\begin{aligned}
\psi(\mathbf{r},\boldsymbol{\sigma}) &= \hat{\mathcal{A}}_n \left(\phi_1(\mathbf{r}_1)\sigma_1(1), \cdots, \phi_n(\mathbf{r}_n)\sigma_n(n)\right) \\
&= \frac{1}{\sqrt{n!}} \begin{vmatrix} \phi_1(\mathbf{x}_1) & \phi_2(\mathbf{x}_1) & \cdots & \phi_n(\mathbf{x}_1) \\ \phi_1(\mathbf{x}_2) & \phi_2(\mathbf{x}_2) & \cdots & \phi_n(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(\mathbf{x}_n) & \phi_2(\mathbf{x}_n) & \cdots & \phi_n(\mathbf{x}_n) \end{vmatrix}
\end{aligned}$$

- Determinantal wave functions are always eigenfunctions of $\hat{S}_z$ (they have a fixed number of α and β electrons), but they are not guaranteed to be eigenvalues of $\hat{S}^2$.
- Determinants have many mathematically convenient properties.

Properties of determinants

- Interchanging two matrix rows or columns (permuting two electrons) results in a sign change $\det|\hat{P}_{12}A| = -\det|A|$.
- Unitary linear transformations of the orbitals leave the wave function unchanged.

$$\det|UA| = \det|U|\det|A| = \det|A|$$

- Even though the determinant contains $n!$ terms, integrals over determinants are easy to evaluate. E.g.

$$\begin{aligned}\langle E\rangle &= \langle \mathcal{A}\Phi|\hat{H}|\mathcal{A}\Phi\rangle = \langle\Phi|\hat{H}|\sum_u^{n!} p_u\hat{P}_u\Phi\rangle \\ &= \sum_i^n\langle\phi_i|\hat{h}|\phi_i\rangle + \tfrac{1}{2}\sum_{ij}^n\langle\phi_i\phi_j|(1-\hat{P}_{12})\hat{g}|\phi_i\phi_j\rangle\end{aligned}$$

- All permutations where the orbital ordering in the ket is different to the ordering in the ket are zero, unless the differing orbitals are affected by $\hat{H}$.

Configuration state functions

- Wave functions that are eigenfunctions of $\hat{S}^2$ can be constructed from linear combinations of determinants. These are called *configuration state functions* (CSF).
- Let us consider again the lowest three states of helium.

$$\begin{aligned}\psi^{0,0}_{1^1S} &= \tfrac{1}{\sqrt{2}}\det|1s\alpha 1s\beta| \\ \psi^{1,1}_{1^3S} &= \tfrac{1}{\sqrt{2}}\det|1s\alpha 2s\alpha| \\ \psi^{1,0}_{1^3S} &= \tfrac{1}{2}\det|1s\alpha 2s\beta| + \tfrac{1}{2}\det|1s\beta 2s\alpha| \\ \psi^{1,-1}_{1^3S} &= \tfrac{1}{\sqrt{2}}\det|1s\beta 2s\beta| \\ \psi^{0,0}_{2^1S} &= \tfrac{1}{2}\det|1s\alpha 2s\beta| - \tfrac{1}{2}\det|1s\beta 2s\alpha|\end{aligned}$$

- Closed shell and high spin open shell states are represented by single determinants, with well defined S and M_S. Low spin open shell states are linear combinations.
- These conclusions are general to n-electron systems.

Hartree-Fock theory

- The determinant representation of the wave function is most the practical for many electron systems.
- Single determinants correctly describe Fermi holes for like spin electrons in closed shell or high spin open shell states. Single Slater determinants cannot describe Fermi heaps, but they do not occur in these states.
- In the *Hartree-Fock method* the orbitals are variationally optimized, subject to remaining orthonormal.
- Consider an infinitesimal change to the spin-orbitals.

$$\begin{aligned}
E[\psi+\delta\psi] &= \sum_i \langle \phi_i+\delta\phi_i|\hat{h}|\phi_i+\delta\phi_i\rangle \\
&\quad +\tfrac{1}{2}\sum_{ij}\langle(\phi_i+\delta\phi_i)(\phi_j+\delta\phi_j)|\hat{g}|(\phi_i+\delta\phi_i)(\phi_j+\delta\phi_j)\rangle \\
&\quad -\tfrac{1}{2}\sum_{ij}\langle(\phi_i+\delta\phi_i)(\phi_j+\delta\phi_j)|\hat{g}|(\phi_j+\delta\phi_j)(\phi_i+\delta\phi_i)\rangle
\end{aligned}$$

- To get the first order variation $\delta^1 E[\psi]$ we collect terms linear in $\delta\phi$.

$$\begin{aligned}
\delta^1 E[\psi] &= \sum_i \langle\delta\phi_i|\hat{h}|\phi_i\rangle + \sum_{ij}\Big(\langle\delta\phi_i\phi_j|\hat{g}|\phi_i\phi_j\rangle - \langle\delta\phi_i\phi_j|\hat{g}|\phi_j\phi_i\rangle\Big) + \text{c.c.} \\
&= \sum_i \langle\delta\phi_i|\hat{h}|\phi_i\rangle + \sum_i \langle\delta\phi_i|\hat{J}-\hat{K}|\phi_i\rangle + \text{c.c.} \\
&= \sum_i \langle\delta\phi_i|\hat{F}|\phi_i\rangle + \text{c.c.}
\end{aligned}$$

- $\hat{F}$ is the *Fock operator* and it is Hermitian.
- The optimum orbitals minimize $E[\psi]$ so $\delta^1 E[\psi]$ vanishes. We therefore have the *Hartree-Fock equation* for each orbital

$$\langle\delta\phi_i|\hat{F}|\phi_i\rangle = 0$$

- Let us expand $\delta\phi_i$ in terms of a complete orthonormal orbital basis, partitioned into the current orbitals and a complementary set.

$$\delta\phi_i = \sum_j^n U_{ij}\phi_j + \sum_a^\infty U_{ia}\phi_a$$

- The first term is a unitary transformation of the occupied orbitals and leaves ψ unchanged.
- From the second term we arrive at the set of *general Hartree-Fock equations* for the optimum orbitals ϕ_i.

$$\langle\phi_a|\hat{F}|\phi_i\rangle = 0$$

- This is satisfied if the function $\hat{F}\phi_i$ is orthogonal to all ϕ_a

$$\hat{F}\phi_i = \sum_j^n \lambda_{ji}\phi_j \qquad \lambda_{ji} = \lambda_{ji}^* = \langle\phi_j|\hat{F}|\phi_i\rangle$$

- We can transform the occupied orbitals among themselves to diagonalize the Hermitian matrix λ_{ji}, arriving at the familiar *canonical Hartree-Fock equations*

$$\hat{F}\phi_i = \varepsilon_i\phi_i$$

The self consistent field procedure

- The Fock operator that defines the orbitals in fact depends on the very orbitals it defines.

$$\hat{F}_1 = -\tfrac{1}{2}\nabla_1^2 - \sum_I \frac{Z_I}{r_{I1}} + \sum_j^n \int \phi_j(\mathbf{r}_2)(1-\hat{P}_{12})\frac{1}{r_{12}}\phi_j(\mathbf{r}_2)d\mathbf{r}_2$$

- The Hartree-Fock equations must therefore be solved self consistently.
- An initial set of orbitals are used to construct the Fock operator, the solution of which yields a new set of orbitals.
- A new Fock operator is constructed and so on until the equations are self consistent.
- Physically this means that each orbital adjusts to the mean repulsive field due to the electrons in the other orbitals.

The Roothaan-Hall equations

- The above equations define the orbitals that give the best Slater determinant wave function.
- The are coupled integro-differential equations and are difficult to solve directly.
- If we expand the orbitals in terms of a finite set of basis functions then the problem is transformed to one of standard linear algebra.
- We expand our orbitals as linear combinations of atomic orbital basis functions.

$$\phi_i(\mathbf{r}) = \sum_\alpha C_{\alpha i}\chi_\alpha(\mathbf{r})$$

- The generalized Hartree-Fock equation becomes

$$\langle \phi_a|\hat{F}|\phi_i\rangle = \sum_{\alpha\beta} C^*_{\alpha a} F_{\alpha\beta} C_{\beta i} = (\mathbf{C}^\dagger \mathbf{F}\mathbf{C})_{ai} = 0$$

- These equations must be solved under the orthonormality constraint

$$\mathbf{C}^\dagger\mathbf{S}\mathbf{C} = 1$$

- The solutions to the *Roothaan-Hall equations* satisfy both requirements

$$\mathbf{F}\mathbf{C} = \mathbf{S}\mathbf{C}\varepsilon$$

- This is a generalized matrix eigenvalue problem. We may transform it to conventional matrix eigenvalue form by transforming the AOs to an (arbitrary) orthonormal set $\{\tilde{\phi}_i\}$.

$$\tilde{\phi}_i = \sum_\alpha U_{\alpha i}\chi_\alpha \qquad \mathbf{U}^\dagger\mathbf{S}\mathbf{U} = 1$$

$$\begin{aligned}(\mathbf{U}^\dagger\mathbf{F}\mathbf{U})(\mathbf{U}^{-1}\mathbf{C}) &= (\mathbf{U}^\dagger\mathbf{S}\mathbf{U})(\mathbf{U}^{-1}\mathbf{C})\varepsilon \\ \tilde{\mathbf{F}}\tilde{\mathbf{C}} &= \tilde{\mathbf{C}}\varepsilon\end{aligned}$$

The density matrix

- It is efficient to reformulate the HF equations in terms of the AO basis, using the density matrix.
- In a RHF calculation the density matrix is defined as

$$D_{\alpha\beta} = \sum_{i}^{n} C_{\alpha i} C_{\beta i}$$

- The Fock matrix is

$$\langle \alpha | \hat{F} | \beta \rangle = h_{\alpha\beta} + \sum_{\gamma\delta} D_{\alpha\beta} (2 g_{\alpha\beta\gamma\delta} - g_{\alpha\gamma\beta\delta})$$

- The energy is evaluated through

$$E = 2 \sum_{\alpha\beta} D_{\alpha\beta} h_{\alpha\beta} + \sum_{\alpha\beta\gamma\delta} D_{\alpha\beta} D_{\gamma\delta} (2 g_{\alpha\beta\gamma\delta} - g_{\alpha\gamma\beta\delta})$$

- It is also possible to optimize the density matrix directly.

Coulomb Correlation: Coupled Cluster Theory

- In the same way as for He and H_2 we introduce Coulomb correlation among the electrons by expanding ψ as a linear combination of Slater determinants.

$$\psi_{\mathrm{CI}} = \sum_{pq\cdots} C_{pq\cdots} \,\mathrm{det}\, |pq \cdots|$$

- The coefficients $C_{pq\cdots}$ may be variationally minimized to give the best wave function within a given orbital basis.
- Each Slater determinant may be viewed as generated from the Hartree-Fock wave function by orbital replacements (*excitations*).
- By including all excitations from occupied to virtual orbitals we arrive at an accurate description of the system.
- The number of virtual excitations grows factorially with the size of the system. The direct variational optimization of all coefficients is impossible in practice.

- However, even in large systems, correlation predominantly occurs through pairwise interactions between electrons.
- When the Hartree-Fock wave function is a good zeroth order reference, the orbitals are only slightly modified by the interactions.
- The perturbation of the orbitals is an excitation $\hat{\tau}_{ij}^{ab}$ from a pair of occupied orbitals ij to a pair of virtual orbitals ab.
- Each pair excitation occurs with an *amplitude* t_{ij}^{ab}, representing the contribution (*probability*) of this excitation.
- In many electron systems such pair excitations occur not only in isolation, but also in combination with one another in all possible ways.

$$\psi_{\text{CCD}} = \left[\prod_{aibj}(1 + t_{ij}^{ab}\hat{\tau}_{ij}^{ab})\right] \text{det}\,|ij\cdots|$$

- This is the *coupled cluster* wave function in its simplest form: the *coupled cluster doubles (CCD) model*.

- Due to the product form ψ_{CCD} is composed of all even order virtual excitations.

$$\psi_{\text{CCD}} = \psi_{\text{HF}} + \sum_{aibj} t_{ij}^{ab}\hat{\tau}_{ij}^{ab}\psi_{\text{HF}} + \sum_{aibjckdl} t_{ij}^{ab}t_{kl}^{cd}\hat{\tau}_{ij}^{ab}\hat{\tau}_{kl}^{cd}\psi_{\text{HF}} + \cdots$$

- The coefficients for quadruple excitations are products of double excitation amplitudes and so on.
- In reality the quadruple excitations are also affected by 3- and 4-electron interactions that have not been included in our pair model, but these contributions are small.
- We may refine our model by including amplitudes for single, triple and higher excitations.
- The singles amplitudes represent the response of the HF orbitals to the Coulomb correlation and triples represent 3-electron interactions etc.
- Each successive excitation level included reduces the error by approximately a factor of 4.

- The quality of the correlation description does not only depend on the level of excitation included, it is also critically dependent on the orbital basis from which the excitations are constructed.
- The convergence of coupled cluster methods as the orbital basis set increases is slow due to the electron cusps.
- There is little point in including higher and higher excitations unless the basis set is large enough to ensure that the basis set errors are smaller or of similar magnitude to errors due to neglecting higher excitations.
- In the following lectures we will discuss the coupled cluster methods in detail, and we will address the issue of basis set convergence through explicitly correlated methods.
- This discussion is most conveniently expressed in the elegant language of second quantization.