Mock Exam Discussion
+
Q&A Session

Written Exam Details

Content

- The written exam will be approximately 5-7 questions with a bonus question.
- The written exam will cover all chapters from 1 to 4 (through HF theory)
- Review recommendation - youtube videos by David Sherrill from Georgia Tech: https://www.youtube.com/@DavidSherrill1

Time & Date

- Your written exam will take place on **Monday October 28th**.
- The exam will start at 10.15, and the duration is **2 hours**.
- We will be in the room from 10h, so you will have few minutes to arrive and settle before starting.

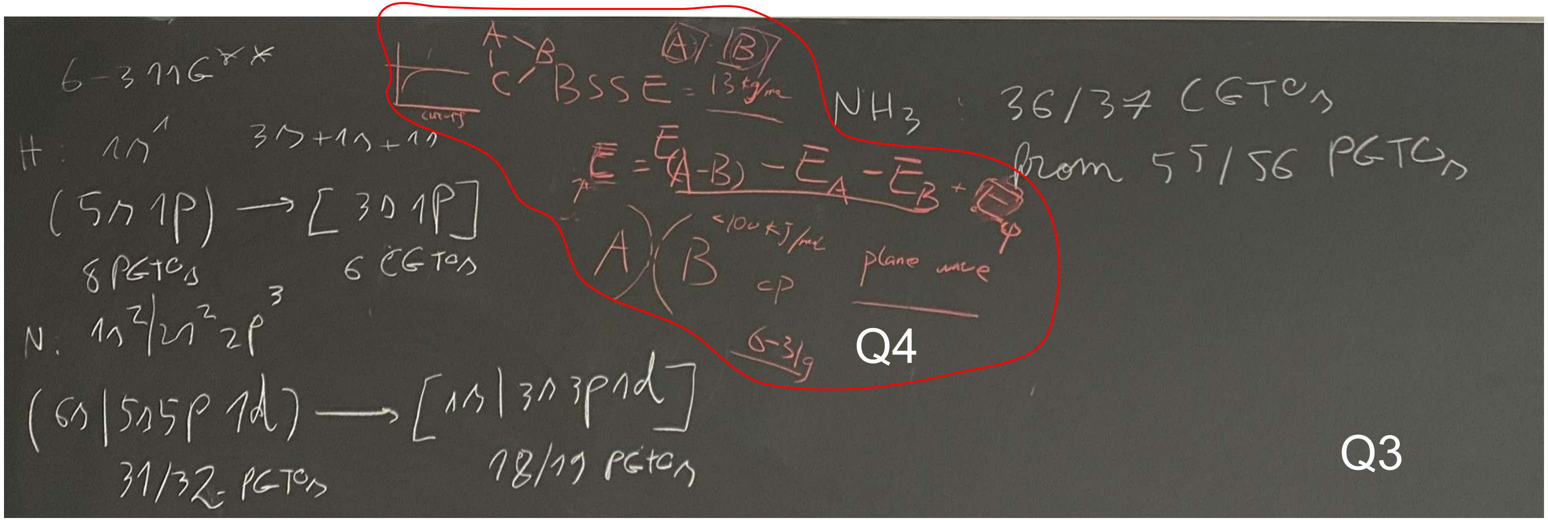
Location

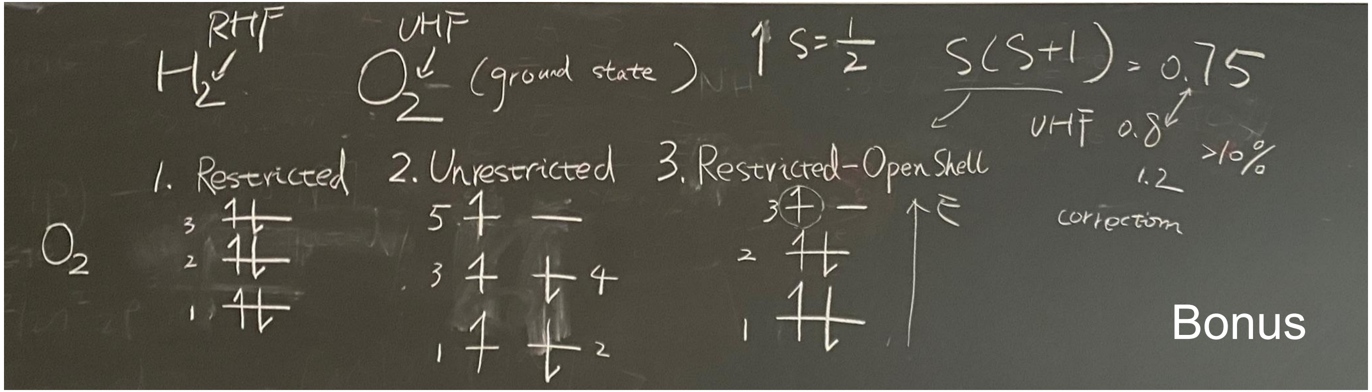
- The exam will be held in **BCH 1103** (where we have interviews).

Materials

- You are permitted to bring **two A4-sized sheets of notes front & back** (handwritten or typed)
- Please also bring scratch paper and writing utensils, no calculators will be needed

Photos of the black board during the Q&A session





Mock Exam Question 1

All standard quantum chemical electronic structure methods are based on three basic assumptions. Which ones? How/when are they justified and when not?

- Time-independent
    - Applies if the properties of interest are not time-dependent

- Non-relativistic
    - Does not apply in systems where spin orbit-coupling is relevant (heavy atoms)

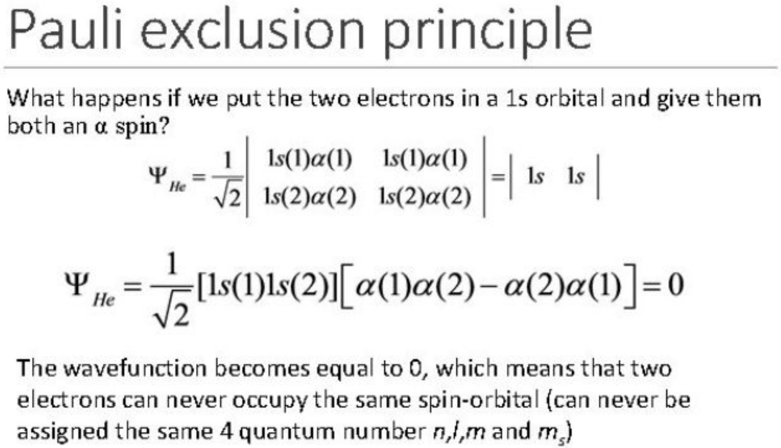
- Separability of electronic and nuclear components (Born-Oppenheimer approximation)
    - Applies: heavy-ish atoms; ground state; no conical sections electronic states
    - Does not apply: super light atoms; excited states; mixed electronic states;l description of nuclear effects (tunneling, zero point vibrations, nuclear wavefunctions)

Mock Exam Question 2

Show that the hypothetical Slater determinant for a He atom is identical to zero

$$\Psi = 1/\sqrt{2}\,|\varphi_{1s}^{\alpha}(1)\varphi_{1s}^{a}(2)|$$

$$\Psi = \frac{1}{\sqrt{2}}\,|\,\phi_{1S}^{\alpha}(1)\phi_{1S}^{\alpha}(2)\,| = \frac{1}{\sqrt{2}}\begin{vmatrix}\phi_{1S}^{\alpha}(1) & \phi_{1S}^{\alpha}(1)\\ \phi_{1S}^{\alpha}(2) & \phi_{1S}^{\alpha}(2)\end{vmatrix} = \frac{1}{\sqrt{2}}(\phi_{1S}^{\alpha}(1)\phi_{1S}^{\alpha}(2) - \phi_{1S}^{\alpha}(1)\phi_{1S}^{\alpha}(2)) = 0$$



Pauli exclusion principle

What happens if we put the two electrons in a 1s orbital and give them both an α spin?

$$\Psi_{He} = \frac{1}{\sqrt{2}}\begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\alpha(1)\\ 1s(2)\alpha(2) & 1s(2)\alpha(2)\end{vmatrix} = \begin{vmatrix} 1s & 1s \end{vmatrix}$$

$$\Psi_{He} = \frac{1}{\sqrt{2}}[1s(1)1s(2)]\left[\alpha(1)\alpha(2) - \alpha(2)\alpha(1)\right] = 0$$

The wavefunction becomes equal to 0, which means that two electrons can never occupy the same spin-orbital (can never be assigned the same 4 quantum number n,l,m and m_s)

Mock Exam Question 2 Previous Student Question

“The Slater determinant in problem 2: Is $\varphi_{1s}^{\alpha}(1)$ *equivalent to the product of spatial orbital* $\varphi_{1s}(1)$ *times spin orbital* α*?”*

Short answer: **Yes**, the $\varphi_{1s}^{\alpha}(1)$ orbital is the “simple” product of spatial orbital $\varphi_{1s}(1)$ times spin orbital α

Why: Quantum mechanics

- The state of a particle is a vector in an Hilbert space
- If the Hamiltonian can be split into the sum of orbital and spin terms, i.e. orbital and spin angular momenta of the particle are separable in the Hamiltonian operator
  → state of the system can be written using tensor product factorization ⇒ **“simple” product**

$$\underbrace{\boxed{|\Psi(t)\rangle}}_{\text{state of the system}} = \underbrace{\boxed{|\psi(t)\rangle}}_{\text{position state vector}} \otimes \underbrace{\boxed{|\xi(t)\rangle}}_{\text{spin state vector}} \longrightarrow \underbrace{\Psi(\mathbf{r}, s_z, t)}_{\text{wavefunction}} = \psi(\mathbf{r}, t)\,\xi(s_z, t)$$

Mock Exam Question 3

How many basis functions are included in the calculation of the molecule NH_3 with the basis set 6-311G**? From how many primitive Gaussians is this basis constructed?

What does **6-311G**** tell us?

- Split-valence with one basis function for each core orbital (**left** of the hyphen) and three functions for each valence orbital (**right** of the hyphen)
- Core basis function is comprised of **6** primitive Gaussians
- Three basis functions are comprised of **3**, **1**, and **1** primitive Gaussians respectively
- ** means we add polarization functions on both light (H) and heavy (everything else) atoms

Don't forget that the hydrogen atom's 1s is its **valence** orbital :)

Mock Exam Question 3

Counting the functions and the primitive Gaussians:

- H 1s → 3 basis functions, 3+1+1 primitive Gaussians
- H polarization (*) → 3 polarization functions (p), 1+1+1 primitive Gaussians

Each H is comprised of 6 basis functions, 8 primitive Gaussians and because there are three H atoms in the NH_3 molecule, they collectively contribute 18 basis functions and 24 primitive Gaussians

- N 1s → 1 basis function, 6 primitive Gaussians
- N 2s → 3 basis functions, 3+1+1 primitive Gaussians
- N 2px, 2py, 2pz→ THREE of: 3 basis functions, 3+1+1 primitive Gaussians
- N polarization (*) → 5 or 6 polarization functions[1] (d), 1+1+1+1+1(+1) primitive Gaussians

The N is comprised of 18 or 19 basis functions, 31 or 32 primitive Gaussians

Total for the NH_3 molecule: 36 or 37 basis functions, 55 or 56 primitive Gaussians

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[1] For d orbitals, 5 or 6 polarization functions depending on whether spherical/cartesian coordinates are used (both answer accepted, always better to specify!)

Mock Exam Question 3 Previous Student Question

“How does the counting of basis functions work with diffuse functions?”

Diffuse functions are shallow basis functions, typically 1 GTO with small exponent, which more accurately represent the "tail" portion of the atomic orbitals, which are distant from the atomic nuclei. 6-31**+**G and 6-31**++**G or a basis set with “**aug**.”

Example with H_2O

STO-3G: 1s, 2s, 2p of 1 basis function (bf) each => 5 bf for O, 1 bf for each H => 7 bf total

6-31G:

O: 1s 1bf, 2s, 2p 2 bf => 9 bf
H: 2bf
total 13 bf (1xO + 2xH)

6-31+G = 6-31G and s and p diffuse functions for non-hydrogen atoms (so for oxygen)

We add diffuse functions for all valence orbitals - one bf each of s and p shape of oxygen

O: 4bf
total: 17 bf (6-31G plus 4)

6-31++G = 6-31G and s and p diffuse functions for all atoms,

so in addition to the previous example, we add 1 diffuse bf per hydrogen
total: 19 bf (6-31+G plus 2)

Extra Basis Set Function Counting Practice

Consider formaldehyde, H_2CO. Count the number of contractions and the number of GTOs in these basis sets:	Solutions (contracted and primitives):
1a. STO-3G	**1a.** 12 and 36
1b. 3-21G	**1b.** 22 and 36 ***(# primitives corrected from 26 to 36 on 19.11.2023!)***
1c. 6-31G* (Spherical)	**1c.** 32 and 62
1d. 6-31G* (Cartesian)	**1d.** 34 and 64
1e. 6-31++G** (Cartesian)	**1e.** 50 and 80

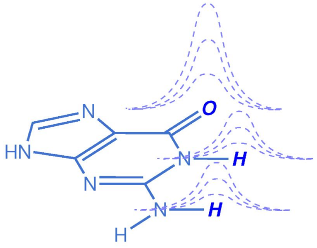
Borrowed from: https://www.theochem.ru.nl/quantumchemistry/2015/qc-wk3-ans.pdf

Mock Exam Question 4 + Previous Student Questions

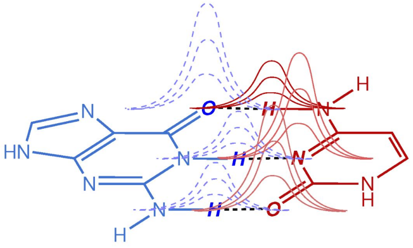
What is the Basis Set Superposition Error (BSSE)? How can one avoid/correct BSSE? In which systems is BSSE a serious problem?

“Does BSSE only occur, as soon as we compare the energy of a complex with the energy of monomer? Or is it also possible to have BSSE in other situations?”

- BSSE is related to certain atoms "borrowing" basis functions from other nearby components, effectively increasing their basis set and improving the calculation by chance
- It can also occur if you look at complexes at different distances e.g H_2 at 10A distance will suffer from less BSSE compared to H_2 at 2.5A distance
- Also different parts in the same molecule can present BSSE (intramolecular BSSE)



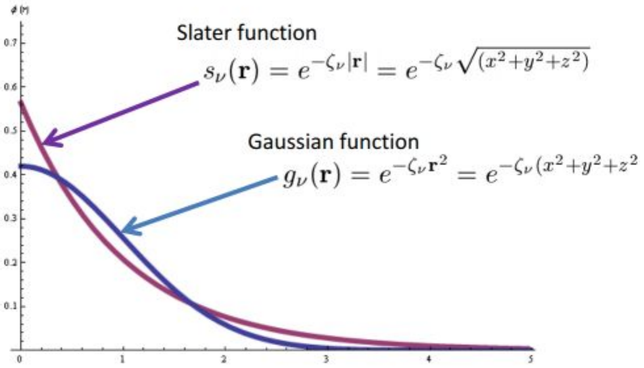
Guanine

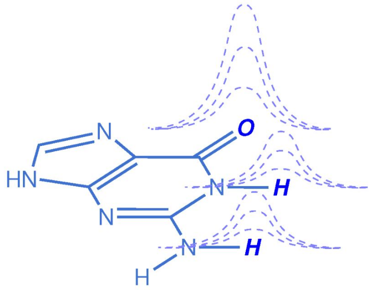


Guanine---Cytosine
Watson-Crick base pair

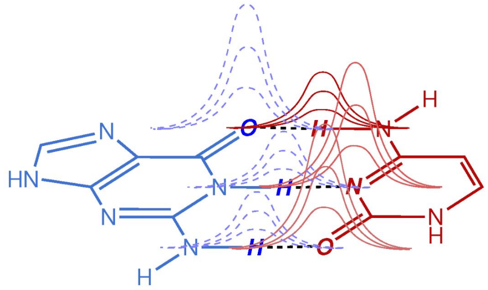
When we compare different species, the effective basis set size is different because an atom, ex. O in Guanine, can use basis functions of the other atoms (as they overlap). The same possibility in the isolated molecule as in the base pair.

“Could you please explain the basis set truncation error and its difference in comparison to the basis set superposition error?”





Guanine



Guanine---Cytosine
Watson-Crick base pair

For example, if we approximate a Slater function with two few gaussian functions we get an inaccurate description for the tail and the cusp. A basis set **truncation error** relates to the fact that a finite linear combination of functions can not fully represent the true system.

Solution:
Make basis set bigger (add more basis functions)

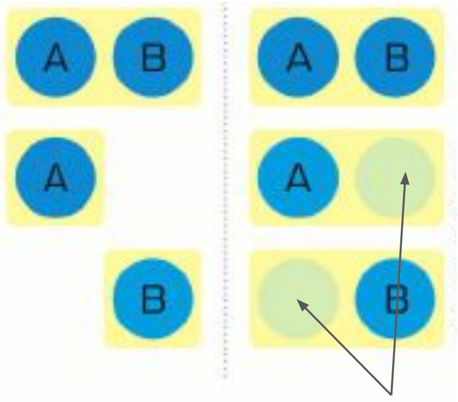
When we compare different types of systems, the effective basis set size may different. For example, the O atom in the G-C complex case can use overlapping basis functions from other atoms. These overlapping basis functions are not available in the isolated molecule and can be create inconsistencies when comparing calculations. This is a basis set **superposition error**.

Solution:
Mimic the basis set to be artificially larger via counterpoise correction.

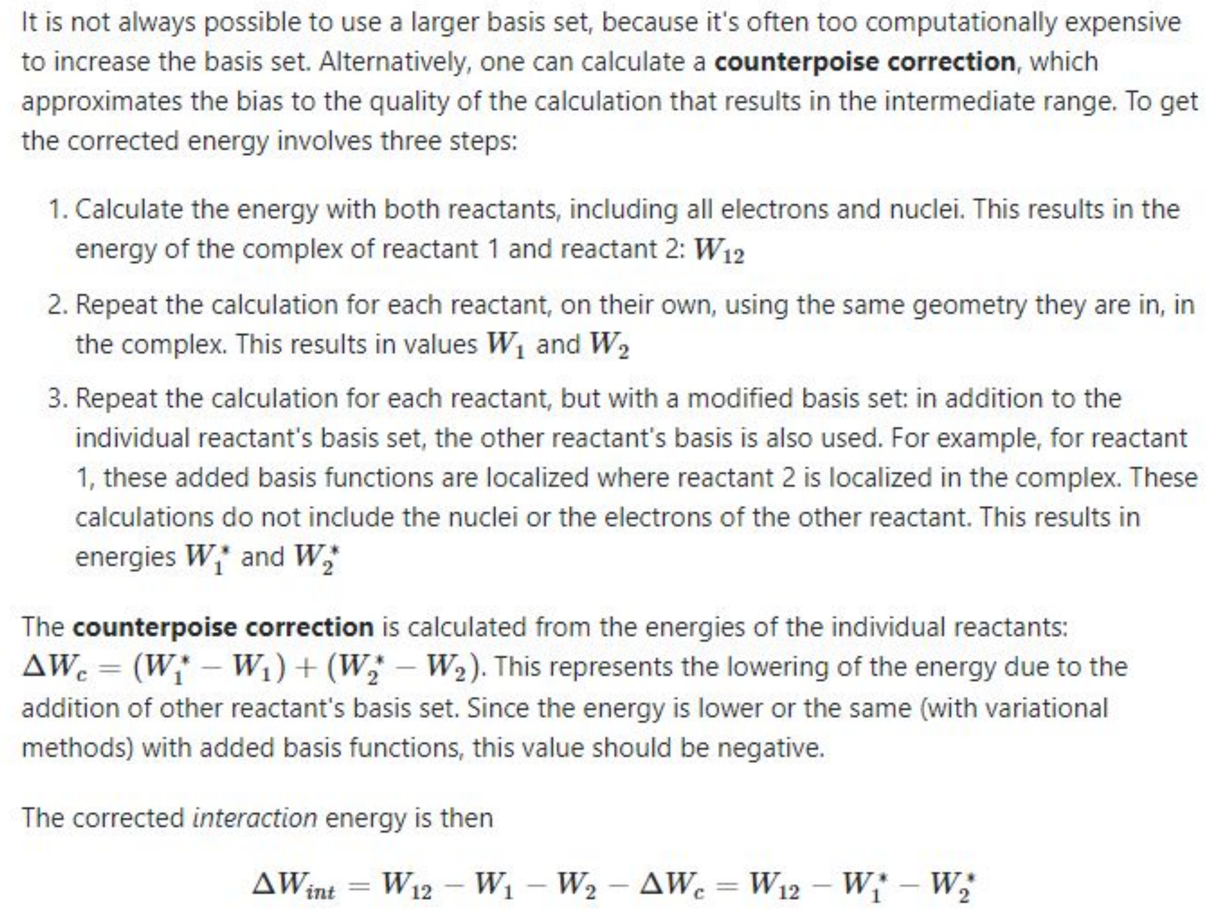
“For counterpoise correction, is the term E^{CP} an additional parameter that we have to add in the final result?”

CP correction is an *a posteriori* correction.

Instead of 3 (or 2 if homodimer) calculations you run 5 calculations and calculate a **correction** energy



Ghost basis functions without an atom present



It is not always possible to use a larger basis set, because it's often too computationally expensive to increase the basis set. Alternatively, one can calculate a **counterpoise correction**, which approximates the bias to the quality of the calculation that results in the intermediate range. To get the corrected energy involves three steps:

1. Calculate the energy with both reactants, including all electrons and nuclei. This results in the energy of the complex of reactant 1 and reactant 2: W_{12}
2. Repeat the calculation for each reactant, on their own, using the same geometry they are in, in the complex. This results in values W_1 and W_2
3. Repeat the calculation for each reactant, but with a modified basis set: in addition to the individual reactant's basis set, the other reactant's basis is also used. For example, for reactant 1, these added basis functions are localized where reactant 2 is localized in the complex. These calculations do not include the nuclei or the electrons of the other reactant. This results in energies W_1^* and W_2^*

The **counterpoise correction** is calculated from the energies of the individual reactants: $\Delta W_c = (W_1^* - W_1) + (W_2^* - W_2)$. This represents the lowering of the energy due to the addition of other reactant's basis set. Since the energy is lower or the same (with variational methods) with added basis functions, this value should be negative.

The corrected *interaction* energy is then

$$\Delta W_{int} = W_{12} - W_1 - W_2 - \Delta W_c = W_{12} - W_1^* - W_2^*$$

Mock Exam Question 5 + Previous Student Question

According to Hund’s rule, states with maximum spin multiplicity are energetically preferred. Give a justification of this empirical rule based on the Hartree-Fock energy expression.

For question 5 “give a justification of Hund’s rule based on HF energy expression”, I used the exchange integral as my argument. Physically speaking, I would also argument that having electrons in different spatial orbitals minimizes the electrostatic repulsion. However, I have troubles integrating this idea using E_{HF} *expression.*

$$E_{HF} = \sum_{i} \langle i | \hat{h} | i \rangle + \frac{1}{2} \sum_{ij} [ii|jj] - [ij|ji]$$

The exact Coulomb interaction among electrons depends on the form of the orbital. However, Coulomb interaction between electrons is <u>always</u> repulsive (two negatively charges) and is minimized at infinite distance ($q_1 q_2 / r_{12}$). If electrons occupy different spatial orbitals, the numerical value for the J integral will differ, but it will be a <u>positive contribution in any case</u>.

The exchange component (K) lowers the energy. However we can only exchange α with α and β with β. Higher multiplicity systems provide more exchange partners making them more stable than lower multiplicity systems with the same # electrons.

Mock Exam Question 6

Why is the Hartree Fock Method sometimes called SCF (self consistent field)?

In general, a SCF method iteratively solves the given problem, using the results from the previous steps in the input until the orbital coefficients do not change (within a given threshold).

In the HF case, we have to solve HF equations for each ϕ_i

$$\left[h(\mathbf{x}_1) + \sum_{\boxed{j \neq i}} \mathcal{J}_j(\mathbf{x}_1) - \sum_{\boxed{j \neq i}} \mathcal{K}_j(\mathbf{x}_1)\right] \phi_{\boxed{i}}(\mathbf{x}_1) = \epsilon_i \phi_{\boxed{i}}(\mathbf{x}_1)$$

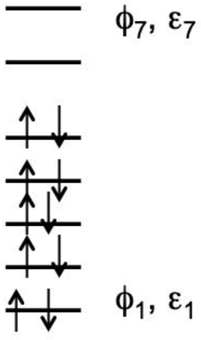
where the sums involving the Coulomb and exchange operators involve all the ϕ_js at the same time, when solving the HF equation for ϕ_j

$$\mathcal{J}_j(\mathbf{x}_1) = \int d\mathbf{x}_2 |\phi_j(\mathbf{x}_2)|^2 r_{12}^{-1} \qquad \mathcal{K}_j(\mathbf{x}_1)\phi_i(\mathbf{x}_1) = \left[\int d\mathbf{x}_2 \phi_j^*(\mathbf{x}_2) r_{12}^{-1} \phi_i(\mathbf{x}_2)\right] \phi_j(\mathbf{x}_1)$$

Hence, the need to solve them self-consistently.

“Could you please explain one more time why having a basis set composed of M functions implies that the Fock Matrix will be M*M sized? (where M is the number of HF orbitals/eigenvectors and M eigenvalues).”

For a water molecule in exercise 4, there are 5 doubly occupied and 2 virtual (“unoccupied”) molecular orbitals.



HF ground state configuration

The **virtual** orbitals are also solutions to the Roothaan equations. However, they do not enter the Fock operator.

In Exercise 4, our C matrix (which indirectly describes the system wavefunction) is always 7 x 7 but we only use the first 5 columns. i.e a 7x5 matrix to construct the next density matrix (7x7). The rows are our basis functions, each column represents an orbital.

Reminder about Hartree-Fock-Roothan equations

We usually need to solve Hartree-Fock equations

$$h(\mathbf{x}_1)\phi_i(\mathbf{x}_1) + \sum_{j\neq i}\left[\int d\mathbf{x}_2 |\phi_j(\mathbf{x}_2)|^2 r_{12}^{-1}\right]\phi_i(\mathbf{x}_1) - \sum_{j\neq i}\left[\int d\mathbf{x}_2 \phi_j^*(\mathbf{x}_2)\phi_i(\mathbf{x}_2) r_{12}^{-1}\right]\phi_j(\mathbf{x}_1) = \epsilon_i \phi_i(\mathbf{x}_1)$$

in the space spanned by a set of basis functions. Introducing a basis set “transforms” the Hartree-Fock equations into the Hartree-Fock-Roothaan equations (detailed derivation in class, on the slides/lecture script)

$$\phi_i = \sum_{\mu=1}^{K} D_{\mu i}\chi_\mu \longrightarrow \sum_\nu F_{\mu\nu}D_{\nu i} = \epsilon_i \sum_\nu S_{\mu\nu}D_{\nu i} \longleftrightarrow \mathbf{FD} = \mathbf{SD}\epsilon$$

where ϵ is a diagonal matrix of the orbital energies. This is like an eigenvalue equation except for the overlap matrix **S** (hence called “pseudo eigenvalue equation”).

By performing a transformation of basis to go to an orthogonal basis, **S=1** (identity matrix), Then it’s just a matter of solving an eigenvalue equation (or, equivalently, diagonalizing the **F** matrix). Since **F** depends on it’s own solution (through the orbitals), the process must be done iteratively in a self-consistent way!

Mock Exam Bonus Question + Previous Student Questions

Explain the terms “restricted”, “unrestricted” and “restricted-open shell” Hartree-Fock calculations.

Restricted

electrons reside as pairs in spatial orbitals of an α paired with β, i.e. we only need to generate information about half of the electrons or one complete set of orbitals. For a closed-shell system, the mean-field approach of Hartree–Fock theory gives rise to the same equations for electrons in the same orbital.

Unrestricted

electrons reside in separate spatial orbitals for α and β, i.e. two complete sets of orbitals, one for the α electrons and one for the β electrons are used. For an open-shell system, the mean-field approach of Hartree–Fock theory gives rise to different equations for the α and β orbitals.

Restricted-Open Shell

electrons reside as pairs in spatial orbitals of an α paired with β until no longer possible. When necessary, separate spatial orbitals are used for α and β.

“For UHF, we talked about how spin contamination can occur. Could you please explain again what it is?”

Spin contamination = artificial mixing of different electronic spin-states, i.e. the wave function is “contaminated” to some extent by higher order spin eigenstates: the wavefunction appears to be the desired spin state, but has a bit of some other spin state mixed in, with possible consequences in energy and also geometry/spin density

This can occur when the spatial parts of α and β spin-orbitals are permitted to differ (as in UHF) and has the disadvantage of producing wavefunction which are not eigenfunctions of the total spin-squared operator. As a check for the presence of spin contamination, most ab initio programs will print out the expectation value of the total spin ($<S^2>$). If there is no spin contamination this should equal S(S+1).

Possible solution: force double occupation of the lowest orbitals by constraining the α and β spatial distributions to be the same (restricted open-shell Hartree–Fock, **ROHF**) → Avoids spin contamination, but is computationally more expensive

“Why are the wavefunctions still eigenfunctions of <S^2> in RHF and ROHF, but no more in UHF?”

Compute the expectation value of the S^2 operator for the RHF/UHF wavefunctions:

$$\langle S^2\rangle_{\mathrm{ROHF}} = \left(\frac{N_\alpha - N_\beta}{2}\right)\left(\frac{N_\alpha - N_\beta}{2}+1\right) = \boxed{\langle S^2\rangle_{\mathrm{exact}}} = s(s+1)$$

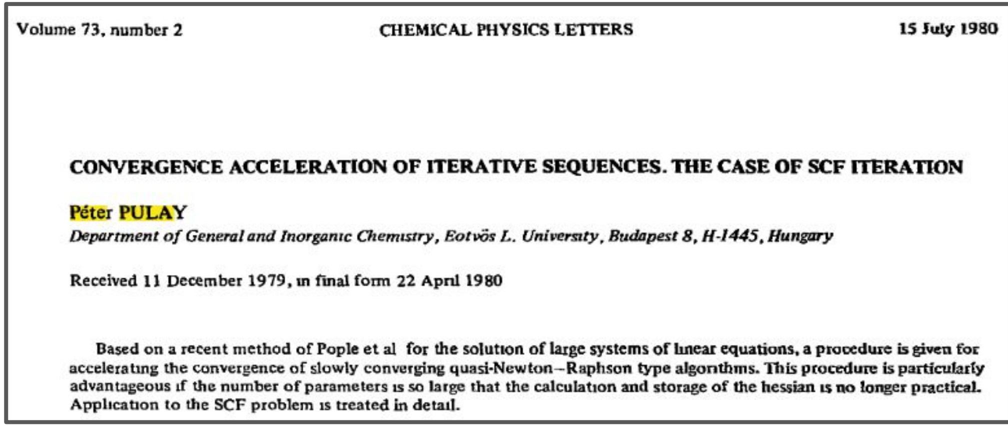
(where $S = N_\alpha - N_\beta$)

$$\langle S^2\rangle_{\mathrm{UHF}} = \boxed{\langle S^2\rangle_{\mathrm{exact}}}\ \boxed{+ N_\beta - \sum_{i,j}^{\mathrm{occupied}} |\langle\psi_i^\alpha|\psi_j^\beta\rangle|^2}$$

“degree of contamination”: measure of the extent of spin contamination in the UHF approach, always non-negative → the wavefunction is usually contaminated to some extent by higher order spin eigenstates

Previous Student Question

“What is DIIS and why we use that?”



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CONVERGENCE ACCELERATION OF ITERATIVE SEQUENCES. THE CASE OF SCF ITERATION

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Based on a recent method of Pople et al for the solution of large systems of linear equations, a procedure is given for accelerating the convergence of slowly converging quasi-Newton–Raphson type algorithms. This procedure is particularly advantageous if the number of parameters is so large that the calculation and storage of the hessian is no longer practical. Application to the SCF problem is treated in detail.

<u>Note</u>: this question is quite specific for the exercises and in any case quite technical, don’t stress too much about it, especially for the written exam!

DIIS (**direct inversion in the iterative subspace**) is a computational technique developed by **Peter Pulay** in the field of computational quantum chemistry with the intent to <u>accelerate and stabilize the convergence of the Hartree–Fock SCF method</u>.

At a given iteration, the approach constructs a linear combination of approximate error vectors from previous iterations, which are then used to extrapolate the function variable for the next iteration.

When used together, SAD (Superposition of Atomic Densities) guess technique and DIIS are usually sufficient to converge the SCF for all but the most difficult systems. DIIS is one of the convergence stabilization techniques supported by Psi4 (on by default).

Other Questions?