Question 1: Counting basis functions

Consider formaldehyde, H_2CO. Count the number of contractions and the number of GTOs in these basis sets:

1a. STO-3G

1b. SV 3-21G

1c. SV 6-31G* (Spherical)

1d. SV 6-31G* (Cartesian)

1e. SV 6-31++G** (Cartesian)

Note: the "+" adds and an extra GTO on valence orbitals. For C/O that is extra orbitals for 2s and for 2p.

Answer: *Contractions (dimension of set of Roothaan equations):*

basis	H		C/O			H_2CO
	s	p	s	p	d	total
STO-3G	1		2	3		12
SV 3-21G	2		3	6		22
SV 6-31G* (Spherical)	2		3	6	5	32
SV 6-31G* (Cartesian)	2		3	6	6	34
SV 6-31++G**(Cartesian)	3	3	4	9	6	50

Note: the star in SV 6-31G indicates polarization functions of second row elements, i.e., d-orbitals for C and O. Two stars (**) indicate also polarization functions on H, i.e., p-orbitals. Similarly for diffuse functions: one + means diffuse s and p functions on C and O, two ++ means also diffuse s functions on H.*

Primitive GTOs:

basis	H		C/O			H_2CO
	s	p	s	p	d	total
STO-3G	3		6	9		36
SV 3-21G	3		6	9		36
SV 6-31G* (Spherical)	4		10	12	5	62
SV 6-31G* (Cartesian)	4		10	12	6	64
SV 6-31++G**(Cartesian)	5	3	11	15	6	80

Question 2: Roothaan equations

The Roothaan equations for a closed shell wave function of a molecule with 16 electrons in a $m = 50$-dimensional one electron basis $\{\phi_1(\boldsymbol{r}), \ldots, \phi_m(\boldsymbol{r})\}$ is given by

$$\boldsymbol{F}[\boldsymbol{P}]\boldsymbol{C} = \boldsymbol{S}\boldsymbol{C}\boldsymbol{\epsilon},$$

where, $\boldsymbol{\epsilon}$ is a diagonal matrix.

2a. Give the dimensions of each of the matrices in this equation.

Answer: *A closed shell wave function with 16 electrons has 8 occupied MOs. Dimensions of $\boldsymbol{F}$, $\boldsymbol{P}$, and $\boldsymbol{S}$:* 50×50. *Dimension of $\boldsymbol{C}$:* 50×8. *Dimension of $\boldsymbol{\epsilon}$:* 8×8.
Sometimes the unoccupied orbitals are also needed, e.g., for a subsequent configuration interaction calculation. In that case all matrices are 50×50.

2b. What is meant by $\boldsymbol{F}[\boldsymbol{P}]$?

Answer: *To compute the Fock matrix $\boldsymbol{F}$ the density matrix $\boldsymbol{P}$ is needed, so $\boldsymbol{F}$ can be considered to be a function of $\boldsymbol{P}$.*

2c. Assuming the equation has been solved, write down the highest occupied molecular orbital.

Answer: *The HOMO is orbital number 8:*

$$\chi_8(\boldsymbol{r}) = \sum_{i=1}^{50} \phi_i(\boldsymbol{r}) C_{i,8}.$$

Question 3: Electron density

A four-electron wave function is given by a single Slater-determinant,

$$\Phi(1,2,3,4) = \frac{1}{\sqrt{n!}} |\chi_1 \overline{\chi}_1 \chi_2 \overline{\chi}_2|. \tag{1}$$

3a. Give the expression for the electron density in point $\boldsymbol{r}$ in terms of the molecular orbitals χ_1 and χ_2.

Answer: *Electron density is a one-electron property. A one-electron property of a single Slater-determinant wave function is the sum of the contributions of the occupied MOs:*

$$\rho(\boldsymbol{r}) = 2|\chi_1(\boldsymbol{r})|^2 + 2|\chi_2(\boldsymbol{r})|^2.$$

Question 4: Antisymmetrizer

The antisymmetrizer for n electrons is given by

$$\hat{\mathcal{A}} = a_n \sum_{i=1}^{n!} (-1)^{p_i} \hat{P}_i. \tag{2}$$

The antisymmetrizer can be defined with different normalizations a_n. Sometimes, a_n is chosen such that the antisymmetrizer is an *idempotent* operator, i.e.,

$$\hat{\mathcal{A}}^2 = \hat{\mathcal{A}}. \tag{3}$$

4a. Determine the normalization factor a_n such that $\hat{\mathcal{A}}$ is idempotent.

Answer: *From question 4b of week 2 we have:*

$$(-1)^q \hat{Q} \sum_{i=1}^{n!} (-1)^p \hat{P} = \sum_{i=1}^{n!} (-1)^p \hat{P}.$$

So we find

$$\hat{\mathcal{A}}^2 = a_n^2 \, n! \sum_{i=1}^{n!} (-1)^p \hat{P}$$

and hence $\hat{\mathcal{A}}$ is idempotent if

$$a_n^2 \, n! = a_n,$$

i.e., if

$$a_n = \frac{1}{n!}.$$

Question 5: Bosons

The wave function for a system of four bosons with spins $s = 0$ is given by

$$\Phi(1,2,3,4) = \frac{1}{\sqrt{4!}} \phi(\boldsymbol{r}_1)\phi(\boldsymbol{r}_3)\phi(\boldsymbol{r}_3)\phi(\boldsymbol{r}_4). \tag{4}$$

The norm of the one-particle wave function ϕ is 2.

5a. Compute the norm of Φ.

Answer: *The square norm of norm of ϕ equals 4,*

$$|\phi|^2 \equiv \iiint |\phi(\boldsymbol{r})|^2 d\boldsymbol{r} = 4.$$

The square of the norm of Φ is

$$\begin{aligned}|\Phi|^2 &= \iiint \iiint \iiint \iiint |\Phi(1,2,3,4)|^2 d\boldsymbol{r}_1\, d\boldsymbol{r}_2\, d\boldsymbol{r}_3\, d\boldsymbol{r}_4 \\ &= \frac{1}{4!}\left(|\phi|^2\right)^4 = \frac{4^4}{4!} = \frac{32}{3}\end{aligned}$$

so the norm of Φ is

$$|\Phi| = 4\sqrt{\frac{2}{3}}.$$

Wave functions for bosons must be symmetric under permutations of particles. In analogy to the antisymmetrizer for Fermions, one may define a *symmetrizer* to turn a product of n one-particle functions $\phi_i(\boldsymbol{r})$ into a proper n-boson wave function:

$$\Phi_{\text{boson}}(1,\ldots,n) = \hat{S}\phi_1(\boldsymbol{r}_1)\phi_2(\boldsymbol{r}_2)\cdots\phi_n(\boldsymbol{r}_n) \tag{5}$$

5b. Give the expression for $\hat{S}$, such that Φ_{boson} is normalized, assuming $\langle\phi_i|\phi_j\rangle = \delta_{ij}$.

Answer: *The symmetrizer is proportional to the sum of permutation operators $\hat{P}_i$*

$$\hat{S} = b_n \sum_{i=1}^{n!} \hat{P}_i.$$

The symmetrizer is Hermitian, just like the anti-symmetrizer, so the square of the norm of $\Phi = \Phi_{\text{boson}}$ is

$$\langle\hat{S}\Phi|\hat{S}\Phi\rangle = \langle\Phi|\hat{S}^2\Phi\rangle.$$

In analogy to question 4 we may derive

$$\hat{S}^2 = b_n^2\, n! \sum_{i=1}^{n!} \hat{P}_i.$$

Since the one-particle wave functions are orthonormal only $\hat{P}_i = \hat{\mathbf{1}}$ contributes:

$$\langle\Phi|\hat{S}^2\Phi\rangle = b_n^2\, n!\langle\phi_1\phi_2\cdots\phi_n|\phi_1\phi_2\cdots\phi_n\rangle = b_n^2\, n!$$

and so the wave function is normalized for $b_n = 1/\sqrt{n!}$