

Chapter 1: Answer Key

Electron-Integral View of Quantum Chemistry
2302638 Advanced Quantum Chemistry

Department of Chemistry, Chulalongkorn University

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1 Checkpoint Question Answers

This section provides detailed answers to all checkpoint questions from Chapter 1, organized by their location in the chapter.

1.1 Checkpoint 1.1: Electron Count in Nonorthonormal Basis

Section 1.7 – Electron Count

Question: Why is the electron count $\text{tr}\{\mathbf{PS}\}$ and not $\text{tr}\{\mathbf{P}\}$ in a nonorthonormal AO basis?

Answer: The electron count formula depends on the orthonormality properties of the basis set. Let us derive both cases to understand why the overlap matrix \mathbf{S} must appear.

Case 1: Orthonormal MO basis. In an orthonormal molecular orbital (MO) basis $\{\phi_p\}$ with $\langle\phi_p|\phi_q\rangle = \delta_{pq}$, the electron density is

$$\rho(\mathbf{r}) = \sum_p n_p |\phi_p(\mathbf{r})|^2, \quad (1)$$

where n_p is the occupation number of orbital p (0, 1, or 2 for RHF). The total electron count is

$$N_e = \int \rho(\mathbf{r}) d\mathbf{r} = \sum_p n_p \underbrace{\int |\phi_p(\mathbf{r})|^2 d\mathbf{r}}_{=1} = \sum_p n_p = \text{tr}\{\mathbf{P}^{\text{MO}}\}, \quad (2)$$

where $P_{pq}^{\text{MO}} = n_p \delta_{pq}$ is diagonal. Here, $\text{tr}\{\mathbf{P}\}$ gives the correct electron count because the orbitals are orthonormal.

Case 2: Nonorthonormal AO basis. In the atomic orbital (AO) basis $\{\chi_\mu\}$ with overlap $S_{\mu\nu} = \langle\chi_\mu|\chi_\nu\rangle \neq \delta_{\mu\nu}$, the MOs are expanded as

$$\phi_i(\mathbf{r}) = \sum_\mu C_{\mu i} \chi_\mu(\mathbf{r}). \quad (3)$$

For closed-shell RHF with n_{occ} doubly-occupied orbitals, the electron density becomes

$$\rho(\mathbf{r}) = 2 \sum_{i=1}^{n_{\text{occ}}} |\phi_i(\mathbf{r})|^2 = 2 \sum_{i=1}^{n_{\text{occ}}} \sum_{\mu\nu} C_{\mu i} C_{\nu i} \chi_\mu(\mathbf{r}) \chi_\nu(\mathbf{r}) = \sum_{\mu\nu} P_{\mu\nu} \chi_\mu(\mathbf{r}) \chi_\nu(\mathbf{r}), \quad (4)$$

where $P_{\mu\nu} = 2 \sum_i^{\text{occ}} C_{\mu i} C_{\nu i}$ is the AO density matrix.

The electron count is then

$$N_e = \int \rho(\mathbf{r}) d\mathbf{r} = \sum_{\mu\nu} P_{\mu\nu} \underbrace{\int \chi_\mu(\mathbf{r}) \chi_\nu(\mathbf{r}) d\mathbf{r}}_{=S_{\mu\nu}} = \sum_{\mu\nu} P_{\mu\nu} S_{\nu\mu} = \text{tr}\{\mathbf{PS}\}. \quad (5)$$

Physical Interpretation

The overlap matrix \mathbf{S} acts as a **metric tensor** that properly accounts for the non-Euclidean geometry of the AO space. Just as we need a metric tensor in curved coordinates to compute distances, we need \mathbf{S} to correctly “count” the electron probability density when our basis functions overlap with each other.

If we incorrectly used $\text{tr}\{\mathbf{P}\}$ in a nonorthonormal basis, we would overcount electrons in regions where basis functions overlap significantly.

Numerical verification for $\text{H}_2/\text{STO-3G}$:

For H_2 at 0.74 Å in the STO-3G basis:

$$\mathbf{P} = \begin{pmatrix} 0.6025 & 0.6025 \\ 0.6025 & 0.6025 \end{pmatrix}, \quad (6)$$

$$\mathbf{S} = \begin{pmatrix} 1.0000 & 0.6599 \\ 0.6599 & 1.0000 \end{pmatrix}. \quad (7)$$

Computing the traces:

- $\text{tr}\{\mathbf{P}\} = 0.6025 + 0.6025 = 1.205$ (incorrect!)
- $\text{tr}\{\mathbf{PS}\} = \sum_{\mu\nu} P_{\mu\nu} S_{\nu\mu} = 0.6025(1.0) + 0.6025(0.6599) + 0.6025(0.6599) + 0.6025(1.0) = 2.000$

The correct electron count of 2 is obtained only when using $\text{tr}\{\mathbf{PS}\}$.

1.2 Checkpoint 1.2: ERI Symmetry Identification

Section 1.7 – ERI Symmetries

Question: The code verifies that `eri[0,1,0,1]` equals `eri[1,0,0,1]`. Which of the 8-fold ERI symmetries does this demonstrate? (Hint: which indices are being swapped?)

Answer: Let us first establish the index correspondence in chemist's notation:

$$\text{eri}[\mu, \nu, \lambda, \sigma] \leftrightarrow (\mu\nu|\lambda\sigma) = \iint \chi_\mu(\mathbf{r}_1)\chi_\nu(\mathbf{r}_1) \frac{1}{r_{12}} \chi_\lambda(\mathbf{r}_2)\chi_\sigma(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2. \quad (8)$$

Comparing the two array elements:

$$\text{eri}[0,1,0,1] \leftrightarrow (01|01), \quad (9)$$

$$\text{eri}[1,0,0,1] \leftrightarrow (10|01). \quad (10)$$

The indices being swapped are $\mu \leftrightarrow \nu$ (positions 0 and 1), while λ and σ remain unchanged. This corresponds to the **permutation symmetry in the first electron coordinate (bra)**:

$$(\mu\nu|\lambda\sigma) = (\nu\mu|\lambda\sigma) \quad (\text{swap first two indices}) \quad (11)$$

Physical origin: This symmetry arises because the product $\chi_\mu(\mathbf{r}_1)\chi_\nu(\mathbf{r}_1)$ is invariant under exchange of μ and ν —we are simply multiplying two functions at the same point \mathbf{r}_1 , and multiplication is commutative:

$$\chi_\mu(\mathbf{r}_1)\chi_\nu(\mathbf{r}_1) = \chi_\nu(\mathbf{r}_1)\chi_\mu(\mathbf{r}_1). \quad (12)$$

Complete 8-fold Symmetry

For real basis functions, ERIs possess 8-fold permutation symmetry:

1. $(\mu\nu|\lambda\sigma) = (\nu\mu|\lambda\sigma)$ (swap in bra) — **this is the one tested**
2. $(\mu\nu|\lambda\sigma) = (\mu\nu|\sigma\lambda)$ (swap in ket)
3. $(\mu\nu|\lambda\sigma) = (\lambda\sigma|\mu\nu)$ (swap bra \leftrightarrow ket)
4. All combinations of the above generate 8 equivalent orderings.

The code also tests:

- `eri[0,1,0,1] = eri[0,1,1,0]`: swap $\lambda \leftrightarrow \sigma$ (symmetry 2)
- `eri[0,1,1,0] = eri[1,0,0,1]`: combination of symmetries

Numerical verification for H₂/STO-3G:

$$\text{eri}[0,1,0,1] = 0.29759055094924614, \quad (13)$$

$$\text{eri}[1,0,0,1] = 0.29759055094924614, \quad (14)$$

$$\text{eri}[0,1,1,0] = 0.29759055094924614. \quad (15)$$

All three values are identical to machine precision, confirming the symmetries.

1.3 Checkpoint 1.3: Factor of 1/2 in Energy Reconstruction

Section 1.7 – Energy Expression

Question: PySCF's `get_veff()` returns $\mathbf{J} - \frac{1}{2}\mathbf{K}$ for RHF. In the energy reconstruction, we compute $E_{\text{elec}} = \text{tr}\{\mathbf{P}\mathbf{h}\} + \frac{1}{2}\text{tr}\{\mathbf{P} \cdot \mathbf{vhf}\}$. Why is there a factor of $\frac{1}{2}$ in front of the `vhf` term?

Answer: This factor of $\frac{1}{2}$ has a deep physical origin related to avoiding **double-counting** of electron-electron interactions.

The problem of double-counting:

The Coulomb operator \mathbf{J} represents the electrostatic interaction of an electron with the total electron density $\rho(\mathbf{r})$:

$$J_{\mu\nu} = \sum_{\lambda\sigma} (\mu\nu|\lambda\sigma) P_{\lambda\sigma}. \quad (16)$$

If we computed the two-electron energy as $\text{tr}\{\mathbf{P}\mathbf{J}\}$, we would count each electron pair (i, j) twice: once when electron i interacts with the density from electron j , and again when electron j interacts with the density from electron i . Therefore:

$$E_J = \frac{1}{2} \text{tr}\{\mathbf{P}\mathbf{J}\} = \frac{1}{2} \sum_{\mu\nu\lambda\sigma} P_{\mu\nu} (\mu\nu|\lambda\sigma) P_{\lambda\sigma}. \quad (17)$$

The same reasoning applies to the exchange term \mathbf{K} .

Derivation of the energy expression:

The RHF electronic energy can be written as:

$$E_{\text{elec}} = \text{tr}\{\mathbf{P}\mathbf{h}\} + \frac{1}{2} \text{tr}\{\mathbf{P}\mathbf{J}\} - \frac{1}{4} \text{tr}\{\mathbf{P}\mathbf{K}\}, \quad (18)$$

where the $\frac{1}{4}$ for exchange comes from $\frac{1}{2}$ (double-counting) times $\frac{1}{2}$ (the RHF exchange coefficient).

Grouping terms:

$$E_{\text{elec}} = \text{tr}\{\mathbf{P}\mathbf{h}\} + \frac{1}{2} \text{tr}\left\{\mathbf{P}\left(\mathbf{J} - \frac{1}{2}\mathbf{K}\right)\right\} = \text{tr}\{\mathbf{P}\mathbf{h}\} + \frac{1}{2} \text{tr}\{\mathbf{P} \cdot \mathbf{vhf}\}. \quad (19)$$

Alternative Formulation

The energy can also be written as:

$$E_{\text{elec}} = \frac{1}{2} \text{tr}\{\mathbf{P}(\mathbf{h} + \mathbf{F})\}, \quad (20)$$

where $\mathbf{F} = \mathbf{h} + \mathbf{J} - \frac{1}{2}\mathbf{K} = \mathbf{h} + \mathbf{vhf}$.

This is equivalent because:

$$\frac{1}{2} \text{tr}\{\mathbf{P}(\mathbf{h} + \mathbf{F})\} = \frac{1}{2} \text{tr}\{\mathbf{P}\mathbf{h}\} + \frac{1}{2} \text{tr}\{\mathbf{P}\mathbf{F}\} \quad (21)$$

$$= \frac{1}{2} \text{tr}\{\mathbf{P}\mathbf{h}\} + \frac{1}{2} \text{tr}\{\mathbf{P}\mathbf{h}\} + \frac{1}{2} \text{tr}\{\mathbf{P}(\mathbf{J} - \frac{1}{2}\mathbf{K})\} \quad (22)$$

$$= \text{tr}\{\mathbf{P}\mathbf{h}\} + \frac{1}{2} \text{tr}\{\mathbf{P} \cdot \mathbf{vhf}\}. \quad (23)$$

Physical interpretation:

The factor of $\frac{1}{2}$ ensures we count each unique electron pair *exactly once*. This is analogous to computing the electrostatic self-energy of a charge distribution:

$$E_{\text{Coulomb}} = \frac{1}{2} \iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}', \quad (24)$$

where the $\frac{1}{2}$ prevents double-counting of the (i, j) and (j, i) contributions.

Numerical verification for H₂/STO-3G:

Computing energy components:

$$\text{tr}\{\mathbf{P}\mathbf{h}\} = -2.5066 \text{ E}_h, \quad (25)$$

$$\frac{1}{2} \text{tr}\{\mathbf{P} \cdot \mathbf{vhf}\} = 0.6748 \text{ E}_h, \quad (26)$$

$$E_{\text{elec}} = -2.5066 + 0.6748 = -1.8319 \text{ E}_h, \quad (27)$$

$$E_{\text{nuc}} = 0.7151 \text{ E}_h, \quad (28)$$

$$E_{\text{tot}} = -1.8319 + 0.7151 = -1.1168 \text{ E}_h. \quad (29)$$

This matches the PySCF RHF energy to machine precision, confirming the correct treatment of the $\frac{1}{2}$ factor.

2 Lab 1A: AO Integral Inventory and Sanity Checks

This section provides the complete expected output and analysis for Lab 1A, using H₂ in the STO-3G basis at a bond length of 0.74 Å.

2.1 System Specification

Parameter	Value
Molecule	H ₂
Geometry	H at (0, 0, 0); H at (0, 0, 0.74) Å
Basis set	STO-3G (minimal basis)
Number of electrons	2
Number of AOs	2 (one 1s function per H)

2.2 One-Electron Integrals

2.2.1 Overlap Matrix S

$$\mathbf{S} = \begin{pmatrix} 1.00000000 & 0.65987312 \\ 0.65987312 & 1.00000000 \end{pmatrix} \quad (30)$$

Observations:

- Diagonal elements are 1.0 (normalized basis functions)
- Off-diagonal element $S_{12} = 0.660$ indicates significant overlap between the two 1s functions at 0.74 Å separation
- Matrix is symmetric: $S_{\mu\nu} = S_{\nu\mu}$

2.2.2 Kinetic Energy Matrix \mathbf{T}

$$\mathbf{T} = \begin{pmatrix} 0.76003188 & 0.23696027 \\ 0.23696027 & 0.76003188 \end{pmatrix} \quad (31)$$

Observations:

- Diagonal elements $T_{11} = T_{22} = 0.760 \text{ E}_h$ represent kinetic energy of each $1s$ orbital
- Off-diagonal elements are positive (kinetic coupling)
- Matrix is symmetric

2.2.3 Nuclear Attraction Matrix \mathbf{V}

$$\mathbf{V} = \begin{pmatrix} -1.88099134 & -1.19633604 \\ -1.19633604 & -1.88099134 \end{pmatrix} \quad (32)$$

Observations:

- All elements are **negative** (attractive potential)
- Diagonal elements include attraction to both nuclei
- Matrix is symmetric

2.2.4 Core Hamiltonian $\mathbf{h} = \mathbf{T} + \mathbf{V}$

$$\mathbf{h} = \begin{pmatrix} -1.12095946 & -0.95937577 \\ -0.95937577 & -1.12095946 \end{pmatrix} \quad (33)$$

Observations:

- Net negative values indicate nuclear attraction dominates kinetic energy
- This is expected for a bound system

2.3 Two-Electron Integrals (ERIs)

2.3.1 ERI Tensor Properties

Property	Value
Shape	$(2, 2, 2, 2)$
Total elements	$2^4 = 16$
Memory (s1, full)	128 bytes
Unique elements (8-fold symmetry)	3

2.3.2 Representative ERI Values

Element	Value (E_h)	Physical Meaning
$(00 00)$	0.7746059	On-site Coulomb (H_1)
$(11 11)$	0.7746059	On-site Coulomb (H_2)
$(01 01)$	0.2976	Two-center Coulomb
$(00 11)$	0.5697	Two-center Coulomb (different)

2.3.3 Symmetry Verification

The 8-fold symmetry is verified numerically:

$$(01|01) = (10|01) = 0.29759055 \quad (\text{swap } \mu \leftrightarrow \nu), \quad (34)$$

$$(01|01) = (01|10) = 0.29759055 \quad (\text{swap } \lambda \leftrightarrow \sigma), \quad (35)$$

$$(01|10) = (10|01) = 0.29759055 \quad (\text{swap bra } \leftrightarrow \text{ket}). \quad (36)$$

2.4 RHF Calculation Results

2.4.1 Energy Components

Quantity	Value	Units
One-electron energy $\text{tr}\{\mathbf{P}\mathbf{h}\}$	-2.5066	E_h
Two-electron energy $\frac{1}{2} \text{tr}\{\mathbf{P} \cdot \mathbf{vhf}\}$	+0.6748	E_h
Electronic energy E_{elec}	-1.8319	E_h
Nuclear repulsion E_{nuc}	+0.7151	E_h
Total energy E_{tot}	-1.1168	E_h

2.4.2 Density Matrix \mathbf{P}

$$\mathbf{P} = \begin{pmatrix} 0.60245569 & 0.60245569 \\ 0.60245569 & 0.60245569 \end{pmatrix} \quad (37)$$

Observations:

- All elements are equal (symmetric bonding MO contributes equally to both AOs)
- This reflects the equal sharing of electrons in a homonuclear diatomic

2.4.3 MO Coefficients and Energies

$$\mathbf{C} = \begin{pmatrix} 0.5488 & 1.2125 \\ 0.5488 & -1.2125 \end{pmatrix}, \quad \boldsymbol{\varepsilon} = \begin{pmatrix} -0.5786 \\ 0.6711 \end{pmatrix} E_h \quad (38)$$

Interpretation:

- Column 1: Bonding MO (σ_g) with equal coefficients (symmetric combination)
- Column 2: Antibonding MO (σ_u^*) with opposite signs (antisymmetric combination)
- HOMO-LUMO gap: $0.6711 - (-0.5786) = 1.250 E_h \approx 34 \text{ eV}$

2.4.4 Electron Count Verification

$$N_e = \text{tr}\{\mathbf{P}\mathbf{S}\} = 0.6025 \times 1.0 + 0.6025 \times 0.6599 + 0.6025 \times 0.6599 + 0.6025 \times 1.0 = 2.0000 \quad (39)$$

The electron count is exactly 2, confirming correct construction of the density matrix.

2.4.5 MO Orthonormality Check

$$\mathbf{C}^\top \mathbf{S} \mathbf{C} = \begin{pmatrix} 1.0000 & 0.0000 \\ 0.0000 & 1.0000 \end{pmatrix} \quad (40)$$

The MOs are orthonormal under the \mathbf{S} metric, as required.

2.5 Energy Reconstruction Verification

The electronic energy can be reconstructed from integrals:

```

1 # Method 1: Using get_veff()
2 vhf = mf.get_veff(mol, dm) # Returns J - 0.5*K for RHF
3 E_elec = np.einsum("ij,ji->", dm, h) + 0.5 * np.einsum("ij,ji->", dm,
4   vhf)
5 E_tot_1 = E_elec + mol.energy_nuc()
6
7 # Method 2: Using explicit J and K
8 J = np.einsum('ijkl,kl->ij', eri, dm)
9 K = np.einsum('ikjl,kl->ij', eri, dm)
10 F = h + J - 0.5*K
11 E_elec = 0.5 * np.einsum("ij,ji->", dm, h + F)
12 E_tot_2 = E_elec + mol.energy_nuc()
13
14 # Both should give -1.1167593073964255 Eh

```

Listing 1: Energy reconstruction verification

Both methods yield $E_{\text{tot}} = -1.1167593073964255 E_h$, matching the SCF result to machine precision (difference $< 10^{-15} E_h$).

2.6 Memory Scaling Analysis

Storage Mode	Elements	Memory	Reduction Factor
aosym="s1" (full)	$N^4 = 16$	128 bytes	1.0
aosym="s8" (packed)	3	24 bytes	$5.3\times$

For larger systems, the 8-fold symmetry becomes increasingly important:

- Water/STO-3G: $N = 7$, reduction from 2401 to ~ 300 unique elements
- Benzene/cc-pVDZ: $N \approx 114$, reduction from 1.7×10^8 to $\sim 2 \times 10^7$ unique elements

3 Common Errors and Debugging Guide

3.1 Factor of 2 Errors in RHF

The most common source of errors in RHF calculations involves factors of 2:

Quantity	Correct Expression	Common Error
Density matrix	$P_{\mu\nu} = 2 \sum_i C_{\mu i} C_{\nu i}$	Missing factor of 2
Fock matrix	$\mathbf{F} = \mathbf{h} + \mathbf{J} - \frac{1}{2}\mathbf{K}$	Using $-\mathbf{K}$ instead
Electron count	$N_e = \text{tr}\{\mathbf{P}\mathbf{S}\}$	Using $\text{tr}\{\mathbf{P}\}$

3.2 Chemist's vs Physicist's Notation

PySCF uses **chemist's notation**:

$$\text{eri}[\mu, \nu, \lambda, \sigma] \equiv (\mu\nu|\lambda\sigma) = \iint \chi_\mu(1)\chi_\nu(1)\frac{1}{r_{12}}\chi_\lambda(2)\chi_\sigma(2). \quad (41)$$

Physicist's notation (NOT used in PySCF):

$$\langle \mu\lambda|\nu\sigma \rangle = \iint \chi_\mu^*(1)\chi_\lambda^*(2)\frac{1}{r_{12}}\chi_\nu(1)\chi_\sigma(2). \quad (42)$$

The index ordering differs! When translating from physics textbooks:

$$\langle \mu\lambda | \nu\sigma \rangle_{\text{phys}} = (\mu\nu | \lambda\sigma)_{\text{chem}}. \quad (43)$$

3.3 Unit Errors

Common Mistake	Symptom	Fix
Geometry in wrong units	Energy off by factor	Check <code>unit=</code> setting
Mixing Å and Bohr	Bond lengths wrong	PySCF defaults to Å

4 Reference: Complete Numerical Output

For reproducibility, here is the complete expected output from Lab 1A:

```

1 Number of AOs (nao): 2
2 S symmetric: True
3 h symmetric: True
4
5 --- ERI Symmetry Checks ---
6 (01|01) = (10|01): True
7 (01|01) = (01|10): True
8 (01|10) = (10|01): True
9
10 ERI shape: (2, 2, 2, 2)
11 ERI memory (MB): 0.0001220703125
12
13 ERI (s8) shape: (3,)
14 ERI (s8) memory (MB): 2.288818359375e-05
15
16 RHF total energy (Eh): -1.1167593073964255
17 Electron count Tr[PS]: 2.0000000000000004
18
19 E_tot rebuilt (Eh): -1.1167593073964255
20 Difference (Eh): 0.0

```

5 Exercise Answer Keys

Brief answers for the end-of-chapter exercises (Section 1.9).

5.1 Exercise 1.1: Identifying Hamiltonian Terms [Core]

Operator Identification

From the electronic Hamiltonian (Eq. 1.3 in the notes):

$$\hat{H}_e = \sum_{i=1}^{N_e} \left(-\frac{1}{2} \nabla_i^2 - \sum_{A=1}^{N_n} \frac{Z_A}{r_{iA}} \right) + \sum_{i < j}^{N_e} \frac{1}{r_{ij}}$$

- (a) The kinetic energy matrix **T** comes from the $-\frac{1}{2}\nabla^2$ operators.
- (b) The nuclear attraction matrix **V** comes from the $-Z_A/r_{iA}$ terms.
- (c) The ERIs arise from the electron–electron repulsion r_{ij}^{-1} .
- (d) Operator counts for N_e electrons and M nuclei:

- Kinetic energy operators: N_e (one per electron)
- Nuclear attraction operators: $N_e \times M$ (each electron with each nucleus)

- Electron–electron operators: $\binom{N_e}{2} = \frac{N_e(N_e-1)}{2}$ (unique pairs)

5.2 Exercise 1.2: Tracing the Computational Pipeline [Core]

Expected results for H₂O/STO-3G:

Quantity	Value
Bond length r_{OH}	0.96 Å
Bond angle $\angle\text{HOH}$	104.5°
E_{nuc}	9.08804 E _h
Number of AOs (N)	7
SCF iterations	10–12 (with DIIS)
Default threshold	10 ^{−9} E _h
E_{elec}	−84.03 E _h
E_{tot}	−74.94 E _h

Basis Function Count

STO-3G assigns:

- Oxygen: 1 (1s) + 1 (2s) + 3 (2p) = 5 functions
- Each hydrogen: 1 (1s) = 1 function
- Total: 5 + 1 + 1 = 7 AO basis functions

The matrices **S**, **h**, **F**, **P** are all 7 × 7.

5.3 Exercise 1.3: Scaling Snapshot [Core]

Example results for H₂O:

Basis	N	s1 (MB)	s8 (MB)
STO-3G	7	0.018	0.003
cc-pVDZ	24	2.65	0.35

Memory Scaling

The ratio of s1 to s8 storage:

$$\frac{N^4}{N^4/8} = 8 \quad (\text{in the limit of large } N)$$

For small N , the ratio is less than 8 because indexing overhead matters. Observed ratios: STO-3G \approx 6, cc-pVDZ \approx 7.6. As N grows, the ratio approaches 8.

5.4 Exercise 1.4: Electron Count and Orthonormality [Core]

Role of the Overlap Matrix

The overlap matrix \mathbf{S} appears in both formulas because it defines the metric (inner product) in the nonorthonormal AO basis:

$$\langle u, v \rangle_S = u^\top \mathbf{S} v$$

MO Orthonormality: $\mathbf{C}^\top \mathbf{S} \mathbf{C} = \mathbf{I}$

The MOs are orthonormal *under the \mathbf{S} -metric*, not the Euclidean metric. This means $\langle \phi_p | \phi_q \rangle = \delta_{pq}$ when computed with proper overlap.

Electron Count: $\text{tr}\{\mathbf{P}\mathbf{S}\} = N_e$

Without \mathbf{S} , we would overcount electrons in regions where AOs overlap. The overlap matrix “corrects” for the redundancy in non-orthogonal descriptions.

Physical interpretation: \mathbf{S} acts as a metric tensor that properly weights the contribution of each AO according to its overlap with others. In an orthonormal basis (e.g., MO basis), $\mathbf{S} = \mathbf{I}$ and these formulas reduce to simple traces.

5.5 Exercise 1.5: ERI Symmetry Spot Check [Advanced]

Physical Origins of ERI Symmetry

The 8-fold ERI symmetry arises from three independent physical properties:

1. Commutativity of multiplication (real basis):

$$\chi_\mu(\mathbf{r}_1)\chi_\nu(\mathbf{r}_1) = \chi_\nu(\mathbf{r}_1)\chi_\mu(\mathbf{r}_1)$$

This gives: $(\mu\nu|\lambda\sigma) = (\nu\mu|\lambda\sigma)$ and $(\mu\nu|\lambda\sigma) = (\mu\nu|\sigma\lambda)$

2. Symmetry of Coulomb operator:

$$\frac{1}{r_{12}} = \frac{1}{r_{21}}$$

This gives: $(\mu\nu|\lambda\sigma) = (\lambda\sigma|\mu\nu)$

3. Real basis functions: All basis functions are real, so complex conjugation has no effect.

Combining these three 2-fold symmetries: $2 \times 2 \times 2 = 8$ -fold total.

Numerical verification: For any randomly chosen $(\mu, \nu, \lambda, \sigma)$, all 8 permutations should agree to machine precision ($< 10^{-14}$).

5.6 Exercise 1.6: Back-of-Envelope ERI Scaling [Advanced]

Benzene cc-pVDZ Estimates

(a) Basis function count:

$$N \approx 6 \times 14 + 6 \times 5 = 84 + 30 = 114 \text{ functions}$$

(b) Full ERI memory:

$$\begin{aligned} \text{Memory} &= N^4 \times 8 \text{ bytes} \\ &= 114^4 \times 8 = 1.35 \times 10^9 \text{ bytes} \approx 1.3 \text{ GB} \end{aligned}$$

(c) **Maximum N for 16 GB RAM:**

$$N^4 \times 8 \leq 16 \times 10^9$$

$$N \leq \left(\frac{16 \times 10^9}{8} \right)^{1/4} \approx 212$$

(d) **Motivation for alternative methods:**

- **Direct SCF:** Never store ERIs; recompute each iteration. Trades compute time for memory.
- **Density Fitting:** Approximate 4-index ERIs with 3-index quantities. Reduces $O(N^4)$ storage to $O(N^2 N_{\text{aux}})$.

5.7 Exercise 1.7: Physical Interpretation of J and K [Advanced]

Coulomb Matrix

(a) **J** represents classical electrostatic repulsion:

$$J_{\mu\nu} = \int \chi_{\mu}(\mathbf{r}_1) \chi_{\nu}(\mathbf{r}_1) \left[\int \frac{\rho(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_2 \right] d\mathbf{r}_1$$

This is the Coulomb potential from density $\rho(\mathbf{r}) = \sum_{\lambda\sigma} P_{\lambda\sigma} \chi_{\lambda} \chi_{\sigma}$. Unlike classical point charges, quantum ρ is a smooth, delocalized distribution.

Exchange Matrix

(b) **K** arises from antisymmetry (Pauli exclusion):

$$\Psi(1, 2) = -\Psi(2, 1)$$

When two electrons have the same spin, their spatial wavefunction must be antisymmetric. This creates an “exchange hole”—a depletion of same-spin electron density near each electron. There is no classical analog because classical particles are distinguishable.

Factor of 1/2 in RHF

(c) In closed-shell RHF with doubly-occupied orbitals:

- Coulomb: All N_e^2 electron pairs contribute (including opposite spins)
- Exchange: Only $N_e^2/2$ same-spin pairs contribute

The factor $\frac{1}{2}$ in $\mathbf{F} = \mathbf{h} + \mathbf{J} - \frac{1}{2}\mathbf{K}$ reflects that exchange only occurs between electrons of the same spin.

Self-Interaction Cancellation

(d) For a single doubly-occupied orbital (e.g., He $1s^2$):

$$J_{11} = (11|11) = K_{11}$$

In the energy: $J_{11} - \frac{1}{2}K_{11} - \frac{1}{2}K_{11} = J_{11} - K_{11} = 0$

This shows that HF is **self-interaction free**: an electron does not repel itself. The exchange term exactly cancels the spurious self-Coulomb contribution.

5.8 Exercise 1.8: Energy Reconstruction Without get_veff [Challenge]

Key verification points:

```

1 # For H2/STO-3G at 0.74 Angstrom
2 # 1. Get converged density
3 dm = mf.make_rdm1()
4
5 # 2. Build J matrix
6 J = np.einsum('mnlsls->mn', eri, dm)
7
8 # 3. Build K matrix (note index order!)
9 K = np.einsum('mlnsls->mn', eri, dm)
10
11 # 4. Fock matrix
12 F = h + J - 0.5*K
13
14 # 5. Electronic energy
15 E_elec = 0.5 * np.einsum('ij,ji->', dm, h + F)
16
17 # Expected: E_elec = -1.8319 Eh, E_tot = -1.1168 Eh

```

Index Contraction Patterns

The critical difference between **J** and **K**:

$$J_{\mu\nu} = \sum_{\lambda\sigma} (\mu\nu|\lambda\sigma) P_{\lambda\sigma} \rightarrow \text{einsum('mnlsls->mn', eri, dm)}$$

$$K_{\mu\nu} = \sum_{\lambda\sigma} (\mu\lambda|\nu\sigma) P_{\lambda\sigma} \rightarrow \text{einsum('mlnsls->mn', eri, dm)}$$

The indices being contracted (λ, σ) are in positions (2,3) for **J** but positions (1,3) for **K**. This reflects the different physical origins: **J** is a local potential; **K** is nonlocal (depends on orbital shape).

5.9 Exercise 1.9: Debugging an SCF Calculation [Challenge]

Bug Identification

The buggy code contains **three errors**:

Bug 1: Missing factor of 2 in density matrix

```

1 # Wrong:
2 P = np.einsum('mi,ni->mn', C_occ, C_occ)
3 # Correct:
4 P = 2 * np.einsum('mi,ni->mn', C_occ, C_occ)

```

For RHF, each spatial orbital is doubly occupied. The density matrix must include the factor of 2: $P_{\mu\nu} = 2 \sum_i C_{\mu i} C_{\nu i}$.

Bug 2: Missing factor of 1/2 on exchange in Fock matrix

```

1 # Wrong:
2 F = h + J - K
3 # Correct:

```

```
4 F = h + J - 0.5*K
```

Exchange only occurs between same-spin electrons. With double occupation, only half the electron pairs are same-spin.

Bug 3: Missing factor of 1/2 in energy formula

```
1 # Wrong:
2 E_elec = np.trace(P @ (h + F))
3 # Correct:
4 E_elec = 0.5 * np.trace(P @ (h + F))
```

The factor of $\frac{1}{2}$ prevents double-counting electron pairs. When summing over all μ, ν , each pair (i, j) is counted as both (i, j) and (j, i) .

Debugging Strategy

To catch these errors systematically:

1. Check $\text{tr}\{\mathbf{PS}\} = N_e$ (catches Bug 1)
2. Compare \mathbf{F} against `mf.get_fock()` (catches Bug 2)
3. Compare E_{elec} against `mf.energy_elec()[0]` (catches Bug 3)

End of Chapter 1 Solutions