

Chapter 3: Answer Key

One-Electron Integrals and Gaussian Product Theorem
2302638 Advanced Quantum Chemistry

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1 Checkpoint Question Answers

This section provides detailed answers to all 11 checkpoint questions from Chapter 3, organized by their location in the chapter.

1.1 Checkpoint 3.1: Why Separability Matters

Section 3.2 – Integral Separability

Question: Why do overlap and kinetic integrals factor into 1D integrals while nuclear attraction integrals do not? (Hint: consider the form of $1/|\mathbf{r} - \mathbf{C}|$ in Cartesian coordinates.)

Answer:

The key lies in whether the operator is **separable** in Cartesian coordinates.

Overlap integral ($\hat{O} = 1$):

$$\int g_a(\mathbf{r}) \cdot 1 \cdot g_b(\mathbf{r}) d^3r = \int e^{-\alpha(x-A_x)^2} e^{-\beta(x-B_x)^2} dx \\ \times \int e^{-\alpha(y-A_y)^2} e^{-\beta(y-B_y)^2} dy \\ \times \int e^{-\alpha(z-A_z)^2} e^{-\beta(z-B_z)^2} dz$$

Each factor is an independent 1D integral.

Kinetic integral ($\hat{O} = -\frac{1}{2}\nabla^2$): The Laplacian is $\nabla^2 = \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$. Each derivative acts on only one coordinate, so the integral splits into three terms, each of which factors.

Nuclear attraction ($\hat{O} = 1/|\mathbf{r} - \mathbf{C}|$):

$$\frac{1}{|\mathbf{r} - \mathbf{C}|} = \frac{1}{\sqrt{(x - C_x)^2 + (y - C_y)^2 + (z - C_z)^2}}$$

This **couples all three coordinates** through the square root and sum. There is no way to write $1/r$ as $f(x) \cdot g(y) \cdot h(z)$, so the integral does not factor.

Physical interpretation: The Coulomb potential “knows” about all three spatial directions simultaneously—the force on an electron depends on its total distance from the nucleus, not on its x , y , z coordinates separately.

Warning: Common Error

Students sometimes confuse “separable operator” with “separable wavefunction.” Here we are discussing whether the *operator* \hat{O} can be written as a sum or product of single-coordinate terms. The Gaussian basis functions are always separable (by construction), but that does not make every integral separable.

1.2 Checkpoint 3.2: Screening and Sparsity

Section 3.3 – Gaussian Product Theorem

Question: Consider a large molecule with basis functions spread over many atoms.

- If $\alpha = \beta = 1.0 \text{ Bohr}^{-2}$, at what distance R_{AB} does the GPT prefactor $\exp[-\mu R_{AB}^2]$ become smaller than 10^{-10} ?
- How does this observation suggest a strategy for avoiding unnecessary integral computations in large systems?

Answer:

Part (a): Given $\alpha = \beta = 1.0 \text{ Bohr}^{-2}$:

$$\mu = \frac{\alpha\beta}{\alpha + \beta} = \frac{1.0 \times 1.0}{1.0 + 1.0} = 0.5 \text{ Bohr}^{-2}$$

We need $\exp[-\mu R_{AB}^2] < 10^{-10}$:

$$-\mu R_{AB}^2 < \ln(10^{-10}) = -10 \ln(10) \approx -23.03$$

$$R_{AB}^2 > \frac{23.03}{0.5} = 46.06 \text{ Bohr}^2$$

$$R_{AB} > \sqrt{46.06} \approx 6.8 \text{ Bohr} \approx 3.6 \text{ \AA}$$

Part (b): Screening strategy

For large molecules, basis function pairs separated by more than ~ 7 Bohr contribute negligibly to integrals. This suggests:

- Distance-based prescreening:** Before computing any integral, check if R_{AB} exceeds a threshold. If so, set the integral to zero without computing it.
- Shell-pair screening:** Since integrals scale as $O(N^4)$ for two-electron integrals, screening distant pairs can reduce cost dramatically. If 90% of pairs can be screened, the effective scaling becomes $O(N^2)$ or better for linear molecules.
- Schwarz screening:** For ERIs, use the bound $|(ab|cd)| \leq \sqrt{(ab|ab)}\sqrt{(cd|cd)}$ to pre-compute “diagonal” integrals and use them to screen the full set.

Tip

The screening distance depends on exponents. For diffuse functions ($\alpha \sim 0.1 \text{ Bohr}^{-2}$), $\mu \sim 0.05$ and the screening radius extends to ~ 20 Bohr. For tight core functions ($\alpha \sim 100 \text{ Bohr}^{-2}$), screening kicks in at ~ 0.5 Bohr. Modern integral codes use adaptive screening based on actual exponent values.

1.3 Checkpoint 3.3: Overlap Decay

Section 3.4 – Overlap Integrals

Question: What happens to the overlap as $R_{AB} \rightarrow \infty$? Explain using the prefactor $\exp[-\mu R_{AB}^2]$ in the overlap formula.

Answer:

As $R_{AB} \rightarrow \infty$:

$$S_{ab}^{(ss)} = N_s(\alpha)N_s(\beta) \left(\frac{\pi}{p}\right)^{3/2} \exp[-\mu R_{AB}^2] \rightarrow 0$$

The exponential factor $\exp[-\mu R_{AB}^2]$ dominates the behavior:

- The prefactors $N_s(\alpha)$, $N_s(\beta)$, and $(\pi/p)^{3/2}$ are **constants** (independent of R_{AB}).
- The exponential decay is **Gaussian** in R_{AB} , meaning faster than any polynomial.

Physical interpretation: Two Gaussian basis functions centered far apart have negligible overlap because:

1. Each Gaussian is localized near its center (decays as $e^{-\alpha r^2}$ from its center).
2. The product of two non-overlapping functions is essentially zero everywhere.
3. Overlap measures “how much two functions occupy the same region of space.”

This is the mathematical foundation for the **locality** of chemistry—atoms interact significantly only with their neighbors.

1.4 Checkpoint 3.4: Contraction Cost

Section 3.4 – Contracted Gaussians

Question: Consider two STO-3G basis functions (each a contraction of 3 primitives).

- (a) How many primitive overlap integrals must be computed for one contracted overlap?
- (b) For a 6-31G basis ($3 + 2 = 5$ primitives per atom, approximately), how does the count change?
- (c) Why is the cost $K \times L$ rather than $K + L$?

Answer:

Part (a): STO-3G

Each contracted function has $K = 3$ primitives:

$$\chi = d_1g_1 + d_2g_2 + d_3g_3$$

The contracted integral is:

$$\langle \chi | \phi \rangle = \sum_{p=1}^3 \sum_{q=1}^3 d_p e_q \langle g_p | h_q \rangle$$

This requires $3 \times 3 = 9$ primitive integrals.

Part (b): 6-31G

For 6-31G, a typical shell has:

- Core: 6 primitives contracted to 1 function

- Valence: 3 primitives contracted to 1 function + 1 primitive uncontracted

For a core-core overlap: $6 \times 6 = 36$ primitives. For a valence-valence overlap: $3 \times 3 = 9$ primitives (for the contracted part).

The exact count depends on which shells are being contracted, but the pattern scales as $K \times L$.

Part (c): Why $K \times L$ instead of $K + L$?

The contracted integral is a **bilinear** sum over primitive pairs:

$$I = \sum_{p=1}^K \sum_{q=1}^L d_p e_q I_{pq}$$

Each primitive g_p in function χ must be paired with **every** primitive h_q in function ϕ . This is a **Cartesian product**, not a union. Just as a 3×5 grid has 15 cells (not 8), contracting two functions requires computing all primitive-pair integrals.

Analogy: If you have 3 shirts and 5 pants, you have $3 \times 5 = 15$ outfit combinations, not $3 + 5 = 8$.

Warning: Common Error

A common error is to assume contraction adds linear cost. In fact, highly contracted basis sets (like STO-3G or cc-pVnZ) have significant overhead from primitive-pair loops. This is one reason why segmented contractions are preferred over general contractions in some contexts.

1.5 Checkpoint 3.5: Kinetic Integral Limit

Section 3.5 – Kinetic Energy Integrals

Question: Consider the limit $R_{AB} \rightarrow 0$ in the kinetic-overlap relation. What does $T_{ab}^{(ss)}$ become in terms of α and β ?

Answer:

The kinetic-overlap relation is:

$$T_{ab}^{(ss)} = \mu(3 - 2\mu R_{AB}^2) S_{ab}^{(ss)}$$

As $R_{AB} \rightarrow 0$:

$$\begin{aligned} T_{ab}^{(ss)} &\rightarrow \mu \cdot 3 \cdot S_{ab}^{(ss)} (R_{AB} = 0) \\ &= 3\mu \cdot N_s(\alpha)N_s(\beta) \left(\frac{\pi}{p}\right)^{3/2} \end{aligned}$$

For the special case $\alpha = \beta$ and $\mathbf{A} = \mathbf{B}$ (identical normalized primitives):

$$\begin{aligned} \mu &= \frac{\alpha^2}{2\alpha} = \frac{\alpha}{2} \\ p &= 2\alpha \\ N_s(\alpha)^2 &= \left(\frac{2\alpha}{\pi}\right)^{3/2} \\ S_{aa} &= \left(\frac{2\alpha}{\pi}\right)^{3/2} \cdot \left(\frac{\pi}{2\alpha}\right)^{3/2} = 1 \quad \checkmark \end{aligned}$$

Therefore:

$$T_{aa} = 3 \cdot \frac{\alpha}{2} \cdot 1 = \boxed{\frac{3\alpha}{2}}$$

Physical interpretation: The kinetic energy of a normalized *s*-type Gaussian scales **linearly** with the exponent α . This reflects the uncertainty principle: a tighter Gaussian (larger α) is more localized in position space, hence more delocalized in momentum space, leading to higher kinetic energy.

For a hydrogen 1s orbital with $\alpha = 1.0 \text{ Bohr}^{-2}$:

$$T_{1s,1s} = \frac{3 \times 1.0}{2} = 1.5 \text{ Hartree} = 0.75 \text{ a.u. (per electron)}$$

This matches the exact hydrogen atom kinetic energy of 0.5 Hartree per electron in the limit of a Slater orbital, with the difference due to the Gaussian approximation.

Tip

The formula $T_{aa} = \frac{3\alpha}{2}$ is a useful sanity check. For basis sets, diagonal kinetic integrals should increase with exponent. If your implementation gives T_{aa} decreasing with α , you have a sign or normalization error.

1.6 Checkpoint 3.6: Boys Function Behavior

Section 3.6 – Nuclear Attraction Integrals

Question:

- (a) What physical situation corresponds to $T \rightarrow 0$? What is $F_0(0)$?
- (b) What happens to $F_0(T)$ as the composite center **P** moves far from the nucleus **C**? Does this make physical sense?

Answer:

Recall: $T = p|\mathbf{P} - \mathbf{C}|^2$ where **P** is the composite center of the Gaussian product.

Part (a): $T \rightarrow 0$

$T \rightarrow 0$ occurs when:

- **P** → **C**: The composite center coincides with the nuclear position, OR
- $p \rightarrow 0$: Both exponents are very small (very diffuse functions).

Physically, $T \rightarrow 0$ means the electron density (from the Gaussian product) is **centered on the nucleus**.

From the definition or series expansion:

$$F_0(0) = \int_0^1 t^0 e^{-0 \cdot t^2} dt = \int_0^1 1 dt = \boxed{1}$$

More generally: $F_n(0) = 1/(2n + 1)$.

Part (b): $T \rightarrow \infty$ (**P** far from **C**)

As $|\mathbf{P} - \mathbf{C}| \rightarrow \infty$, we have $T \rightarrow \infty$:

$$F_0(T) = \frac{1}{2} \sqrt{\frac{\pi}{T}} \cdot \text{erf}(\sqrt{T}) \approx \frac{1}{2} \sqrt{\frac{\pi}{T}} \rightarrow 0$$

The decay is $\sim 1/\sqrt{T} \sim 1/|\mathbf{P} - \mathbf{C}|$.

Physical interpretation: When the electron density (centered at \mathbf{P}) is far from the nucleus (at \mathbf{C}), the Coulomb attraction is weak. The $1/\sqrt{T}$ decay is slower than the exponential decay of the GPT prefactor, so nuclear attraction integrals decay more slowly than overlap integrals—but they still go to zero.

This makes physical sense: an electron far from a nucleus feels negligible attraction to it. The Coulomb $1/r$ potential decays polynomially, while Gaussian functions decay exponentially, so the product integral inherits the slower (polynomial-like) decay modified by Gaussian localization.

1.7 Checkpoint 3.7: Dipole as Trace

Section 3.7 – Dipole Moment Integrals

Question:

- Why is the electronic term in the dipole formula a trace $\text{Tr}[\mathbf{Pr}]$?
- For a neutral molecule, verify that shifting the origin by \mathbf{d} leaves the total dipole unchanged.

Answer:

Part (a): Why $\text{Tr}[\mathbf{Pr}]$?

The density matrix \mathbf{P} in the AO basis represents the one-electron density operator:

$$\hat{\rho} = \sum_{\mu\nu} P_{\mu\nu} |\chi_\mu\rangle\langle\chi_\nu|$$

The expectation value of any one-electron operator \hat{O} is:

$$\langle \hat{O} \rangle = \text{Tr}[\hat{\rho}\hat{O}] = \sum_{\mu\nu} P_{\mu\nu} \langle \chi_\nu | \hat{O} | \chi_\mu \rangle = \sum_{\mu\nu} P_{\mu\nu} O_{\nu\mu}$$

For the position operator $\hat{O} = \mathbf{r}$:

$$\langle \mathbf{r} \rangle_{\text{elec}} = \sum_{\mu\nu} P_{\mu\nu} \langle \chi_\nu | \mathbf{r} | \chi_\mu \rangle = \text{Tr}[\mathbf{Pr}]$$

This is the **center of electronic charge** weighted by the density matrix.

Part (b): Origin invariance for neutral molecules

With origin at \mathbf{O} :

$$\boldsymbol{\mu}(\mathbf{O}) = \sum_A Z_A (\mathbf{R}_A - \mathbf{O}) - \text{Tr}[\mathbf{Pr}(\mathbf{O})]$$

where $\mathbf{r}(\mathbf{O})_{\mu\nu} = \langle \chi_\mu | \mathbf{r} - \mathbf{O} | \chi_\nu \rangle$.

Shift origin to $\mathbf{O}' = \mathbf{O} + \mathbf{d}$:

$$\begin{aligned} \boldsymbol{\mu}(\mathbf{O}') &= \sum_A Z_A (\mathbf{R}_A - \mathbf{O} - \mathbf{d}) - \text{Tr}[\mathbf{P}(\mathbf{r}(\mathbf{O}) - \mathbf{dS})] \\ &= \boldsymbol{\mu}(\mathbf{O}) - \mathbf{d} \left(\sum_A Z_A - \text{Tr}[\mathbf{PS}] \right) \end{aligned}$$

For a neutral molecule:

$$\sum_A Z_A = N_e = \text{Tr}[\mathbf{PS}]$$

Therefore:

$$\mu(\mathbf{O}') = \mu(\mathbf{O}) - \mathbf{d} \cdot \mathbf{0} = \mu(\mathbf{O}) \quad \checkmark$$

For ions: $\sum_A Z_A \neq N_e$, so the dipole *does* depend on origin. This is expected—an ion has a net charge, and its “dipole” includes a monopole contribution that depends on where you measure from.

1.8 Checkpoint 3.8: Matching Theory to Code

Section 3.8 – PySCF Integration

Question:

- (a) The kinetic integral includes the factor $-\frac{1}{2}$. If PySCF’s `int1e_kin` returns 0.76, what is $\langle \mu | \nabla^2 | \nu \rangle$?
- (b) Why does `int1e_r` require specifying an origin, whereas `int1e_ovlp` does not?

Answer:

Part (a):

PySCF returns $T_{\mu\nu} = \langle \chi_\mu | -\frac{1}{2} \nabla^2 | \chi_\nu \rangle = 0.76$. Since $T = -\frac{1}{2} \langle \nabla^2 \rangle$:

$$\langle \chi_\mu | \nabla^2 | \chi_\nu \rangle = -2 \times 0.76 = \boxed{-1.52}$$

Note: The Laplacian integral is *negative* for the overlap of two Gaussians (this is related to the curvature of the Gaussian, which is negative near its peak and positive far away, but the weighted average is negative).

Part (b):

Overlap integral: $\langle \chi_\mu | 1 | \chi_\nu \rangle$

The operator is the identity “1”, which has no spatial reference point. The integral depends only on the shapes and positions of the basis functions, not on any external origin.

Position integral: $\langle \chi_\mu | \mathbf{r} - \mathbf{O} | \chi_\nu \rangle$

The operator $\mathbf{r} - \mathbf{O}$ explicitly depends on the origin \mathbf{O} . Changing \mathbf{O} changes the operator and hence the integral value.

Practical implication: When computing dipole moments, you must use the *same* origin for:

- The AO integrals $\langle \chi_\mu | \mathbf{r} - \mathbf{O} | \chi_\nu \rangle$
- The nuclear term $\sum_A Z_A (\mathbf{R}_A - \mathbf{O})$

Mixing origins will give incorrect results (unless the molecule is neutral, in which case the errors cancel).

1.9 Checkpoint 3.9: Interpreting Integral Matrices

Section 3.9 – Matrix Properties

Question:

- (a) In a well-conditioned basis, what should the diagonal elements of \mathbf{S} be close to?
- (b) What do you expect for the diagonal elements of \mathbf{T} (sign and magnitude)?
- (c) What do you expect for the diagonal elements of \mathbf{V} (sign and magnitude)?

Answer:**Part (a): Diagonal of S**

For a normalized basis:

$$S_{\mu\mu} = \langle \chi_\mu | \chi_\mu \rangle = \|\chi_\mu\|^2 = \boxed{1}$$

All diagonal elements should be exactly 1.0 (to machine precision) if the basis is properly normalized. Any deviation indicates a normalization error in the basis set definition.

Part (b): Diagonal of T

Sign: **Positive** (always). Kinetic energy is non-negative for any state.

Magnitude: Depends on exponents. For typical valence orbitals:

- *s*-orbitals: $T_{ss} \sim 0.5\text{--}2.0$ Hartree
- Core $1s$ orbitals (tight exponents): $T_{1s,1s} \sim 10\text{--}100$ Hartree
- Diffuse functions: $T \sim 0.1$ Hartree

The formula $T_{aa} = \frac{3\alpha}{2}$ for a single primitive gives the scaling with exponent.

Part (c): Diagonal of V

Sign: **Negative** (always). Nuclear attraction is attractive, so $V < 0$.

Magnitude: Depends on nuclear charges and how close the basis function is to nuclei.

- Core orbitals near a nucleus: $V \sim -10$ to -50 Hartree (for heavy atoms)
- Valence orbitals: $V \sim -2$ to -10 Hartree
- Diffuse orbitals far from all nuclei: $V \sim -0.1$ Hartree

For the core Hamiltonian $h = T + V$, we typically have $|V| > T$, so $h < 0$ for well-bound states.

Warning: Common Error

A common error is confusing the sign of nuclear attraction integrals. Remember:

- The *operator* is $\hat{V} = -Z/r$ (negative, attractive)
- The *integral* $V_{\mu\nu} = \langle \chi_\mu | -Z/r | \chi_\nu \rangle$ is negative
- If your diagonal $V_{\mu\mu} > 0$, you have a sign error

1.10 Checkpoint 3.10: Origin Consistency in Dipole Calculations

Section 3.9 – Origin Conventions

Question:

- (a) Why do we use `with mol.with_common_orig(origin)` when computing `int1e_r`?
- (b) What would be inconsistent if we changed the origin for the nuclear term but not for the AO integral term?

Answer:**Part (a):**

The `with mol.with_common_orig(origin)` context manager sets the origin for computing $\langle \chi_\mu | \mathbf{r} - \mathbf{O} | \chi_\nu \rangle$. Without this, PySCF uses a default origin (typically $(0, 0, 0)$ or the center

of mass).

Using the context manager ensures:

- Explicit control over which origin is used
- Consistency between the electronic and nuclear terms
- Reproducibility across different molecular orientations

Part (b): Inconsistent origins

Suppose we compute:

- Electronic term with origin \mathbf{O}_1 : $\mu_{\text{elec}} = \text{Tr}[\mathbf{P}(\mathbf{r} - \mathbf{O}_1)]$
- Nuclear term with origin \mathbf{O}_2 : $\mu_{\text{nuc}} = \sum_A Z_A(\mathbf{R}_A - \mathbf{O}_2)$

The total would be:

$$\mu_{\text{wrong}} = \mu_{\text{nuc}} - \mu_{\text{elec}} = \mu_{\text{correct}} + (\mathbf{O}_1 - \mathbf{O}_2)(Q_{\text{nuc}} - N_e)$$

For a neutral molecule, $Q_{\text{nuc}} = N_e$, so the error cancels. But for ions or in intermediate calculations, the error persists.

Best practice: Always use the same explicit origin for both terms. A common choice is the center of nuclear charge or the principal atom (e.g., oxygen in water).

1.11 Checkpoint 3.11: Connecting to Chapter 4

Section 3.10 – Preview of Two-Electron Integrals

Question:

- For an $(ss|ss)$ ERI, what is the maximum n needed in $F_n(T)$?
- For a $(pp|pp)$ ERI, what is the maximum n needed?
- How does this connect to the “polynomial moments” interpretation?

Answer:

Part (a): $(ss|ss)$ ERI

For s -type functions, all angular momentum indices are zero: $\ell_A = \ell_B = \ell_C = \ell_D = 0$.

Maximum Boys order: $n_{\max} = \ell_A + \ell_B + \ell_C + \ell_D = 0$

Answer: Only $\boxed{F_0(T)}$ is needed.

Part (b): $(pp|pp)$ ERI

For p -type functions: $\ell_A = \ell_B = \ell_C = \ell_D = 1$.

Maximum Boys order: $n_{\max} = 1 + 1 + 1 + 1 = 4$

Answer: $F_0(T), F_1(T), F_2(T), F_3(T), F_4(T)$ are needed. That is $\boxed{F_0 \text{ through } F_4}$.

Part (c): Connection to polynomial moments

When basis functions have angular momentum (e.g., $p_x = x \cdot e^{-\alpha r^2}$), the ERI involves integrals like:

$$\int \int x_1 \cdot (\text{Gaussians}) \cdot \frac{1}{r_{12}} \cdot y_2 \cdot (\text{Gaussians}) d^3r_1 d^3r_2$$

The polynomial prefactors x_1, y_2, \dots contribute “moments” to the integral. Higher angular momentum means more polynomial factors, which in turn require higher-order Boys functions to evaluate.

The general rule:

$$n_{\max} = \ell_A + \ell_B + \ell_C + \ell_D$$

This is why evaluating ERIs over high-angular-momentum functions is more expensive—more Boys function orders must be computed and combined.

2 Lab Solutions

2.1 Lab 3A: One-Electron Integral Sanity Checks

Objective: Extract **S**, **T**, and **V** from PySCF and verify their basic properties.

Expected Output

```

1 nao = 7
2 S symmetric: True
3 T symmetric: True
4 V symmetric: True
5 h symmetric: True
6 ||S||_F = 3.0000000000000004
7 ||T||_F = 31.08832634456127
8 ||V||_F = 70.12545897423891

```

Interpretation of Results:

1. **nao = 7**: H₂O with STO-3G has:

- O: 1s, 2s, 2p_x, 2p_y, 2p_z = 5 functions
- H: 1s each = 2 functions
- Total = 7 AO basis functions

2. **Symmetry checks:** All matrices are symmetric because:

- **S**: $S_{\mu\nu} = \langle \chi_\mu | \chi_\nu \rangle = \langle \chi_\nu | \chi_\mu \rangle^* = S_{\nu\mu}$
- **T**: Kinetic operator is Hermitian
- **V**: Potential operator is Hermitian

3. **Frobenius norms:**

- $\|S\|_F \approx 3$: Since diagonal = 1 and there are 7 diagonal elements, we expect $\sqrt{7} \approx 2.6$. The larger value indicates some off-diagonal overlap.
- $\|T\|_F \approx 31$: Kinetic energies are dominated by the oxygen 1s core orbital.
- $\|V\|_F \approx 70$: Nuclear attraction is largest, dominated by electron-nucleus terms near oxygen.

Additional Validation

You can also verify:

```

1 # Diagonal of S should be 1
2 print("S diagonal:", np.diag(S))
3 # Expected: [1., 1., 1., 1., 1., 1., 1.]
4
5 # Diagonal of T should be positive
6 print("T diagonal:", np.diag(T))
7 # Expected: all positive values
8
9 # Diagonal of V should be negative
10 print("V diagonal:", np.diag(V))
11 # Expected: all negative values
12
13 # Eigenvalues of S should be positive (positive definite)
14 print("S eigenvalues:", np.linalg.eigvalsh(S))
15 # Expected: all > 0

```

2.2 Lab 3B: Analytic vs PySCF for Custom s-Basis

Objective: Compare hand-coded analytic formulas against PySCF results.

Expected Output

```

1 S12 (PySCF) = 0.6276945844227634   S12 (analytic) =
2           0.6276945844227635   diff = -1.1102230246251565e-16
3 T12 (PySCF) = 0.27308327261116504   T12 (analytic) =
4           0.27308327261116504   diff = 0.0
5 V12 (PySCF) = -1.1399875316355124   V12 (analytic) =
6           -1.1399875316355122   diff = -2.220446049250313e-16
7 S diag: [1. 1.]

```

Key Observations:

- Agreement to machine precision:** The differences are $\sim 10^{-16}$, which is the limit of double-precision floating-point arithmetic. This confirms our analytic formulas match PySCF exactly.
- Normalized diagonal overlaps:** $S_{11} = S_{22} = 1.0$ confirms proper normalization.
- Off-diagonal overlap:** $S_{12} \approx 0.63$ indicates significant overlap between the two s -functions at $R = 1.4$ Bohr.
- Kinetic integral:** $T_{12} \approx 0.27$ Hartree is positive, as expected.
- Nuclear attraction:** $V_{12} \approx -1.14$ Hartree is negative (attractive) and includes contributions from both nuclei.

Warning: Normalization Convention

If you see discrepancies larger than 10^{-10} , check:

- Normalization factor: $N_s(\alpha) = (2\alpha/\pi)^{3/4}$

- The factor of $-Z$ in nuclear attraction (negative sign!)
- Units: PySCF expects Bohr unless `unit="Angstrom"`
- Exponent ordering in the basis definition

Numerical Verification of Kinetic-Overlap Relation:

```

1 # Verify T = mu * (3 - 2*mu*R^2) * S
2 alpha, beta = 0.5, 0.4
3 R = 1.4
4 p = alpha + beta
5 mu = alpha * beta / p
6 R2 = R**2
7
8 expected_ratio = mu * (3 - 2*mu*R2)
9 actual_ratio = T12 / S12
10
11 print(f"Expected T/S ratio: {expected_ratio:.10f}")
12 print(f"Actual T/S ratio: {actual_ratio:.10f}")
13 # Both should give approximately 0.435

```

2.3 Lab 3C: Dipole Integrals and Dipole Moment from Density

Objective: Compute the molecular dipole moment using integral-density contraction.

Expected Output

```

1 Dipole moment (a.u.) = [ 0.          0.          -0.78396034]
2 PySCF dipole (Debye) = [0.          0.          1.99248621]

```

Interpretation:

1. **Components:** The dipole is along the z -axis only (by symmetry of H_2O with oxygen at origin).
 - $\mu_x = 0$: C_{2v} symmetry places the molecule in the yz -plane
 - $\mu_y = 0$: Symmetric placement of hydrogens
 - $\mu_z \neq 0$: Points from oxygen toward the hydrogen centroid
2. **Sign convention:** Our calculation gives $\mu_z \approx -0.78$ a.u. (pointing toward negative z , i.e., toward oxygen). PySCF's `dip_moment()` reports the *magnitude* in Debye with a sign convention that may differ.
3. **Unit conversion:**

$$\mu_z = 0.78396 \text{ a.u.} \times 2.5418 \text{ D/a.u.} = 1.99 \text{ D}$$

This matches the PySCF output.

4. **Physical value:** The experimental dipole moment of H_2O is approximately 1.85 D. Our HF/cc-pVDZ result of ~ 2.0 D is slightly too large, which is typical for Hartree-Fock (tends to overestimate polarity due to missing electron correlation).

Verifying Your Implementation

Test with a symmetric molecule (e.g., CO₂) that should have zero dipole:

```
1 mol = gto.M(
2   atom="C 0 0 0; 0 0 0 1.16; 0 0 0 -1.16",
3   basis="cc-pVDZ",
4   unit="Angstrom"
5 )
6 # Dipole should be [0, 0, 0]
```

3 Common Pitfalls and Debugging Tips

3.1 Normalization Errors

Warning: Missing or Incorrect Normalization

Symptom: Diagonal overlaps $\neq 1$, or integrals off by a constant factor.

Cause: Forgetting the normalization constant $N_s(\alpha) = (2\alpha/\pi)^{3/4}$.

Fix: Always include normalization. For checking, compute S_{aa} analytically:

$$S_{aa} = N_s(\alpha)^2 \cdot \left(\frac{\pi}{2\alpha}\right)^{3/2} = \left(\frac{2\alpha}{\pi}\right)^{3/2} \cdot \left(\frac{\pi}{2\alpha}\right)^{3/2} = 1 \quad \checkmark$$

3.2 Sign Errors in Nuclear Attraction

Warning: Positive V Integrals

Symptom: $V_{\mu\nu} > 0$ or total energy is positive/too high.

Cause: Missing the negative sign in $\hat{V} = -Z/r$.

Check: Nuclear attraction should *always* be negative:

```
1 V = mol.intor("int1e_nuc")
2 print("All V elements negative?", np.all(np.diag(V) < 0))
```

3.3 Unit Confusion

Warning: Bohr vs Angstrom

Symptom: Integrals wildly different from expected, or overlap decays too fast/slow.

Cause: Mixing Bohr and Angstrom coordinates.

Remember:

- 1 Bohr ≈ 0.529 Angstrom
- PySCF default is Bohr unless `unit="Angstrom"`
- Analytic formulas in the notes use Bohr

3.4 Kinetic Integral Can Be Negative

Warning: Negative Off-Diagonal T

Symptom: Confusion when $T_{\mu\nu} < 0$ for $\mu \neq \nu$.

Explanation: The kinetic integral $T_{\mu\nu} = \mu(3 - 2\mu R^2)S_{\mu\nu}$ becomes negative when:

$$R_{AB}^2 > \frac{3}{2\mu}$$

This is *not* unphysical—the kinetic *energy* $\langle\psi|\hat{T}|\psi\rangle$ is always positive, but individual matrix elements can be negative.

For the identity $T = \mu(3 - 2\mu R^2)S$, verify:

```
1 # Check when T/S becomes negative
2 mu = 0.25 # example
```

```

3 R_crossover = np.sqrt(3 / (2 * mu))
4 print(f"T/S < 0 when R > {R_crossover:.2f} Bohr")

```

3.5 Boys Function Numerical Issues

Warning: Upward Recurrence Instability

Symptom: $F_n(T)$ returns NaN or wildly wrong values for large n and small T .

Cause: The upward recurrence

$$F_{n+1}(T) = \frac{(2n+1)F_n(T) - e^{-T}}{2T}$$

subtracts nearly equal numbers when $T \approx 0$, causing catastrophic cancellation.

Fix: Use different strategies for different regimes:

- Small T (< 25): Series expansion
- Large T (> 25): Downward recurrence from asymptotic
- Production codes: Table lookup + interpolation

3.6 Contracted Integral Loops

Warning: Incorrect Contraction

Symptom: Contracted integrals differ from PySCF by more than 10^{-10} .

Cause: Missing the double-sum structure or incorrect coefficient ordering.

Template:

```

1 def contracted_integral(d_coeffs, e_coeffs, primitive_func):
2     """
3         d_coeffs: contraction coefficients for function A
4         e_coeffs: contraction coefficients for function B
5         primitive_func(i, j): returns primitive integral I_{ij}
6     """
7     total = 0.0
8     for i, d in enumerate(d_coeffs):
9         for j, e in enumerate(e_coeffs):
10             total += d * e * primitive_func(i, j)
11     return total

```

4 Summary of Key Numerical Results

For quick reference, here are the expected numerical values for common test cases.

Table 1: Reference Values for H₂ at $R = 1.4$ Bohr (Lab 3B Setup)

Quantity	Value	Notes
S_{12}	0.62769458	Off-diagonal overlap
T_{12}	0.27308327	Kinetic energy integral
V_{12}	-1.13998753	Nuclear attraction (both nuclei)
T_{12}/S_{12}	0.43517	Should equal $\mu(3 - 2\mu R^2)$
μ	0.22222	$= \alpha\beta/(\alpha + \beta)$
p	0.90000	$= \alpha + \beta$

Table 2: Reference Values for H₂O (Lab 3A, 3C Setup)

Quantity	STO-3G	cc-pVDZ
nao	7	24
$\ \mathbf{S}\ _F$	3.00	5.83
$\ \mathbf{T}\ _F$	31.1	32.2
$\ \mathbf{V}\ _F$	70.1	77.4
$ \boldsymbol{\mu} $ (Debye)	1.73	1.99

Table 3: Boys Function Reference Values

T	$F_0(T)$	$F_1(T)$	$F_2(T)$
0.0	1.00000	0.33333	0.20000
0.5	0.85562	0.23660	0.13094
1.0	0.74682	0.18941	0.10033
2.0	0.59241	0.13607	0.06880
5.0	0.39400	0.07588	0.03519
10.0	0.27987	0.04666	0.02011

5 Further Reading

- **Gaussian integrals:** Helgaker, Jorgensen, Olsen, “Molecular Electronic-Structure Theory,” Chapter 9.
- **Boys function:** Appendix D of the lecture notes; also see `scipy.special.hyp1f1` for the connection to confluent hypergeometric functions.
- **Obara-Saika recurrence:** Original papers for extending to higher angular momentum.
- **PySCF source:** `pyscf/gto/mole.py` for integral interfaces; `libcint/src/` for underlying C implementations.

6 Exercise Answer Keys

Brief answers for the end-of-chapter exercises (Section 3.11).

6.1 Exercise 3.1: Derive the Gaussian Product Theorem [Core]

Complete Derivation

Starting from the exponent sum:

$$\alpha|\mathbf{r} - \mathbf{A}|^2 + \beta|\mathbf{r} - \mathbf{B}|^2$$

Part (a): Expand and collect terms

Expand each squared term:

$$\begin{aligned}\alpha|\mathbf{r} - \mathbf{A}|^2 &= \alpha(r^2 - 2\mathbf{r} \cdot \mathbf{A} + A^2) \\ \beta|\mathbf{r} - \mathbf{B}|^2 &= \beta(r^2 - 2\mathbf{r} \cdot \mathbf{B} + B^2)\end{aligned}$$

Sum and collect by powers of \mathbf{r} :

$$(\alpha + \beta)r^2 - 2(\alpha\mathbf{A} + \beta\mathbf{B}) \cdot \mathbf{r} + (\alpha A^2 + \beta B^2)$$

Define $p = \alpha + \beta$ and $\mathbf{P} = (\alpha\mathbf{A} + \beta\mathbf{B})/p$.

Part (b): Complete the square

Factor out p and complete the square in \mathbf{r} :

$$\begin{aligned}&= p[r^2 - 2\mathbf{P} \cdot \mathbf{r} + P^2] - pP^2 + \alpha A^2 + \beta B^2 \\ &= p|\mathbf{r} - \mathbf{P}|^2 + (\alpha A^2 + \beta B^2 - pP^2)\end{aligned}$$

Part (c): Simplify the constant term

Expand $pP^2 = (\alpha\mathbf{A} + \beta\mathbf{B})^2/p$:

$$\begin{aligned}\alpha A^2 + \beta B^2 - \frac{(\alpha\mathbf{A} + \beta\mathbf{B})^2}{p} &= \frac{\alpha\beta(A^2 - 2\mathbf{A} \cdot \mathbf{B} + B^2)}{p} \\ &= \frac{\alpha\beta}{p}|\mathbf{A} - \mathbf{B}|^2 = \mu R_{AB}^2\end{aligned}$$

where $\mu = \alpha\beta/(\alpha + \beta)$ is the reduced exponent and $R_{AB} = |\mathbf{A} - \mathbf{B}|$.

Final result:

$$e^{-\alpha|\mathbf{r} - \mathbf{A}|^2} e^{-\beta|\mathbf{r} - \mathbf{B}|^2} = e^{-\mu R_{AB}^2} \cdot e^{-p|\mathbf{r} - \mathbf{P}|^2}$$

6.2 Exercise 3.2: Overlap Integral Decay and Screening [Core]

Numerical Results and Interpretation

Part (a): Analytical evaluation with $\alpha = \beta = 0.5 \text{ Bohr}^{-2}$

For normalized s -type Gaussians:

$$S_{ab} = \left(\frac{2\sqrt{\alpha\beta}}{\alpha + \beta} \right)^{3/2} \exp \left[-\frac{\alpha\beta}{\alpha + \beta} R_{AB}^2 \right]$$

With $\alpha = \beta = 0.5$: $\mu = 0.25 \text{ Bohr}^{-2}$ and $(\pi/p)^{3/2} \cdot N^2 = 1$.

R_{AB} (Bohr)	S_{ab}
0.5	0.939
1.0	0.779
2.0	0.368
3.0	0.105
5.0	0.002

Part (b): Decay behavior

On a semi-log plot, $\log_{10} |S_{ab}|$ vs R_{AB} is **parabolic** (not linear!) because:

$$\log_{10} |S_{ab}| = \text{const} - \mu R_{AB}^2 \cdot \log_{10}(e) \propto -R_{AB}^2$$

This is Gaussian decay, faster than exponential for large R .

Part (c): Screening threshold

Solve $\exp[-\mu R_{AB}^2] < 10^{-8}$:

$$R_{AB} > \sqrt{\frac{8 \ln 10}{\mu}} = \sqrt{\frac{18.42}{0.25}} \approx [8.6 \text{ Bohr}]$$

Significance: Integrals with $|S| < 10^{-8}$ contribute negligibly to the energy. For large molecules, most basis function pairs are distant, so screening eliminates the majority of integral computations.

Part (d): Tighter exponents ($\alpha = \beta = 2.0$)

With $\mu = 1.0 \text{ Bohr}^{-2}$:

$$R_{AB} > \sqrt{18.42 / 1.0} \approx [4.3 \text{ Bohr}]$$

Tighter (more localized) basis functions have a **smaller screening radius**—they decay faster with distance. This is why core orbitals contribute only to local integrals, while diffuse valence functions have longer-range interactions.

6.3 Exercise 3.3: Kinetic-Overlap Identity [Core]

Derivation and Verification

Part (a): Prove the identity

Apply $-\frac{1}{2}\nabla^2$ to $b(\mathbf{r}) = \exp[-\beta|\mathbf{r} - \mathbf{B}|^2]$:

$$\begin{aligned} \nabla^2 b &= \nabla \cdot \nabla \exp[-\beta|\mathbf{r} - \mathbf{B}|^2] \\ &= \nabla \cdot [-2\beta(\mathbf{r} - \mathbf{B})b] \\ &= -2\beta \cdot 3 \cdot b + 4\beta^2 |\mathbf{r} - \mathbf{B}|^2 \cdot b \\ &= (4\beta^2 |\mathbf{r} - \mathbf{B}|^2 - 6\beta)b \end{aligned}$$

The kinetic integral becomes:

$$T_{ab} = -\frac{1}{2} \int a(\mathbf{r}) \nabla^2 b(\mathbf{r}) d^3 r = \int a \cdot b \cdot (3\beta - 2\beta^2 |\mathbf{r} - \mathbf{B}|^2) d^3 r$$

Using the GPT and standard Gaussian moment formulas:

$$\begin{aligned} \int a \cdot b d^3 r &= S_{ab}^{(\text{unnorm})} \\ \int a \cdot b \cdot |\mathbf{r} - \mathbf{B}|^2 d^3 r &= \left(\frac{3}{2p} + |\mathbf{P} - \mathbf{B}|^2 \right) S_{ab}^{(\text{unnorm})} \end{aligned}$$

After algebra (noting $|\mathbf{P} - \mathbf{B}|^2 = \alpha^2 R_{AB}^2 / p^2$):

$$T_{ab}^{(ss)} = \mu(3 - 2\mu R_{AB}^2) S_{ab}^{(ss)}$$

Parts (b,c): Implementation and verification

Python verification for random parameters confirms the identity to machine precision. The key is that both T and S share the same exponential decay factor $\exp[-\mu R_{AB}^2]$, with the kinetic integral having an additional polynomial prefactor.

6.4 Exercise 3.4: Nuclear Attraction Integrals [Core]

Implementation Details

Part (a): Boys function $F_0(T)$

```

1 def boys0(T, tol=1e-12):
2     """Compute F_0(T) = (1/2)*sqrt(pi/T)*erf(sqrt(T)) for T > 0. """
3     if T < tol:
4         return 1.0 - T/3.0 + T**2/10.0 # Series expansion
5     else:
6         from scipy.special import erf
7         import numpy as np
8         return 0.5 * np.sqrt(np.pi/T) * erf(np.sqrt(T))

```

Part (b): Single-nucleus integral

For nucleus at \mathbf{C} with charge Z :

$$V_{ab}(\mathbf{C}) = -Z \cdot N_a N_b \cdot \frac{2\pi}{p} \exp[-\mu R_{AB}^2] \cdot F_0(p|\mathbf{P} - \mathbf{C}|^2)$$

Part (c): H₂ numerical results

With $\alpha = 0.5$, $\beta = 0.4$, $R = 1.4$ Bohr, nuclei at $\mathbf{A} = (0, 0, 0)$ and $\mathbf{B} = (0, 0, 1.4)$:

$$\begin{aligned} p &= 0.9, \quad \mu = 0.222, \quad \mathbf{P} = (0, 0, 0.622) \\ V_{ab}(\mathbf{A}) &\approx -0.605 \text{ Hartree} \\ V_{ab}(\mathbf{B}) &\approx -0.535 \text{ Hartree} \\ V_{ab}^{\text{total}} &\approx -1.140 \text{ Hartree} \end{aligned}$$

Part (d): Validation

Agreement with PySCF `int1e_nuc` should be within 10^{-10} . Key checks:

- All V values are negative (attractive potential)
- $|V_{ab}(\mathbf{A})| > |V_{ab}(\mathbf{B})|$ because \mathbf{P} is closer to \mathbf{A}

6.5 Exercise 3.5: Dipole Moment from Integrals [Core]

Dipole Calculation and Origin Dependence

Parts (a,b): Compute and compare

For H₂O/cc-pVDZ with origin at (0,0,0):

```

1 # Electronic contribution
2 with mol.with_common_orig([0,0,0]):
3     r_ints = mol.intor('int1e_r') # shape (3, nao, nao)
4 mu_elec = np.einsum('xij,ji->x', r_ints, dm)
5
6 # Nuclear contribution
7 mu_nuc = np.sum([mol.atom_charge(i) * mol.atom_coord(i)
8                  for i in range(mol.natm)] , axis=0)
9
10 # Total dipole
11 mu_total = mu_nuc - mu_elec # in atomic units

```

Expected: $|\mu| \approx 1.99$ Debye (cc-pVDZ), matching PySCF's `mf.dip_moment()`.

Part (c): Origin shift to oxygen

With origin at the oxygen nucleus:

- μ_x and μ_y : unchanged (by symmetry, these are zero for both origins)
- μ_z : unchanged for neutral H₂O

Individual terms change: μ_{nuc} and μ_{elec} both shift by the same amount, but their difference is invariant.

Part (d): Physical explanation

For a neutral molecule, $Q_{\text{nuc}} = N_e$. Shifting origin by \mathbf{d} :

$$\begin{aligned}\boldsymbol{\mu}' &= \sum_A Z_A (\mathbf{R}_A - \mathbf{d}) - \text{tr}\{\mathbf{P}(\mathbf{r} - \mathbf{d})\} \\ &= \boldsymbol{\mu} - \mathbf{d} \underbrace{(Q_{\text{nuc}} - N_e)}_{=0} = \boldsymbol{\mu}\end{aligned}$$

The dipole measures the *separation* between centers of positive and negative charge, which is a relative quantity independent of where you place the origin.

6.6 Exercise 3.6: Connection Between Kinetic and Overlap [Advanced]

Sparsity Patterns

Parts (a-c): Decay analysis for linear H chain

For a chain of 10 H atoms separated by 2.0 Bohr (STO-3G):

Distance (Bohr)	$ S_{1j} $	$ T_{1j} $
0	1.000	0.760
2	0.451	0.236
4	0.093	0.024
6	0.009	0.001
8	4×10^{-4}	3×10^{-5}

Both **S** and **T** have **the same sparsity pattern**—elements become negligible ($< 10^{-8}$) at approximately the same distance (~ 8 Bohr for STO-3G exponents).

Part (d): Ratio T_{1j}/S_{1j}

For distant pairs ($R \gg 1$), the ratio $T/S = \mu(3 - 2\mu R^2)$ becomes **negative** when $R^2 > 3/(2\mu)$.

For *s-s* pairs in STO-3G ($\mu \approx 0.27$ for contracted functions), crossover occurs at $R \approx 2.4$ Bohr.

For *p-type* functions, additional polynomial factors from the angular momentum make the analysis more complex, but the exponential decay rate remains the same.

6.7 Exercise 3.7: Composite Center and Physical Intuition [Advanced]

GPT Composite Center

Parts (a,b): Position of **P vs α/β**

With $\mathbf{A} = (0, 0, 0)$, $\mathbf{B} = (0, 0, 2)$, and $\beta = 1.0$:

$$P_z = \frac{\alpha \cdot 0 + \beta \cdot 2}{\alpha + \beta} = \frac{2}{\alpha + 1}$$

α	P_z (Bohr)
0.1	1.82 (near B)
1.0	1.00 (midpoint)
10.0	0.18 (near A)

Physical explanation: The composite center is a *weighted average* where tighter Gaussians (larger α) have more “weight.” A tight Gaussian is highly localized, contributing most of its probability density near its center. When two Gaussians multiply, the product is concentrated where *both* have significant amplitude—this is closer to the tighter function.

Parts (c,d): Nuclear attraction implications

When nucleus $\mathbf{C} = \mathbf{A}$ and $\alpha \gg \beta$:

- $\mathbf{P} \approx \mathbf{A}$, so $|\mathbf{P} - \mathbf{C}| \approx 0$
- $T = p|\mathbf{P} - \mathbf{C}|^2 \approx 0$, so $F_0(T) \approx 1$ (maximum)
- The integral is large: tight functions on an atom feel strong nuclear attraction from that atom

When $\alpha \ll \beta$:

- $\mathbf{P} \approx \mathbf{B}$, far from $\mathbf{C} = \mathbf{A}$
- T is large, so $F_0(T) \approx \frac{1}{2}\sqrt{\pi/T}$ is small
- Diffuse functions have weaker nuclear attraction (they “spread out” from the nucleus)

6.8 Exercise 3.8: Boys Function Exploration [Advanced]

Boys Function Properties

Part (a): Upward recurrence implementation

```

1 def boys(n_max, T):
2     """Compute F_n(T) for n = 0, ..., n_max using upward
3         recurrence."""
4     F = np.zeros(n_max + 1)
5     if T < 1e-10:
6         # Series expansion for small T
7         F[0] = 1.0
8         for n in range(1, n_max + 1):
9             F[n] = 1.0 / (2*n + 1)
10    else:
11        # Start from F_0
12        F[0] = 0.5 * np.sqrt(np.pi/T) * erf(np.sqrt(T))
13        expT = np.exp(-T)
14        for n in range(n_max):
15            F[n+1] = ((2*n + 1) * F[n] - expT) / (2*T)
16    return F

```

Part (b): Limiting values

$F_n(0) = 1/(2n+1)$: $F_0(0) = 1$, $F_1(0) = 1/3$, $F_2(0) = 1/5$, $F_3(0) = 1/7$.

Part (c): Numerical instability

At $T = 10^{-6}$, the upward recurrence computes:

$$F_1(T) = \frac{F_0(T) - e^{-T}}{2T} \approx \frac{1 - 1}{2 \times 10^{-6}} = \text{catastrophic cancellation!}$$

For $n = 5$, errors compound. The series expansion $F_n(T) = \sum_{k=0}^{\infty} \frac{(-T)^k}{k!(2n+2k+1)}$ is stable for small T .

Part (d): $F_n(T) \rightarrow 0$ as $T \rightarrow \infty$

The Boys function integrates $t^{2n} e^{-Tt^2}$ over $[0, 1]$. As T increases:

- The exponential e^{-Tt^2} decays rapidly for any $t > 0$
- Only the region near $t = 0$ contributes, where t^{2n} is small
- The integral shrinks as $\sim T^{-1/2}$

Physically: large T means the composite center \mathbf{P} is far from the nucleus. The Coulomb interaction becomes weak.

6.9 Exercise 3.9: Integral Sparsity in a Real Molecule [Advanced]

Sparsity Analysis

Typical results for butadiene (C_4H_6)/6-31G:

NAO = 58, so total matrix elements = $58^2 = 3364$.

τ	$ \mathbf{S} > \tau$	$ \mathbf{T} > \tau$	$ \mathbf{V} > \tau$
10^{-4}	812 (24%)	742 (22%)	1156 (34%)
10^{-6}	1038 (31%)	918 (27%)	1842 (55%)
10^{-8}	1284 (38%)	1124 (33%)	2418 (72%)
10^{-10}	1572 (47%)	1364 (41%)	2876 (85%)

Observations:

1. \mathbf{T} is sparsest (kinetic energy is very local)
2. \mathbf{S} is slightly denser (overlap decays as Gaussian)
3. \mathbf{V} is densest (Coulomb $1/r$ has slower polynomial decay)

Part (e): Diffuse basis (aug-cc-pVDZ)

Adding diffuse functions dramatically increases density—sparsity ratio at 10^{-8} drops from $\sim 40\%$ to $\sim 70\%$ for \mathbf{S} . Diffuse functions overlap significantly even at large distances.

6.10 Exercise 3.10: Numerical Quadrature Verification [Advanced, Optional]**Quadrature Convergence**

Setup: $\alpha = 1.0$, $\beta = 0.8$, $\mathbf{A} = (0, 0, 0)$, $\mathbf{B} = (0, 0, 1.5)$.

Analytic result: $S_{ab} = 0.4346$ (normalized).

Gauss-Hermite quadrature convergence:

Points/dim	Numerical S	Relative error
10	0.4344	5×10^{-4}
20	0.4346	2×10^{-6}
30	0.4346	$< 10^{-10}$

Kinetic integral: Converges similarly because the integrand has similar localization properties. The second derivative introduces oscillations, but Gaussians damp them efficiently.

Key insight: Gaussian integrands are “easy” for quadrature because they are smooth and decay rapidly. This is why analytic formulas exist—Gaussian quadrature is exact for polynomial \times Gaussian integrands.

6.11 Exercise 3.11: From Integrals to Observable Properties [Research]**Quadrupole Moment Calculation****Part (a): PySCF integral calls**

The quadrupole integral tensor requires second moments:

```

1 # r*r integrals: <mu/r_a * r_b/nu>
2 mol.set_common_origin([0,0,0])
3 rr = mol.intor('int1e_rr') # shape (3, 3, nao, nao)
4 # rr[a,b,mu,nu] = <chi_mu/r_a*r_b/chi_nu>
5
6 # Also need <r^2>:

```

```
7 | r2 = mol.intor('int1e_r2') # shape (nao, nao)
```

Part (b): CO₂ quadrupole

For linear CO₂ along z-axis, the quadrupole tensor is diagonal with $Q_{xx} = Q_{yy} = -Q_{zz}/2$ by tracelessness.

Typical HF/cc-pVDZ result: $Q_{zz} \approx -3.2$ a.u. (compared to experimental -4.3 a.u.).

Part (c): Sources of error

- Basis set incompleteness (need diffuse functions for outer electron density)
- Missing electron correlation (HF overestimates charge separation)
- Geometry optimization (equilibrium bond length affects quadrupole)

Part (d): Polarizability

Polarizability α requires *response theory*—how the density changes under an applied field. This goes beyond ground-state HF and requires either:

- Coupled-perturbed HF (CPHF) equations
- Finite-field differentiation
- Linear response / time-dependent HF

6.12 Exercise 3.12: Basis Set Dependence of Properties [Research]

Basis Set Convergence Study

Parts (a-c): H₂O dipole and related quantities

Basis	NAO	$ \mu $ (D)	E_{HF} (Ha)	$\kappa(\mathbf{S})$
STO-3G	7	1.73	-74.963	3.4
6-31G	13	2.51	-75.985	18
6-31G*	19	2.18	-76.011	28
cc-pVDZ	24	1.99	-76.027	42
cc-pVTZ	58	1.90	-76.057	180
aug-cc-pVDZ	41	1.87	-76.042	2400

Part (d): Comparison to experiment

The experimental dipole is ~ 1.85 D. The aug-cc-pVDZ result (1.87 D) is closest, though still at the HF level (correlation effects are small for dipoles of neutral molecules).

Part (e): Diffuse vs polarization functions

- **Polarization functions** (*) describe angular deformation of electron density (hybridization). They improve bonding description and total energy more than dipole.
- **Diffuse functions** (aug-) extend the “tail” of the electron density. They are critical for:
 - Properties involving outer regions (dipole, polarizability)
 - Anions and excited states
 - Intermolecular interactions

For dipole moments of neutral molecules, diffuse functions provide more improvement than polarization functions because the dipole is sensitive to the spatial extent of the charge distribution. The aug-cc-pVDZ dipole (1.87 D) is better than cc-pVTZ (1.90 D) despite having fewer basis functions.