

1. Evaluate each of the following using the definition of contraction.

$\overline{a_p a_q} = ?$	$\overline{a_p^\dagger a_q} = ?$	$\overline{a_p a_q^\dagger} = ?$	$\overline{a_p^\dagger a_q^\dagger} = ?$
$\overline{a_a a_b} = ?$	$\overline{a_a^\dagger a_b} = ?$	$\overline{a_a a_b^\dagger} = ?$	$\overline{a_a^\dagger a_b^\dagger} = ?$
$\overline{a_a a_i} = ?$	$\overline{a_a^\dagger a_i} = ?$	$\overline{a_a a_i^\dagger} = ?$	$\overline{a_a^\dagger a_i^\dagger} = ?$
$\overline{a_i a_a} = ?$	$\overline{a_i^\dagger a_a} = ?$	$\overline{a_i a_a^\dagger} = ?$	$\overline{a_i^\dagger a_a^\dagger} = ?$
$\overline{a_i a_j} = ?$	$\overline{a_i^\dagger a_j} = ?$	$\overline{a_i a_j^\dagger} = ?$	$\overline{a_i^\dagger a_j^\dagger} = ?$

2. Assuming Wick's theorem, prove the following corollaries in your own words.
- A product of normal-ordered operators equals the normal-ordering of their product plus all cross-contractions.
  - The vacuum expectation value of an operator is the sum of its complete contractions.
3. Visually illustrate the proof of the phase factor for completely contracted products with a non-trivial example – something with more than two line intersections.
4. Derive the expansion of  $H_e$  in terms of  $\Phi$ -normal-ordered excitations.
5. Derive Slater's rules using Wick's theorem.

$$\langle \Phi | H_e | \Phi \rangle = \sum_i h_{ii} + \frac{1}{2} \sum_{ij} \langle ij || ij \rangle \quad \langle \Phi | H_e | \Phi_i^a \rangle = h_{ia} + \sum_j \langle ij || aj \rangle \quad \langle \Phi | H_e | \Phi_{ij}^{ab} \rangle = \langle ij || ab \rangle$$

Also, explain why the second equation evaluates to zero for canonical Hartree-Fock orbitals.<sup>1</sup> This is known as *Brillouin's theorem*.

6. Derive the CIS matrix elements using Wick's theorem.

<sup>1</sup>Hint: Project the canonical Hartree-Fock equation by another spin-orbital and expand  $f_{pq} = \langle \psi_p | \hat{f} | \psi_q \rangle$  in terms of one- and two-electron integrals.