Question 1a (0.5 pts). Write down the CID Schrödinger equation.

$$H_c(1 + C_2)\Phi = E_c(1 + C_2)\Phi$$

where $C_2 = \frac{1}{4}c^{ij}_{ab}\tilde{a}^{ab}_{ij}$

Question 1b (1.5 pts). Project the CID Schrödinger equation on the left by $\langle\Phi|$ and $\langle\Phi^{ab}_{ij}|$ to obtain expressions for E_c and c^{ij}_{ab}.

$$\begin{aligned} E_c &= \langle\Phi|H_c(1 + C_2)|\Phi\rangle \\ E_c c^{ij}_{ab} &= \langle\Phi^{ab}_{ij}|H_c(1 + C_2)|\Phi\rangle \end{aligned}$$

Question 1c (5 pts). Use Wick's theorem to evaluate each matrix element obtained in part b. You do not have to convert the KM contraction dots into η's and γ's, nor do you have to expand the index antisymmetrizers $\hat{P}$. For example, an acceptable place to stop for your answer would be something like

$$\langle\Phi|\tilde{a}^{j}_{b}\tilde{a}^{pq}_{rs}\tilde{a}^{a}_{i}|\Phi\rangle = \hat{P}^{(p/q)}_{(r/s)}\tilde{a}^{j\circ\circ}_{a\bullet}\tilde{a}^{p\circ q\bullet}_{r\bullet\bullet s\circ\circ}\tilde{a}^{a\bullet\bullet}_{i\circ}$$

$$\begin{aligned} E_c &= \langle\Phi|H_c(1 + C_2)|\Phi\rangle \\ &= \langle\Phi|(f^q_p\tilde{a}^p_q + \tfrac{1}{4}\bar{g}^{rs}_{pq}\tilde{a}^{pq}_{rs})(1 + \tfrac{1}{4}c^{ij}_{ab}\tilde{a}^{ab}_{ij})|\Phi\rangle \\ &= \langle\Phi|\tfrac{1}{4}\bar{g}^{rs}_{pq}\tilde{a}^{pq}_{rs}\tfrac{1}{4}c^{ij}_{ab}\tilde{a}^{ab}_{ij}|\Phi\rangle \\ &= \tfrac{1}{16}\bar{g}^{rs}_{pq}c^{ij}_{ab}\hat{P}^{(p/q)}_{(r/s)}\tilde{a}^{p^{\circ}q^{\circ\circ}}_{r^{\bullet}s^{\bullet\bullet}}\tilde{a}^{a^{\bullet}b^{\bullet\bullet}}_{i^{\circ}j^{\circ\circ}} \end{aligned}$$

$$\begin{aligned} E_c c^{ij}_{ab} &= \langle\Phi^{ab}_{ij}|H_c(1 + C_2)|\Phi\rangle \\ &= \langle\Phi|\tilde{a}^{ij}_{ab}(f^q_p\tilde{a}^p_q + \tfrac{1}{4}\bar{g}^{rs}_{pq}\tilde{a}^{pq}_{rs})(1 + \tfrac{1}{4}c^{kl}_{cd}\tilde{a}^{cd}_{kl})|\Phi\rangle \\ &= \langle\Phi|\tilde{a}^{ij}_{ab}(\tfrac{1}{4}\bar{g}^{rs}_{pq}\tilde{a}^{pq}_{rs})|\Phi\rangle + \langle\Phi|\tilde{a}^{ij}_{ab}(f^q_p\tilde{a}^p_q)\tfrac{1}{4}c^{kl}_{cd}\tilde{a}^{cd}_{kl}|\Phi\rangle + \langle\Phi|\tilde{a}^{ij}_{ab}(\tfrac{1}{4}\bar{g}^{rs}_{pq}\tilde{a}^{pq}_{rs})\tfrac{1}{4}c^{kl}_{cd}\tilde{a}^{cd}_{kl}|\Phi\rangle \\ &= \tfrac{1}{4}\bar{g}^{rs}_{pq}\hat{P}^{(p/q)}_{(r/s)}\tilde{a}^{i^{\circ1}j^{\circ2}}_{a^{\bullet1}b^{\bullet2}}\tilde{a}^{p^{\bullet1}q^{\bullet2}}_{r^{\circ1}s^{\circ2}} \\ &\quad + \tfrac{1}{4}f^q_p c^{kl}_{cd}\left(\hat{P}^{(c/d)}_{(a/b|k/l)}\tilde{a}^{i^{\circ1}j^{\circ2}}_{a^{\bullet1}b^{\bullet3}}\tilde{a}^{p^{\bullet1}}_{q^{\bullet2}}\tilde{a}^{c^{\bullet2}d^{\bullet3}}_{k^{\circ1}l^{\circ2}} + \hat{P}^{(i/j|c/d)}_{(k/l)}\tilde{a}^{i^{\circ2}j^{\circ3}}_{a^{\bullet1}b^{\bullet2}}\tilde{a}^{p^{\circ1}}_{q^{\circ2}}\tilde{a}^{c^{\bullet1}d^{\bullet2}}_{k^{\circ1}l^{\circ3}}\right) \\ &\quad + \tfrac{1}{16}\bar{g}^{rs}_{pq}c^{kl}_{cd}\left(\hat{P}^{(c/d)}_{(a/b|k/l)}\tilde{a}^{i^{\circ1}j^{\circ2}}_{a^{\bullet1}b^{\bullet2}}\tilde{a}^{p^{\bullet1}q^{\bullet2}}_{r^{\bullet3}s^{\bullet4}}\tilde{a}^{c^{\bullet3}d^{\bullet4}}_{k^{\circ1}l^{\circ2}} + \hat{P}^{(i/j|c/d)}_{(k/l)}\tilde{a}^{i^{\circ1}j^{\circ2}}_{a^{\bullet1}b^{\bullet2}}\tilde{a}^{p^{\circ3}q^{\circ4}}_{r^{\circ1}s^{\circ2}}\tilde{a}^{c^{\bullet1}d^{\bullet2}}_{k^{\circ3}l^{\circ4}} + \hat{P}^{(i/j|p/q|c/d)}_{(a/b|r/s|k/l)}\tilde{a}^{i^{\circ1}j^{\circ3}}_{a^{\bullet1}b^{\bullet3}}\tilde{a}^{p^{\circ2}q^{\bullet1}}_{r^{\circ1}s^{\bullet2}}\tilde{a}^{c^{\bullet2}d^{\bullet3}}_{k^{\circ2}l^{\circ3}}\right) \end{aligned}$$

Question 2 (3 pts). Explain in your own words how perturbation theory works, as applied to the time-independent Schrödinger equation. Be sure to include a brief discussion of the following in your answer:

- the Hamiltonian
- λ
- The perturbation expansion

In perturbation theory, we split our Hamiltonian into two (or more) parts, $H = H_0 + V$, where H_0 is a system which is easier to solve and V is the perturbation. We introduce a parameter λ in front of V, so that $H = H_0 + \lambda V$. So long as the perturbation is small, we can expand the eigenstates and eigenvalues as a Taylor expansion in λ. We can plug this into the Schrödinger equation to find an infinite series of simultaneous equations, which can be used to find corrections to the wavefunction/energy at various orders.

Question 3 (3 pts). Derive an expression for $\Phi_0^{(3)}$ by explicitly pulling out terms from the perturbation expansion using the resolvent formalism. Explain you steps.

The perturbation expansion of the wavefunction is:

$$|\Psi_0\rangle = |\Phi_0\rangle + \sum_{n=0}^{\infty}(R_0 V^1)^n R_0 V\,|\Phi_0\rangle$$

At $n = 2$, we have a V and two V' in our term. To make the term third order overall (this is our target for constructing $|\Phi_0^{(3)}\rangle$), we require that each V' is 1st order, so we only take out the first order energy and V in our V' expansion $V' = V - E_0^{(1)}$. Let's now write this $n = 2$ term down before moving on,

$$|\Phi_0^{(3)}\rangle = (\mathcal{R}_0(V - E_0^{(1)}))^2 \mathcal{R}_0 V\,|\Phi_0\rangle + (\text{...more})$$

There is also a third-order term which appears when $n = 1$, $(\mathcal{R}_0 V')^1 \mathcal{R}_0 V\,|\Phi_0\rangle$. That V' has a second order contribution from $E_0^{(2)}$, therefore we set $V' = -E_0^{(2)}$ and pick up an additional term $\mathcal{R}_0 E_0^{(2)} \mathcal{R}_0 V\,|\Phi_0\rangle$ for $|\Phi_0^{(3)}\rangle$

$$|\Phi_0^{(3)}\rangle = (\mathcal{R}_0(V - E_0^{(1)}))^2 \mathcal{R}_0 V\,|\Phi_0\rangle - \mathcal{R}_0 E_0^{(2)} \mathcal{R}_0 V\,|\Phi_0\rangle$$

Expanding this and simplifying yields

$$|\Phi_0^{(3)}\rangle = \mathcal{R}_0 V \mathcal{R}_0 V \mathcal{R}_0 V\,|\Phi_0\rangle - \mathcal{R}_0 E_0^{(1)} \mathcal{R}_0 V \mathcal{R}_0 V\,|\Phi_0\rangle - \mathcal{R}_0 V \mathcal{R}_0 E_0^{(1)} \mathcal{R}_0 V\,|\Phi_0\rangle + \mathcal{R}_0 E_0^{(1)} \mathcal{R}_0 E_0^{(1)} \mathcal{R}_0 V\,|\Phi_0\rangle - \mathcal{R}_0 E_0^{(2)} \mathcal{R}_0 V\,|\Phi_0\rangle$$

Question 4 (2 pts). Derive $\Phi_0^{(4)}$ using the energy substitution trick.

$$\begin{aligned}
|\Phi_0^{(4)}\rangle = \quad & \mathcal{R}_0 V \mathcal{R}_0 V \mathcal{R}_0 V \mathcal{R}_0 V\,|\Phi_0\rangle - \mathcal{R}_0 E_0^{(1)} \mathcal{R}_0 V \mathcal{R}_0 V \mathcal{R}_0 V\,|\Phi_0\rangle - \mathcal{R}_0 V \mathcal{R}_0 E_0^{(1)} \mathcal{R}_0 V \mathcal{R}_0 V\,|\Phi_0\rangle \\
& - \mathcal{R}_0 V \mathcal{R}_0 V \mathcal{R}_0 E_0^{(1)} \mathcal{R}_0 V\,|\Phi_0\rangle + \mathcal{R}_0 E_0^{(1)} \mathcal{R}_0 V \mathcal{R}_0 E_0^{(1)} \mathcal{R}_0 V\,|\Phi_0\rangle + \mathcal{R}_0 E_0^{(1)} \mathcal{R}_0 E_0^{(1)} \mathcal{R}_0 V \mathcal{R}_0 V\,|\Phi_0\rangle \\
& + \mathcal{R}_0 V \mathcal{R}_0 E_0^{(1)} \mathcal{R}_0 E_0^{(1)} \mathcal{R}_0 V\,|\Phi_0\rangle - \mathcal{R}_0 E_0^{(2)} \mathcal{R}_0 V \mathcal{R}_0 V\,|\Phi_0\rangle - \mathcal{R}_0 V \mathcal{R}_0 E_0^{(2)} \mathcal{R}_0 V\,|\Phi_0\rangle \\
& - \mathcal{R}_0 E_0^{(1)} \mathcal{R}_0 E_0^{(1)} \mathcal{R}_0 E_0^{(1)} \mathcal{R}_0 V\,|\Phi_0\rangle + \mathcal{R}_0 E_0^{(2)} \mathcal{R}_0 E_0^{(1)} \mathcal{R}_0 V\,|\Phi_0\rangle + \mathcal{R}_0 E_0^{(1)} \mathcal{R}_0 E_0^{(2)} \mathcal{R}_0 V\,|\Phi_0\rangle \\
& - \mathcal{R}_0 E_0^{(3)} \mathcal{R}_0 V\,|\Phi_0\rangle
\end{aligned}$$

Question 5 (2 pts). Derive an expression for $E_0^{(5)}$ using Löwdin's PT formalism.

$E_0^{(5)} = \langle \Phi_0 | V | \Phi_0^{(4)} \rangle$

where $|\Phi_0^{(4)}\rangle$ is the result of question 4.