Suppose we choose to describe an atom in lowest order using a potential $U(r)$ other than the HF potential.

1. Show that the correction to the first-order energy from the single-particle part of the potential (V_1) for a one electron atom in a state v is
$$E_v^{(1)} = \Delta_{vv},$$
where $\Delta = V_{\text{HF}} - U$.

   We use the fact that the contribution to the first-order energy from V_1 is
$$\begin{aligned} E^{(1)} &= \langle \Psi_0 | V_1 | \Psi_0 \rangle \\ &= \sum_{ij} \Delta_{ij} \, \langle 0_c | a_v :a_i^\dagger a_j : a_v^\dagger | 0_c \rangle \\ &= \sum_{ij} \Delta_{ij} \, \delta_{iv} \, \delta_{jv} \\ &= \Delta_{vv}. \end{aligned}$$

2. Show that the corresponding second-order correction is
$$E_v^{(2)} = \sum_{na} \frac{\Delta_{na} \tilde{g}_{avnv} + \tilde{g}_{nvnv} \Delta_{an}}{\epsilon_n - \epsilon_a} - \sum_{i \neq v} \frac{\Delta_{vi} \Delta_{iv}}{\epsilon_i - \epsilon_v}.$$

   Here, i runs over a and n.

   First, we note that if we add V_1 to the potential, then the expression for the correlation function becomes
$$\chi^{(1)} = \sum_{ma} \chi_{ma}^{(1)} a_m^\dagger a_a + \sum_m \chi_{mv}^{(1)} a_m a_v + \sum_{mnab} \chi_{mnab}^{(1)} a_m^\dagger a_n^\dagger a_b a_a + \sum_{mnb} \chi_{mnvb}^{(1)} a_m^\dagger a_n^\dagger a_b a_v,$$
   where,
$$\begin{aligned} \chi_{ma}^{(1)} &= -\frac{\Delta_{ma}}{\epsilon_m - \epsilon_a} \\ \chi_{va}^{(1)} &= -\frac{\Delta_{mv}}{\epsilon_m - \epsilon_v} \\ \chi_{mnab}^{(1)} &= -\frac{1}{2} \frac{g_{mnab}}{\epsilon_m + \epsilon_n - \epsilon_a - \epsilon_b} \\ \chi_{mnab}^{(1)} &= -\frac{1}{2} \frac{\tilde{g}_{mnvb}}{\epsilon_m + \epsilon_n - \epsilon_v - \epsilon_b} \end{aligned}$$

The extra terms in the second-order energy from V_1 are

$$
\begin{aligned}
E^{(2)} &= \langle 0_c | a_v V_1 \left(\sum_{abmn} \chi^{(1)}_{mnab} a^\dagger_m a^\dagger_n a_b a_a + \sum_{mnb} \chi^{(1)}_{mnvb} a^\dagger_m a^\dagger_n a_b a_v \right) a^\dagger_v | 0_c \rangle \\
&+ \langle 0_c | a_v V_1 \left(\sum_{am} \chi^{(1)}_{ma} a^\dagger_m a_a + \sum_{m} \chi^{(1)}_{mv} a^\dagger_m a_v \right) a^\dagger_v | 0_c \rangle \\
&+ \langle 0_c | a_v V_2 \left(\sum_{am} \chi^{(1)}_{ma} a^\dagger_m a_a + \sum_{m} \chi^{(1)}_{mv} a^\dagger_m a_v \right) a^\dagger_v | 0_c \rangle \\
&= \sum_{ij} \Delta_{ij} \sum_{mnab} \chi^{(1)}_{mnab} \; \langle 0_c | a_v : a^\dagger_i a_j : a^\dagger_m a^\dagger_n a_b a_a a^\dagger_v | 0_c \rangle \\
&+ \sum_{ij} \Delta_{ij} \sum_{mnb} \chi^{(1)}_{mnvb} \; \langle 0_c | a_v : a^\dagger_i a_j : a^\dagger_m a^\dagger_n a_b | 0_c \rangle \\
&+ \sum_{ij} \Delta_{ij} \sum_{ma} \chi^{(1)}_{ma} \; \langle 0_c | a_v : a^\dagger_i a_j : a^\dagger_m a_a a^\dagger_v | 0_c \rangle \\
&+ \sum_{ij} \Delta_{ij} \sum_{m} \chi^{(1)}_{mv} \; \langle 0_c | a_v : a^\dagger_i a_j : a^\dagger_m | 0_c \rangle \\
&+ \frac{1}{2} \sum_{ijkl} g_{ijkl} \sum_{ma} \chi^{(1)}_{ma} \; \langle 0_c | a_v : a^\dagger_i a^\dagger_j a_l a_k : a^\dagger_m a_a a^\dagger_v | 0_c \rangle \\
&+ \frac{1}{2} \sum_{ijkl} g_{ijkl} \sum_{m} \chi^{(1)}_{mv} \; \langle 0_c | a_v : a^\dagger_i a^\dagger_j a_l a_k : a^\dagger_m | 0_c \rangle .
\end{aligned}
$$

The first and sixth terms above cannot contribute. The remaining terms give, in order,

$$
E^{(2)} = \sum_{bn} \Delta_{bn} \tilde{\chi}^{(1)}_{vnvb} + \sum_{ma} \Delta_{am} \chi^{(1)}_{ma} - \sum_{a} \Delta_{av} \chi^{(1)}_{va} + \sum_{m} \Delta_{vm} \chi^{(1)}_{mv} + \sum_{ma} \tilde{g}_{vavm} \chi^{(1)}_{ma} .
$$

Substituting the values of the correlation coefficients, we find

$$
E^{(2)} = -\sum_{bn} \frac{\Delta_{bn} \; \tilde{g}_{vnvb}}{\epsilon_n - \epsilon_b} - \sum_{ma} \frac{\Delta_{am} \Delta_{ma}}{\epsilon_m - \epsilon_a} + \sum_{a} \frac{\Delta_{av} \Delta_{va}}{\epsilon_v - \epsilon_a} - \sum_{m} \frac{\Delta_{vm} \Delta_{mv}}{\epsilon_m - \epsilon_v} - \sum_{ma} \frac{\tilde{g}_{vavm} \; \Delta_{ma}}{\epsilon_m - \epsilon_a} .
$$

The second term, which is independent of v is the contribution of Δ to the core energy. The remaining terms are contributions to the valence energy. We therefore find

$$
E^{(2)}_v = -\sum_{bn} \frac{\Delta_{bn} \; \tilde{g}_{vnvb} + \tilde{g}_{vbvn} \Delta_{nb}}{\epsilon_n - \epsilon_b} - \sum_{i \neq v} \frac{\Delta_{vi} \Delta_{iv}}{\epsilon_i - \epsilon_v} .
$$

n.b. The indices in the first factor Δ_{na} in the question were reversed; the factor should have been Δ_{an}. The result in the above equation is correct.