P2

a) $IP = E_{N-1} - E_N$

In a closed shell, each orbital has $2e^-$.
Therefore we can use Koopman's Theorem
(see notes page 123)

So

$$-IP = \epsilon_i = \langle i|h|i\rangle + \sum_{b=1}^{N} \langle ib||ib\rangle$$

$$= h_{ii} + \sum_{b=1}^{N} \left(\langle ib|ib\rangle - \langle ib|bi\rangle\right)$$

$$= h_{ii} + \sum_{b=1}^{N/2} (2J_{ib} - K_{ib})$$

Note: i) First we sum over the N electron orbitals (spatial + spin). In the spatial orbital representation we have 2 contributions from each orbital to J_{ib} (there are two e^- in ψ_i, one spin up and one spin down)

ii) There is only one J_{ii} term (as it should be), since $J_{ii} = K_{ii}$.

b) Here we can use the three rules in problem 1b), because both systems are closed shells.

$IP_2 = E_{N-2} - E_N$

$$E_N = 2\sum_{p=1}^{N/2} h_{pp} + \sum_{p=1}^{N/2} J_{pp} + 2\sum_{\substack{p=1 \\ p\neq q}}^{N/2}\sum_{q=1}^{N/2} J_{pq} - \sum_{\substack{p=1 \\ p\neq q}}^{N/2}\sum_{q=1}^{N/2} K_{pq}$$

and

$$E_{N-2} = E_N - 2h_{ii} - 4\sum_{\substack{p=1 \\ p\neq i}}^{N/2} J_{ip} + 2\sum_{\substack{p=1 \\ p\neq i}}^{N/2} K_{ip} - J_{ii}$$

I subtract all terms w a subscript i

$$\boxed{\begin{aligned} \Rightarrow -IP_2 &= 2h_{ii} + 4\sum_{p=1}^{N/2} J_{ip} - 2\sum_{p=1}^{N/2} K_{ip} - 3J_{ii} + 2K_{ii} \\ &= 2h_{ii} + 4\sum_{p=1}^{N/2} J_{ip} - 2\sum_{p=1}^{N/2} K_{ip} - J_{ii} \end{aligned}}$$

$$\left(= 2h_{ii} + 2\sum_{p=1}^{N/2} (2J_{ip} - K_{ip}) - J_{ii} \right)$$

Note: $|\ldots \psi_p \bar{\psi}_p \ldots \psi_q \bar{\psi}_q \ldots\rangle = |\Phi_0\rangle$

According to the rules in problem 1b):
~~Each~~ The two pairs $\psi_p \bar{\psi}_p$ and $\psi_q \bar{\psi}_q$ in a closed shell system ~~give~~ contribute

$$h_{pp} + h_{pp} + h_{qq} + h_{qq} + J_{pp} + J_{qq} + J_{pq} + J_{pq} + J_{pq} + J_{pq} - K_{pq} - K_{pq}$$

$$= 2h_{pp} + 2h_{qq} + J_{pp} + J_{qq} + 4J_{pq} - 2K_{pq}$$

to E_N. ~~Thus~~ Therefore we arrive at the formula as it is on page 5. A factor of 2 is absorbed in the double sums.