Partitition the space up into three subspaces :

- (R) : Reference space; constructed from CASSCF wavefunctions corresponded to the states of interest.
- (A) : CASCI space minus the reference space.
- (X) : External space constructed from determinants obtained by applying excitation operators to the determinants within the CASCI space.

These three spaces are orthogonal to one another.

Use them to write the eigenvalue problem:

$$\mathbf{Hc} = \mathbf{cE} \tag{1}$$

$$\begin{bmatrix} [H^{(RR)}] & [H^{(RA)}] & [H^{(RX)}] \\ [H^{(AR)}] & [H^{(AA)}] & [H^{(AX)}] \\ [H^{(XR)}] & [H^{(XA)}] & [H^{(XX)}] \end{bmatrix} \begin{bmatrix} [c^{(RR)}] & [c^{(RA)}] & [c^{(RX)}] \\ [c^{(AR)}] & [c^{(AA)}] & [c^{(AX)}] \\ [c^{(XR)}] & [c^{(XA)}] & [c^{(XX)}] \end{bmatrix}$$
$$= \begin{bmatrix} [c^{(RR)}] & [c^{(RA)}] & [c^{(RX)}] \\ [c^{(AR)}] & [c^{(AA)}] & [c^{(AX)}] \\ [c^{(XR)}] & [c^{(XA)}] & [c^{(XX)}] \end{bmatrix} \begin{bmatrix} [E^{RR}] & [0] & [0] \\ [0] & [E^{AA}] & [0] \\ [0] & [0] & [E^{CC}] \end{bmatrix} \tag{2}$$

From which we can get the set of equations :

$$H^{(RR)}c^{(RR)} + H^{(RA)}c^{(AR)} + H^{(RX)}c^{(XR)} = c^{(RR)}E^{(RR)} \tag{3}$$

$$H^{(AR)}c^{(RA)} + H^{(AA)}c^{(AA)} + H^{(AX)}c^{(XA)} = c^{(AA)}E^{(AA)} \tag{4}$$

$$H^{(XR)}c^{(RX)} + H^{(XA)}c^{(AX)} + H^{(XX)}c^{(XX)} = c^{(XX)}E^{(XX)} \tag{5}$$

For a particular state, ν, this can be written in index notation as

$$\sum_k H_{ik}c_{k\nu} + \sum_f H_{if}c_{f\nu} + \sum_x H_{iz}c_{z\nu} = \sum_k c_{ik}E_\nu, \tag{6}$$

$$\sum_k H_{ik}c_{k\nu} + \sum_f H_{df}c_{f\nu} + \sum_x H_{iz}c_{z\nu} = \sum_f c_{f\nu}E_\nu, \tag{7}$$

$$\sum_k H_{wk}c_{k\nu} + \sum_f H_{wf}c_{f\nu} + \sum_x H_{wz}c_{z\nu} = \sum_z c_{z\nu}E_\nu. \tag{8}$$

In the above and from now on the following convention is used for indexes; $i, j, k, l \in R$, $d, e, f \in A$, and $w, x, y, z \in X$.

If the reference space, R, is well seperated energetically from the remainder of the active space then we can assume that $[c^{(RA)}] \approx [c^{(AR)}] \approx 0$. This leaves us with the following equations for a state

$\nu \in R$:

$$\sum_k H_{ik}c_{k\nu} + \sum_z H_{iz}c_{z\nu} = \sum_k c_{\nu k}E_\nu \tag{9}$$

$$\sum_k H_{wk}c_{k\nu} + \sum_x H_{wz}c_{z\nu} = \sum_z c_{\nu z}E_{z\nu}. \tag{10}$$

Rearranging (10) to get an expression for $c_{y\nu}^{(XR)}$ ($y \in X$, $\nu \in R$);

$$c_{y\nu} = -\sum_{zk}[[H^{(XX)}] - E_\nu[I^{(XX)}]]^{-1}_{yz}H_{zk}c_{k\nu}, \tag{11}$$

where $[I^{(XX)}]$ is the representation of the identity on the external space X. This expression for $c_{y\nu}$ may be substitued back into (9) to obtain

$$\sum_k H_{ik}c_{k\nu} + \sum_y H_{iy}\sum_{zk}([H^{(XX)}] - E_\nu[I^{(XX)}])^{-1}_{yz}H_{zk}c_{k\nu} = \sum_k c_{\nu k}E_\nu \tag{12}$$

This would need to be solved iteratively, due to appearance of E_ν on both sides of the equation. This is problematic as calculating matrix inverses can prove expensive, and we would need to calculate the inverse again for every new guess at E_ν. To try and deal with this we write

$$E_\nu = E_\nu^0 + \Delta E_\nu \tag{13}$$

leading to

$$[[H^{(XX)}] - E_\nu[I^{(XX)}]]^{-1} = ([C] + [D])^{-1}, \tag{14}$$

where

$$[C] = [H^{(XX)}] - E_\nu^0[I^{(XX)}] \tag{15}$$

$$[D] = \Delta E_\nu[I^{(XX)}] \tag{16}$$

Now using the identity $(C + D)^{-1} = (1 + C^{-1}D)D^{-1}$ we write :

$$([H^{(XX)}] - E_\nu[I^{(XX)}])^{-1} = (1 - \Delta E_\nu V^{-1})V, \tag{17}$$

where $V = (H^{(XX)} - E_\nu^0[I^{(XX)}])$. Provided ΔE_ν is small we can write this as a series;

$$(1 - \Delta E_\nu V^{-1}) = \sum_q^\infty (\Delta E_\nu V^{-1})^q \tag{18}$$

Substituing back into (12) and approximating to terms in (ΔE^2) we get

$$\sum_k H_{ik}c_{k\nu} + \sum_y H_{iy}\sum_{zkx}(1 + E_\nu V^{-1} + (E_\nu V^{-1})^2)_{yx}V_{xz}H_{zk}c_{k\nu} = \sum_k c_{\nu k}E_\nu \tag{19}$$

The advantage of this is that we need only calculate the inverse of V, which is independent of ΔE, and so need only be calculated once during the determination of $c_{k\nu}$.

The members, $|w\rangle$, of space X are given by applying excitation operators to the wavefunctions $|\nu\rangle$, which form the reference space;

$$|w\rangle = a_s^\dagger a_t^\dagger a_p a_s |I\rangle c_{I\nu} \tag{20}$$

where I is a determinant in the active space, s and t may be virtual or active indexes, whilst p and s may be core or active indexes. It is forbidden for both s and t to be active. Hence the elements of the $[H^{XX}]$ block are given by

$$\sum_{IJ} d_{I\nu}^\dagger \langle I|a_s a_t a_p^\dagger a_s^\dagger \hat{H} a_s^\dagger a_t^\dagger a_p a_s|J\rangle d_{J\nu} = d_{I\nu}^\dagger \langle I|\hat{E}_\Omega^\dagger \hat{H} \hat{E}^\dagger|I\rangle d_{J\nu}. \tag{21}$$

It is notable that this means that the definition of the external space is dependent upon the reference state ν, which is obviously rather bad...