Derivation of Quadratic Response Time Dependent Hartree-Fock (TDHF) Equations

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November 21, 2014

1 Derivation of Equations of Motion through Second Order

Expand the Fock matrix, $\mathbf{F}$ and the density matrix, $\mathbf{P}$, in a perturbative series as a function of arbitrary λ. Let μ and ν be arbitrary perturbation indicies. We use Einstein notation, recognizing that λ_μ is a sum over all possible μ, which includes λ_ν.

$$\mathbf{P} = \mathbf{P}^{(0)} + \lambda_\mu \mathbf{P}^{(1)} + \lambda_\mu \lambda_\nu \mathbf{P}^{(2)} + \cdots$$
$$\mathbf{F} = \mathbf{F}^{(0)} + \lambda_\mu \mathbf{F}^{(1)} + \lambda_\mu \lambda_\nu \mathbf{F}^{(2)} + \cdots$$

In a similar fashion, expand the Fock matrix and the density matrix, as a Taylor series in arbitrary λ.

$$\mathbf{P}(t,\lambda) = \mathbf{P}^{(0)} + \lambda_\mu \frac{\partial \mathbf{P}}{\partial \lambda_\mu}\bigg|_{\lambda=0} + \frac{\lambda_\mu \lambda_\nu}{2} \frac{\mathbf{P}}{\partial^2 \lambda_\mu \partial \lambda_\nu}\bigg|_{\lambda=0} + \cdots$$
$$\mathbf{F}(t,\lambda) = \mathbf{F}^{(0)} + \lambda_\mu \frac{\partial \mathbf{F}}{\partial \lambda_\mu}\bigg|_{\lambda=0} + \frac{\lambda_\mu \lambda_\nu}{2} \frac{\mathbf{F}}{\partial^2 \lambda_\mu \partial \lambda_\nu}\bigg|_{\lambda=0} + \cdots$$

This suggests that the following relations hold (with the factor of 2 absorbing into the expressions λ; upon collecting terms later on it cancels.):

$$\mathbf{P}^{(1)} = \frac{\partial}{\partial \lambda_\mu} \mathbf{P}_\lambda(t)\bigg|_{\lambda=0} \qquad \mathbf{P}^{(2)} = \frac{\partial^2}{\partial \lambda_\mu \lambda_\nu} \mathbf{P}_\lambda(t)\bigg|_{\lambda=0}$$
$$\mathbf{F}^{(1)} = \frac{\partial}{\partial \lambda_\mu} \mathbf{F}_\lambda(t)\bigg|_{\lambda=0} \qquad \mathbf{F}^{(2)} = \frac{\partial^2}{\partial \lambda_\mu \lambda_\nu} \mathbf{F}_\lambda(t)\bigg|_{\lambda=0}$$

Recalling the definition of the Fourier transform:

$$f(t) = \int_{-\infty}^{\infty} f(\omega)\; e^{-i\omega t}\, d\omega$$

And using the postulate that any real observable corresponds to a Hermitian operator (e.g. Fock and Density operators are Hermitian), gives, in the frequency domain:

$$\mathbf{P}^{(1)} = \frac{\partial}{\partial \lambda_\mu} \mathbf{P}_\lambda(t)\bigg|_{\lambda=0} = \mathbf{P}^{(\mu)}(\omega_\mu) e^{-i\omega_\mu t} + \mathbf{P}^{(\mu)}(-\omega_\mu) e^{i\omega_\mu t}$$

$$\mathbf{F}^{(1)} = \frac{\partial}{\partial\lambda_\mu}\mathbf{F}_\lambda(t)\Big|_{\lambda=0} = \mathbf{F}^{(\mu)}(\omega_\mu)e^{-i\omega_\mu t} + \mathbf{F}^{(\mu)}(-\omega_\mu)e^{i\omega_\mu t}$$

$$\begin{aligned}\mathbf{P}^{(2)} = \frac{\partial^2}{\partial\lambda_\mu\lambda_\nu}\mathbf{P}_\lambda(t)\Big|_{\lambda=0} &= \mathbf{P}^{\mu\nu}(\omega_\mu,\omega_\nu)e^{-i(\omega_\mu+\omega_\nu)t}\\ &+ \mathbf{P}^{\mu\nu}(\omega_\mu,-\omega_\nu)e^{-i(\omega_\mu-\omega_\nu)t}\\ &+ \mathbf{P}^{\mu\nu}(-\omega_\mu,\omega_\nu)e^{-i(-\omega_\mu+\omega_\nu)t}\\ &+ \mathbf{P}^{\mu\nu}(-\omega_\mu,-\omega_\nu)e^{i(\omega_\mu+\omega_\nu)t}\end{aligned}$$

$$\begin{aligned}\mathbf{F}^{(2)} = \frac{\partial^2}{\partial\lambda_\mu\lambda_\nu}\mathbf{F}_\lambda(t)\Big|_{\lambda=0} &= \mathbf{F}^{\mu\nu}(\omega_\mu,\omega_\nu)e^{-i(\omega_\mu+\omega_\nu)t}\\ &+ \mathbf{F}^{\mu\nu}(\omega_\mu,-\omega_\nu)e^{-i(\omega_\mu-\omega_\nu)t}\\ &+ \mathbf{F}^{\mu\nu}(-\omega_\mu,\omega_\nu)e^{-i(-\omega_\mu+\omega_\nu)t}\\ &+ \mathbf{F}^{\mu\nu}(-\omega_\mu,-\omega_\nu)e^{i(\omega_\mu+\omega_\nu)t}\end{aligned}$$

The von-Neumann type equation of motion is:

$$i\frac{\partial}{\partial t}\mathbf{P}(t) = [\mathbf{F}(t), \mathbf{P}(t)] \tag{1}$$

Plugging in above expressions for left hand side:

$$\begin{aligned}i\frac{\partial}{\partial t}\mathbf{P}(t) = i\frac{\partial}{\partial t}\mathbf{P}^{(0)}&\\ &+ \frac{\partial}{\partial t}\lambda_\mu\mathbf{P}^{(\mu)}(\omega_\mu)e^{-i\omega_\mu t} + \frac{\partial}{\partial t}\lambda_\mu\mathbf{P}^{(\mu)}(-\omega_\mu)e^{i\omega_\mu t}\\ &+ \frac{\partial}{\partial t}\lambda_\mu\lambda_\nu\mathbf{P}^{\mu\nu}(\omega_\mu,\omega_\nu)e^{-i(\omega_\mu+\omega_\nu)t}\\ &+ \frac{\partial}{\partial t}\lambda_\mu\lambda_\nu\mathbf{P}^{\mu\nu}(\omega_\mu,-\omega_\nu)e^{-i(\omega_\mu-\omega_\nu)t}\\ &+ \frac{\partial}{\partial t}\lambda_\mu\lambda_\nu\mathbf{P}^{\mu\nu}(-\omega_\mu,\omega_\nu)e^{-i(-\omega_\mu+\omega_\nu)t}\\ &+ \frac{\partial}{\partial t}\lambda_\mu\lambda_\nu\mathbf{P}^{\mu\nu}(-\omega_\mu,-\omega_\nu)e^{i(\omega_\mu+\omega_\nu)t}\end{aligned}$$

Which is to say that

$$\begin{aligned}i\frac{\partial}{\partial t}\mathbf{P}(t) = \lambda_\mu\omega_\mu&\left(\mathbf{P}^{(\mu)}(\omega_\mu)e^{-i\omega_\mu t} - \mathbf{P}^{(\mu)}(-\omega_\mu)e^{i\omega_\mu t}\right)\\ &+ \lambda_\mu\lambda_\nu[(\omega_\mu+\omega_\nu)\mathbf{P}^{\mu\nu}e^{-i(\omega_\mu+\omega_\nu)t}\\ &+ (\omega_\mu-\omega_\nu)\mathbf{P}^{\mu\nu}e^{-i(\omega_\mu-\omega_\nu)t}\\ &+ (-\omega_\mu+\omega_\nu)\mathbf{P}^{\mu\nu}e^{-i(-\omega_\mu+\omega_\nu)t}\\ &- (\omega_\mu+\omega_\nu)\mathbf{P}^{\mu\nu}e^{i(\omega_\mu+\omega_\nu)t}\end{aligned}$$

Solving for the right hand side:

$$
\begin{aligned}
[\mathbf{F}(t), \mathbf{P}(t)] = [\mathbf{F}^{(0)}, \mathbf{P}^{(0)}] \\
&+ \lambda_\mu [\mathbf{F}^{(0)}, \mathbf{P}^{(\mu)}] + \lambda_\mu [\mathbf{F}^{(\mu)}, \mathbf{P}^{(0)}] \\
&+ \lambda_\mu \lambda_\nu [\mathbf{F}^{(0)}, \mathbf{P}^{(\mu\nu)}] + \lambda_\mu \lambda_\nu [\mathbf{F}^{(\mu\nu)}, \mathbf{P}^{(0)}] \\
&+ \lambda_\mu \lambda_\nu [\mathbf{F}^{(\mu)}, \mathbf{P}^{(\nu)}] + \lambda_\mu \lambda_\nu [\mathbf{F}^{(\nu)}, \mathbf{P}^{(\mu)}]
\end{aligned}
$$

Therefore, to second order

$$
\begin{aligned}
[\mathbf{F}(t), \mathbf{P}(t)] = [\mathbf{F}^{(0)}, \mathbf{P}^{(0)}] \\
&+ \lambda_\mu \left\{ [\mathbf{F}^{(0)}, \mathbf{P}^{(\mu)}] + [\mathbf{F}^{(\mu)}, \mathbf{P}^{(0)}] \right\} \\
&+ \lambda_\mu \lambda_\nu \left\{ [\mathbf{F}^{(0)}, \mathbf{P}^{(\mu\nu)}] + [\mathbf{F}^{(\mu\nu)}, \mathbf{P}^{(0)}] + [\mathbf{F}^{(\mu)}, \mathbf{P}^{(\nu)}] + [\mathbf{F}^{(\nu)}, \mathbf{P}^{(\mu)}] \right\}
\end{aligned}
$$

Expanding the expression in terms of the frequency dependent response yields

$$
\begin{aligned}
[\mathbf{F}(t), \mathbf{P}(t)] = [\mathbf{F}^{(0)}, \mathbf{P}^{(0)}] \\
&+ \lambda_\mu [\mathbf{F}^{(0)}, \mathbf{P}^{(\mu)}(\omega_\mu) e^{-i\omega_\mu t} + \mathbf{P}^{(\mu)}(-\omega_\mu) e^{i\omega_\mu t}] \\
&+ \lambda_\mu [\mathbf{F}^{(\mu)}(\omega_\mu) e^{-i\omega_\mu t} + \mathbf{F}^{(\mu)}(-\omega_\mu) e^{i\omega_\mu t}, \mathbf{P}^{(0)}] \\
&+ \lambda_\mu \lambda_\nu [\mathbf{F}^{(0)}, \mathbf{P}^{(\mu\nu)}(\omega_\mu, \omega_\nu)] e^{-i(\omega_\mu + \omega_\nu)t} \\
&+ \lambda_\mu \lambda_\nu [\mathbf{F}^{(0)}, \mathbf{P}^{(\mu\nu)}(\omega_\mu, -\omega_\nu)] e^{-i(\omega_\mu - \omega_\nu)t} \\
&+ \lambda_\mu \lambda_\nu [\mathbf{F}^{(0)}, \mathbf{P}^{(\mu\nu)}(-\omega_\mu, \omega_\nu)] e^{-i(-\omega_\mu + \omega_\nu)t} \\
&+ \lambda_\mu \lambda_\nu [\mathbf{F}^{(0)}, \mathbf{P}^{(\mu\nu)}(-\omega_\mu, -\omega_\nu)] e^{i(\omega_\mu + \omega_\nu)t} \\
&+ \lambda_\mu \lambda_\nu [\mathbf{F}^{(\mu\nu)}(\omega_\mu, \omega_\nu), \mathbf{P}^{(0)}] e^{-i(\omega_\mu + \omega_\nu)t} \\
&+ \lambda_\mu \lambda_\nu [\mathbf{F}^{(\mu\nu)}(\omega_\mu, -\omega_\nu), \mathbf{P}^{(0)}] e^{-i(\omega_\mu - \omega_\nu)t} \\
&+ \lambda_\mu \lambda_\nu [\mathbf{F}^{(\mu\nu)}(-\omega_\mu, \omega_\nu), \mathbf{P}^{(0)}] e^{-i(-\omega_\mu + \omega_\nu)t} \\
&+ \lambda_\mu \lambda_\nu [\mathbf{F}^{(\mu\nu)}(-\omega_\mu, -\omega_\nu), \mathbf{P}^{(0)}] e^{i(\omega_\mu + \omega_\nu)t} \\
&+ \lambda_\mu \lambda_\nu [\mathbf{F}^{(\mu)}(\omega_\mu), \mathbf{P}^{(\nu)}(\omega_\nu)] e^{-i(\omega_\mu + \omega_\nu)t} \\
&+ \lambda_\mu \lambda_\nu [\mathbf{F}^{(\nu)}(\omega_\nu), \mathbf{P}^{(\mu)}(\omega_\mu)] e^{-i(\omega_\mu + \omega_\nu)t} \\
&+ \lambda_\mu \lambda_\nu [\mathbf{F}^{(\mu)}(\omega_\mu), \mathbf{P}^{(\nu)}(-\omega_\nu)] e^{-i(\omega_\mu - \omega_\nu)t} \\
&+ \lambda_\mu \lambda_\nu [\mathbf{F}^{(\nu)}(-\omega_\nu), \mathbf{P}^{(\mu)}(\omega_\mu)] e^{-i(\omega_\mu - \omega_\nu)t} \\
&+ \lambda_\mu \lambda_\nu [\mathbf{F}^{(\mu)}(-\omega_\mu), \mathbf{P}^{(\nu)}(\omega_\nu)] e^{-i(-\omega_\mu + \omega_\nu)t} \\
&+ \lambda_\mu \lambda_\nu [\mathbf{F}^{(\nu)}(\omega_\nu), \mathbf{P}^{(\mu)}(-\omega_\mu)] e^{-i(-\omega_\mu + \omega_\nu)t} \\
&+ \lambda_\mu \lambda_\nu [\mathbf{F}^{(\mu)}(-\omega_\mu), \mathbf{P}^{(\nu)}(-\omega_\nu)] e^{i(\omega_\mu + \omega_\nu)t} \\
&+ \lambda_\mu \lambda_\nu [\mathbf{F}^{(\nu)}(-\omega_\nu), \mathbf{P}^{(\mu)}(-\omega_\mu)] e^{i(\omega_\mu + \omega_\nu)t}
\end{aligned}
$$

Setting the left and right hand sides equal, we can collect terms with like λ. After the perturbative orders have been collected, we further collect based off of the exponential terms. Justification for collection based off of the exponential factors can be illustrated by considering the first order terms:

$$
\begin{aligned}
\omega_\mu \left(\mathbf{P}^{(\mu)}(\omega_\mu) e^{-i\omega_\mu t} - \mathbf{P}^{(\mu)}(-\omega_\mu) e^{i\omega_\mu t} \right) = [\mathbf{F}^{(0)}, \mathbf{P}^{(\mu)}(\omega_\mu) e^{-i\omega_\mu t} + \mathbf{P}^{(\mu)}(-\omega_\mu) e^{i\omega_\mu t}] \\
&+ [\mathbf{F}^{(\mu)}(\omega_\mu) e^{-i\omega_\mu t} + \mathbf{F}^{(\mu)}(-\omega_\mu) e^{i\omega_\mu t}, \mathbf{P}^{(0)}]
\end{aligned}
$$

Multiplying the above expression by $e^{i\omega_\mu t}$ yields

$$\omega_\mu \left(\mathbf{P}^{(\mu)}(\omega_\mu) - \mathbf{P}^{(\mu)}(-\omega_\mu)e^{2i\omega_\mu t} \right) = [\mathbf{F}^{(0)}, \mathbf{P}^{(\mu)}(\omega_\mu) + \mathbf{P}^{(\mu)}(-\omega_\mu)e^{2i\omega_\mu t}] + [\mathbf{F}^{(\mu)}(\omega_\mu) + \mathbf{F}^{(\mu)}(-\omega_\mu)e^{2i\omega_\mu t}, \mathbf{P}^{(0)}]$$

Which is true if and only if the time dependent terms are independent of the time independent terms. Thus the equation is separable into two first order response equations:

$$\omega_\mu \mathbf{P}^{(\mu)}(\omega_\mu) = [\mathbf{F}^{(0)}, \mathbf{P}^{(\mu)}(\omega_\mu)] + [\mathbf{F}^{(\mu)}(\omega_\mu), \mathbf{P}^{(0)}]$$

Plus the complex conjugate. The same procedure of collecting terms based off of exponential is valid for any number of exponential terms. Thus collecting the second order terms yields, in summary:

$$0 = [\mathbf{F}^{(0)}, \mathbf{P}^{(0)}] \tag{2}$$

$$\omega_\mu \mathbf{P}^{(\mu)} = [\mathbf{F}^{(0)}, \mathbf{P}^{(\mu)}] + [\mathbf{F}^{(\mu)}, \mathbf{P}^{(0)}] \tag{3}$$

$$(\omega_\mu + \omega_\nu)\mathbf{P}^{(\mu\nu)} = [\mathbf{F}^{(0)}, \mathbf{P}^{(\mu\nu)}] + [\mathbf{F}^{(\mu)}, \mathbf{P}^{(\nu)}] + [\mathbf{F}^{(\nu)}, \mathbf{P}^{(\mu)}] + [\mathbf{F}^{(\mu\nu)}, \mathbf{P}^{(0)}] \tag{4}$$

Plus their complex conjugates. Frequency arguments have been dropped for clarity. These are the equations of motion up to second order.

2 Derivation of second order response working equations

Assuming a converged solution to the Hartree-Fock equations in the canonical molecular orbital basis, $\mathbf{P}^{(0)}$ and $\mathbf{F}^{(0)}$ are the density and Fock/Kohn-Sham matrices. The density matrix is given as

$$\mathbf{P}^{(0)} = \left[\begin{array}{c|c} \mathbf{I} & \mathbf{0} \\ \hline \mathbf{0} & \mathbf{0} \end{array}\right] \tag{5}$$

$$\mathbf{F}^{(0)} = \left[\begin{array}{c|c} \mathbf{\Sigma}_{\mathrm{O}} & \mathbf{0} \\ \hline \mathbf{0} & \mathbf{\Sigma}_{\mathrm{V}} \end{array}\right] \tag{6}$$

with $\mathbf{I}$ equal to the identity matrix of dimension number of occupied orbitals, and $\mathbf{\Sigma}_O$ and $\mathbf{\Sigma}_V$ are the diagonal matrices containing occupied orbital and virtual orbital eigenvalues, respectively. The total dimension of each matrix is (number occupied + number virtual). The first order idempotency constraint

$$\mathbf{P}^{(\mu)} = \mathbf{P}^{(0)}\mathbf{P}^{(\mu)} + \mathbf{P}^{(\mu)}\mathbf{P}^{(0)} \tag{7}$$

Results in

$$\mathbf{P}^{(\mu)} = \left[\begin{array}{c|c} \mathbf{I} & \mathbf{0} \\ \hline \mathbf{0} & \mathbf{0} \end{array}\right] \left[\begin{array}{c|c} \mathbf{P}^{(\mu)}_{\mathrm{OO}} & \mathbf{P}^{(\mu)}_{\mathrm{OV}} \\ \hline \mathbf{P}^{(\mu)}_{\mathrm{VO}} & \mathbf{P}^{(\mu)}_{\mathrm{VV}} \end{array}\right] - \left[\begin{array}{c|c} \mathbf{P}^{(\mu)}_{\mathrm{OO}} & \mathbf{P}^{(\mu)}_{\mathrm{OV}} \\ \hline \mathbf{P}^{(\mu)}_{\mathrm{VO}} & \mathbf{P}^{(\mu)}_{\mathrm{VV}} \end{array}\right] \left[\begin{array}{c|c} \mathbf{I} & \mathbf{0} \\ \hline \mathbf{0} & \mathbf{0} \end{array}\right] = \left[\begin{array}{c|c} \mathbf{0} & \mathbf{P}^{(\mu)}_{\mathrm{OV}} \\ \hline \mathbf{P}^{(\mu)}_{\mathrm{VO}} & \mathbf{0} \end{array}\right] \tag{8}$$

The second-order density matrix idempotency constraint is

$$\mathbf{P}^{(\mu\nu)} = \mathbf{P}^{(0)}\mathbf{P}^{(\mu\nu)} + \mathbf{P}^{(\mu\nu)}\mathbf{P}^{(0)} + \mathbf{P}^{(\mu)}\mathbf{P}^{(\nu)} + \mathbf{P}^{(\nu)}\mathbf{P}^{(\mu)} \tag{9}$$

Which gives

$$
\begin{aligned}
\mathbf{P}^{(\mu)} = \left[\begin{array}{c|c} \mathbf{P}^{(\mu\nu)}_{\mathrm{OO}} & \mathbf{P}^{(\mu\nu)}_{\mathrm{OV}} \\ \hline \mathbf{P}^{(\mu\nu)}_{\mathrm{VO}} & \mathbf{P}^{(\mu\nu)}_{\mathrm{VV}} \end{array}\right] &= \left[\begin{array}{c|c} \mathbf{I} & \mathbf{0} \\ \hline \mathbf{0} & \mathbf{0} \end{array}\right] \left[\begin{array}{c|c} \mathbf{P}^{(\mu\nu)}_{\mathrm{OO}} & \mathbf{P}^{(\mu\nu)}_{\mathrm{OV}} \\ \hline \mathbf{P}^{(\mu\nu)}_{\mathrm{VO}} & \mathbf{P}^{(\mu\nu)}_{\mathrm{VV}} \end{array}\right] + \left[\begin{array}{c|c} \mathbf{P}^{(\mu\nu)}_{\mathrm{OO}} & \mathbf{P}^{(\mu\nu)}_{\mathrm{OV}} \\ \hline \mathbf{P}^{(\mu\nu)}_{\mathrm{VO}} & \mathbf{P}^{(\mu\nu)}_{\mathrm{VV}} \end{array}\right] \left[\begin{array}{c|c} \mathbf{I} & \mathbf{0} \\ \hline \mathbf{0} & \mathbf{0} \end{array}\right] \\
&\quad + \left[\begin{array}{c|c} \mathbf{0} & \mathbf{P}^{(\mu)}_{\mathrm{OV}} \\ \hline \mathbf{P}^{(\mu)}_{\mathrm{VO}} & \mathbf{0} \end{array}\right] \left[\begin{array}{c|c} \mathbf{0} & \mathbf{P}^{(\nu)}_{\mathrm{OV}} \\ \hline \mathbf{P}^{(\nu)}_{\mathrm{VO}} & \mathbf{0} \end{array}\right] + \left[\begin{array}{c|c} \mathbf{0} & \mathbf{P}^{(\nu)}_{\mathrm{OV}} \\ \hline \mathbf{P}^{(\nu)}_{\mathrm{VO}} & \mathbf{0} \end{array}\right] \left[\begin{array}{c|c} \mathbf{0} & \mathbf{P}^{(\mu)}_{\mathrm{OV}} \\ \hline \mathbf{P}^{(\mu)}_{\mathrm{VO}} & \mathbf{0} \end{array}\right] \qquad (10) \\
&= \left[\begin{array}{c|c} \mathbf{P}^{(\mu\nu)}_{\mathrm{OO}} & \mathbf{P}^{(\mu\nu)}_{\mathrm{OV}} \\ \hline \mathbf{0} & \mathbf{0} \end{array}\right] + \left[\begin{array}{c|c} \mathbf{P}^{(\mu\nu)}_{\mathrm{OO}} & \mathbf{0} \\ \hline \mathbf{P}^{(\mu\nu)}_{\mathrm{VO}} & \mathbf{0} \end{array}\right] \\
&\quad + \left[\begin{array}{c|c} \mathbf{P}^{(\mu)}_{\mathrm{OV}}\mathbf{P}^{(\nu)}_{\mathrm{VO}} & \mathbf{0} \\ \hline \mathbf{0} & \mathbf{P}^{(\mu)}_{\mathrm{VO}}\mathbf{P}^{(\nu)}_{\mathrm{OV}} \end{array}\right] + \left[\begin{array}{c|c} \mathbf{P}^{(\nu)}_{\mathrm{OV}}\mathbf{P}^{(\mu)}_{\mathrm{VO}} & \mathbf{0} \\ \hline \mathbf{0} & \mathbf{P}^{(\nu)}_{\mathrm{VO}}\mathbf{P}^{(\mu)}_{\mathrm{OV}} \end{array}\right] \qquad (11)
\end{aligned}
$$

This implies the following relation

$$\mathbf{P}^{(\mu\nu)}_{\mathrm{OO}} = -(\mathbf{P}^{(\mu)}_{\mathrm{OV}}\mathbf{P}^{(\nu)}_{\mathrm{VO}} + \mathbf{P}^{(\mu)}_{\mathrm{OV}}\mathbf{P}^{(\nu)}_{\mathrm{VO}}) \tag{12}$$

and

$$\mathbf{P}^{(\mu\nu)}_{\mathrm{VV}} = \mathbf{P}^{(\mu)}_{\mathrm{VO}}\mathbf{P}^{(\nu)}_{\mathrm{OV}} + \mathbf{P}^{(\mu)}_{\mathrm{VO}}\mathbf{P}^{(\nu)}_{\mathrm{OV}} \tag{13}$$

which is to say that the occupied-occupied and virtual-virtual blocks of the second-order density matrix can be completely specified from the solutions to the first-order density matrix. We will make use of this fact when formulating the final second-order response working equations.

The final working equations are specified using the second order equation of motion eq. (4):

$$(\omega_\mu + \omega_\nu)\mathbf{P}^{(\mu\nu)} = [\mathbf{F}^{(0)}, \mathbf{P}^{(\mu\nu)}] + [\mathbf{F}^{(\mu)}, \mathbf{P}^{(\nu)}] + [\mathbf{F}^{(\nu)}, \mathbf{P}^{(\mu)}] + [\mathbf{F}^{(\mu\nu)}, \mathbf{P}^{(0)}]$$

The second-order Fock/KS matrix $\mathbf{F}^{(\mu\nu)}$ is given by the expression

$$\mathbf{F}^{(\mu\nu)} = \mathbf{F}^{(1)}\left\{\mathbf{P}^{(\mu\nu)}\right\} + \mathbf{F}^{(2)}\left\{\mathbf{P}^{(\mu)}, \mathbf{P}^{(\nu)}\right\} \tag{14}$$

The first term, $\mathbf{F}^{(1)}\left\{\mathbf{P}^{(\mu\nu)}\right\}$ is the same as the first order change in the Fock/KS matrix, as we dealt with in the linear response derivation:

$$\mathbf{F}^{(1)}\left\{\mathbf{P}^{(\mu\nu)}\right\} = \frac{\partial \mathbf{F}}{\partial \mathbf{P}}\mathbf{P}^{(\mu\nu)} \tag{15}$$

where $\frac{\partial \mathbf{F}}{\partial \mathbf{P}}$ is given, in the TDHF method, as:

$$
\begin{aligned}
\sum_{rs} \frac{\partial F_{pq}}{\partial P_{rs}} &= \sum_{rs} \frac{\partial}{\partial P_{rs}} \left(H^{core}_{pq} + P_{rs}[(pq|sr) - (pr|sq)]\right) \\
&= (pq|sr) - (pr|sq) = (pq||sr) \qquad (16)
\end{aligned}
$$

or for TDKS,

$$\frac{\partial F_{pq}}{\partial P_{rs}} = (pq|sr) + (pq|f_{xc}|sr) \tag{17}$$

with f_{xc}, called the exchange kernel, defined as:

$$f_{xc}(\mathbf{r}_1, \mathbf{r}_2) = \frac{\partial^2 E_{(xc)}[\rho]}{\partial\rho(\mathbf{r}_1)\partial\rho(\mathbf{r}_2)} \tag{18}$$

where $E_{xc}[\rho]$ is the adiabatic exchange-correlation energy functional. From this, it is clear that $\mathbf{F}^{(1)}\{\mathbf{P}\}$ depends linearly on $\mathbf{P}$, such that $\mathbf{F}^{(1)}\left\{\mathbf{P}^{(\mu)} + \mathbf{P}^{(\nu)}\right\} = \mathbf{F}^{(1)}\left\{\mathbf{P}^{(\mu)}\right\} + \mathbf{F}^{(1)}\left\{\mathbf{P}^{(\nu)}\right\}$.

The second term $\mathbf{F}^{(2)}\left\{\mathbf{P}^{(\mu)},\mathbf{P}^{(\nu)}\right\}$ for the KS matrix depends only on the first-order density matrices, and is given as

$$\left[\mathbf{F}^{(2)}\left\{\mathbf{P}^{(\mu)},\mathbf{P}^{(\nu)}\right\}\right]_{pq} = \int\int\int \phi_p^*(\mathbf{r}_1)\phi_q(\mathbf{r}_1)g_{xc}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)\rho^{(\mu)}(\mathbf{r}_2)\rho^{(\nu)}(\mathbf{r}_3)dr_1dr_2dr_3 \tag{19}$$

with $g_{xc}(\mathbf{r}_1.\mathbf{r}_2,\mathbf{r}_3)$ as the third-order derivative of the adiabatic exchange-correlation functional (compare to f_{xc}), defined as

$$g_{xc}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3) = \frac{\partial^3 E_{(xc)}[\rho]}{\partial\rho(\mathbf{r}_1)\partial\rho(\mathbf{r}_2)\partial\rho(\mathbf{r}_3)} \tag{20}$$

Because $\rho^{(\mu)}$ and $\rho^{(\nu)}$ are the first-order changes in the density matrix, given as

$$\rho^{(\mu)}(\mathbf{r}) = \sum_{ia}\left[P_{ia}^{(\mu)}\phi_i(\mathbf{r})\phi_a^*(\mathbf{r}) + P_{ai}^{(\mu)}\phi_a(\mathbf{r})\phi_i^*(\mathbf{r})\right] \tag{21}$$

substitution of the above yields, for real orbitals

$$\left[\mathbf{F}^{(2)}\left\{\mathbf{P}^{(\mu)},\mathbf{P}^{(\nu)}\right\}\right]_{pq} = \sum_{ia,jb} G_{pq,ia,jb}\left(P_{ai}^{(\mu)} + P_{ia}^{(\mu)}\right)\left(P_{bj}^{(\nu)} + P_{jb}^{(\nu)}\right) \tag{22}$$

with

$$G_{pq,ia,jb} = \int\int\int \phi_p(\mathbf{r}_1)\phi_q(\mathbf{r}_1)\phi_i(\mathbf{r}_2)\phi_a(\mathbf{r}_2)\phi_j(\mathbf{r}_3)\phi_b(\mathbf{r}_3)g_{xc}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)dr_1dr_2dr_3 \tag{23}$$

The important result is that $\mathbf{F}^{(2)}\left\{\mathbf{P}^{(\mu)},\mathbf{P}^{(\nu)}\right\}$ for the KS matrix depends only on the first-order density matrices, which are determined directly from a linear-response TDKS calculation. For TDHF, the result is even simpler: $\mathbf{F}^{(2)}\left\{\mathbf{P}^{(\mu)},\mathbf{P}^{(\nu)}\right\}$ is zero.

Plugging eq. (14) into eq. (4), and rearranging yields

$$(\omega_\mu+\omega_\nu)\mathbf{P}^{(\mu\nu)} - [\mathbf{F}^{(0)},\mathbf{P}^{(\mu\nu)}] = [\mathbf{F}^{(\mu)},\mathbf{P}^{(\nu)}] + [\mathbf{F}^{(\nu)},\mathbf{P}^{(\mu)}] + [\mathbf{F}^{(1)}\left\{\mathbf{P}^{(\mu\nu)}\right\} + \mathbf{F}^{(2)}\left\{\mathbf{P}^{(\mu)},\mathbf{P}^{(\nu)}\right\},\mathbf{P}^{(0)}] \tag{24}$$

Making use of the linearity of $\mathbf{F}^{(1)}\{\mathbf{P}\}$, we substitute the second order density matrix partition, such that

$$\mathbf{F}^{(1)}\{\mathbf{P}^{\mu\nu}\} = \mathbf{F}^{(1)}\left\{\mathbf{P}_{\mathrm{OO}}^{(\mu\nu)} + \mathbf{P}_{\mathrm{VV}}^{(\mu\nu)}\right\} + \mathbf{F}^{(1)}\left\{\mathbf{P}_{\mathrm{OV}}^{(\mu\nu)} + \mathbf{P}_{\mathrm{VO}}^{(\mu\nu)}\right\} \tag{25}$$

Substituting this result into eq. (24), and rearranging gives

$$\begin{aligned}(\omega_\mu+\omega_\nu)\mathbf{P}^{(\mu\nu)} - [\mathbf{F}^{(0)},\mathbf{P}^{(\mu\nu)}] - [\mathbf{F}^{(1)}\left\{\mathbf{P}_{\mathrm{OV}}^{(\mu\nu)} + \mathbf{P}_{\mathrm{VO}}^{(\mu\nu)}\right\},\mathbf{P}^{(0)}] =\\ [\mathbf{F}^{(\mu)},\mathbf{P}^{(\nu)}] + [\mathbf{F}^{(\nu)},\mathbf{P}^{(\mu)}] + [\mathbf{F}^{(2)}\left\{\mathbf{P}^{(\mu)},\mathbf{P}^{(\nu)}\right\},\mathbf{P}^{(0)}] + [\mathbf{F}^{(1)}\left\{\mathbf{P}_{\mathrm{OO}}^{(\mu\nu)} + \mathbf{P}_{\mathrm{VV}}^{(\mu\nu)}\right\},\mathbf{P}^{(0)}]\end{aligned} \tag{26}$$

Because of eqs. (12), (13) and (22), the whole right hand side of the above equation can be directly determined from first-order density matrices (of which are obtained from a linear response calculation). We will call the right hand side $\mathbf{Q}$, so that

$$\mathbf{Q} = [\mathbf{F}^{(\mu)},\mathbf{P}^{(\nu)}] + [\mathbf{F}^{(\nu)},\mathbf{P}^{(\mu)}] + [\mathbf{F}^{(2)}\left\{\mathbf{P}^{(\mu)},\mathbf{P}^{(\nu)}\right\},\mathbf{P}^{(0)}] + [\mathbf{F}^{(1)}\left\{\mathbf{P}_{\mathrm{OO}}^{(\mu\nu)} + \mathbf{P}_{\mathrm{VV}}^{(\mu\nu)}\right\},\mathbf{P}^{(0)}] \tag{27}$$

and

$$(\omega_\mu+\omega_\nu)\mathbf{P}^{(\mu\nu)} - [\mathbf{F}^{(0)},\mathbf{P}^{(\mu\nu)}] - [\mathbf{F}^{(1)}\left\{\mathbf{P}_{\mathrm{OV}}^{(\mu\nu)} + \mathbf{P}_{\mathrm{VO}}^{(\mu\nu)}\right\},\mathbf{P}^{(0)}] = \mathbf{Q} \tag{28}$$

It can be seen that eq. (28) has a similar form to the linear-response working equations, which, upon rearranging, gives:

$$\begin{bmatrix}\mathbf{A} & \mathbf{B}\\ \mathbf{B}^* & \mathbf{A}^*\end{bmatrix}\begin{bmatrix}\mathbf{P}_{\mathrm{VO}}^{(\mu\nu)}\\ (\mathbf{P}_{\mathrm{OV}}^{(\mu\nu)})^\dagger\end{bmatrix} - (\omega_\mu+\omega_\nu)\begin{bmatrix}\mathbf{1} & \mathbf{0}\\ \mathbf{0} & -\mathbf{1}\end{bmatrix}\begin{bmatrix}\mathbf{P}_{\mathrm{VO}}^{(\mu\nu)}\\ (\mathbf{P}_{\mathrm{OV}}^{(\mu\nu)})^\dagger\end{bmatrix} = \begin{bmatrix}-\mathbf{Q}_{\mathrm{VO}}\\ (\mathbf{Q}_{\mathrm{OV}})^\dagger\end{bmatrix} \tag{29}$$

The elements of **A** and **B** are

$$A_{ia,jb} = \delta_{ij}\delta_{ab}(\epsilon_a - \epsilon_i) + (ia||jb) \tag{30}$$

and

$$B_{ia,jb} = (ia||bj) \tag{31}$$

for Hartree-Fock, and

$$A_{ia,jb} = \delta_{ij}\delta_{ab}(\epsilon_a - \epsilon_i) + (ia|jb) + (ia|f_{xc}|jb) \tag{32}$$

and

$$B_{ia,jb} = (ia|bj) + (ia|f_{xc}|bj) \tag{33}$$

for Kohn-Sham. **Q** will not necessarily equal zero, and so unlike the linear response calculations, **Q** must be determined first, and then the equations are solved iteratively.