or in matrix form

$$\mathcal{P}(t \to 0) = -i \sum_{c,v} |cv\rangle\langle cv| = -i \sum_{t} |t\rangle\langle t|\,.$$

The direction of approach of the limit, $t \to 0^+$ versus $t \to -0^+$, is immaterial as both yield the same answer for real valued Green's functions $G_0(\omega)$ due to time reversal symmetry. We then have our desired result: Φ_{xc}^{GW} written in terms of the time-ordered $\varepsilon(\omega)$,

$$\Phi_{xc}^{GW}[G_0] = E_X[\rho_0] - \frac{1}{2}\sum_t \langle t|V|t\rangle + \frac{1}{2}\int_{-\infty}^{\infty} \frac{d\omega}{2\pi i}\, tr\Big\{ \ln \varepsilon(\omega) \Big\}\,. \tag{23}$$

This expression is our main workhorse. In Sections 7 and 9, we evaluate this integral exactly and approximately to generate alternative forms for Φ_{xc}^{GW}.

6. DERIVATIVES OF F AND Φ_{xc}^{GW}

In this section, we provide expressions for the derivatives of the exchange-correlation functional $\Phi_{xc}^{GW}[G_0]$ and the total energy functional $F[G_0, G_0]$ versus the wave functions ψ_n and eigenenergies ϵ_n or equivalently the potential U_0 that determine G_0. The ϵ_n derivatives are used in Section 8 to prove the unboundedness of the energy functional. Separately, these derivative expressions can prove useful to investigators contemplating variational approaches that extremize $F[G_0, G_0]$ which require analytical derivatives.

We begin with variations of the eigenenergies ϵ_n. The derivative of G_0 is

$$\frac{\partial G_0(\omega)}{\partial \epsilon_n} = \frac{|n\rangle\langle n|}{(\omega - \epsilon_n)^2}\,.$$

As per Section 4, the only non-zero contribution to the variation of $F[G_0, G_0]$ when changing ϵ_n comes from the exchange-correlation functional Φ_{xc}^{GW} so

$$\frac{\partial F[G_0, G_0]}{\partial \epsilon_n} = \frac{\partial \Phi_{xc}^{GW}[G_0]}{\partial \epsilon_n} = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi i} e^{i\omega 0^+} tr\Big\{ \Sigma_{xc}(\omega) \frac{\partial G_0(\omega)}{\partial \epsilon_n} \Big\}\,.$$

We turn this into a contour integral over the upper complex ω half plane. Using Eq. (12), we get contributions from the poles of $\Sigma_{xc}(\omega)$ that are above the real axis and a possible contribution from the pole of $\partial G_0/\partial \epsilon_n$ if n is occupied (if $\epsilon_n < \mu$).

To organize the process, we write $\Sigma_{xc}(\omega)$ in the general form of a sum over poles

$$\Sigma_{xc}(\omega) = \Sigma_x + \sum_\alpha \frac{\sigma_\alpha^+}{\omega - \xi_\alpha^+} + \sum_\beta \frac{\sigma_\beta^-}{\omega - \xi_\alpha^-}\,. \tag{24}$$

Here, Σ_x is the Fock (bare) exchange operator

$$\Sigma_x(x, x') = -\sum_v \psi_v(x)\psi_v(x')^* V(x, x')$$