Supplemental Material: Ensemble Time-Dependent Density Functional Theory

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S1. RELATION BETWEEN COUPLING-CONSTANT DEPENDENCE AND SCALING

We derive the relation for the density matrix in general TDDFT, and specialize to XC quantities. We start from a fully general time dependent density matrix, $\langle \mathbf{R}|\hat{\Gamma}(t)|\mathbf{R}'\rangle = \Gamma(\mathbf{R},\mathbf{R}',t)$ with $\mathbf{R} = (\mathbf{r},\mathbf{r}_2,\ldots,\mathbf{r}_n)$, which satisfies a Von-Neumann-type equation of motion as

$$i\frac{\partial}{\partial t}\hat{\Gamma}(t) = \left[\hat{H}(t),\hat{\Gamma}(t)\right], \tag{S1}$$

with $\hat{H}(t)$ being the time dependent Hamiltonian

$$\hat{H}(t) = \hat{T} + \hat{V}_{\text{ee}} + \hat{V}(t), \tag{S2}$$

with kinetic energy $\hat{T}$, Coulomb interaction $\hat{V}_{\text{ee}}$ and time-dependent one-body potential $\hat{V}(t)$. In the Runge-Gross framework generalized to ensemble density matrices [1, 2], the time-dependent ensemble density matrix is both a functional of the initial density matrix $\hat{\Gamma}(0)$ as well as time-dependent density, $n_t = n(\mathbf{r},t)$, which can be written as $\Gamma[n_t,\hat{\Gamma}(0)]$. We define the uniformly coordinate scaled $\Gamma(\mathbf{R},\mathbf{R}',t)$ as,

$$\Gamma_\gamma(\mathbf{R},\mathbf{R}',t) = \gamma^{3N}\Gamma(\gamma\mathbf{R},\gamma\mathbf{R}',\gamma^2 t) \quad \text{with} \;\; 0<\gamma<\infty. \tag{S3}$$

Writing Eq. (S1) explicitly in coordinate space:

$$i\frac{\partial\Gamma(\mathbf{R},\mathbf{R}',t)}{\partial t} = \left(\hat{H}(\mathbf{R},t) - \hat{H}(\mathbf{R}',t)\right)\Gamma(\mathbf{R},\mathbf{R}',t), \tag{S4}$$

with Hamiltonian $\hat{H}(\mathbf{R},t) = \hat{T}(\mathbf{R}) + \hat{V}(\mathbf{R},t) + \hat{V}_{\text{ee}}(\mathbf{R})$ and corresponding coordinate basis representations

$$\hat{T}(\mathbf{R}) = -\frac{1}{2}\sum_i \nabla^2_{\mathbf{r}_i}, \quad \hat{V}_{\text{ee}}(\mathbf{R}) = \sum_{i>j}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}, \quad \hat{V}(\mathbf{R},t) = \sum_i v(\mathbf{r}_i,t). \tag{S5}$$

Replacing $\mathbf{R}$ by $\gamma\mathbf{R}$, $\mathbf{R}'$ by $\gamma\mathbf{R}'$ and t by $\gamma^2 t$ and multiplying through by γ^2 yields

$$i\frac{\partial\Gamma_\gamma(\mathbf{R},\mathbf{R}',t)}{\partial t} = \left[\left(\hat{T}(\mathbf{R}) - \hat{T}(\mathbf{R}')\right) + \gamma^2\left(\hat{V}(\gamma\mathbf{R},\gamma^2 t) - \hat{V}(\gamma\mathbf{R},\gamma^2 t)\right) + \gamma\left(\hat{V}_{\text{ee}}(\mathbf{R}) - \hat{V}_{\text{ee}}(\mathbf{R}')\right)\right]\Gamma_\gamma(\mathbf{R},\mathbf{R}',t). \tag{S6}$$

Defining $V_\gamma(\mathbf{R},t) = \gamma^2 V(\gamma\mathbf{R},\gamma^2 t)$, we rewrite Eq. (S6) as

$$i\frac{\partial\hat{\Gamma}_\gamma}{\partial t} = \left[\hat{H}^\gamma_{v_\gamma}(t),\hat{\Gamma}_\gamma(t)\right], \tag{S7}$$

where $\hat{H}^{\gamma}_{v_\gamma}(t)$ has scaled interaction $\gamma \hat{V}_{\rm ee}$ and one-body potential $V_\gamma(\mathbf{R}, t)$. Since $\Gamma_\gamma(\mathbf{R}, \mathbf{R}', t)$ has density $n_\gamma(\mathbf{R}, t) = \gamma^3 n(\gamma\mathbf{r}, \gamma^2 t)$ and initial density matrix $\hat{\Gamma}_\gamma(0)$, visual comparison of Eq. (S7) with Eq. (S1) tell us

$$\hat{\Gamma}^{\gamma}[n_{t,\gamma}, \hat{\Gamma}_\gamma(0)] = \hat{\Gamma}_\gamma[n_t, \hat{\Gamma}(0)]. \tag{S8}$$

Thus, replacing γ with λ and swapping functional arguments,

$$\hat{\Gamma}^{\lambda}[n_t, \hat{\Gamma}(0)] = \hat{\Gamma}_\lambda[n_{t,1/\lambda}, \hat{\Gamma}_{1/\lambda}(0)], \tag{S9}$$

and

$$v^{\lambda}[n_t, \hat{\Gamma}(0)](\mathbf{r}, t) = \lambda^2 v[n_{t,1/\lambda}, \hat{\Gamma}_{1/\lambda}(0)](\lambda\mathbf{r}, \lambda^2 t), \tag{S10}$$

where superscript λ denotes scaled interaction while keeping the density fixed, i.e., the usual adiabatic connection [3, 4]. These are the generalizations of the classic relation between coupling constant and coordinate scaling in ground-state DFT [5]. As the KS system has no interaction, its density matrix is independent of λ, and Eq. (S8) yields,

$$\hat{\Gamma}^{\rm S}[n_{t\gamma}, \hat{\Gamma}^{\rm S}_\gamma(0)] = \hat{\Gamma}^{\rm S}_\gamma[n_t, \hat{\Gamma}^{\rm S}(0)] \tag{S11}$$

and

$$v_{\rm S}[n_{t\gamma}, \hat{\Gamma}^{\rm S}_\gamma(0)](\mathbf{r}, t) = \gamma^2 v_{\rm S}[n_t, \hat{\Gamma}^{\rm S}(0)](\mathbf{r}, t). \tag{S12}$$

As the HXC potential is the difference between the KS and physical potentials, we find

$$v^{\lambda}_{\rm HXC}[n_t, \hat{\Gamma}(0), \hat{\Gamma}^{\rm S}(0)](\mathbf{r}, t) = \lambda^2 v_{\rm HXC}[n_{t,1/\lambda}, \hat{\Gamma}_{1/\lambda}(0), \hat{\Gamma}^{\rm S}_{1/\lambda}(0)](\lambda\mathbf{r}, \lambda^2 t), \tag{S13}$$

and for the eHXC kernel

$$f^{\lambda}_{\rm HXC,\mathbf{w}}[n_t, \hat{\Gamma}(0), \hat{\Gamma}^{\rm S}(0)](\mathbf{r}, t, \mathbf{r}', t') = \left.\frac{\delta v^{\lambda}_{\rm HXC}[n](\mathbf{r}, t)}{\delta n(\mathbf{r}', t)}\right|_{n=n_0} = \lambda^2 f_{\rm HXC}[n_{t,1/\lambda}, \hat{\Gamma}_{1/\lambda}(0), \hat{\Gamma}^{\rm S}_{1/\lambda}(0)](\lambda\mathbf{r}, \lambda^2 t, \lambda\mathbf{r}', \lambda^2 t'), \tag{S14}$$

which is completely general and holds for any initial density matrix.

In the very very special case in which the initial density matrix (see Eq. (2)) is the sum of the eigenstates of the initial Hamiltonian with normalized, non-negative and non-increasing weights, GOK [6–8] tells us the initial density matrix is a functional of the initial density ($\hat{\Gamma}_{\mathbf{w}}[n_t](0)$), so that the eHXC potential becomes a pure w-dependent density functional,

$$v_{\rm HXC,\mathbf{w}}[n_t](\mathbf{r}, t) = v_{\rm HXC,\mathbf{w}}[n_t, \hat{\Gamma}[n_t](0), \hat{\Gamma}^{\rm S}[n_t](0)]](\mathbf{r}, t). \tag{S15}$$

This simplifies Eq. (S13) to

$$v^{\lambda}_{\rm HXC,\mathbf{w}}[n_t](\mathbf{r}, t) = \lambda^2 v_{\rm HXC,\mathbf{w}}[n_{t,1/\lambda}](\lambda\mathbf{r}, \lambda^2 t), \tag{S16}$$

and for the eHXC kernel as,

$$f^{\lambda}_{\rm HXC,\mathbf{w}}[n_t](\mathbf{r}, t, \mathbf{r}', t') = \left.\frac{\delta v^{\lambda}_{\rm HXC,\mathbf{w}}[n](\mathbf{r}, t)}{\delta n(\mathbf{r}', t')}\right|_{n=n_0} = \lambda^2 f_{\rm HXC,\mathbf{w}}[n_{t,1/\lambda}](\lambda\mathbf{r}, \lambda^2 t, \lambda\mathbf{r}', \lambda^2 t'), \tag{S17}$$

which gives Eq. (15).

S2. DEFINITIONS OF HUBBARD MODEL QUANTITIES

Most of the derivations were based on the original derivation of Ref. [9], but some errors were fixed and the ensemble DFT versions were derived. The Hubbard Hamiltonian of Eq. (17) can be written, for singlet states only, as the following cubic equation [10],

$$-U + (1 + \Delta v^2 - U^2)\epsilon + 2U\epsilon^2 - \epsilon^3 = 0, \tag{S18}$$

with U the on-site potential, t the hopping parameter, Δv the potential difference and ϵ the energy eigenvalue. For exact solutions for the energy and wavefunction, we refer to Refs. [9, 11]. We can define the numerators ($A_{mk} = |\langle m|\,\Delta\hat{n}\,|k\rangle|^2$) of Eq. 19 and Eq. 20 as,

$$\sqrt{A_{ij}} = \frac{2xc_3}{c_i^2 c_j^2} \tag{S19}$$

where $c_3 = c_0c_1c_2$ and c_i is defined in Eq. (S2) from Ref. [11] with $x = \Delta v/2t$. The transition frequencies are given by $\nu_k = \epsilon_k - \epsilon_0$, and $\Delta\nu = \nu_2 - \nu_1 = \epsilon_2 - \epsilon_1$ with ϵ_i being the energy of the ith eigenstate.

For the Kohn-Sham system, we can find the $\chi_s(\nu)$ as,

$$\chi_{\mathrm{S},w}(\nu) = (1-2w)\frac{2\nu_{\mathrm{S}}A_{\mathrm{S},1}}{\nu_+^2 - \nu_{\mathrm{S}}^2} + w\frac{2\Delta\nu_{\mathrm{S}}A_{\mathrm{S},2}}{\nu_+^2 - \Delta\nu_{\mathrm{S}}^2}, \tag{S20}$$

with $v_+ = \nu + i\eta$, $\nu = \omega/2t$, $\nu_{\mathrm{S}} = \Delta\nu_{\mathrm{S}} = 1$ as $\nu_d = 2\nu_s$ and $A_{\mathrm{S},i} = 2$ in the symmetric limit. Due to it being $\chi_{\mathrm{S}}(\nu)$ the transitions to the second excited states are per definition zero. For the derivation, we refer to Ref. [9].

We can use any approximation to the $f_{\mathrm{HXC},w}(\nu)$ to construct an approximate susceptibility:

$$\chi_w^{\mathrm{app}}(\nu) = \frac{1}{\chi_{\mathrm{S},w}(\nu)^{-1} - f_{\mathrm{HXC},w}^{\mathrm{app}}(\nu)} \tag{S21}$$

where we are now tasked to find the poles of $\chi_w^{\mathrm{app}}(\nu)$, which is equivalent to the solving the matrix formulation. However, this $\chi_w^{\mathrm{app}}(\nu)$ can also be inserted in the ACFD theorem in order to get a new set of corrections to the transition frequencies.

To derive the Matrix Formulation, we make use of the fact that at the exact transition frequencies, the inverse of the physical density-density response function is 0, i.e. $\chi_w(\nu_{01,02,12})^{-1} = 0$. This leads to

$$f_{\mathrm{HXC,w}}(\nu) = \chi_{\mathrm{S},w}(\nu)^{-1}, \tag{S22}$$

which can be used to find the Casida equation, with some simple algebra into as Eq. 21, which has solutions at ν_1, ν_2 and $\Delta\nu$.

S3. ENSEMBLE ADIABATIC CONNECTION FLUCTUATION DISSIPATION THEOREM

It was derived in Ref [9] that the correlation energy can be calculated via the ACFD as,

$$E_c^{\mathrm{ACFD}}[n] = -\frac{U}{4\pi}\int_0^1 d\lambda \int_0^\infty d\omega\,\mathrm{Im}\left[\chi_w^\lambda[n](\omega) - \chi_{\mathrm{S},w}[n](\omega)\right]. \tag{S23}$$

We first start with the integration over $d\omega$, which can be done as,

$$-\frac{1}{\pi}\int_0^\infty d\omega\,\mathrm{Im}\left[\chi_w^\lambda[n](\omega) - \chi_{\mathrm{S},w}[n](\omega)\right] = A_{01}(U\lambda) + wA_{12}(U\lambda) - A_{\mathrm{S},1} - wA_{\mathrm{S},2}. \tag{S24}$$

With this, we can now perform the integral over λ as

$$E_c = \frac{U}{4}\int_0^1 d\lambda\left(A_{01}(U\lambda) + wA_{12}(U\lambda) - A_{\mathrm{S},1} - wA_{\mathrm{S},2}\right) = 2t\bar{w}\left(1 - \sqrt{1 + \left(\frac{U}{4t}\right)^2}\right), \tag{S25}$$

which is the exact correlation energy that was derived in Ref. [10].

S4. ENSEMBLE ENERGIES

To calculate the transition energies, obtained from approximated correlation energies, we need find exact ensemble equations from all the terms in Eq. (4). These are given in Ref. [10–12] as

$$T_{\mathrm{S},w} = -2t\sqrt{\bar{w} - \Delta n_w^2/4} \tag{S26}$$

$$E_{\mathrm{H}} = U(1 + \Delta n_w^2/4) \tag{S27}$$

$$E_{\mathrm{x},w} = -\frac{U\bar{w}}{2}\left(1 + \frac{\bar{w} + 2w^2}{\bar{w}^3}\frac{\Delta n_w^2}{4}\right) \tag{S28}$$

$$V_w = -\Delta v \Delta n_w/2 = -tx\Delta n_w, \tag{S29}$$

so that one can find the total energy as,

$$E_w = T_{\mathrm{S},w} + E_{\mathrm{H}} + E_{x,w} + E_{c,w}^{\mathrm{app}} - \Delta v \Delta n_w/2, \tag{S30}$$

where $E_{c,w}^{\mathrm{app}}$ is the approximate w dependent correlation energy obtained from the ACFD (Eq. (S23)). The exact $E_{c,w}$ for the Hubbard, up to leading order, has been found as,

$$E_{c,w} = 2t\bar{w}\left(1 - \sqrt{1 + \left(\frac{U}{4t}\right)^2}\right) \tag{S31}$$

by Ref. [10]. The transition energies can then be obtained in two ways, by either

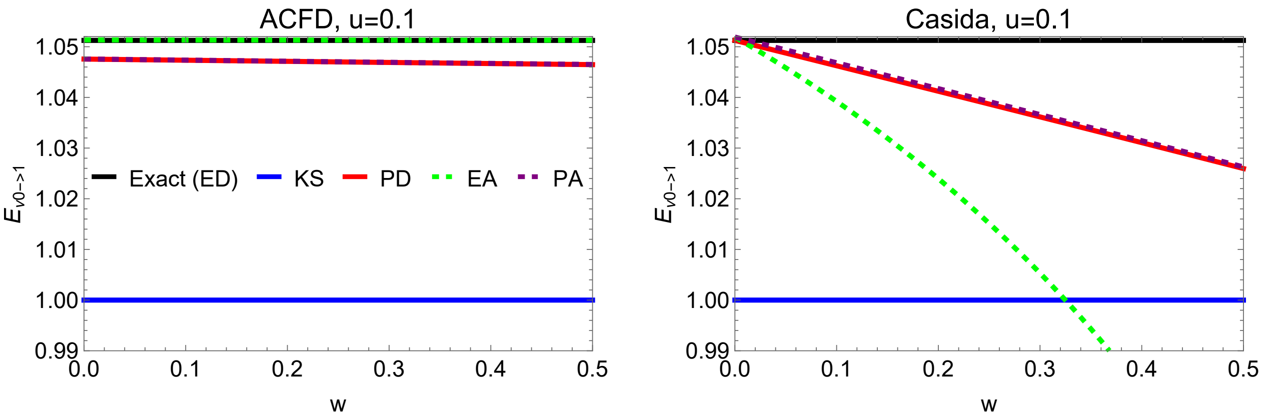
$$\nu_{\mathrm{dif}} = \frac{E_w - E_0}{w} \tag{S32}$$

or

$$\nu_{\mathrm{der}} = \frac{dE_w}{dw}, \tag{S33}$$

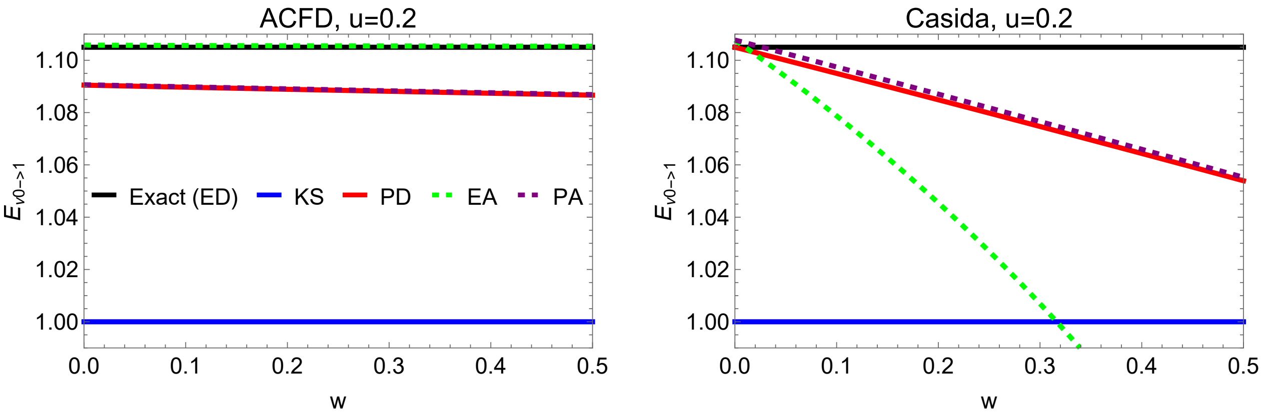
which coincide in the exact case.

S5. EXTRA FIGURES FOR DIFFERENT U



(b) (c)

FIG. S1: The w dependence of the transition frequency of the ground state to first excited state transition for $U = 0.1$ for the exact, KS and 3 approximations (pure dynamic, ensemble adiabatic and pure adiabatic).



(b) (c)

FIG. S2: The w dependence of the transition frequency of the ground state to first excited state transition for $U = 0.2$ for the exact, KS and 3 approximations (pure dynamic, ensemble adiabatic and pure adiabatic).

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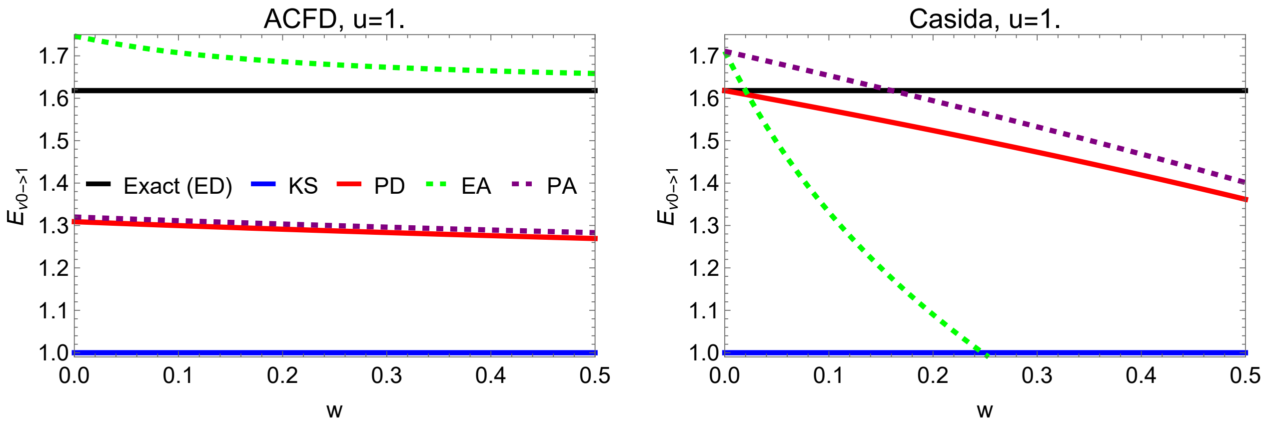
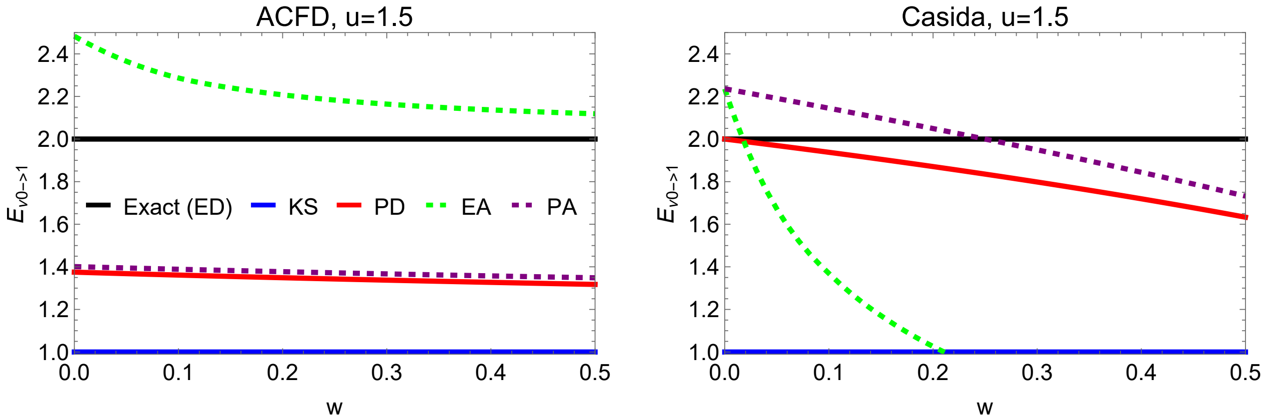


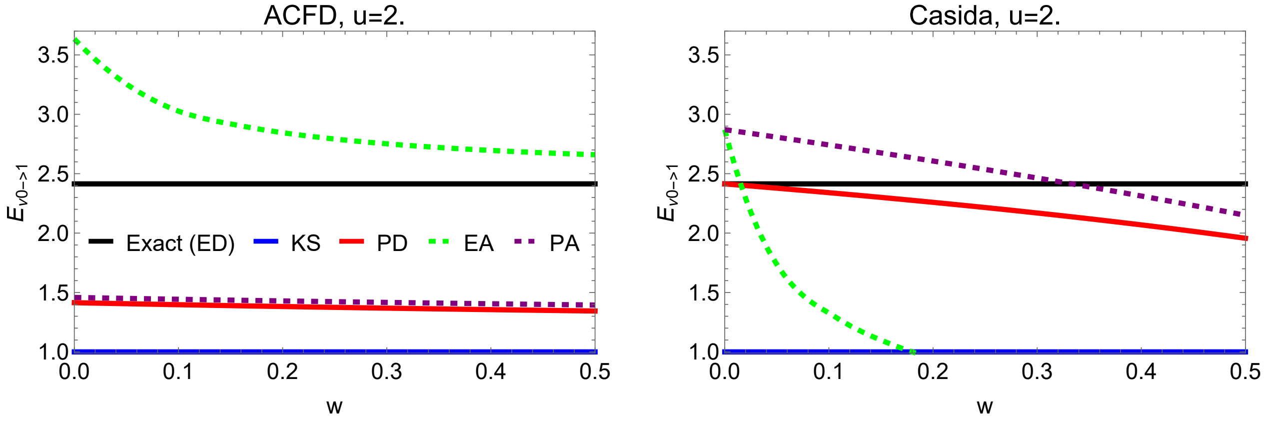
(b) (c)

FIG. S3: The w dependence of the transition frequency of the ground state to first excited state transition for $U = 1$ for the exact, KS and 3 approximations (pure dynamic, ensemble adiabatic and pure adiabatic)..



(b) (c)

FIG. S4: The w dependence of the transition frequency of the ground state to first excited state transition for $U = 1.5$ for the exact, KS and 3 approximations (pure dynamic, ensemble adiabatic and pure adiabatic).



(b) (c)

FIG. S5: The w dependence of the transition frequency of the ground state to first excited state transition for $U = 2$ for the exact, KS and 3 approximations (pure dynamic, ensemble adiabatic and pure adiabatic).

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