Supplementary Material

Inclusion of Nuclear Quantum Effects for Simulations of Nonlinear Spectroscopy

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I. FOURIER RELATIONS OF TWO-TIME CORRELATION FUNCTIONS

A. Standard correlation function

The standard two-time correlation function for Hermitian operators $\hat{A}$, $\hat{B}$ and $\hat{C}$ is given by

$$\langle AB(t)C(t')\rangle = \frac{1}{Z}Tr[e^{-\beta\hat{H}}\hat{A}\hat{B}(t)\hat{C}(t')]. \tag{1}$$

Working in the basis of energy eigenstates of $\hat{H}$ (i.e. $\hat{H}\,|n\rangle = E_n\,|n\rangle$) it follows that

$$\langle AB(t)C(t')\rangle = \frac{1}{Z}\sum_{q,r,s} e^{-\beta E_q} A_{qr}B_{rs}C_{sq}e^{+i\omega_{rs}t}e^{+i\omega_{sq}t'}, \tag{2}$$

where $O_{nm} = \langle n|\,\hat{O}\,|m\rangle$ and $\omega_{nm} = (E_n - E_m)/\hbar$.

The double Fourier transform of the previous expression is given by

$$\langle AB(\omega)C(\omega')\rangle = \frac{1}{Z}\sum_{q,r,s} e^{-\beta E_q} A_{qr}B_{rs}C_{sq}\delta(\omega-\omega_{rs})\delta(\omega'-\omega_{sq}), \tag{3}$$

Enforcing the second delta function in Eq. (3) we have

$$\langle AB(\omega)C(\omega')\rangle = e^{+\beta\hbar\omega'}\frac{1}{Z}\sum_{q,r,s} e^{-\beta E_s} C_{sq}A_{qr}B_{rs}\delta(\omega-\omega_{rs})\delta(\omega'-\omega_{sq}), \tag{4}$$

$$= e^{+\beta\hbar\omega'}\,\langle C(\omega')AB(\omega)\rangle\,. \tag{5}$$

If instead we enforce both delta functions in (3) we get

$$\langle AB(\omega)C(\omega')\rangle = e^{+\beta\hbar(\omega'+\omega)}\frac{1}{Z}\sum_{q,r,s} e^{-\beta E_r} B_{rs}C_{sq}A_{qr}\delta(\omega-\omega_{rs})\delta(\omega'-\omega_{sq}), \tag{6}$$

$$= e^{+\beta\hbar(\omega'+\omega)}\,\langle B(\omega)C(\omega')A\rangle\,. \tag{7}$$

Summarizing, in Fourier space the following relation holds between 'cyclic permutations' of this standard two-time TCF

$$\langle AB(\omega)C(\omega')\rangle = e^{+\beta\hbar\omega'}\,\langle C(\omega')AB(\omega)\rangle \tag{8}$$

$$= e^{+\beta\hbar\bar{\omega}}\,\langle B(\omega)C(\omega')A\rangle\,, \tag{9}$$

where $\bar{\omega} = \omega + \omega'$.

Following a similar procedure for the correlation function $\langle\hat{A}\hat{C}(t')\hat{B}(t)\rangle$, the following relations can be found between cyclic permutations of the TCF:

$$\langle\hat{A}\hat{C}(\omega')\hat{B}(\omega)\rangle = e^{+\beta\hbar\omega}\langle\hat{B}(\omega)\hat{A}\hat{C}(\omega')\rangle \tag{10}$$

$$= e^{+\beta\hbar\bar{\omega}}\langle\hat{C}(\omega')\hat{B}(\omega)\hat{A}\rangle. \tag{11}$$

Note that Eqs. (8-9) and Eq. (10-11) relate all the possible standard two-time TCFs that can be generated from the operators $\hat{A}$, $\hat{B}(t)$ and $\hat{C}(t')$.

B. Double Kubo Transform

Following a similar procedure as before, it is possible to relate the DKT to the standard TCF.[1] In particular, for the DKT defined by

$$\langle A; B(t); C(t')\rangle = \frac{1}{\beta^2}\int_0^\beta d\lambda \int_0^\lambda d\lambda' Tr\left[e^{-(\beta-\lambda)\hat{H}}\hat{A}e^{-(\lambda-\lambda')\hat{H}}\hat{B}(t)e^{-\lambda'\hat{H}}\hat{C}(t')\right], \tag{12}$$

working in the basis of energy eigenstates it follows that

$$\left\langle \hat{A}; \hat{B}(t); \hat{C}(t)\right\rangle = \frac{1}{Z\beta^2}\int_0^\beta d\lambda \int_0^\lambda d\lambda' \sum_{q,r,s} e^{-\beta E_q+\lambda\hbar\omega_{qr}+\lambda'\hbar\omega_{rs}} A_{qr}B_{rs}C_{sq}e^{+i\omega_{rs}t}e^{+i\omega_{sq}t'}. \tag{13}$$

Performing the double Fourier transform and enforcing the delta functions, it follows that

$$\langle A; B(\omega); C(\omega')\rangle = F_1(\omega,\omega')\sum_{q,r,s} e^{-\beta E_q}A_{qr}B_{rs}C_{sq}\delta(\omega-\omega_{rs})\delta(\omega'-\omega_{sq}) \tag{14}$$

$$= F_1(\omega,\omega')\left\langle AB(\omega)C(\omega')\right\rangle, \tag{15}$$

where

$$F_1(\omega,\omega') = \frac{1}{\beta^2}\int_0^\beta \mathrm{d}\lambda \int_0^\lambda \mathrm{d}\lambda'\; e^{-\lambda\hbar(\omega+\omega')}e^{+\lambda'\hbar\omega} \tag{16}$$

$$= \frac{1}{\beta^2\hbar^2}\left(\frac{e^{-\beta\hbar\bar{\omega}}}{\bar{\omega}\omega} - \frac{e^{-\beta\hbar\omega'}}{\omega'\omega} + \frac{1}{\bar{\omega}\omega'}\right). \tag{17}$$

Similarly, for the DKT defined by $\langle B(t); A; C(t')\rangle$ a similar derivation gives the relation

$$\langle B(\omega); A; C(\omega')\rangle = F_2(\omega,\omega')\left\langle B(\omega)AC(\omega')\right\rangle, \tag{18}$$

with

$$F_2(\omega,\omega') = \frac{1}{\beta^2\hbar^2}\left[\frac{e^{\beta\hbar\omega}}{\overline{\omega}\omega} + \frac{e^{-\beta\hbar\omega'}}{\overline{\omega}\omega'} - \frac{1}{\omega\omega'}\right]. \tag{19}$$

II. PROPERTIES OF THE DOUBLE KUBO TRANSFORM

The DKT defined by Eq. (12) presents some interesting symmetries, that can be proved by exploiting the symmetry of the integration limits and cyclic properties of the trace. Here, we summarized them.

A. Stationary

The DKT is stationary with respect to an overall shift of the time origin. In fact, since

$$\left\langle \hat{A}; \hat{B}(t); \hat{C}(t') \right\rangle = \frac{1}{Z\beta^2} \int_0^\beta \mathrm{d}\lambda \int_0^\lambda \mathrm{d}\lambda' \ \left\langle \hat{A}(-i\lambda\hbar)\hat{B}(t - i\lambda'\hbar)\hat{C}(t') \right\rangle \tag{20}$$

and

$$\begin{aligned}
\left\langle \hat{A}(-i\lambda\hbar)\hat{B}(t - i\lambda'\hbar)\hat{C}(t') \right\rangle &= \frac{1}{Z} Tr[e^{-\beta\hat{H}} \hat{A}(-i\lambda\hbar) e^{+\frac{i}{\hbar}\hat{H}t} \hat{B}(-i\lambda'\hbar) e^{-\frac{i}{\hbar}\hat{H}t} \hat{C}(t')] \\
&= \frac{1}{Z} Tr[e^{-\beta\hat{H}} e^{-\frac{i}{\hbar}\hat{H}t} \hat{A}(-i\lambda\hbar) e^{+\frac{i}{\hbar}\hat{H}t} \hat{B}(-i\lambda'\hbar) e^{-\frac{i}{\hbar}\hat{H}t} \hat{C}(t') e^{+\frac{i}{\hbar}\hat{H}t}] \\
&= \left\langle \hat{A}(-t - i\lambda\hbar)\hat{B}(-i\lambda'\hbar)\hat{C}(t' - t) \right\rangle
\end{aligned} \tag{21}$$

it follows that

$$\left\langle \hat{A}; \hat{B}(t); \hat{C}(t') \right\rangle = \left\langle \hat{A}(-t); \hat{B}; \hat{C}(t' - t) \right\rangle \tag{22}$$

B. Cyclic permutations

The DKT is invariant to cyclic permutations of the argument. In fact, by making the change of variables $\lambda = \beta - \mu$ and $\lambda' = \mu' - \mu$, making use of the cyclic properties of the trace and interchanging the order of integration it follows that

$$\left\langle \hat{A}; \hat{B}(t); \hat{C}(t') \right\rangle = \frac{1}{\beta^2} \int_0^\beta \mathrm{d}\lambda \int_0^\lambda \mathrm{d}\lambda' \ \left\langle \hat{A}(-i\lambda\hbar)\hat{B}(t - i\lambda'\hbar)\hat{C}(t') \right\rangle \tag{23}$$

$$= \frac{1}{\beta^2} \int_0^\beta \mathrm{d}\mu \int_\mu^\beta \mathrm{d}\mu' \ \left\langle \hat{B}\left(t - i\mu'\hbar\right) \hat{C}(t' - i\mu\hbar)\hat{A} \right\rangle \tag{24}$$

$$= \frac{1}{\beta^2} \int_0^\beta \mathrm{d}\mu' \int_0^{\mu'} \mathrm{d}\mu \ \left\langle \hat{B}\left(t - i\mu'\hbar\right) \hat{C}(t' - i\mu\hbar)\hat{A} \right\rangle \tag{25}$$

$$\equiv \left\langle \hat{B}(t); \hat{C}(t'); \hat{A} \right\rangle . \tag{26}$$

Following the same procedure, it also follows that:

$$\left\langle \hat{B}(t); \hat{C}(t'); \hat{A} \right\rangle = \left\langle \hat{C}(t'); \hat{A}; \hat{B}(t) \right\rangle . \tag{27}$$

C. Complex conjugate

The complex conjugate of Eq. (12) is given by:

$$\left\langle \hat{A}; \hat{B}(t); \hat{C}(t') \right\rangle^* = \frac{1}{\beta^2} \int_0^\beta \mathrm{d}\lambda \int_0^\lambda \mathrm{d}\lambda' \ \left\langle \hat{C}(t') \hat{B}(t + i\lambda'\hbar) \hat{A}(+i\lambda\hbar) \right\rangle \tag{28}$$

$$= \frac{1}{\beta^2} \int_0^\beta \mathrm{d}\mu \int_\mu^\beta \mathrm{d}\mu' \ \left\langle \hat{B}(t - i\mu'\hbar) \hat{A}(-i\mu\hbar) \hat{C}(t') \right\rangle \tag{29}$$

$$= \frac{1}{\beta^2} \int_0^\beta \mathrm{d}\mu' \int_0^{\mu'} \mathrm{d}\mu \ \left\langle \hat{B}(t - i\mu'\hbar) \hat{A}(-i\mu\hbar) \hat{C}(t') \right\rangle \tag{30}$$

$$= \left\langle \hat{B}(t); \hat{A}; \hat{C}(t') \right\rangle, \tag{31}$$

where the passage from Eq. (28) to Eq. (29) is achieved by using a change of variables ($\mu = \beta - \lambda$ and $\mu' = \beta - \lambda'$) and cyclic properties of the trace.

Since the operators only depend on the position and, hence, are chosen to be real in the basis of eigenstates of $\hat{H}$, it also follows that:

$$\left\langle \hat{A}; \hat{B}(t); \hat{C}(t') \right\rangle^* = \frac{1}{\beta^2} \int_0^\beta \mathrm{d}\lambda \int_0^\lambda \mathrm{d}\lambda' \ Tr \left[\frac{e^{-\beta\hat{H}}}{Z} \hat{C}(t') e^{-\lambda'\hat{H}} \hat{B}(t) e^{+\lambda'\hat{H}} e^{-\lambda\hat{H}} \hat{A} e^{+\lambda\hat{H}} \right] \tag{32}$$

$$= \frac{1}{\beta^2} \int_0^\beta \mathrm{d}\lambda \int_0^\lambda \mathrm{d}\lambda' \ \sum_{q,r,s} \frac{e^{-\beta E_q}}{Z} C_{qr} B_{rs} A_{sq} e^{+i\omega_{rs}t} e^{+i\omega_{qr}t'} e^{\lambda'\hbar\omega_{sr}} e^{\lambda\hbar\omega_{qs}} \tag{33}$$

$$= \frac{1}{\beta^2} \int_0^\beta \mathrm{d}\lambda \int_0^\lambda \mathrm{d}\lambda' \ \sum_{q,r,s} \frac{e^{-\beta E_q}}{Z} A_{qs} B_{sr} C_{rq} e^{-i\omega_{sr}t} e^{-i\omega_{rq}t'} e^{\lambda'\hbar\omega_{sr}} e^{\lambda\hbar\omega_{qs}} \tag{34}$$

$$= \left\langle \hat{A}; \hat{B}(-t); \hat{C}(-t') \right\rangle. \tag{35}$$

D. Symmetrized DKT

It is straightforward to show that the symmetrized DKT defined as

$$\left\langle \hat{A}; \hat{B}(t); \hat{C}(t') \right\rangle^{sym} = \left\langle \hat{A}; \hat{B}(t); \hat{C}(t') \right\rangle + \left\langle \hat{B}(t); \hat{A}; \hat{C}(t') \right\rangle \tag{36}$$

is a real and even function of time. In fact, using Eq. (31) it follows that

$$\left\langle \hat{A}; \hat{B}(t); \hat{C}(t') \right\rangle^{sym} = \left\langle \hat{A}; \hat{B}(t); \hat{C}(t') \right\rangle + \left\langle \hat{A}; \hat{B}(t); \hat{C}(t') \right\rangle^* \tag{37}$$

$$= 2\Re \left\{ \left\langle \hat{A}; \hat{B}(t); \hat{C}(t') \right\rangle \right\}. \tag{38}$$

From Eq. (35) it also easy to show that

$$\left\langle \hat{A}; \hat{B}(t); \hat{C}(t') \right\rangle^{sym} = \left\langle \hat{A}; \hat{B}(t); \hat{C}(t') \right\rangle + \left\langle \hat{A}; \hat{B}(-t); \hat{C}(-t') \right\rangle \tag{39}$$

$$= \left\langle \hat{A}; \hat{B}(-t); \hat{C}(-t') \right\rangle^{sym}. \tag{40}$$

From the stationary of the DKT to an overall time shift Eq. (22) and the definition of the symmetrized DKT Eq. (36) it follows that

$$\left\langle \hat{A};\hat{B}(t);\hat{C}(t')\right\rangle^{sym} = \left\langle \hat{A};\hat{B}(t);\hat{C}(t')\right\rangle + \left\langle \hat{B}(t);\hat{A};\hat{C}(t')\right\rangle \tag{41}$$

$$= \left\langle \hat{A}(-t);\hat{B};\hat{C}(t'-t)\right\rangle + \left\langle \hat{B};\hat{A}(-t);\hat{C}(t'-t)\right\rangle \tag{42}$$

$$= \left\langle \hat{B};\hat{A}(-t);\hat{C}(t'-t)\right\rangle^{sym} \tag{43}$$

which is the time version of the detail balance relation presented in the main text.

Finally, it is straightforward to show that when one of the operator is unity, the symmetrized DKT reduces to the simple Kubo transform.[2] For example, when $\hat{B}(t) = 1$ this follows from

$$\langle A;1;C(t)\rangle^{sym} = \frac{1}{Z\beta^2}\int_0^\beta d\lambda \int_0^\lambda d\lambda' Tr[e^{-(\beta-\lambda)\hat{H}}\hat{A}e^{-\lambda\hat{H}}\hat{C}(t) + e^{-(\beta-\lambda')\hat{H}}\hat{A}e^{-\lambda'\hat{H}}\hat{C}(t)] \tag{44}$$

$$= \frac{1}{Z\beta^2}\left[\int_0^\beta d\lambda \int_0^\lambda d\lambda' Tr[e^{-(\beta-\lambda)\hat{H}}\hat{A}e^{-\lambda\hat{H}}\hat{C}(t)] + \int_0^\beta d\lambda' \int_{\lambda'}^\beta d\lambda Tr[e^{-(\beta-\lambda')\hat{H}}\hat{A}e^{-\lambda'\hat{H}}\hat{C}(t)]\right] \tag{45}$$

$$= \frac{1}{Z\beta^2}\int_0^\beta d\lambda \int_0^\beta d\lambda' Tr[e^{-(\beta-\lambda)\hat{H}}\hat{A}e^{-\lambda\hat{H}}\widehat{C}(t)] \tag{46}$$

$$= \frac{1}{Z\beta}\int_0^\beta d\lambda Tr[e^{-(\beta-\lambda)\hat{H}}\hat{A}e^{-\lambda\hat{H}}\widehat{C}(t)] \tag{47}$$

$$= \langle A;C(t)\rangle\,. \tag{48}$$

Due to the relations given by Eq. (26-27) and Eq. (43) it is straightforward to generalize this for the cases where $\hat{A} = 1$ or $\hat{C}(t') = 1$.

E. Asymmetrized DKT

Similar properties can be derived for the asymmetric DKT defined by

$$\left\langle \hat{A};\hat{B}(t);\hat{C}(t')\right\rangle^{asym} = \left\langle \hat{A};\hat{B}(t);\hat{C}(t')\right\rangle - \left\langle \hat{B}(t);\hat{A};\hat{C}(t')\right\rangle. \tag{49}$$

Using Eq. (31) it follows that the asymmetric DKT is a purely imaginary function

$$\left\langle \hat{A};\hat{B}(t);\hat{C}(t')\right\rangle^{asym} = \left\langle \hat{A};\hat{B}(t);\hat{C}(t')\right\rangle - \left\langle \hat{A};\hat{B}(t);\hat{C}(t')\right\rangle^{*} \tag{50}$$

$$= 2i\Im\left\{\left\langle \hat{A};\hat{B}(t);\hat{C}(t')\right\rangle\right\}. \tag{51}$$

From Eq. (35) it also follows that asymmetric DKT is an odd function of time

$$\left\langle \hat{A}; \hat{B}(t); \hat{C}(t') \right\rangle^{asym} = \left\langle \hat{A}; \hat{B}(t); \hat{C}(t') \right\rangle - \left\langle \hat{A}; \hat{B}(-t); \hat{C}(-t') \right\rangle \tag{52}$$

$$= - \left\langle \hat{A}; \hat{B}(-t); \hat{C}(-t') \right\rangle^{asym}. \tag{53}$$

III. SYMMETRIZED DKT AND ASYMMETRIC DKT IN THE HARMONIC LIMIT

The Fourier transform of the DKT in the energy representation is given by (see Eqs. (13-14))

$$\tilde{K}_{ABC}(\omega, \omega') = \frac{1}{Z\beta^2} \sum_{qrs} e^{-\beta E_q} A_{qr} B_{rs} C_{sq} \int_0^\beta \int_0^\lambda e^{\lambda(E_q - E_r)} e^{\lambda'(E_r - E_s)} \times \delta\left[\omega - (E_r - E_s)/\hbar\right] \delta\left[\omega' - (E_s - E_q)/\hbar\right], \tag{54}$$

where we defined $\tilde{K}_{ABC}(\omega, \omega') \equiv \langle A; B(\omega); C(\omega') \rangle$ for notation simplicity.

For the case of a harmonic potential $V = \frac{1}{2} m\Omega^2 x^2$ with eigenvalues $E_n = \hbar\Omega(n + \frac{1}{2})$ we have

$$\tilde{K}_{ABC}(\omega, \omega') = \frac{e^{-\beta\hbar\Omega/2}}{Z\beta^2} \sum_{qrs} e^{-\beta\hbar\Omega q} A_{qr} B_{rs} C_{sq} I_{q,r,s}(\beta) \Big\{ \delta\left[\omega - (r-s)\Omega\right] \delta\left[\omega' - (s-q)\Omega\right] \Big\}, \tag{55}$$

where

$$I_{q,r,s}(\beta) = \int_0^\beta d\lambda \int_0^\lambda d\lambda' e^{\lambda\hbar\Omega(q-r)} e^{\lambda'\hbar\Omega(r-s)}. \tag{56}$$

To proceed we expand each of the operators to second order in the coordinate $\hat{x}$, namely

$$\hat{A} = A^0 + A'\hat{x} + \frac{1}{2} A''\hat{x}^2, \tag{57}$$

$$\hat{B} = B^0 + B'\hat{x} + \frac{1}{2} B''\hat{x}^2, \tag{58}$$

$$\hat{C} = C^0 + C'\hat{x} + \frac{1}{2} C''\hat{x}^2, \tag{59}$$

where the primes represent derivatives with respect to the coordinate. When the matrix elements of the operators inside Eq. (55) are expanded according to Eqs. (57-59), the DKT splits into different terms that depend on the order to which each element is taken. The lowest order term that contribute to the DKT (and the response function) involves one x^2 operator and two x operators[3–5] and there will be three possible combinations, namely

$$\tilde{K}_{ABC}(\omega, \omega') \approx \tilde{K}_{211}(\omega, \omega') + \tilde{K}_{121}(\omega, \omega') + \tilde{K}_{112}(\omega, \omega') \tag{60}$$

where the notation $\tilde{K}_{211}$ denotes that $\hat{A}$ is replaced by $\hat{x}^2$, $\hat{B}$ with $\hat{x}$ and $\hat{C}$ with $\hat{x}$. Note that terms involving the (static) zero order terms A^0, B^0, C^0, $\tilde{K}_{000}$, $\tilde{K}_{110}$, $\tilde{K}_{101}$ and $\tilde{K}_{011}$ in principle contribute to the DKT, although they do not contribute to the response function.[4,5] Since these terms can be excluded from the DKT by computing the time correlation function of the fluctuations of the operators $\hat{A}$, $\hat{B}$,$\hat{C}$, i.e. $\Delta\hat{A} = \hat{A} - \left\langle \hat{A} \right\rangle$, they will no longer be considered here.[3] Note that the response function $R(t,t')$ defined in the main text is unaffected by the substitution of all the operators by its fluctuations.

Using the fact that for a harmonic oscillator

$$x_{ij} = \sqrt{\frac{\hbar}{2m\Omega}} \left[\delta_{i,j+1}\sqrt{j+1} + \delta_{i,j-1}\sqrt{j}\right], \tag{61}$$

and

$$x_{ij}^2 = \frac{\hbar}{2m\Omega} \left[\delta_{i,j+2}\sqrt{j+1}\sqrt{j+2} + \delta_{i,j}(2j+1) + \delta_{i,j-2}\sqrt{j}\sqrt{j-1}\right], \tag{62}$$

each term in Eq. (60) can be further expanded. For example, the first term

$$\tilde{K}_{211}(\omega,\omega') = \frac{A''B'C'e^{-\beta\hbar\Omega/2}}{2Z\beta^2} \sum_{qrs} e^{-\beta\hbar\Omega q} x_{qr}^2 x_{rs} x_{sq} I_{q,r,s}(\beta) \Big\{ \delta\left[\omega - (r-s)\Omega\right] \delta\left[\omega' - (s-q)\Omega\right] \Big\}, \tag{63}$$

can be expanded as

$$\begin{aligned}\tilde{K}_{211}(\omega,\omega') = &\left(\frac{\hbar}{2m\Omega}\right)^2 \frac{A''B'C'e^{-\beta\hbar\Omega/2}}{2Z\beta^2} \sum_{qrs} e^{-\beta\hbar\Omega q} \Big[\delta_{q,r+2}\sqrt{r+1}\sqrt{r+2} + \\ &\delta_{q,r-2}\sqrt{r}\sqrt{r-1} + \delta_{q,r}(2r+1)\Big] \\ &\times \left[\delta_{r,s+1}\sqrt{s+1} + \delta_{r,s-1}\sqrt{s}\right] \left[\delta_{s,q+1}\sqrt{q+1} + \delta_{s,q-1}\sqrt{q}\right] I_{q,r,s}(\beta) \\ &\times \Big\{ \delta\left[\omega - (r-s)\Omega\right] \delta\left[\omega' - (s-q)\Omega\right] \Big\}.\end{aligned} \tag{64}$$

There are only four cases in which Eq. (64) does not vanish. These cases and the corresponding correlation functions are:

(1) $q = r-2$, $s = q+1$, $r = s+1$

$$\begin{aligned}\tilde{K}_{211}^{(1)}(\omega,\omega') &= \left(\frac{\hbar}{2m\Omega}\right)^2 \frac{A''B'C'e^{-\beta\hbar\Omega/2}(1-e^{-\beta\hbar\Omega})^2}{4Z(\beta\hbar\Omega)^2} \sum_q e^{-\beta\hbar\Omega q}(q+2)(q+1)\delta(\omega-\Omega)\delta(\omega'-\Omega) \\ &= \left(\frac{\hbar}{2m\Omega}\right)^2 \frac{A''B'C'e^{-\beta\hbar\Omega/2}(1-e^{-\beta\hbar\Omega})^2}{4Z(\beta\hbar\Omega)^2} \frac{2}{(1-e^{-\beta\hbar\Omega})^3}\delta(\omega-\Omega)\delta(\omega'-\Omega) \\ &= \left(\frac{\hbar}{2m\Omega}\right)^2 \frac{A''B'C'}{2(\beta\hbar\Omega)^2}\delta(\omega-\Omega)\delta(\omega'-\Omega)\end{aligned} \tag{65}$$

(2) $q = r + 2,\ s = q - 1,\ r = s - 1$

$$\tilde{K}^{(2)}_{211}(\omega,\omega') = \left(\frac{\hbar}{2m\Omega}\right)^2 \frac{A''B'C'e^{-\beta\hbar\Omega/2}(1-e^{\beta\hbar\Omega})^2}{4Z(\beta\hbar\Omega)^2}\sum_q e^{-\beta\hbar\Omega q} q(q-1)\delta(\omega+\Omega)\delta(\omega'+\Omega)$$
$$= \left(\frac{\hbar}{2m\Omega}\right)^2 \frac{A''B'C'e^{-\beta\hbar\Omega/2}(1-e^{\beta\hbar\Omega})^2}{4Z(\beta\hbar\Omega)^2}\frac{2e^{-2\beta\hbar\Omega}}{(1-e^{-\beta\hbar\Omega})^3}\delta(\omega+\Omega)\delta(\omega'+\Omega)$$
$$= \left(\frac{\hbar}{2m\Omega}\right)^2 \frac{A''B'C'}{2(\beta\hbar\Omega)^2}\delta(\omega+\Omega)\delta(\omega'+\Omega) \tag{66}$$

(3) $q = r,\ s = q - 1,\ r = s + 1$

$$\tilde{K}^{(3)}_{211}(\omega,\omega') = \left(\frac{\hbar}{2m\Omega}\right)^2 \frac{A''B'C'e^{-\beta\hbar\Omega/2}(e^{\beta\hbar\Omega}-\beta\hbar\Omega-1)}{2Z(\beta\hbar\Omega)^2}\sum_q e^{-\beta\hbar\Omega q} q(2q+1)\delta(\omega-\Omega)\delta(\omega'+\Omega)$$
$$= \left(\frac{\hbar}{2m\Omega}\right)^2 \frac{A''B'C'(e^{\beta\hbar\Omega}-\beta\hbar\Omega-1)(3e^{-\beta\hbar\Omega}+e^{-2\beta\hbar\Omega})}{2(\beta\hbar\Omega)^2(1-e^{-\beta\hbar\Omega})^2}\delta(\omega-\Omega)\delta(\omega'+\Omega) \tag{67}$$

(4) $q = r,\ s = q + 1,\ r = s - 1$

$$\tilde{K}^{(4)}_{211}(\omega,\omega') = \left(\frac{\hbar}{2m\Omega}\right)^2 \frac{A''B'C'e^{-\beta\hbar\Omega/2}(e^{-\beta\hbar\Omega}+\beta\hbar\Omega-1)}{2Z(\beta\hbar\Omega)^2}\sum_q e^{-\beta\hbar\Omega q}(q+1)(2q+1)\delta(\omega+\Omega)\delta(\omega'-\Omega)$$
$$= \left(\frac{\hbar}{2m\Omega}\right)^2 \frac{A''B'C'(e^{-\beta\hbar\Omega}+\beta\hbar\Omega-1)(3e^{-\beta\hbar\Omega}+1)}{2(\beta\hbar\Omega)^2(1-e^{-\beta\hbar\Omega})^2}\delta(\omega+\Omega)\delta(\omega'-\Omega) \tag{68}$$

The notation here is defined such that

$$\tilde{K}_{211}(\omega,\omega') = \tilde{K}^{(1)}_{211}(\omega,\omega') + \tilde{K}^{(2)}_{211}(\omega,\omega') + \tilde{K}^{(3)}_{211}(\omega,\omega') + \tilde{K}^{(4)}_{211}(\omega,\omega'). \tag{69}$$

Similar manipulations can be made for the second and third terms in Eq. (60). Here we summarize the results:

$$\tilde{K}^{(1)}_{121}(\omega,\omega') = \left(\frac{\hbar}{2m\Omega}\right)^2 \frac{A'B''C'(1+\beta\hbar\Omega e^{\beta\hbar\Omega}-e^{\beta\hbar\Omega})(3e^{-2\beta\hbar\Omega}+e^{-\beta\hbar\Omega})}{2(\beta\hbar\Omega)^2(1-e^{-\beta\hbar\Omega})^2}\delta(\omega)\delta(\omega'+\Omega) \tag{70}$$

$$\tilde{K}^{(2)}_{121}(\omega,\omega') = \left(\frac{\hbar}{2m\Omega}\right)^2 \frac{A'B''C'(1-\beta\hbar\Omega e^{-\beta\hbar\Omega}-e^{-\beta\hbar\Omega})(3+e^{-\beta\hbar\Omega})}{2(\beta\hbar\Omega)^2(1-e^{-\beta\hbar\Omega})^2}\delta(\omega)\delta(\omega'-\Omega) \quad (71)$$

$$\tilde{K}^{(3)}_{121}(\omega,\omega') = \left(\frac{\hbar}{2m\Omega}\right)^2 \frac{A'B''C'e^{-\beta\hbar\Omega}\left[\cosh(\beta\hbar\Omega)-1\right]}{(\beta\hbar\Omega)^2(1-e^{-\beta\hbar\Omega})^2}\delta(\omega-2\Omega)\delta(\omega'+\Omega) \quad (72)$$

$$\tilde{K}^{(4)}_{121}(\omega,\omega') = \left(\frac{\hbar}{2m\Omega}\right)^2 \frac{A'B''C'e^{-\beta\hbar\Omega}\left[\cosh(\beta\hbar\Omega)-1\right]}{(\beta\hbar\Omega)^2(1-e^{-\beta\hbar\Omega})^2}\delta(\omega+2\Omega)\delta(\omega'-\Omega) \quad (73)$$

$$\tilde{K}^{(1)}_{112}(\omega,\omega') = \left(\frac{\hbar}{2m\Omega}\right)^2 \frac{A'B'C''(e^{\beta\hbar\Omega}-\beta\hbar\Omega-1)(3e^{-\beta\hbar\Omega}+e^{-2\beta\hbar\omega})}{2(\beta\hbar\Omega)^2(1-e^{-\beta\hbar\Omega})^2}\delta(\omega+\Omega)\delta(\omega') \quad (74)$$

$$\tilde{K}^{(2)}_{112}(\omega,\omega') = \left(\frac{\hbar}{2m\Omega}\right)^2 \frac{A'B'C''(e^{-\beta\hbar\Omega}+\beta\hbar\Omega-1)(3e^{-\beta\hbar\Omega}+1)}{2(\beta\hbar\Omega)^2(1-e^{-\beta\hbar\Omega})^2}\delta(\omega-\Omega)\delta(\omega') \quad (75)$$

$$\tilde{K}^{(3)}_{112}(\omega,\omega') = \left(\frac{\hbar}{2m\Omega}\right)^2 \frac{A'B'C''}{2(\beta\hbar\Omega)^2}\delta(\omega-\Omega)\delta(\omega'+2\Omega) \quad (76)$$

$$\tilde{K}^{(4)}_{112}(\omega,\omega') = \left(\frac{\hbar}{2m\Omega}\right)^2 \frac{A'B'C''}{2(\beta\hbar\Omega)^2}\delta(\omega+\Omega)\delta(\omega'-2\Omega) \quad (77)$$

Note that all relations presented above can be expressed as a prefactor $\tilde{F}^{(n)}_{abc}(\omega,\omega')$ multiply by a set of delta functions

$$\tilde{K}^{(d)}_{abc}(\omega,\omega') = \tilde{F}^{(d)}_{abc}(\omega,\omega')\delta(\omega+n\Omega)\delta(\omega'+m\Omega), \quad (78)$$

where the particular values of n, m depend on the particular term considered.

From the relations presented above it is straightforward to obtain the symmetrized and asymmetric DKT for the harmonic reference potential. In fact, since (see Eq. 39)

$$\tilde{K}^{sym}_{ABC}(\omega,\omega') = \tilde{K}_{ABC}(\omega,\omega') + \tilde{K}_{ABC}(-\omega,-\omega') \quad (79)$$

the symmetrized DKT is given by

$$\tilde{K}^{sym}_{ABC}(\omega,\omega') = \tilde{R}^{(a)} + \tilde{R}^{(b)} + \tilde{R}^{(c)} + \tilde{R}^{(d)} + \tilde{R}^{(e)} + \tilde{R}^{(f)} \tag{80}$$

where

$$\tilde{R}^{(a)} = (\tilde{F}^{(1)}_{211} + \tilde{F}^{(2)}_{211})\left[\delta(\omega-\Omega)\delta(\omega'-\Omega) + \delta(\omega+\Omega)\delta(\omega'+\Omega)\right], \tag{81}$$

$$\tilde{R}^{(b)} = (\tilde{F}^{(3)}_{211} + \tilde{F}^{(4)}_{211})\left[\delta(\omega-\Omega)\delta(\omega'+\Omega) + \delta(\omega+\Omega)\delta(\omega'-\Omega)\right], \tag{82}$$

$$\tilde{R}^{(c)} = (\tilde{F}^{(1)}_{121} + \tilde{F}^{(2)}_{121})\left[\delta(\omega)\delta(\omega'+\Omega) + \delta(\omega)\delta(\omega'-\Omega)\right], \tag{83}$$

$$\tilde{R}^{(d)} = (\tilde{F}^{(3)}_{121} + \tilde{F}^{(4)}_{121})\left[\delta(\omega-2\Omega)\delta(\omega'+\Omega) + \delta(\omega+2\Omega)\delta(\omega'-\Omega)\right], \tag{84}$$

$$\tilde{R}^{(e)} = (\tilde{F}^{(1)}_{112} + \tilde{F}^{(2)}_{112})\left[\delta(\omega+\Omega)\delta(\omega') + \delta(\omega-\Omega)\delta(\omega')\right], \tag{85}$$

$$\tilde{R}^{(f)} = (\tilde{F}^{(3)}_{112} + \tilde{F}^{(4)}_{112})\left[\delta(\omega-\Omega)\delta(\omega'+2\Omega) + \delta(\omega+\Omega)\delta(\omega'-2\Omega)\right]. \tag{86}$$

In the previous equations we suppressed the frequency dependence of the prefactors functions for notation simplicity. Note that all six terms contribute to the symmetric DKT.

Similarly, since (see Eq. 52)

$$\tilde{K}^{asym}_{ABC}(\omega,\omega') = \tilde{K}_{ABC}(\omega,\omega') - \tilde{K}_{ABC}(-\omega,-\omega'), \tag{87}$$

the asymmetric DKT is given by

$$\tilde{K}^{asym}_{ABC}(\omega,\omega') = \tilde{I}^{(a)} + \tilde{I}^{(b)} + \tilde{I}^{(c)} + \tilde{I}^{(d)} + \tilde{I}^{(e)} + \tilde{I}^{(f)} \tag{88}$$

where

$$\tilde{I}^{(a)} = (\tilde{F}^{(1)}_{211} - \tilde{F}^{(2)}_{211})\left[\delta(\omega-\Omega)\delta(\omega'-\Omega) + \delta(\omega+\Omega)\delta(\omega'+\Omega)\right] = 0, \tag{89}$$

$$\tilde{I}^{(b)} = (\tilde{F}^{(3)}_{211} - \tilde{F}^{(4)}_{211})\left[\delta(\omega-\Omega)\delta(\omega'+\Omega) + \delta(\omega+\Omega)\delta(\omega'-\Omega)\right], \tag{90}$$

$$\tilde{I}^{(c)} = (\tilde{F}^{(1)}_{121} - \tilde{F}^{(2)}_{121})\left[\delta(\omega)\delta(\omega'+\Omega) + \delta(\omega)\delta(\omega'-\Omega)\right], \tag{91}$$

$$\tilde{I}^{(d)} = (\tilde{F}^{(3)}_{121} - \tilde{F}^{(4)}_{121})\left[\delta(\omega-2\Omega)\delta(\omega'+\Omega) + \delta(\omega+2\Omega)\delta(\omega'-\Omega)\right] = 0, \tag{92}$$

$$\tilde{I}^{(e)} = (\tilde{F}^{(1)}_{112} - \tilde{F}^{(2)}_{112})\left[\delta(\omega+\Omega)\delta(\omega') + \delta(\omega-\Omega)\delta(\omega')\right], \tag{93}$$

$$\tilde{I}^{(f)} = (\tilde{F}^{(3)}_{112} - \tilde{F}^{(4)}_{112})\left[\delta(\omega-\Omega)\delta(\omega'+2\Omega) + \delta(\omega+\Omega)\delta(\omega'-2\Omega)\right] = 0. \tag{94}$$

Note that, due to the form of the prefactors, three terms are identically zero and do not contribute to the asymmetric DKT and hence the response function. If we further consider

not just $\tilde{K}^{asym}_{ABC}(\omega,\omega')$ but $Q_-(\omega,\omega')\tilde{K}^{asym}_{ABC}(\omega,\omega')$, the contribution of $\tilde{I}^{(b)}$ to the overall response function is also zero, since $Q_-(\omega,\omega')$ vanishes when $\omega = -\omega'$ (which is enforced by the delta functions in $\tilde{I}^{(b)}$).

From the analysis presented below, in the harmonic limit four out of the six low-order terms are zero for the $Q_-(\omega,\omega')\tilde{K}^{asym}_{ABC}(\omega,\omega')$ term and, hence, do not contribute to the response. This analysis suggest that neglecting the contribution of the asymmetric DKT to the response may not be a bad approximation and we choose to do so in the main text. Although these relations were derived for a harmonic potential we expect this approximation to be valid even for moderately anharmonic potentials.

IV. ADDITIONAL FIGURES COMPARING THE EXACT AND APPROXIMATE SECOND ORDER RESPONSE FUNCTION

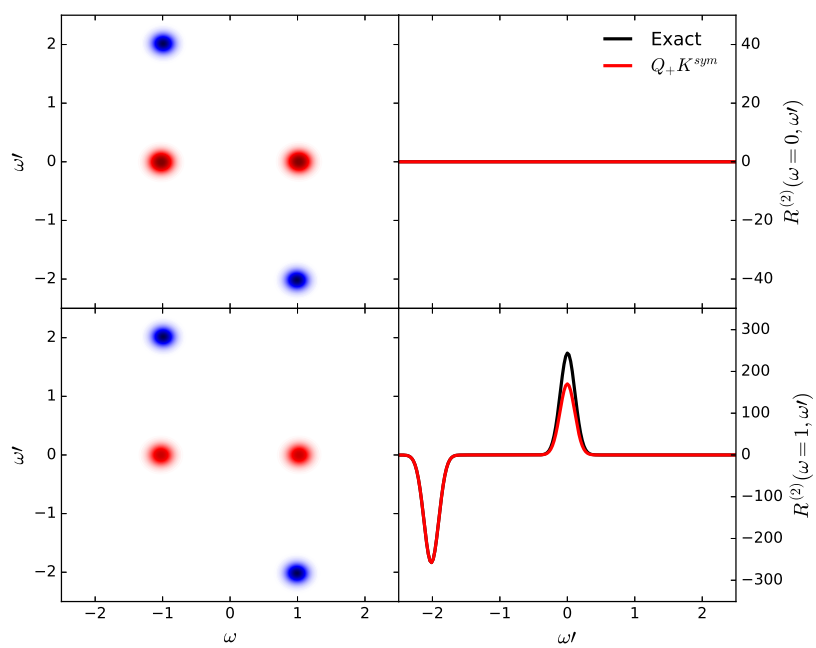

FIG. 1. Top Left: Exact Response. Bottom Left: The approximate response. Top Right: A projection at $\omega = 0$ comparing the exact and approximate response. Bottom Right: A projection at $\omega = 1$ comparing the exact and approximate response. The potential is defined as $V(x) = \frac{1}{2}x^2$ with a temperature $\beta = 1$ with $\hat{A} = \hat{B} = \hat{x}$ and $\hat{C} = \hat{x}^2$.

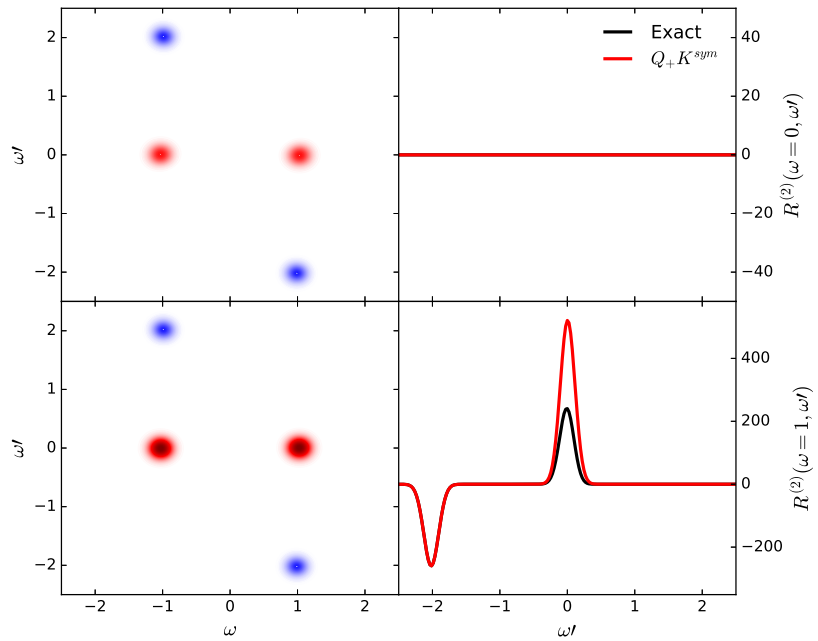

FIG. 2. Top Left: Exact Response. Bottom Left: The approximate response. Top Right: A projection at $\omega = 0$ comparing the exact and approximate response. Bottom Right: A projection at $\omega = 1$ comparing the exact and approximate response. The potential is defined as $V(x) = \frac{1}{2}x^2$ with a temperature $\beta = 8$ with $\hat{A} = \hat{B} = \hat{x}$ and $\hat{C} = \hat{x}^2$.

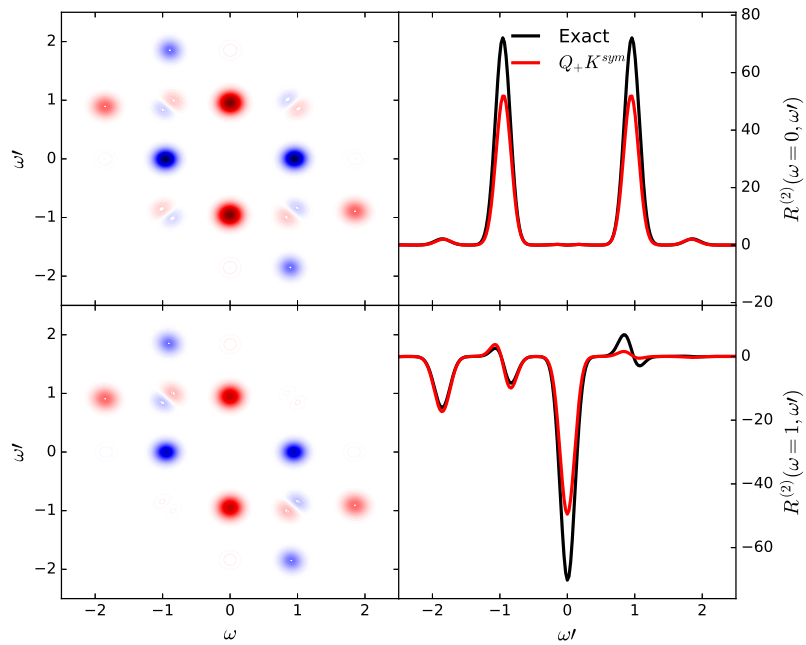

FIG. 3. Top Left: Exact Response. Bottom Left: The approximate response. Top Right: A projection at $\omega = 0$ comparing the exact and approximate response. Bottom Right: A projection at $\omega = 1$ comparing the exact and approximate response. The potential is defined as $V(x) = \frac{1}{2}x^2 + \frac{1}{10}x^3 + \frac{1}{100}x^4$ with a temperature $\beta = 1$ with $\hat{A} = \hat{B} = \hat{C} = \hat{x}$.

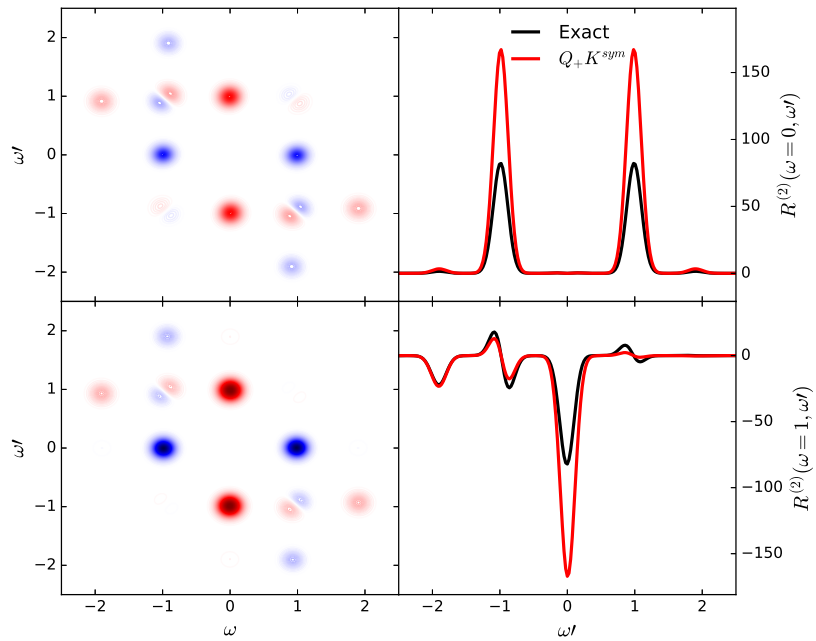

FIG. 4. Top Left: Exact Response. Bottom Left: The approximate response. Top Right: A projection at $\omega = 0$ comparing the exact and approximate response. Bottom Right: A projection at $\omega = 1$ comparing the exact and approximate response. The potential is defined as $V(x) = \frac{1}{2}x^2 + \frac{1}{10}x^3 + \frac{1}{100}x^4$ with a temperature $\beta = 8$ with $\hat{A} = \hat{B} = \hat{C} = \hat{x}$.

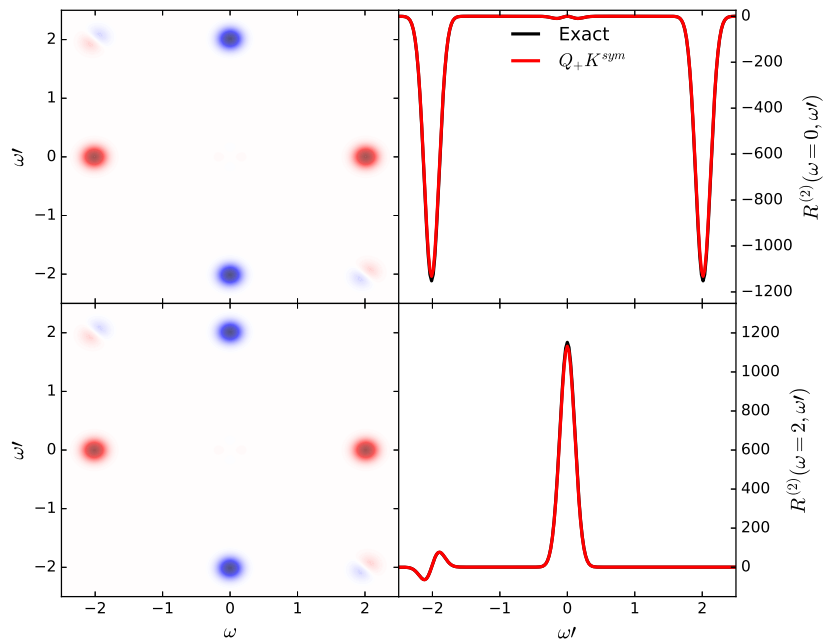

FIG. 5. Top Left: Exact Response. Bottom Left: The approximate response. Top Right: A projection at $\omega = 0$ comparing the exact and approximate response. Bottom Right: A projection at $\omega = 2$ comparing the exact and approximate response. The potential is defined as $V(x) = \frac{1}{2}x^2$ with a temperature $\beta = 1$ with $\hat{A} = \hat{B} = \hat{C} = \hat{x}^2$.

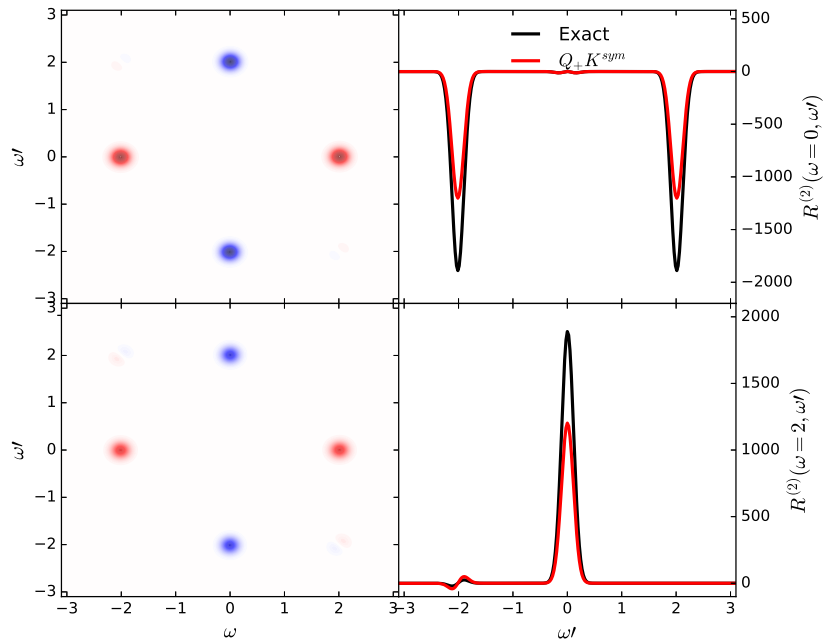

FIG. 6. Top Left: Exact Response. Bottom Left: The approximate response. Top Right: A projection at $\omega = 0$ comparing the exact and approximate response. Bottom Right: A projection at $\omega = 2$ comparing the exact and approximate response. The potential is defined as $V(x) = \frac{1}{2}x^2$ with a temperature $\beta = 8$ with $\hat{A} = \hat{B} = \hat{C} = \hat{x}^2$.

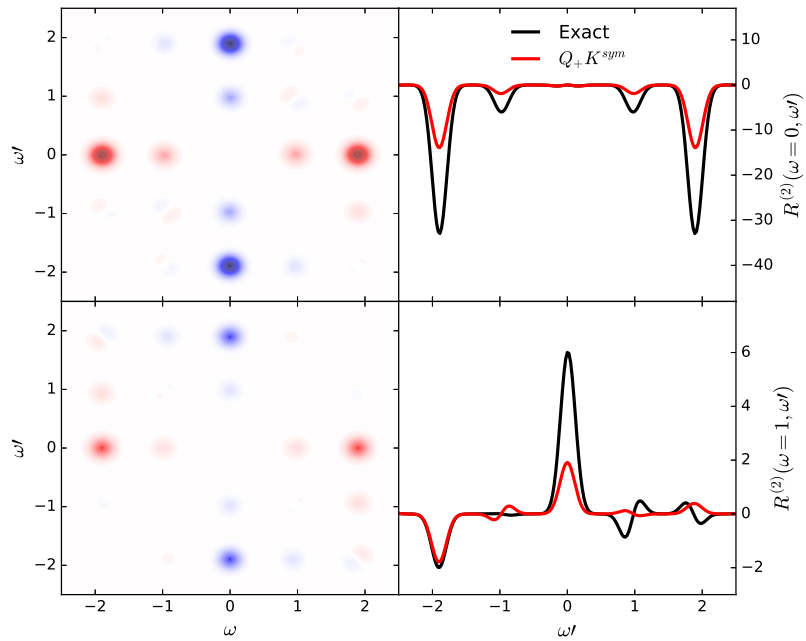

FIG. 7. Top Left: Exact Response. Bottom Left: The approximate response. Top Right: A projection at $\omega = 0$ comparing the exact and approximate response. Bottom Right: A projection at $\omega = 1$ comparing the exact and approximate response. The potential is defined as $V(x) = \frac{1}{4}x^4$ with a temperature $\beta = 1$ with $\hat{A} = \hat{B} = \hat{C} = \hat{x}^2$.

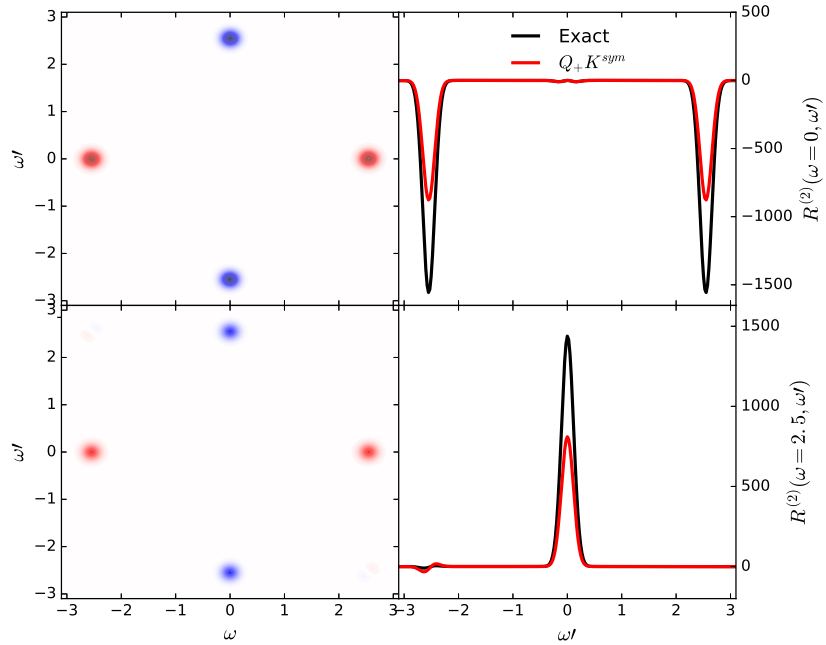

FIG. 8. Top Left: Exact Response. Bottom Left: The approximate response. Top Right: A projection at $\omega = 0$ comparing the exact and approximate response. Bottom Right: A projection at $\omega = 2.5$ comparing the exact and approximate response. The potential is defined as $V(x) = \frac{1}{4}x^4$ with a temperature $\beta = 8$ with $\hat{A} = \hat{B} = \hat{C} = \hat{x}^2$.

V. ADDITIONAL FIGURES COMPARING THE SYMMETRIZED DKT AND RPMD APPROXIMATION

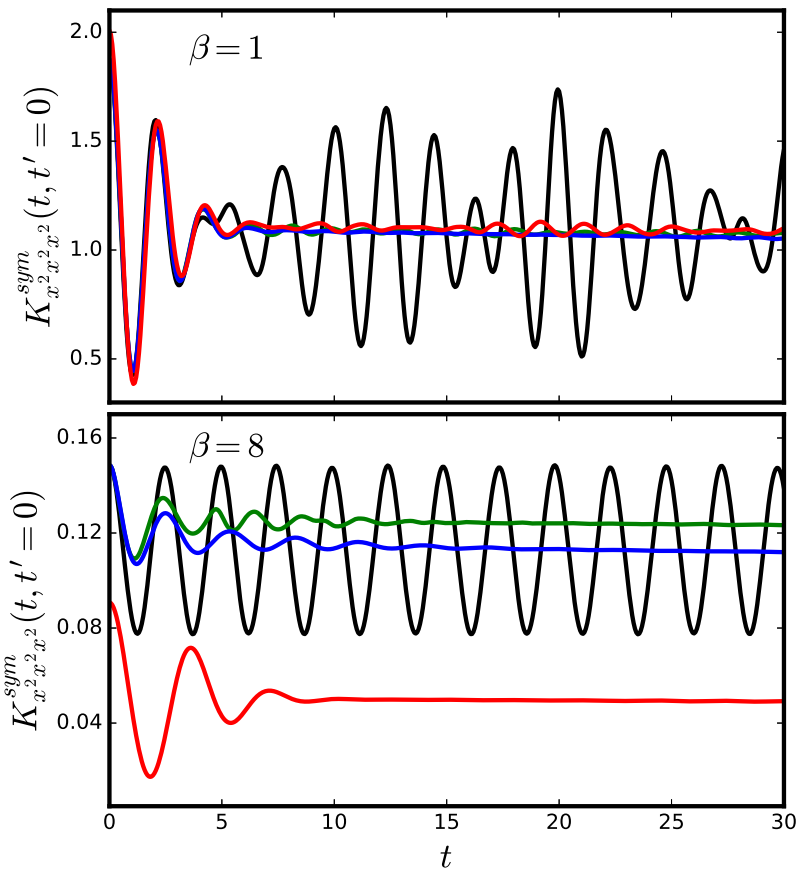

FIG. 9. $t' = 0$ cut of the symmetrized DKT x^2 auto-correlation for the quartic potential. Black line: exact result, $K^{sym}_{x^2x^2x^2}(t, 0)$. Red line: Classical result. Green line: RPMD result. Blue line: TRPMD result.

VI. ADDITIONAL FIGURES COMPARING THE EXACT AND RPMD APPROXIMATE SECOND ORDER RESPONSE FUNCTION

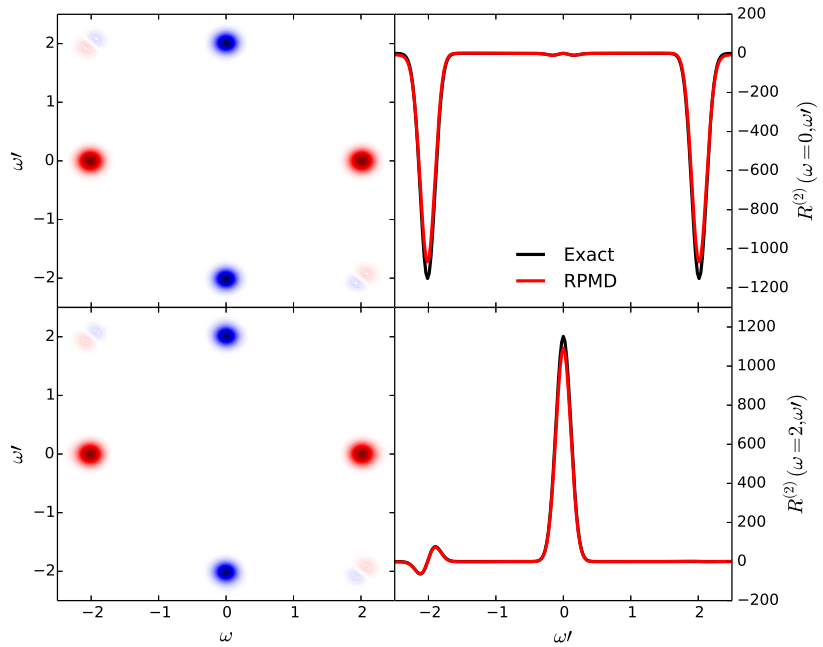

FIG. 10. Top Left: Exact Response. Bottom Left: The RPMD approximate response. Top Right: A projection at $\omega = 0$ comparing the exact and RPMD approximate response. Bottom Right: A projection at $\omega = 2$ comparing the exact and RPMD approximate response. The potential is defined as $V(x) = \frac{1}{2}x^2$ with a temperature $\beta = 1$ with $\hat{A} = \hat{B} = \hat{C} = \hat{x}^2$.

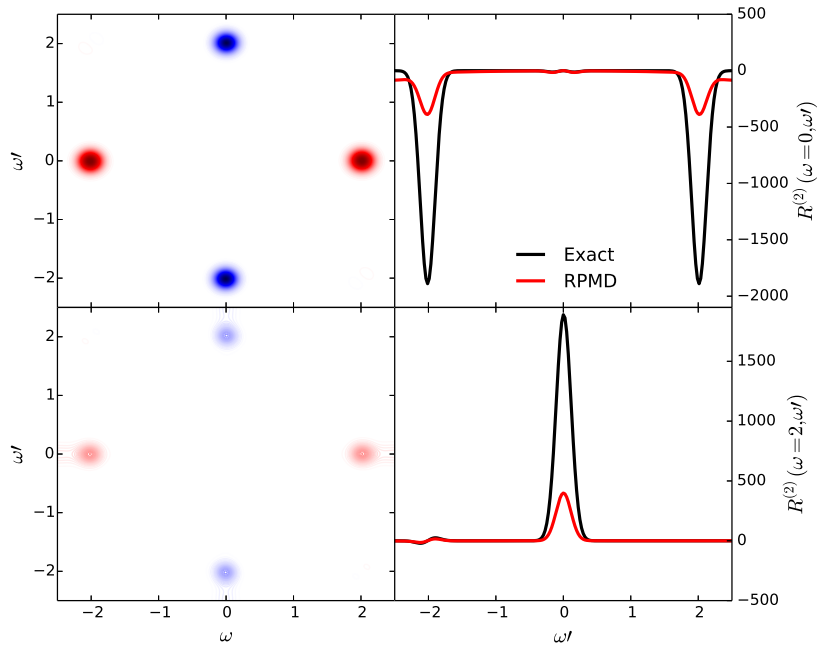

FIG. 11. Top Left: Exact Response. Bottom Left: The RPMD approximate response. Top Right: A projection at $\omega = 0$ comparing the exact and RPMD approximate response. Bottom Right: A projection at $\omega = 2$ comparing the exact and RPMD approximate response. The potential is defined as $V(x) = \frac{1}{2}x^2$ with a temperature $\beta = 8$ with $\hat{A} = \hat{B} = \hat{C} = \hat{x}^2$.

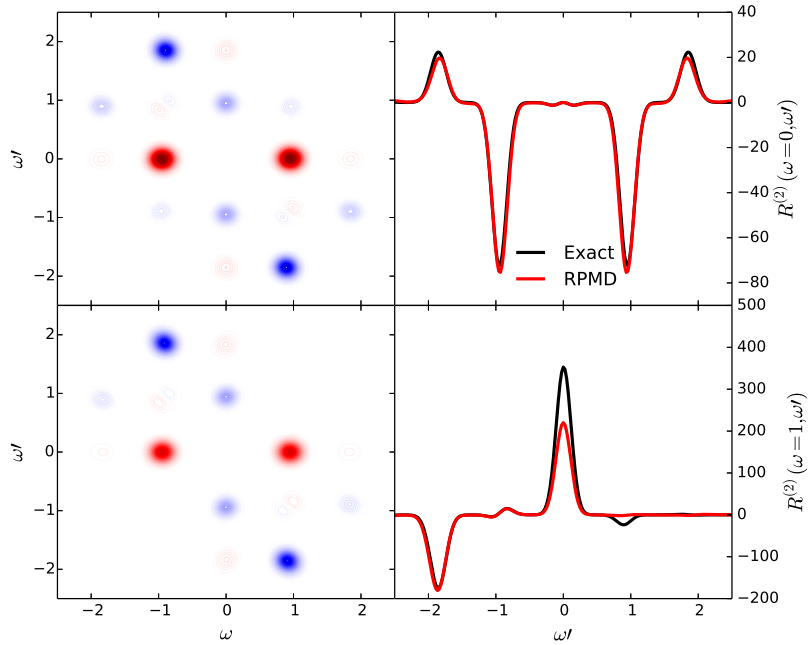

FIG. 12. Top Left: Exact Response. Bottom Left: The RPMD approximate response. Top Right: A projection at $\omega = 0$ comparing the exact and RPMD approximate response. Bottom Right: A projection at $\omega = 1$ comparing the exact and RPMD approximate response. The potential is defined as $V(x) = \frac{1}{2}x^2 + \frac{1}{10}x^3 + \frac{1}{100}x^4$ with a temperature $\beta = 1$ with $\hat{A} = \hat{B} = \hat{x}$ and $\hat{C} = \hat{x}^2$.

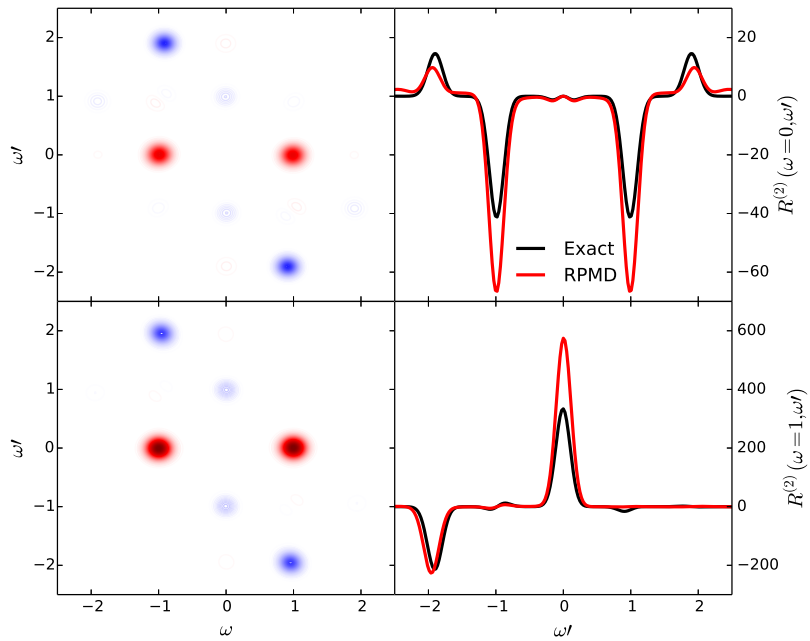

FIG. 13. Top Left: Exact Response. Bottom Left: The RPMD approximate response. Top Right: A projection at $\omega = 0$ comparing the exact and RPMD approximate response. Bottom Right: A projection at $\omega = 1$ comparing the exact and RPMD approximate response. The potential is defined as $V(x) = \frac{1}{2}x^2 + \frac{1}{10}x^3 + \frac{1}{100}x^4$ with a temperature $\beta = 8$ with $\hat{A} = \hat{B} = \hat{x}$ and $\hat{C} = \hat{x}^2$.

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