Gaussian time-dependent variational principle for the finite-temperature anharmonic lattice dynamics

Jae-Mo Lihm 1, 2, 3, * and Cheol-Hwan Park 1, 2, 3, †
1 Center for Correlated Electron Systems, Institute for Basic Science, Seoul 08826, Korea
2 Department of Physics and Astronomy, Seoul National University, Seoul 08826, Korea
3 Center for Theoretical Physics, Seoul National University, Seoul 08826, Korea
(Dated: July 27, 2021)

The anharmonic lattice is a representative example of an interacting, bosonic, many-body system. The self-consistent harmonic approximation has proven versatile for the study of the equilibrium properties of anharmonic lattices. However, the study of dynamical properties therein resorts to an ansatz, whose validity has not yet been theoretically proven. Here, we apply the time-dependent variational principle, a recently emerging useful tool for studying the dynamic properties of interacting many-body systems, to the anharmonic lattice Hamiltonian at finite temperature using the Gaussian states as the variational manifold. We derive an analytic formula for the position-position correlation function and the phonon self-energy, proving the dynamical ansatz of the self-consistent harmonic approximation. We establish a fruitful connection between time-dependent variational principle and the anharmonic lattice Hamiltonian, providing insights in both fields. Our work expands the range of applicability of the time-dependent variational principle to first-principles lattice Hamiltonians and lays the groundwork for the study of dynamical properties of the anharmonic lattice using a fully variational framework.

Introduction — Variational methods form the basis of our understanding of quantum mechanical many-body systems. In a variational method, the wavefunctions or density matrices of a system are parametrized by a set of parameters whose size is much smaller than the dimension of the Hilbert space. Static and time-dependent [1–3] variational methods are being actively used to study interacting many-body model Hamiltonians [4–13].

The anharmonic lattice is a representative example of an interacting bosonic many-body system in materials science. The self-consistent harmonic approximation (SCHA) is a variational method for approximately finding the ground or thermal equilibrium state of an anharmonic lattice Hamiltonian [14, 15]. Recently, a stochastic implementation of SCHA [16–19] was developed and attracted considerable attention. SCHA has been successfully applied to study structural phase transitions [18–21], superconductivity [16, 22–25], and charge density waves [26–31], as well as to the dynamical properties such as the phonon spectral function [20, 21, 32–34] and infrared and Raman spectra [35].

However, SCHA is limited in that one needs to resort to a specific ansatz to study the dynamical properties. It is known that the SCHA ansatz for the position-position Green function is correct in the static limit of zero frequency and the perturbative limit of weak anharmonicity [18]. However, the validity of the SCHA ansatz in the nonperturbative and dynamic regime [20, 21, 33, 35], where the dynamical theory is most necessary, has not been theoretically justified.

In this Letter, we solve this important problem by applying the time-dependent variational principle (TDVP) with Gaussian variational states [7, 13, 36, 37] to the anharmonic lattice Hamiltonian at finite temperature. Gaussian TDVP expands the static variational states of SCHA to states with nonzero momenta. We use the linearized time evolution to derive the position-position correlation function and prove the SCHA dynamical ansatz. We illustrate that the Gaussian TDVP is successful in describing the dynamics because it includes the 2-phonon states as true dynamical excitations. Our work connects the TDVP theory, whose application was mostly focused on model Hamiltonians for cold atoms, with anharmonic lattice dynamics and the SCHA method. Such connection gives fruitful results on both sides. In TDVP theory, the linearized time evolution and the projected Hamiltonian method [4, 6, 9] are two different ways to compute the excitation spectrum, whose superiority over the other varies across systems [4, 7, 13]. We use the anharmonic lattice model to show that only the linearized time evolution gives correct excitation energies in the perturbative limit. On the SCHA side, we illustrate ways to systematically expand the SCHA theory by leveraging recent developments of non-Gaussian TDVP [6, 11, 12].

Self-consistent harmonic approximation — We briefly review the key results of SCHA. Within the adiabatic Born-Oppenheimer approximation, the anharmonic lattice Hamiltonian is

$$\hat{H} = \sum_{a=1}^{N} \frac{p_a^2}{2M_a} + \hat{V}(\hat{r}_1, \ldots, \hat{r}_N).$$

Here, $a$ is the combined index for atoms and Cartesian directions, $N = N_{\text{atm}} \times d$ with $N_{\text{atm}}$ and $d$ the numbers of the atoms and the spatial dimensions, respectively, $M_a$ the atomic mass, $\hat{r}_a$ and $\hat{p}_a$ the position and momentum operators, and $\hat{V}$ the Born-Oppenheimer potential energy. We set $\hbar = 1$.

In SCHA, the true thermal equilibrium state of the
The anharmonic Hamiltonian is approximated by that of a harmonic Hamiltonian $\hat{H}^{(H)}$:
\[
\hat{H}^{(H)} = \sum_{a=1}^{N} \frac{\hat{p}_a^2}{2M_a} + \tilde{V}^{(H)}(\tilde{\mathbf{r}}),
\]
where $\tilde{V}^{(H)}(\tilde{\mathbf{r}})$ is the potential energy in the normal-mode representation. The anharmonic Hamiltonian [Eq. (1)] and the density matrix as the variational manifold:
\[
\hat{H}^{(H)} = \sum_{m=1}^{N} \frac{\omega_m}{2} (\hat{p}_m^2 + \tilde{r}_m^2),
\]
with $\omega_m$ the eigenvalue of the SCHA dynamical matrix, and $\tilde{r}_m$ and $\hat{p}_m$ the normal-mode position and momentum operators. The anharmonic Hamiltonian [Eq. (1)] can be written as
\[
\hat{H} = \sum_{m=1}^{N} \frac{\omega_m}{2} \hat{p}_m^2 + V(\tilde{\mathbf{r}}),
\]
with $V(\tilde{\mathbf{r}}) = \tilde{V}(\tilde{\mathbf{r}})$ the potential energy in the normal-mode representation.

In the normal-mode representation, the SCHA self-consistency equations [18] become
\[
\left\langle \frac{\partial \tilde{V}}{\partial \tilde{r}_m} \right\rangle_0 = 0, \quad \left\langle \frac{\partial^2 \tilde{V}}{\partial \tilde{r}_m \partial \tilde{r}_n} \right\rangle_0 = \omega_m \delta_{m,n}.
\]
Also, since $\hat{\rho}_0$ is a thermal state, we find
\[
\langle \hat{p}_m \rangle_0 = 0, \quad \langle \hat{p}_m \hat{p}_n \rangle_0 = \left( n_m + \frac{1}{2} \right) \delta_{m,n},
\]
with $n_m = 1/(e^{\beta \omega_m} - 1)$ the occupation number.

**Gaussian time-dependent variational principle** — Next, we discuss the general principles of Gaussian TDVP for a multimode bosonic system at finite temperature. We use the set of states obtained by applying a Gaussian unitary transformation $\hat{U}(\mathbf{x})$ to the SCHA density matrix as the variational manifold:
\[
\hat{\rho}(\mathbf{x}) = \hat{U}(\mathbf{x}) \hat{\rho}_0 \hat{U}^\dagger(\mathbf{x}).
\]
Here, $\mathbf{x}$ is a real-valued vector that encodes all the variational parameters. We parametrize the Gaussian transformation as
\[
\hat{U}(\mathbf{x}) = \hat{D}(\alpha) \hat{S}(\beta, \gamma),
\]
where $\hat{D}$ and $\hat{S}$ are the displacement and squeezing operators, respectively:
\[
\hat{D}(\alpha) = \exp \left( \frac{1}{\sqrt{2}} \sum_m (\alpha_m \hat{a}_m^\dagger - \alpha_m^* \hat{a}_m) \right),
\]
\[
\hat{S}(\beta, \gamma) = \exp \left[ \sum_{m,n} \left( b_{mn} (\beta_{mn} \hat{a}_m^\dagger \hat{a}_n - \beta_{mn}^* \hat{a}_m \hat{a}_n^\dagger) + c_{mn} (\gamma_{mn} \hat{a}_m^\dagger \hat{a}_n^\dagger - \gamma_{mn}^* \hat{a}_m \hat{a}_n) \right) \right],
\]
where
\[
b_{mn} = \begin{cases} 1/\sqrt{4(n_m + n_n + 1)} & \text{if } m = n, \\ 1/\sqrt{2(n_m + n_n + 1)} & \text{if } m \neq n, \end{cases}
\]
\[
c_{mn} = 1/\sqrt{2(n_m - n_n)}.
\]
The variational parameters $\alpha_m$, $\beta_{mn}$, and $\gamma_{mn}$ are complex numbers. The parameter $\beta_{mn}$ ($\gamma_{mn}$) is defined only for $m \leq n$ ($m < n$). Here, we assume for simplicity that $\omega_m$’s are nondegenerate and satisfy $\omega_1 < \omega_2 < \cdots < \omega_N$. The total number of complex variational parameters is $N^2 + N$. In the linear response regime, degeneracy does not pose any theoretical difficulty: if modes $m$ and $n$ are degenerate, one just needs to exclude $\gamma_{mn}$ from the set of variational parameters. This exclusion is done because the infinitesimal transformation parametrized by $\gamma_{mn}$ does not change $\hat{\rho}_0$ [38].

Each group of parameters describes a different type of excitation. Parameters $\alpha$, $\beta$, and $\gamma$ correspond to 1-phonon excitations, 2-phonon excitations with two creations or two annihilations of phonons, and 2-phonon excitations with one creation and one annihilation, respectively.

The imaginary parts of the parameters generate dynamics. For example, $\Im \alpha$ generates a finite atomic momentum through the displacement operator. The SCHA theory does not contain these imaginary parameters because the variational states are limited to the thermal state of a harmonic Hamiltonian. In contrast, Gaussian TDVP, which allows both the real and imaginary parts of the variational parameters to vary, naturally allows one to study the dynamics.

We define $\mathbf{x}$, the vector of variational parameters as
\[
\mathbf{x} = (\Re \alpha \ \Im \alpha \ \Re \beta \ \Im \beta \ \Re \gamma \ \Im \gamma)^\dagger.
\]
Since $\hat{\rho}(\mathbf{x} = 0) = \hat{\rho}_0$ is the variational solution that minimizes the SCHA free energy, $\mathbf{x} = 0$ is a stationary point of the variational time evolution [38].

To apply TDVP to mixed states, we map the variational density matrices to wavefunctions by purification [11, 39]. For each physical state in the number basis,
we add an auxiliary state so that the purified wavefunction becomes

$$|\Psi(x)\rangle = \sqrt{\hat{\rho}_0} \otimes 1 |\Phi^+\rangle,$$

(15)

where $\otimes$ denotes a tensor product, and $|\Phi^+\rangle$ is a maximally entangled state [39] between the physical and the auxiliary modes [see Eq. (S15) and related discussions]. For the purified wavefunction, the expectation value of a physical operator $A_0$ is

$$A(x) \equiv \langle \Psi(x)|A_0 \otimes 1|\Psi(x)\rangle = \langle \hat{A}(x) \rangle_0,$$

(16)

where

$$\hat{A}(x) = \hat{U}^\dagger(x) \hat{A}_0 \hat{U}(x).$$

(17)

The variational time evolution is obtained by projecting the true dynamics of the wavefunction to the tangent space of the variational manifold. The tangent space is spanned by the tangent vectors, which at $x = 0$ are

$$|V_\rho\rangle = \left((\partial_\rho \hat{U}) \sqrt{\hat{\rho}_0} \otimes 1\right) |\Phi^+\rangle.$$

(18)

Using the variational linear response theory [13, 38], one can show that the retarded correlation function $G^{(R)}(\omega)$ between operators $\hat{A}$ and $\hat{B}$ is

$$G^{(R)}(\omega)_{\hat{A}\hat{B}}(\omega) = \lim_{\eta \to 0^+} -i(\partial_\rho \hat{B})G^{\mu}_\rho(\omega + i\eta)(\Omega^{\mu\rho}\partial_\rho A).$$

(19)

Here, the matrix Green function $\mathcal{G}(z)$ is defined as

$$(z - i\mathbf{K})\mathcal{G}(z) = 1,$$

(20)

where $\mathbf{K}$ is the linearized time-evolution generator defined as

$$K^{\mu}_\nu = -\Omega^{\mu\rho}\partial_\rho \partial_\nu E,$$

(21)

with $E(x) = \text{Tr}[\hat{\rho}(x)\hat{H}]$. The symplectic form $\Omega$ is defined by

$$\Omega^{\mu\rho} \text{Im} \langle V_\rho|V_\nu\rangle = \frac{1}{2} \delta^{\mu}_\nu.$$

(22)

By computing $\mathbf{K}$ and the corresponding matrix Green function $\mathcal{G}(z)$, one can find the physical correlation function $G^{(R)}_{\hat{A}\hat{B}}(\omega)$ using Eq. (19).

**Anharmonic lattice dynamics** — Now, we study the dynamical properties of the anharmonic lattice Hamiltonian using Gaussian TDVP. First, the symplectic form is [38]

$$\Omega = \begin{pmatrix} 0 & 1 & 0 & 0 & -1 \\ -1 & 0 & 1 & 0 & 0 \\ 0 & -1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 & -1 \\ 0 & 0 & 0 & 0 & 0 \end{pmatrix},$$

(23)

with $\oplus$ the direct sum.

The three matrices correspond to the subspace spanned by the tangent vectors for the variation of $\alpha$, $\beta$, and $\gamma$, respectively. In each matrix, the bases for the first (second) block of rows and columns are the tangent vectors for the real (imaginary) parts of the parameters.

For later use, we define $P_1$, $P_{2+}$, and $P_{2-}$ as the projection operators to the bases of each of the three matrices. The subscripts 1, 2+, and 2− indicate the nature of the tangent vectors: 1-phonon excitations, 2-phonon excitations with two creations or two annihilations, and 2-phonon excitations with one creation and one annihilation. We also define the projection to the whole 2-phonon sector: $P_2 = P_{2+} + P_{2-}$.

Evaluating Eq. (21), we find that the time evolution generator $\mathbf{K}$ is the sum of the non-interacting part, 3-phonon interaction, and 4-phonon interaction (see Sec. S4 C of the Supplementary Material [38]):

$$i\mathbf{K} = \mathbf{H}^{(0)} + \mathbf{V}^{(3)} + \mathbf{V}^{(4)},$$

(24)

where

$$\mathbf{H}^{(0)} = \begin{pmatrix} 0 & i\omega \\ -i\omega & 0 \end{pmatrix} \oplus \begin{pmatrix} 0 & i\omega_+ \\ -i\omega_+ & 0 \end{pmatrix} \oplus \begin{pmatrix} 0 & i\omega_- \\ -i\omega_- & 0 \end{pmatrix},$$

(25)

$$\mathbf{V}^{(3)} = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -i\Phi^{(3)} B & 0 & -i\Phi^{(3)} C & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ -iB\Phi^{(3)} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ -iC\Phi^{(3)} & 0 & 0 & 0 & 0 & 0 \end{pmatrix},$$

(26)

$$\mathbf{V}^{(4)} = \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix} \oplus \begin{pmatrix} 0 & 0 & 0 & 0 \\ -iB\Phi^{(4)} B & 0 & -iB\Phi^{(4)} C & 0 \\ 0 & 0 & 0 & 0 \\ -iC\Phi^{(4)} B & 0 & -iC\Phi^{(4)} C & 0 \end{pmatrix}. $$

(27)

Here, we defined the diagonal matrices:

$$\omega_{m,n} = \omega_m \delta_{m,n},$$

(28)

$$[\omega_{\pm}]_{mn,pq} = (\omega_m \pm \omega_n) \delta_{mn,pq},$$

(29)

$$B_{mn,pq} = b_{mn}(n_m + n_n + 1) \delta_{mn,pq},$$

(30)

$$C_{mn,pq} = -c_{mn}(n_m - n_n) \delta_{mn,pq}.$$  

(31)

The implicit summation over a pair of mode indices $m$ and $n$ implies the constraint $m \leq n$ unless otherwise noted. We also defined the anharmonicity tensor

$$\Phi^{(m)}_{n_1,\ldots,n_m} = \left\langle \frac{\partial^m V}{\partial r_{n_1} \cdots \partial r_{n_m}} \right\rangle_0.$$
The non-interacting part $H^{(0)}$ describes the free evolution of 1- and 2-phonon excitations in the SCHA Hamiltonian. The 3-phonon interaction $V^{(3)}$ couples the 1- and 2-phonon excitations. The 4-phonon interaction $V^{(4)}$ couples the 2-phonon excitations to each other.

Finally, we study the linear response of the anharmonic lattice and compute the position-position correlation function. First, we define the non-interacting Green function $G^{(0)}$:

$$ (z - H^{(0)})G^{(0)}(z) = 1. \quad (33) $$

From Eq. (25), one finds

$$ G^{(0)}(z) = G_1^{(0)}(z) \oplus G_{2+}^{(0)}(z) \oplus G_{2-}^{(0)}(z), \quad (34) $$

where

$$ G_1^{(0)}(z) = \frac{1}{z^2 - \omega^2} \begin{pmatrix} z & i \omega \\ -i \omega & z \end{pmatrix}, \quad (35) $$

and

$$ G_{2 \pm}^{(0)}(z) = \frac{1}{z^2 - \omega_{\pm}^2} \begin{pmatrix} z & i \omega_{\pm} \\ -i \omega_{\pm} & z \end{pmatrix}. \quad (36) $$

Next, we include the 4-phonon interaction $V^{(4)}$. We define the partially interacting Green function $G^{(4)}(z)$:

$$ (z - H^{(0)} - V^{(4)})G^{(4)}(z) = 1. \quad (37) $$

Since the 4-phonon interaction $V^{(4)}$ does not act on the 1-phonon sector, we find

$$ P_1G^{(4)}P_1 = G_1^{(0)} \oplus 0. \quad (38) $$

For the 2-phonon sector, we obtain the Dyson equation

$$ P_2G^{(4)}P_2 = P_2G_2^{(0)}P_2 + P_2G^{(4)}V^{(4)}G^{(0)}P_2. \quad (39) $$

Finally, we study the fully interacting Green function $G(z)$ by including the 3-phonon interaction $V^{(3)}$. From the definitions of $G$ and $G^{(4)}$, we obtain the Dyson equation

$$ P_1GP_1 = P_1G^{(4)}P_1 + P_1G^{(4)}P_1V^{(3)}P_2V^{(4)}G^{(0)}P_1. \quad (40) $$

One can solve the Dyson equations [Eqs. (39, 40)] to find [38]

$$ P_1GP_1 = G_1^{(0)} \quad (41) $$

$$ -G_1^{(0)} \left( \sum_{s,s', \pm} \Phi^{(3)}B_s[G^{(4)}]_{s's}B_s'\Phi^{(3)} \right) P_1GP_1. $$

Here, we defined $B_+ = B$ and $B_- = C$. In Eq. (41), we omitted the direct sum of the zero matrix in the $P_2$ subspace for brevity.

From Eqs. (S1, S2), one finds that the matrix elements for the position operator is nonzero only for the variation of $\Re \alpha$:

$$ \partial_\mu r = (1 0 0 0 0)^T. \quad (42) $$

Then, from Eqs. (19, 41), one can derive the Dyson equation for the interacting retarded position-position correlation function [38]:

$$ C^{(R)}_{rr} = C^{(R)}_{rr} + G^{(R)}_{rr} \Pi_{rr}G^{(R)}_{rr}. \quad (43) $$

The self-energy is

$$ \Pi_{rr}(z) = \Phi^{(3)}W(\bar{z} - \Phi^{(4)}W)^{-1}\Phi^{(3)}, \quad (44) $$

where $W$ is a diagonal matrix defined as

$$ W = \sum_{s=\pm} B_s \frac{\omega_s}{z^2 - \omega^2_s} B_s. \quad (45) $$

By recovering the mode indices and defining

$$ \chi_{mn,pq}(z) = \frac{1}{2} \left[ \frac{(\omega_m + \omega_n)(n_m + n_n + 1)}{(\omega_m + \omega_n)^2 - z^2} \right. $$

$$ - \left. \frac{(\omega_m - \omega_n)(n_m - n_n)}{(\omega_m - \omega_n)^2 - z^2} \right] \delta_{mn,pq}. \quad (46) $$

one can rewrite Eq. (44) in a form identical to the SCHA dynamical ansatz [38]:

$$ \Pi_{rr}(z) = \Phi^{(3)} \left( -\frac{1}{2} \chi(z) \right) \left[ 1 - \Phi^{(4)} \left( -\frac{1}{2} \chi(z) \right) \right]^{-1} \Phi^{(3)}. \quad (47) $$

In Eq. (47), the implicit summation over the mode indices is done without any constraints. Equation (47) and its derivation is the main result of this Letter. When transformed to the Cartesian representation, Eq. (47) becomes identical to the SCHA dynamical ansatz [Eq. (70) of Ref. 18]. We emphasize that we rigorously derived the phonon self-energy $\Pi_{rr}(z)$ using Gaussian TDVP. Our derivation theoretically proves the SCHA dynamical ansatz.

The physical interpretation of the self-energy formula we obtained varies significantly from that of the SCHA dynamical ansatz. In Gaussian TDVP, the 2-phonon states are true dynamical excitations. However, in SCHA, the 2-phonon states do not have their own dynamics and appear only indirectly through the position dependence of the SCHA force constants. The presence of the dynamical 2-phonon excitations is the essential reason why Gaussian TDVP can describe dynamical properties while the SCHA theory cannot.

For example, the phonon lifetime is an important dynamical property of an anharmonic lattice. In Gaussian TDVP, the 1-phonon states acquire a finite lifetime by decaying to the continuum of 2-phonon states through the 3-phonon interaction. In contrast, in SCHA, there are no
Perturbation theory $\omega_0 - \lambda^2 a_0^2/12\omega_0 + O(\lambda^4)$
Linearized time evolution $\omega_0 - \lambda^2 a_0^2/12\omega_0 + O(\lambda^4)$
Projected Hamiltonian $\omega_0 - \lambda^2 a_0^2/16\omega_0 + O(\lambda^4)$

| Process | Perturbation theory | Linearized time evolution | Projected Hamiltonian |
|---------|---------------------|---------------------------|-----------------------|
| $t_1 < t_2$ | $\omega_0 - \lambda^2 a_0^2/12\omega_0 + O(\lambda^4)$ | $\omega_0 - \lambda^2 a_0^2/12\omega_0 + O(\lambda^4)$ | $\omega_0 - \lambda^2 a_0^2/16\omega_0 + O(\lambda^4)$ |
| $t_2 < t_1$ | $\omega_0 - \lambda^2 a_0^2/12\omega_0 + O(\lambda^4)$ | $\omega_0 - \lambda^2 a_0^2/12\omega_0 + O(\lambda^4)$ | $\omega_0 - \lambda^2 a_0^2/16\omega_0 + O(\lambda^4)$ |

In contrast, in the linearized time evolution, the coupling describes a process involving a 4-phonon state. Since the Gaussian projected Hamiltonian method completely neglects the 3- and 4-phonon excitations, it only includes the process described in Fig. 1(a), not that of Fig. 1(b). In contrast, in the linearized time evolution, the coupling of the 1- and 2-phonon states to virtual 3- and 4-phonon states is included by an additional term related to the derivative of the tangent vectors, which is neglected in the projected Hamiltonian method [13]. Thanks to this additional term, the linearized time evolution gives the correct perturbative limit, while the projected Hamiltonian cannot.

A promising future research direction based on our study is a rigorous, systematic expansion of the SCHA method to go beyond the harmonic approximation by using non-Gaussian variational transformations [6]. Also, the use of mixed fermionic and bosonic variational states [6, 11, 12] will allow the study of nontrivial electron-phonon correlation such as in phonon-mediated superconductivity or polarons in anharmonic lattices.

Recently, Monacelli and Mauri also reported a proof of the SCHA dynamical self-energy in an independent work [41]. While Ref. [41] additionally presents a numerical algorithm to compute the correlation functions, our work focuses on the link between TDVP and SCHA. Also, while the proof for the finite-temperature case in Ref. [41] is based on an analogy with the $T=0$ case, our proof uses purification to rigorously derive the finite-temperature equation of motion. The results of the two works are consistent when there is an overlap.

**Conclusion** — In summary, we developed a variational theory for the dynamical properties of anharmonic lattices using Gaussian TDVP, establishing a firm link between Gaussian TDVP and SCHA. We provided solid theoretical groundwork for the use of the SCHA dynamical ansatz in studying spectral properties. The presence of dynamical 2-phonon excitations in Gaussian TDVP was essential to obtain correct dynamics of the 1-phonon excitations. We compared the linearized time evolution and the projected Hamiltonian methods to find that only the former is correct in the perturbative limit. Our work establishes a useful connection between TDVP and SCHA, allowing further developments in both fields.

This work was supported by the Creative-Pioneering Research Program through Seoul National University, Korean NRF No-2020R1A2C1014760, and the Institute for Basic Science (No. IBSR009-D1).

---

* jaemo.lihm@gmail.com
† cheolhwan@snu.ac.kr
[1] P. A. M. Dirac, “Note on exchange phenomena in the thomas atom,” Mathematical Proceedings of the Cambridge Philosophical Society 26, 376–385 (1930).
[2] P Kramer, “A review of the time-dependent variational principle,” Journal of Physics: Conference Series 99, 012009 (2008).
[3] Jutho Haegeman, J. Ignacio Cirac, Tobias J. Osborne, Iztok Pižorn, Henri Verschelde, and Frank Verstraete, “Time-dependent variational principle for quantum lat-
tices," Phys. Rev. Lett. 107, 070601 (2011).
[4] Jutho Haegeman, Tobias J. Osborne, and Frank Verstraete, “Post-matrix product state methods: To tangent space and beyond,” Phys. Rev. B 88, 075133 (2013).
[5] Yuto Ashida, Tao Shi, Mari Carmen Bañuls, J. Ignacio Cirac, and Eugene Demler, “Solving quantum impurity problems in and out of equilibrium with the variational approach,” Phys. Rev. Lett. 121, 026805 (2018).
[6] Tao Shi, Eugene Demler, and J. Ignacio Cirac, “Variational study of fermionic and bosonic systems with non-Gaussian states: Theory and applications,” Annals of Physics 390, 245–302 (2018).
[7] Tommaso Guaita, Lucas Hackl, Tao Shi, Claudius Hubig, Eugene Demler, and J. Ignacio Cirac, “Gaussian time dependent variational principle for the Bose-Hubbard model,” Physical Review B 100, 094529 (2019).
[8] Nicholas Rivera, Johannes Flick, and Prineha Narang, “Variational theory of nonrelativistic quantum electrodynamics,” Phys. Rev. Lett. 122, 193003 (2019).
[9] Laurens Vanderstraeten, Jutho Haegeman, and Frank Verstraete, “Simulating excitation spectra with projected entangled pair states,” Phys. Rev. B 99, 165121 (2019).
[10] Laurens Vanderstraeten, Jutho Haegeman, and Frank Verstraete, “Tangent-space methods for uniform matrix product states,” SciPost Phys. Lect. Notes, 7 (2019).
[11] Tao Shi, Eugene Demler, and J. Ignacio Cirac, “Variational approach for many-body systems at finite temperature,” Phys. Rev. Lett. 125, 180602 (2020).
[12] Yao Wang, Ilya Esterlis, Tao Shi, J. Ignacio Cirac, and Eugene Demler, “Zero-temperature phases of the two-dimensional hubbard-holstein model: A non-Gaussian exact diagonalization study,” Phys. Rev. Research 2, 043258 (2020).
[13] Lucas Hackl, Tommaso Guaita, Tao Shi, Jutho Haegeman, Eugene Demler, and Ignacio Cirac, “Geometry of variational methods: dynamics of closed quantum systems,” SciPost Physics 9 (2020), 10.21468/scipost-phys.9.4.048.
[14] D.J. Hooton, “II. A new treatment of anharmonicity in lattice thermodynamics: I,” The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science 46, 422–432 (1955).
[15] Ion Errea, Bruno Rousseau, and Aitor Bergara, “Anharmonic Stabilization of the High-Pressure Simple Cubic Phase of Calcium,” Physical Review Letters 106, 165501 (2011).
[16] Ion Errea, Matteo Calandra, and Francesco Mauri, “First-Principles Theory of Anharmonicity and the Inverse Isotope Effect in Superconducting Palladium-Hydride Compounds,” Physical Review Letters 111, 177002 (2013).
[17] Ion Errea, Matteo Calandra, and Francesco Mauri, “Anharmonic free energies and phonon dispersions from the stochastic self-consistent harmonic approximation: Application to platinum and palladium hydrides,” Physical Review B 89, 064302 (2014).
[18] Raffaello Bianco, Ion Errea, Lorenzo Paulatto, Matteo Calandra, and Francesco Mauri, “Second-order structural phase transitions, free energy curvature, and temperature-dependent anharmonic phonons in the self-consistent harmonic approximation: Theory and stochastic implementation,” Physical Review B 96, 014111 (2017).
[19] Lorenzo Monacelli, Ion Errea, Matteo Calandra, and Francesco Mauri, “Pressure and stress tensor of complex anharmonic crystals within the stochastic self-consistent harmonic approximation,” Physical Review B 98, 024106 (2018).
[20] Raffaello Bianco, Ion Errea, Matteo Calandra, and Francesco Mauri, “High-pressure phase diagram of hydrogen and deuterium sulfides from first principles: Structural and vibrational properties including quantum and anharmonic effects,” Physical Review B 97, 214101 (2018).
[21] Unai Aseginolaza, Raffaello Bianco, Lorenzo Monacelli, Lorenzo Paulatto, Matteo Calandra, Francesco Mauri, Aitor Bergara, and Ion Errea, “Phonon Collapse and Second-Order Phase Transition in Thermoelectric SnSe,” Physical Review Letters 122, 075901 (2019).
[22] Ion Errea, Matteo Calandra, Chris J. Pickard, Joseph Nelson, Richard J. Needs, Yinwei Li, Hanyu Liu, Yunwei Zhang, Yannig Ma, and Francesco Mauri, “High-Pressure Hydrogen Sulffide from First Principles: A Strongly Anharmonic Phonon-Mediated Superconductor,” Physical Review Letters 114, 157004 (2015).
[23] Ion Errea, Matteo Calandra, Chris J. Pickard, Joseph R. Nelson, Richard J. Needs, Yinwei Li, Hanyu Liu, Yunwei Zhang, Yannig Ma, and Francesco Mauri, “Quantum hydrogen-bond symmetrization in the superconducting hydrogen sulfide system,” Nature 532, 81–84 (2016).
[24] Miguel Borinaga, Unai Aseginolaza, Ion Errea, Matteo Calandra, Francesco Mauri, and Aitor Bergara, “Anharmonicity and the isotope effect in superconducting lithium at high pressures: A first-principles approach,” Physical Review B 96, 184505 (2017).
[25] Ion Errea, Francesco Belli, Lorenzo Monacelli, Antonio Sanna, Takashi Koretsune, Terumasa Tadano, Raffaello Bianco, Matteo Calandra, Ryotaro Arita, Francesco Mauri, and José A. Flores-Livas, “Quantum crystal structure in the 250-kelvin superconducting lanthanum hydride,” Nature 578, 66–69 (2020).
[26] Maxime Leroux, Ion Errea, Mathieu Le Tacon, Sofia-Michaela Soulouliou, Gaston Garbarino, Laurent Cario, Alexey Bosak, Francesco Mauri, Matteo Calandra, and Pierre Rodière, “Strong anharmonicity induces quantum melting of charge density wave in 2H - NbSe2 under pressure,” Physical Review B 92, 140303 (2015).
[27] Raffaello Bianco, Ion Errea, Lorenzo Monacelli, Matteo Calandra, and Francesco Mauri, “Quantum Enhancement of Charge Density Wave in NbS2 in the Two-Dimensional Limit,” Nano Letters 19, 3098–3103 (2019).
[28] Jianqiang Sky Zhou, Lorenzo Monacelli, Raffaello Bianco, Ion Errea, Francesco Mauri, and Matteo Calandra, “Anharmonicity and Doping Melt the Charge Density Wave in Single-Layer TiSe2,” Nano Letters 20, 4809–4815 (2020).
[29] Raffaello Bianco, Lorenzo Monacelli, Matteo Calandra, Francesco Mauri, and Ion Errea, “Weak Dimensionality Dependence and Dominant Role of Ionic Fluctuations in the Charge-Density-Wave Transition of NbSe2,” Physical Review Letters 125, 106101 (2020).
[30] Jianqiang Sky Zhou, Raffaello Bianco, Lorenzo Monacelli, Ion Errea, Francesco Mauri, and Matteo Calandra, “Theory of the thickness dependence of the charge density wave transition in 1T-TiTe2,” 2D Materials 7, 045032 (2020).
[31] Josu Diego, AH Said, SK Mahatha, Raffaello Bianco, Lorenzo Monacelli, Matteo Calandra, Francesco Mauri,
K Rossnagel, Ion Errea, and S Blanco-Canosa, “van der waals driven anharmonic melting of the 3D charge density wave in VSe$_2$,” Nature communications 12, 1–7 (2021).

[32] Lorenzo Paulatto, Ion Errea, Matteo Calandra, and Francesco Mauri, “First-principles calculations of phonon frequencies, lifetimes, and spectral functions from weak to strong anharmonicity: The example of palladium hydrides,” Physical Review B 91, 054304 (2015).

[33] Unai Aseginolaza, Raffaello Bianco, Lorenzo Monacelli, Lorenzo Paulatto, Matteo Calandra, Francesco Mauri, Aitor Bergara, and Ion Errea, “Strong anharmonicity and high thermoelectric efficiency in high-temperature SnS from first principles,” Physical Review B 100, 214307 (2019).

[34] Unai Aseginolaza, Tommaso Cea, Raffaello Bianco, Lorenzo Monacelli, Matteo Calandra, Aitor Bergara, Francesco Mauri, and Ion Errea, “Bending rigidity and sound propagation in graphene,” arXiv:2005.12047 [cond-mat] (2020), arXiv:2005.12047 [cond-mat].

[35] Lorenzo Monacelli, Ion Errea, Matteo Calandra, and Francesco Mauri, “Black metal hydrogen above 360 GPa driven by proton quantum fluctuations,” Nature Physics 17, 63 (2021).

[36] Christian Weedbrook, Stefano Pirandola, Raúl García-Patrón, Nicolas J. Cerf, Timothy C. Ralph, Jeffrey H. Shapiro, and Seth Lloyd, “Gaussian quantum information,” Rev. Mod. Phys. 84, 621–669 (2012).

[37] Gerardo Adesso, Sammy Ragy, and Antony R. Lee, “Continuous variable quantum information: Gaussian states and beyond,” Open Systems & Information Dynamics 21, 1440001 (2014).

[38] See Supplemental Material, which includes Refs. [42], at [URL will be inserted by publisher] for the analysis of the variational parameters, technical details of the derivations, a note on degeneracies, a note on the zero-temperature case, and the calculation of the excitation energy of the single-mode anharmonic Hamiltonian.

[39] Michael A. Nielsen and Isaac L. Chuang, Quantum Computation and Quantum Information (Cambridge University Press, Cambridge, England, 2000).

[40] http://gkantonius.github.io/feynman/, accessed: 2020-05-31.

[41] Lorenzo Monacelli and Francesco Mauri, “Time-dependent self-consistent harmonic approximation: Anharmonic nuclear quantum dynamics and time correlation functions,” Phys. Rev. B 103, 104305 (2021).

[42] R Pathria and PD Beale, Statistical Mechanics, 3rd ed. (Academic Press, Boston, MA, 2011).
CONTENTS

S1. Physical meaning of the variational parameters 1
S2. Linear response formulation of TDVP at finite temperatures 3
S3. Derivation of the symplectic form 5
S4. Derivatives of the energy 6
   A. Useful identities 7
   B. First derivatives 8
   C. Second derivatives 9
S5. Calculation of the interacting Green function 14
   A. Partially interacting Green function: 4-phonon interaction 14
   B. Fully interacting Green function: 3-, 4-phonon interactions 15
S6. Derivation of the SCHA ansatz from the TDVP self-energy 16
S7. Degenerate and near-degenerate modes 17
S8. Zero temperature case 18
S9. Single-mode anharmonic Hamiltonian 18
References 19

S1. PHYSICAL MEANING OF THE VARIATIONAL PARAMETERS

In this section, we detail the physical meaning of the transformations and the tangent vectors by inspecting the infinitesimal transformation of the position and momentum operators. Using the definition of the operator transformation [Eq. (17)] and \( \partial_\mu \hat{U} \big|_{x=0} = - \partial_\mu \hat{U} \big|_{x=0} \), one finds that the derivative of \( \hat{A}(x) \) at \( x = 0 \) is

\[
\partial_\mu \hat{A}(x) \bigg|_{x=0} = \left[ \hat{A}(0), \partial_\mu \hat{U} \big|_{x=0} \right].
\]

(S1)

Hereafter, all derivatives with respect to the variational parameters are evaluated at \( x = 0 \) unless otherwise stated.

The derivatives of the Gaussian transformation operator at \( x = 0 \) are

\[
\frac{\partial \hat{U}}{\partial \alpha_m} = \frac{1}{\sqrt{2}} (\hat{a}_m^\dagger - \hat{a}_m) = -i \hat{p}_m,
\]

(S2)
\[
\frac{\partial \hat{U}}{\partial \alpha_{im}} = \frac{i}{\sqrt{2}} (\hat{a}_m^\dagger + \hat{a}_m) = i \hat{r}_m, \quad (S3)
\]

\[
\frac{\partial \hat{U}}{\partial \beta_{mn}} = b_{mn} (\hat{a}_m^\dagger \hat{a}_n^\dagger - \hat{a}_n \hat{a}_m) = -ib_{mn}(\hat{r}_m \hat{p}_n + \hat{p}_m \hat{r}_n), \quad (S4)
\]

\[
\frac{\partial \hat{U}}{\partial \beta_{im}} = i b_{mn} (\hat{a}_m^\dagger \hat{a}_n^\dagger + \hat{a}_n \hat{a}_m) = i b_{mn}(\hat{r}_m \hat{r}_n - \hat{p}_m \hat{p}_n), \quad (S5)
\]

\[
\frac{\partial \hat{U}}{\partial \gamma_{mn}} = c_{mn} (\hat{a}_m^\dagger \hat{a}_{n} - \hat{a}_n^\dagger \hat{a}_m) = ic_{mn}(\hat{r}_m \hat{p}_n - \hat{p}_m \hat{r}_n), \quad (S6)
\]

\[
\frac{\partial \hat{U}}{\partial \gamma_{im}} = -ic_{mn}(\hat{a}_m \hat{a}_n^\dagger + \hat{a}_n \hat{a}_m^\dagger) = -ic_{mn}(\hat{r}_m \hat{r}_n + \hat{p}_m \hat{p}_n). \quad (S7)
\]

We calculate how the position and momentum operators transform for an infinitesimal change of each variational parameter. For conciseness, we write the real and imaginary parts of the variational parameters as follows:

\[
\alpha^r_m \equiv \text{Re} \alpha_m, \quad \beta^r_{mn} \equiv \text{Re} \beta_{mn}, \quad \gamma^r_{mn} \equiv \text{Re} \gamma_{mn}, \quad (S8)
\]

\[
\alpha^i_m \equiv \text{Im} \alpha_m, \quad \beta^i_{mn} \equiv \text{Im} \beta_{mn}, \quad \gamma^i_{mn} \equiv \text{Im} \gamma_{mn}.
\]

First, for the displacement parameter \( \alpha \), the infinitesimal transformation of the position and momentum operators are

\[
\left. \frac{\partial \hat{r}_p(x)}{\partial \alpha^r_m} \right|_{x=0} = \delta_{m,p}, \quad \left. \frac{\partial \hat{p}(x)}{\partial \alpha^r_m} \right|_{x=0} = 0, \quad (S9)
\]

\[
\left. \frac{\partial \hat{r}_p(x)}{\partial \alpha^i_m} \right|_{x=0} = 0, \quad \left. \frac{\partial \hat{p}(x)}{\partial \alpha^i_m} \right|_{x=0} = \delta_{m,p}. \quad (S10)
\]

For the real part of the squeezing parameters \( \beta \) and \( \gamma \), the infinitesimal transformation of \( \hat{r} \) and \( \hat{p} \) are

\[
\left. \frac{\partial \hat{r}_p(x)}{\partial \beta^r_{mn}} \right|_{x=0} = b_{mn}(\hat{r}_m \delta_{n,p} + \hat{r}_n \delta_{m,p}), \quad \left. \frac{\partial \hat{p}(x)}{\partial \beta^r_{mn}} \right|_{x=0} = b_{mn}(-\hat{p}_m \delta_{n,p} - \hat{p}_n \delta_{m,p}), \quad (S11)
\]

\[
\left. \frac{\partial \hat{r}_p(x)}{\partial \gamma^r_{mn}} \right|_{x=0} = c_{mn}(-\hat{r}_m \delta_{n,p} + \hat{r}_n \delta_{m,p}), \quad \left. \frac{\partial \hat{p}(x)}{\partial \gamma^r_{mn}} \right|_{x=0} = c_{mn}(-\hat{p}_m \delta_{n,p} + \hat{p}_n \delta_{m,p}). \quad (S12)
\]

Finally, for the imaginary part of the squeezing parameters \( \beta \) and \( \gamma \), the infinitesimal transformation of \( \hat{r} \) and \( \hat{p} \) are

\[
\left. \frac{\partial \hat{r}_p(x)}{\partial \beta^i_{mn}} \right|_{x=0} = b_{mn}(\hat{p}_m \delta_{n,p} + \hat{p}_n \delta_{m,p}), \quad \left. \frac{\partial \hat{p}(x)}{\partial \beta^i_{mn}} \right|_{x=0} = b_{mn}(\hat{r}_m \delta_{n,p} + \hat{r}_n \delta_{m,p}), \quad (S13)
\]

\[
\left. \frac{\partial \hat{r}_p(x)}{\partial \gamma^i_{mn}} \right|_{x=0} = c_{mn}(\hat{p}_m \delta_{n,p} + \hat{p}_n \delta_{m,p}), \quad \left. \frac{\partial \hat{p}(x)}{\partial \gamma^i_{mn}} \right|_{x=0} = -c_{mn}(\hat{r}_m \delta_{n,p} + \hat{r}_n \delta_{m,p}). \quad (S14)
\]

From Eqs. (S9-S14), one can understand the role of each variational parameter. The real part of the displacement parameter \( \alpha^r_m \), parametrizes the displacement of the position operator for mode \( m \). These \( N \) degrees of freedom correspond to the center position \( \hat{R} \) in the SCHA harmonic Hamiltonian. The real parts of the squeezing parameters, \( \beta^r_{mn} \) and \( \gamma^r_{mn} \), parametrize the change in the normal mode frequency and eigenvectors. Especially, \( \gamma^r_{mn} \) parametrizes the linear combination of the two eigenmodes \( m \) and \( n \).

If modes \( m \) and \( n \) are nondegenerate, setting \( \gamma^r_{mn} \neq 0 \) mixes two modes with different frequencies, inducing a nontrivial transformation of the thermal density matrix. In contrast, if modes \( m \) and \( n \) are degenerate (i.e. \( \omega_m = \omega_n \)), the linear combination parametrized by \( \gamma^r_{mn} \) is a gauge transformation that does not change the density matrix. Hence, it is justified to exclude \( \gamma^r_{mn} \) from the variational parameters when modes \( m \) and \( n \) are degenerate, as mentioned in the main text. From a theoretical point of view, including \( \gamma_{mn} \) in the set of variational parameters for degenerate modes \( m \) and \( n \) makes the symplectic form [Eq. (22) of the main text] noninvertible and thus should be avoided [S1].

The imaginary parts of the Gaussian parameters generate dynamics of the variational states. The displacement parameter \( \alpha^i_m \) parametrizes the generation of finite atomic momentum. The squeezing parameters \( \beta^i_{mn} \) and \( \gamma^i_{mn} \) parametrize the linear combination of the position coordinates with the momentum coordinates and vice versa.
S2. LINEAR RESPONSE FORMULATION OF TDVP AT FINITE TEMPERATURES

In this section, we derive and summarize the key results of the linear response formulation of TDVP at finite temperatures, following Ref. [S1].

In Eq. (15) of the main text, we mapped the variational density matrices to pure state wavefunctions by purification. The maximally entangled state $|\Phi^+\rangle$ is defined as

$$|\Phi^+\rangle = \sum_{n_1, \ldots, n_N} |n_1, \ldots, n_N\rangle \otimes |n_1, \ldots, n_N\rangle.$$  \hfill (S15)

Thanks to the unitarity of $\hat{U}$, the variational wavefunction $|\Psi(x)\rangle$ is always normalized to unity. The original density matrix is recovered by taking a partial trace of the auxiliary system:

$$\hat{\rho}(x) = \text{Tr}_{\text{aux}} |\Psi(x)\rangle \langle \Psi(x)|.$$ \hfill (S16)

Note that although $|\Psi(0)\rangle$ is a purification of the thermal state $\hat{\rho}_0$ of the harmonic Hamiltonian $\hat{H}^{(H)}$, it is not a stationary state of the time evolution with $\hat{H}^{(H)}$:

$$(e^{-i\hat{H}^{(H)} t} \otimes 1) |\Psi(0)\rangle = (\sqrt{\hat{\rho}_0} e^{-i\hat{H}^{(H)} t} \otimes 1) |\Phi^+\rangle$$

$$= (\sqrt{\hat{\rho}_0} \otimes e^{-i\hat{H}^{(H)} t}) |\Phi^+\rangle$$

$$\neq |\Psi(0)\rangle e^{i\phi(t)}$$ \hfill (S17)

for any choice of the phase $\phi(t)$. In the second equality of Eq. (S17), we used the fact that $\hat{H}^{(H)}$ is diagonal in the eigenmode basis. Still, the corresponding density matrix that is obtained by taking the partial trace of the auxiliary system is time-independent. Hence, the time evolution of the purified wavefunction is not a true dynamics in the physical system. It is an auxiliary dynamics that occurs due to the non-uniqueness of the purification up to a unitary transformation at the auxiliary system. This artificial dynamics does not occur in our variational approach because we do not allow any variational degree of freedom to the auxiliary system.

The time evolution of the variational wavefunction is obtained by projecting the change in the wavefunction to the tangent space of the variational manifold. The tangent space is spanned by the tangent vectors, which are the derivatives of the variational wavefunction orthogonalized to the original wavefunction. Formally, the tangent vectors are defined as

$$|V_\mu(x)\rangle = \hat{Q}(x) \left. \frac{\partial |\Psi(x)\rangle}{\partial x^\mu} \right|_x.$$ \hfill (S18)

where $\hat{Q}(x)$ a projection operator:

$$\hat{Q}(x) = 1 - |\Psi(x)\rangle \langle \Psi(x)|.$$ \hfill (S19)

According to TDVP, the dynamics of the variational parameters can be described by a classical Hamilton equation of motion. To determine the equation of motion, we need the symplectic form and the derivatives of the energy expectation value $E(x) = \langle \Psi(x) | H | \Psi(x) \rangle$ [S1].

The symplectic form $\Omega^{\mu\nu}(x)$ is the inverse of $\omega_{\mu\nu}(x)$, which is twice the imaginary part of the inner product of the tangent vectors:

$$\Omega^{\mu\rho}(x) \omega_{\mu\nu}(x) = \delta^\rho_\nu,$$ \hfill (S20)

$$\omega_{\mu\nu}(x) = 2 \text{Im} \langle V_\mu(x)|V_\nu(x)\rangle.$$ \hfill (S21)

We use Greek indices to denote the components of the real-valued vector $x$ defined in Eq. (14) of the main text. We use Einstein’s summation convention for repeated indices.

According to the Lagrangian action principle, the equation of motion of the variational parameters is [S1, S2]

$$\frac{dx^\mu}{dt} = -\Omega^{\mu\nu}(x) \left. \frac{\partial E(x)}{\partial x^\nu} \right|_x.$$ \hfill (S22)

We note that since the Gaussian variational manifold is a Kähler manifold, the Lagrangian, McLachlan, and Dirac-Frenkel TDVP equations are all equivalent [S1].
Now, we illustrate how to compute dynamical and spectral properties using the linear response formulation of TDVP. As we are interested only in small changes of the wavefunction around the stationary state, we linearize the equation of motion Eq. (S22) around \( x = 0 \) to find \[ S1–S3 \]

\[ \frac{dx^\mu}{dt} = K^\mu_\nu x^\nu, \]  

(S23)

where the linearized time-evolution generator \( K \) is

\[ K^\mu_\nu = \frac{\partial}{\partial x^\nu} \left( -\Omega^\mu\rho(x) \frac{\partial E}{\partial x^\rho} \right) \bigg|_{x=0} = -\Omega^\mu\rho(x = 0) \frac{\partial^2 E}{\partial x^\rho \partial x^\nu} \bigg|_{x=0}, \]  

(S24)

as shown in Eq. (21) of the main text. Here, we used \( \frac{\partial E}{\partial x^\rho} \bigg|_{x=0} = 0 \) which is true because \( x = 0 \) is a stationary point. From now on, we denote \( \frac{\partial}{\partial x^\mu} \) by \( \partial_{\mu} \). Also, we use \( \Omega_{\mu\rho} \) to refer to \( \Omega^\mu\rho(x = 0) \) unless otherwise noted. The solution of the linearized equation of motion is

\[ x^\mu(t) = [d\Phi(t)]^\mu_\nu x^\nu(0), \]  

(S25)

where \( d\Phi(t) \) is the linearized free evolution flow defined as

\[ d\Phi(t) = e^{Kt}. \]  

(S26)

Let us consider a standard linear response setting, where an infinitesimal time-dependent perturbation is added to the Hamiltonian:

\[ \hat{H}_\epsilon(t) = \hat{H} + \epsilon \varphi(t) \hat{A}. \]  

(S27)

Here, \( \hat{A} \) is an arbitrary Hermitian operator in the Hilbert space of purified wavefunctions, \( \varphi(t) \) is a real-valued function, and \( \epsilon \) is a real variable parametrizing the strength of the perturbation. We write the solution of the corresponding variational time evolution as \( |\Psi_\epsilon(t)\rangle \equiv |\Psi(x_\epsilon(t))\rangle \) .

The linear response of the variational parameter is defined as

\[ \delta_A x^\mu(t) = \frac{d}{d\epsilon} x^\mu_\epsilon(t) \bigg|_{\epsilon=0}. \]  

(S28)

According to Proposition 8 of Ref. [S1], \( \delta_A x^\mu(t) \) is given as

\[ \delta_A x^\mu(t) = -\Omega^\nu\rho \partial_{\rho} A \int_{-\infty}^{t} dt' [d\Phi(t - t')]^\mu_\nu \varphi(t'), \]  

(S29)

where

\[ \partial_{\rho} A \equiv \frac{\partial}{\partial x^\rho} \langle \Psi(x) | \hat{A} | \Psi(x) \rangle \bigg|_{x=0}. \]  

(S30)

The linear response of the expectation value of an operator \( \hat{B} \) at time \( t \) is [S1]

\[ \delta_A B(t) = \frac{d}{d\epsilon} \langle \Psi_\epsilon(t) | \hat{B} | \Psi_\epsilon(t) \rangle \bigg|_{\epsilon=0} = \delta_A x^\mu(t) \partial_{\mu} B \]  

(S31)

\[ = - (\partial_{\mu} B)(\Omega^\nu\rho \partial_{\rho} A) \int_{-\infty}^{t} dt' [d\Phi(t - t')]^\mu_\nu \varphi(t'). \]

Now, we use the spectral decomposition of \( K \) to compute \( d\Phi(t) \). One can decompose \( iK \) with eigenvalues \( \lambda_l \), eigenvectors \( \mathcal{E}^\mu(\lambda_l) \) and dual eigenvectors \( \overline{\mathcal{E}}_\nu(\lambda_l) \) [S1]:

\[ iK^\mu_\nu = \sum_l \lambda_l \mathcal{E}^\mu(\lambda_l) \overline{\mathcal{E}}_\nu(\lambda_l). \]  

(S32)

The dual eigenvectors satisfy

\[ \overline{\mathcal{E}}_\mu(\lambda_l) \mathcal{E}^\mu(\lambda_{l'}) = \delta_{l,l'}. \]  

(S33)
Then, the linearized free evolution flow becomes
\[
[d\Phi(t)]^\mu_\nu = \sum_l e^{-i\lambda_l t} \mathcal{E}^\mu(\lambda_l) \mathcal{E}^\nu(\lambda_l). \tag{S34}
\]

Using Eq. (S31) and Eq. (S34), we find
\[
\delta A_B(t) = -\sum_l [\mathcal{E}^\mu(\lambda_l) \partial_\mu B|\mathcal{E}^\nu(\lambda_l) \Omega^{\nu\rho} \partial_\rho A|] \int_{-\infty}^t dt' e^{-i\lambda_l (t-t')} \varphi(t'). \tag{S35}
\]

By taking the Fourier transform of Eq. (S35), we find
\[
\delta A_B(\omega) = -i\varphi(\omega) \sum_l [\mathcal{E}^\mu(\lambda_l) \partial_\mu B|\mathcal{E}^\nu(\lambda_l) \Omega^{\nu\rho} \partial_\rho A] \lim_{\eta \to 0^+} \frac{1}{\omega - \lambda_l + i\eta}. \tag{S36}
\]

The retarded correlation function \(G_{AB}^{(R)}(\omega)\) is defined as
\[
\delta A_B(\omega) = G_{AB}^{(R)}(\omega) \varphi(\omega). \tag{S37}
\]

From Eqs. (S37) and (S36), we find
\[
G_{AB}^{(R)}(\omega) = \lim_{\eta \to 0^+} -i \sum_l [\mathcal{E}^\mu(\lambda_l) \partial_\mu B|\mathcal{E}^\nu(\lambda_l) \Omega^{\nu\rho} \partial_\rho A] \omega + i\eta - \lambda_l. \tag{S38}
\]

Then, using the definition of the matrix Green function [Eq. (20)], we find Eq. (19) of the main text.

**S3. DERIVATION OF THE SYMPLECTIC FORM**

In this section, we calculate the overlap of the tangent vectors to calculate the metric and the symplectic form. From the definition of the tangent vectors [Eq. (18)], one finds
\[
\langle V_\mu | V_\nu \rangle = \langle \Phi^+ \left| \mathcal{E}^{\mu\nu} \right| \Phi^+ \rangle = \langle \frac{\partial U^\dag}{\partial x^\mu} \frac{\partial U}{\partial x^\nu} \rangle_0. \tag{S39}
\]

To evaluate Eq. (S39), we use the derivatives of the variational transformation, Eqs. (S2-S7).

Now, we compute the overlap. First, since the thermal expectation value of an operator containing uneven numbers of creation and annihilation operators is zero, one finds
\[
\langle \frac{\partial U^\dag}{\partial \alpha_r^m} \frac{\partial U}{\partial \alpha_r^n} \rangle_0 = 0. \tag{S40}
\]

and
\[
\langle \frac{\partial U^\dag}{\partial \beta_{rn}^m} \frac{\partial U}{\partial \beta_{pq}^n} \rangle_0 = 0. \tag{S41}
\]

Next, we calculate the nonzero inner products. First, for two displacement parameters \(\alpha_m\) and \(\alpha_n\), we find
\[
\langle \frac{\partial U^\dag}{\partial \alpha_m^r} \frac{\partial U}{\partial \alpha_n^s} \rangle_0 = \langle \hat{p}_m \hat{p}_n \rangle_0 = \left( n_m + \frac{1}{2} \right) \delta_{m,n}, \tag{S42}
\]

\[
\langle \frac{\partial U^\dag}{\partial \alpha_m^r} \frac{\partial U}{\partial \alpha_n^r} \rangle_0 = -\langle \hat{p}_m \hat{r}_n \rangle_0 = \frac{i}{2} \delta_{m,n}. \tag{S43}
\]
and
\[
\left\langle \frac{\partial \hat{U}^\dagger}{\partial \alpha_m} \frac{\partial \hat{U}}{\partial \alpha_n} \right\rangle_0 = (\hat{r}_m \hat{r}_n)_0 = \left( n_m + \frac{1}{2} \right) \delta_{m,n}.
\] (S44)

Next, we consider the tangent vectors of the squeezing parameters \( \beta^r_{mn} \) and \( \beta^r_{pq} \). Note that
\[
\delta_{m,p} \delta_{n,q} + \delta_{m,q} \delta_{n,p} = \begin{cases} 
\delta_{mn,pq} & \text{if } m \neq n \\
2\delta_{mn,pq} & \text{if } m = n
\end{cases}
\] (S45)
holds since \( m \leq n \) and \( p \leq q \). Then, using Eqs. (S4, S5), we find
\[
\left\langle \frac{\partial \hat{U}^\dagger}{\partial \beta^r_{mn}} \frac{\partial \hat{U}}{\partial \beta^r_{pq}} \right\rangle_0 = b_{mn} b_{pq} \left( \hat{a}_n \hat{a}_m \hat{a}_p \hat{a}_q + \hat{a}_m \hat{a}_n \hat{a}_q \hat{a}_p \right)_0
= b_{mn} b_{pq} (\delta_{m,p} \delta_{n,q} + \delta_{m,q} \delta_{n,p}) (2n_m n_n + n_m + n_n + 1)
= \frac{2n_m n_n + n_m + n_n + 1}{2(n_m + n_n + 1)} \delta_{mn,pq},
\] (S46)
and
\[
\left\langle \frac{\partial \hat{U}^\dagger}{\partial \tau^r_{mn}} \frac{\partial \hat{U}}{\partial \tau^r_{pq}} \right\rangle_0 = i b_{mn} b_{pq} \left( \hat{a}_n \hat{a}_m \hat{a}_p \hat{a}_q - \hat{a}_m \hat{a}_n \hat{a}_q \hat{a}_p \right)_0
= i b_{mn} b_{pq} (\delta_{m,p} \delta_{n,q} + \delta_{m,q} \delta_{n,p}) (n_m + n_n + 1)
= \frac{i}{2} \delta_{mn,pq}.
\] (S47)

Finally, for the tangent vectors of the squeezing parameters \( \gamma^r_{mn} \) and \( \gamma^r_{pq} \), \( m < n \) and \( p < q \) holds by definition. Thus, we find
\[
\left\langle \frac{\partial \hat{U}^\dagger}{\partial \gamma^r_{mn}} \frac{\partial \hat{U}}{\partial \gamma^r_{pq}} \right\rangle_0 = \left\langle \frac{\partial \hat{U}^\dagger}{\partial \gamma^r_{mn}} \frac{\partial \hat{U}}{\partial \gamma^r_{pq}} \right\rangle_0 = c_{mn} c_{pq} (\hat{a}_m \hat{a}_n - \hat{a}_n \hat{a}_m) (\hat{a}_p \hat{a}_q - \hat{a}_q \hat{a}_p)_0
= c_{mn} c_{pq} \delta_{m,p} \delta_{n,q} (2n_m n_n + n_m + n_n)
= \frac{2n_m n_n + n_m + n_n}{2(n_m - n_n)} \delta_{mn,pq},
\] (S48)
and
\[
\left\langle \frac{\partial \hat{U}^\dagger}{\partial \gamma^r_{mn}} \frac{\partial \hat{U}}{\partial \gamma^r_{pq}} \right\rangle_0 = - i c_{mn} c_{pq} \left( (\hat{a}_n \hat{a}_m - \hat{a}_m \hat{a}_n)(\hat{a}_p \hat{a}_q + \hat{a}_q \hat{a}_p)_0
= - i c_{mn} c_{pq} \delta_{m,p} \delta_{n,q} (n_m - n_n)
= \frac{i}{2} \delta_{mn,pq}.
\] (S49)

The only inner products with nonzero imaginary parts are those in Eqs. (S43, S47, S49) and their complex conjugates. Using this result and the definition of the symplectic form [Eq. (22)], one obtains Eq. (23) of the main text.

S4. DERIVATIVES OF THE ENERGY

In this section, we calculate the first and second derivatives of the energy expectation value with respect to the variational parameters. In this section, all derivatives are evaluated at \( x = 0 \) unless otherwise noted.
A. Useful identities

Before actually calculating the derivatives, we derive useful identities. Using the normal mode representation of the anharmonic Hamiltonian [Eq. (5)], we find

\[
[H, \hat{r}_m] = -i\omega_m \hat{p}_m,
\]

(S50)

and

\[
[H, \hat{p}_m] = i \frac{\partial V}{\partial r_m}.
\]

(S51)

Also, given an observable \( \hat{O} = O(\hat{r}) \) which is a function of the position operators, one finds

\[
\left\langle \hat{r}_m \hat{O} \right\rangle_0 = \int \! dr \rho_0(r) \hat{r}_m O(r) = -\left( n_m + \frac{1}{2} \right) \int \! dr \frac{\partial \rho_0(r)}{\partial r_m} O(r) = \left( n_m + \frac{1}{2} \right) \int \! dr \rho_0(r) \frac{\partial O(r)}{\partial r_m} = \left( n_m + \frac{1}{2} \right) \left\langle \frac{\partial \hat{O}}{\partial r_m} \right\rangle_0.
\]

(S52)

Here, \( \rho_0(r) \) is the diagonal part of \( \hat{\rho}_0 \) in the normal mode position basis [S4]:

\[
\rho_0(r) = \langle r | \rho_0 | r \rangle = \prod_{m=1}^{N} \sqrt{\frac{1}{\pi(2n_m + 1)}} \exp \left( -\frac{r_m^2}{2n_m + 1} \right).
\]

(S53)

In the third equality of Eq. (S52), we used a partial integration with respect to \( r_m \) [see also Eqs. (C1-C3) of Ref. [S5]].

In addition, using

\[
e^{-\beta \hat{H}^{(n)}} \hat{a}_m = e^{\beta \omega_m} \hat{a}_m e^{-\beta \hat{H}^{(n)}},
\]

(S54)

one can show

\[
\left\langle \hat{a}_m \hat{O} \right\rangle_0 = e^{\beta \omega_m} \left\langle \hat{O} \hat{a}_m \right\rangle_0
\]

(S55)

and

\[
\left\langle \hat{a}_m \hat{O} \right\rangle_0 = e^{-\beta \omega_m} \left\langle \hat{O} \hat{a}_m \right\rangle_0.
\]

(S56)

From Eqs. (S55) and (S56), one can show

\[
\left\langle \hat{O} \hat{r}_m \right\rangle_0 = \frac{e^{\beta \omega_m}}{\sqrt{2}} \left\langle \hat{a}_m \hat{O} \right\rangle_0 + \frac{e^{-\beta \omega_m}}{\sqrt{2}} \left\langle \hat{a}_m \hat{O} \right\rangle_0 = \frac{e^{\beta \omega_m} + e^{-\beta \omega_m}}{2} \left\langle \hat{r}_m \hat{O} \right\rangle_0 + \frac{e^{\beta \omega_m} - e^{-\beta \omega_m}}{2i} \left\langle \hat{p}_m \hat{O} \right\rangle_0.
\]

(S57)

Using Eq. (S57) and \([\hat{r}_m, O(\hat{r})] = 0\), one finds

\[
\left\langle \hat{p}_m \hat{O} \right\rangle_0 = -\frac{i}{2n_m + 1} \left\langle \hat{r}_m \hat{O} \right\rangle_0 = -\frac{i}{2} \left\langle \frac{\partial \hat{O}}{\partial r_m} \right\rangle_0.
\]

(S58)

Taking complex conjugate of Eq. (S58), one also finds

\[
\left\langle \hat{O} \hat{p}_m \right\rangle_0 = \frac{i}{2} \left\langle \frac{\partial \hat{O}}{\partial r_m} \right\rangle_0.
\]

(S59)

Using a logic similar to Eq. (S57), one can also show

\[
\left\langle \hat{p}_m \hat{O} \hat{p}_n \right\rangle_0 = -\frac{i}{2n_m + 1} \left\langle \hat{r}_m \hat{O} \hat{p}_n \right\rangle_0 + \frac{2n_m(n_m + 1)}{2n_m + 1} \delta_{m,n} \left\langle \hat{O} \right\rangle_0
\]

\[
= \frac{1}{2(2n_m + 1)} \left( \delta_{m,n} \left\langle \hat{O} \right\rangle_0 + \left\langle \hat{r}_m \frac{\partial \hat{O}}{\partial r_n} \right\rangle_0 \right) + \frac{2n_m(n_m + 1)}{2n_m + 1} \delta_{m,n} \left\langle \hat{O} \right\rangle_0
\]

\[
= \frac{1}{4} \left\langle \frac{\partial^2 \hat{O}}{\partial r_m \partial r_n} \right\rangle_0 + \left( n_m + \frac{1}{2} \right) \delta_{m,n} \left\langle \hat{O} \right\rangle_0.
\]

(S60)

We use Eq. (S60) only in Eq. (S83).
B. First derivatives

Now, we compute the first derivatives of the energy expectation value and show that the SCHA solution is also the stationary state of the Gaussian TDVP. By setting $\hat{O} = \hat{H}$ in Eq. (S1) and taking the equilibrium expectation value, the first-order derivative of the energy expectation value becomes

$$\frac{\partial E}{\partial x^\mu} = \left\langle \left[ \hat{H}, \frac{\partial \hat{U}}{\partial x^\mu} \right] \right\rangle_0 .$$  \hspace{1cm} (S61)

So, the first-order derivatives can be computed using the derivatives of the Gaussian transformation operator, Eqs. (S2-S7).

Using the identities [Eqs. (S50-S59)] as well as the properties of the SCHA density matrix [Eqs. (6, 7)], the first-order derivatives of energy at $x = 0$ can be computed as follows. We find that all first-order derivatives of the energy are zero. For the variational parameters included in the SCHA theory, the centroid position and the force constants, the stationarity of $\hat{\rho}_0$ is expected since $\hat{\rho}_0$ is the variational solution that minimizes the SCHA free energy. $\hat{\rho}_0$ is also stationary with respect to the variation of other parameters such as the atomic momentum parameter $\alpha_{im}$ because it is a thermal density matrix whose momentum expectation value is zero.

$$\frac{\partial E}{\partial \alpha_{im}} = \left\langle \left[ \hat{H}, -i\hat{p}_m \right] \right\rangle_0 = \left\langle \frac{\partial \hat{V}}{\partial r_m} \right\rangle_0 = 0 \hspace{1cm} (S62)$$

$$\frac{\partial E}{\partial \alpha_{im}} = \left\langle \left[ \hat{H}, i\hat{r}_m \right] \right\rangle_0 = \omega_m \langle \hat{p}_m \rangle_0 = 0 \hspace{1cm} (S63)$$

$$\frac{\partial E}{\partial \beta^{rm}} = -ib_{mn} \left\langle \left[ \hat{H}, \hat{r}_m \hat{p}_n + \hat{p}_m \hat{r}_n \right] \right\rangle_0 = 0 \hspace{1cm} (S64)$$

$$\frac{\partial E}{\partial \beta^{rm}} = ib_{mn} \left\langle \left[ \hat{H}, \hat{r}_m \hat{r}_n - \hat{p}_m \hat{p}_n \right] \right\rangle_0 = 0 \hspace{1cm} (S65)$$

$$\frac{\partial E}{\partial \gamma^{rm}} = ic_{mn} \left\langle \left[ \hat{H}, \hat{r}_m \hat{p}_n - \hat{p}_m \hat{r}_n \right] \right\rangle_0 = 0 \hspace{1cm} (S66)$$

$$\frac{\partial E}{\partial \gamma^{rm}} = -ic_{mn} \left\langle \left[ \hat{H}, \hat{r}_m \hat{p}_n + \hat{p}_m \hat{r}_n \right] \right\rangle_0 = 0 \hspace{1cm} (S67)$$

Equations (S66) and (S67) can be derived in the same way as Eqs. (S64) and (S65), respectively.
C. Second derivatives

Next, we calculate the second derivatives of energy. The result of this subsection can be summarized in a matrix form:

\[
\frac{\partial^2 E}{\partial x^\mu \partial x^\nu} = \begin{pmatrix}
\omega & 0 & \Phi^{(3)} B & 0 & \Phi^{(3)} C & 0 \\
0 & \omega & 0 & 0 & 0 & 0 \\
B \Phi^{(3)} & 0 & \omega_+ + B \Phi^{(4)} B & 0 & B \Phi^{(4)} C & 0 \\
0 & 0 & 0 & \omega_+ & 0 & 0 \\
C \Phi^{(3)} & 0 & C \Phi^{(4)} B & 0 & \omega_- + C \Phi^{(4)} C & 0 \\
0 & 0 & 0 & 0 & 0 & \omega_- \\
\end{pmatrix}.
\]  
(S68)

The remaining part of this subsection is the derivation of Eq. (S68). By taking derivative of Eq. (17) with \( \hat{O} = \hat{H} \), the second derivative of energy at \( x = 0 \) is given by

\[
\frac{\partial^2 E}{\partial x^\mu \partial x^\nu} = \left\langle \frac{\partial^2 \hat{H}}{\partial x^\mu \partial x^\nu} + \frac{\partial^2 \hat{U}^\dagger}{\partial x^\mu \partial x^\nu} \hat{H} + \frac{\partial^2 \hat{U}}{\partial x^\mu \partial x^\nu} \hat{U} \partial \hat{H} + \frac{\partial \hat{U}^\dagger}{\partial x^\mu} \hat{H} \frac{\partial \hat{U}}{\partial x^\nu} \right\rangle_0.
\]  
(S69)

When the two derivatives are for the same parameter type (displacement or squeezing), the second derivative of the transformation matrix becomes

\[
\frac{\partial^2 \hat{U}}{\partial x^\mu \partial x^\nu} = \frac{1}{2} \left\langle \frac{\partial \hat{U}}{\partial x^\mu}, \frac{\partial \hat{U}}{\partial x^\nu} \right\rangle.
\]  
(S70)

In this case, using \( \partial \hat{U}^\dagger = -\partial \hat{U} \), the second derivative of the energy can be written as

\[
\frac{\partial^2 E}{\partial x^\mu \partial x^\nu} = \frac{1}{2} \left\langle \frac{\partial \hat{H}}{\partial x^\mu}, \frac{\partial \hat{U}^\dagger}{\partial x^\nu} \right\rangle_0 - \frac{1}{2} \left\langle \frac{\partial \hat{H}}{\partial x^\mu}, \frac{\partial \hat{U}}{\partial x^\nu} \right\rangle_0.
\]  
(S71)

For mixed second derivatives in which the derivatives are with respect to one displacement and one squeezing parameter, one finds

\[
\frac{\partial^2 \hat{U}}{\partial \alpha_{t/\xi}^m \partial \beta_{m/n}^{\xi/\xi}} = \frac{\partial \hat{U}}{\partial \alpha_{t/\xi}^m},
\]  
(S72)

and the same for \( \gamma \) instead of \( \beta \). In this case, the second derivative of energy becomes

\[
\frac{\partial^2 E}{\partial \alpha_{t/\xi}^m \partial \beta_{m/n}^{\xi/\xi}} = \left\langle \frac{\partial \hat{H}}{\partial \alpha_{t/\xi}^m}, \frac{\partial \hat{U}^\dagger}{\partial \beta_{m/n}^{\xi/\xi}} \right\rangle_0 + \frac{\partial^2 \hat{H}}{\partial \alpha_{t/\xi}^m \partial \beta_{m/n}^{\xi/\xi}} \hat{H} - \frac{\partial^2 \hat{U}}{\partial \alpha_{t/\xi}^m \partial \beta_{m/n}^{\xi/\xi}} \hat{H} \}
\]  
(S73)

and the same for \( \gamma \) instead of \( \beta \).

For the second derivatives with respect to two displacement parameters \( \alpha_m \) and \( \alpha_n \), we use Eq. (S71) to find

\[
\frac{\partial^2 E}{\partial \alpha_m \partial \alpha_n} = -\frac{1}{2} \left\langle \left[ \hat{H}, \hat{\alpha}_m \right], \hat{\alpha}_n \right\rangle_0 + (m \leftrightarrow n) = \frac{1}{2} \left\langle \left[ \partial \hat{V} / \partial \alpha_m \right], \hat{\alpha}_n \right\rangle_0 + (m \leftrightarrow n) = \frac{\partial^2 \hat{V}}{\partial \alpha_m \partial \alpha_n} = 0,
\]  
(S74)

\[
\frac{\partial^2 E}{\partial \alpha_m \partial \alpha_n} = \frac{1}{2} \left\langle \left[ \hat{H}, \hat{\alpha}_m \right], \hat{\alpha}_n \right\rangle_0 = \frac{1}{2} \left\langle \left[ \hat{H}, \hat{\alpha}_n \right], \hat{\alpha}_m \right\rangle_0 = \frac{1}{2} \left\langle \left[ \partial \hat{V} / \partial \alpha_m \right], \hat{\alpha}_n \right\rangle_0 = \frac{i}{2} \omega_n \left\langle \hat{\alpha}_m, \hat{\alpha}_n \right\rangle_0 = 0,
\]  
(S75)
\[\frac{\partial^2 E}{\partial \alpha_m^i \partial \alpha_n^i} = -\frac{1}{2} \left\langle \left[ \hat{H}, \hat{r}_m \right], \hat{r}_n \right\rangle_0 + (m \leftrightarrow n) = \frac{i}{2} \omega_m \left\langle \left[ \hat{p}_m, \hat{r}_n \right] \right\rangle_0 + (m \leftrightarrow n) = \omega_m \delta_{m,n}. \quad (S76)\]

Similarly, one can also calculate the second derivatives with respect to two squeezing parameters. Before going on, we first list some useful identities related to nested commutators.

\[\left[ \hat{H}, \hat{r}_m \hat{r}_n \right] = \hat{r}_m \left[ \hat{H}, \hat{r}_n \right] + \left[ \hat{H}, \hat{r}_m \right] \hat{r}_n = -i(\omega_n \hat{r}_m \hat{p}_n + \omega_m \hat{p}_m \hat{r}_n) \quad (S77)\]

\[\left[ \hat{H}, \hat{r}_m \hat{p}_n \right] = \hat{r}_m \left[ \hat{H}, \hat{p}_n \right] + \left[ \hat{H}, \hat{r}_m \right] \hat{p}_n = i\hat{r}_m \frac{\partial \hat{V}}{\partial r_n} - i\omega_m \hat{p}_m \hat{p}_n \quad (S78)\]

\[\left[ \hat{H}, \hat{p}_m \hat{p}_n \right] = \hat{p}_m \left[ \hat{H}, \hat{p}_n \right] + \left[ \hat{H}, \hat{p}_m \right] \hat{p}_n = i\hat{p}_m \frac{\partial \hat{V}}{\partial r_n} + i \frac{\partial \hat{V}}{\partial r_m} \hat{p}_n \quad (S79)\]

\[\left\langle \left[ \hat{H}, \hat{r}_m \hat{r}_n \right], \hat{r}_p \hat{r}_q \right\rangle_0 = \left\langle \left[ (-i(\omega_n \hat{r}_m \hat{p}_n + \omega_m \hat{p}_m \hat{r}_n), \hat{r}_p \hat{r}_q) \right] \right\rangle_0 \]
\[= -i\omega_m \left\langle \left[ \hat{r}_m \hat{p}_n, \hat{r}_p \hat{r}_q \right] \right\rangle_0 - i\omega_m \left\langle \left[ \hat{p}_m \hat{r}_n, \hat{r}_p \hat{r}_q \right] \right\rangle_0 \]
\[= -(\delta_{m,p} \delta_{n,q} + \delta_{m,q} \delta_{n,p}) \left[ \omega_m \left( n_m + \frac{1}{2} \right) + \omega_n \left( n_n + \frac{1}{2} \right) \right] \quad (S80)\]

\[\left\langle \left[ \hat{H}, \hat{r}_m \hat{p}_n \right], \hat{r}_p \hat{r}_q \right\rangle_0 = \left\langle \left[ (-i(\omega_n \hat{r}_m \hat{p}_n + \omega_m \hat{p}_m \hat{r}_n), \hat{r}_p \hat{r}_q) \right] \right\rangle_0 \]
\[= -i\omega_n \left\langle \left[ \hat{r}_m \hat{p}_n, \hat{r}_p \hat{r}_q \right] \right\rangle_0 - i\omega_m \left\langle \left[ \hat{p}_m \hat{r}_n, \hat{r}_p \hat{r}_q \right] \right\rangle_0 \]
\[= (\delta_{m,p} \delta_{n,q} + \delta_{m,q} \delta_{n,p}) \left[ \omega_m \left( n_m + \frac{1}{2} \right) + \omega_n \left( n_n + \frac{1}{2} \right) \right] \quad (S81)\]

\[\left\langle \left[ \hat{H}, \hat{p}_m \hat{p}_n \right], \hat{r}_p \hat{r}_q \right\rangle_0 = \left\langle \left[ i\hat{p}_m \frac{\partial \hat{V}}{\partial r_n} + i \frac{\partial \hat{V}}{\partial r_m} \hat{p}_n, \hat{r}_p \hat{r}_q \right] \right\rangle_0 \]
\[= i \left\langle \left[ \hat{p}_m, \hat{r}_p \hat{r}_q \right] \frac{\partial \hat{V}}{\partial r_n} \right\rangle_0 + i \left\langle \frac{\partial \hat{V}}{\partial r_m} \hat{p}_n, \hat{r}_p \hat{r}_q \right\rangle_0 \]
\[= \delta_{m,p} \left\langle \hat{r}_p \frac{\partial \hat{V}}{\partial r_n} \right\rangle_0 + \delta_{m,q} \left\langle \hat{r}_p \frac{\partial \hat{V}}{\partial r_n} \right\rangle_0 + \delta_{n,p} \left\langle \frac{\partial \hat{V}}{\partial r_m} \hat{r}_p \right\rangle_0 + \delta_{n,q} \left\langle \frac{\partial \hat{V}}{\partial r_m} \hat{r}_p \right\rangle_0 \]
\[= \delta_{m,p} \delta_{n,q} + \delta_{m,q} \delta_{n,p} \left[ \omega_m \left( n_m + \frac{1}{2} \right) + \omega_n \left( n_n + \frac{1}{2} \right) \right] \quad (S82)\]

\[\left\langle \left[ \hat{H}, \hat{p}_m \hat{p}_n \right], \hat{p}_p \hat{p}_q \right\rangle_0 = \left\langle \left[ i\hat{p}_m \frac{\partial \hat{V}}{\partial r_n} + i \frac{\partial \hat{V}}{\partial r_m} \hat{p}_n, \hat{p}_p \hat{p}_q \right] \right\rangle_0 \]
\[= i \left\langle \hat{p}_m \frac{\partial \hat{V}}{\partial r_n} \hat{p}_p \hat{p}_q \right\rangle_0 + i \left\langle \frac{\partial \hat{V}}{\partial r_m} \hat{p}_n \hat{p}_p \hat{p}_q \right\rangle_0 \]
\[= - \left\langle \hat{p}_m \frac{\partial^2 \hat{V}}{\partial r_n \partial r_p} \hat{p}_q \right\rangle_0 - \left\langle \hat{p}_m \frac{\partial \hat{V}}{\partial r_n} \hat{p}_p \hat{p}_q \right\rangle_0 - \left\langle \hat{p}_p \frac{\partial^2 \hat{V}}{\partial r_m \partial r_q} \hat{p}_n \right\rangle_0 - \left\langle \frac{\partial^2 \hat{V}}{\partial r_m \partial r_q} \hat{p}_n \hat{p}_p \right\rangle_0 \]
\[= - \left[ \left\langle \hat{p}_m \frac{\partial \hat{V}}{\partial r_n} \hat{p}_q \right\rangle_0 \right] \left[ (m \leftrightarrow n) + (p \leftrightarrow q) \right] + i \left\langle \hat{p}_m \frac{\partial \hat{V}}{\partial r_n} \hat{p}_q \right\rangle_0 \]
\[= - \left[ \frac{1}{4} \Phi_{mpnq}^{(4)} + \delta_{m,p} \delta_{n,q} \omega_n \left( n_n + \frac{1}{2} \right) + (m \leftrightarrow n) + (p \leftrightarrow q) \right] + \Phi_{mpnq}^{(4)} \]
\[= -(\delta_{m,p} \delta_{n,q} + \delta_{m,q} \delta_{n,p}) \left[ \omega_m \left( n_m + \frac{1}{2} \right) + \omega_n \left( n_n + \frac{1}{2} \right) \right] \quad (S83)\]
In the fifth equality of Eq. (S83), we used Eq. (S60).

\[
\left\langle \left[ \hat{H}, \hat{r}_m \hat{p}_n \right] , \hat{r}_p \hat{p}_q \right\rangle_0 = \left\langle \left[ i \hat{r}_m \frac{\partial \hat{V}}{\partial r_n} - i \omega_m \hat{p}_m \hat{p}_n , \hat{r}_p \hat{p}_q \right] \right\rangle_0 \\
= i \left\langle \hat{r}_p \left( \hat{r}_m \frac{\partial \hat{V}}{\partial r_n} , \hat{p}_q \right) \right\rangle_0 - i \omega_m \langle [\hat{p}_m \hat{p}_n , \hat{r}_p \hat{p}_q] \rangle_0 \\
= - \left\langle \hat{r}_p \left( \delta_{m,q} \frac{\partial \hat{V}}{\partial r_n} + \hat{r}_m \frac{\partial^2 \hat{V}}{\partial r_n \partial r_q} \right) \right\rangle_0 - \omega_m \left[ \delta_{m,p} \delta_{n,q} \left( n_m + \frac{1}{2} \right) + \delta_{m,q} \delta_{n,p} \left( n_m + \frac{1}{2} \right) \right] \\
= - \delta_{m,q} \delta_{n,p} \left[ \omega_m \left( n_m + \frac{1}{2} \right) + \omega_n \left( n_n + \frac{1}{2} \right) \right] - \delta_{m,p} \delta_{n,q} \left[ \omega_m \left( n_m + \frac{1}{2} \right) + \omega_n \left( n_n + \frac{1}{2} \right) \right] \\
- \left( n_p + \frac{1}{2} \right) \left( n_n + \frac{1}{2} \right) \Phi_{mnpq}^{(4)}, \tag{S84}
\]

\[
\left\langle \left[ \hat{H}, \hat{r}_m \hat{p}_n \right] , \hat{r}_p \hat{r}_q \right\rangle_0 = \left\langle \left[ i \hat{r}_m \frac{\partial \hat{V}}{\partial r_n} - i \omega_m \hat{p}_m \hat{p}_n , \hat{r}_p \hat{r}_q \right] \right\rangle_0 \\
= - i \omega_m \left( \langle [\hat{p}_m \hat{p}_n , \hat{r}_p \hat{r}_q] \rangle_0 + \langle \hat{r}_p \hat{p}_m \hat{p}_n , \hat{r}_q \rangle_0 \right) \\
= 0 \tag{S85}
\]

\[
\left\langle \left[ \hat{H}, \hat{r}_m \hat{p}_n \right] , \hat{p}_p \hat{q}_n \right\rangle_0 = \left\langle \left[ i \hat{r}_m \frac{\partial \hat{V}}{\partial r_n} - i \omega_m \hat{p}_m \hat{p}_n , \hat{p}_p \hat{q}_n \right] \right\rangle_0 \\
= i \left\langle \hat{p}_p \left( \hat{r}_m \frac{\partial \hat{V}}{\partial r_n} , \hat{p}_q \right) \right\rangle_0 + i \left\langle \hat{r}_m \frac{\partial \hat{V}}{\partial r_n} \hat{p}_q \right\rangle_0 \\
= - \left\langle \hat{p}_p \left( \delta_{m,q} \frac{\partial \hat{V}}{\partial r_n} + \hat{r}_m \frac{\partial^2 \hat{V}}{\partial r_n \partial r_q} \right) \right\rangle_0 - \left\langle \left[ \delta_{m,p} \frac{\partial \hat{V}}{\partial r_n} + \hat{r}_m \frac{\partial^2 \hat{V}}{\partial r_n \partial r_p} \right] \hat{p}_q \right\rangle_0 \\
= 0 \tag{S86}
\]

\[
\left\langle \left[ \hat{H}, \hat{r}_m \hat{r}_n \right] , \hat{r}_p \hat{p}_q \right\rangle_0 = - i \left\langle \left[ \omega_n \hat{r}_m \hat{p}_n + \omega_m \hat{r}_m \hat{r}_n , \hat{r}_p \hat{p}_q \right] \right\rangle_0 \\
= - i \omega_m \langle [\hat{p}_m \hat{r}_n , \hat{r}_p \hat{p}_q] \rangle_0 - i \omega_n \langle [\hat{r}_m \hat{r}_n , \hat{p}_p \hat{q}_n] \rangle_0 \\
= - i \omega_n (- i \delta_{n,p} \hat{r}_m \hat{p}_q + i \delta_{m,q} \hat{r}_p \hat{p}_n) - i \omega_m (i \delta_{n,q} \hat{p}_m \hat{r}_p - i \delta_{m,p} \hat{p}_q \hat{r}_n) \rangle_0 \\
= \frac{i}{2} \omega_n (- \delta_{n,p} \delta_{m,q} + \delta_{m,q} \delta_{p,n}) + \frac{i}{2} \omega_m (- \delta_{n,q} \delta_{m,p} + \delta_{m,p} \delta_{q,n}) \\
= 0 \tag{S87}
\]
\[
\left<\left[\hat{H}, \hat{p}_m \hat{p}_n\right], \hat{r}_p \hat{r}_q\right> = \left<\left[i\hat{p}_m \frac{\partial \hat{V}}{\partial r_n} + i\frac{\partial \hat{V}}{\partial r_m} \hat{p}_n, \hat{r}_p \hat{r}_q\right]\right> = i \left<\hat{p}_m \hat{r}_p \frac{\partial \hat{V}}{\partial r_n} \hat{p}_q\right> + i \left<\left[\hat{p}_m, \hat{r}_p\right] \hat{p}_q \frac{\partial \hat{V}}{\partial r_n}\right> + i \left<\hat{p}_m \frac{\partial \hat{V}}{\partial r_m} \hat{p}_n, \hat{r}_p \hat{p}_q\right> = -i \hat{p}_m \hat{r}_p \frac{\partial^2 \hat{V}}{\partial r_n \partial r_q} + \delta_{m,p} \left<\hat{p}_q \frac{\partial \hat{V}}{\partial r_n}\right> + \delta_{n,p} \left<\hat{p}_q \frac{\partial \hat{V}}{\partial r_m}\right> = \frac{i}{2} \delta_{p,m} \left<\frac{\partial^2 \hat{V}}{\partial r_n \partial r_q}\right> + \frac{r_p}{\partial r_m} \frac{\partial^2 \hat{V}}{\partial r_q} \hat{r}_p \frac{\partial \hat{V}}{\partial r_n} = 0
\]

Now, we actually calculate the second derivatives of energy. Using Eq. (S71), and Eqs. (S80-S83), one finds

\[
\frac{\partial^2 E}{\partial \beta_{mn} \partial \beta_{pq}} = -\frac{1}{2} b_{mn} b_{pq} \left\langle \left[\left[\hat{H}, \hat{r}_m \hat{r}_n - \hat{p}_m \hat{p}_n\right], \hat{r}_p \hat{r}_q - \hat{p}_p \hat{p}_q\right]\right> + \left<\left[\hat{H}, \hat{r}_m \hat{r}_n + \hat{p}_m \hat{p}_n\right], \hat{r}_p \hat{r}_q + \hat{p}_p \hat{p}_q\right]\rangle = \left<\left[\hat{H}, \hat{r}_m \hat{r}_n + \hat{p}_m \hat{p}_n\right], \hat{r}_p \hat{r}_q + \hat{p}_p \hat{p}_q\right]\rangle + \left<\left[\hat{H}, \hat{r}_m \hat{r}_n - \hat{p}_m \hat{p}_n\right], \hat{r}_p \hat{r}_q - \hat{p}_p \hat{p}_q\right]\rangle
\]

where in the last equality we have used \(m \leq n\) and \(p \leq q\),

\[
\frac{\partial^2 E}{\partial \beta_{mn} \partial \beta_{pq}} = \frac{1}{2} c_{mn} c_{pq} \left\langle \left[\left[\hat{H}, \hat{r}_m \hat{r}_n + \hat{p}_m \hat{p}_n\right], \hat{r}_p \hat{r}_q + \hat{p}_p \hat{p}_q\right]\right> + \left<\left[\hat{H}, \hat{r}_m \hat{r}_n - \hat{p}_m \hat{p}_n\right], \hat{r}_p \hat{r}_q - \hat{p}_p \hat{p}_q\right]\rangle
\]

where in the last equality we have used \(m < n\) and \(p < q\), and

\[
\frac{\partial^2 E}{\partial \beta_{mn} \partial \beta_{pq}} = \frac{1}{2} b_{mn} c_{pq} \left\langle \left[\left[\hat{H}, \hat{r}_m \hat{r}_n + \hat{p}_m \hat{p}_n\right], \hat{r}_p \hat{r}_q + \hat{p}_p \hat{p}_q\right]\right> + \left<\left[\hat{H}, \hat{r}_m \hat{r}_n - \hat{p}_m \hat{p}_n\right], \hat{r}_p \hat{r}_q - \hat{p}_p \hat{p}_q\right]\rangle = 0
\]

Also, using Eq. (S84), one finds

\[
\frac{\partial^2 E}{\partial \beta_{mn} \partial \beta_{pq}} = \frac{1}{2} b_{mn} b_{pq} \left\langle \left[\left[\hat{H}, \hat{r}_m \hat{p}_n + \hat{p}_m \hat{r}_n\right], \hat{r}_p \hat{p}_q + \hat{p}_p \hat{p}_q\right]\right> + \left<\left[\hat{H}, \hat{r}_m \hat{p}_n + \hat{p}_m \hat{r}_n\right], \hat{r}_p \hat{p}_q + \hat{p}_p \hat{p}_q\right]\rangle = \left<\left[\hat{H}, \hat{r}_m \hat{p}_n + \hat{p}_m \hat{r}_n\right], \hat{r}_p \hat{p}_q + \hat{p}_p \hat{p}_q\right]\rangle + \left<\left[\hat{H}, \hat{r}_m \hat{p}_n + \hat{p}_m \hat{r}_n\right], \hat{r}_p \hat{p}_q + \hat{p}_p \hat{p}_q\right]\rangle
\]

(S88)
and
\[
\frac{\partial^2 E}{\partial \gamma_{mn} \partial \gamma_{pq}} = -\frac{1}{2} c_{mn} c_{pq} \left\langle \left[ \left[ \hat{H}, \hat{r}_m \hat{p}_n - \hat{p}_m \hat{r}_n \right], \hat{r}_p \hat{p}_q - \hat{p}_p \hat{r}_q \right] \right\rangle_0 + ((m, n) \leftrightarrow (p, q))
\]
\[
= - c_{mn} c_{pq} \left\langle \left[ \left[ \hat{H}, \hat{r}_m \hat{p}_n \right], \hat{r}_p \hat{p}_q - \hat{p}_p \hat{r}_q \right] \right\rangle_0 - (p \leftrightarrow q) - (m \leftrightarrow n)
\]
\[
= - 2 c_{mn} c_{pq} \left( \delta_{m,p} \delta_{n,q} - \delta_{m,q} \delta_{n,p} \right) (\omega_m - \omega_n) (n_m - n_n) - (n_p - n_q) \left( n_m + \frac{1}{2} \right) \Phi^{(4)}_{mnpq} - (m \leftrightarrow n)
\]
\[
= - 2 c_{mn} c_{pq} \left( \delta_{m,p} \delta_{n,q} - \delta_{m,q} \delta_{n,p} \right) (\omega_m - \omega_n) (n_m - n_n) + c_{mn} c_{pq} (n_p - n_q) (n_m - n_n) \Phi^{(4)}_{mnpq}
\]
\[
= (\omega_n - \omega_m) \delta_{mn, pq} + c_{mn} c_{pq} (n_p - n_q) (n_m - n_n) \Phi^{(4)}_{mnpq}.
\] (S94)

Using Eqs. (S85-S88), one finds
\[
\frac{\partial^2 E}{\partial \beta_{mn} \partial \beta_{pq}} = \frac{1}{2} b_{mn} b_{pq} \left\langle \left[ \left[ \left[ \hat{H}, \hat{r}_m \hat{p}_n \right], \hat{r}_p \hat{p}_q - \hat{p}_p \hat{r}_q \right] \right], \hat{r}_m \hat{p}_n \right\rangle_0 + \left\langle \left[ \left[ \left[ \hat{H}, \hat{r}_m \hat{p}_n \right], \hat{r}_m \hat{p}_n \right], \hat{r}_p \hat{p}_q - \hat{p}_p \hat{r}_q \right] \right\rangle_0 = 0, \quad \text{(S95)}
\]
\[
\frac{\partial^2 E}{\partial \gamma_{mn} \partial \beta_{pq}} = \frac{1}{2} c_{mn} c_{pq} \left\langle \left[ \left[ \left[ \hat{H}, \hat{r}_m \hat{p}_n \right], \hat{r}_p \hat{p}_q - \hat{p}_p \hat{r}_q \right] \right], \hat{r}_m \hat{p}_n \right\rangle_0 + \left\langle \left[ \left[ \left[ \hat{H}, \hat{r}_m \hat{p}_n \right], \hat{r}_m \hat{p}_n \right], \hat{r}_p \hat{p}_q - \hat{p}_p \hat{r}_q \right] \right\rangle_0 = 0, \quad \text{(S96)}
\]
\[
\frac{\partial^2 E}{\partial \gamma_{mn} \partial \beta_{pq}} = \frac{1}{2} c_{mn} c_{pq} \left\langle \left[ \left[ \left[ \hat{H}, \hat{r}_m \hat{p}_n \right], \hat{r}_p \hat{p}_q - \hat{p}_p \hat{r}_q \right] \right], \hat{r}_m \hat{p}_n \right\rangle_0 + \left\langle \left[ \left[ \left[ \hat{H}, \hat{r}_m \hat{p}_n \right], \hat{r}_m \hat{p}_n \right], \hat{r}_p \hat{p}_q - \hat{p}_p \hat{r}_q \right] \right\rangle_0 = 0, \quad \text{(S97)}
\]
and
\[
\frac{\partial^2 E}{\partial \gamma_{mn} \partial \gamma_{pq}} = \frac{1}{2} c_{mn} c_{pq} \left\langle \left[ \left[ \left[ \hat{H}, \hat{r}_m \hat{p}_n \right], \hat{r}_p \hat{p}_q - \hat{p}_p \hat{r}_q \right] \right], \hat{r}_m \hat{p}_n \right\rangle_0 + \left\langle \left[ \left[ \left[ \hat{H}, \hat{r}_m \hat{p}_n \right], \hat{r}_m \hat{p}_n \right], \hat{r}_p \hat{p}_q - \hat{p}_p \hat{r}_q \right] \right\rangle_0 = 0. \quad \text{(S98)}
\]

Finally, for mixed second derivatives for one displacement and one squeezing parameter, the relevant expectation values are
\[
\left\langle \left[ \hat{H}, \hat{r}_{pq} \right] \right\rangle_0 = -i \omega_p (\hat{p}_p, \hat{r}_m \hat{r}_n) = 0, \quad \text{(S99)}
\]
\[
\left\langle \left[ \hat{H}, \hat{r}_{pq} \right] \right\rangle_0 = -i \omega_p (\hat{p}_p, \hat{r}_m \hat{r}_n) = 0, \quad \text{(S100)}
\]
\[
\left\langle \left[ \hat{H}, \hat{r}_{pq} \right] \right\rangle_0 = -i \omega_p (\hat{p}_p, \hat{r}_m \hat{r}_n) = 0, \quad \text{(S101)}
\]
\[
\left\langle \left[ \hat{H}, \hat{r}_{pq} \right] \right\rangle_0 = i \left\langle \left[ \hat{V}, \hat{r}_m \hat{r}_n \right] \right\rangle_0 = 0, \quad \text{(S102)}
\]
\[
\left\langle \left[ \hat{H}, \hat{r}_{pq} \right] \right\rangle_0 = i \left\langle \left[ \hat{V}, \hat{r}_m \hat{r}_n \right] \right\rangle_0 = 0, \quad \text{(S103)}
\]
and
\[
\left\langle \left[ \hat{H}, \hat{r}_{pq} \right] \right\rangle_0 = i \left\langle \left[ \hat{V}, \hat{r}_m \hat{r}_n \right] \right\rangle_0 = 0, \quad \text{(S104)}
\]
Using Eq. (S73), the mixed second derivatives of the energy become

$$\frac{\partial^2 E}{\partial \alpha \partial \beta mn} = -b_{mn} \left\langle \left[ \left[ \hat{H}, \hat{p}_m \right], \hat{r}_n \hat{p}_n + \hat{p}_m \hat{r}_n \right] \right\rangle = b_{mn} \left[ \left( n_m + \frac{1}{2} \right) \Phi^{(3)}_{mn} + (n \leftrightarrow m) \right] = b_{mn} (n_m + n_n + 1) \Phi^{(3)}_{mn},$$

(S105)

$$\frac{\partial^2 E}{\partial \alpha \partial \gamma mn} = c_{mn} \left\langle \left[ \left[ \hat{H}, \hat{p}_m \right], \hat{r}_m \hat{p}_n - \hat{p}_m \hat{r}_n \right] \right\rangle = -c_{mn} \left[ \left( n_m + \frac{1}{2} \right) \Phi^{(3)}_{mn} - (n \leftrightarrow m) \right] = -c_{mn} (n_m - n_n) \Phi^{(3)}_{mn},$$

(S106)

$$\frac{\partial^2 E}{\partial \alpha \partial \beta mn} = b_{mn} \left\langle \left[ \left[ \hat{H}, \hat{p}_p \right], \hat{r}_m \hat{p}_n - \hat{p}_m \hat{r}_n \right] \right\rangle = 0,$$

(S107)

$$\frac{\partial^2 E}{\partial \alpha \partial \gamma mn} = -c_{mn} \left\langle \left[ \left[ \hat{H}, \hat{p}_p \right], \hat{r}_m \hat{p}_n + \hat{p}_m \hat{r}_n \right] \right\rangle = 0,$$

(S108)

$$\frac{\partial^2 E}{\partial \alpha \partial \beta mn} = b_{mn} \left\langle \left[ \left[ \hat{H}, \hat{r}_p \right], \hat{r}_m \hat{p}_n + \hat{p}_m \hat{r}_n \right] \right\rangle = 0,$$

(S109)

$$\frac{\partial^2 E}{\partial \alpha \partial \gamma mn} = -c_{mn} \left\langle \left[ \left[ \hat{H}, \hat{r}_p \right], \hat{r}_m \hat{p}_n - \hat{p}_m \hat{r}_n \right] \right\rangle = 0,$$

(S110)

$$\frac{\partial^2 E}{\partial \alpha \partial \beta mn} = -b_{mn} \left\langle \left[ \left[ \hat{H}, \hat{r}_p \right], \hat{r}_m \hat{p}_n - \hat{p}_m \hat{r}_n \right] \right\rangle = 0,$$

(S111)

and

$$\frac{\partial^2 E}{\partial \alpha \partial \gamma mn} = c_{mn} \left\langle \left[ \left[ \hat{H}, \hat{r}_p \right], \hat{r}_m \hat{p}_n + \hat{p}_m \hat{r}_n \right] \right\rangle = 0.$$

(S112)

## S5. Calculation of the Interacting Green Function

In this section, we detail the solution of the Dyson equations.

### A. Partially interacting Green function: 4-phonon interaction

First, let us consider the Dyson equation for the partially interacting Green function [(39)]. Substituting Eq. (27) and Eq. (34) into Eq. (39), one can directly solve the Dyson equation to find

$$P_2 G^{(4)}(z) P_2 = 0 \oplus (G^{(0)}_2, \oplus G^{(0)}_2) \times \begin{pmatrix}
1 & B \Phi^{(4)} \frac{\omega}{z - \omega} & 0 & 0 & 0 & -B \Phi^{(4)} \frac{\omega}{z - \omega} \\
0 & 0 & 0 & iB \Phi^{(4)} C \frac{z}{z - \omega} & -B \Phi^{(4)} C \frac{\omega}{z - \omega} & 1 \\
iC \Phi^{(4)} \frac{\omega}{z - \omega} & -C \Phi^{(4)} \frac{\omega}{z - \omega} & iC \Phi^{(4)} \frac{z}{z - \omega} & 1 & 0 & 0
\end{pmatrix}^{-1}.$$

(S113)

From Eq. (S113), one finds
\[
\begin{pmatrix}
G^{(0)}_{2_+}(z) & 0 \\
0 & G^{(0)}_{2_-}(z)
\end{pmatrix} = \begin{pmatrix}
G^{(4)}_{2_+}(z) & G^{(4)}_{2_+}(z) \\
G^{(4)}_{2_-}(z) & G^{(4)}_{2_-}(z)
\end{pmatrix} \times \begin{pmatrix}
1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
iB\Phi^{(4)} B \frac{z}{\sqrt{\omega^2 - \omega^2_+}} & -B\Phi^{(4)} B \frac{z}{\sqrt{\omega^2 - \omega^2_-}} & iB\Phi^{(4)} C \frac{z}{\sqrt{\omega^2 - \omega^2_+}} & -B\Phi^{(4)} C \frac{z}{\sqrt{\omega^2 - \omega^2_-}} \\
iC\Phi^{(4)} B \frac{z}{\sqrt{\omega^2 - \omega^2_+}} & -C\Phi^{(4)} B \frac{z}{\sqrt{\omega^2 - \omega^2_-}} & iC\Phi^{(4)} C \frac{z}{\sqrt{\omega^2 - \omega^2_+}} & -C\Phi^{(4)} C \frac{z}{\sqrt{\omega^2 - \omega^2_-}}
\end{pmatrix},
\]
where we defined
\[
G^{(4)}_{ss'}(z) = P_{ss'}G^{(4)}_{ss'}(z)P_{ss'},
\]
with \(s, s' \in \{+, -\} \).

By explicitly writing the odd rows and even columns of Eq. (S114), one finds
\[
\begin{pmatrix}
\frac{i\omega_+}{\sqrt{\omega^2 - \omega^2_+}} & 0 \\
0 & \frac{i\omega_-}{\sqrt{\omega^2 - \omega^2_-}}
\end{pmatrix} = \begin{pmatrix}
G^{(4)}_{++}(z) & G^{(4)}_{++}(z) \\
G^{(4)}_{+-}(z) & G^{(4)}_{+-}(z)
\end{pmatrix} \times \begin{pmatrix}
1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
iB\Phi^{(4)} B \frac{\omega_+}{\sqrt{\omega^2 - \omega^2_+}} & -B\Phi^{(4)} C \frac{\omega_+}{\sqrt{\omega^2 - \omega^2_-}} & iB\Phi^{(4)} C \frac{\omega_+}{\sqrt{\omega^2 - \omega^2_+}} & -B\Phi^{(4)} C \frac{\omega_+}{\sqrt{\omega^2 - \omega^2_-}} \\
iC\Phi^{(4)} B \frac{\omega_-}{\sqrt{\omega^2 - \omega^2_+}} & -C\Phi^{(4)} B \frac{\omega_-}{\sqrt{\omega^2 - \omega^2_-}} & iC\Phi^{(4)} C \frac{\omega_-}{\sqrt{\omega^2 - \omega^2_+}} & -C\Phi^{(4)} C \frac{\omega_-}{\sqrt{\omega^2 - \omega^2_-}}
\end{pmatrix}.
\]

Here, the subscript 11 and 12 denotes the row and column index of the blocks in the \(2 \times 2\) representation of \(G^{(4)}_{ss'}(z)\). Since the first and third rows of the last matrix of Eq. (S116) is zero, one finds
\[
\begin{pmatrix}
\frac{i\omega_+}{\sqrt{\omega^2 - \omega^2_+}} & 0 \\
0 & \frac{i\omega_-}{\sqrt{\omega^2 - \omega^2_-}}
\end{pmatrix} = \begin{pmatrix}
G^{(4)}_{++}(z) & G^{(4)}_{++}(z) \\
G^{(4)}_{+-}(z) & G^{(4)}_{+-}(z)
\end{pmatrix} \times \begin{pmatrix}
1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
iB\Phi^{(4)} B \frac{\omega_+}{\sqrt{\omega^2 - \omega^2_+}} & -B\Phi^{(4)} C \frac{\omega_+}{\sqrt{\omega^2 - \omega^2_-}} & iB\Phi^{(4)} C \frac{\omega_+}{\sqrt{\omega^2 - \omega^2_+}} & -B\Phi^{(4)} C \frac{\omega_+}{\sqrt{\omega^2 - \omega^2_-}} \\
iC\Phi^{(4)} B \frac{\omega_-}{\sqrt{\omega^2 - \omega^2_+}} & -C\Phi^{(4)} B \frac{\omega_-}{\sqrt{\omega^2 - \omega^2_-}} & iC\Phi^{(4)} C \frac{\omega_-}{\sqrt{\omega^2 - \omega^2_+}} & -C\Phi^{(4)} C \frac{\omega_-}{\sqrt{\omega^2 - \omega^2_-}}
\end{pmatrix}.
\]

By inverting the last matrix of Eq. (S117) and using Eq. (S119), one finds
\[
\begin{pmatrix}
G^{(4)}_{++}(z) & G^{(4)}_{++}(z) \\
G^{(4)}_{+-}(z) & G^{(4)}_{+-}(z)
\end{pmatrix} = i \begin{pmatrix}
g_+^{(4)}(z) & 0 \\
0 & g_-^{(4)}(z)
\end{pmatrix} \begin{pmatrix}
1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
iB\Phi^{(4)} B g_+(z) & B\Phi^{(4)} C g_-(z) & iB\Phi^{(4)} C g_+(z) & B\Phi^{(4)} C g_-(z)
\end{pmatrix}^{-1}
\]
where
\[
\mathbf{g}_\pm^{(4)}(z) = \frac{\omega_\pm}{z^2 - \omega_\pm^2}.
\]

### B. Fully interacting Green function: 3-, 4-phonon interactions

Next, we derive the Dyson equation for the interacting retarded position-position correlation function starting from the Dyson equation in Eq. (41).

Using Eq. (S1) and Eqs. (S2-S7), one can easily show that the matrix elements of the position operator is nonzero only for the variation of \(\alpha^i_m\):
\[
\partial_{\mathbf{r}} \mathbf{r} = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 \end{pmatrix}^T.
\]
Similarly, the matrix element for the momentum operator is nonzero only for the variation of \(\alpha^i_m\):
\[
\partial_{\mathbf{p}} \mathbf{p} = \begin{pmatrix} 0 & 1 & 0 & 0 & 0 \end{pmatrix}^T,
\]
By substituting \(\mathbf{r}_m\) or \(\mathbf{p}_n\) to \(\hat{A}\) and \(\hat{B}\) of the general linear response formula Eq. (19), we find
\[
\mathbf{P}_1 \mathbf{G}(\omega + i\eta) \mathbf{P}_1 = i \begin{pmatrix}
-G^{(R)}_{rr}(\omega) & G^{(R)}_{rp}(\omega) \\
-G^{(R)}_{rp}(\omega) & G^{(R)}_{pp}(\omega)
\end{pmatrix} \oplus 0.
\]
Therefore, to calculate the position-position correlation function, it suffices to compute the upper right block of \(\mathbf{P}_1 \mathbf{G} \mathbf{P}_1\); the 1-phonon sector of the fully interacting Green function.
By viewing the upper right block of Eq. (41), one finds

$$iG_{rr}^{(R)} = iG_{rr}^{(R0)} - iG_{rr}^{(R0)} \times \left( \sum_{s,s'=\pm} \Phi(3) B_s \mathbf{G}_{s'r'}(z) \right)_{12} B_{s'} \Phi(3) \right) \times iG_{rr}^{(R)}.$$  

(S123)

Then, the self-energy for the fully interacting retarded position-position correlation function reads

$$\Pi_{rr}(z) = -i \sum_{s,s'=\pm} \Phi^{(3)} B_s \mathbf{G}_{s'r'}^{(4)}(z) \right)_{12} B_{s'} \Phi^{(3)}.$$

(S124)

Substituting Eq. (S118) into Eq. (S124) and using

$$(B g_+ C g_-) \left[ \mathbb{1} - \left( \frac{B}{C} \right) \Phi^{(4)} (B g_+ C g_-) \right]^{-1} \left( \frac{B}{C} \right) = (B g_+ B + C g_- C) \left[ \mathbb{1} - \Phi^{(4)} (B g_+ B + C g_- C) \right]^{-1},$$

we find Eq. (44) of the main text:

$$\Pi_{rr}(z) = \Phi^{(3)} W (\mathbb{1} - \Phi^{(4)} W)^{-1} \Phi^{(3)}.$$

(S126)

Here, we used the diagonal matrix $W$ defined in Eq. (45) of the main text:

$$W_{mn,pq} \equiv \left[ B g_+ (z) B + C g_- (z) C \right]_{mn,pq}$$

$$= -\frac{1}{2} \frac{2 - \delta_{m,n}}{2} \frac{(\omega_m + \omega_n)(n_m + n_n + 1)}{(\omega_m + \omega_n)^2 - z^2} - \frac{(\omega_m - \omega_n)(n_m - n_n)}{(\omega_m - \omega_n)^2 - z^2} \delta_{mn,pq}. \quad (S127)$$

In Eq. (44), all the sum over indices in the matrix-matrix product should be constrained by $m \leq n$.

**S6. DERIVATION OF THE SCBA ANSATZ FROM THE TDVP SELF-ENERGY**

In this section, we derive the SCBA ansatz Eq. (47) from the self-energy formula Eq. (44) which is derived from TDVP. In this section, the constraint $m \leq n$ in the summation over mode indices $m$ and $n$ is not implied. The constraint is made explicit whenever necessary by using smaller matrices which are defined only on the constrained indices:

$$\tilde{\Phi}_{p,m'n'}^{(3)} = \Phi_{pm'n'}, \quad (S128)$$

$$\tilde{\Phi}_{m'n',r's'}^{(4)} = \Phi_{m'n'r's'}, \quad (S129)$$

and

$$\tilde{W}_{m'n',r's'} = W_{m'n',r's'}. \quad (S130)$$

Here and in the remaining part of this section, we denote the constrained indices with primes: the index $m'n'$ implies the constraint $m' \leq n'$. Using these smaller matrices, Eq. (44) can be written as

$$\Pi_{rr}(z) = \tilde{\Phi}^{(3)} \tilde{W} (\mathbb{1} - \tilde{\Phi}^{(4)} \tilde{W})^{-1} \tilde{\Phi}^{(3)\dagger}. \quad (S131)$$

Next, we define a rectangular matrix $R$ with matrix elements

$$R_{m'n',rs} = \begin{cases} 1 & \text{if } (r,s) = (m',n') \text{ or } (r,s) = (n',m') \\ 0 & \text{otherwise} \end{cases}. \quad (S132)$$

By multiplying $R$ to the smaller matrices, one can recover the full matrix:

$$\tilde{\Phi}^{(3)} R = R^\dagger \tilde{\Phi}^{(3)\dagger} = \Phi^{(3)}, \quad (S133)$$
and

$$R^\top \Phi^{(4)} R = \Phi^{(4)}.$$  \hfill (S134)

These identities hold because $\Phi_{mn}^{(3)}$ and $\Phi_{mns}^{(4)}$ are invariant to the permutation of the indices. In addition, from the definition of $\chi$ [Eq. (46)], one finds

$$(R \chi R^\top)_{m'n',r's'} = (R \chi R^\top)_{m'n',m's'} \delta_{m'n',r's'}$$  \hfill (S135)

and

$$(R \chi R^\top)_{m'n',m'n'} = \begin{cases} \chi_{m'n'} & \text{if } m' = n' \\ 2\chi_{m'n'} & \text{if } m' \neq n' \end{cases}$$

$$= (2 - \delta_{m,n})\chi_{m'n'}$$

$$= -2\tilde{W}_{m'n'}.$$  \hfill (S136)

Equations (S135) and (S136) imply

$$R \chi R^\top = -2\tilde{W}.$$  \hfill (S137)

Using Eqs. (S133), (S134), and (S137), we can write Eq. (S131) as

$$\Pi_{rr}(z) = -\frac{1}{2} \Phi^{(3)} R \chi R^\top \left( \mathbb{1} + \frac{1}{2} \Phi^{(4)} R \chi R^\top \right)^{-1} \Phi^{(3)\top}$$

$$= -\frac{1}{2} \Phi^{(3)} R \chi \left( \mathbb{1} + \frac{1}{2} R^\top \Phi^{(4)} R \chi \right)^{-1} R^\top \Phi^{(3)\top}$$

$$= -\frac{1}{2} \Phi^{(3)} \chi \left( \mathbb{1} + \frac{1}{2} \Phi^{(4)} \chi \right)^{-1}.$$  \hfill (S138)

Equation (S138) is identical to Eq. (47) of the main text.

### S7. DEGENERATE AND NEAR-DEGENERATE MODES

In this section, we detail the treatment of degenerate and near-degenerate modes.

First, let us assume that states $m$ and $n$ are almost but not exactly degenerate. Although it is true that $c_{mn}$ [Eq. (13)] becomes large, what is important in the dynamics of the variational parameter $\gamma_{mn}$ in the linear response regime is the linearized time-evolution generator $K$. When computing $K$, the large $c_{mn}$ factors are counteracted by the small $(n_m - n_n)$ factors that appear when taking derivatives of $E(x)$. Equations (S49, S90, S94) are examples of such counteraction. The fact that the equation of motion does not suffer any problems can be seen from Eqs. (26, 27, 31). One finds that $c_{mn}$ enters the time-evolution generator $K$ only through $C_{mn,pq}$ [Eq. (31)]. There, the $c_{mn}$ factor is multiplied by $(n_m - n_n)$, so that $C_{mn,pq}$ is proportional to $\sqrt{n_m - n_n}$. Hence, the matrix element of $K$ involving near-degenerate states converges to zero in the limit of degeneracy.

Next, let us consider exactly degenerate states. In the main text, we explained that if modes $m$ and $n$ degenerate, one needs to exclude $\gamma_{mn}$ from the set of variational parameters when studying the linear response regime. The reason is that the infinitesimal transformation parametrized by $\gamma_{mn}$ does not change the variational equilibrium density matrix $\rho_0$. One should exclude parameters that do not change the variational density matrix $\rho(x)$ at that given $x$. The parameter $\gamma_{mn}$ for degenerate $m$ and $n$ is such a parameter for the equilibrium, $x = 0$. We note that such exclusion is necessary and justified only in the linear response regime. When considering large deviations from $x = 0$, one must include $\gamma_{mn}$ in the set of variational parameters.

Even if the energy of degenerate states $m$ and $n$ are slightly perturbed due to numerical inaccuracies, no problem will occur. As explained in the near-degenerate case, the corresponding equation of motion will be suppressed by a factor of $\sqrt{n_m - n_n}$, so that $\gamma_{mn}$ stays at equilibrium value, $\gamma_{mn} = 0$. 
S8. ZERO TEMPERATURE CASE

In the main text, we have focused only on the finite temperature case. At zero temperature, one should apply TDVP directly to the Gaussian wavefunctions without purification. The main difference with the finite temperature case is that the squeezing transformation parametrized by $\gamma$ becomes a do-nothing operation at $T = 0$. This difference can be noticed by calculating the tangent vector by applying $\partial \hat{U} / \partial \gamma$ [Eqs. (S6, S7)] to the stationary state wavefunction. At $T > 0$, the purified stationary state wavefunction in the number basis has nonzero coefficients for states with nonzero phonon populations; hence, the tangent vectors do not vanish. On the contrary, at $T = 0$, the stationary state wavefunction is a vacuum state of the SCHA harmonic Hamiltonian. Hence, the rightmost annihilation operators in Eqs. (S6, S7) nullify the wavefunction and the corresponding tangent vectors become null vectors. So, at zero temperature, only $\alpha$ and $\beta$ should be used as the variational parameters.

One can follow the same steps as in the finite temperature case to calculate the linearized time evolution generator and the position-position correlation function at zero temperature. The final form of the phonon self-energy is identical to the finite-temperature result, Eq. (47). The only difference is that the second term in the definition of $\chi$ [Eq. (46)] that originates from the variation of the $\gamma$ parameter vanishes. Still, the equations need not be modified because the second term of Eq. (46) is already zero at $T = 0$ since $n_m = n_n = 0$.

S9. SINGLE-MODE ANHARMONIC HAMILTONIAN

In this section, we compute the excitation energy of the single-mode anharmonic Hamiltonian [Eq. (48)] using three different methods: perturbation theory, linearized time evolution, and projected Hamiltonian.

First, using standard second-order perturbation theory, the ground state and first-excited state energy are

$$E_{\text{ground}} = \frac{\omega_0}{2} - \frac{\lambda^2 a^2}{144 \omega_0} + \mathcal{O}(\lambda^3)$$

and

$$E_{\text{1st exc.}} = \frac{3 \omega_0}{2} - \frac{13 \lambda^2 a^2}{144 \omega_0} + \mathcal{O}(\lambda^3).$$

One can also show that the third-order perturbative correction to energy is zero because of the parity of the unperturbed wavefunctions. Thus, the excitation energy is

$$\omega_{\text{pert}} = E_{\text{1st exc.}} - E_{\text{ground}} = \omega_0 - \frac{\lambda^2 a^2}{12 \omega_0} + \mathcal{O}(\lambda^4).$$

Next, let us use the linearized time evolution method. The third- and fourth-order force constants of the Hamiltonian are

$$\Phi^{(3)} = \lambda a, \quad \Phi^{(4)} = \lambda^2 b.$$ (S142)

Using the self-energy formula [Eq. (47)], we find

$$\Pi(z) = -\frac{\omega_0 \lambda^2 a^2}{2(4 \omega_0^2 - z^2)} \times \frac{1}{1 + \frac{\lambda^2 a^2}{2(4 \omega_0^2 - z^2)}}.$$ (S143)

The excitation energy $\omega_{\text{lin}}$ is the position of the pole of the interacting Green function. From the Dyson equation [Eq. (43)], one finds

$$1 = \frac{\omega_0}{(\omega_{\text{lin}})^2 - \omega_0^2} \Pi(\omega_{\text{lin}}).$$ (S144)

In the perturbative limit of small $\lambda$, one finds

$$\omega_{\text{lin}} \approx \omega_0 + \frac{1}{2} \Pi(\omega_0) = \omega_0 - \frac{\lambda^2 a^2}{12 \omega_0} + \mathcal{O}(\lambda^4).$$ (S145)

Finally, we use the projected Hamiltonian method. The tangent space of the Gaussian variational manifold at zero temperature is spanned by the 1- and 2-phonon states:

$$\mathcal{T}_{\text{Gaussian}} = \text{span}\{|1\rangle, |2\rangle\}.$$ (S146)
The Hamiltonian projected to this subspace is

\[ H_{\text{proj}} = \begin{pmatrix} \frac{3\omega_0}{2} & 0 \\ 0 & \frac{\omega_0}{2} \end{pmatrix} + \begin{pmatrix} 0 & \frac{\lambda a}{4} \\ \frac{\lambda a}{4} & \frac{\lambda^2 b}{8} \end{pmatrix}. \]  

(S147)

One can find the excitation energy by subtracting the variational ground state energy, \(\omega_0/2\), from the lower eigenvalue of \(H_{\text{proj}}\):

\[
\omega_{\text{proj}} = \frac{3\omega_0}{2} + \frac{\lambda^2 b}{16} - \sqrt{\left(\frac{\omega_0}{2} + \frac{\lambda^2 b}{16}\right)^2 + \left(\frac{\lambda a}{4}\right)^2} - \frac{\omega_0}{2} \\
= \omega_0 - \frac{\lambda^2 a^2}{16\omega_0} + O(\lambda^4).
\]  

(S148)

These results are summarized in Table I of the main text. By comparing \(\omega_{\text{lin}}\) [Eq. (S145)] and \(\omega_{\text{proj}}\) [Eq. (S148)] to \(\omega_{\text{pert}}\) [Eq. (S141)], we find that only the linearized time evolution method gives the correct leading order correction to the excitation energy.

---

[S1] Lucas Hackl, Tommaso Guaita, Tao Shi, Jutho Haegeman, Eugene Demler, and Ignacio Cirac, “Geometry of variational methods: dynamics of closed quantum systems,” SciPost Physics 9 (2020), 10.21468/scipostphys.9.4.048.

[S2] Tao Shi, Eugene Demler, and J. Ignacio Cirac, “Variational study of fermionic and bosonic systems with non-Gaussian states: Theory and applications,” Annals of Physics 390, 245–302 (2018).

[S3] Tommaso Guaita, Lucas Hackl, Tao Shi, Claudius Hubig, Eugene Demler, and J. Ignacio Cirac, “Gaussian time dependent variational principle for the Bose-Hubbard model,” Physical Review B 100, 094529 (2019).

[S4] R Pathria and PD Beale, Statistical Mechanics, 3rd ed. (Academic Press, Boston, MA, 2011).

[S5] Raffaello Bianco, Ion Errea, Lorenzo Paulatto, Matteo Calandra, and Francesco Mauri, “Second-order structural phase transitions, free energy curvature, and temperature-dependent anharmonic phonons in the self-consistent harmonic approximation: Theory and stochastic implementation,” Physical Review B 96, 014111 (2017).