

## Supporting Information for Unphysical Solutions in Coupled-Cluster-Based Random Phase Approximation and How to Avoid Them

Ruiheng Song,<sup>1</sup> Xiliang Gong,<sup>1</sup> and Hong-Zhou Ye<sup>1,2, a)</sup>

<sup>1)</sup>*Department of Chemistry and Biochemistry, University of Maryland, College Park,  
MD 20742*

<sup>2)</sup>*Institute for Physical Science and Technology, University of Maryland, College Park,  
MD 20742*

---

<sup>a)</sup>Electronic mail: [hzye@umd.edu](mailto:hzye@umd.edu)

Note: figures, tables, and equations in the main text will be referred to as Fig. M1, Table M2, and Eq. M3.

## I. COMPUTATIONAL DETAILS

All calculations reported in this work using RPA and drCCD are performed using a developer version of the PySCF code<sup>1,2</sup> with Libcint<sup>3</sup> for integral evaluation. The mean-field calculations are performed at zero-temperature with integer occupation. The reference RPA correlation energy is calculated using AC-RPA as implemented in PySCF with 60 quadrature points for the imaginary frequency integration. The cc-pVDZ basis sets<sup>4</sup> and the associated cc-pVDZ-JKFIT auxiliary basis sets<sup>5</sup> are used for both the mean-field and correlated calculations, along with the frozen-core approximation for the latter. Molecular structures optimized at B3LYP<sup>6</sup>+D3<sup>7</sup>/def2-SVP<sup>8</sup> level using ORCA<sup>9-11</sup> can be found below in section IV. For the factorized drCCD, the Cholesky decomposition (Eq. M28) vectors reproduce the matrix elements of the preconditioner to a precision better than  $10^{-9}$  Ha<sup>-1</sup>. For the iterative solution of both full and factorized drCCD equations, the maximum DIIS space is set to 6. The iteration is deemed converged if both the energy change between two iterations drops below  $10^{-7}$  Ha and the amplitudes ( $T$  for full drCCD and  $U$  for factorized drCCD) drops below  $10^{-6}$  (a.u.).

## II. EXTENSION TO OTHER FLAVORS OF RPA

The discussion in the main text for direct particle-hole RPA (ph-RPA) relies only on the mathematical properties of the RPA eigenvalue equation (Eq. M2), which is a symplectic eigenvalue equation. As a consequence, all results developed in the main text apply immediately to other flavors of RPA that can be formulated using a symplectic eigenvalue equation. This includes ph-RPA with exchange (commonly referred to as RPAX or full RPA), particle-particle RPA<sup>12,13</sup> (pp-RPA), and quasi-particle RPA<sup>12</sup> (qp-RPA), to name a few. Our discussion below for qp and pp-RPA follows closely Ref 12.

### A. RPAX

The RPAX equation is the same as Eq. M2 except that  $A$  and  $B$  contain anti-symmetrized electron repulsion integrals. The RPAX correlation energy can be reproduced by the physical solution

of ring CCD, whose amplitude  $T$  also satisfies the condition  $\lambda_{\max}(T^\dagger T) < 1$ .

## B. qp-RPA

The qp-RPA is RPA for a Hartree-Fock-Bogoliubov state.<sup>12</sup> The qp-RPA eigenvalue equation is also formally the same as Eq. M2,

$$\begin{bmatrix} \mathcal{A} & \mathcal{B} \\ -\mathcal{B}^* & -\mathcal{A}^* \end{bmatrix} \begin{bmatrix} \mathcal{X} & \mathcal{Y}^* \\ \mathcal{Y} & \mathcal{X}^* \end{bmatrix} = \begin{bmatrix} \mathcal{X} & \mathcal{Y}^* \\ \mathcal{Y} & \mathcal{X}^* \end{bmatrix} \begin{bmatrix} \Omega & 0 \\ 0 & -\Omega^* \end{bmatrix}, \quad (1)$$

with  $\mathcal{A}$  and  $\mathcal{B}$  matrices given by

$$\begin{aligned} A_{pq,rs} &= \langle [\alpha_q \alpha_p, [H, \alpha_r^\dagger \alpha_s^\dagger]] \rangle, \\ B_{pq,rs} &= \langle [\alpha_q \alpha_p, [H, \alpha_s \alpha_r]] \rangle, \end{aligned} \quad (2)$$

where  $\alpha_p$  and  $\alpha_p^\dagger$  are quasi-particle annihilation and creation operators, respectively. All matrices,  $\mathcal{A}$ ,  $\mathcal{B}$ ,  $\mathcal{X}$ ,  $\mathcal{Y}$ ,  $\Omega$ , are of size  $N_{\text{orb}} \times N_{\text{orb}}$  with  $N_{\text{orb}} = N_{\text{occ}} + N_{\text{vir}}$ . Under the assumption that the underlying HFB state is stable, the qp-RPA eigenvalues are all real, and a physical qp-RPA correlation energy is given by the plasmonic formula,

$$E_c^{\text{qp-RPA}} = \frac{1}{2} \text{Tr} (\Omega - \mathcal{A}) = \frac{1}{2} \text{Tr} \mathcal{B} \mathcal{T} \quad (3)$$

where in the second equality, we introduced the physical solution

$$\mathcal{T} = \mathcal{Y} \mathcal{X}^{-1} \quad (4)$$

to the Ricatti equation corresponding to the qp-RPA problem,

$$\mathcal{B}^* + \mathcal{A}^* \mathcal{T} + \mathcal{T} \mathcal{A} + \mathcal{T} \mathcal{B} \mathcal{T} = 0. \quad (5)$$

The physical solution  $\mathcal{T}$  satisfies the same condition,  $\lambda_{\max}(\mathcal{T}^\dagger \mathcal{T}) < 1$ .

## C. pp-RPA

When qp-RPA is applied to a stable HF (rather than HFB) state, the  $\mathcal{A}$  and  $\mathcal{B}$  matrices have the following block structure,

$$\mathcal{A} = \begin{bmatrix} \mathcal{A}_{\text{oo,oo}} & 0 & 0 \\ 0 & \mathcal{A}_{\text{ov,ov}} & 0 \\ 0 & 0 & \mathcal{A}_{\text{vv,vv}} \end{bmatrix}, \quad \mathcal{B} = \begin{bmatrix} 0 & 0 & \mathcal{B}_{\text{oo,vv}} \\ 0 & \mathcal{B}_{\text{ov,ov}} & 0 \\ \mathcal{B}_{\text{vv,oo}} & 0 & 0 \end{bmatrix} \quad (6)$$

where  $\mathcal{A}_{\text{ov,ov}}$  and  $\mathcal{B}_{\text{ov,ov}}$  are the  $A$  and  $B$  matrices in ph-RPA (Eq. M3). Using the notation from Ref 12,

$$\begin{aligned} \mathcal{A}_{\text{oo,oo}} &= D, & D_{ij,kl} &= -(\epsilon_i + \epsilon_j)\delta_{ik}\delta_{jl} + \langle kl||ij \rangle, \\ \mathcal{A}_{\text{vv,vv}} &= C, & C_{ab,cd} &= (\epsilon_a + \epsilon_b)\delta_{ac}\delta_{bd} + \langle ab||cd \rangle, \\ \mathcal{B}_{\text{oo,vv}} &= \bar{B}, & \bar{B}_{ij,ab} &= \langle ab||ij \rangle. \end{aligned} \quad (7)$$

Note that both  $C$  and  $D$  are Hermitian matrices. This block structure leads to three independent eigenvalue problem: the ov-ov blocks give the ph-RPA presented in the main text, while the other blocks give pp-RPA,

$$\begin{bmatrix} C & -\bar{B} \\ \bar{B}^\dagger & -D^* \end{bmatrix} \begin{bmatrix} X_1 & Y_2 \\ Y_1 & X_2 \end{bmatrix} = \begin{bmatrix} X_1 & Y_2 \\ Y_1 & X_2 \end{bmatrix} \begin{bmatrix} \Omega_1 & 0 \\ 0 & \Omega_2 \end{bmatrix} \quad (8)$$

and its particle-hole conjugate, the hole-hole RPA (hh-RPA),

$$\begin{bmatrix} D & -\bar{B}^\top \\ \bar{B}^* & -C^* \end{bmatrix} \begin{bmatrix} X_2^* & Y_1^* \\ Y_2^* & X_1^* \end{bmatrix} = \begin{bmatrix} X_2^* & Y_1^* \\ Y_2^* & X_1^* \end{bmatrix} \begin{bmatrix} -\Omega_2 & 0 \\ 0 & -\Omega_1 \end{bmatrix}, \quad (9)$$

where  $\Omega_1$  is positive and  $\Omega_2$  is negative for a stable HF reference. The pp-RPA and hh-RPA have the same correlation energy

$$E_c^{\text{pp-RPA}} = \text{Tr}(\Omega_1 - C) = \text{Tr}(-\Omega_2 - D) = E_c^{\text{hh-RPA}} \quad (10)$$

which is reproduced by the physical solution

$$T_1 = -Y_1 X_1^{-1} = -(Y_2 X_2^{-1})^\dagger = T_2^\dagger \quad (11)$$

to the ladder CCD equation

$$\bar{B}^\dagger + D^* T_1 + T_1 C + T_1 \bar{B} T_1 = 0. \quad (12)$$

To derive the condition for the physical ladder CCD solution, we note that while neither pp-RPA (8) nor hh-RPA (9) corresponds to a symplectic eigenvalue equation, the combined problem

$$\begin{bmatrix} D & 0 & 0 & -\bar{B}^\top \\ 0 & C & -\bar{B} & 0 \\ 0 & \bar{B}^\dagger & -D^* & 0 \\ \bar{B}^* & 0 & 0 & -C^* \end{bmatrix} \begin{bmatrix} X_2^* & 0 & 0 & Y_1^* \\ 0 & X_1 & Y_2 & 0 \\ 0 & Y_1 & X_2 & 0 \\ Y_2^* & 0 & 0 & X_1^* \end{bmatrix} = \begin{bmatrix} X_2^* & 0 & 0 & Y_1^* \\ 0 & X_1 & Y_2 & 0 \\ 0 & Y_1 & X_2 & 0 \\ Y_2^* & 0 & 0 & X_1^* \end{bmatrix} \begin{bmatrix} -\Omega_2 & 0 & 0 & 0 \\ 0 & \Omega_1 & 0 & 0 \\ 0 & 0 & \Omega_2 & 0 \\ 0 & 0 & 0 & -\Omega_1 \end{bmatrix} \quad (13)$$

gives a symplectic eigenvalue equation. The plasmonic correlation energy of this pp+hh-RPA theory is equal to both the pp-RPA and the hh-RPA correlation energy,

$$E_{\text{cc}}^{\text{pp+hh-RPA}} = \frac{1}{2} \text{Tr}(\Omega_1 - \Omega_2 - C - D) = \underbrace{\text{Tr}(\Omega_1 - C)}_{E_{\text{cc}}^{\text{pp-RPA}}} = \underbrace{\text{Tr}(-\Omega_2 - D)}_{E_{\text{cc}}^{\text{hh-RPA}}}, \quad (14)$$

which is therefore also reproduced by the physical solution of ladder CCD. Since eq. (13) is a symplectic eigenvalue problem, we define

$$\bar{T} = - \begin{bmatrix} 0 & Y_1 \\ Y_2^* & 0 \end{bmatrix} \begin{bmatrix} X_2^* & 0 \\ 0 & X_1 \end{bmatrix}^{-1} = \begin{bmatrix} 0 & T_1 \\ T_1^\top & 0 \end{bmatrix} \quad (15)$$

which admits an Autonne-Takagi decomposition similar to Eq. M13. We thus conclude that  $\lambda_{\text{max}}(\bar{T}^\dagger \bar{T}) < 1$  is a sufficient and necessary condition for the physical solution. Noting that

$$\bar{T}^\dagger \bar{T} = \begin{bmatrix} T_1^* T_1^\top & 0 \\ 0 & T_1^\dagger T_1 \end{bmatrix}, \quad (16)$$

the condition for physical pp-RPA solution can be further simplified to be

$$\lambda_{\text{max}}(T_1^\dagger T_1) = \lambda_{\text{max}}(T_1^* T_1^\top) < 1. \quad (17)$$

### III. EXTENSION TO UNSTABLE MEAN-FIELD REFERENCES

The derivation in the main text for ph-RPA and in section II for other flavors of RPA assumes a stable mean-field reference (HF for ph-RPA and pp-RPA and HFB for qp-RPA), which guarantees that all RPA eigenvalues are real. However, a stable mean-field reference is not a necessary condition for real RPA frequencies; see e.g., the Appendix of Ref 12 for a counterexample. In this section, we show that all results derived in the main text and in section II are valid as long as the RPA frequencies are real, regardless of stability of the underlying mean-field reference.

For an unstable mean-field reference with real RPA eigenvalues, the RPA eigenvalue equation (Eq. M2) still holds. However, in this case,  $\Omega$  contains both positive and negative RPA frequencies.

Let

$$V_1 = \begin{bmatrix} X \\ Y \end{bmatrix}, \quad V_2 = \begin{bmatrix} Y^* \\ X^* \end{bmatrix} = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} V_1^* \quad (18)$$

be the eigenvectors corresponding to  $\Omega$  and  $-\Omega$ . We follow Ref 12 and define  $\Omega$  to be those RPA frequencies whose corresponding eigenvector has a *positive norm*, i.e.,

$$V_1^\dagger \eta V_1 = X^\dagger X - Y^\dagger Y = 1, \quad (19)$$

which automatically implies that  $V_2$  has a negative norm,

$$V_2^\dagger \eta V_2 = -(V_1^\dagger \eta V_1)^* = -1, \quad (20)$$

where the metric matrix is

$$\eta = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}. \quad (21)$$

With this definition, the RPA correlation energy is formally the same as Eq. M1, i.e.,

$$E_c^{\text{RPA}} = \frac{1}{2} \text{Tr}(\Omega - A). \quad (22)$$

But again,  $\Omega$  now contains some negative frequencies. This RPA correlation energy is reproduced by the Riccati equation (Eq. M7) with the physical solution  $T = YX^{-1}$ , where  $X$  and  $Y$  are from  $V_1$  with positive norm. The family of Riccati solutions are then  $T_\eta = Y_\eta X_\eta^{-1}$ , where  $\eta_n = \pm 1$  now corresponds to taking the  $n$ -th column from  $V_1$  (which has a positive norm) and  $V_2$  (which has a negative norm), respectively. With this modified definition of physical and unphysical solutions, all other conclusions derived in the main text and in section II naturally apply to this special case of unstable mean-field references.

#### IV. SUPPLEMENTARY DATA

The following GitHub repository

[https://github.com/hongzhouye/supporting\\_data/tree/main/2025/RPA\\_Stability](https://github.com/hongzhouye/supporting_data/tree/main/2025/RPA_Stability)

collects (i) optimized molecular structures and (ii) data presented in Fig. M1 and M2.

#### V. SUPPLEMENTARY FIGURES

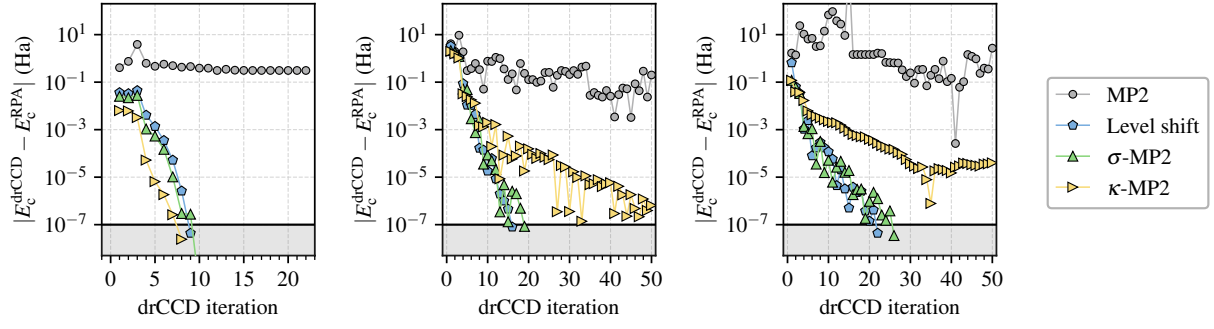


FIG. S1. The same figures as Fig. M1A, C, and E except that the two-stage algorithm is not used.

## REFERENCES

- <sup>1</sup>Q. Sun, T. C. Berkelbach, N. S. Blunt, G. H. Booth, S. Guo, Z. Li, J. Liu, J. D. McClain, E. R. Sayfutyarova, S. Sharma, S. Wouters, and G. K.-L. Chan, “Pyscf: the python-based simulations of chemistry framework,” [Wiley Interdiscip. Rev. Comput. Mol. Sci](#) **8**, e1340 (2018).
- <sup>2</sup>Q. Sun, X. Zhang, S. Banerjee, P. Bao, M. Barbry, N. S. Blunt, N. A. Bogdanov, G. H. Booth, J. Chen, Z.-H. Cui, J. J. Eriksen, Y. Gao, S. Guo, J. Hermann, M. R. Hermes, K. Koh, P. Koval, S. Lehtola, Z. Li, J. Liu, N. Mardirossian, J. D. McClain, M. Motta, B. Mussard, H. Q. Pham, A. Pulkin, W. Purwanto, P. J. Robinson, E. Ronca, E. R. Sayfutyarova, M. Scheurer, H. F. Schurkus, J. E. T. Smith, C. Sun, S.-N. Sun, S. Upadhyay, L. K. Wagner, X. Wang, A. White, J. D. Whitfield, M. J. Williamson, S. Wouters, J. Yang, J. M. Yu, T. Zhu, T. C. Berkelbach, S. Sharma, A. Y. Sokolov, and G. K.-L. Chan, “Recent developments in the PySCF program package,” [J. Chem. Phys.](#) **153**, 024109 (2020).
- <sup>3</sup>Q. Sun, “Libcint: An efficient general integral library for gaussian basis functions,” [J. Comput. Chem.](#) **36**, 1664–1671 (2015).
- <sup>4</sup>T. H. Dunning, “Gaussian basis sets for use in correlated molecular calculations. i. the atoms boron through neon and hydrogen,” [J. Chem. Phys.](#) **90**, 1007–1023 (1989).
- <sup>5</sup>F. Weigend, “A fully direct ri-hf algorithm: Implementation, optimised auxiliary basis sets, demonstration of accuracy and efficiency,” [Phys. Chem. Chem. Phys.](#) **4**, 4285–4291 (2002).
- <sup>6</sup>A. D. Becke, “Density-functional thermochemistry. iii. the role of exact exchange,” [J. Chem. Phys.](#) **98**, 5648–5652 (1993).
- <sup>7</sup>S. Grimme, J. Antony, S. Ehrlich, and H. Krieg, “A consistent and accurate ab initio parametrization of density functional dispersion correction (dft-d) for the 94 elements h-pu,” [J. Chem. Phys.](#) **132**, 154104 (2010).
- <sup>8</sup>F. Weigend and R. Ahlrichs, “Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for h to rn: Design and assessment of accuracy,” [Phys. Chem. Chem. Phys.](#) **7**, 3297 (2005).
- <sup>9</sup>F. Neese, “The orca program system,” [Wiley Interdiscip. Rev. Comput. Mol. Sci](#) **2**, 73–78 (2012).
- <sup>10</sup>F. Neese, “Software update: the orca program system, version 4.0,” [Wiley Interdiscip. Rev. Comput. Mol. Sci](#) **8**, e1327 (2018).
- <sup>11</sup>F. Neese, F. Wennmohs, U. Becker, and C. Riplinger, “The ORCA quantum chemistry program package,” [J. Chem. Phys.](#) **152**, 224108 (2020).



- <sup>12</sup>G. E. Scuseria, T. M. Henderson, and I. W. Bulik, “Particle-particle and quasiparticle random phase approximations: Connections to coupled cluster theory,” [J. Chem. Phys. \*\*139\*\*, 104113 \(2013\)](#).
- <sup>13</sup>D. Peng, S. N. Steinmann, H. van Aggelen, and W. Yang, “Equivalence of particle-particle random phase approximation correlation energy and ladder-coupled-cluster doubles,” [J. Chem. Phys. \*\*139\*\*, 104112 \(2013\)](#).