Supporting information of

Exchange-Correlation Energy from Pairing Matrix Fluctuation and the Particle-Particle Random Phase Approximation

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I. THEORY IN DETAIL

A. The paring matrix fluctuation, particle-particle Green function, and the particle-particle Random Phase Approximation

In the absence of a pairing field, the pairing matrix

$$\kappa_{ij}(t) = \langle \Psi_0^N | a_{H_i}(t) a_{H_j}(t) | \Psi_0^N \rangle$$

where $|\Psi_0^N\rangle$ is the N-electron ground state, is identically zero. The operators $a_{H_i}^\dagger(t)$ are the creation operators in the Heisenberg picture, $a_{H_i}^\dagger(t) = e^{\frac{i}{\hbar}(\hat{H}-\nu\hat{N})t} a_i^\dagger e^{\frac{-i}{\hbar}(\hat{H}-\nu\hat{N})t}$ and the term $-\nu\hat{N}$, with ν the chemical potential, is added to the Hamiltonian such that the N-electron state is the minimum under the total Hamiltonian $\hat{H} - \nu\hat{N}$ when the particle number is allowed to change. Under a perturbation $\hat{F}(t)$ in the form of a pairing field, $\hat{F}(t') = \sum_{kl} f_{kl} a_{H_l}^\dagger(t') a_{H_k}^\dagger(t') \theta(t')$, the retarded Green function $\bar{\mathbf{K}}^R$

$$\bar{K}_{ijkl}^R(t-t') = \frac{-i}{\hbar}\theta(t-t')\langle \Psi_0^N |[a_{H_i}(t) a_{H_j}(t), a_{H_l}^\dagger(t') a_{H_k}^\dagger(t')]|\Psi_0^N\rangle, \tag{1}$$

describes the linear change in the paring matrix $\langle \Psi_0^N | a_{H_i}(t) a_{H_j}(t) | \Psi_0^N \rangle$:

$$\kappa_{ij}(t) = \frac{-i}{\hbar}\int_0^t \langle \Psi_0^N |[a_{H_i}(t) a_{H_j}(t), \hat{F}(t')]|\Psi_0^N\rangle dt'$$
$$= \sum_{kl} \bar{K}^R(t-t')_{ijkl} f_{kl}$$

Since the paring matrix $\langle \Psi_0^N | a_{H_i}(t) a_{H_j}(t) | \Psi_0^N \rangle = \langle \Psi_0^N | a_i a_j | \Psi_0^N \rangle = 0$ in the absence of the pairing field, the retarded Green function is identical to the dynamic pairing matrix fluctuation, $\bar{\mathbf{K}}(t-t')$

$$\bar{K}_{ijkl}(t-t') = \frac{-i}{\hbar}\theta(t-t')\langle \Psi_0^N |[\left(a_{H_i}(t) a_{H_j}(t) - \langle \Psi_0^N | a_i a_j | \Psi_0^N \rangle\right), \left(a_{H_l}^\dagger(t') a_{H_k}^\dagger(t') - \langle \Psi_0^N | a_l^\dagger a_k^\dagger | \Psi_0^N \rangle\right)]|\Psi_0^N\rangle,$$

The dynamic pairing matrix fluctuation is the pairing interaction counterpart of the polarization propagator, which determines the correlation energy via the well-known adiabatic-connection fluctuation-dissipation (ACFD) theorem [4, 12]. In section I B, we will formulate a similar adiabatic connection in terms of the dynamic pairing matrix fluctuation. The particle-particle Green function $\mathbf{K}(t-t')$, defined as [2]

$$K_{ijkl}(t-t') = \frac{-i}{\hbar}\langle \Psi_0^N |\mathcal{T}[a_{H_i}(t) a_{H_j}(t) a_{H_l}^\dagger(t') a_{H_k}^\dagger(t')]|\Psi_0^N\rangle \tag{2}$$

where $\mathcal{T}$ is the time-ordering operator, is a closely related quantity. The dynamic paring matrix fluctuation $\bar{\mathbf{K}}(t-t')$ and the pp-Green function $\mathbf{K}(t-t')$ contain information on the same physical properties, namely 2-electron removal and addition energies and their corresponding transition amplitudes. This becomes apparent from their Fourier Transform

$$
\begin{aligned}
K_{ijkl}(E) &= \int_{-\infty}^{+\infty} e^{\frac{i}{\hbar}E(t-t')}K_{ijkl}(t-t')d(t-t') \\
&= \frac{-i}{\hbar}\sum_n \int_{-\infty}^{\infty} e^{\frac{i}{\hbar}(E_0^N - E_n^{n+2} + 2\nu + E)(t-t')}\theta(t-t')d(t-t')\langle\Psi_0^N|a_i a_j|\Psi_n^{N+2}\rangle\langle\Psi_n^{N+2}|a_l^\dagger a_k^\dagger|\Psi_0^N\rangle \\
&\quad -\frac{i}{\hbar}\sum_n \int_{-\infty}^{\infty} e^{\frac{i}{\hbar}(E_0^N - E_n^{N-2} - 2\nu - E)(t'-t)}\theta(t'-t)d(t-t')\langle\Psi_0^N|a_l^\dagger a_k^\dagger|\Psi_n^{N-2}\rangle\langle\Psi_n^{N-2}|a_i a_j|\Psi_0^N\rangle.
\end{aligned}
$$

where the last line invokes the completeness of the $N-2$ and $N+2$ electron wavefunction basis. At this point, it is convenient to introduce a short-hand notation for the transition pairing matrix elements

$$
\begin{aligned}
\chi_{ij}^{n,N-2} &= \langle\Psi_n^{N-2}|a_i a_j|\Psi_0^N\rangle \\
\chi_{ij}^{n,N+2} &= \langle\Psi_0^N|a_i a_j|\Psi_n^{N+2}\rangle
\end{aligned}
\tag{3}
$$

and the transition energies

$$
\begin{aligned}
\omega_n^{N-2} &= E_0^N - E_n^{N-2} - 2\nu \\
\omega_n^{N+2} &= E_n^{N+2} - E_0^N - 2\nu.
\end{aligned}
\tag{4}
\tag{5}
$$

For a physical system, the energy decreases monotonically with the number of electrons, so the term -2ν makes it possible to distinguish the 2-electron removal energies from the 2-electron addition energies by their sign: the 2-electron removal energies $\omega_n^{N-2} = E_0^N - E_n^{N-2} - 2\nu$ are negative and the 2-electron addition energies $\omega_n^{N+2} = E_n^{N+2} - E_0^N - 2\nu$ are positive. The particle-particle Green function expressed in the energy domain is then

$$
\begin{aligned}
K_{ijkl}(E) &= \frac{-i}{\hbar}\sum_n \int_{-\infty}^{\infty} e^{\frac{i}{\hbar}(-\omega_n^{N+2}+E)(t-t')}\theta(t-t')d(t-t')\chi_{ij}^{n,N+2}\left(\chi_{kl}^{n,N+2}\right)^* \\
&\quad -\frac{i}{\hbar}\sum_n \int_{-\infty}^{\infty} e^{\frac{i}{\hbar}(\omega_n^{N-2}-E)(t'-t)}\theta(t'-t)d(t-t')\left(\chi_{kl}^{n,N-2}\right)^*\chi_{ij}^{n,N-2} \\
&= \sum_n \frac{\chi_{ij}^{n,N+2}(\chi_{kl}^{n,N+2})^*}{E - \omega_n^{N+2} + i\eta} \\
&\quad -\sum_n \frac{(\chi_{kl}^{n,N-2})^*\chi_{ij}^{n,N-2}}{E - \omega_n^{N-2} - i\eta}.
\end{aligned}
\tag{6}
$$

Similarly, the dynamic paring matrix fluctuation and the retarded particle-particle Green function in energy domain are

$$
\bar{K}_{ijkl}(E) = \bar{K}_{ijkl}^R(E) = \sum_n \frac{\chi_{ij}^{n,N+2}(\chi_{kl}^{n,N+2})^*}{E - \omega_n^{N+2} + i\eta} - \sum_n \frac{(\chi_{kl}^{n,N-2})^*\chi_{ij}^{n,N-2}}{E - \omega_n^{N-2} + i\eta}
$$

This form of the particle-particle Green function and the dynamic pairing matrix fluctuation reveals their most interesting properties: they contain information on the vectors $\chi^{\mathbf{n},N-2}$ and $\chi^{\mathbf{n},N+2}$ with the amplitudes defined in (3) and the 2-electron removal and addition energies, ω_n^{N-2} and ω_n^{N+2}. Since the particle-particle Green function and the dynamic pairing matrix fluctuation contain the same physical information, the following derivations can be expressed equivalently in terms of the dynamic pairing matrix fluctuation. While we feel that the dynamic pairing matrix fluctuation has a more straightforward interpretation as the response to a pairing perturbation than the pp-Green function, the majority of the literature on many-body perturbation theory uses the language of Green functions. We will therefore adopt the Green function formalism in the following derivations as well.

There are several ways to derive the pp-RPA equations, which are similar in nature to their ph-RPA counterparts [2, 19]. In the same way the particle-hole Green function can be approximated by an infinite series in terms of the non-interacting Green function in the ph-RPA, the particle-particle Green function $\mathbf{K}(E)$ can be approximated in terms of the non-interacting Green function $\mathbf{K}^0(E)$ by

$$\mathbf{K}(E) = \mathbf{K}^0(E) + \mathbf{K}^0(E)\mathbf{V}\mathbf{K}(E), \tag{7}$$

an equivalent form of which can be found in Ref. ([2]). In Eq. (7) all quantities, including the two-electron integrals

$$
\begin{aligned}
V_{ijkl} &= \langle ij||kl\rangle \\
&= \langle ij|kl\rangle - \langle ji|kl\rangle \\
&= \int \frac{\phi_i^*(\mathbf{x}_1)\phi_j^*(\mathbf{x}_2)(1-\hat{P}_{12})\phi_k(\mathbf{x}_1)\phi_l(\mathbf{x}_2)}{|\mathbf{r_1}-\mathbf{r_2}|}d\mathbf{x}_1 d\mathbf{x}_2,
\end{aligned}
$$

where $\mathbf{x}$ represents the one-electron spatial vector and spin coordinate, are expressed in an antisymmetrized basis, so only matrix indices ab with $a < b$ and ij with $i < j$ need to be considered. All matrix operations, such as the trace operation and matrix multiplication, are defined accordingly. The non-interacting particle-particle Green function, expressed in an antisymmetrical basis, is the particle-particle Green function in the non-interacting limit,

$$
\begin{aligned}
K_{ijkl}^0(t-t') &= \frac{-i}{\hbar}\langle \Phi_0^N|\mathcal{T}[a_{I_i}(t)a_{I_j}(t)a_{I_l}^\dagger(t')a_{I_k}^\dagger(t')]|\Phi_0^N\rangle \\
&= \frac{-i}{\hbar}(\delta_{jl}\delta_{ik}-\delta_{il}\delta_{jk})\left(e^{-\frac{i}{\hbar}(\epsilon_i+\epsilon_j-2\nu)(t-t')}\theta(i-F)\theta(j-F)\theta(t-t') + e^{\frac{i}{\hbar}(\epsilon_i+\epsilon_j+2\nu)(t'-t)}\theta(F-i)\theta(F-j)\theta(t'-t)\right) \\
&= \frac{-i}{\hbar}(\delta_{jl}\delta_{ik}-\delta_{il}\delta_{jk})e^{-\frac{i}{\hbar}(\epsilon_i+\epsilon_j-2\nu)(t-t')}\left(\theta(i-F)\theta(j-F)\theta(t-t') + \theta(F-i)\theta(F-j)\theta(t'-t)\right),
\end{aligned}
$$

where $|\Phi_0^N\rangle$ is the N-electron non-interacting reference state and the operators $a_{I_i}^\dagger(t)$ are the creation operators in the interaction picture, $a_{I_i}^\dagger(t) = e^{\frac{i}{\hbar}(\hat{H}_0-\nu\hat{N})}a_i^\dagger e^{\frac{-i}{\hbar}(\hat{H}_0-\nu\hat{N})}$ with $\hat{H}_0$ the non-interacting (one-electron) Hamiltonian. Note that the non-interacting particle-particle Green function can also be written in terms of the non-interacting one-particle Green function $\mathbf{G}^0$,

$$
\begin{aligned}
G_{ij}^0(t-t') &= \frac{-i}{\hbar}\langle \Phi_0^N|\mathcal{T}[a_{I_i}(t)a_{I_j}^\dagger(t')]|\Phi_0^N\rangle \\
&= \frac{-i}{\hbar}\delta_{ij}e^{\frac{-i}{\hbar}(\epsilon_i-\nu)(t-t')}\left(\theta(i-F)\theta(t-t') - \theta(F-i)\theta(t'-t)\right),
\end{aligned}
$$

namely

$$
\begin{aligned}
K_{ijkl}^0(t-t') &= \frac{-\hbar}{i}(\delta_{ik}\delta_{jl}-\delta_{il}\delta_{jk})G_{ik}^0(t-t')G_{jl}^0(t-t') \\
&= \frac{-\hbar}{i}\left(G_{ik}^0(t-t')G_{jl}^0(t-t') - G_{il}^0(t-t')G_{jk}^0(t-t')\right).
\end{aligned}
$$

The Fourier Transform of the non-interacting particle-particle Green function is

$$
\begin{aligned}
K_{ijkl}^0(E) &= (\delta_{ik}\delta_{jl}-\delta_{il}\delta_{jk})\frac{-\hbar}{i}\int_{-\infty}^{+\infty}e^{\frac{i}{\hbar}Et}G_{ik}^0(t)G_{jl}^0(t)dt \\
&= (\delta_{ik}\delta_{jl}-\delta_{il}\delta_{jk})\frac{-i}{\hbar}\int_{-\infty}^{+\infty}e^{\frac{-i}{\hbar}(\epsilon_i+\epsilon_j-2\nu-E)t}\left(\theta(i-F)\theta(j-F)\theta(t) + \theta(F-i)\theta(F-j)\theta(-t)\right)dt \quad (8) \\
&= (\delta_{ik}\delta_{jl}-\delta_{il}\delta_{jk})\left[\frac{\theta(i-F)\theta(j-F)}{E-(\epsilon_i+\epsilon_j-2\nu)+i\eta} - \frac{\theta(F-i)\theta(F-j)}{E-(\epsilon_i+\epsilon_j-2\nu)-i\eta}\right] \tag{9}
\end{aligned}
$$

where $\{\epsilon_i\}$ are the orbital energies of the non-interacting reference system.

Eq. (7) can be solved by multiplying each side of the equation by $(E - \omega_n^{N-2})$ and subsequently taking the limit $E \to \omega_n^{N-2}$

$$\underbrace{lim}_{E \to \omega_n^{N-2}} (E - \omega_n^{N-2})K(E)_{ijkl} = \underbrace{lim}_{E \to \omega_n^{N-2}} (E - \omega_n^{N-2})\left(K^0(E)_{ijkl} + \sum_{m<n,o<p} K^0(E)_{ijmn}V_{mnop}K(E)_{opkl}\right).$$

This will separate out one single term on both sides of the equation: the term that has $(E-\omega_n^{N-2})$ in the denominator.

$$(\chi_{kl}^{n,N-2})^*\chi_{ij}^{n,N-2} = \sum_{m<n,o<p} K^0(\omega_n^{N-2})_{ijmn}V_{mnop}(\chi_{kl}^{n,N-2})^*\chi_{op}^{n,N-2}.$$

The factor $(\chi_{kl}^{n,N-2})^*$ that appears on both sides of the equation can then be canceled out

$$\chi_{ij}^{n,N-2} = \sum_{m<n,o<p} K^0(\omega_n^{N-2})_{ijmn}V_{mnop}\chi_{op}^{n,N-2}$$

$$= \sum_{o<p} \left(\frac{\theta(i-F)\theta(j-F)}{\omega_n^{N-2} - (\epsilon_i + \epsilon_j - 2\nu) + i\eta} - \frac{\theta(F-i)\theta(F-j)}{\omega_n^{N-2} - (\epsilon_i + \epsilon_j - 2\nu) - i\eta}\right) V_{ijop}\chi_{op}^{n,N-2}. \tag{10}$$

This leads to a set of equations for the pp-indices ab and a set of equations for the hh-indices hi

$$\chi_{ab}^{n,N-2} = \frac{1}{\omega_n^{N-2} - (\epsilon_a + \epsilon_b - 2\nu)} \left(\sum_{c<d}^{N_p} V_{abcd}\chi_{cd}^{n,N-2} + \sum_{h<i}^{N_h} V_{abhi}\chi_{hi}^{n,N-2}\right)$$

$$\chi_{hi}^{n,N-2} = \frac{-1}{\omega_n^{N-2} - (\epsilon_h + \epsilon_i - 2\nu)} \left(\sum_{c<d}^{N_p} V_{hicd}\chi_{cd}^{n,N-2} + \sum_{h<i}^{N_h} V_{hijk}\chi_{jk}^{n,N-2}\right).$$

which can be rearranged to reveal a generalized eigenvalue problem in the eigenvalues ω_n and the eigenvectors χ^n

$$\sum_{c<d} \chi_{cd}^{n,N-2}\left(V_{abcd} + \delta_{ac}\delta_{bd}(\epsilon_a + \epsilon_b - 2\nu)\right) + \sum_{h<i} \chi_{hi}^{n,N-2}V_{abhi} = \chi_{ab}^{n,N-2}\omega_n^{N-2}$$

$$-\sum_{c<d} \chi_{cd}^{n,N-2}V_{hicd} - \sum_{j<k} \chi_{jk}^{n,N-2}\left(V_{hijk} - \delta_{jh}\delta_{ik}(\epsilon_h + \epsilon_i - 2\nu)\right) = \chi_{hi}^{n,N-2}\omega_n^{N-2},$$

where a, b, c, d are particle indices, h, i, j, k are hole indices and m, n, o, p are general indices. This can be written in matrix form by defining $\chi^\mathbf{n} \equiv \begin{pmatrix} \mathbf{X^n} \\ \mathbf{Y^n} \end{pmatrix}$, where $\mathbf{X}^n$ contains the elements of the vector χ^n with pp-labels and the vector $\mathbf{Y}^n$ contains the elements with hh-labels,

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^\dagger & \mathbf{C} \end{pmatrix} \begin{pmatrix} \mathbf{X^n} \\ \mathbf{Y^n} \end{pmatrix} = \omega_n \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{pmatrix} \begin{pmatrix} \mathbf{X^n} \\ \mathbf{Y^n} \end{pmatrix} \tag{11}$$

with

$$A_{abcd} = \langle ab\|cd\rangle + \delta_{ac}\delta_{bd}(\epsilon_a + \epsilon_b - 2\nu)$$
$$B_{abij} = \langle ab\|ij\rangle$$
$$C_{ijkl} = \langle ij\|kl\rangle - \delta_{ik}\delta_{jl}(\epsilon_i + \epsilon_j - 2\nu). \tag{12}$$

In our implementation, we have used $\nu = \frac{\epsilon_{HOMO} + \epsilon_{LUMO}}{2}$, which corresponds to the average chemical potential for the physical system under the non-interacting KS or generalized KS DFA [5]. The constant ν does not affect the correlation energy; it only ensures that the pp-RPA matrix on the left hand side of Eq. (11) is positive semidefinite. This implies that the 2-electron removal energies are negative and the two-electron addition energies are positive, which makes it easier to separate them among the entire set of eigenvalues ω_n. Since the pp-RPA matrix is expressed

in an anti-symmetric basis, only ordered pp-indices ab with $a < b$ and hh-indices hi with $h < i$ are included. The dimension of the A and C matrix is therefore the number of ordered pp and hh pairs:

$$dim(\mathbf{A}) = \frac{1}{2}N_p(N_p - 1)$$

$$dim(\mathbf{C}) = \frac{1}{2}N_h(N_h - 1)$$

where N_p and N_h are the number of particles (unoccupied orbitals) and holes (occupied orbitals) respectively. Since in general, $N_p > N_h$, the dimension of the pp-RPA matrix is $O(N_p^2)$, so a straightforward diaonalization of the pp-RPA matrix leads to an $O(N_p^6)$ scaling. Nonetheless, the cost of computing the correlation energy is actually $O(N_h^2 N_p^4)$ because only $\frac{1}{2}N_h(N_h - 1)$ eigenvalues are needed to compute the correlation energy. Eq. (7) can be rearranged for the $N + 2$ electron states in a similar manner, by multiplying by $(E - \omega_n^{N+2})$ and taking the limit $E \to \omega_n^{N+2}$. This leads to the same set of equations for the 2-electron addition energies;

$$\chi_{ij}^{n,N+2} = \sum_{m<n,o<p} K^0(\omega_n^{N+2})_{ijmn} V_{mnop} \chi_{op}^{n,N+2}$$

$$\chi_{ij}^{n,N+2} = \sum_{o<p} \left(\frac{\theta(i-F)\theta(j-F)}{\omega_n^{N+2} - (\epsilon_i + \epsilon_j - 2\nu) + i\eta} - \frac{\theta(F-i)\theta(F-j)}{\omega_n^{N+2} - (\epsilon_i + \epsilon_j - 2\nu) - i\eta} \right) V_{ijop} \chi_{op}^{n,N+2},$$

which has the exact same form as Eq. (10) for the 2-electron removal energies. The eigenvectors $\mathbf{X^n}$ and $\mathbf{Y^n}$ that satisfy Eq. (12) may thus involve either the $N+2$ electron states or $N-2$ electron states. The generalized eigenvalues ω_n are either positive 2-electron addition energies, $\omega_n^{N+2} = E_n^{N+2} - E_0^N - 2\nu$, or negative 2-electron removal energies, $\omega_n^{N-2} = E_0^N - E_n^{N-2} - 2\nu$.

B. Exchange-correlation energy from dynamic pairing matrix fluctuations

In this section, we develop an exact expression for the exchange-correlation energy in terms of dynamic pairing matrix fluctuations via the adiabatic connection [11–13]. The result is the dynamic pairing matrix fluctuation counterpart of the well-known adiabatic-connection fluctuation-dissipation (ACFD) theorem [4, 12] which expresses the exchange-correlation energy in terms of dynamic density fluctuations. Just like the ACFD theorem, it formulates the exact correlation energy in terms of dynamic fluctuations; it only considers different correlation channels: the dynamic pairing matrix fluctuation involves the pp- and hh-correlation channels, while the dynamic density fluctuation involves the ph-correlation channel. These two different types of correlation channels are closely related to the division of the second order density matrix space into P-, Q- and G-matrices [14]. The energy can be expressed in either one of these matrices, which naturally leads to equivalent formulations for the exchange-correlation energy in terms of dynamic pairing matrix fluctuations and dynamic density fluctuations via the adiabatic connection. The resulting adiabatic-connection formulae are in principle exact. In section I C, we show that the approximate exchange-correlation energy that follows from the pp-RPA is equivalent to the summation of ladder diagrams in many body perturbation theory.

The adiabatic connection considers a non-interacting reference system, described by the Hamiltonian

$$\hat{H}_0 = \hat{h} + \hat{u},$$

where $\hat{h}$ is the core Hamiltonian and $\hat{u}$ is the – local or non-local, and possibly spin-dependent – one-body operator that defines the non-interacting system. The adiabatic connection then defines a path from the non-interacting model to the fully interacting system, parametrized by the interaction strength λ:

$$\hat{H}_\lambda = \hat{H}_0 + \lambda(\hat{V} - \hat{u}_\lambda).$$

The operator $\hat{u}_\lambda$ is restricted to satisfy $\hat{u}_1 = \hat{u}$ such that $\hat{H}_1$ is the Hamiltonian for the fully interacting system. The Hellmann-Feynman theorem

$$\frac{\partial E}{\partial \lambda} = \langle \Psi^\lambda | \frac{\partial \hat{H}_\lambda}{\partial \lambda} | \Psi^\lambda \rangle$$

then formulates the correlation energy $E^1 - E^0$ as an integration along the adiabatic connection path

$$E^1 - E^0 = \int_0^1 \langle \Psi^\lambda | \frac{\partial \hat{H}_\lambda}{\partial \lambda} | \Psi^\lambda \rangle d\lambda$$
$$= \int_0^1 \langle \Psi^\lambda | \hat{V} - \hat{u}_\lambda - \lambda \frac{\partial \hat{u}_\lambda}{\partial \lambda} | \Psi^\lambda \rangle d\lambda.$$

Since $\hat{V}$ is a two-body operator and $\hat{u}_\lambda$ is a one-body operator, this can be written more compactly in terms of the second-order density matrix Γ^λ and the first-order density matrix γ^λ for the system with interaction strength λ:

$$E^1 - E^0 = \text{tr} \int_0^1 \mathbf{V}\mathbf{\Gamma}^\lambda d\lambda - \text{tr} \int_0^1 \mathbf{u}_\lambda \gamma^\lambda d\lambda - \text{tr} \int_0^1 \lambda \frac{\partial \mathbf{u}_\lambda}{\partial \lambda} \gamma^\lambda d\lambda.$$

Given that $E^0 = \text{tr } \mathbf{h}\gamma^\mathbf{0} + \text{tr } \mathbf{u}\gamma^\mathbf{0}$, the energy for the fully interacting system is

$$E^1 = \text{tr } \mathbf{h}\gamma^\mathbf{0} + \text{tr} \int_0^1 \mathbf{V}\mathbf{\Gamma}^\lambda d\lambda - \text{tr} \int_0^1 (\mathbf{u}_\lambda \gamma^\lambda - \mathbf{u}\gamma^\mathbf{0}) d\lambda - \text{tr} \int_0^1 \lambda \frac{\partial \mathbf{u}_\lambda}{\partial \lambda} \gamma^\lambda d\lambda.$$

Relative to the Hartree-Fock/Exact Exchange energy functional, $E^{HF} = \text{tr } \mathbf{h}\gamma^\mathbf{0} + \text{tr } \mathbf{V}\mathbf{\Gamma}^\mathbf{0}$, the correlation energy functional $E^c \equiv E^1 - E^{HF}$ is then

$$E^c = \text{tr} \int_0^1 \mathbf{V}(\mathbf{\Gamma}^\lambda - \mathbf{\Gamma}^\mathbf{0}) d\lambda - \text{tr} \int_0^1 (\mathbf{u}_\lambda \gamma^\lambda - \mathbf{u}\gamma^\mathbf{0}) d\lambda - \text{tr} \int_0^1 \lambda \frac{\partial \mathbf{u}_\lambda}{\partial \lambda} \gamma^\lambda d\lambda$$

The two-body part of the energy can be written equivalently in terms of the second-order density matrix, the Q-matrix or the G-matrix, defined by

$$\Gamma_{ijkl} = \langle \Psi | a_k^+ a_l^+ a_j a_i | \Psi \rangle$$
$$Q_{ijkl} = \langle \Psi | a_k a_l a_j^+ a_i^+ | \Psi \rangle$$
$$G_{ijkl} = \langle \Psi | a_k^+ a_l a_j^+ a_i | \Psi \rangle,$$

because the anti-commutation properties of the creation and annihilation operators define maps between the second-order density matrix, the Q-matrix and the G-matrix:

$$\Gamma_{ijkl} = Q_{lkji} + (\delta \wedge \gamma)_{ijkl} - (\delta \wedge \delta)_{ijkl}$$
$$\Gamma_{ijkl} = -G_{ilkj} + \delta_{jl}\gamma_{ik} = G_{jlki} - \delta_{il}\gamma_{jk},$$

where $\wedge$ denotes the wedge product, which includes all unique anti-symmetrical product terms, $(\delta \wedge \gamma)_{ijkl} = \delta_{ik}\gamma_{jl} + \delta_{jl}\gamma_{ik} - \delta_{il}\gamma_{jk} - \delta_{jk}\gamma_{il}$ and $(\delta \wedge \delta)_{ijkl} = \delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk}$. This results in three equivalent expressions for the correlation energy

$$E^c = \text{tr} \int_0^1 \mathbf{V}(\mathbf{\Gamma}^\lambda - \mathbf{\Gamma}^\mathbf{0}) d\lambda - \text{tr} \int_0^1 (\mathbf{u}_\lambda \gamma^\lambda - \mathbf{u}\gamma^\mathbf{0}) d\lambda - \text{tr} \int_0^1 \lambda \frac{\partial \mathbf{u}_\lambda}{\partial \lambda} \gamma^\lambda d\lambda, \tag{13}$$

$$E^c = \text{tr} \int_0^1 \mathbf{V}(\mathbf{Q}^\lambda - \mathbf{Q}^\mathbf{0}) d\lambda + \text{tr} \int_0^1 \mathbf{V}(\delta \wedge (\gamma^\lambda - \gamma^\mathbf{0}) d\lambda - \text{tr} \int_0^1 (\mathbf{u}_\lambda \gamma^\lambda - \mathbf{u}\gamma^\mathbf{0}) d\lambda - \text{tr} \int_0^1 \lambda \frac{\partial \mathbf{u}_\lambda}{\partial \lambda} \gamma^\lambda d\lambda, \tag{14}$$

and

$$E^c = \text{tr} \int_0^1 \tilde{\mathbf{V}}(\mathbf{G}^\lambda - \mathbf{G^0})d\lambda - \sum_{ijk}\int_0^1 \langle ij|ki\rangle(\gamma_{jk}^\lambda - \gamma_{jk}^0)d\lambda - \text{tr} \int_0^1 (\mathbf{u}_\lambda\gamma^\lambda - \mathbf{u}\gamma^\mathbf{0})d\lambda - \text{tr}\int_0^1 \lambda\frac{\partial \mathbf{u}_\lambda}{\partial\lambda}\gamma^\lambda d\lambda. \quad (15)$$

In Eq. (15), $\tilde{\mathbf{V}}$ is a rearranged form of the two-electron integral matrix that pairs up indices associated to the same electron, $\tilde{V}_{ijkl} = \langle il|jk\rangle$. Equations (13-15) are general expressions for the correlation energy functional, valid for any adiabatic connection path.

In the context of KS-DFT, these formulae can be simplified by assuming that the potential $\hat{u}_\lambda = \hat{u}_\lambda(\mathbf{x})$ is local and chosing a constant-density adiabatic connection path, such that the spin density remains constant: $\rho^\lambda(\mathbf{x}) = \rho^0(\mathbf{x}) = \rho(\mathbf{x})$. The terms $\text{tr}\int_0^1 (\mathbf{u}_\lambda\gamma^\lambda - \mathbf{u}\gamma^\mathbf{0})d\lambda$ can then be expressed in terms of the density $\rho^\lambda = \rho$ instead of the density matrix γ^λ

$$\text{tr}\int_0^1 (\mathbf{u}_\lambda\gamma^\lambda - \mathbf{u}\gamma^\mathbf{0})d\lambda = \text{tr}\int_0^1 (\mathbf{u}_\lambda\rho - \mathbf{u}\rho)d\lambda$$

and the last term $\text{tr}\int_0^1 \lambda\frac{\partial \mathbf{u}_\lambda}{\partial\lambda}\gamma^\lambda d\lambda$ can be simplified through partial integration

$$\text{tr}\int_0^1 \lambda\frac{\partial \mathbf{u}_\lambda}{\partial\lambda}\gamma^\lambda d\lambda = \text{tr}\int_0^1 \lambda\frac{\partial \mathbf{u}_\lambda}{\partial\lambda}d\lambda\rho$$

$$= \text{tr}\,[\lambda\mathbf{u}_\lambda]_0^1\rho - \text{tr}\int_0^1 \mathbf{u}_\lambda d\lambda\rho$$

$$= \text{tr}\,\mathbf{u}\rho - \text{tr}\int_0^1 \mathbf{u}_\lambda d\lambda\rho$$

All terms involving $\hat{u}_\lambda$ cancel out:

$$-\text{tr}\int_0^1 (\mathbf{u}_\lambda\gamma^\lambda - \mathbf{u}\gamma^\mathbf{0})d\lambda - \text{tr}\int_0^1 \lambda\frac{\partial \mathbf{u}_\lambda}{\partial\lambda}\gamma^\lambda d\lambda = -\text{tr}\int_0^1 (\mathbf{u}_\lambda - \mathbf{u})d\lambda\rho - \text{tr}\,\mathbf{u}\rho + \text{tr}\int_0^1 \mathbf{u}_\lambda d\lambda\rho$$

$$= 0.$$

Furthermore, the terms $\text{tr}\int_0^1 \mathbf{V}(\delta \wedge (\gamma^\lambda - \gamma^\mathbf{0})d\lambda$ and $\sum_{ijk}\int_0^1 \langle ij|ki\rangle(\gamma_{jk}^\lambda - \gamma_{jk}^0)d\lambda$ vanish because of the following:

$$\sum_{ijk}\langle ij|ik\rangle(\gamma_{jk}^\lambda - \gamma_{jk}^0) = \int \frac{\sum_i \phi_i^*(\mathbf{x}')\phi_i(\mathbf{x}')\sum_{jk}\phi_j^*(\mathbf{x})\phi_k(\mathbf{x})(\gamma_{jk}^\lambda - \gamma_{jk}^0)}{|\mathbf{r} - \mathbf{r}'|}d\mathbf{x}d\mathbf{x}'$$

$$= \int \delta(0)\frac{\gamma^\lambda(\mathbf{x},\mathbf{x}) - \gamma^0(\mathbf{x},\mathbf{x})}{|\mathbf{r} - \mathbf{r}'|}d\mathbf{x}d\mathbf{x}'$$

$$= \int \delta(0)\frac{\rho^\lambda(\mathbf{x}) - \rho^0(\mathbf{x})}{|\mathbf{r} - \mathbf{r}'|}d\mathbf{x}d\mathbf{x}'$$

$$= 0$$

$$\sum_{ijk}\langle ij|ki\rangle(\gamma_{jk}^\lambda - \gamma_{jk}^0) = \int \frac{\sum_i \phi_i^*(\mathbf{x})\phi_i(\mathbf{x}')\sum_{jk}\phi_j^*(\mathbf{x}')\phi_k(\mathbf{x})(\gamma_{jk}^\lambda - \gamma_{jk}^0)}{|\mathbf{r} - \mathbf{r}'|}d\mathbf{x}d\mathbf{x}'$$

$$= \int \delta(\mathbf{x} - \mathbf{x}')\frac{\gamma^\lambda(\mathbf{x}',\mathbf{x}) - \gamma^0(\mathbf{x}',\mathbf{x})}{|\mathbf{r} - \mathbf{r}'|}d\mathbf{x}d\mathbf{x}'$$

$$= \int \delta(\mathbf{x} - \mathbf{x}')\frac{\rho^\lambda(\mathbf{x}) - \rho^0(\mathbf{x})}{|\mathbf{r} - \mathbf{r}'|}d\mathbf{x}d\mathbf{x}'$$

$$= 0.$$

Thus for a local potential $\hat{u}_\lambda(r)$ the adiabatic connection along the constant-density path leads to the equivalent formulae

$$E^c = \text{tr} \int_0^1 \mathbf{V}(\mathbf{\Gamma}^\lambda - \mathbf{\Gamma^0}) d\lambda$$

$$E^c = \text{tr} \int_0^1 \mathbf{V}(\mathbf{Q}^\lambda - \mathbf{Q^0}) d\lambda$$

$$E^c = \text{tr} \int_0^1 \tilde{\mathbf{V}}(\mathbf{G}^\lambda - \mathbf{G^0}) d\lambda.$$

The correlation energy can then be expressed in terms of dynamic fluctuations: the P- and Q-matrix can be written in terms of the pairing matrix fluctuation and the G-matrix in terms of the density matrix fluctuation. The second-order density matrix can be related to the transition paring matrix elements $\chi_{ij}^{n,N-2} = \langle \Psi_n^{N-2} | a_i a_j | \Psi_0^N \rangle$ through the completeness of the $N-2$ electron wavefunction basis,

$$
\begin{aligned}
\Gamma_{ijkl} &= \langle \Psi_0^N | a_k^+ a_l^+ a_j a_i | \Psi_0^N \rangle \\
&= \sum_n \langle \Psi_0^N | a_k^+ a_l^+ | \Psi_n^{N-2} \rangle \langle \Psi_n^{N-2} | a_j a_i | \Psi_0^N \rangle \\
&= \sum_n \chi_{ji}^{n,N-2} (\chi_{lk}^{n,N-2})^*,
\end{aligned}
\tag{16}
$$

and the Q-matrix can be related to the transition pairing matrix elements $\chi_{ij}^{n,N+2} = \langle \Psi_n^N | a_i a_j | \Psi_0^{N+2} \rangle$ through the completeness of the $N+2$ electron wavefunction basis,

$$
\begin{aligned}
Q_{ijkl} &= \langle \Psi_0^N | a_k a_l a_j^+ a_i^+ | \Psi_0^N \rangle \\
&= \sum_n \langle \Psi_0^N | a_k a_l | \Psi_n^{N+2} \rangle \langle \Psi_n^{N+2} | a_j^+ a_i^+ | \Psi_0^N \rangle \\
&= \sum_n \chi_{kl}^{n,N+2} (\chi_{ij}^{n,N+2})^*,
\end{aligned}
\tag{17}
$$

and the G-matrix can be written in terms of the transition density matrix elements $\chi_{ij}^{n,N} \equiv \langle \Psi_n^N | a_j^+ a_i | \Psi_0^N \rangle$ through the completeness of the N-electron wavefunction basis

$$
\begin{aligned}
G_{ijkl} &= \langle \Psi_0^N | a_k^+ a_l a_j^+ a_i | \Psi_0^N \rangle \\
&= \sum_n \langle \Psi_0^N | a_k^+ a_l | \Psi_n^N \rangle \langle \Psi_n^N | a_j^+ a_i | \Psi_0^N \rangle \\
&= \sum_{n \neq 0} \chi_{ij}^{n,N} (\chi_{kl}^{n,N})^* + \gamma_{ij} \gamma_{kl}.
\end{aligned}
\tag{18}
$$

The exact correlation energy can thus be expressed in terms of transition pairing matrix elements,

$$
\begin{aligned}
E^c &= \sum_n \sum_{ijkl} \int_0^1 \left((\chi_\lambda^{n,N-2})_{ji} (\chi_\lambda^{n,N-2})_{lk}^* - (\chi_0^{n,N-2})_{ji} (\chi_0^{n,N-2})_{lk}^* \right) V_{ijkl} d\lambda \\
&= \sum_n \int_0^1 \int d\mathbf{x} d\mathbf{x}' \frac{\chi_\lambda^{n,N-2}(\mathbf{x},\mathbf{x}') \chi_\lambda^{n,N-2}(\mathbf{x},\mathbf{x}')^* - \chi_0^{n,N-2}(\mathbf{x},\mathbf{x}') \chi_0^{n,N-2}(\mathbf{x},\mathbf{x}')^*}{|\mathbf{r} - \mathbf{r}'|} d\lambda,
\end{aligned}
\tag{19}
$$

and

$$E^c = \sum_n \sum_{ijkl} \int_0^1 \left((\chi_\lambda^{n,N+2})^*_{ij} (\chi_\lambda^{n,N+2})_{kl} - (\chi_0^{n,N+2})^*_{ij} (\chi_0^{n,N+2})_{kl} \right) V_{ijkl} d\lambda$$

$$= \sum_n \int_0^1 \int d\mathbf{x} d\mathbf{x}' \frac{\chi_\lambda^{n,N+2}(\mathbf{x},\mathbf{x}')^* \chi_\lambda^{n,N+2}(\mathbf{x},\mathbf{x}') - \chi_0^{n,N+2}(\mathbf{x},\mathbf{x}')^* \chi_0^{n,N+2}(\mathbf{x},\mathbf{x}')}{|\mathbf{r} - \mathbf{r}'|} d\lambda, \tag{20}$$

or in terms of transition density matrix elements,

$$E^c = \sum_{n\neq0} \sum_{ijkl} \int_0^1 \left((\chi_\lambda^{n,N})_{ij} (\chi_\lambda^{n,N})^*_{kl} - (\chi_0^{n,N})_{ij} (\chi_0^{n,N})^*_{kl} \right) \tilde{V}_{ijkl} d\lambda$$

$$= \sum_{n\neq0} \int_0^1 \int d\mathbf{x} d\mathbf{x}' \frac{\chi_\lambda^{n,N}(\mathbf{x})\chi_\lambda^{n,N}(\mathbf{x}')^* - \chi_0^{n,N}(\mathbf{x})\chi_0^{n,N}(\mathbf{x}')^*}{|\mathbf{r} - \mathbf{r}'|} d\lambda. \tag{21}$$

Note that the ground-state density matrix elements in Eq. (18) do not contribute along the constant-density adiabatic-connection path.

Equation (21) for the correlation energy in terms of transition density matrix elements has been exploited in the context of ph-RPA, because the transition density matrix elements involved can be extracted from the polarization propagator $\mathbf{\Pi}$, defined as [2]

$$\Pi(E)_{ijkl} = \sum_{n\neq0} \frac{\langle \Psi_0^N | a_k^+ a_l | \Psi_n^N \rangle \langle \Psi_n^N | a_j^+ a_i | \Psi_0^N \rangle}{E - \omega_n^N + i\eta} - \sum_{n\neq0} \frac{\langle \Psi_0^N | a_j^+ a_i | \Psi_n^N \rangle \langle \Psi_n^N | a_k^+ a_l | \Psi_0^N \rangle}{E + \omega_n^N - i\eta}$$

$$= \sum_{n\neq0} \frac{\langle \Psi_0^N | a_k^+ a_l | \Psi_n^N \rangle \langle \Psi_n^N | a_j^+ a_i | \Psi_0^N \rangle}{E - \omega_n^N + i\eta} - \sum_{n\neq0} \frac{\langle \Psi_0^N | a_j^+ a_i | \Psi_n^N \rangle \langle \Psi_n^N | a_k^+ a_l | \Psi_0^N \rangle}{E + \omega_n^N - i\eta}$$

$$= \sum_{n\neq0} \frac{(\chi_{kl}^{n,N})^* \chi_{ij}^{n,N}}{E - \omega_n^N + i\eta} - \sum_{n\neq0} \frac{(\chi_{ji}^{n,N})^* \chi_{lk}^{n,N}}{E + \omega_n^N - i\eta}.$$

Integrating over a semi-circular path in the positive real plane gives

$$\frac{-1}{2\pi i} \int_{-i\infty}^{+i\infty} e^{-E\eta} \Pi(E)_{ijkl} dE = \sum_{n\neq0} \chi_{ij}^{n,N} (\chi_{kl}^{n,N})^* \tag{22}$$

while integrating over a semi-circular path in the negative real plane gives

$$\frac{-1}{2\pi i} \int_{-i\infty}^{+i\infty} e^{E\eta} \Pi(E)_{ijkl} dE = \sum_{n\neq0} \chi_{lk}^{n,N} (\chi_{ji}^{n,N})^*.$$

Using Eqs. (21) and (22), the correlation energy can be expressed in terms of the polarization propagator:

$$E^c = \sum_{ijkl} \tilde{V}_{ijkl} \sum_{n\neq0} \int_0^1 (\chi_\lambda^{n,N})_{ij} (\chi_\lambda^{n,N})^*_{kl} d\lambda - (\chi_0^{n,N})_{ij} (\chi_0^{n,N})^*_{kl}$$

$$= \frac{-1}{2\pi i} \int_0^1 \int_{-i\infty}^{+i\infty} e^{-E\eta} \mathrm{tr}\, \tilde{\mathbf{V}}[\mathbf{\Pi}^\lambda(E) - \mathbf{\Pi^0}(E)] dE d\lambda$$

$$= \frac{-1}{2\pi i} \int_0^1 \int_{-i\infty}^{+i\infty} e^{-E\eta} \int d\mathbf{x} d\mathbf{x}' \int \frac{\Pi^\lambda(\mathbf{x},\mathbf{x}',E) - \Pi^0(\mathbf{x},\mathbf{x}',E)}{|\mathbf{r} - \mathbf{r}'|} dE d\lambda. \tag{23}$$

This result is in principle exact, but requires an expression for $\Pi^\lambda(\mathbf{x}, \mathbf{x}', E)$. The ph-RPA approximates the polarization propagator for the interacting strength λ by the Dyson-like equation $\mathbf{\Pi}^\lambda = \mathbf{\Pi}^0 + \lambda \mathbf{\Pi}^0 \tilde{\mathbf{V}} \mathbf{\Pi}^\lambda$, which leads to the well-known energy expression for the RPA [3, 12].

The correlation energy can also be expressed in terms of pairing matrix fluctuations or the particle-particle Green function, based on Eqs. (16,17). The transition pairing matrix elements involved can be extracted from the particle-particle Green function, Eq. (6): integrating the particle-particle Green function over a semi-circular path in the negative real plane gives

$$\frac{-1}{2\pi i} \int_{-i\infty}^{+i\infty} e^{E\eta} K(E)_{ijkl} dE = \sum_n (\chi_{lk}^{n,N-2})^* \chi_{ji}^{n,N-2} \tag{24}$$

while closing the contour in the positive real plane gives

$$\frac{-1}{2\pi i} \int_{-i\infty}^{+i\infty} e^{-E\eta} K(E)_{ijkl} dE = \sum_n (\chi_{kl}^{n,N+2})^* \chi_{ij}^{n,N+2}. \tag{25}$$

Equations (16) and (24) then lead to an expression for the correlation energy in terms of the particle-particle Green function, integrated over a contour in the negative real plane:

$$
\begin{aligned}
E^c &= \sum_{ijkl} V_{ijkl} \sum_n \int_0^1 (\chi_\lambda^{n,N-2})_{ij} (\chi_\lambda^{n,N-2})_{kl}^* d\lambda - (\chi_0^{n,N-2})_{ij} (\chi_0^{n,N-2})_{kl}^* \\
&= \frac{-1}{2\pi i} \int_0^1 \int_{-i\infty}^{+i\infty} e^{E\eta} \operatorname{tr} \mathbf{V}[\mathbf{K}^\lambda(E) - \mathbf{K^0}(E)] dE d\lambda \\
&= \frac{-1}{2\pi i} \int_0^1 \int_{-i\infty}^{+i\infty} e^{E\eta} \int d\mathbf{x} d\mathbf{x}' \frac{K^\lambda(\mathbf{x}, \mathbf{x}', E) - K^0(\mathbf{x}, \mathbf{x}', E)}{|\mathbf{r} - \mathbf{r}'|} dE
\end{aligned} \tag{26}
$$

where

$$K^\lambda(\mathbf{x}_1, \mathbf{x}_2, E) = \frac{1}{2} \sum_{ijkl} K(E)_{ijkl} \phi_i(\mathbf{x}_1) \phi_j(\mathbf{x}_2) \phi_k^*(\mathbf{x}_1) \phi_l^*(\mathbf{x}_2) \tag{27}$$

Equations (17) and (25) lead to the same formula, integrated over a contour in the positive real plane:

$$
\begin{aligned}
E^c &= \sum_{ijkl} V_{ijkl} \sum_n \int_0^1 (\chi_\lambda^{n,N+2})_{ij}^* (\chi_\lambda^{n,N+2})_{kl} d\lambda - (\chi_0^{n,N+2})_{ij}^* (\chi_0^{n,N+2})_{kl} \\
&= \frac{-1}{2\pi i} \int_0^1 \int_{-i\infty}^{+i\infty} e^{-E\eta} \operatorname{tr} \mathbf{V}[\mathbf{K}^\lambda(E) - \mathbf{K^0}(E)] dE d\lambda \\
&= \frac{-1}{2\pi i} \int_0^1 \int_{-i\infty}^{+i\infty} e^{-E\eta} \int d\mathbf{x} d\mathbf{x}' \frac{\mathbf{K}^\lambda(\mathbf{x}, \mathbf{x}', E) - \mathbf{K^0}(\mathbf{x}, \mathbf{x}', E)}{|\mathbf{r} - \mathbf{r}'|} dE d\lambda.
\end{aligned} \tag{28}
$$

The equivalence of (26) and (28) shows that the integration path can be closed in either half plane. Although the previous equations integrate the Green functions along the imaginary axis, similar equations hold for integration along the real axis, namely

$$
\begin{aligned}
E^c &= \frac{-1}{2\pi i} \int_0^1 \int_{-\infty}^{+\infty} e^{-iE\eta} \operatorname{tr} \tilde{\mathbf{V}}[\mathbf{\Pi}^\lambda(E) - \mathbf{\Pi^0}(E)] dE d\lambda \\
&= \frac{-1}{2\pi i} \int_0^1 \int_{-\infty}^{+\infty} e^{-iE\eta} \int d\mathbf{x} d\mathbf{x}' \int \frac{\Pi^\lambda(\mathbf{x}, \mathbf{x}', E) - \Pi^0(\mathbf{x}, \mathbf{x}', E)}{|\mathbf{r} - \mathbf{r}'|} dE d\lambda,
\end{aligned} \tag{29}
$$

$$E^c = \frac{-1}{2\pi i} \int_0^1 \int_{-\infty}^{+\infty} e^{iE\eta} \text{tr } \mathbf{V}[\mathbf{K}^\lambda(E) - \mathbf{K^0}(E)]dEd\lambda$$

$$= \frac{-1}{2\pi i} \int_0^1 \int_{-\infty}^{+\infty} e^{iE\eta} \int d\mathbf{x}d\mathbf{x}' \frac{K^\lambda(\mathbf{x}, \mathbf{x}', E) - K^0(\mathbf{x}, \mathbf{x}', E)}{|\mathbf{r} - \mathbf{r}'|} dE, \tag{30}$$

and

$$E^c = \frac{-1}{2\pi i} \int_0^1 \int_{-\infty}^{+\infty} e^{-iE\eta} \text{tr } \mathbf{V}[\mathbf{K}^\lambda(E) - \mathbf{K^0}(E)]dEd\lambda$$

$$= \frac{-1}{2\pi i} \int_0^1 \int_{-\infty}^{+\infty} e^{-iE\eta} \int d\mathbf{x}d\mathbf{x}' \frac{K^\lambda(\mathbf{x}, \mathbf{x}', E) - K^0(\mathbf{x}, \mathbf{x}', E)}{|\mathbf{r} - \mathbf{r}'|} dEd\lambda. \tag{31}$$

From the numerical point of view, integration along the imaginary axis is more convenient because it avoids the poles on the real axis. The integration along the imaginary energy axis is also valid for the retarded Green function or the paring matrix fluctuation, such that Eq. (23,26 and 28) also apply to the retarded Green function or the pairing matrix fluctuation.

C.   Exchange-correlation energy from the particle-particle RPA

Expressions (26) and (28) for the correlation energy in terms of the particle-particle Green function are in principle exact, but require knowledge of the Green function $\mathbf{K}^\lambda(E)$ as a function of the interaction strength λ. The pp-RPA approximates $\mathbf{K}^\lambda(E)$ through the Dyson-like equation

$$\mathbf{K}^\lambda(E) = \mathbf{K}^0(E) + \lambda\mathbf{K}^0(E)\mathbf{V}\mathbf{K}^\lambda(E) \tag{32}$$

such that, based on Eq. (26),

$$E_{pp}^c = \frac{-1}{2\pi i} \int_0^1 \int_{-i\infty}^{+i\infty} \text{tr } [\mathbf{K}^\lambda(E)\mathbf{V} - \mathbf{K}^0(E)\mathbf{V}]dEd\lambda$$

$$= \frac{-1}{2\pi i} \int_0^1 \int_{-i\infty}^{+i\infty} \left(\lambda\text{tr } [\mathbf{K}^0(E)\mathbf{V}\mathbf{K}^0(E)\mathbf{V}] + \lambda^2\text{tr } [\mathbf{K}^0(E)\mathbf{V}\mathbf{K}^0(E)\mathbf{V}\mathbf{K}^0(E)\mathbf{V}] + \dots\right)dEd\lambda$$

$$= \frac{-1}{2\pi i} \int_0^1 \int_{-i\infty}^{+i\infty} \sum_{n=2}^\infty \lambda^{n-1}\text{tr } [(\mathbf{K}^0\mathbf{V})^n]dEd\lambda$$

$$= \frac{-1}{2\pi i} \int_{-i\infty}^{+i\infty} \left[\sum_{n=2}^\infty \frac{1}{n}(\lambda)^n\text{tr } [(\mathbf{K}^0\mathbf{V})^n]dE\right]_0^1$$

$$= -\frac{1}{2\pi i} \int_{-i\infty}^{+i\infty} \sum_{n=2}^\infty \frac{1}{n}\text{tr } [(\mathbf{K}^0\mathbf{V})^n]dE$$

$$= \frac{1}{2\pi i} \int_{-i\infty}^{+i\infty} \text{tr } [\ln(\mathbf{I} - \mathbf{K}^0\mathbf{V}) + \mathbf{K}^0\mathbf{V}]dE. \tag{33}$$

Note that no convergence factors $e^{\pm E\eta}$ are needed here, since the third line shows that no first-order poles are included. This expression is consistent with the diagrammatic expansion of the particle-particle Green function in many body perturbation theory. Similarly to the ph-RPA, which approximates the ground-state correlation energy by the sum of all ring diagrams, the pp-RPA approximates the correlation energy by the sum of all ladder diagrams[2]:

$$E_{Ladder}^c = \frac{-1}{2\pi i} \sum_{n=2}^\infty \frac{1}{n} \int_{-i\infty}^{+i\infty} \text{tr } [\mathbf{K}^0(E))\mathbf{V}]^n \ dE$$

$$= \frac{-1}{2\pi i} \sum_{n=1}^\infty \frac{1}{n} \int_{-i\infty}^{+i\infty} \text{tr } [\mathbf{K}^0(E))\mathbf{V}]^n \ dE + \frac{1}{2\pi i} \int_{-i\infty}^{+i\infty} \text{tr } \mathbf{K}^0(E))\mathbf{V} \ dE \tag{34}$$

$$= \frac{1}{2\pi i} \int_{-i\infty}^{+i\infty} \text{tr } [\ln(\mathbf{I} - \mathbf{K}^0(E)\mathbf{V}) + \mathbf{K}^0(E)\mathbf{V}] \ dE. \tag{35}$$

This expression is equivalent to adiabatic connection result, Eq. (33). The pp-RPA equations have an equivalent real space representation. To derive their real space counterpart, it is convenient to rewrite the Dyson-like equation in terms of the two-electron integrals that are not antisymmetrized

$$\frac{1}{2}K_{ijkl}^{\lambda} = \frac{1}{2}K_{ijkl}^{0} + \lambda \sum_{mnop} \frac{1}{2}K_{ijmn}^{0} \langle mn|op \rangle \frac{1}{2}K_{opkl}^{\lambda}$$

Because $v(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}$ is diagonal the real space representation, the real-space equivalent of Eq. (32) is a four-point equation

$$K^{\lambda}(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_1', \mathbf{x}_2', E) = K^{0}(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_1', \mathbf{x}_2', E) + \lambda \int d\mathbf{x}_1" d\mathbf{x}_2" K^{0}(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_1", \mathbf{x}_2", E)v(\mathbf{x}_1", \mathbf{x}_2")K^{\lambda}(\mathbf{x}_1", \mathbf{x}_2", \mathbf{x}_1', \mathbf{x}_2', E).$$

This leads to the correlation energy expression

$$
\begin{aligned}
E_{pp}^c &= \frac{-1}{2\pi i} \int_0^1 \int_{-i\infty}^{+i\infty} \lambda \int\int K^0(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_1', \mathbf{x}_2', E)v(\mathbf{x}_1', \mathbf{x}_2')K^0(\mathbf{x}_1', \mathbf{x}_2', \mathbf{x}_1, \mathbf{x}_2, E)v(\mathbf{x}_1, \mathbf{x}_2)d\mathbf{x}_1 d\mathbf{x}_2 d\mathbf{x}_1' d\mathbf{x}_2' \; dEd\lambda \\
&\quad - \frac{1}{2\pi i} \int_0^1 \int_{-i\infty}^{+i\infty} \lambda^2 \int\int\int K^0(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_1', \mathbf{x}_2', E)v(\mathbf{x}_1', \mathbf{x}_2')K^0(\mathbf{x}_1', \mathbf{x}_2', \mathbf{x}_1", \mathbf{x}_2", E)v(\mathbf{x}_1", \mathbf{x}_2") \\
&\quad \times K^0(\mathbf{x}_1", \mathbf{x}_2", \mathbf{x}_1, \mathbf{x}_2, E)v(\mathbf{x}_1, \mathbf{x}_2)d\mathbf{x}_1 d\mathbf{x}_2 d\mathbf{x}_1' d\mathbf{x}_2' d\mathbf{x}_1" d\mathbf{x}_2" \; dEd\lambda \\
&\quad - \frac{1}{2\pi i} \int_0^1 \int_{-i\infty}^{+i\infty} \lambda^3 \int\int\int\int \cdots \\
&\quad - \cdots \\
&= \frac{-1}{2\pi i} \int_{-i\infty}^{+i\infty} \frac{1}{2} \int\int K^0(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_1', \mathbf{x}_2', E)v(\mathbf{x}_1', \mathbf{x}_2')K^0(\mathbf{x}_1', \mathbf{x}_2', \mathbf{x}_1, \mathbf{x}_2, E)v(\mathbf{x}_1, \mathbf{x}_2)d\mathbf{x}_1 d\mathbf{x}_2 d\mathbf{x}_1' d\mathbf{x}_2' \; dE \\
&\quad - \frac{1}{2\pi i} \int_{-i\infty}^{+i\infty} \frac{1}{3} \int\int\int K^0(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_1', \mathbf{x}_2', E)v(\mathbf{x}_1', \mathbf{x}_2')K^0(\mathbf{x}_1', \mathbf{x}_2', \mathbf{x}_1", \mathbf{x}_2", E)v(\mathbf{x}_1", \mathbf{x}_2") \\
&\quad \times K^0(\mathbf{x}_1", \mathbf{x}_2", \mathbf{x}_1, \mathbf{x}_2, E)v(\mathbf{x}_1, \mathbf{x}_2)d\mathbf{x}_1 d\mathbf{x}_2 d\mathbf{x}_1' d\mathbf{x}_2' d\mathbf{x}_1" d\mathbf{x}_2" \; dE \\
&\quad - \frac{1}{2\pi i} \int_{-i\infty}^{+i\infty} \frac{1}{4} \int\int\int\int \cdots \\
&\quad - \cdots \\
&= \frac{1}{2\pi i} \int_{-i\infty}^{+i\infty} \mathrm{tr}\left(\ln(\mathbf{I} - \mathbf{S}) + \mathbf{S}\right) dE
\end{aligned}
\tag{36}
$$

where $\mathbf{S}$ is a matrix represented in real space with its elements

$$S(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_1', \mathbf{x}_2', E) = K^0(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_1', \mathbf{x}_2', E)v(\mathbf{x}_1', \mathbf{x}_2')$$

The correlation energy can be computed directly from Eq. (35) or (36) through numerical integration, since the non-interacting pp-function $\mathbf{K}^0$ has a simple, known structure (Eq. (9)), but it can also be reformulated in terms of the eigenvalues of equation (12)[2]:

$$E_{pp}^c = \frac{1}{2\pi i} \int_{-i\infty}^{+i\infty} \text{tr} \left[\ln(\mathbf{I} - \mathbf{K}^0(E)\mathbf{V}) + \mathbf{K}^0(E)\mathbf{V}\right] dE$$

$$= \sum_n^{N_{pp}} \omega_n^{N+2} - \text{tr } \mathbf{A} \tag{37}$$

$$= -\sum_n^{N_{hh}} \omega_n^{N-2} - \text{tr } \mathbf{C} \tag{38}$$

$$= \frac{1}{2}\sum_n^{N_{pp}} \omega_n^{N+2} - \frac{1}{2}\text{tr } \mathbf{A} - \frac{1}{2}\sum_n^{N_{hh}} \omega_n^{N-2} - \frac{1}{2}\text{tr } \mathbf{C}. \tag{39}$$

In order to show how the expression Eq. (35), or equivalently Eq. (33), reduces to the three equivalent expressions in terms of the eigenvalues ω_n^{N+2} or ω_n^{N-2}, we will consider the integrals of the two terms, $\text{tr } [\ln(\mathbf{I} - \mathbf{K}^0(E)\mathbf{V})]$ and $\text{tr } [\mathbf{K}^0(E)\mathbf{V}]$, separately. First of all,

$$\frac{1}{2\pi i} \int_{-i\infty}^{+i\infty} \text{tr } \mathbf{K}^0(E)\mathbf{V} \, dE$$

$$= \frac{1}{2\pi i} \int_{-i\infty}^{+i\infty} \sum_{a<b}^{N_p} V_{abab} \frac{1}{E - (\epsilon_a + \epsilon_b - 2\nu) + i\eta} - \sum_{h<i}^{N_h} V_{hihi} \frac{1}{E - (\epsilon_h + \epsilon_i - 2\nu) - i\eta} \, dE.$$

Integrating this over a semi-circle in the positive real plane – a negatively oriented curve – gives

$$\frac{1}{2\pi i} \int_{-i\infty}^{+i\infty} \text{tr } \mathbf{K}^0(E)\mathbf{V} \, dE$$

$$= -\sum_{a<b}^{N_p} V_{abab},$$

whereas integrating this over a semi-circle in the negative real plane – a positively oriented curve – gives

$$\frac{1}{2\pi i} \int_{-i\infty}^{+i\infty} \text{tr } \mathbf{K}^0(E)\mathbf{V} \, dE$$

$$= -\sum_{h<i}^{N_h} V_{hihi}.$$

The remaining integral of $\text{tr } [\ln(\mathbf{I} - \mathbf{K}^0(E)\mathbf{V})]$ can be evaluated using partial integration.

$$\frac{1}{2\pi i} \int_{-i\infty}^{+i\infty} \text{tr } [\ln(\mathbf{I} - \mathbf{K}^0(E)\mathbf{V})]dE = \frac{1}{2\pi i} \left[E \text{ tr } \ln(\mathbf{I} - \mathbf{K}^0(E)\mathbf{V})\right]_{-i\infty}^{+i\infty} - \frac{1}{2\pi i} \int_{-i\infty}^{+i\infty} E \text{ tr } [\frac{\partial}{\partial E}\ln(\mathbf{I} - \mathbf{K}^0(E)\mathbf{V})]dE$$

$$= -\frac{1}{2\pi i} \int_{-i\infty}^{+i\infty} E \text{ tr } [\frac{\partial}{\partial E}\ln(\mathbf{I} - \mathbf{K}^0(E)\mathbf{V})]dE. \tag{40}$$

In order to tackle the integrand, the identity $\mathbf{I} - \mathbf{K}^0\mathbf{V} = \mathbf{K}^0\mathbf{K}^{-1}$, which follows simply from Eq. (7), can be applied:

$$\frac{\partial}{\partial E}\ln(\mathbf{I} - \mathbf{K}^0(E)\mathbf{V}) = \frac{\partial}{\partial E}\ln \mathbf{K}^0\mathbf{K}^{-1}$$

$$= \mathbf{K}(\mathbf{K}^0)^{-1} \left(\frac{\partial \mathbf{K}^0}{\partial E}\mathbf{K}^{-1} + \mathbf{K}^0\frac{\partial \mathbf{K}^{-1}}{\partial E}\right)$$

$$= \mathbf{K}(\mathbf{K}^0)^{-1} \left(\frac{\partial \mathbf{K}^0}{\partial E}\mathbf{K}^{-1} + \mathbf{K}^0\frac{\partial (\mathbf{K}^0)^{-1}}{\partial E}\right). \tag{41}$$

In the last line, the relationship $\mathbf{K}^{-1} = (\mathbf{K}^0)^{-1} - \mathbf{V}$, which implies that $\frac{\partial \mathbf{K}^{-1}}{\partial E} = \frac{\partial (\mathbf{K}^0)^{-1}}{\partial E}$, has been used. The integral then becomes

$$-\frac{1}{2\pi i} \int_{-i\infty}^{+i\infty} E \ \text{tr} \ [\frac{\partial}{\partial E}\ln(\mathbf{I} - \mathbf{K}^0(E)\mathbf{V})]dE = -\frac{1}{2\pi i} \int_{-i\infty}^{+i\infty} E \ \text{tr} \ \left[\mathbf{K}(\mathbf{K}^0)^{-1} \left(\frac{\partial \mathbf{K}^0}{\partial E}\mathbf{K}^{-1} + \mathbf{K}^0\frac{\partial (\mathbf{K}^0)^{-1}}{\partial E}\right)\right] dE$$

$$= -\frac{1}{2\pi i} \int_{-i\infty}^{+i\infty} E \ \text{tr} \ \left[(\mathbf{K}^0)^{-1}\frac{\partial \mathbf{K}^0}{\partial E} + \mathbf{K}\frac{\partial (\mathbf{K}^0)^{-1}}{\partial E}\right] dE. \qquad (42)$$

The terms needed to compute the integrand are

$$\left(\frac{\partial K^0}{\partial E}\right)_{ijkl} = -(\delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk}) \left[\frac{\theta(i - F)\theta(j - F)}{(E - (\epsilon_i + \epsilon_j - 2\nu) + i\eta)^2} - \frac{\theta(F - i)\theta(F - j)}{(E - (\epsilon_i + \epsilon_j - 2\nu) - i\eta)^2}\right]$$

$$\left(K^0\right)_{ijkl}^{-1} = (\delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk}) \left[\theta(i - F)\theta(j - F)\left(E - (\epsilon_i + \epsilon_j - 2\nu) + i\eta\right) - \theta(F - i)\theta(F - j)\left(E - (\epsilon_i + \epsilon_j - 2\nu) - i\eta\right)\right]$$

$$\frac{\partial \left(K^0\right)_{ijkl}^{-1}}{\partial E} = (\delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk}) \left[\theta(i - F)\theta(j - F) - \theta(F - i)\theta(F - j)\right]. \qquad (43)$$

With the aid of expressions (40), (41) and (42), the first part of the integral (40) becomes

$$-\frac{1}{2\pi i} \int_{-i\infty}^{+i\infty} E \ \text{tr} \ \left[(\mathbf{K}^0)^{-1}\frac{\partial \mathbf{K}^0}{\partial E}\right] dE = -\frac{1}{2\pi i} \int_{-i\infty}^{+i\infty} E \sum_{i<j}^{K} \left[-\frac{\theta(i - F)\theta(j - F)}{E - (\epsilon_i + \epsilon_j - 2\nu) + i\eta} - \frac{\theta(F - i)\theta(F - j)}{E - (\epsilon_i + \epsilon_j - 2\nu) - i\eta}\right] dE.$$

Integration over a semi-circular path in the positive real plane gives

$$-\frac{1}{2\pi i} \int_{-i\infty}^{+i\infty} E \sum_{i<j}^{K} \left[-\frac{\theta(i - F)\theta(j - F)}{E - (\epsilon_i + \epsilon_j - 2\nu) + i\eta} - \frac{\theta(F - i)\theta(F - j)}{E - (\epsilon_i + \epsilon_j - 2\nu) - i\eta}\right] dE = -\sum_{a<b}^{N_p}(\epsilon_b + \epsilon_a - 2\nu),$$

whereas integration over a semi-circular path in the negative real plane gives

$$-\frac{1}{2\pi i} \int_{-i\infty}^{+i\infty} E \sum_{i<j}^{K} \left[-\frac{\theta(i - F)\theta(j - F)}{E - (\epsilon_i + \epsilon_j - 2\nu) + i\eta} - \frac{\theta(F - i)\theta(F - j)}{E - (\epsilon_i + \epsilon_j - 2\nu) - i\eta}\right] dE = \sum_{h<i}^{N_h}(\epsilon_h + \epsilon_i - 2\nu).$$

The second part of the integral (40) becomes

$$-\frac{1}{2\pi i} \int_{-i\infty}^{+i\infty} E \ \text{tr} \ \left[\mathbf{K}\frac{\partial (\mathbf{K}^0)^{-1}}{\partial E}\right] dE = -\frac{1}{2\pi i} \int_{-i\infty}^{+i\infty} E \left(\sum_{a<b}^{N_p} K(E)_{abab} - \sum_{h<i}^{N_h} K(E)_{hihi}\right) dE.$$

Integration over a semi-circular path in the positive real plane gives

$$-\frac{1}{2\pi i} \int_{-i\infty}^{+i\infty} E \ \text{tr} \ \left[\mathbf{K}\frac{\partial (\mathbf{K}^0)^{-1}}{\partial E}\right] dE = \sum_n \omega_n^{N+2} \left(\sum_{a<b}^{N_p} \chi_{ab}^{n,N+2} \left(\chi_{ab}^{n,N+2}\right)^* - \sum_{h<i}^{N_h} \chi_{hi}^{n,N+2} \left(\chi_{hi}^{n,N+2}\right)^*\right)$$

$$= \sum_n \omega_n^{N+2}$$

and integration over a semi-circular path in the negative real plane gives

$$-\frac{1}{2\pi i}\int_{-i\infty}^{+i\infty} E \text{ tr }\left[\mathbf{K}\frac{\partial(\mathbf{K}^0)^{-1}}{\partial E}\right]dE = -\sum_n \omega_n^{N-2}\left(-\sum_{a<b}^{N_p}\chi_{ab}^{n,N-2}\left(\chi_{ab}^{n,N-2}\right)^* + \sum_{h<i}^{N_h}\chi_{hi}^{n,N-2}\left(\chi_{hi}^{n,N-2}\right)^*\right)$$

$$= -\sum_n \omega_n^{N-2}.$$

where we have used the normalization conditions, Eqs. (45-46).

To summarize, by closing a semi-circular path in the positive real plane, we find

$$E_{pp}^c = \sum_n^{N_{pp}}\omega_n^{N+2} - \sum_{a<b}^{N_p}(\epsilon_b + \epsilon_a - 2\nu) - \sum_{a<b}^{N_p}V_{abab}$$

$$= \sum_n^{N_{pp}}\omega_n^{N+2} - \text{tr }\mathbf{A}$$

and by closing a semi-circular path in the negative real plane,

$$E_{pp}^c = -\sum_n^{N_{hh}}\omega_n^{N-2} + \sum_{h<i}^{N_h}(\epsilon_h + \epsilon_i - 2\nu) - \sum_{h<i}^{N_h}V_{hihi}$$

$$= -\sum_n^{N_{hh}}\omega_n^{N-2} - \text{tr }\mathbf{C}.$$

The two expressions for the correlation energy are equivalent, which follows from the orthonormality and completeness of the pp-RPA eigenvector basis. At this point, it is convenient to introduce a simplified notation for the pp-RPA matrix,

$$\mathbf{R} = \begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^\dagger & \mathbf{C} \end{pmatrix}$$

and for its eigenvectors,

$$\chi^{\mathbf{n}} = \begin{pmatrix} \mathbf{X^n} \\ \mathbf{Y^n} \end{pmatrix}.$$

The norm matrix can be denoted as $\mathbf{M} = \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{pmatrix}$ so that the pp-RPA equations take the form

$$\mathbf{R}\chi^{\mathbf{n}} = \omega_n \mathbf{M}\chi^{\mathbf{n}}, \tag{44}$$

for both the 2-electron addition and the 2-electron removal. The orthonormality and completeness of the eigenvector basis can then be expressed as

$$\left(\chi^{\mathbf{n},N+2}\right)^\dagger \mathbf{M}\chi^{\mathbf{m},N+2} = \delta_{mn} \tag{45}$$

$$\left(\chi^{\mathbf{n},N-2}\right)^\dagger \mathbf{M}\chi^{\mathbf{m},N-2} = -\delta_{mn} \tag{46}$$

$$\sum_n^{N_{pp}}\chi^{\mathbf{n},N+2}\left(\chi^{n,N+2}\right)^\dagger - \sum_n^{N_{hh}}\chi^{\mathbf{n},N-2}\left(\chi^{n,N-2}\right)^\dagger = \mathbf{M}$$

The pp-RPA equations imply that

$$\sum_n^{N_{pp}} \left(\chi^{\mathbf{n},N+2}\right)^\dagger \begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^\dagger & \mathbf{C} \end{pmatrix} \chi^{\mathbf{n},N+2} = \sum_n^{N_{pp}} \omega_n^{N+2} \left(\chi^{\mathbf{n},N+2}\right)^\dagger \mathbf{M}\chi^{\mathbf{n},N+2}$$

$$-\sum_n^{N_{hh}} \left(\chi^{\mathbf{n},N-2}\right)^\dagger \begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^\dagger & \mathbf{C} \end{pmatrix} \chi^{\mathbf{n},N-2} = -\sum_n^{N_{hh}} \omega_n^{N-2} \left(\chi^{\mathbf{n},N-2}\right)^\dagger \mathbf{M}\chi^{\mathbf{n},N-2}.$$

This, together with the normalization and completeness of the eigenvectors, and Eq.(45), leads to the following relation between the $N-2$ electron quantities and $N+2$ electron quantities

$$\text{tr } \mathbf{A} - \text{tr } \mathbf{C} = \sum_n^{N_{pp}} \omega_n^{N+2} + \sum_n^{N_{hh}} \omega_n^{N-2}. \tag{47}$$

The correlation energy can be viewed as a functional $E[\{\phi_i\}, n_i]$ because equation (12) depends only on the orthonormal set of orbitals $\{\phi_i\}$ and their occupations n_i. The total pp-RPA energy expression combines the HF-energy functional with the pp-RPA correlation energy:

$$E^{pp}[\{\phi_i\}, n_i] = E^{HF}[\{\phi_i\}, n_i] + E_{pp}^c[\{\phi_i\}, n_i]$$

$$= \sum_i h_{ii} n_i + \frac{1}{2} \sum_{ij} \langle ij||ij\rangle n_i n_j + E_{pp}^c[\{\phi_i\}, n_i]$$

with $\mathbf{h}$ the core Hamiltonian matrix.

D. Perturbation analysis of the pp-RPA energy

In the context of many-body perturbation theory, the pp-RPA energy arises as the sum of all ladder diagrams up to infinite order [2]:

$$E_{pp}^c = \frac{-1}{2\pi i} \sum_{n=2}^\infty \frac{1}{n} \int_{-i\infty}^{+i\infty} \text{tr } [\mathbf{K}^0(E))\mathbf{V}]^n \, dE$$

$$= \frac{-1}{2\pi i} \sum_{n=1}^\infty \frac{1}{n} \int_{-i\infty}^{+i\infty} \text{tr } [\mathbf{K}^0(E))\mathbf{V}]^n \, dE + \frac{1}{2\pi i} \int_{-i\infty}^{+i\infty} \text{tr } \mathbf{K}^0(E))\mathbf{V} \, dE \tag{48}$$

$$= \frac{1}{2\pi i} \int_{-i\infty}^{+i\infty} \text{tr } [\ln(\mathbf{I} - \mathbf{K}^0(E)\mathbf{V}) + \mathbf{K}^0(E)\mathbf{V}] \, dE. \tag{49}$$

In contrast, the ph-RPA energy originates from the summation of all ring diagrams [2]:

$$E_{ph}^c = \frac{1}{2\pi i} \sum_{n=2}^\infty \frac{-1}{2n} \int_{-i\infty}^{+i\infty} \text{tr } [\mathbf{\Pi}^0(E))\tilde{\mathbf{V}}]^n \, dE$$

$$= \frac{1}{2\pi i} \sum_{n=1}^\infty \frac{-1}{2n} \int_{-i\infty}^{+i\infty} \text{tr } [\mathbf{\Pi}^0(E))\tilde{\mathbf{V}}]^n \, dE + \frac{1}{4\pi i} \int_{-i\infty}^{+i\infty} \text{tr } \mathbf{\Pi}^0(E))\tilde{\mathbf{V}} \, dE \tag{50}$$

$$= \frac{1}{4\pi i} \int_{-i\infty}^{+i\infty} \text{tr } [\ln(\mathbf{I} - \mathbf{\Pi}^0(E)\tilde{\mathbf{V}}) + \mathbf{\Pi}^0(E)\tilde{\mathbf{V}}] \, dE \tag{51}$$

where $\tilde{V}_{ahib} = \langle ab|hi\rangle$ does not include exchange. The ph-RPAX uses antisymmetrized two-electron integrals and the coresponding correlation energy can be derived from the adiabatic connection to be [8]:

$$E_{phX}^c = \frac{1}{4\pi i} \sum_{n=2}^{\infty} \frac{-1}{2n} \int_{-i\infty}^{+i\infty} \text{tr } [\mathbf{\Pi}^0(E))\tilde{\mathbf{V}}]^n \, dE$$

$$= \frac{1}{4\pi i} \sum_{n=1}^{\infty} \frac{-1}{2n} \int_{-i\infty}^{+i\infty} \text{tr } [\mathbf{\Pi}^0(E))\tilde{\mathbf{V}}]^n \, dE + \frac{1}{4\pi i} \int_{-i\infty}^{+i\infty} \text{tr } \mathbf{\Pi}^0(E))\tilde{\mathbf{V}} \, dE \tag{52}$$

$$= \frac{1}{8\pi i} \int_{-i\infty}^{+i\infty} \text{tr } [\ln(\mathbf{I} - \mathbf{\Pi}^0(E)\tilde{\mathbf{V}}) + \mathbf{\Pi}^0(E)\tilde{\mathbf{V}}] \, dE \tag{53}$$

where $\bar{V}_{ahib} = \langle ab\|hi\rangle$ now includes exchange.

The pp-RPA energy is correct through second order:

$$E_{pp}^{(2)} = -\frac{1}{2}\frac{1}{2\pi i} \int_{-i\infty}^{+i\infty} tr \, [\mathbf{K}^0(E)\mathbf{V}]^2 dE$$

$$= -\frac{1}{2}\frac{1}{2\pi i} \int_{-i\infty}^{+i\infty} \sum_{a<b,c<d} \frac{V_{abcd}V_{cdab}}{(E-(\epsilon_a+\epsilon_b))(E-(\epsilon_c+\epsilon_d))} + \sum_{h<i,j<k} \frac{V_{hijk}V_{jkhi}}{(E-(\epsilon_h+\epsilon_i))(E-(\epsilon_j+\epsilon_k))}$$

$$-2\sum_{a<b,h<i} \frac{V_{abhi}V_{hiab}}{(E-(\epsilon_a+\epsilon_b))(E-(\epsilon_h+\epsilon_i))}dE$$

$$= -\sum_{a<b,h<i} \frac{V_{abhi}V_{hiab}}{\epsilon_a+\epsilon_b-\epsilon_h-\epsilon_i}$$

$$= -\frac{1}{4}\sum_{abhi} \frac{|\langle hi\|ab\rangle|^2}{\epsilon_a+\epsilon_b-\epsilon_h-\epsilon_i}$$

where only the third term in the second line makes a non-zero contribution. This expression includes all possible second-order diagrams, and is hence exact. The ph-RPAX has the same second-order energy contribution,

$$E_{phX}^{(2)} = -\frac{1}{4}\frac{1}{4\pi i} \int_{-i\infty}^{+i\infty} tr \, [\mathbf{\Pi}^0(E)\bar{\mathbf{V}}]^2 dE$$

$$= -\frac{1}{4}\frac{1}{4\pi i} \int_{-i\infty}^{+i\infty} \sum_{abqi} \frac{\bar{V}_{ahbi}\bar{V}_{biah}}{(E-(\epsilon_a-\epsilon_h))(E-(\epsilon_b-\epsilon_i))} + \sum_{hijk} \frac{\bar{V}_{haib}\bar{V}_{ibha}}{(E-(\epsilon_h-\epsilon_a))(E-(\epsilon_i-\epsilon_b))}$$

$$-2\sum_{pqhi} \frac{\bar{V}_{ahib}\bar{V}_{ibah}}{(E-(\epsilon_a-\epsilon_h))(E-(\epsilon_i-\epsilon_b))}dE$$

$$= -\frac{1}{4}\sum_{abhi} \frac{\bar{V}_{ahib}\bar{V}_{ibah}}{\epsilon_a-\epsilon_h-\epsilon_i+\epsilon_b}$$

$$= -\frac{1}{4}\sum_{abhi} \frac{|\langle hi\|ab\rangle|^2}{\epsilon_a+\epsilon_b-\epsilon_h-\epsilon_i}$$

but an inherent drawback of the ph-RPAX is its sensitivity to instabilities in the non-interacting reference state: when the non-interacting reference state is unstable with respect to orbital rotations, the ph-RPAX breaks down and produces imaginary eigenvalues [19]. For this reason, molecular calculations are done almost exclusively using the 'direct' ph-RPA[8, 10, 18], which does not suffer from such instabilities. The ph-RPA, however, does not have the correct second-order energy expression because it does not consider antisymmetrized two-electron integrals:

$$
\begin{aligned}
E_{ph}^{(2)} &= -\frac{1}{4}\frac{1}{2\pi i}\int_{-i\infty}^{+i\infty} tr\,[\mathbf{\Pi}^0(E)\tilde{\mathbf{V}}]^2 dE \\
&= -\frac{1}{4}\frac{1}{2\pi i}\int_{-i\infty}^{+i\infty}\sum_{abqi}\frac{\tilde{V}_{ahbi}\tilde{V}_{biah}}{(E-(\epsilon_a-\epsilon_h))(E-(\epsilon_b-\epsilon_i))} + \sum_{hijk}\frac{\tilde{V}_{haib}\tilde{V}_{ibha}}{(E-(\epsilon_h-\epsilon_a))(E-(\epsilon_i-\epsilon_b))} \\
&\quad -2\sum_{pqhi}\frac{\tilde{V}_{ahib}\tilde{V}_{ibah}}{(E-(\epsilon_a-\epsilon_h))(E-(\epsilon_i-\epsilon_b))} dE \\
&= -\frac{1}{2}\sum_{abhi}\frac{\tilde{V}_{ahib}\tilde{V}_{ibah}}{\epsilon_a-\epsilon_h-\epsilon_i+\epsilon_b} \\
&= -\frac{1}{2}\sum_{abhi}\frac{|\langle hi|ab\rangle|^2}{\epsilon_a+\epsilon_b-\epsilon_h-\epsilon_i}
\end{aligned}
$$

Only the last term in the second line does not vanish upon integration.

E. The particle-particle RPA for systems with fractional electron number

While equation (12) describes the pp-RPA for systems with integer electron number, the behavior of the pp-RPA for systems with fractional electron number or spin can be quantified by taking the fractional orbital occupations into account explicitly in the pp-RPA equations (12)

$$
\begin{aligned}
A_{abcd} &= \sqrt{(1-n_a)(1-n_b)}\langle ab\|cd\rangle\sqrt{(1-n_c)(1-n_d)} \\
&\quad + \delta_{ac}\delta_{bd}(\epsilon_a+\epsilon_b-2\nu) \\
B_{abij} &= \sqrt{(1-n_a)(1-n_b)}\langle ab\|ij\rangle\sqrt{n_i n_j} \\
C_{ijkl} &= \sqrt{n_i n_j}\langle ij\|kl\rangle\sqrt{n_k n_l} - \delta_{ij}\delta_{kl}(\epsilon_i+\epsilon_j-2\nu).
\end{aligned}
\tag{54}
$$

This extension to fractional occupation number follows the same approach as the one taken in previous work by Cohen, Mori-Sanchez and Yang [6, 15] and is explained in more detail in Ref. [22]. When all orbital occupation numbers are integer these equations reduce to the usual pp-RPA equations.

II.   ADDITIONAL FIGURES AND TABLES

We computed the KS reference wavefunctions with Gaussian03 [9] for the systems with integer electron number and with the QM4D package for systems with fractional electron number or spin [1]. For the subsequent pp-RPA calculation, we used our implementation, which diagonalizes the pp-RPA matrix. Since the diagonalization is computationally expensive, we used a cc-pVDZ basis set for all calculations, except for the Ar and Ne atoms, for which we used an aug-cc-pVDZ (FC) basis set. For the calculations on thermodynamical properties, we used a cc-pVTZ basis set limited to F-functions because the pp-RPA energy converges slowly with the basis set size (Fig. 12 of ref. ([21])) and geometries from the G2 test set [7]. Accurate potential energy functions for the dimers of the noble gases have been taken from the work of Ogilvie et al. [16, 17] and the MRCI potential energy function for the N_2 in the cc-pVDZ basis set has been taken from previous work [20].
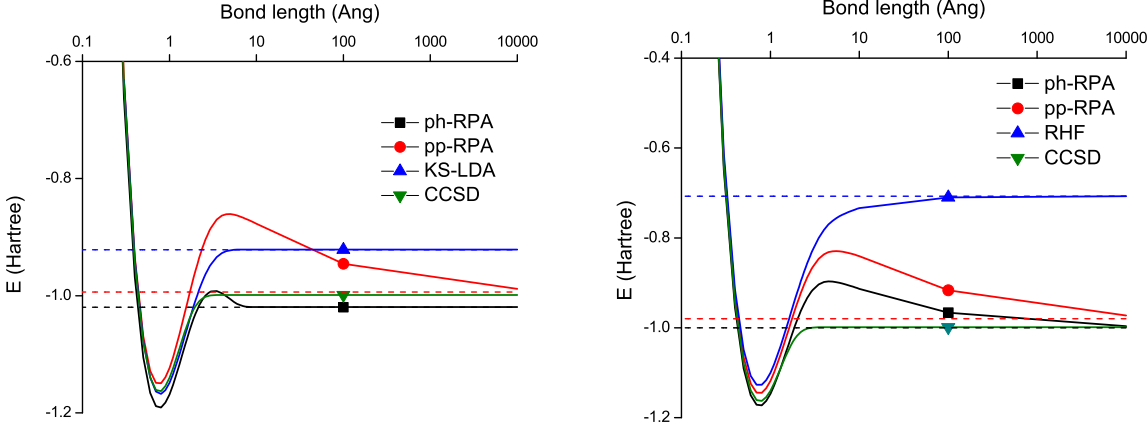

FIG. 1: The pp-RPA energy (left: restricted LDA reference, right: restricted HF reference) for the H_2 molecule approaches the correct value in the dissociation limit, but has an unphysical 'bump', much more so than ph-RPA. The dashed lines indicate the dissociation limit from the fractional analysis of the H atom.
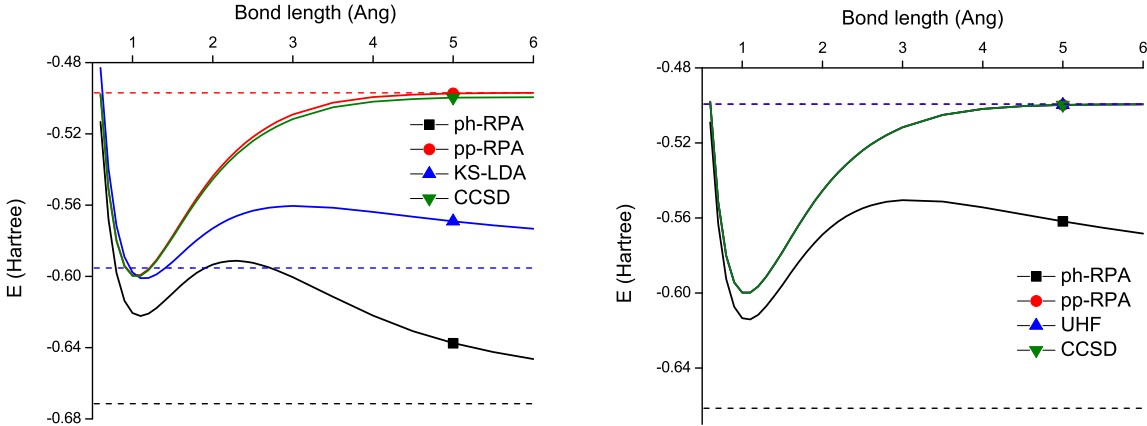

FIG. 2: In contrast to the ph-RPA, the pp-RPA dissociates H_2^+ correctly (left: LDA reference, right: HF reference). The dashed lines indicate the dissociation limit from the fractional analysis of the H atom.
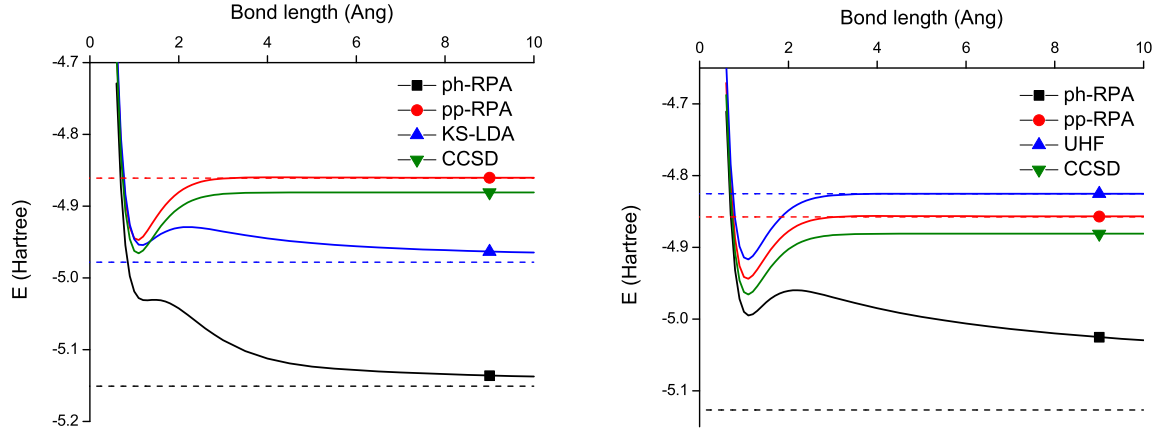
FIG. 3: The pp-RPA also gives a correct energy profile for He_2^+, in contrast to the ph-RPA (left: LDA reference, right: HF reference). The dashed lines indicate the dissociation limit from the fractional analysis of the He atom.
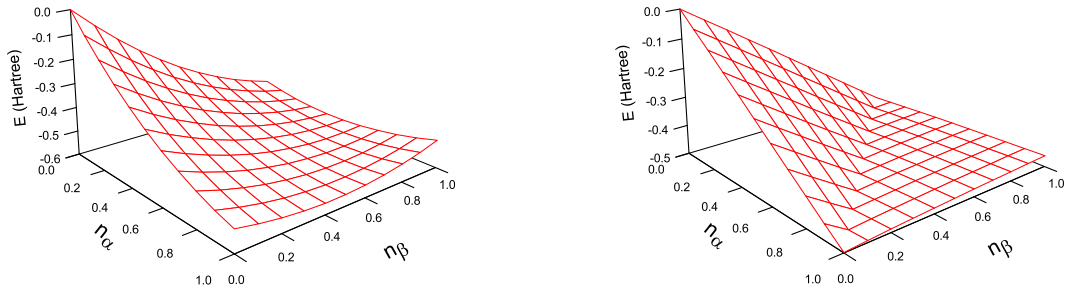

FIG. 4: The ph-RPA energy for the H atom (left) is a nearly constant function of the fractional spin projection, but is a convex function of the fractional electron number. The pp-RPA energy (right) is physically correct: it has a nearly constant function of the fractional spin projection and a linear function of the fractional electron number. Like the exact functional, its derivative has a discontinuity at N=1.
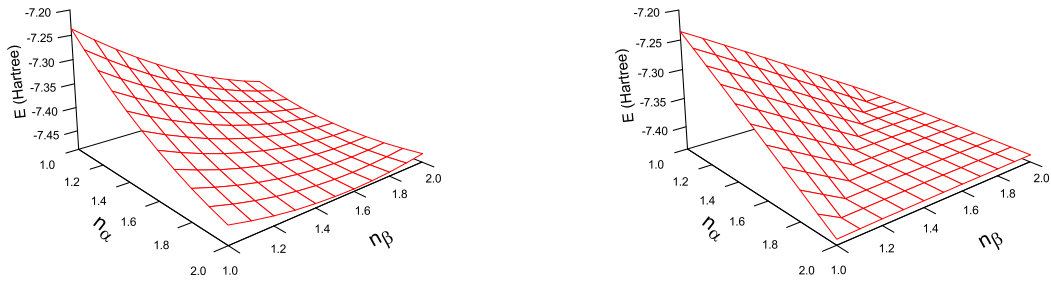

FIG. 5: The ph-RPA energy for the Li atom (left) is a nearly constant function of the fractional spin projection, but is a convex function of the fractional electron number. The pp-RPA energy (right) is a nearly constant function of the fractional spin projection and a nearly linear function of the fractional electron number. Like the exact functional, its derivative has a discontinuity at N=3.
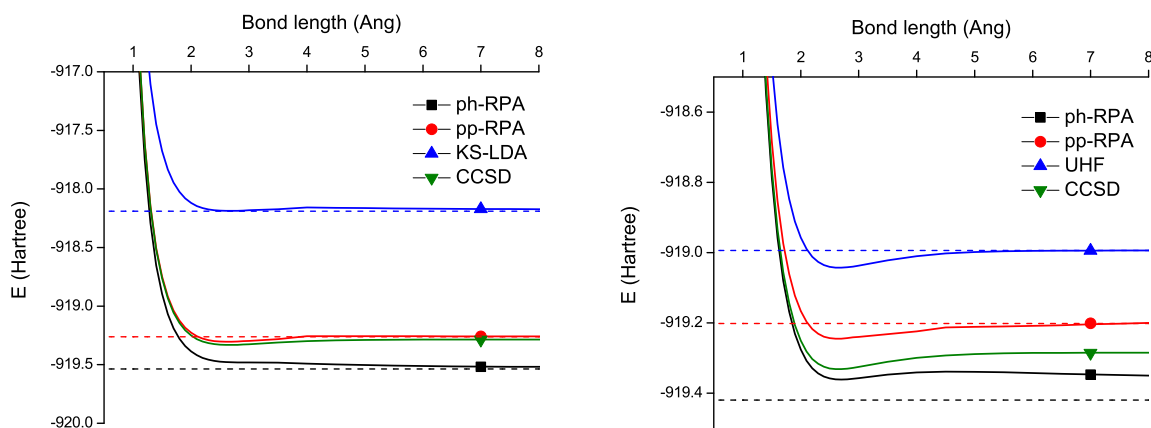
FIG. 6: The pp-RPA also gives a correct energy profile for Cl_2^-, in contrast to the ph-RPA (left: LDA reference, right: HF reference). The dashed lines indicate the dissociation limit from the fractional analysis of the He atom.
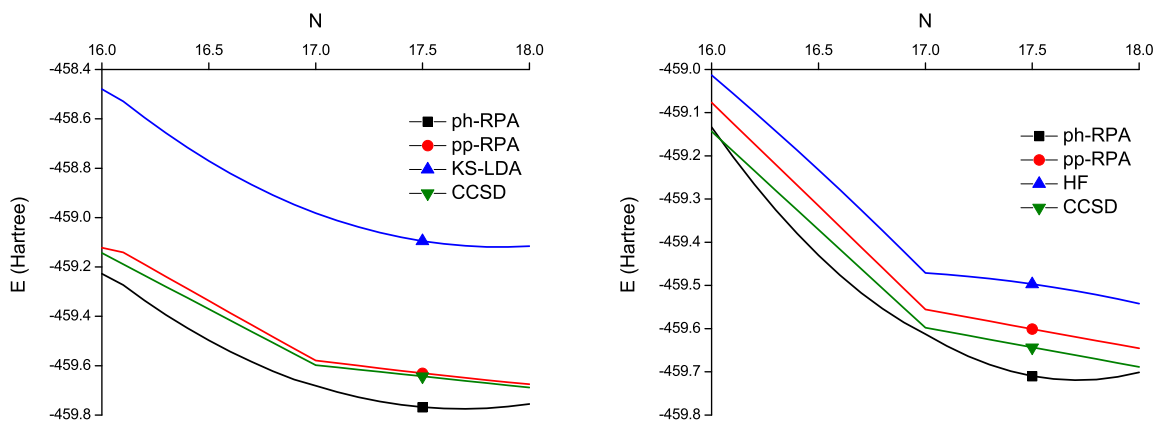

FIG. 7: The pp-RPA energy for the Cl atom is nearly linear in between integer electron numbers, as opposed to the ph-RPA energy (left: LDA reference, right: HF reference). The 'accurate' graph consists of line segments between the CCSD energies for the integer occupations.
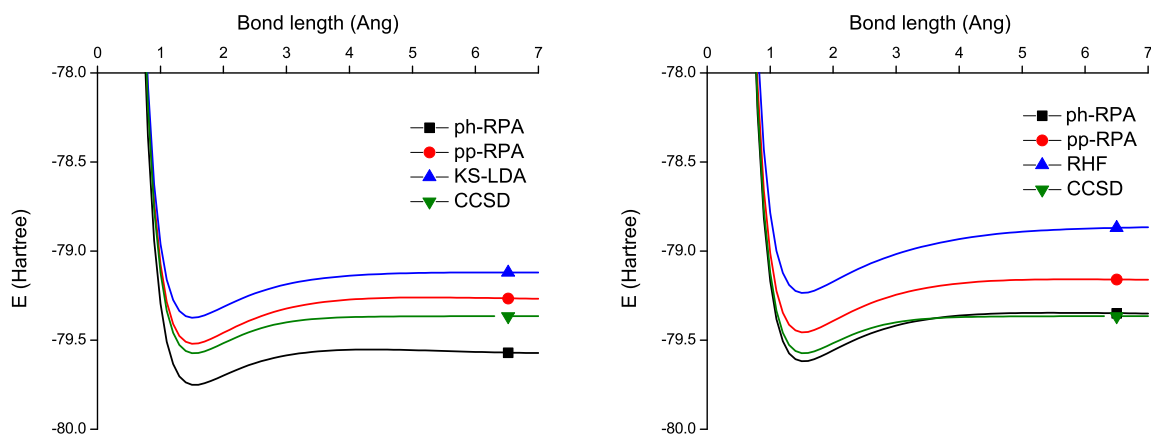
FIG. 8: The pp-RPA describes the stretching of the C-C bond in C_2H_6 correctly (left: restricted LDA reference, right: restricted HF reference). The positions of the H atoms are kept fixed at their equilibrium position.
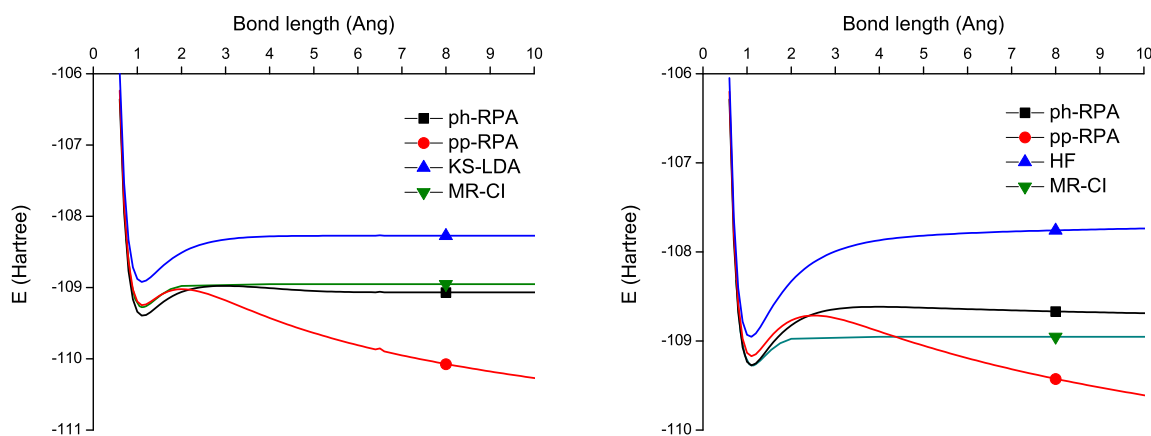

FIG. 9: The pp-RPA leads to a decreasing energy in the dissociation limit of the triple bond in N_2 (left: restricted LDA reference, right: restricted HF reference).
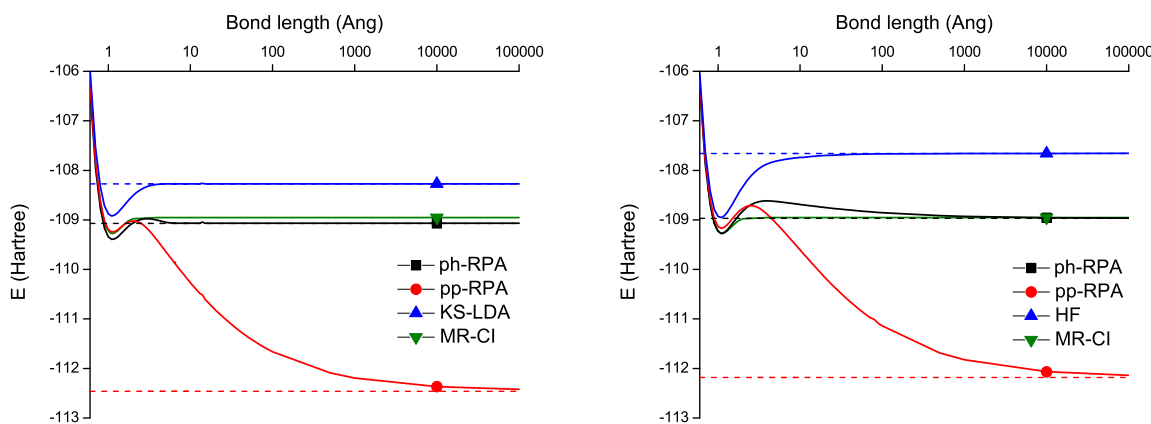

FIG. 10: The dissociation limit of the pp-RPA and ph-RPA energy for N_2 corresponds to the energy of two spin and angular momentum unpolarized N atoms, indicated with dashed lines (left: restricted LDA reference, right: restricted HF reference).

FIG. 11: The ph-RPA and pp-RPA both describe the van der Waals interactions in the Ar dimer well (left: LDA reference, right: HF reference).
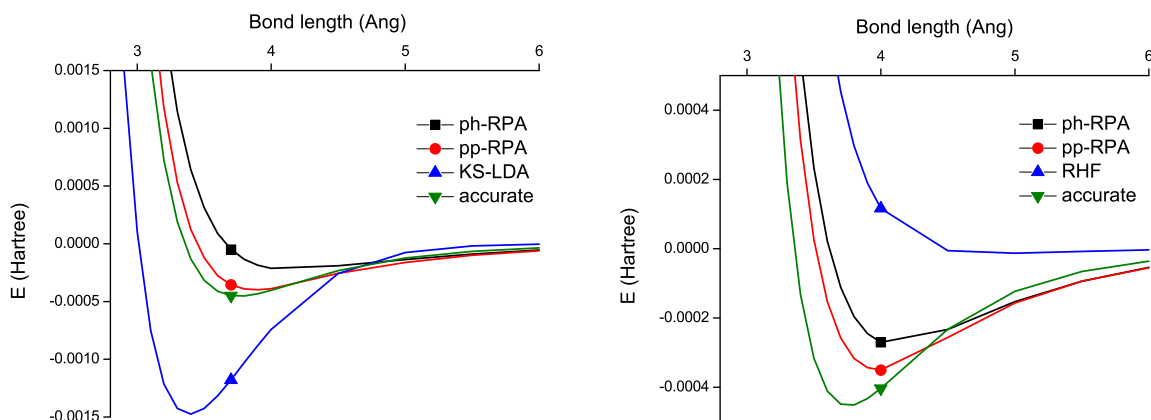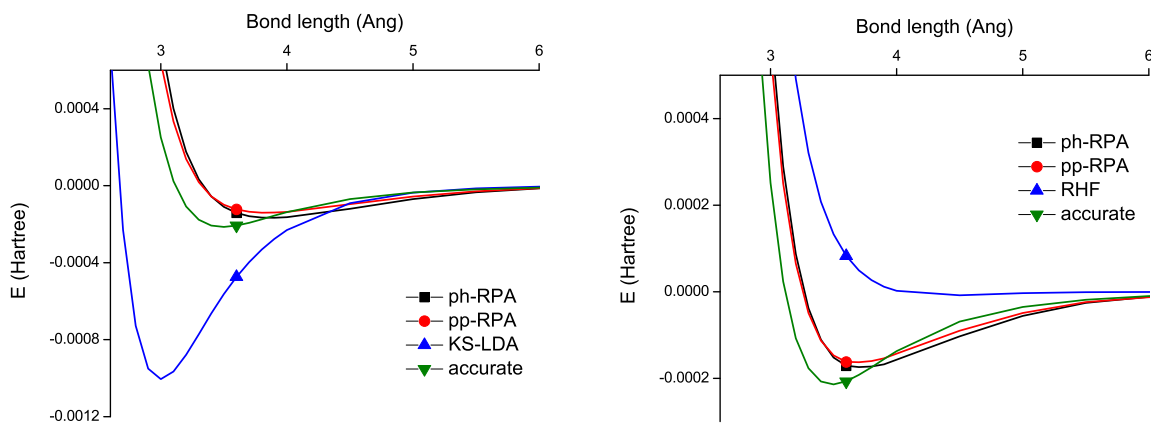

FIG. 12: The pp-RPA also describes the van der Waals interactions in the heteronuclear NeAr well (left: LDA reference, right: HF reference).
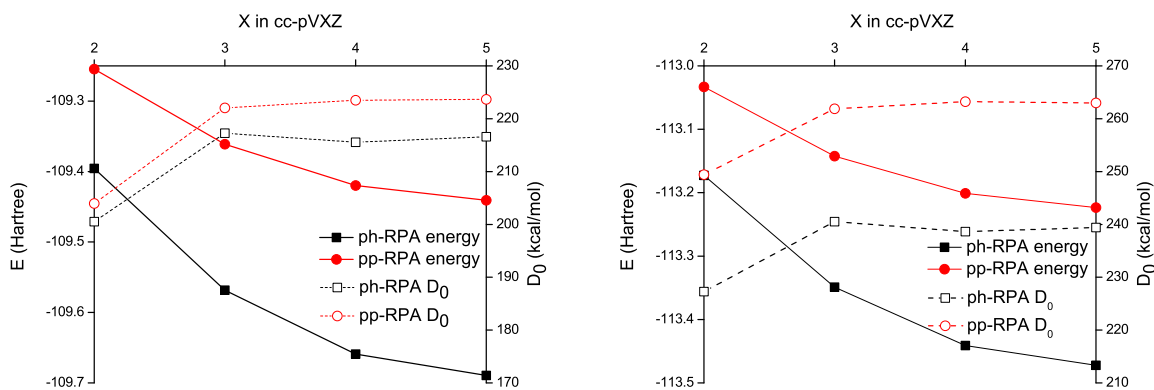

FIG. 13: The basis set convergence of the pp-RPA energy is rather slow, similar to that of ph-RPA. The atomization energy D_0 converges faster to its basis set limit than the absolute energies (left: N_2, right: CO).

TABLE I: The left and right derivatives of the pp-RPA(LDA) and ph-RPA(LDA) energy in eV, computed by finite difference (with $\Delta = 0.001$), agree well with experiment, especially the derivatives with respect to the HOMO orbital occupation.

	$\left(\frac{\partial E}{\partial n_f}\right)_{N-\delta}$ pp-RPA(LDA)	$\left(\frac{\partial E}{\partial n_f}\right)_{N-\delta}$ ph-RPA(LDA)	ϵ_{HOMO} KS-LDA	$-I$ expt.	$\left(\frac{\partial E}{\partial n_f}\right)_{N+\delta}$ pp-RPA(LDA)	$\left(\frac{\partial E}{\partial n_f}\right)_{N+\delta}$ ph-RPA(LDA)	ϵ_{LUMO} KS-LDA	A expt.
Li	-5.395	-3.130	-3.581	-5.392	0.125	-3.013	-2.169	-0.618
Be	-8.628	-5.379	-6.042	-9.323	1.185	-2.811	-2.515	-0.295
B	-8.184	-3.668	-4.540	-8.298	0.772	-4.010	-3.812	-0.280
C	-11.112	-5.271	-6.564	-11.260	0.177	-4.131	-5.083	-1.262
N	-14.281	-6.636	-8.849	-14.534	0.959	-5.553	-4.910	-0.070
O	-15.137	-8.242	-9.636	-13.618	-1.395	-8.299	-7.709	-1.461
F	-17.803	-10.193	-11.837	-17.423	-4.206	-11.434	-10.812	-3.401
MAE	**0.445**	**5.332**	**4.114**		**0.945**	**4.552**	**4.232**	

TABLE II: The left and right derivatives of the pp-RPA(HF) and ph-RPA(LDA) energy in eV, computed by finite difference (with $\Delta = 0.001$) agree well with experiment.

	$\left(\frac{\partial E}{\partial n_f}\right)_{N-\delta}$ pp-RPA(HF)	$\left(\frac{\partial E}{\partial n_f}\right)_{N-\delta}$ ph-RPA(HF)	ϵ_{HOMO} HF	$-I$ expt.	$\left(\frac{\partial E}{\partial n_f}\right)_{N+\delta}$ pp-RPA(HF)	$\left(\frac{\partial E}{\partial n_f}\right)_{N+\delta}$ ph-RPA(HF)	ϵ_{LUMO} HF	A expt.
Li	-5.349	-2.580	-5.343	-5.392	-0.030	-2.026	0.153	-0.618
Be	-8.528	-4.595	-8.416	-9.323	0.336	-2.054	0.396	-0.295
B	-8.369	-3.013	-8.666	-8.298	0.424	-2.821	0.795	-0.280
C	-11.405	-4.649	-11.941	-11.260	0.377	-3.978	1.025	-1.262
N	-14.696	-6.639	-15.531	-14.534	1.357	-3.273	2.095	-0.070
O	-15.607	-6.948	-16.648	-13.618	0.226	-5.759	1.765	-1.461
F	-18.397	-8.841	-19.921	-17.423	-1.787	-8.885	0.967	-3.401
MAE	**0.597**	**6.083**	**1.219**		**1.184**	**3.058**	**2.083**	

TABLE III: The errors in the atomization energies D_0 and the heats of formation ΔH (in kcal/mol) relative to the experimental values $\Delta H_{expt.}$, computed with pp-RPA in the cc-pVTZ basis set, are significantly better than those computed with ph-RPA.

	D_0^{pp-RPA}	D_0^{ph-RPA}	ΔH^{pp-RPA}	ΔH^{ph-RPA}	ΔH^{expt}
C_2H_2	406.3	387.3	53.2	72.2	54.2
CH_4	410.6	410.8	-9.3	-9.6	-17.9
Cl_2	56.6	44.2	1.4	13.7	0.0
CO	265.0	243.6	-32.1	-10.7	-26.4
F_2	37.5	27.9	1.0	10.6	0.0
H_2	100.4	108.3	8.8	0.9	0.0
H_2O	225.8	218.8	-51.3	-44.4	-57.8
HCl	102.4	98.3	-18.1	-14.0	-22.1
HF	139.2	128.5	-63.5	-52.8	-65.1
HOCl	161.7	148.5	-15.1	-1.9	-17.8
HOOH	262.7	250.6	-26.4	-14.3	-32.5
LiH	47.9	52.6	43.2	38.5	33.3
N_2	225.6	221.8	3.0	6.8	0.0
NaCl	94.2	82.2	-39.8	-27.8	-43.6
NH	75.7	81.3	93.0	87.3	85.2
NH_2	170.6	177.5	56.0	49.1	45.1
NH_3	284.5	288.9	1.9	-2.5	-11.0
O_2	129.4	111.3	-8.8	9.2	0.0
MAE			**5.8**	**10.4**	
MAX			**12.9**	**18.0**	

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