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Extension of many-body theory and approximate density functionals to fractional charges and fractional spins

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The exact conditions for density functionals and density matrix functionals in terms of fractional charges and fractional spins are known, and their violation in commonly used functionals has been shown to be the root of many major failures in practical applications. However, approximate functionals are designed for physical systems with integer charges and spins, not in terms of the fractional variables. Here we develop a general framework for extending approximate density functionals and many-electron theory to fractional-charge and fractional-spin systems. Our development allows for the fractional extension of any approximate theory that is a functional of G^0, the one-electron Green's function of the non-interacting reference system. The extension to fractional charge and fractional spin systems is based on the ensemble average of the basic variable, G^0. We demonstrate the fractional extension for the following theories: (1) any explicit functional of the one-electron density, such as the local density approximation and generalized gradient approximations; (2) any explicit functional of the one-electron density matrix of the non-interacting reference system, such as the exact exchange functional (or Hartree-Fock theory) and hybrid functionals; (3) many-body perturbation theory; and (4) random-phase approximations. A general rule for such an extension has also been derived through scaling the orbitals and should be useful for functionals where the link to the Green's function is not obvious. The development thus enables the examination of approximate theories against known exact conditions on the fractional variables and the analysis of their failures in chemical and physical applications in terms of violations of exact conditions of the energy functionals. The present work should facilitate the calculation of chemical potentials and fundamental bandgaps with approximate functionals and many-electron theories through the energy derivatives with respect to the fractional charge. It should play an important role in developing accurate approximate density functionals and many-body theory. © *2013 AIP Publishing LLC.* [http://dx.doi.org/10.1063/1.4817183]

I. INTRODUCTION

Exact conditions for the ground-state energy of many-electron systems play a very important role in the development and understanding of approximate density functional and many body theories. Particularly relevant are the exact conditions for fractional charges[1] and fractional spins,[2,3] that have highlighted some key failures of approximate density functionals which are connected to major failures in chemical and physical applications[4] associated with the dissociation of molecular ions, polarizabilities, barrier heights, magnetic properties, fundamental bandgaps, and strongly correlated systems.

The main problem of density functional theory (DFT) to give accurate energy gaps in finite and bulk systems can be traced to the delocalization error, which is defined as the deviation of a given approximate functional from the exact linear behavior in fractional charges.[5] Consequently, most approximate functionals tend to over-delocalize the added electron or hole to give unphysically low energies for delocalized electrons. The consequences of the delocalization error can be seen not only in the prediction of derivative properties such as bandgaps and charge transfer excitations,[6] or

the energy of stretched molecular ions,[7] but also in thermochemistry and structures of molecules at equilibrium.[8,9] Progress has been made in designing functionals with reduced delocalization error.[10–14] Because of the delocalization error, currently, reliable bandgap prediction is dependent on the use of many-body Green's function theory, such as the GW approximation.[15]

Analogously, it has been proven[2] that fractional spins arise in systems with large static correlation energy (strongly correlated systems). Static correlation error of approximate functionals is defined as the deviation in the energy of fractional-spin states from the constancy condition defined by the energy of the comprising pure spin states. This leads to another set of different failures in DFT such as incorrect chemical bond dissociation or failure for the band structure prediction of Mott insulators.[2,3]

The simple physical picture of fractional charges and fractional spins comes from molecular dissociation.[16] For example, fractional-charge hydrogen atoms result from the dissociation of H_2^+,[7] and fractional-spin hydrogen atoms from the dissociation of H_2.[2] This is key as it makes possible the direct numerical verification for the fractional extensions of approximate theories: The fractional-charge or fractional-spin

calculations have to yield energies that agree with the limits of the corresponding molecular dissociation.[17]

For the extension of approximate functionals of the density or the first-order density matrix to fractional charges, $N + \delta$ ($0 < \delta < 1$), the ensemble average of the density[1] or the one-electron density matrix[16] can be used

$$\rho_1(N + \delta) = (1 - \delta)\rho_1(N) + \delta\rho_1(N + 1). \quad (1)$$

This leads to the use of fractional occupation of the orbitals, $\rho_1(\mathbf{r}, \mathbf{r}') = \sum_i n_i \phi_i(\mathbf{r})\phi_i(\mathbf{r}')$, which extends local density approximation (LDA), generalized gradient approximation (GGA) or Hartree-Fock method (HF) to fractional charges and fractional spins.[2,18,19]

These exact conditions for fractional charges and fractional spins are just as important for many-body theory based methods, where an extension to fractional occupations is still required. However, this generalization is not always a trivial question because the basic variable is no longer the density or the one-particle density matrix. Furthermore, the extension to fractional occupations does not correspond to a finite temperature formulation of the theory evaluated at T = 0. For Møller-Plesset theory (MP2) and the random phase approximation (RPA),[20–22] which depend on the unoccupied orbitals and eigenvalues, the basic variable is the one-electron Green's function, which now plays the same role as the one-electron density matrix for approximate density functionals. The fractional extensions have been made for the MP2[23] and for the random phase approximation,[24,25] but without rigorous derivation.

In this work, we will show that the basic variable is an ensemble average of the one-electron Green's function for the non-interacting systems. As it will be shown, this result agrees with Eq. (1) and allows the correct extension of many-body methods to fractional charges and fractional spins.

II. FRACTIONAL CHARGES AND FRACTIONAL SPINS BASED ON ONE-ELECTRON GREEN'S FUNCTIONS

There is a large class of approximate functionals or many-body theories, which can be cast as functionals of the one-electron Green's function of the non-interacting reference system. Because the electron density and the first-order density matrix for the non-interacting reference system is given by the one-electron Green's function, thus common functionals of the density or the one-electron density matrix are included.

The one-electron Green's function of an N-electron system in its ground state $|\Psi_0^N\rangle$ is defined as[20]

$$G^N(i, j; t - t') = -i\langle\Psi_0^N|T(a_i(t)a_j^\dagger(t'))|\Psi_0^N\rangle, \quad (2)$$

in terms of the time ordering operator T and the creation $a\dagger$ and annihilation a operators. Note that the index i includes spin. In terms of combined spatial and spin coordinates $\mathbf{x}$,

$$G^N(\mathbf{x}, \mathbf{x}'; t - t') = -i\langle\Psi_0^N|T(\hat{\psi}(\mathbf{x}, t)\hat{\psi}^\dagger(\mathbf{x}', t'))|\Psi_0^N\rangle$$
$$= \sum_{ij} G^N(i, j; t - t')\phi_i(\mathbf{x})\phi_j^*(\mathbf{x}'), \quad (3)$$

with the field operators,

$$\hat{\psi}(\mathbf{x}, t) = \sum_i \phi_i(\mathbf{x})a_i(t) \quad (4)$$

and

$$\hat{\psi}^\dagger(\mathbf{x}, t) = \sum_i \phi_i^*(\mathbf{x})a_i^\dagger(t), \quad (5)$$

expressed as linear combinations of creation and annihilation operators where the coefficients are the single particle spin orbitals $\{|\phi_i\rangle\}$ and the sums run over all possible single particle states.

The one-electron Green's function can also be expressed in terms of a complete set of eigenstates $\{|\Psi_m^{N+1}\rangle\}$ and eigenvalues $\{E_m^{N+1}\}$ of the system Hamiltonian:

$$G^N(i, j; t - t') = -i \left\{ \theta(t - t') \sum_m e^{i(E_0^N - E_m^{N+1})(t-t')}\langle\Psi_0^N|a_i|\Psi_m^{N+1}\rangle\langle\Psi_m^{N+1}|a_j^\dagger|\Psi_0^N\rangle \right.$$
$$\left. - \theta(t' - t) \sum_n e^{i(E_0^N - E_n^{N-1})(t'-t)}\langle\Psi_0^N|a_j^\dagger|\Psi_n^{N-1}\rangle\langle\Psi_n^{N-1}|a_i|\Psi_0^N\rangle \right\}, \quad (6)$$

which leads to the Lehmann representation in energy, given by the Fourier transform

$$G^N(i, j; E) = \int_{-\infty}^{+\infty} d(t - t')e^{iE(t-t')}G^N(i, j; t - t')$$
$$= \sum_m \frac{\langle\Psi_0^N|a_i|\Psi_m^{N+1}\rangle\langle\Psi_m^{N+1}|a_j^\dagger|\Psi_0^N\rangle}{E - (E_m^{N+1} - E_0^N) + i\eta}$$
$$+ \sum_n \frac{\langle\Psi_0^N|a_j^\dagger|\Psi_n^{N-1}\rangle\langle\Psi_n^{N-1}|a_i|\Psi_0^N\rangle}{E - (E_0^N - E_n^{N-1}) - i\eta}. \quad (7)$$

For a non-interacting system that is described by a normalized Slater determinant Φ_0^N with one-electron orbitals $\{|\phi_i\rangle\}$ and orbital energies $\{\varepsilon_i\}$, its single-particle Green's function is given by

$$G^{0,N}(i, j; t - t')$$
$$= -i\langle\Phi_0^N|T(a_i(t)a_j^\dagger(t'))|\Phi_0^N\rangle$$
$$= -i\delta_{ij}e^{-i\varepsilon_i(t-t')}\{\theta(t - t')\theta(i - F) - \theta(t' - t)\theta(F - i)\}, \quad (8)$$

where F is a number larger than the index for the highest occupied orbital but smaller than the index for the lowest unoccupied orbital. In coordinate and spin space

$$G^{0,N}(\mathbf{x}, \mathbf{x}'; t - t') = -i \langle \Phi_0^N | T(\hat{\psi}(\mathbf{x}, t) \hat{\psi}^\dagger(\mathbf{x}', t')) | \Phi_0^N \rangle \quad (9)$$

$$= \sum_{ij} G^{0,N}(i, j; t - t') \phi_i(\mathbf{x}) \phi_j^*(\mathbf{x}'). \quad (10)$$

In energy representation,

$$G^{0,N}(i, j; E) = \int_{-\infty}^{+\infty} d(t - t') e^{iE(t-t')} G^{0,N}(i, j; t - t') \quad (11)$$

$$= \delta_{ij} \left\{ \frac{\theta(i - F)}{E - \varepsilon_i + i\eta} + \frac{\theta(F - i)}{E - \varepsilon_i - i\eta} \right\}, \quad (12)$$

and

$$G^{0,N}(\mathbf{x}, \mathbf{x}'; E) = \sum_{ij} G^{0,N}(i, j; E) \phi_i(\mathbf{x}) \phi_j^*(\mathbf{x}')$$

$$= \sum_{i>F} \frac{1}{E - \varepsilon_i + i\eta} \phi_i(\mathbf{x}) \phi_i(\mathbf{x}')^*$$

$$+ \sum_{i<F} \frac{1}{E - \varepsilon_i - i\eta} \phi_i(\mathbf{x}) \phi_i(\mathbf{x}')^*$$

$$= \sum_a \frac{1}{E - \varepsilon_a + i\eta} \phi_a(\mathbf{x}) \phi_a(\mathbf{x}')^*$$

$$+ \sum_i \frac{1}{E - \varepsilon_i - i\eta} \phi_i(\mathbf{x}) \phi_i(\mathbf{x}')^*, \quad (13)$$

where a, b, c, d are particle indexes (unoccupied), i, j, k, l are hole indexes (occupied), and m, n, o, p are general indexes. Sometimes, i, j, k, l are used for general indexes, in specific cases as in Eq. (2).

To make the extension to fractional charge and fractional spin systems, we construct an ensemble of systems that are described with the *same* non-interacting reference Hamiltonian. For a fractionally charged system with $N + \delta$ electrons, where the spin character of the additional fractional charge δ is expressed through the orbital and its corresponding occupation number n_i, we define the single-particle Green's function as the following ensemble average:

$$G^{0,N+\delta}(i, j; t - t')$$
$$= (1 - \delta) G^{0,N}(i, j; t - t') + \delta G^{0,N+1}(i, j; t - t')$$
$$= -i \delta_{ij} e^{-i\varepsilon_i(t-t')} \{ \theta(t - t')(1 - n_i) - \theta(t' - t) n_i \} \quad (14)$$

or

$$G^{0,N+\delta}(i, j; E) = (1 - \delta) G^{0,N}(i, j; E) + \delta G^{0,N+1}(i, j; E)$$

$$= \delta_{ij} \left\{ \frac{(1 - n_i)}{E - \varepsilon_i + i\eta} + \frac{n_i}{E - \varepsilon_i - i\eta} \right\}, \quad (15)$$

where

$$\sum_i n_i = N + \delta. \quad (16)$$

In coordinate and spin space,

$$G^{0,N+\delta}(\mathbf{x}, \mathbf{x}'; E) = \sum_{ij} G^{0,N+\delta}(i, j; E) \phi_i(\mathbf{x}) \phi_j^*(\mathbf{x}')$$

$$= \sum_{i \geq F} \frac{(1 - n_i)}{E - \varepsilon_i + i\eta} \phi_i(\mathbf{x}) \phi_i(\mathbf{x}')^*$$

$$+ \sum_{i \leq F} \frac{n_i}{E - \varepsilon_i - i\eta} \phi_i(\mathbf{x}) \phi_i(\mathbf{x}')^*$$

$$= \sum_a \frac{1}{E - \varepsilon_a + i\eta} \tilde{\phi}_a(\mathbf{x}) \tilde{\phi}_a(\mathbf{x}')^*$$

$$+ \sum_i \frac{1}{E - \varepsilon_i - i\eta} \tilde{\phi}_i(\mathbf{x}) \tilde{\phi}_i(\mathbf{x}')^*. \quad (17)$$

Fractional occupations occur only at the frontier levels, because we require the non-interacting ground state representation of an interacting system.

We have *extended* the index a for unoccupied orbital (particle) to include fractionally unoccupied states, and index i for occupied states (hole) to include fractionally occupied states. We also introduce the occupation-scaled unoccupied orbitals

$$\tilde{\phi}_a(\mathbf{x}_1) = \sqrt{1 - n_a} \phi_a(\mathbf{x}_1) \quad (18)$$

and the occupation-scaled occupied orbitals

$$\tilde{\phi}_i(\mathbf{x}_2) = \sqrt{n_i} \phi_i(\mathbf{x}_2). \quad (19)$$

Our extension allows the direct incorporation of fractional charges and spins into many-body theories based on Green's functions.

The expression $G^{0,N+\delta}(\mathbf{x}, \mathbf{x}'; E)$ Eq. (17), is the key result, which underlies *a simple rule* for extending approximate density functionals and many-body theories to fractional charges and fractional spins: Notice that $G^{0,N+\delta}(\mathbf{x}, \mathbf{x}'; E)$ has the same form as $G^{0,N}(\mathbf{x}, \mathbf{x}'; E)$, except that (i) the parent orbitals need to be replaced by the occupation-scaled orbitals, (ii) the set of occupied orbitals includes fractionally occupied ones, and (iii) the set of unoccupied orbitals includes the fractionally unoccupied ones. Thus, fractional orbitals enter into both sets: as fractionally occupied, and as fractionally unoccupied.

Because the fractional orbitals enter into the formalism as fractional hole/occupied orbital and also as fractional particle/unoccupied orbital, the matrix representation for $G^{0,N+\delta}(i, j; E)$ can be written in the extended matrix of $(n_o + n_f + n_f + n_u)$, where n_o is the number of (fully) occupied orbitals, n_f is the number of fractional orbitals, and n_u is the number of fully unoccupied orbitals. $G^{0,N+\delta}(i, j; E)$ is a diagonal matrix with four blocks of states: occupied states of the size n_o, fractional occupied state of the size n_f, fractional unoccupied states of the size n_f, and unoccupied states of the size n_u. The structure is

$$\mathbf{G}^{0,N+\delta} = \begin{pmatrix} \frac{1}{E-\varepsilon_i-i\eta} & & & \\ & \frac{n_i}{E-\varepsilon_i-i\eta} & & \\ & & \frac{(1-n_i)}{E-\varepsilon_i+i\eta} & \\ & & & \frac{1}{E-\varepsilon_i+i\eta} \end{pmatrix}. \quad (20)$$

Note that in Eq. (20), the Green's function has been unfolded into a matrix with the dimension of $(n_o + n_f + n_f + n_u)$, larger than $(n_o + n_f + n_u)$, which is the dimension of all one-electron states. In this way, the matrix elements in orbital space in Eq. (20) are different from those in Eq. (15), but they have the same real-space representation of Eq. (17).

In the following, we apply the fractional extension $G^{0, N+\delta}$ in various approximations and work out the details applied to various types of approximate functionals in many-body theory. Remarkably, in all the cases the simple extension rule applies.

III. HARTREE FOCK AND PERTURBATION THEORY

A. The density and density matrix from one-particle Green's functions

The non-interacting one-electron density matrix, corresponding the hole part in the many-body language, is given by

$$
\begin{aligned}
\rho_s(i, j) &= \int_{-\infty}^{+\infty} \frac{dE}{2\pi i} e^{iE\eta} G^{0, N+\delta}(i, j; E) \\
&= \int_{C\uparrow} \frac{dE}{2\pi i} G^{0, N+\delta}(i, j; E) \\
&= -i G^{0, N+\delta}(i, j; t, t^+) \\
&= \delta_{ij} n_i,
\end{aligned}
\tag{21}
$$

where the integration along the path $C\uparrow$ is the integration from $-\infty$ to $+\infty$ and closed on the negative side of the complex E plane. Analogously the non-interacting particle matrix of many body-theory (the virtual state density) is

$$
\begin{aligned}
\bar{\rho}_s(i, j) &= \int_{-\infty}^{+\infty} \frac{dE}{2\pi i} e^{-iE\eta} G^{0, N+\delta}(i, j; E) \\
&= i G^{0, N+\delta}(i, j; t^+ - t) \\
&= \delta_{ij}(1 - n_i).
\end{aligned}
\tag{22}
$$

In coordinate and spin space

$$
\begin{aligned}
\rho_s(\mathbf{x}, \mathbf{x}') &= \sum_{ij} \rho_s(i, j) \phi_i(\mathbf{x}) \phi_j^*(\mathbf{x}') \\
&= -i G^{0, N+\delta}(\mathbf{x}, \mathbf{x}'; t, t^+) \\
&= \sum_i n_i \phi_i(\mathbf{x}) \phi_i^*(\mathbf{x}'),
\end{aligned}
\tag{23}
$$

and

$$
\begin{aligned}
\bar{\rho}_s(\mathbf{x}, \mathbf{x}') &= \sum_{ij} \bar{\rho}_{i, j} \phi_i(\mathbf{x}) \phi_j^*(\mathbf{x}') \\
&= \sum_i (1 - n_i) \phi_i(\mathbf{x}) \phi_i^*(\mathbf{x}'),
\end{aligned}
\tag{24}
$$

such that

$$
\rho_s(\mathbf{x}, \mathbf{x}') + \bar{\rho}_s(\mathbf{x}, \mathbf{x}') = \delta(\mathbf{x} - \mathbf{x}').
\tag{25}
$$

The electron density can thus be expressed in terms of the occupation numbers as

$$
\rho(\mathbf{x}) = \sum_i n_i \phi_i(\mathbf{x}) \phi_i^*(\mathbf{x}).
\tag{26}
$$

This equation is consistent with previous work[2,3,18] for any functional of $\rho(\mathbf{x})$ or $\rho_s(\mathbf{x}, \mathbf{x}')$ such as LDA, GGA or HF. Here and hereafter, we suppress the superscripts "$N + \delta$" for the density and particle matrix for the non-interacting fractional reference systems, when the fractional context is unambiguous.

B. Perturbation theory based on one-particle Green's functions

We will derive energy functionals of $G^{0, N+\delta}$ within the perturbation theory. The many-electron Hamiltonian is given by

$$
H = \sum_i \left(-\frac{1}{2} \nabla_i^2 + v_{ext}(\mathbf{r}_i) \right) + \sum_{i \neq j} v(r_{ij}),
\tag{27}
$$

or equivalently in Fock space,

$$
\begin{aligned}
H &= \sum_{ij} h_{ij} a_i^\dagger a_j + \frac{1}{2} \sum_{ijkl} \langle ij|kl \rangle a_i^\dagger a_j^\dagger a_l a_k \\
&= \sum_{ij} h_{ij} a_i^\dagger a_j + \frac{1}{4} \sum_{ijkl} \langle ij||kl \rangle a_i^\dagger a_j^\dagger a_l a_k,
\end{aligned}
\tag{28}
$$

where

$$
h_{ij} = \langle \phi_i | -\frac{1}{2} \nabla^2 + v_{ext}(\mathbf{r}) | \phi_j \rangle = \langle i | -\frac{1}{2} \nabla^2 + v_{ext}(\mathbf{r}) | j \rangle,
\tag{29}
$$

and

$$
\langle ij|kl \rangle = \iint d\mathbf{x}_1 d\mathbf{x}_2 \phi_i^*(\mathbf{x}_1) \phi_j^*(\mathbf{x}_2) v(r_{12}) \phi_k(\mathbf{x}_1) \phi_l(\mathbf{x}_2),
\tag{30}
$$

$$
\langle ij||kl \rangle = \langle ij|kl \rangle - \langle ij|lk \rangle.
\tag{31}
$$

Consider a non-interacting reference system which can have a local or non-local potential $v_s = v_{ext} + u$, of the form $v_s(\mathbf{x})$ or $v_s(\mathbf{x}, \mathbf{x}')$ respectively, as determined by the nature of u,

$$
\left(-\frac{1}{2} \nabla^2 + v_{ext} + u \right) | \phi_i \rangle = \varepsilon_i | \phi_i \rangle.
\tag{32}
$$

The equation for the Green's function of the physical interacting system is

$$
[E - (h + u + \Sigma^*)] G(E) = I
\tag{33}
$$

and the corresponding Dyson equation

$$
G(E) = G^0(E) + G^0(E) \Sigma^*(E) G(E).
\tag{34}
$$

The irreducible self-energy $\Sigma^*(E)$, expanded up to second-order perturbation in the electron-electron interaction,[26] is given by

$$
\Sigma^*(k, l, E) = -\langle k|u|l \rangle + \lambda \Sigma^{*(1)}(k, l, E) + \lambda^2 \Sigma^{*(2)}(k, l, E),
\tag{35}
$$

where λ is the order parameter representing the electron-electron interaction, and the first- and second-order contributions are

$$\Sigma^{*(1)}(i, j, E) = \int_{C\uparrow} \frac{dE'}{2\pi i} \sum_{kl} \langle ik||jl\rangle G^0(l, k; E') \tag{36}$$

$$= \sum_{kl} \langle ik||jl\rangle \rho_s(l, k)$$

$$= \sum_{k} \langle ik||jk\rangle n_k$$

$$= J_{ij} - K_{ij}, \tag{37}$$

and

$$\Sigma^{*(2)}(i, j, E) = -\frac{1}{2} \int_{-\infty}^{+\infty} \frac{dE_1}{2\pi i} \int_{-\infty}^{+\infty} \frac{dE_2}{2\pi i}$$

$$\sum_{klm} \sum_{npq} \langle ik||lm\rangle \langle np||jq\rangle G^0(l, n; E_1) G^0(m, p; E_2) G^0(q, k; E_1 + E_2 - E)$$

$$= \frac{1}{2} \sum_{lmq} \langle iq||lm\rangle \langle lm||jq\rangle \left\{ \frac{(1 - n_l)(1 - n_m)n_q}{E - \varepsilon_l - \varepsilon_m + \varepsilon_q + i\eta} + \frac{n_l n_m (1 - n_q)}{E - \varepsilon_l - \varepsilon_m + \varepsilon_q - i\eta} \right\}. \tag{38}$$

For the details of the integration leading to Eq. (38), see Subsection 2 of the Appendix.

Now we introduce the Hamiltonian $H(\lambda)$ as a function of the coupling parameter λ,

$$H(\lambda) = H_0 + \lambda H_1, \tag{39}$$

where

$$H_0 = \sum_{ij} (h_{ij} + u_{ij}) a_i^\dagger a_j$$

$$= \sum_{i} \varepsilon_i a_i^\dagger a_i, \tag{40}$$

and

$$H_1 = \frac{1}{2} \sum_{ijkl} \langle ij|kl\rangle a_i^\dagger a_j^\dagger a_l a_k - \sum_{ij} u_{ij} a_i^\dagger a_j \tag{41}$$

Thus, $H(0) = H_0, H(1) = H_0 + H_1 = H$. Then the total energy as a function of λ is

$$E(\lambda) = \langle \Psi_0^N(\lambda) | H(\lambda) | \Psi_0^N(\lambda) \rangle, \tag{42}$$

and its derivative is

$$\frac{dE(\lambda)}{d\lambda} = \langle \Psi_0^N(\lambda) | H_1 | \Psi_0^N(\lambda) \rangle. \tag{43}$$

The total energy $E(1)$ for the physical system is given by

$$E(1) - E(0)$$

$$= \int_0^1 d\lambda \langle \Psi_0^N(\lambda) | H_1 | \Psi_0^N(\lambda) \rangle$$

$$= \int_0^1 d\lambda \left\{ -\sum_{ij} u_{ij} \langle \Psi_0^N(\lambda) | a_i^\dagger a_j | \Psi_0^N(\lambda) \rangle \right.$$

$$\left. + \frac{1}{2} \sum_{ijkl} \langle ij|kl\rangle \langle \Psi_0^N(\lambda) | a_i^\dagger a_j^\dagger a_l a_k | \Psi_0^N(\lambda) \rangle \right\}, \tag{44}$$

where we suppress the index of λ in a_i. This equation will lead to various useful expressions of the total energy in terms of Green's functions, $\mathbf{G}^0(E)$ and $\mathbf{G}(E)$, and the self-energies.

Using the equation of motion, we obtain, with details given in Subsection 3 of the Appendix, $E(1)$ in terms of $\mathbf{G}^\lambda(E)$ and the irreducible self-energy $\mathbf{\Sigma}^{*\lambda}(E)$,

$$E(1) - E(0)$$

$$= \frac{1}{2} \int_0^1 d\lambda \int_{-\infty}^{+\infty} \frac{dE}{2\pi i} e^{iE\eta} \mathrm{Tr} \left(-\mathbf{u} + \frac{1}{\lambda} \mathbf{\Sigma}^{*\lambda}(E) \right) \mathbf{G}^\lambda(E). \tag{45}$$

Using the Dyson equation

$$\mathbf{G}^\lambda(E) = \mathbf{G}^0(E) + \mathbf{G}^0(E) \mathbf{\Sigma}^\lambda(E) \mathbf{G}^0(E), \tag{46}$$

in terms of the reducible self-energy $\mathbf{\Sigma}^\lambda(E)$,

$$\mathbf{\Sigma}^\lambda(E) = \mathbf{\Sigma}^{*\lambda}(E) + \mathbf{\Sigma}^\lambda(E) \mathbf{G}^0(E) \mathbf{\Sigma}^{*\lambda}(E)$$

$$= \mathbf{\Sigma}^{*\lambda}(E) + \mathbf{\Sigma}^{*\lambda}(E) \mathbf{G}^0(E) \mathbf{\Sigma}^\lambda(E), \tag{47}$$

we obtain $E(1)$ in terms of the reducible self-energy $\boldsymbol{\Sigma}^\lambda(E)$ and $\mathbf{G}^0(E)$,

$$
E(1) - E(0) = \frac{1}{2}\int_0^1 d\lambda \int_{-\infty}^{+\infty} \frac{dE}{2\pi i} e^{iE\eta} \mathrm{Tr}\Big[-\mathbf{u}(\mathbf{G}^0(E)
$$
$$
+ \mathbf{G}^0(E)\boldsymbol{\Sigma}^\lambda(E)\mathbf{G}^0(E)) + \frac{1}{\lambda}\boldsymbol{\Sigma}^\lambda(E)\mathbf{G}^0(E)\Big]
\tag{48}
$$

We now use Eq. (47) and express $\boldsymbol{\Sigma}^\lambda(E)$ in terms of the irreducible self-energy $\boldsymbol{\Sigma}^{*\lambda}(E)$ and $\mathbf{G}^0(E)$,

$$
\boldsymbol{\Sigma}^\lambda(E) = \boldsymbol{\Sigma}^{*\lambda}(E)\big[1 - \mathbf{G}^0(E)\boldsymbol{\Sigma}^{*\lambda}(E)\big]^{-1},
\tag{49}
$$

which can be used to obtain the perturbation expansion for $\boldsymbol{\Sigma}^\lambda(E)$ to input into Eq. (48) to obtain the total energy. In addition, from Eq. (45), and using $(\mathbf{G}^\lambda(E))^{-1} = (\mathbf{G}^0(E))^{-1} - \boldsymbol{\Sigma}^{*\lambda}(E)$, we have

$$
E(1) - E(0) = \frac{1}{2}\int_0^1 d\lambda \int_{-\infty}^{+\infty} \frac{dE}{2\pi i} e^{iE\eta} \mathrm{Tr}\left(-\mathbf{u} + \frac{1}{\lambda}\boldsymbol{\Sigma}^{*\lambda}(E)\right)
$$
$$
\times \left((\mathbf{G}^0(E))^{-1} - \boldsymbol{\Sigma}^{*\lambda}(E)\right)^{-1},
\tag{50}
$$

which expresses the total energy directly in terms of the irreducible self-energy $\boldsymbol{\Sigma}^*(E)$ and $\mathbf{G}^0(E)$.

To second order, using Eq. (35) in Eq. (47),

$$
\boldsymbol{\Sigma}^\lambda(E) = [-\lambda\mathbf{u} + \lambda\boldsymbol{\Sigma}^{*(1)}(E) + \lambda^2\boldsymbol{\Sigma}^{*(2)}(E)]
$$
$$
+ [-\lambda\mathbf{u} + \lambda\boldsymbol{\Sigma}^{*(1)}(E) + \lambda^2\boldsymbol{\Sigma}^{*(2)}(E)]\mathbf{G}^o(E)
$$
$$
\times [-\lambda\mathbf{u} + \lambda\boldsymbol{\Sigma}^{*(1)}(E) + \lambda^2\boldsymbol{\Sigma}^{*(2)}(E)] + \cdots
$$
$$
= [-\lambda\mathbf{u} + \lambda\boldsymbol{\Sigma}^{*(1)}(E) + \lambda^2\boldsymbol{\Sigma}^{*(2)}(E)]
$$
$$
+ [-\lambda\mathbf{u} + \lambda\boldsymbol{\Sigma}^{*(1)}(E)]\mathbf{G}^o(E)
$$
$$
\times [-\lambda\mathbf{u} + \lambda\boldsymbol{\Sigma}^{*(1)}(E)] + \cdots
$$
$$
= \lambda[-\mathbf{u} + \boldsymbol{\Sigma}^{*(1)}(E)] + \lambda^2\{\boldsymbol{\Sigma}^{*(2)}(E)
$$
$$
+ [-\mathbf{u} + \boldsymbol{\Sigma}^{*(1)}(E)]\mathbf{G}^o(E)[-\mathbf{u} + \boldsymbol{\Sigma}^{*(1)}(E)]\} + \cdots,
\tag{51}
$$

which will be used to derive the perturbation energy functional.

1. Perturbation energy up to the first order

We now consider Eq. (51) up to first order, $\boldsymbol{\Sigma}^\lambda(E) = \lambda[-\mathbf{u} + \boldsymbol{\Sigma}^{*(1)}(E)]$. Then, collecting the terms of order λ^0

in the integrand of Eq. (48) gives

$$
E^{(1)} = E(0) + \frac{1}{2}\int_0^1 \frac{d\lambda}{\lambda}\int_{-\infty}^{+\infty} \frac{dE}{2\pi i} e^{iE\eta}
$$
$$
\times \mathrm{Tr}\{\lambda[-2\mathbf{u} + \boldsymbol{\Sigma}^{*(1)}(E)]\mathbf{G}^0(E)\}
$$
$$
= \sum_i (h_{ii} + u_{ij})n_i + \left[-\sum_i u_{ii}n_i + \frac{1}{2}\sum_k \langle ik||ik\rangle n_k n_i\right]
$$
$$
= \sum_i h_{ii}n_i + \frac{1}{2}\sum_{ki} \langle ik||ik\rangle n_k n_i,
\tag{52}
$$

which is just the Hartree-Fock energy functional for fractional systems.

2. Perturbation energy up to the second order

Consider Eq. (51) up to second order and collect the terms of order λ^1 in the integrand of Eq. (48), then

$$
E^{(2)} = \frac{1}{2}\int_0^1 d\lambda \int_{-\infty}^{+\infty} \frac{dE}{2\pi i} e^{iE\eta}
$$
$$
\times \mathrm{Tr}\{-\mathbf{u}(\mathbf{G}^0(E)(\lambda[-\mathbf{u} + \boldsymbol{\Sigma}^{*(1)}(E)])\mathbf{G}^0(E))
$$
$$
+ \frac{1}{\lambda}\lambda^2(\boldsymbol{\Sigma}^{*(2)}(E) + [-\mathbf{u} + \boldsymbol{\Sigma}^{*(1)}(E)]\mathbf{G}^o(E)[-\mathbf{u}
$$
$$
+ \boldsymbol{\Sigma}^{*(1)}(E)])\mathbf{G}^0(E)\}
$$
$$
= \frac{1}{4}\int_{-\infty}^{+\infty} \frac{dE}{2\pi i} e^{iE\eta}\mathrm{Tr}\{\boldsymbol{\Sigma}^{*(2)}(E)\mathbf{G}^0(E)
$$
$$
+ [-2\mathbf{u} + \boldsymbol{\Sigma}^{*(1)}(E)]\mathbf{G}^o(E)[-\mathbf{u} + \boldsymbol{\Sigma}^{*(1)}(E)]\mathbf{G}^0(E)\}.
\tag{53}
$$

Using Eq. (A20),

$$
\frac{1}{4}\int_{-\infty}^{+\infty} \frac{dE}{2\pi i} e^{iE\eta}\mathrm{Tr}\{\boldsymbol{\Sigma}^{*(2)}(E)\mathbf{G}^0(E)\}
$$
$$
= \frac{1}{4}\sum_{ilmq} \langle iq||lm\rangle\langle lm||iq\rangle \frac{(1-n_l)(1-n_m)n_q n_i}{\varepsilon_i + \varepsilon_q - \varepsilon_l - \varepsilon_m}.
$$

With HF orbitals where $-\mathbf{u} + \boldsymbol{\Sigma}^{*(1)}(E) = 0$, the second order energy is given by

$$
E^{(2)} = \frac{1}{4}\sum_{ilmq} \langle iq||lm\rangle\langle lm||iq\rangle \frac{(1-n_l)(1-n_m)n_q n_i}{\varepsilon_i + \varepsilon_q - \varepsilon_l - \varepsilon_m},
\tag{54}
$$

which is the fractional extension of the MP2 energy used previously.[23] We attributed initially this fractional extension to the finite-temperature extension of second-order perturbation theory,[27] with the fractional occupations from finite temperature excitations. For a recent discussion on the finite-temperature MP2 theory, see Ref. 28. However, the current derivation has been developed for systems with fractional charges and spins at zero temperature.

Straightforwardly, we can obtain the derivatives with respect to the occupation numbers of the MP2 second

order energy

$$\frac{\partial E^{(2)}}{\partial n_i} = \frac{1}{4}\sum_{lmj}\langle ij||lm\rangle\langle lm||ij\rangle 2\frac{(1-n_l)(1-n_m)n_j}{\varepsilon_i+\varepsilon_j-\varepsilon_l-\varepsilon_m} - \frac{1}{4}\sum_{jkm}\langle jk||im\rangle\langle lm||im\rangle 2\frac{(1-n_m)n_jn_k}{\varepsilon_j+\varepsilon_k-\varepsilon_i-\varepsilon_m}$$

$$= \frac{1}{2}\sum_{lmq}\langle iq||lm\rangle\langle lm||iq\rangle\left\{\frac{(1-n_l)(1-n_m)n_q}{\varepsilon_i-\varepsilon_l-\varepsilon_m+\varepsilon_q}+\frac{n_ln_m(1-n_q)}{\varepsilon_i-\varepsilon_l-\varepsilon_m+\varepsilon_q}\right\}$$

$$= \Sigma^{*(2)}(i,i,\varepsilon_i), \tag{55}$$

where $-\mathbf{u}+\boldsymbol{\Sigma}^{*(1)}(E)=0$ has again been used. These derivatives have previously been used to calculate the MP2 gap of some atoms and molecules.[23]

IV. POLARIZATION PROPAGATORS AND RANDOM PHASE APPROXIMATIONS

Moving forward, we consider partial summation of perturbation theory based on the random phase approximation. The particle-hole two-particle Green's function is defined as

$$G_{ph}(\mathbf{x}_1,\mathbf{x}_2,t_1-t_2) = -i\big\langle\Psi_0^N\big|T(\hat{\psi}^\dagger(1)\hat{\psi}(1)\hat{\psi}^\dagger(2)\hat{\psi}(2))\big|\Psi_0^N\big\rangle$$

$$= -i\big\langle\Psi_0^N\big|T(\hat{\rho}(1)\hat{\rho}(2))\big|\Psi_0^N\big\rangle$$

$$= -i\big\{\theta(t_1-t_2)\big\langle\Psi_0^N\big|\hat{\rho}(1)\hat{\rho}(2)\big|\Psi_0^N\big\rangle + \theta(t_2-t_1)\big\langle\Psi_0^N\big|\hat{\rho}(2)\hat{\rho}(1)\big|\Psi_0^N\big\rangle\big\}$$

$$= -i\left\{\theta(t_1-t_2)\sum_n e^{i\left(E_0^N-E_n^N\right)(t_1-t_2)}\big\langle\Psi_0^N\big|\hat{\rho}(\mathbf{x}_1)\big|\Psi_n^N\big\rangle\big\langle\Psi_n^N\big|\hat{\rho}(\mathbf{x}_2)\big|\Psi_0^N\big\rangle\right.$$

$$\left.+\theta(t_2-t_1)\sum_n e^{i\left(E_0^N-E_n^N\right)(t_2-t_1)}\big\langle\Psi_0^N\big|\hat{\rho}(\mathbf{x}_2)\big|\Psi_n^N\big\rangle\big\langle\Psi_n^N\big|\hat{\rho}(\mathbf{x}_1)\big|\Psi_0^N\big\rangle\right\}. \tag{56}$$

The Lehmann representation in energy is given by

$$G_{ph}(\mathbf{x}_1,\mathbf{x}_2,E) = \int_{-\infty}^{+\infty} d(t_1-t_2)e^{iE(t_1-t_2)}G_{ph}(\mathbf{x}_1,\mathbf{x}_2,t_1-t_2)$$

$$= \sum_n\frac{\big\langle\Psi_0^N\big|\hat{\rho}(\mathbf{x}_1)\big|\Psi_n^N\big\rangle\big\langle\Psi_n^N\big|\hat{\rho}(\mathbf{x}_2)\big|\Psi_0^N\big\rangle}{E-\left(E_n^N-E_0^N\right)+i\eta} - \sum_n\frac{\big\langle\Psi_0^N\big|\hat{\rho}(\mathbf{x}_2)\big|\Psi_n^N\big\rangle\big\langle\Psi_n^N\big|\hat{\rho}(\mathbf{x}_1)\big|\Psi_0^N\big\rangle}{E-\left(E_0^N-E_n^N\right)-i\eta}. \tag{57}$$

Considering the density operator in terms of the field operators

$$\hat{\rho}(\mathbf{x}_1) = \hat{\psi}^\dagger(1)\hat{\psi}(1)$$

$$= \sum_j\phi_j^*(\mathbf{x}_1)a_j^\dagger(t_1)\sum_i\phi_i(\mathbf{x}_1)a_i(t_1)$$

leads to the diagonal elements

$$G_{ph}(\mathbf{x}_1,\mathbf{x}_2;t_1-t_2) = \sum_{ijkl}\phi_j^*(\mathbf{x}_1)\phi_i(\mathbf{x}_1)\phi_k^*(\mathbf{x}_2)\phi_l(\mathbf{x}_2)G_{ph}(i,j;k,l;t_1-t_2), \tag{58}$$

and

$$G_{ph}(\mathbf{x}_1,\mathbf{x}_2;E) = \sum_{ijkl}\phi_j^*(\mathbf{x}_1)\phi_i(\mathbf{x}_1)\phi_k^*(\mathbf{x}_2)\phi_l(\mathbf{x}_2)G_{ph}(i,j;k,l;E), \tag{59}$$

where we have used the four-point Green's function

$$G_{ph}(i, j; k, l; t_1 - t_2) = -i\langle\Psi_0^N|T(a_j^\dagger(t_1)a_i(t_1)a_k^\dagger(t_2)a_l(t_2))|\Psi_0^N\rangle$$

$$= -i\Big\{\theta(t_1 - t_2)\sum_n e^{i\left(E_0^N - E_n^N\right)(t_1 - t_2)}\langle\Psi_0^N|a_j^\dagger a_i|\Psi_n^N\rangle\langle\Psi_n^N|a_k^\dagger a_l|\Psi_0^N\rangle$$

$$+ \theta(t_2 - t_1)\sum_n e^{i\left(E_0^N - E_n^N\right)(t_2 - t_1)}\langle\Psi_0^N|a_k^\dagger a_l|\Psi_n^N\rangle\langle\Psi_n^N|a_j^\dagger a_i|\Psi_0^N\rangle\Big\}. \tag{60}$$

Thus,

$$G_{ph}(i, j; k, l; E) = \sum_n \frac{\langle\Psi_0^N|a_j^\dagger a_i|\Psi_n^N\rangle\langle\Psi_n^N|a_k^\dagger a_l|\Psi_0^N\rangle}{E - \left(E_n^N - E_0^N\right) + i\eta} - \sum_n \frac{\langle\Psi_0^N|a_k^\dagger a_l|\Psi_n^N\rangle\langle\Psi_n^N|a_j^\dagger a_i|\Psi_0^N\rangle}{E - \left(E_0^N - E_n^N\right) - i\eta}. \tag{61}$$

Similarly the polarization propagator in the spin and coordinate space is defined as

$$\Pi(\mathbf{x}_1, \mathbf{x}_2; t_1 - t_2) = -i\{\langle\Psi_0^N|T(\hat\rho(1)\hat\rho(2))|\Psi_0^N\rangle - \langle\Psi_0^N|\hat\rho(1)|\Psi_0^N\rangle\langle\Psi_0^N|\hat\rho(2)|\Psi_0^N\rangle\}$$

$$= -i\Big\{\theta(t_1 - t_2)\sum_{n\neq 0} e^{i\left(E_0^N - E_n^N\right)(t_1 - t_2)}\langle\Psi_0^N|\hat\rho(\mathbf{x}_1)|\Psi_n^N\rangle\langle\Psi_n^N|\hat\rho(\mathbf{x}_2)|\Psi_0^N\rangle$$

$$+ \theta(t_2 - t_1)\sum_{n\neq 0} e^{i\left(E_0^N - E_n^N\right)(t_2 - t_1)}\langle\Psi_0^N|\hat\rho(\mathbf{x}_2)|\Psi_n^N\rangle\langle\Psi_n^N|\hat\rho(\mathbf{x}_1)|\Psi_0^N\rangle\Big\}, \tag{62}$$

or

$$\Pi(\mathbf{x}_1, \mathbf{x}_2; E) = \sum_{n\neq 0} \frac{\langle\Psi_0^N|\hat\rho(\mathbf{x}_1)|\Psi_n^N\rangle\langle\Psi_n^N|\hat\rho(\mathbf{x}_2)|\Psi_0^N\rangle}{E - \left(E_n^N - E_0^N\right) + i\eta} - \sum_{n\neq 0} \frac{\langle\Psi_0^N|\hat\rho(\mathbf{x}_2)|\Psi_n^N\rangle\langle\Psi_n^N|\hat\rho(\mathbf{x}_1)|\Psi_0^N\rangle}{E - \left(E_0^N - E_n^N\right) - i\eta}. \tag{63}$$

The four-point polarization propagators are

$$\Pi(i, j; k, l; t_1 - t_2) = -i\{\langle\Psi_0^N|T(a_j^\dagger(t_1)a_i(t_1)a_k^\dagger(t_2)a_l(t_2))|\Psi_0^N\rangle - \langle\Psi_0^N|a_j^\dagger a_i|\Psi_0^N\rangle\langle\Psi_0^N|a_k^\dagger a_l|\Psi_0^N\rangle\}$$

$$= -i\Big\{\theta(t_1 - t_2)\sum_n e^{i\left(E_0^N - E_n^N\right)(t_1 - t_2)}\langle\Psi_0^N|a_j^\dagger a_i|\Psi_n^N\rangle\langle\Psi_n^N|a_k^\dagger a_l|\Psi_0^N\rangle$$

$$+ \theta(t_2 - t_1)\sum_n e^{i\left(E_0^N - E_n^N\right)(t_2 - t_1)}\langle\Psi_0^N|a_k^\dagger a_l|\Psi_n^N\rangle\langle\Psi_n^N|a_j^\dagger a_i|\Psi_0^N\rangle\Big\}$$

$$- \langle\Psi_0^N|a_j^\dagger a_i|\Psi_0^N\rangle\langle\Psi_0^N|a_k^\dagger a_l|\Psi_0^N\rangle$$

$$= G_{ph}(j, i; k, l; t_1 - t_2) - \langle\Psi_0^N|a_j^\dagger a_i|\Psi_0^N\rangle\langle\Psi_0^N|a_k^\dagger a_l|\Psi_0^N\rangle, \tag{64}$$

or

$$\Pi(i, j; k, l; E) = \sum_{n\neq 0} \frac{\langle\Psi_0^N|a_j^\dagger a_i|\Psi_n^N\rangle\langle\Psi_n^N|a_k^\dagger a_l|\Psi_0^N\rangle}{E - \left(E_n^N - E_0^N\right) + i\eta} - \sum_{n\neq 0} \frac{\langle\Psi_0^N|a_k^\dagger a_l|\Psi_n^N\rangle\langle\Psi_n^N|a_j^\dagger a_i|\Psi_0^N\rangle}{E - \left(E_0^N - E_n^N\right) - i\eta}$$

$$= G_{ph}(i, j; k, l; E) - 2\pi\delta(E)\langle\Psi_0^N|a_j^\dagger a_i|\Psi_0^N\rangle\langle\Psi_0^N|a_k^\dagger a_l|\Psi_0^N\rangle. \tag{65}$$

In coordinate and spin representation $\mathbf{x}_1$, the diagonal elements are

$$\Pi(\mathbf{x}_1, \mathbf{x}_2; t_1 - t_2) = \sum_{ijkl} \phi_j^*(\mathbf{x}_1)\phi_i(\mathbf{x}_1)\phi_k^*(\mathbf{x}_2)\phi_l(\mathbf{x}_2)\Pi(i, j; k, l; t_1 - t_2), \tag{66}$$

and

$$\Pi(\mathbf{x}_1, \mathbf{x}_2; E) = \sum_{ijkl} \phi_j^*(\mathbf{x}_1)\phi_i(\mathbf{x}_1)\phi_k^*(\mathbf{x}_2)\phi_l(\mathbf{x}_2)\Pi(i, j; k, l; E). \tag{67}$$

The polarization propagator describes the dynamic density-density fluctuation, which can be approximated in the random phase approximation and leads to an approximate ground state correlation energy.

A. Non-interacting systems

The non-interacting propagator can be evaluated from Eqs. (64) and (65), or it is given by[26]

$$
\begin{aligned}
\Pi^0&(i, j; k, l; t_1 - t_2) \\
&= -i G^0(i, k; t_1 - t_2) G^0(l, j; t_2 - t_1) \\
&= -i(-i)\delta_{ik} e^{-i\varepsilon_i(t_1 - t_2)} \{\theta(t_1 - t_2)\theta(i - F) \\
&\quad - \theta(t_2 - t_1)\theta(F - i)\} \\
&\quad (-i)\delta_{jl} e^{-i\varepsilon_j(t_2 - t_1)} \{\theta(t_2 - t_1)\theta(j - F) \\
&\quad - \theta(t_1 - t_2)\theta(F - j)\} \\
&= -i\delta_{ik}\delta_{jl} e^{i(\varepsilon_j - \varepsilon_i)(t_1 - t_2)} \{\theta(t_1 - t_2)\theta(i - F)\theta(F - j) \\
&\quad + \theta(t_2 - t_1)\theta(F - i)\theta(j - F)\},
\end{aligned}
\tag{68}
$$

and

$$
\begin{aligned}
\Pi^0&(i, j; k, l; E) \\
&= \int_{-\infty}^{+\infty} \frac{dE'}{2\pi i} G^0(i, k; E + E') G^0(l, j; E') \\
&= \delta_{ik}\delta_{jl} \left\{ \frac{\theta(F - j)\theta(i - F)}{E - (\varepsilon_i - \varepsilon_j) + i\eta} - \frac{\theta(F - i)\theta(j - F)}{E + (\varepsilon_j - \varepsilon_i) - i\eta} \right\}.
\end{aligned}
\tag{69}
$$

B. Non-interacting systems with fractional charge and fractional spin

Using the key equations, Eqs. (14) and (15), and following the same relationship as the integer cases in Sec. IV A, we obtain the propagator for fractional systems,

$$
\begin{aligned}
\Pi^{0,N+\delta}&(i, j; k, l; t_1 - t_2) \\
&= -i G^{0,N+\delta}(i, k; t_1 - t_2) G^{0,N+\delta}(l, j; t_2 - t_1) \\
&= -i\delta_{ik}\delta_{jl} e^{i(\varepsilon_j - \varepsilon_i)(t_1 - t_2)} \{\theta(t_1 - t_2)(1 - n_i)n_j \\
&\quad + \theta(t_2 - t_1)n_i(1 - n_j)\},
\end{aligned}
\tag{70}
$$

and

$$
\begin{aligned}
\Pi^{0,N+\delta}&(i, j; k, l; E) \\
&= \int_{-\infty}^{+\infty} \frac{dE'}{2\pi i} G^{0,N+\delta}(i, k; E + E') G^{0,N+\delta}(l, j; E') \\
&= \delta_{ik}\delta_{jl} \left\{ \frac{(1 - n_i)n_j}{E - (\varepsilon_i - \varepsilon_j) + i\eta} - \frac{n_i(1 - n_j)}{E + (\varepsilon_j - \varepsilon_i) - i\eta} \right\}.
\end{aligned}
\tag{71}
$$

This is another key equation, which raises several interesting points:

1. $\Pi^{0,N+\delta}$ is not the ensemble average of the N and $N + \delta$ systems, whereas $G^{0,N+\delta}$ is.
2. In $\Pi^0(i, j; k, l; E)$, Eq. (69), for integer systems it is obtained that $\Pi^0(i, j; k, l; E) = (1 - \delta_{ij})\Pi^0(i, j; E)$, because

of $\theta(F - j)\theta(i - F)$. However, for the $\Pi^{0,N+\delta}(i, j; k, l; E)$, the term $i = j$ is non vanishing in general, because $(1 - n_i)n_i$ can be non-zero for fractionally occupied orbitals.

3. The index i can be divided into three sets: particle (p) (or unoccupied u), hole (h) (or occupied, o), and fractional (f). Note the somewhat confusing many-body terms of hole state for $i < F$, and particle state for $F < i$. The particle and hole concept is from the "vacuum" of the Fermi sea, a particle is obtained by adding it to the state above F and hole is obtained for states below F. In normal terms, the occupied states (o) are below F, and the unoccupied states (u) are above F. When appropriate, we will use $\{a, b, c, d, \dots\}$ to denote unoccupied (particle) and fractional unoccupied states, $\{i, j, k, l, \dots\}$ to denote occupied (hole) and fractional occupied states, and $\{m, n, o, p, \dots\}$ to denote arbitrary states. In the concept of the "vacuum" of the Fermi sea, the fractional occupied states are both particle and hole states. In the normal occupied/unoccupied concept, the fractional occupied states are both occupied and unoccupied (fractionally).

4. $\Pi^{0,N+\delta}(i, j; k, l; E)$ is non-vanishing for the following cases:
    (a) $(1 - n_i)n_j \neq 0$, when $j \leq F \leq i$; that is j is a hole state ($j < F$) or a fractionally occupied state ($j = F$), and i is a particle ($F < i$) or a fractionally occupied state ($F = i$).
    (b) $n_i(1 - n_j) \neq 0$, when $i \leq F \leq j$; that is i is a hole state or a fractionally occupied state, j is a particle or a fractionally occupied state.

5. $\Pi^{0,N+\delta}(i, j; k, l; E)$ is a diagonal matrix in the space of ($ij \times kl$) because of $\delta_{ik}\delta_{jl}$. Similarly to Eq. (20), we will use the unfolded matrix representation of the propagator, whose dimension is $d_{ij} = 2(n_o + n_f)(n_u + n_f)$, where n_o is the number of (fully) occupied orbitals, n_f the number of fractionally occupied orbitals, and n_u the number of fully unoccupied orbitals. Its structure is given in Table I.

In the two-point spin coordinate representation, the fractional propagator is given by

$$
\begin{aligned}
\Pi^{0,N+\delta}&(\mathbf{x}_1, \mathbf{x}_2; t_1 - t_2) \\
&= \sum_{ijkl} \phi_j^*(\mathbf{x}_1)\phi_i(\mathbf{x}_1)\phi_k^*(\mathbf{x}_2)\phi_l(\mathbf{x}_2)\Pi^{0,N+\delta}(i, j; k, l; t_1 - t_2),
\end{aligned}
\tag{72}
$$

which in the energy form is

$$
\begin{aligned}
\Pi^{0,N+\delta}&(\mathbf{x}_1, \mathbf{x}_2; E) \\
&= \sum_{ijkl} \phi_j^*(\mathbf{x}_1)\phi_i(\mathbf{x}_1)\phi_k^*(\mathbf{x}_2)\phi_l(\mathbf{x}_2)\Pi^{0,N+\delta}(i, j; k, l; E) \\
&= \sum_{ij} \phi_j^*(\mathbf{x}_1)\phi_i(\mathbf{x}_1)\phi_i^*(\mathbf{x}_2)\phi_j(\mathbf{x}_2) \left\{ \frac{(1 - n_i)n_j}{E - (\varepsilon_i - \varepsilon_j) + i\eta} \right. \\
&\quad \left. - \frac{n_i(1 - n_j)}{E + (\varepsilon_j - \varepsilon_i) - i\eta} \right\} \\
&= \sum_{ij} \frac{\bar{\rho}_i(\mathbf{x}_1, \mathbf{x}_2)\rho_j(\mathbf{x}_2, \mathbf{x}_1)}{E - (\varepsilon_i - \varepsilon_j) + i\eta} - \frac{\rho_i(\mathbf{x}_1, \mathbf{x}_2)\bar{\rho}_j(\mathbf{x}_2, \mathbf{x}_1)}{E + (\varepsilon_j - \varepsilon_i) - i\eta},
\end{aligned}
$$

TABLE I. Structure of $\Pi^{0,N+\delta}(i,j;k,l;E)$.

i index	j index			
	o (occupied)	of (occupied fractionally)	uf (unoccupied fractionally)	u (unoccupied)
o	0	0	$-\frac{(1-n_j)}{E+(\varepsilon_j-\varepsilon_i)-i\eta}$	$-\frac{1}{E+(\varepsilon_j-\varepsilon_i)-i\eta}$
of	0	0	$-\frac{n_i(1-n_j)}{E+(\varepsilon_j-\varepsilon_i)-i\eta}$	$-\frac{n_i}{E+(\varepsilon_j-\varepsilon_i)-i\eta}$
uf	$\frac{(1-n_i)}{E-(\varepsilon_i-\varepsilon_j)+i\eta}$	$\frac{(1-n_i)n_j}{E-(\varepsilon_i-\varepsilon_j)+i\eta}$	0	0
u	$\frac{1}{E-(\varepsilon_i-\varepsilon_j)+i\eta}$	$\frac{n_j}{E-(\varepsilon_i-\varepsilon_j)+i\eta}$	0	0

where the occupied density matrix (hole) is

$$\rho_i(\mathbf{x}_1,\mathbf{x}_2) = n_i\phi_i(\mathbf{x}_1)\phi_i^*(\mathbf{x}_2), \tag{73}$$

and the unoccupied density matrix (particle) is

$$\bar\rho_i(\mathbf{x}_1,\mathbf{x}_2) = (1-n_i)\phi_i(\mathbf{x}_1)\phi_i^*(\mathbf{x}_2). \tag{74}$$

If the orbitals are real, then

$$\rho_i(\mathbf{x}_1,\mathbf{x}_2) = \rho_i(\mathbf{x}_2,\mathbf{x}_1), \tag{75}$$

and the second part in $\Pi^{0,N+\delta}(\mathbf{x}_1,\mathbf{x}_2;E)$ can be rearranged as

$$\sum_{ij}\frac{\rho_i(\mathbf{x}_1,\mathbf{x}_2)\bar\rho_j(\mathbf{x}_2,\mathbf{x}_1)}{E+(\varepsilon_j-\varepsilon_i)-i\eta} = \sum_{ij}\frac{\rho_j(\mathbf{x}_1,\mathbf{x}_2)\bar\rho_i(\mathbf{x}_2,\mathbf{x}_1)}{E+(\varepsilon_i-\varepsilon_j)-i\eta}$$
$$= \sum_{ij}\frac{\rho_j(\mathbf{x}_2,\mathbf{x}_1)\bar\rho_i(\mathbf{x}_1,\mathbf{x}_2)}{E+(\varepsilon_i-\varepsilon_j)-i\eta}, \tag{76}$$

therefore

$$\Pi^{0,N+\delta}(\mathbf{x}_1,\mathbf{x}_2;E)$$
$$= \sum_{ij}\bar\rho_i(\mathbf{x}_1,\mathbf{x}_2)\rho_j(\mathbf{x}_2,\mathbf{x}_1)\left(\frac{1}{E-(\varepsilon_i-\varepsilon_j)+i\eta}\right.$$
$$\left. - \frac{1}{E+(\varepsilon_i-\varepsilon_j)-i\eta}\right). \tag{77}$$

C. Ground state energy from the polarization propagators

A nice property of the polarization propagator is that it is connected directly to ground state density matrix and hence the total energy.

1. Potential energy from $\Pi(\mathbf{x},\mathbf{y};E)$

Consider the interaction energies

$$\langle\Psi_0^N|V|\Psi_0^N\rangle = \langle\Psi_0^N(1)|V|\Psi_0^N(1)\rangle$$
$$= \int_0^1 d\lambda\langle\Psi_0^N(\lambda)|V|\Psi_0^N(\lambda)\rangle$$
$$+ \langle\Psi_0^N(0)|V|\Psi_0^N(0)\rangle, \tag{78}$$

and

$$\langle\Psi_0^N(\lambda)|\lambda V|\Psi_0^N(\lambda)\rangle$$

$$= \frac{1}{2}\lambda\sum_{ijkl}\langle ij|kl\rangle\langle\Psi_0^N(\lambda)|a_i^\dagger(t)a_j^\dagger(t)a_l(t)a_k(t)|\Psi_0^N(\lambda)\rangle$$

$$= \frac{1}{2}\lambda\iint d\mathbf{x}d\mathbf{y}v(\mathbf{x},\mathbf{y})\langle\Psi_0^N(\lambda)|\hat\psi^\dagger(\mathbf{x},t)\hat\psi^\dagger(\mathbf{y},t)$$

$$\times \hat\psi(\mathbf{y},t)\hat\psi(\mathbf{x},t)|\Psi_0^N(\lambda)\rangle. \tag{79}$$

The diagonal part of the two particle reduced density matrix (2-rdm) is

$$2\gamma_2(\mathbf{y},\mathbf{x})$$

$$= \langle\Psi_0^N|\hat\psi^\dagger(\mathbf{x})\hat\psi^\dagger(\mathbf{y})\hat\psi(\mathbf{y})\hat\psi(\mathbf{x})|\Psi_0^N\rangle$$

$$= \langle\Psi_0^N| - \hat\psi^\dagger(\mathbf{x})\hat\psi^\dagger(\mathbf{y})\hat\psi(\mathbf{x})\hat\psi(\mathbf{y})|\Psi_0^N\rangle$$

$$= \langle\Psi_0^N| - \hat\psi^\dagger(\mathbf{x})\big(\delta(\mathbf{x}-\mathbf{y}) - \hat\psi(\mathbf{x})\hat\psi^\dagger(\mathbf{y})\big)\hat\psi(\mathbf{y})|\Psi_0^N\rangle$$

$$= -\delta(\mathbf{x}-\mathbf{y})\langle\Psi_0^N|\hat\psi^\dagger(\mathbf{x})\hat\psi(\mathbf{y})|\Psi_0^N\rangle$$

$$+ \langle\Psi_0^N|\hat\psi^\dagger(\mathbf{x})\big(\hat\psi(\mathbf{x})\hat\psi^\dagger(\mathbf{y})\big)\hat\psi(\mathbf{y})|\Psi_0^N\rangle$$

$$= -\delta(\mathbf{x}-\mathbf{y})\rho(\mathbf{x}) + \langle\Psi_0^N|\hat\rho(\mathbf{x})\hat\rho(\mathbf{y})|\Psi_0^N\rangle$$

$$= \rho(\mathbf{x})\rho(\mathbf{y}) - \delta(\mathbf{x}-\mathbf{y})\rho(\mathbf{x})$$

$$+ \langle\Psi_0^N|\big(\hat\rho(\mathbf{x})-\rho(\mathbf{x})\big)\big(\hat\rho(\mathbf{y})-\rho(\mathbf{y})\big)|\Psi_0^N\rangle$$

$$= \rho(\mathbf{x})\rho(\mathbf{y}) - \delta(\mathbf{x}-\mathbf{y})\rho(\mathbf{x})$$

$$+ \sum_{n\neq0}\langle\Psi_0^N|\hat\rho(\mathbf{x})|\Psi_n^N\rangle\langle\Psi_n^N|\hat\rho(\mathbf{y})|\Psi_0^N\rangle. \tag{80}$$

The last term in the previous equation can be rewritten as

$$\sum_{n\neq 0}\langle\Psi_0^N|\hat{\rho}(\mathbf{x})|\Psi_n^N\rangle\langle\Psi_n^N|\hat{\rho}(\mathbf{y})|\Psi_0^N\rangle$$

$$=\sum_{n\neq 0}\int_0^\infty dE\frac{-1}{\pi}\text{Im}\frac{\langle\Psi_0^N|\hat{\rho}(\mathbf{x})|\Psi_n^N\rangle\langle\Psi_n^N|\hat{\rho}(\mathbf{y})|\Psi_0^N\rangle}{E-\left(E_n^N-E_0^N\right)+i\eta}$$

$$=\sum_{n\neq 0}\int_0^\infty dE\frac{-1}{\pi}\text{Im}\left[\frac{\langle\Psi_0^N|\hat{\rho}(\mathbf{x})|\Psi_n^N\rangle\langle\Psi_n^N|\hat{\rho}(\mathbf{y})|\Psi_0^N\rangle}{E-\left(E_n^N-E_0^N\right)+i\eta}\right.$$

$$\left.-\frac{\langle\Psi_0^N|\hat{\rho}(\mathbf{y})|\Psi_n^N\rangle\langle\Psi_n^N|\hat{\rho}(\mathbf{x})|\Psi_0^N\rangle}{E+\left(E_n^N-E_0^N\right)-i\eta}\right]$$

$$=\sum_{n\neq 0}\int_{-\infty}^\infty dE\frac{-1}{2\pi}\text{Im}\left[\frac{\langle\Psi_0^N|\hat{\rho}(\mathbf{x})|\Psi_n^N\rangle\langle\Psi_n^N|\hat{\rho}(\mathbf{y})|\Psi_0^N\rangle}{E-\left(E_n^N-E_0^N\right)+i\eta}\right.$$

$$\left.-\frac{\langle\Psi_0^N|\hat{\rho}(\mathbf{y})|\Psi_n^N\rangle\langle\Psi_n^N|\hat{\rho}(\mathbf{x})|\Psi_0^N\rangle}{E+\left(E_n^N-E_0^N\right)-i\eta}\right]$$

$$=\frac{-1}{2\pi}\int_{-\infty}^\infty dE\,\text{Im}\Pi(\mathbf{x},\mathbf{y};E)$$

$$=\frac{-1}{2\pi i}\int_{-i\infty}^{i\infty} dE\,e^{\pm\eta}\Pi(\mathbf{x},\mathbf{y};E), \tag{81}$$

where we have used $\sum_{n\neq 0}\langle\Psi_0^N|\hat{\rho}(\mathbf{x})|\Psi_n^N\rangle\langle\Psi_n^N|\hat{\rho}(\mathbf{y})|\Psi_0^N\rangle$ $=\sum_{n\neq 0}\langle\Psi_0^N|\hat{\rho}(\mathbf{y})|\Psi_n^N\rangle\langle\Psi_n^N|\hat{\rho}(\mathbf{x})|\Psi_0^N\rangle$ as the 2-rdm is symmetric, $\gamma_2(\mathbf{y},\mathbf{x})=\gamma_2(\mathbf{x},\mathbf{y})$.

Now from the previous equations, we have

$$2\gamma_2(\mathbf{y},\mathbf{x})=\rho(\mathbf{x})\rho(\mathbf{y})-\delta(\mathbf{x}-\mathbf{y})\rho(\mathbf{x})$$

$$-\frac{1}{2\pi}\int_{-\infty}^\infty dE\,\text{Im}\Pi(\mathbf{x},\mathbf{y};E)$$

$$=\rho(\mathbf{x})\rho(\mathbf{y})-\delta(\mathbf{x}-\mathbf{y})\rho(\mathbf{x})$$

$$-\frac{1}{2\pi i}\int_{-i\infty}^{i\infty} dE\,e^{\pm i\eta}\Pi(\mathbf{x},\mathbf{y};E). \tag{82}$$

Hence,

$$\langle\Psi_0^N|V|\Psi_0^N\rangle$$

$$=\iint d\mathbf{x}d\mathbf{y}v(\mathbf{x},\mathbf{y})\gamma_2(\mathbf{y},\mathbf{x})$$

$$=\frac{1}{2}\iint d\mathbf{x}d\mathbf{y}v(\mathbf{x},\mathbf{y})\left[-\frac{1}{2\pi}\int_{-\infty}^\infty dE\,\text{Im}\Pi(\mathbf{x},\mathbf{y}_2;E)\right.$$

$$\left.+\rho(\mathbf{x})\rho(\mathbf{y})-\delta(\mathbf{x}-\mathbf{y})\rho(\mathbf{x})\right]$$

$$=\frac{1}{2}\iint d\mathbf{x}d\mathbf{y}v(\mathbf{x},\mathbf{y})\left[-\frac{1}{2\pi i}\int_{-i\infty}^{i\infty} dE\,e^{\pm\eta}\Pi(\mathbf{x},\mathbf{y};E)\right.$$

$$\left.+\rho(\mathbf{x})\rho(\mathbf{y})-\delta(\mathbf{x}-\mathbf{y})\rho(\mathbf{x})\right]. \tag{83}$$

2. Potential energy from $\Pi(i, j; k, l; E)$

Sometime it is desirable to work in the 4-point index space. We can express the potential energy as

$$\langle\Psi_0^N|V|\Psi_0^N\rangle=\frac{1}{2}\sum_{ijkl}\langle ij|kl\rangle\langle\Psi_0^N|a_i^\dagger a_j^\dagger a_l a_k|\Psi_0^N\rangle$$

$$=\frac{1}{4}\sum_{ijkl}\langle ij||kl\rangle\langle\Psi_0^N|a_i^\dagger a_j^\dagger a_l a_k|\Psi_0^N\rangle$$

$$=\sum_{ijkl}\langle ij|kl\rangle\gamma(ij,kl)$$

$$=\sum_{ijkl}\langle ij|\bar{V}_{ph}|kl\rangle\gamma(il,jk)$$

$$=\frac{1}{2}\sum_{ijkl}\langle ij||kl\rangle\gamma(ij,kl)$$

$$=\frac{1}{2}\sum_{ijkl}\langle ij|V_{ph}|kl\rangle\gamma(il,jk), \tag{84}$$

where we use
$$\gamma(ij,kl)=\frac{1}{2}\langle\Psi_0^N|a_i^\dagger a_j^\dagger a_l a_k|\Psi_0^N\rangle, \tag{85}$$

$$\langle ij|kl\rangle=\iint d\mathbf{x}_1 d\mathbf{x}_2\phi_i^*(\mathbf{x}_1)\phi_j^*(\mathbf{x}_2)v(r_{12})\phi_k(\mathbf{x}_1)\phi_l(\mathbf{x}_2),$$

and

$$\langle ij||kl\rangle=\langle ij|kl\rangle-\langle ij|lk\rangle, \tag{86}$$

$$\langle ij|V_{ph}|kl\rangle=\langle il||jk\rangle$$

$$=\iint d\mathbf{x}_1 d\mathbf{x}_2\phi_i^*(\mathbf{x}_1)\phi_l^*(\mathbf{x}_2)v(r_{12})$$

$$\times(1-P_{12})\phi_j(\mathbf{x}_1)\phi_k(\mathbf{x}_2), \tag{87}$$

$$\langle ij|\bar{V}_{ph}|kl\rangle=\langle il|jk\rangle$$

$$=\iint d\mathbf{x}_1 d\mathbf{x}_2\phi_i^*(\mathbf{x}_1)\phi_l^*(\mathbf{x}_2)v(r_{12})\phi_j(\mathbf{x}_1)\phi_k(\mathbf{x}_2). \tag{88}$$

Using Eq. (65), we have

$$\frac{-1}{\pi}\int_{-\infty}^\infty dE\,\text{Im}\Pi(i,j;k,l;E)$$

$$=\delta_{ki}\rho_{jl}+\delta_{lj}\rho_{ki}-2\rho_{kl}\rho_{ji}+4\gamma_{jk,il},$$

which is derived in details in Subsection 5 in the Appendix. Thus,

$$2\gamma_{jk,il}=\frac{-1}{2\pi}\int_{-\infty}^\infty dE\,\text{Im}\Pi(i,j;k,l;E)+\rho_{kl}\rho_{ji}$$

$$-\frac{1}{2}\left(\delta_{ki}\rho_{jl}+\delta_{lj}\rho_{ki}\right).$$

and for real orbitals, $\gamma_{jk,il}=\gamma_{il,jk}$.

We now can express the potential energy as

$$\langle \Psi_0^N | V | \Psi_0^N \rangle = \sum_{ijkl} \langle ij | \bar{V}_{ph} | kl \rangle \gamma_{il,jk}$$

$$= \frac{1}{2} \sum_{ijkl} \langle ij | \bar{V}_{ph} | kl \rangle \left[\frac{-1}{2\pi} \int_{-\infty}^{\infty} dE \operatorname{Im}\Pi(i,j;k,l;E) + \rho_{kl}\rho_{ji} - \frac{1}{2} \left(\delta_{ki}\rho_{jl} + \delta_{lj}\rho_{ki} \right) \right]$$

$$= \frac{-1}{4\pi} \int_{-\infty}^{\infty} dE \operatorname{Im}\operatorname{Tr} \bar{\mathbf{V}}_{ph}\Pi + \frac{1}{2} \iint d\mathbf{x}d\mathbf{y}v(\mathbf{x},\mathbf{y}) \left[\rho(\mathbf{x})\rho(\mathbf{y}) - \delta(\mathbf{x}-\mathbf{y})\rho(\mathbf{x}) \right]. \tag{89}$$

Equivalently,

$$\langle \Psi_0^N | V | \Psi_0^N \rangle = \frac{1}{2} \sum_{ijkl} \langle ij | V_{ph} | kl \rangle \gamma_{il,jk}$$

$$= \frac{-1}{8\pi} \int_{-\infty}^{\infty} dE \operatorname{Im}\operatorname{Tr} \mathbf{V}_{ph}\Pi$$

$$+ \frac{1}{4} \iint d\mathbf{x}_1 d\mathbf{x}_2 \phi_i^*(\mathbf{x}_1)\phi_l^*(\mathbf{x}_2)v(\mathbf{x}_1,\mathbf{x}_2)(1-P_{12})\phi_j(\mathbf{x}_1)\phi_k(\mathbf{x}_2) \left[\rho_{kl}\rho_{ji} - \frac{1}{2} \left(\delta_{ki}\rho_{jl} + \delta_{lj}\rho_{ki} \right) \right]$$

$$= \frac{-1}{8\pi} \int_{-\infty}^{\infty} dE \operatorname{Im}\operatorname{Tr} \mathbf{V}_{ph}\Pi$$

$$+ \frac{1}{4} \iint d\mathbf{x}_1 d\mathbf{x}_2 v(\mathbf{x}_1,\mathbf{x}_2) \left(\rho(\mathbf{x}_1)\rho(\mathbf{x}_2) - \rho(\mathbf{x}_2,\mathbf{x}_1)\rho(\mathbf{x}_1,\mathbf{x}_2) \right)$$

$$+ \frac{1}{4} \iint d\mathbf{x}_1 d\mathbf{x}_2 v(\mathbf{x}_1,\mathbf{x}_2) \left(\rho(\mathbf{x}_1)\delta(\mathbf{x}_2-\mathbf{x}_1) - \rho(\mathbf{x}_1)\delta(0) \right). \tag{90}$$

See Subsection 6 in the Appendix for details of the derivation.

3. HF energy from $\Pi^{0,N+\delta}(\mathbf{x}_1;\mathbf{x}_2;E)$

Given the HF determinant wavefunction Φ_0^N, the potential energy in HF theory is given by

$$E_{\text{pot}}^0 = \langle \Phi_0^N | V | \Phi_0^N \rangle$$

$$= \iint d\mathbf{x}d\mathbf{y}v(\mathbf{x},\mathbf{y})\gamma_2(\mathbf{y},\mathbf{x})$$

$$= \frac{1}{2} \iint d\mathbf{x}d\mathbf{y}v(\mathbf{x},\mathbf{y}) \left[\rho(\mathbf{x})\rho(\mathbf{y}) - \delta(\mathbf{x}-\mathbf{y})\rho(\mathbf{x}) \right.$$

$$\left. - \frac{1}{2\pi} \int_{-\infty}^{\infty} dE \operatorname{Im}\Pi^0(\mathbf{x};\mathbf{y};E) \right]. \tag{91}$$

To extend this expression to fractional charges and fractional spins, simply use $\Pi^{0,N+\delta}(\mathbf{x}_1;\mathbf{x}_2;E)$ of Eq. (77), and

$$-\frac{1}{2\pi} \int_{-\infty}^{\infty} dE \operatorname{Im}\Pi^{0,N+\delta}(\mathbf{x}_1;\mathbf{x}_2;E)$$

$$= -\frac{1}{2\pi} \int_{-\infty}^{\infty} dE \operatorname{Im} \sum_{ij} \bar{\rho}_i(\mathbf{x}_1,\mathbf{x}_2)\rho_j(\mathbf{x}_2,\mathbf{x}_1)$$

$$\times \left(\frac{1}{E-(\varepsilon_i-\varepsilon_j)+i\eta} - \frac{1}{E+(\varepsilon_i-\varepsilon_j)-i\eta} \right)$$

$$= \sum_{ij} \bar{\rho}_i(\mathbf{x}_1,\mathbf{x}_2)\rho_j(\mathbf{x}_2,\mathbf{x}_1)$$

$$= \bar{\rho}(\mathbf{x}_1,\mathbf{x}_2)\rho(\mathbf{x}_2,\mathbf{x}_1). \tag{92}$$

Thus the last two terms of Eq. (91),

$$-\delta(\mathbf{x}_1-\mathbf{x}_2)\rho(\mathbf{x}_1) - \frac{1}{2\pi} \int_{-\infty}^{\infty} dE \operatorname{Im}\Pi^{0,N+\delta}(\mathbf{x}_1;\mathbf{x}_2;E)$$

$$= -\delta(\mathbf{x}_1-\mathbf{x}_2)\rho(\mathbf{x}_2,\mathbf{x}_1) - \frac{1}{2\pi} \int_{-\infty}^{\infty} dE \operatorname{Im}\Pi^{0,N+\delta}(\mathbf{x}_1;\mathbf{x}_2;E)$$

$$= -\left(\bar{\rho}(\mathbf{x}_1,\mathbf{x}_2) + \rho(\mathbf{x}_1,\mathbf{x}_2) \right) \rho(\mathbf{x}_2,\mathbf{x}_1) + \bar{\rho}(\mathbf{x}_1,\mathbf{x}_2)\rho(\mathbf{x}_2,\mathbf{x}_1)$$

$$= -\rho(\mathbf{x}_1,\mathbf{x}_2)\rho(\mathbf{x}_2,\mathbf{x}_1),$$

and we have

$$E_{\text{pot}}^0 = \frac{1}{2} \iint d\mathbf{x}d\mathbf{y}v(\mathbf{x},\mathbf{y}) \left[\rho(\mathbf{x})\rho(\mathbf{y}) - \rho(\mathbf{x}_1,\mathbf{x}_2)\rho(\mathbf{x}_2,\mathbf{x}_1) \right], \tag{93}$$

which recovers the HF potential energy for fractional systems.

4. Correlation energy

We will use an adiabatic connection, which is more general than Eq. (39), to calculate the total energy:

$$\langle \Psi_0^N(\lambda) | H_1 | \Psi_0^N(\lambda) \rangle = \iint d\mathbf{x}d\mathbf{y}v(\mathbf{x},\mathbf{y})\gamma_2^\lambda(\mathbf{y},\mathbf{x}) \tag{94}$$

with corresponding energy

$$E(1) = E(0) + \int_0^1 d\lambda \langle \Psi_0^N(\lambda) | H_1 | \Psi_0^N(\lambda) \rangle. \tag{95}$$

We use a new expression for $H_1(\lambda)$, $H(\lambda) = H_0 + H_1(\lambda)$, such that $H(1) = H_0 + H_1(1)$ is the physical H. Then

$$E(1) = E(0) + \int_0^1 d\lambda \langle \Psi_0^N(\lambda)| \frac{\partial H_1}{\partial \lambda} |\Psi_0^N(\lambda)\rangle.$$

Let $H(\lambda) = H_0 + H_1(\lambda)$, $H(0) = H_0 = \sum_{ij}(h_{ij} + u(1)_{ij})a_i^\dagger a_j$, and $H_1(\lambda) = \lambda V - \sum_{ij} u_{ij}(\lambda)a_i^\dagger a_j$; then $E(0) = \text{Tr}\rho^0(h + u(1))$, and

$$E(1) - E(0)$$

$$= \int_0^1 d\lambda \left[\langle \Psi_0^N(\lambda)|V|\Psi_0^N(\lambda)\rangle - \langle \Psi_0^N(\lambda)| \sum_{ij} \frac{\partial u_{ij}(\lambda)}{\partial \lambda} a_i^\dagger a_j |\Psi_0^N(\lambda)\rangle \right]$$

$$= -\int_0^1 d\lambda \text{Tr}\rho^\lambda \left(\frac{\partial u(\lambda)}{\partial \lambda} \right) + \frac{1}{2} \int_0^1 d\lambda \iint d\mathbf{x} d\mathbf{y} v(\mathbf{x}, \mathbf{y}) \rho^\lambda(\mathbf{x}) \rho^\lambda(\mathbf{y})$$

$$- \frac{1}{2} \int_0^1 d\lambda \iint d\mathbf{x} d\mathbf{y} v(\mathbf{x}, \mathbf{y}) \left[\delta(\mathbf{x} - \mathbf{y})\rho^\lambda(\mathbf{x}) + \frac{1}{2\pi} \int_{-\infty}^\infty dE \text{Im}\Pi^\lambda(\mathbf{x}; \mathbf{y}; E) \right]$$

$$= -\int_0^1 d\lambda \text{Tr}\rho^\lambda \left(\frac{\partial u(\lambda)}{\partial \lambda} \right) + \frac{1}{2} \int_0^1 d\lambda \iint d\mathbf{x} d\mathbf{y} v(\mathbf{x}, \mathbf{y}) \left(\rho^\lambda(\mathbf{x})\rho^\lambda(\mathbf{y}) \right)$$

$$- \frac{1}{2} \int_0^1 d\lambda \iint d\mathbf{x} d\mathbf{y} v(\mathbf{x}, \mathbf{y}) \left[\delta(\mathbf{x} - \mathbf{y}) \left(\rho^\lambda(\mathbf{x}) - \rho^0(\mathbf{x}) \right) + \frac{1}{2\pi} \int_{-\infty}^\infty dE \text{Im} \left(\Pi^\lambda(\mathbf{x}; \mathbf{y}; E) - \Pi^0(\mathbf{x}; \mathbf{y}; E) \right) \right]$$

$$- \frac{1}{2} \iint d\mathbf{x} d\mathbf{y} v(\mathbf{x}, \mathbf{y}) \left[\rho^0(\mathbf{x}_1, \mathbf{x}_2)\rho^0(\mathbf{x}_2, \mathbf{x}_1) \right],$$

where we used the result from Sec. IV C 3 on $\Pi^0(\mathbf{x}; \mathbf{y}; E)$,

$$\frac{1}{2} \iint d\mathbf{x} d\mathbf{y} v(\mathbf{x}, \mathbf{y}) \left[\delta(\mathbf{x} - \mathbf{y})\rho^0(\mathbf{x}) \right.$$

$$\left. - \frac{1}{2\pi} \int_{-\infty}^\infty dE \text{Im}\Pi^0(\mathbf{x}; \mathbf{y}; E) \right]$$

$$= \frac{1}{2} \iint d\mathbf{x} d\mathbf{y} v(\mathbf{x}, \mathbf{y}) \left[\rho^0(\mathbf{x}_1, \mathbf{x}_2)\rho^0(\mathbf{x}_2, \mathbf{x}_1) \right].$$

Thus we have the general expression for calculating the ground state energy from polarization propagator,

$$E(1)$$

$$= \text{Tr}\rho^0(h + u(1)) - \int_0^1 d\lambda \text{Tr}\rho^\lambda \left(\frac{\partial u(\lambda)}{\partial \lambda} \right)$$

$$+ \frac{1}{2} \int_0^1 d\lambda \iint d\mathbf{x} d\mathbf{y} v(\mathbf{x}, \mathbf{y})(\rho^\lambda(\mathbf{x})\rho^\lambda(\mathbf{y}) - \rho^0(\mathbf{x}, \mathbf{y})\rho^0(\mathbf{y}, \mathbf{x}))$$

$$- \frac{1}{2} \int_0^1 d\lambda \iint d\mathbf{x} d\mathbf{y} v(\mathbf{x}, \mathbf{y})(\delta(\mathbf{x} - \mathbf{y}) \left(\rho^\lambda(\mathbf{x}) - \rho^0(\mathbf{x}) \right)$$

$$+ \frac{1}{2\pi} \int_{-\infty}^\infty dE \text{Im} \left(\Pi^\lambda(\mathbf{x}; \mathbf{y}; E) - \Pi^0(\mathbf{x}; \mathbf{y}; E) \right)). \quad (96)$$

In general $u(1) = (v_s - v)$, $u(0) = 0$, where v_s is the non-interacting reference potential. In between both limits we can have any $u(\lambda)$, so that $\int_0^1 d\lambda \rho^\lambda \left(\frac{\partial u(\lambda)}{\partial \lambda} \right) = \rho^1 u(1) - \int_0^1 u(\lambda) \frac{\partial \rho^\lambda}{\partial \lambda} d\lambda$, and

$$\text{Tr}\rho^0 (h + u(1)) - \int_0^1 d\lambda \text{Tr}\rho^\lambda \left(\frac{\partial u(\lambda)}{\partial \lambda} \right)$$

$$= \text{Tr}\rho^0 h + \text{Tr} \left(\rho^0 - \rho^1 \right) u(1) + \int_0^1 d\lambda \text{Tr} u(\lambda) \frac{\partial \rho^\lambda}{\partial \lambda}.$$

We then have another general expression for calculating the ground state energy from the polarization propagator

$$E(1)$$

$$= \text{Tr}\rho^0 h + \text{Tr} \left(\rho^0 - \rho^1 \right) u(1) + \int_0^1 d\lambda \text{Tr} u(\lambda) \frac{\partial \rho^\lambda}{\partial \lambda}$$

$$+ \frac{1}{2} \int_0^1 d\lambda \iint d\mathbf{x} d\mathbf{y} v(\mathbf{x}, \mathbf{y})(\rho^\lambda(\mathbf{x})\rho^\lambda(\mathbf{y}) - \rho^0(\mathbf{x}, \mathbf{y})\rho^0(\mathbf{y}, \mathbf{x}))$$

$$- \frac{1}{2} \int_0^1 d\lambda \iint d\mathbf{x} d\mathbf{y} v(\mathbf{x}, \mathbf{y}) \left[\delta(\mathbf{x} - \mathbf{y})(\rho^\lambda(\mathbf{x}) - \rho^0(\mathbf{x})) \right.$$

$$\left. + \frac{1}{2\pi} \int_{-\infty}^\infty dE \text{Im} \left(\Pi^\lambda(\mathbf{x}; \mathbf{y}; E) - \Pi^0(\mathbf{x}; \mathbf{y}; E) \right) \right]. \quad (97)$$

There are various ways to design adiabatic connections,[29–32] that are now considered in this context.

a. Linear potential connection. First, one can follow the linear path for the potential $u(\lambda) = \lambda u(1) = \lambda(v_s - v)$ (Ref. 29), then

$$\text{Tr}\rho^0\left(h + u(1)\right) - \int_0^1 d\lambda \text{Tr}\rho^\lambda \left(\frac{\partial u(\lambda)}{\partial \lambda}\right)$$

$$= \text{Tr}\rho^0\left(h + u(1)\right) - \int_0^1 d\lambda \text{Tr}\rho^\lambda \left(u(1)\right)$$

$$= \text{Tr}\rho^0 h + \int_0^1 d\lambda \text{Tr}\left(\rho^0 - \rho^\lambda\right)u(1)$$

$$= \text{Tr}\rho^0(t + v) + \int_0^1 d\lambda \text{Tr}\left(\rho^0 - \rho^\lambda\right)(v_s - v)$$

$$= \text{Tr}\rho^0 t + \int_0^1 d\lambda \left[\text{Tr}\rho^\lambda v + \text{Tr}\left(\rho^0 - \rho^\lambda\right)v_s\right],$$

and the ground state total energy, Eq. (97), for the linear potential path is

$$E(1)$$

$$= \text{Tr}\rho^0 t + \int_0^1 d\lambda \left[\text{Tr}\rho^\lambda v + \text{Tr}\left(\rho^0 - \rho^\lambda\right)v_s\right]$$

$$+ \frac{1}{2}\int_0^1 d\lambda \iint d\mathbf{x}d\mathbf{y}v(\mathbf{x},\mathbf{y})\left(\rho^\lambda(\mathbf{x})\rho^\lambda(\mathbf{y}) - \rho^0(\mathbf{x},\mathbf{y})\rho^0(\mathbf{y},\mathbf{x})\right)$$

$$- \frac{1}{2}\int_0^1 d\lambda \iint d\mathbf{x}d\mathbf{y}v(\mathbf{x},\mathbf{y})\left[\delta(\mathbf{x}-\mathbf{y})\left(\rho^\lambda(\mathbf{x}) - \rho^0(\mathbf{x})\right)\right.$$

$$\left. + \frac{1}{2\pi}\int_{-\infty}^{\infty} dE\,\text{Im}\left(\Pi^\lambda(\mathbf{x};\mathbf{y};E) - \Pi^0(\mathbf{x};\mathbf{y};E)\right)\right]. \quad (98)$$

Using HF energy expression,

$$E^{HF} = \text{Tr}\rho^0 h + \frac{1}{2}\int_0^1 d\lambda \iint d\mathbf{x}d\mathbf{y}v(\mathbf{x},\mathbf{y})(\rho^0(\mathbf{x})\rho^0(\mathbf{y})$$

$$- \rho^0(\mathbf{x},\mathbf{y})\rho^0(\mathbf{y},\mathbf{x})),$$

the correlation energy $E_c = E(1) - E^{HF}$ is then

$$E_c = -\int_0^1 d\lambda \text{Tr}\left(\rho^\lambda - \rho^0\right)u$$

$$+ \frac{1}{2}\int_0^1 d\lambda \iint d\mathbf{x}d\mathbf{y}v(\mathbf{x},\mathbf{y})\left(\rho^\lambda(\mathbf{x})\rho^\lambda(\mathbf{y}) - \rho^0(\mathbf{x})\rho^0(\mathbf{y})\right)$$

$$- \frac{1}{2}\int_0^1 d\lambda \iint d\mathbf{x}d\mathbf{y}v(\mathbf{x},\mathbf{y})\left[\delta(\mathbf{x}-\mathbf{y})\left(\rho^\lambda(\mathbf{x}) - \rho^0(\mathbf{x})\right)\right.$$

$$\left. + \frac{1}{2\pi}\int_{-\infty}^{\infty} dE\,\text{Im}\left(\Pi^\lambda(\mathbf{x};\mathbf{y};E) - \Pi^0(\mathbf{x};\mathbf{y};E)\right)\right]. \quad (99)$$

b. Constant density connection. The second path is the constant-density adiabatic connection,[30, 31] $\frac{\partial\rho^\lambda}{\partial\lambda} = 0$, $\rho^0 = \rho^\lambda = \rho^1$, namely, the electron density along the adiabatic connection is kept constant and is equal to the density of the physical system. Then, the ground state total energy, Eq. (97), becomes

$$E(1) = \text{Tr}\rho h + \frac{1}{2}\iint d\mathbf{x}d\mathbf{y}v(\mathbf{x},\mathbf{y})(\rho(\mathbf{x})\rho(\mathbf{y})$$

$$- \rho^0(\mathbf{x},\mathbf{y})\rho^0(\mathbf{y},\mathbf{x}))$$

$$- \frac{1}{2}\int_0^1 d\lambda \iint d\mathbf{x}d\mathbf{y}v(\mathbf{x},\mathbf{y})$$

$$\times \left[\frac{1}{2\pi}\int_{-\infty}^{\infty} dE\,\text{Im}\left(\Pi^\lambda(\mathbf{x};\mathbf{y};E) - \Pi^0(\mathbf{x};\mathbf{y};E)\right)\right].$$

Thus, the correlation energy is

$$E_c = -\frac{1}{2}\int_0^1 d\lambda \iint d\mathbf{x}d\mathbf{y}v(\mathbf{x},\mathbf{y})$$

$$\times \left[\frac{1}{2\pi}\int_{-\infty}^{\infty} dE\,\text{Im}\left(\Pi^\lambda(\mathbf{x};\mathbf{y};E) - \Pi^0(\mathbf{x};\mathbf{y};E)\right)\right]. \quad (100)$$

In four-point matrix form, we have

$$E_c = -\frac{1}{2}\int_0^1 d\lambda \frac{1}{2\pi}\int_{-\infty}^{\infty} dE\,\text{Im}\sum_{ijkl}(\Pi^\lambda(i,j;k,l;E)$$

$$- \Pi^0(i,j;k,l;E))\langle kl|\bar{V}_{ph}|ij\rangle$$

$$= -\frac{1}{2}\int_0^1 d\lambda \frac{1}{2\pi}\int_{-\infty}^{\infty} dE\,\text{Im}\text{Tr}\left(\mathbf{\Pi}^\lambda(E) - \mathbf{\Pi}^0(E)\right)\bar{\mathbf{V}}_{ph}$$

$$= -\frac{1}{2}\int_0^1 d\lambda \frac{1}{2\pi}\int_{-i\infty}^{i\infty} dE\,e^{\pm i\eta}\text{Tr}\left(\mathbf{\Pi}^\lambda(E) - \mathbf{\Pi}^0(E)\right)\bar{\mathbf{V}}_{ph}, \quad (101)$$

and

$$E_c = -\frac{1}{4} \int_0^1 d\lambda \frac{1}{2\pi} \int_{-\infty}^{\infty} dE \, \mathrm{Im} \sum_{ijkl} (\Pi^\lambda(i,j;k,l;E)$$

$$- \Pi^0(i,j;k,l;E)) \langle kl|V_{ph}|ij\rangle$$

$$= -\frac{1}{4} \int_0^1 d\lambda \frac{1}{2\pi} \int_{-\infty}^{\infty} dE \, \mathrm{Im} \mathrm{Tr} \left(\boldsymbol{\Pi}^\lambda(E) - \boldsymbol{\Pi}^0(E) \right) \mathbf{V}_{ph}$$

$$= -\frac{1}{4} \int_0^1 d\lambda \frac{1}{2\pi} \int_{-i\infty}^{i\infty} dE \, e^{\pm i\eta} \mathrm{Tr} \left(\boldsymbol{\Pi}^\lambda(E) - \boldsymbol{\Pi}^0(E) \right) \mathbf{V}_{ph}. \tag{102}$$

where we use the anti-symmetric interaction matrix $\langle il||jk\rangle = \langle ij|V_{ph}|kl\rangle$ to calculate the correlation energy, as in Eq. (84). We also replaced the integration along the real axis by integration along the imaginary axis, as they are shown equivalently in Eq. (83).

Equation (100) is convenient for RPA calculations without exchange interaction in two-point real space representation, while Eq. (101) for RPA calculations without exchange interaction, and Eq. (102) for RPA calculations with exchange interaction.

D. Random phase approximations

1. RPA equations

RPA[20] can be written as the equation for the polarization propagator,

$$\Pi^{\mathrm{RPA}}(i,j;k,l;E) = \Pi^0(i,j;k,l;E)$$

$$+ \sum_{pqrs} \Pi^0(i,j;p,q;E)\langle pq|U_{ph}|rs\rangle$$

$$\times \Pi^{\mathrm{RPA}}(r,s;k,l;E), \tag{103}$$

or in condensed notation

$$\boldsymbol{\Pi}^{\mathrm{RPA}} = \boldsymbol{\Pi}^0 + \boldsymbol{\Pi}^0 \mathbf{U}_{ph} \boldsymbol{\Pi}^{\mathrm{RPA}}, \tag{104}$$

where $\langle ij|U_{ph}|kl\rangle$ can be a general energy-independent interaction. $\langle ij|U_{ph}|kl\rangle = \langle ij|\bar{V}_{ph}|kl\rangle$ for RPA with no exchange interaction, and $\langle ij|U_{ph}|kl\rangle = \langle ij|V_{ph}|kl\rangle$ for RPAE, the random phase approximation with exchange interaction.

Assume that Π^{RPA} has a Lehmann representation as that of the exact one in Eq. (65),[20]

$$\Pi^{\mathrm{RPA}}(i,j;k,l;E)$$

$$= \sum_{n\neq0} \frac{\langle \Psi_0^{\mathrm{RPA}}|a_j^\dagger a_i|\Psi_n^{\mathrm{RPA}}\rangle \langle \Psi_n^{\mathrm{RPA}}|a_k^\dagger a_l|\Psi_0^{\mathrm{RPA}}\rangle}{E - \left(E_n^N - E_0^N\right) + i\eta}$$

$$- \sum_{n\neq0} \frac{\langle \Psi_0^{\mathrm{RPA}}|a_k^\dagger a_l|\Psi_n^{\mathrm{RPA}}\rangle \langle \Psi_n^{\mathrm{RPA}}|a_j^\dagger a_i|\Psi_0^{\mathrm{RPA}}\rangle}{E - \left(E_0^N - E_n^N\right) - i\eta}. \tag{105}$$

Within RPA, define the excitation energy

$$\varepsilon_n^\pi = E_n^N - E_0^N, \tag{106}$$

the column matrix $\mathbf{X}^n$ with dimension $(n_u + n_f)(n_o + n_f)$,

$$X_{bi}^n = \langle \Psi_n^{\mathrm{RPA}}|a_b^\dagger a_i|\Psi_0^{\mathrm{RPA}}\rangle^*$$

$$= \langle \Psi_0^{\mathrm{RPA}}|a_i^\dagger a_b|\Psi_n^{\mathrm{RPA}}\rangle, \tag{107}$$

and the column matrix $\mathbf{Y}^n$ with dimension $(n_o + n_f)(n_u + n_f)$,

$$Y_{bi}^n = \langle \Psi_n^{\mathrm{RPA}}|a_i^\dagger a_b|\Psi_0^{\mathrm{RPA}}\rangle, \tag{108}$$

then we can write[20]

$$\boldsymbol{\Pi}^{\mathrm{RPA}} = \sum_{n\neq0} \frac{\begin{pmatrix} \mathbf{X}^n \\ \mathbf{Y}^n \end{pmatrix}(\mathbf{X}^{n\dagger}\mathbf{Y}^{n\dagger})}{E - \varepsilon_n^\pi + i\eta} - \sum_{n\neq0} \frac{\left(\begin{pmatrix} \mathbf{Y}^n \\ \mathbf{X}^n \end{pmatrix}(\mathbf{Y}^{n\dagger}\mathbf{X}^{n\dagger})\right)^*}{E + \varepsilon_n^\pi - i\eta}. \tag{109}$$

It is not necessary to solve the RPA equation, Eq. (104), directly for every energy, because we can use the analytical structure of $\boldsymbol{\Pi}(E)$ from Eq. (109). We multiply Eq. (104) from the left by $\left(\boldsymbol{\Pi}^0\right)^{-1}$,

$$\left(\boldsymbol{\Pi}^0\right)^{-1} \boldsymbol{\Pi}^{\mathrm{RPA}} = \mathbf{I} + \mathbf{U}_{ph}\boldsymbol{\Pi}^{\mathrm{RPA}},$$

thus,

$$\left(\left(\boldsymbol{\Pi}^0\right)^{-1} - \mathbf{U}_{ph}\right)\boldsymbol{\Pi}^{\mathrm{RPA}} = \mathbf{I}.$$

We only need to solve the equations at the singularity of $\boldsymbol{\Pi}^{\mathrm{RPA}}$. Thus

$$\lim_{E\to\varepsilon_n^\pi-i\eta} \left(E - \varepsilon_n^\pi + i\eta\right)\left(\left(\boldsymbol{\Pi}^0\right)^{-1} - \mathbf{U}_{ph}\right)\boldsymbol{\Pi}^{\mathrm{RPA}} = 0.$$

Take the limit

$$\lim_{E\to\varepsilon_n^\pi-i\eta} \left(E - \varepsilon_n^\pi + i\eta\right)\boldsymbol{\Pi}^{\mathrm{RPA}} = \begin{pmatrix} \mathbf{X}^n \\ \mathbf{Y}^n \end{pmatrix}(\mathbf{X}^{n\dagger}\mathbf{Y}^{n\dagger}), \tag{110}$$

$$\left(\left(\boldsymbol{\Pi}^0(\varepsilon_n^\pi - i\eta)\right)^{-1} - \mathbf{U}_{ph}\right)\begin{pmatrix} \mathbf{X}^n \\ \mathbf{Y}^n \end{pmatrix} = 0. \tag{111}$$

Thus, Eq. (111) is valid for any ε_n^π, including the $\varepsilon_n^\pi = 0$ when the ground state is degenerate for both the many-electron and the non-interacting reference system.

Equation (111) can be rewritten in terms of two blocks, corresponding to the $\mathbf{X}^n$ and $\mathbf{Y}^n$ components:

$$\left(\Pi^0(a,i;a,i;\varepsilon_n^\pi - i\eta)\right)^{-1} X_{ai}^n$$

$$= \sum_{bj} \left(\langle ai|U_{ph}|bj\rangle X_{bj}^n + \langle ai|U_{ph}|jb\rangle Y_{bj}^n\right), \tag{112}$$

and

$$\left(\Pi^0(i,a;i,a;\varepsilon_n^\pi - i\eta)\right)^{-1} Y_{ai}^n$$

$$= \sum_{bj} \left(\langle ia|U_{ph}|bj\rangle X_{bj}^n + \langle ia|U_{ph}|jb\rangle Y_{bj}^n\right). \tag{113}$$

Based on Table I, $(\Pi^0(a,i;a,i;\varepsilon_n^\pi - i\eta))^{-1}$
$= \frac{\varepsilon_n^\pi - (\varepsilon_a - \varepsilon_i)}{(1-n_a)n_i}$, then Eq. (112) becomes

$$\frac{\varepsilon_n^\pi - (\varepsilon_a - \varepsilon_i)}{(1-n_a)n_i} X_{ai}^n$$

$$= \frac{1}{\sqrt{(1-n_a)n_i}} \sum_{bj} \left\{ \sqrt{(1-n_a)n_i}\langle ai|U_{ph}|bj\rangle \right.$$

$$\times \sqrt{(1-n_b)n_j}\frac{1}{\sqrt{(1-n_b)n_j}}X_{bj}^n$$

$$+ \sqrt{(1-n_a)n_i}\langle ai|U_{ph}|jb\rangle$$

$$\left. \times \sqrt{(1-n_b)n_j}\frac{1}{\sqrt{(1-n_b)n_j}}Y_{bj}^n \right\}. \quad (114)$$

Define the following fractional-transformed quantities:

$$\sqrt{(1-n_a)n_i}\langle ai|U_{ph}|bj\rangle\sqrt{(1-n_b)n_j} = \langle ai|U_{ph}|bj\rangle_f,$$
$$(115)$$

$$\sqrt{(1-n_a)n_A}\langle ai|U_{ph}|jb\rangle\sqrt{(1-n_b)n_j} = \langle ai|U_{ph}|jb\rangle_f,$$
$$(116)$$

$$\frac{1}{\sqrt{(1-n_a)n_i}}X_{ai}^n = \widetilde{X}_{ai}^n, \quad (117)$$

$$\frac{1}{\sqrt{(1-n_b)n_j}}Y_{bj}^n = \widetilde{Y}_{bj}^n. \quad (118)$$

Then Eq. (114) can be written as

$$\left(\varepsilon_n^\pi - (\varepsilon_a - \varepsilon_i)\right)\widetilde{X}_{ai}^n$$
$$= \sum_{bB} \left\{ \langle ai|U_{ph}|bj\rangle_f \widetilde{X}_{bj}^n + \langle ai|U_{ph}|jb\rangle_f \widetilde{Y}_{bj}^n \right\}. \quad (119)$$

Similarly, using $(\Pi^0(i,a;i,a;\varepsilon_n^\pi - i\eta))^{-1}$
$= -\frac{\varepsilon_n^\pi + (\varepsilon_a - \varepsilon_i)}{n_i(1-n_a)}$ from Table I, we can convert Eq. (113) into

$$- \left(\varepsilon_n^\pi + (\varepsilon_a - \varepsilon_i)\right)\widetilde{Y}_{ai}^n$$
$$= \sum_{bj} \left\{ \langle ia|U_{ph}|bj\rangle_f \widetilde{X}_{bj}^n + \langle ia|U_{ph}|jb\rangle_f \widetilde{Y}_{bj}^n \right\}. \quad (120)$$

In matrix notation

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ -\mathbf{B}^* & -\mathbf{A}^* \end{pmatrix} \begin{pmatrix} \widetilde{\mathbf{X}}^n \\ \widetilde{\mathbf{Y}}^n \end{pmatrix} = \varepsilon_n^\pi \begin{pmatrix} \widetilde{\mathbf{X}}^n \\ \widetilde{\mathbf{Y}}^n \end{pmatrix}, \quad (121)$$

where the A and B matrices including fractional occupations are

$$A_{ia,jb} = (\varepsilon_a - \varepsilon_i)\delta_{ab}\delta_{ij}$$
$$+ \langle ai|U_{ph}|bj\rangle\sqrt{(1-n_a)n_i(1-n_b)n_j}, \quad (122)$$

$$B_{ia,jb} = \langle ai|U_{ph}|jb\rangle\sqrt{(1-n_a)n_i(1-n_b)n_j}. \quad (123)$$

This is the RPA equations for systems with fractional charges and fractional spins, which were developed in our previous work,[24,25] based on just using the occupation-scaled orbitals with Eqs. (18) and (19) and extending the dimension of the matrices to include the fractional orbitals in both the occupied and unoccupied states. The static limiting case of $E = 0$ has also been developed[33] in conjunction with extending the analytical evaluation of Fukui functions[34] and local conditions for the fractional charge and fractional spins. Here we have given the full derivation starting from the basic formula of the single-particle Green's function for fractional systems, Eq. (15). Our derivation also gives clear meaning for the eigenvectors $\widetilde{\mathbf{X}}^n$ and $\widetilde{\mathbf{Y}}^n$ for fractional systems.

2. RPA energy expressions

We now focus on the correlation energy. The RPA equation, Eq. (104), for $\Pi^{\mathrm{RPA},\lambda}$ at the coupling constant λ can be solved as

$$\Pi^{\mathrm{RPA},\lambda} = \frac{1}{((\mathbf{\Pi}^0)^{-1} - \lambda\mathbf{U}_{ph})}.$$

Then, the RPA approximation to correlation energy, based on Eq. (101), is

$$E_c = -\frac{1}{4\pi}\int_{-\infty}^{\infty}dE\,\mathrm{Im}\int_0^1 d\lambda\,\mathrm{Tr}\left[\frac{1}{((\mathbf{\Pi}^0(E))^{-1} - \lambda\mathbf{U}_{ph})} - \mathbf{\Pi}^0(E)\right]\bar{\mathbf{V}}_{ph}$$

$$= -\frac{1}{4\pi}\int_{-\infty}^{\infty}dE\,\mathrm{Im}\int_0^1 d\lambda\,\mathrm{Tr}\left[\frac{1}{(1 - \lambda\mathbf{\Pi}^0(E)\mathbf{U}_{ph})}\mathbf{\Pi}^0(E) - \mathbf{\Pi}^0(E)\right]\bar{\mathbf{V}}_{ph}$$

$$= -\frac{1}{4\pi}\int_{-\infty}^{\infty}dE\,\mathrm{Im}\int_0^1 d\lambda\,\mathrm{Tr}\left[1 + \lambda\mathbf{\Pi}^0(E)\mathbf{U}_{ph} + \lambda^2\mathbf{\Pi}^0(E)\mathbf{U}_{ph}\mathbf{\Pi}^0(E)\mathbf{U}_{ph} + \cdots - 1\right]\mathbf{\Pi}^0(E)\bar{\mathbf{V}}_{ph}$$

$$= -\frac{1}{4\pi}\int_{-\infty}^{\infty}dE\,\mathrm{Im\,Tr}\left[\frac{1}{2}\mathbf{\Pi}^0(E)\mathbf{U}_{ph} + \frac{1}{3}\mathbf{\Pi}^0(E)\mathbf{U}_{ph}\mathbf{\Pi}^0(E)\mathbf{U}_{ph}\cdots\right]\mathbf{\Pi}^0(E)\bar{\mathbf{V}}_{ph}$$

$$= -\frac{1}{4\pi}\int_{-\infty}^{\infty}dE\,\mathrm{Im\,Tr}\left[\frac{1}{2}\left(\mathbf{\Pi}^0(E)\mathbf{U}_{ph}\right)^2 + \frac{1}{3}\left(\mathbf{\Pi}^0(E)\mathbf{U}_{ph}\right)^3 + \cdots\right]\left(\mathbf{U}_{ph}\right)^{-1}\bar{\mathbf{V}}_{ph}$$

$$= \frac{1}{4\pi}\int_{-\infty}^{\infty}dE\,\mathrm{Im\,Tr}\left[\ln(\mathbf{1} - \mathbf{\Pi}^0(E)\mathbf{U}_{ph}) + \mathbf{\Pi}^0(E)\mathbf{U}_{ph}\right]\left(\mathbf{U}_{ph}\right)^{-1}\bar{\mathbf{V}}_{ph}. \quad (124)$$

Note that if we use $\langle jk||il\rangle = \langle kl|V_{ph}|ij\rangle$ instead of $\langle jk|il\rangle = \langle kl|\bar{V}_{ph}|ij\rangle$, there is an additional factor of $\frac{1}{2}$ as in Eq. (102), and therefore

$$E_c^{\text{KS}-\text{DFT}} = \frac{1}{8\pi}\int_{-\infty}^{\infty}dE\,\text{ImTr}[\ln(\mathbf{1} - \mathbf{\Pi}^0(E)\mathbf{U}_{ph})$$
$$+ \mathbf{\Pi}^0(E)\mathbf{U}_{ph}](\mathbf{U}_{ph})^{-1}\mathbf{V}_{ph}. \quad (125)$$

We can see the convenience of using Eq. (124) for conventional RPA without exchange interaction where $\mathbf{U}_{ph} = \bar{\mathbf{V}}_{ph}$ and Eq. (125) for RPAE with exchange where $\mathbf{U}_{ph} = \mathbf{V}_{ph}$. In Subsection 7 of the Appendix, we show that

$$\frac{1}{4\pi}\int_{-\infty}^{\infty}dE\,\text{ImTr}\left[\ln(\mathbf{1} - \mathbf{\Pi}^0(E)\mathbf{U}_{ph}) + \mathbf{\Pi}^0(E)\mathbf{U}_{ph}\right]$$
$$= \frac{1}{2}\sum_{n>0}\varepsilon_n^\pi - \frac{1}{2}\sum_{a\in\text{particle},i\in\text{hole}}(\varepsilon_a - \varepsilon_i) - \frac{1}{2}\sum_{ij}\langle ij|\,U_{ph}\,|ij\rangle_f$$
$$= \frac{1}{2}\sum_{n>0}\varepsilon_n^\pi - \frac{1}{2}\text{Tr}\mathbf{A}. \quad (126)$$

Thus for RPA, $\mathbf{U}_{ph} = \bar{\mathbf{V}}_{ph}$, without exchange

$$E_c^{\text{RPA}} = \frac{1}{2}\sum_{n>0}\varepsilon_n^\pi - \frac{1}{2}\text{Tr}\mathbf{A}. \quad (127)$$

For RPAE, $\mathbf{U}_{ph} = \mathbf{V}_{ph}$, with exchange,

$$E_c^{\text{RPAE}} = \frac{1}{4}\sum_{n>0}\varepsilon_n^\pi - \frac{1}{4}\text{Tr}\mathbf{A}. \quad (128)$$

These are the desired results rigorously derived from the ensemble of the basic variable, which have been used previously in showing the large localization error in the RPA energy.[24,25]

Equation (127) extends the results of previous work[35,36] to fractional systems. Equation (128) clarifies the issue on the proper factor for the RPAE correlation energy. The present derivation shows that the additional factor of $\frac{1}{2}$ is needed for RPAE correlation energy compared with that for RPA.[21,22] Both Eqs. (127) and (128) apply for both the normal RPA and also the RPA with fractionally occupied orbitals.

V. CONCLUSIONS

Many approximate approaches and many-body theoretical methods are explicit functionals of the single particle Green's function of the non-interacting reference system. This work shows the rigorous extension of those methods to fractional charges and fractional spins. This is achieved by taking the appropriate ensemble average of the one-electron Green's function, which is the basic variable, and using this in the corresponding energy expression. We have shown this for methods such as LDA, HF, MP2, and RPA using the fact that the non-interacting one-electron density matrix, Eq. (23), and the non-interacting polarization propagator, Eq. (71), can be expressed in terms of the non-interacting single-particle Green's function, Eq (15). This leads to expressions in terms of fractional charges and fractional spins describing systems that correspond to the dissociation limit of molecules with integer occupation numbers, as has been shown for H_2^+ and H_2.[4]

It should be noted that for many-body methods such as RPA, our development is different from the finite temperature extensions previously considered in the literature.[37] The dimension and structure of our RPA matrix equations, Eq. (121), are uniquely related to fractional systems at zero temperature. The development in this paper is completely consistent with the simple scaling of the orbitals: $\tilde{\phi}_i = \sqrt{n_i}\phi_i$ for the occupied orbitals, and $\tilde{\phi}_a = \sqrt{(1 - n_a)}\phi_a$ for the unoccupied orbitals, and the inclusion of fractional orbitals in both the occupied and unoccupied sets of orbitals. For other methods where the connection to the underlying single particle Green's function is not clear, we expect the occupation scaling to apply. This development should allow examining and developing functionals based on many-body methods to meet the very challenging exact conditions for fractional charges and fractional spins,[3] which is important, as the violation of these conditions explains many dramatic failures of DFT in realistic applications.

ACKNOWLEDGMENTS

APPENDIX: DETAILS OF DERIVATION

1. An identity

Considering

$$\frac{1}{E \pm i\eta} = P\frac{1}{E} \mp i\pi\delta(E), \quad (A1)$$

then

$$\text{Im}G^N(i, j; E) = -\pi\sum_m\langle\Psi_0^N|a_i|\Psi_m^{N+1}\rangle\langle\Psi_m^{N+1}|a_j^\dagger|\Psi_0^N\rangle$$
$$\times\delta\left(E - (E_m^{N+1} - E_0^N)\right)$$
$$+ \pi\sum_n\langle\Psi_0^N|a_j^\dagger|\Psi_n^{N-1}\rangle\langle\Psi_n^{N-1}|a_i|\Psi_0^N\rangle$$
$$\times\delta\left(E - (E_0^N - E_n^{N-1})\right). \quad (A2)$$

Let

$$t^+ = t + \eta, \quad (A3)$$

where the infinitesimal number $\eta > 0$, then

$$\frac{\partial}{\partial t}G^N(i, j; t - t^+)$$
$$= i\sum_n e^{i\left(E_0^N - E_n^{N-1}\right)(t^+ - t)}(-i)\left(E_0^N - E_n^{N-1}\right)$$
$$\times\langle\Psi_0^N|a_j^\dagger|\Psi_n^{N-1}\rangle\langle\Psi_n^{N-1}|a_i|\Psi_0^N\rangle$$
$$= \sum_n\left(E_0^N - E_n^{N-1}\right)\langle\Psi_0^N|a_j^\dagger|\Psi_n^{N-1}\rangle\langle\Psi_n^{N-1}|a_i|\Psi_0^N\rangle. \quad (A4)$$

Thus,

$$\int_{C\uparrow} \frac{dE}{2\pi i} E G^N(i, j; E)$$

$$= \int_{-\infty}^{+\infty} \frac{dE}{2\pi i} e^{iE\eta} E \left\{ \sum_m \frac{\langle \Psi_0^N | a_i | \Psi_m^{N+1} \rangle \langle \Psi_m^{N+1} | a_j^\dagger | \Psi_0^N \rangle}{E - (E_m^{N+1} - E_0^N) + i\eta} \right.$$

$$\left. + \sum_n \frac{\langle \Psi_0^N | a_j^\dagger | \Psi_n^{N-1} \rangle \langle \Psi_n^{N-1} | a_i | \Psi_0^N \rangle}{E - (E_0^N - E_n^{N-1}) - i\eta} \right\}$$

$$= \sum_n (E_0^N - E_n^{N-1}) \langle \Psi_0^N | a_j^\dagger | \Psi_n^{N-1} \rangle \langle \Psi_n^{N-1} | a_i | \Psi_0^N \rangle$$

$$= \frac{\partial}{\partial t} G^N(i, j; t, t^+)$$

$$= \frac{1}{\pi} \int_{-\infty}^{\varepsilon_F^-} dE \, E \mathrm{Im} G^N(i, j; E), \tag{A5}$$

where $\varepsilon_F^- = E_0^N - E_0^{N-1} = \mu^-$, $\varepsilon_F^+ = E_0^{N+1} - E_0^N = \mu^+$.

2. The second order self-energy

The second order self-energy is given in terms of G^0 and we perform the energy integration

$$\Sigma^{*(2)}(i, j, E)$$

$$= -\frac{1}{2} \int_{-\infty}^{+\infty} \frac{dE_1}{2\pi i} \int_{-\infty}^{+\infty} \frac{dE_2}{2\pi i}$$

$$\times \sum_{klm} \sum_{npq} \langle ik||lm \rangle \langle np||jq \rangle G^0(l, n; E_1) G^0(m, p; E_2)$$

$$\times G^0(q, k; E_1 + E_2 - E)$$

$$= -\frac{1}{2} \sum_{klm} \sum_{npq} \langle ik||lm \rangle \langle np||jq \rangle$$

$$\times \int_{-\infty}^{+\infty} \frac{dE_1}{2\pi i} G^0(l, n; E_1) \delta_{mp} \delta_{qk} \left\{ \frac{(1 - n_m)n_q}{E - E_1 + \varepsilon_q - \varepsilon_m + i\eta} \right.$$

$$\left. - \frac{n_q(1 - n_m)}{E - E_1 + \varepsilon_q - \varepsilon_m - i\eta} \right\}$$

$$= -\frac{1}{2} \sum_{klm} \sum_{npq} \langle ik||lm \rangle \langle np||jq \rangle \delta_{mp} \delta_{qk} \delta_{ln}$$

$$\times \left\{ -\frac{(1 - n_l)(1 - n_m)n_q}{E - \varepsilon_l - \varepsilon_m + \varepsilon_q + i\eta} - \frac{n_l n_m (1 - n_q)}{E - \varepsilon_l - \varepsilon_m + \varepsilon_q - i\eta} \right\}$$

$$= \frac{1}{2} \sum_{lmq} \langle iq||lm \rangle \langle lm||jq \rangle \left\{ \frac{(1 - n_l)(1 - n_m)n_q}{E - \varepsilon_l - \varepsilon_m + \varepsilon_q + i\eta} \right.$$

$$\left. + \frac{n_l n_m (1 - n_q)}{E - \varepsilon_l - \varepsilon_m + \varepsilon_q - i\eta} \right\},$$

which is Eq. (38) in the text.

We have used the following integrals:

$$I = \int_{-\infty}^{+\infty} \frac{dE'}{2\pi i} \left\{ \frac{H_1}{E' - h_1 + i\eta} + \frac{P_1}{E' - p_1 - i\eta} \right\}$$

$$\times \left\{ \frac{H_2}{E' - E - h_2 + i\eta} + \frac{P_2}{E' - E - p_2 - i\eta} \right\}$$

$$= \frac{H_1 P_2}{E + p_2 - h_1 + i\eta} - \frac{H_2 P_1}{E + h_2 - p_1 - i\eta}, \tag{A6}$$

such that

$$I_1 = \int_{-\infty}^{+\infty} \frac{dE_2}{2\pi i} \left\{ \frac{(1 - n_m)}{E_2 - \varepsilon_m + i\eta} + \frac{n_m}{E_2 - \varepsilon_m - i\eta} \right\}$$

$$\times \left\{ \frac{(1 - n_q)}{E_1 + E_2 - E - \varepsilon_q + i\eta} + \frac{n_q}{E_1 + E_2 - E - \varepsilon_q - i\eta} \right\}$$

$$= \frac{(1 - n_m)n_q}{E - E_1 + \varepsilon_q - \varepsilon_m + i\eta} - \frac{n_m(1 - n_q)}{E - E_1 + \varepsilon_q - \varepsilon_m - i\eta}, \tag{A7}$$

and

$$I_2 = \int_{-\infty}^{+\infty} \frac{dE_1}{2\pi i} \left\{ \frac{(1 - n_l)}{E_1 - \varepsilon_l + i\eta} + \frac{n_l}{E_1 - \varepsilon_l - i\eta} \right\}$$

$$\times \left\{ \frac{(1 - n_m)n_q}{E - E_1 + \varepsilon_q - \varepsilon_m + i\eta} - \frac{n_m(1 - n_q)}{E - E_1 + \varepsilon_q - \varepsilon_m - i\eta} \right\}$$

$$= \int_{-\infty}^{+\infty} \frac{dE_1}{2\pi i} \left\{ \frac{(1 - n_l)}{E_1 - \varepsilon_l + i\eta} + \frac{n_l}{E_1 - \varepsilon_l - i\eta} \right\}$$

$$\times \left\{ -\frac{(1 - n_m)n_q}{E_1 - E - \varepsilon_q + \varepsilon_m - i\eta} + \frac{n_m(1 - n_q)}{E_1 - E - \varepsilon_q + \varepsilon_m + i\eta} \right\}$$

$$= \frac{(1 - n_l)(1 - n_m)n_q}{\varepsilon_l - E - \varepsilon_q + \varepsilon_m - i\eta} + \frac{n_l n_m (1 - n_q)}{\varepsilon_l - E - \varepsilon_q + \varepsilon_m + i\eta}$$

$$= -\frac{(1 - n_l)(1 - n_m)n_q}{E - \varepsilon_l - \varepsilon_m + \varepsilon_q + i\eta} - \frac{n_l n_m (1 - n_q)}{E - \varepsilon_l - \varepsilon_m + \varepsilon_q - i\eta}. \tag{A8}$$

3. Energy expression from the equation of motion

The equation of motion for $H(\lambda)$, suppressing the index of λ in $a_i(t)$, can be expressed as

$$i \frac{\partial}{\partial t} a_i(t) = [a_i(t), H(\lambda)]$$

$$= \sum_j [h_{ij} + (1 - \lambda)u_{ij}] a_j(t)$$

$$+ \lambda \sum_{jkl} \langle ij|kl \rangle a_j^\dagger(t) a_l(t) a_k(t). \tag{A9}$$

Then

$$\lambda \sum_{jkl} \langle ij|kl \rangle a_j^\dagger(t) a_l(t) a_k(t)$$

$$= i \frac{\partial}{\partial t} a_i(t) - \sum_j [h_{ij} + (1 - \lambda)u_{ij}] a_j(t), \tag{A10}$$

and (using $t^+ = t + 0$),

$$\lambda \sum_{ijkl} \langle ij|kl \rangle a_i^\dagger(t^+) a_j^\dagger(t) a_l(t) a_k(t)$$

$$= \sum_i a_i^\dagger(t^+) \left(i \frac{\partial}{\partial t} \right) a_i(t)$$

$$- \sum_{ij} [h_{ij} + (1-\lambda)u_{ij}] a_i^\dagger(t^+) a_j(t). \quad (A11)$$

Thus,

$$\langle \Psi_0^N(\lambda) | \lambda V | \Psi_0^N(\lambda) \rangle$$

$$= \frac{1}{2} \lambda \sum_{ijkl} \langle ij|kl \rangle \langle \Psi_0^N(\lambda) | a_i^\dagger(t) a_j^\dagger(t) a_l(t) a_k(t) | \Psi_0^N(\lambda) \rangle$$

$$= \frac{1}{2} \sum_i \langle \Psi_0^N(\lambda) | a_i^\dagger(t^+) \left(i \frac{\partial}{\partial t} \right) a_i(t) | \Psi_0^N(\lambda) \rangle$$

$$- \frac{1}{2} \sum_{ij} [h_{ij} + (1-\lambda)u_{ij}] \langle \Psi_0^N(\lambda) | a_i^\dagger(t^+) a_j(t) | \Psi_0^N(\lambda) \rangle$$

$$= \frac{1}{2} \sum_i \left[\left(i \frac{\partial}{\partial t} \right) \langle \Psi_0^N(\lambda) | a_i^\dagger(t^+) a_i(t) | \Psi_0^N(\lambda) \rangle \right]$$

$$- \frac{1}{2} \sum_{ij} [h_{ij} + (1-\lambda)u_{ij}] G^\lambda(j, i; t - t^+)$$

$$= \frac{1}{2} \text{Tr} \left(i \frac{\partial}{\partial t} \right) \mathbf{G}^\lambda(t - t^+) - \frac{1}{2} \text{Tr} [\mathbf{h} + \mathbf{u} - \lambda\mathbf{u}] \mathbf{G}^\lambda(t - t^+)$$

$$= \frac{1}{2} \text{Tr} \left[i \frac{\partial}{\partial t} - (\mathbf{h} + \mathbf{u} - \lambda\mathbf{u}) \right] \mathbf{G}^\lambda(t, t^+)$$

$$= \frac{1}{2} \int_{C\uparrow} \frac{dE}{2\pi i} \text{Tr} \left\{ [E - (\mathbf{h} + \mathbf{u} - \lambda\mathbf{u})] \mathbf{G}^\lambda(E) \right\},$$

using

$$G^\lambda(i, j; t - t^+)$$

$$= \int_{C\uparrow} \frac{dE}{2\pi i} G^\lambda(i, j; E)$$

$$= \int_{C\uparrow} \frac{dE}{2\pi i} \int_{-\infty}^{+\infty} d(t - t^+) e^{iE(t - t^+)} G^\lambda(i, j; t - t^+),$$

$$(A12)$$

and the identity of Eq. (A5).

Therefore at $\lambda = 1$,

$$\langle \Psi_0^N(1) | V | \Psi_0^N(1) \rangle = \frac{1}{2} \int_{C\uparrow} \frac{dE}{2\pi i} \text{Tr} \left\{ [E - \mathbf{h}] \mathbf{G}^{\lambda=1}(E) \right\},$$

$$(A13)$$

and similarly

$$\langle \Psi_0^N(1) | h | \Psi_0^N(1) \rangle = \int_{C\uparrow} \frac{dE}{2\pi i} \text{Tr}\{\mathbf{h} \mathbf{G}^{\lambda=1}(E)\}. \quad (A14)$$

Thus, the ground state energy can be expressed as

$$E_0^N = E(1)$$

$$= \langle \Psi_0^N(1) | h | \Psi_0^N(1) \rangle + \langle \Psi_0^N(1) | V | \Psi_0^N(1) \rangle$$

$$= \int_{C\uparrow} \frac{dE}{2\pi i} \text{Tr} \left\{ \mathbf{h} \mathbf{G}^{\lambda=1}(E) \right\}$$

$$+ \frac{1}{2} \int_{C\uparrow} \frac{dE}{2\pi i} \text{Tr} \left\{ [E - \mathbf{h}] \mathbf{G}^{\lambda=1}(E) \right\}$$

$$= \frac{1}{2} \int_{C\uparrow} \frac{dE}{2\pi i} \text{Tr} \left\{ (E + \mathbf{h}) \mathbf{G}(E) \right\}.$$

Taking the choice of $\mathbf{h} + \mathbf{u}$ as the Hamiltonian for the non-interacting reference system,

$$\left[i \frac{\partial}{\partial t} - (\mathbf{h} + \mathbf{u}) \right] \mathbf{G}^0(t) = \mathbf{I}, \quad (A15)$$

we have

$$\left[i \frac{\partial}{\partial t} - (\mathbf{h} + \mathbf{u} + \mathbf{\Sigma}^{*\lambda}) \right] \mathbf{G}^\lambda(t) = \mathbf{I}, \quad (A16)$$

and

$$\left[E - (\mathbf{h} + \mathbf{u} + \mathbf{\Sigma}^{*\lambda}) \right] \mathbf{G}^\lambda(E) = \mathbf{I}, \quad (A17)$$

then

$$\left(\mathbf{G}^\lambda \right)^{-1}(t) = \left[i \frac{\partial}{\partial t} - (\mathbf{h} + \mathbf{u} + \mathbf{\Sigma}^{*\lambda}) \right]$$

$$= \left(\mathbf{G}^0 \right)^{-1}(t) + \mathbf{\Sigma}^{*\lambda}. \quad (A18)$$

This gives

$$[E - (\mathbf{h} + \mathbf{u} - \lambda\mathbf{u})] \mathbf{G}^\lambda(E) = \mathbf{I} + \left(\mathbf{\Sigma}^{*\lambda} + \lambda u \right) \mathbf{G}^\lambda(E).$$

$$(A19)$$

The expression for the energy can be cast as, using Eqs. (44) and (A13),

$$E(1) - E(0)$$

$$= \int_0^1 d\lambda \langle \Psi_0^N(\lambda) | H_1 | \Psi_0^N(\lambda) \rangle$$

$$= \int_0^1 d\lambda \left[-\sum_{ij} u_{ij} \langle \Psi_0^N(\lambda) | a_i^\dagger a_j | \Psi_0^N(\lambda) \rangle \right.$$

$$\left. + \frac{1}{2} \sum_{ijkl} \langle ij|kl \rangle \langle \Psi_0^N(\lambda) | a_i^\dagger a_j^\dagger a_l a_k | \Psi_0^N(\lambda) \rangle \right]$$

$$= \int_0^1 d\lambda \left[-\sum_{ij} u_{ij} \langle \Psi_0^N(\lambda) | a_i^\dagger a_j | \Psi_0^N(\lambda) \rangle \right.$$

$$+ \frac{1}{2} \frac{1}{\lambda} \sum_{ij} \langle \Psi_0^N(\lambda) | a_i^+(t)$$

$$\left. \times \left(i \frac{\partial}{\partial t} a_i(t) - \sum \left(h_{ij} + u_{ij} - \lambda u_{ij} \right) a_j(t) \right) | \Psi_0^N(\lambda) \rangle \right]$$

$$= -\int_0^1 d\lambda \int_{-\infty}^{+\infty} \frac{dE}{2\pi i} e^{iE\eta} \text{Tr} \left[\mathbf{u} \mathbf{G}^\lambda(E) \right]$$

$$+ \frac{1}{2} \int_0^1 \frac{d\lambda}{\lambda} \int_{-\infty}^{+\infty} \frac{dE}{2\pi i} e^{iE\eta} \text{Tr} \left[\mathbf{I} + \left(\mathbf{\Sigma}^{*\lambda}(E) + \lambda \mathbf{u} \right) \mathbf{G}^\lambda(E) \right]$$

$$= -\int_0^1 d\lambda \int_{-\infty}^{+\infty} \frac{dE}{2\pi i} e^{iE\eta} \text{Tr} \mathbf{u} \mathbf{G}^\lambda(E)$$

$$+ \frac{1}{2} \int_0^1 \frac{d\lambda}{\lambda} \int_{-\infty}^{+\infty} \frac{dE}{2\pi i} e^{iE\eta} \text{Tr} \left(\mathbf{\Sigma}^{*\lambda}(E) + \lambda \mathbf{u} \right) \mathbf{G}^\lambda(E)$$

$$= \frac{1}{2} \int_0^1 d\lambda \int_{-\infty}^{+\infty} \frac{dE}{2\pi i} e^{iE\eta} \text{Tr} \left[\left(-\mathbf{u} + \frac{1}{\lambda} \mathbf{\Sigma}^{*\lambda}(E) \right) \mathbf{G}^\lambda(E) \right],$$

which is Eq. (45) in the text.

4. The second-order energy

The detailed integration needed for the second order energy is as follows:

$$\frac{1}{4} \int_{-\infty}^{+\infty} \frac{dE}{2\pi i} e^{iE\eta} \text{Tr} \{ \mathbf{\Sigma}^{*(2)}(E) \mathbf{G}^0(E) \}$$

$$= \frac{1}{4} \int_{-\infty}^{+\infty} \frac{dE}{2\pi i} e^{iE\eta} \frac{1}{2} \sum_{ilmq} \langle iq||lm \rangle \langle lm||iq \rangle$$

$$\left\{ \frac{(1-n_l)(1-n_m)n_q}{E - \varepsilon_l - \varepsilon_m + \varepsilon_q + i\eta} + \frac{n_l n_m (1-n_q)}{E - \varepsilon_l - \varepsilon_m + \varepsilon_q - i\eta} \right\}$$

$$\times \left\{ \frac{(1-n_i)}{E - \varepsilon_i + i\eta} + \frac{n_i}{E - \varepsilon_i - i\eta} \right\}$$

$$= \frac{1}{8} \sum_{ilmq} \langle iq||lm \rangle \langle lm||iq \rangle \left[n_l n_m (1-n_q) \right.$$

$$\times \left\{ \frac{(1-n_i)}{-(-\varepsilon_l - \varepsilon_m + \varepsilon_q) - \varepsilon_i + i\eta} \right.$$

$$\left. + \frac{n_i}{-(-\varepsilon_l - \varepsilon_m + \varepsilon_q) - \varepsilon_i - i\eta} \right\}$$

$$+ n_i \left\{ \frac{(1-n_l)(1-n_m)n_q}{\varepsilon_i - \varepsilon_l - \varepsilon_m + \varepsilon_q + i\eta} \right.$$

$$\left. \left. + \frac{n_l n_m (1-n_q)}{\varepsilon_i - \varepsilon_l - \varepsilon_m + \varepsilon_q - i\eta} \right\} \right]$$

$$= \frac{1}{8} \sum_{ilmq} \langle iq||lm \rangle \langle lm||iq \rangle$$

$$\times \left[n_l n_m (1-n_q) \left\{ \frac{1}{\varepsilon_l + \varepsilon_m - \varepsilon_q - \varepsilon_i + i\eta} \right. \right.$$

$$\left. \left. + \frac{n_i}{\varepsilon_i - \varepsilon_l - \varepsilon_m + \varepsilon_q - i\eta} \right\} \right.$$

$$\left. + \frac{(1-n_l)(1-n_m)n_q n_i}{\varepsilon_i - \varepsilon_l - \varepsilon_m + \varepsilon_q + i\eta} \right]$$

$$= \frac{1}{8} \sum_{ilmq} \langle iq||lm \rangle \langle lm||iq \rangle \left\{ \frac{n_l n_m (1-n_q)(1-n_i)}{\varepsilon_l + \varepsilon_m - \varepsilon_q - \varepsilon_i} \right.$$

$$\left. + \frac{(1-n_l)(1-n_m)n_q n_i}{\varepsilon_i + \varepsilon_q - \varepsilon_l - \varepsilon_m} \right\}$$

$$= \frac{1}{4} \sum_{ilmq} \langle iq||lm \rangle \langle lm||iq \rangle \frac{(1-n_l)(1-n_m)n_q n_i}{\varepsilon_i + \varepsilon_q - \varepsilon_l - \varepsilon_m}. \quad \text{(A20)}$$

5. The integration of the polarization propagator

$$\frac{-1}{\pi} \int_{-\infty}^{\infty} dE \operatorname{Im} \Pi(i, j; k, l; E)$$

$$= \sum_{n \neq 0} \left[\langle \Psi_0^N | a_j^\dagger a_i | \Psi_n^N \rangle \langle \Psi_n^N | a_k^\dagger a_l | \Psi_0^N \rangle \right.$$

$$\left. + \langle \Psi_0^N | a_k^\dagger a_l | \Psi_n^N \rangle \langle \Psi_n^N | a_j^\dagger a_i | \Psi_0^N \rangle \right]$$

$$= -\langle \Psi_0^N | a_j^\dagger a_i | \Psi_0^N \rangle \langle \Psi_0^N | a_k^\dagger a_l | \Psi_0^N \rangle$$

$$+ \sum_n \langle \Psi_0^N | a_j^\dagger a_i | \Psi_n^N \rangle \langle \Psi_n^N | a_k^\dagger a_l | \Psi_0^N \rangle$$

$$- \langle \Psi_0^N | a_k^\dagger a_l | \Psi_0^N \rangle \langle \Psi_0^N | a_j^\dagger a_i | \Psi_0^N \rangle$$

$$+ \sum_n \langle \Psi_0^N | a_k^\dagger a_l | \Psi_n^N \rangle \langle \Psi_n^N | a_j^\dagger a_i | \Psi_0^N \rangle$$

$$= -\rho_{ji}\rho_{kl} + \langle \Psi_0^N | a_j^\dagger a_i a_k^\dagger a_l | \Psi_0^N \rangle$$

$$- \rho_{kl}\rho_{ji} + \langle \Psi_0^N | a_k^\dagger a_l a_j^\dagger a_i | \Psi_0^N \rangle$$

$$= \delta_{ki} \langle \Psi_0^N | a_j^\dagger a_l | \Psi_0^N \rangle - \langle \Psi_0^N | a_j^\dagger a_k^\dagger a_i a_l | \Psi_0^N \rangle - \rho_{ji}\rho_{kl}$$

$$+ \delta_{lj} \langle \Psi_0^N | a_k^\dagger a_i | \Psi_0^N \rangle - \langle \Psi_0^N | a_k^\dagger a_j^\dagger a_l a_i | \Psi_0^N \rangle - \rho_{kl}\rho_{ji}$$

$$= \delta_{ki}\rho_{jl} - \langle \Psi_0^N | a_j^\dagger a_k^\dagger a_i a_l | \Psi_0^N \rangle - \rho_{ji}\rho_{kl} + \delta_{lj}\rho_{ki}$$

$$- \langle \Psi_0^N | a_k^\dagger a_j^\dagger a_l a_i | \Psi_0^N \rangle - \rho_{kl}\rho_{ji}$$

$$= \delta_{ki}\rho_{jl} - 2\gamma_{jk,li} - \rho_{ji}\rho_{kl} + \delta_{lj}\rho_{ki} - 2\gamma_{kj,il} - \rho_{kl}\rho_{ji}$$

$$= \delta_{ki}\rho_{jl} + \delta_{lj}\rho_{ki} - 2\rho_{kl}\rho_{ji} - 4\gamma_{jk,li}$$

$$= \delta_{ki}\rho_{jl} + \langle \Psi_0^N | a_j^\dagger a_k^\dagger a_l a_i | \Psi_0^N \rangle - \rho_{ji}\rho_{kl} + \delta_{lj}\rho_{ki}$$

$$+ \langle \Psi_0^N | a_k^\dagger a_j^\dagger a_i a_l | \Psi_0^N \rangle - \rho_{kl}\rho_{ji}$$

$$= \delta_{ki}\rho_{jl} + 2\gamma_{jk,il} - \rho_{ji}\rho_{kl} + \delta_{lj}\rho_{ki} + 2\gamma_{kj,li} - \rho_{kl}\rho_{ji}$$

$$= \delta_{ki}\rho_{jl} + \delta_{lj}\rho_{ki} - 2\rho_{kl}\rho_{ji} + 4\gamma_{jk,il},$$

where we used

$$2\gamma_{jk,li} = 2\gamma_{kj,il} = \langle \Psi_0^N | a_j^\dagger a_k^\dagger a_i a_l | \Psi_0^N \rangle,$$

and

$$2\gamma_{jk,il} = -2\gamma_{jk,li} = \langle \Psi_0^N | a_j^\dagger a_k^\dagger a_l a_i | \Psi_0^N \rangle.$$

6. The details of the potential energy expression

$$\frac{1}{2} \sum_{ijkl} \langle ij | \bar{V}_{ph} | kl \rangle \left[\rho_{kl}\rho_{ji} - \frac{1}{2} \left(\delta_{ki}\rho_{jl} + \delta_{lj}\rho_{ki} \right) \right]$$

$$= \frac{1}{2} \sum_{ijkl} \iint d\mathbf{x}_1 d\mathbf{x}_2 \phi_i^*(\mathbf{x}_1) \phi_l^*(\mathbf{x}_2) v(\mathbf{x}_1, \mathbf{x}_2) \phi_j(\mathbf{x}_1) \phi_k(\mathbf{x}_2)$$

$$\times \left[\rho_{kl}\rho_{ji} - \frac{1}{2} \left(\delta_{ki}\rho_{jl} + \delta_{lj}\rho_{ki} \right) \right]$$

$$= \frac{1}{2} \iint d\mathbf{x}_1 d\mathbf{x}_2 v(\mathbf{x}_1, \mathbf{x}_2) \rho(\mathbf{x}_1, \mathbf{x}_1) \rho(\mathbf{x}_2, \mathbf{x}_2)$$

$$- \frac{1}{4} \iint d\mathbf{x}_1 d\mathbf{x}_2 v(\mathbf{x}_1, \mathbf{x}_2) (\rho(\mathbf{x}_1, \mathbf{x}_2)\delta(\mathbf{x}_2 - \mathbf{x}_1)$$

$$+ \rho(\mathbf{x}_2, \mathbf{x}_1)\delta(\mathbf{x}_2 - \mathbf{x}_1))$$

$$= \frac{1}{2} \iint d\mathbf{x}_1 d\mathbf{x}_2 v(\mathbf{x}_1, \mathbf{x}_2) [\rho(\mathbf{x}_1)\rho(\mathbf{x}_2) - \rho(\mathbf{x}_1)\delta(\mathbf{x}_2 - \mathbf{x}_1)].$$

This is just part of Eq. [(89)](#) in the text, and

$$\frac{1}{4} \sum_{ijkl} \langle ij | V_{ph} | kl \rangle \left[\rho_{kl}\rho_{ji} - \frac{1}{2} \left(\delta_{ki}\rho_{jl} + \delta_{lj}\rho_{ki} \right) \right]$$

$$= \frac{1}{4} \sum_{ijkl} \iint d\mathbf{x}_1 d\mathbf{x}_2 \phi_i^*(\mathbf{x}_1) \phi_l^*(\mathbf{x}_2) v(\mathbf{x}_1, \mathbf{x}_2)(1 - P_{12})$$

$$\times \phi_j(\mathbf{x}_1) \phi_k(\mathbf{x}_2) \left[\rho_{kl}\rho_{ji} - \frac{1}{2}(\delta_{ki}\rho_{jl} + \delta_{lj}\rho_{ki}) \right]$$

$$= \frac{1}{4} \iint d\mathbf{x}_1 d\mathbf{x}_2 v(\mathbf{x}_1, \mathbf{x}_2)(\rho(\mathbf{x}_1, \mathbf{x}_1)\rho(\mathbf{x}_2, \mathbf{x}_2)$$

$$- \rho(\mathbf{x}_2, \mathbf{x}_1)\rho(\mathbf{x}_1, \mathbf{x}_2))$$

$$- \frac{1}{8} \iint d\mathbf{x}_1 d\mathbf{x}_2 v(\mathbf{x}_1, \mathbf{x}_2)(\rho(\mathbf{x}_1, \mathbf{x}_2)\delta(\mathbf{x}_2 - \mathbf{x}_1)$$

$$- \rho(\mathbf{x}_2, \mathbf{x}_2)\delta(\mathbf{x}_1 - \mathbf{x}_1) + \rho(\mathbf{x}_2, \mathbf{x}_1)\delta(\mathbf{x}_2 - \mathbf{x}_1)$$

$$- \rho(\mathbf{x}_1, \mathbf{x}_1)\delta(\mathbf{x}_2 - \mathbf{x}_2))$$

$$= \frac{1}{4} \iint d\mathbf{x}_1 d\mathbf{x}_2 v(\mathbf{x}_1, \mathbf{x}_2)(\rho(\mathbf{x}_1)\rho(\mathbf{x}_2)$$

$$- \rho(\mathbf{x}_2, \mathbf{x}_1)\rho(\mathbf{x}_1, \mathbf{x}_2))$$

$$- \frac{1}{8} \iint d\mathbf{x}_1 d\mathbf{x}_2 v(\mathbf{x}_1, \mathbf{x}_2)(2\rho(\mathbf{x}_1)\delta(\mathbf{x}_2 - \mathbf{x}_1)$$

$$- \rho(\mathbf{x}_1)\delta(0) - \rho(\mathbf{x}_2)\delta(0))$$

$$= \frac{1}{4} \iint d\mathbf{x}_1 d\mathbf{x}_2 v(\mathbf{x}_1, \mathbf{x}_2)(\rho(\mathbf{x}_1)\rho(\mathbf{x}_2) - \rho(\mathbf{x}_2, \mathbf{x}_1)\rho(\mathbf{x}_1, \mathbf{x}_2))$$

$$- \frac{1}{4} \iint d\mathbf{x}_1 d\mathbf{x}_2 v(\mathbf{x}_1, \mathbf{x}_2)(\rho(\mathbf{x}_1)\delta(\mathbf{x}_2 - \mathbf{x}_1)$$

$$- \rho(\mathbf{x}_1)\delta(0)).$$

7. RPA correlation energy

Here we will evaluate the integral of Eq. [(126)](#), using some techniques from Ref. [27](#). Based on

$\lim_{E\to\infty}\mathbf{\Pi}^0(E)\sim 1/E$,

$$\lim_{E\to\infty}E\frac{d}{dE}\mathrm{Tr}\left[\ln(\mathbf{1}-\mathbf{\Pi}^0(E)\mathbf{U}_{ph})\right]$$

$$=\lim_{E\to-\infty}E\frac{d}{dE}\mathrm{Tr}\left[\ln(\mathbf{1}-\mathbf{\Pi}^0(E)\mathbf{U}_{ph})\right],$$

because $[\ln(\mathbf{1}-\mathbf{\Pi}^0(E)\mathbf{U}_{ph})]=-\mathbf{\Pi}^0(E)\mathbf{U}_{ph}-\frac{1}{2}(\mathbf{\Pi}^0(E)$ $\mathbf{U}_{ph})^2-\frac{1}{3}(\mathbf{\Pi}^0(E)\mathbf{U}_{ph})^3+\cdots\cdots$ and $\lim_{E\to\infty}E\frac{d}{dE}\mathrm{Tr}[\ln(\mathbf{1}-\mathbf{\Pi}^0(E)\mathbf{U}_{ph})]$ is an even function of E. We thus have

$$\frac{1}{4\pi}\int_{-\infty}^{\infty}dE\,\mathrm{ImTr}\left[\ln(\mathbf{1}-\mathbf{\Pi}^0(E)\mathbf{U}_{ph})+\mathbf{\Pi}^0(E)\mathbf{U}_{ph}\right]$$

$$=-\frac{1}{4\pi}\int_{-\infty}^{\infty}E\,dE\frac{d}{dE}\mathrm{ImTr}\left[\ln(\mathbf{1}-\mathbf{\Pi}^0(E)\mathbf{U}_{ph})\right]$$

$$+\frac{1}{4\pi}\int_{-\infty}^{\infty}dE\,\mathrm{ImTr}\left[\mathbf{\Pi}^0(E)\mathbf{U}_{ph}\right]$$

$$+\frac{1}{4\pi}E\,\mathrm{ImTr}\left[\ln(\mathbf{1}-\mathbf{\Pi}^0(E)\mathbf{U}_{ph})\right]\Big|_{-\infty}^{\infty}$$

$$=-\frac{1}{4\pi}\int_{-\infty}^{\infty}E\,dE\frac{d}{dE}\mathrm{ImTr}\left[\ln(\mathbf{1}-\mathbf{\Pi}^0(E)\mathbf{U}_{ph})\right]$$

$$+\frac{1}{4\pi}\int_{-\infty}^{\infty}dE\,\mathrm{ImTr}\left[\mathbf{\Pi}^0(E)\mathbf{U}_{ph}\right]. \qquad (A21)$$

We will consider the two parts in Eq (A21) separately. Using Eq. (104) we get

$$\left(\mathbf{\Pi}^{\mathrm{RPA}}\right)^{-1}=\left(\mathbf{\Pi}^0\right)^{-1}-\mathbf{U}_{ph}.$$

Then

$$\frac{d}{dE}\mathrm{Tr}\left[\ln(\mathbf{1}-\mathbf{\Pi}^0(E)\mathbf{U}_{ph})\right]$$

$$=\frac{d}{dE}\mathrm{Tr}\left[\ln\left(\mathbf{\Pi}^0\left(\mathbf{\Pi}^{\mathrm{RPA}}\right)^{-1}\right)\right]$$

$$=\mathrm{Tr}\left[\left(\mathbf{\Pi}^0\right)^{-1}\frac{d}{dE}\mathbf{\Pi}^0+\left(\mathbf{\Pi}^{\mathrm{RPA}}\right)\frac{d}{dE}\left(\mathbf{\Pi}^{\mathrm{RPA}}\right)^{-1}\right]$$

$$=\mathrm{Tr}\left[\left(\mathbf{\Pi}^0\right)^{-1}\frac{d}{dE}\mathbf{\Pi}^0+\left(\mathbf{\Pi}^{\mathrm{RPA}}\right)\frac{d}{dE}\left(\mathbf{\Pi}^0\right)^{-1}\right].$$

Using

$$\Pi^{0,N+\delta}(i,j;k,l;E)=\delta_{ik}\delta_{jl}\left\{\frac{(1-n_i)n_j}{E-(\varepsilon_i-\varepsilon_j)+i\eta}-\frac{n_i(1-n_j)}{E+(\varepsilon_j-\varepsilon_i)-i\eta}\right\},$$

$$\mathrm{Tr}\left[\left(\mathbf{\Pi}^0\right)^{-1}\frac{d}{dE}\mathbf{\Pi}^0\right]$$

$$=\sum_{ij}\left\{\frac{(1-n_i)n_j}{E-(\varepsilon_i-\varepsilon_j)+i\eta}-\frac{n_i(1-n_j)}{E+(\varepsilon_j-\varepsilon_i)-i\eta}\right\}^{-1}\frac{d}{dE}\left\{\frac{(1-n_i)n_j}{E-(\varepsilon_i-\varepsilon_j)+i\eta}-\frac{n_i(1-n_j)}{E+(\varepsilon_j-\varepsilon_i)-i\eta}\right\}$$

$$=\sum_{ij}\left\{\frac{(1-n_i)n_j}{E-(\varepsilon_i-\varepsilon_j)+i\eta}-\frac{n_i(1-n_j)}{E+(\varepsilon_j-\varepsilon_i)-i\eta}\right\}^{-1}\left\{-\frac{(1-n_i)n_j}{\left(E-(\varepsilon_i-\varepsilon_j)+i\eta\right)^2}+\frac{n_i(1-n_j)}{\left(E+(\varepsilon_j-\varepsilon_i)-i\eta\right)^2}\right\}$$

$$-\frac{1}{4\pi}\int_{-\infty}^{\infty}E\,dE\,\mathrm{ImTr}\left[\left(\mathbf{\Pi}^0\right)^{-1}\frac{d}{dE}\mathbf{\Pi}^0\right]$$

$$=-\frac{1}{4\pi}\int_{-\infty}^{\infty}E\,dE\sum_{ij}\left\{\frac{(1-n_i)n_j}{E-(\varepsilon_i-\varepsilon_j)+i\eta}-\frac{n_i(1-n_j)}{E+(\varepsilon_j-\varepsilon_i)-i\eta}\right\}^{-1}$$

$$\left\{\frac{(1-n_i)n_j}{\left(E-(\varepsilon_i-\varepsilon_j)+i\eta\right)}\pi\delta(E-(\varepsilon_i-\varepsilon_j))+\frac{n_i(1-n_j)}{\left(E+(\varepsilon_j-\varepsilon_i)-i\eta\right)}\pi\delta(E+(\varepsilon_j-\varepsilon_i))\right\}$$

$$=-\frac{1}{4}\left\{\sum_{ij}(\varepsilon_i-\varepsilon_j)\frac{(1-n_i)n_j}{(1-n_i)n_j-n_i(1-n_j)}+\sum_{ij}(\varepsilon_i-\varepsilon_j)\frac{n_i(1-n_j)}{(1-n_i)n_j-n_i(1-n_j)}\right\}$$

$$=-\frac{1}{4}\left[\sum_{i\in\text{particle},j\in\text{hole}}(\varepsilon_i-\varepsilon_j)\frac{(1-n_i)n_j}{(1-n_i)n_j-n_i(1-n_j)}+\sum_{i\in\text{hole},j\in\text{particle}}(\varepsilon_i-\varepsilon_j)\frac{n_i(1-n_j)}{(1-n_i)n_j-n_i(1-n_j)}\right]$$

$$=-\frac{1}{4}\left[\sum_{i\in\text{particle},j\in\text{hole}}(\varepsilon_i-\varepsilon_j)-\sum_{i\in\text{hole},j\in\text{particle}}(\varepsilon_i-\varepsilon_j)\right]$$

$$=-\frac{1}{2}\sum_{i\in\text{particle},j\in\text{hole}}(\varepsilon_i-\varepsilon_j).$$

Note that $\frac{(1-n_i)n_j}{(1-n_i)n_j - n_i(1-n_j)} = 1$ for $i \in$ particle, $j \in$ hole, because $n_i(1-n_j) = 0$, excluding the frac-frac block, which is zero from $(\varepsilon_i - \varepsilon_j)$. And $\frac{n_i(1-n_j)}{(1-n_i)n_j - n_i(1-n_j)} = -1$, for $i \in$ hole, $j \in$ particle, because $(1-n_i)n_j = 0$, excluding the frac-frac block, which is zero from $(\varepsilon_i - \varepsilon_j)$.

Consider now

$$-\frac{1}{4\pi} \int_{-\infty}^{\infty} E \, dE \, \mathrm{ImTr} \left(\mathbf{\Pi}^{\mathrm{RPA}} \right) \frac{d}{dE} \left(\mathbf{\Pi}^0 \right)^{-1}$$

and

$$\left(\mathbf{\Pi}^0(i, j; k, l; E) \right)^{-1} = \delta_{ik} \delta_{jl} \left\{ \frac{(1-n_i)n_j}{E - (\varepsilon_i - \varepsilon_j) + i\eta} - \frac{n_i(1-n_j)}{E + (\varepsilon_j - \varepsilon_i) - i\eta} \right\}^{-1}.$$

For $i \in$ particle, $j \in$ hole,

$$\frac{d}{dE} \left(\mathbf{\Pi}^0(i, j; k, l; E) \right)^{-1} = \delta_{ik} \delta_{jl} \frac{d}{dE} \left\{ \frac{(1-n_i)n_j}{E - (\varepsilon_i - \varepsilon_j) + i\eta} \right\}^{-1} = \delta_{ik} \delta_{jl} \frac{d}{dE} \frac{E - (\varepsilon_i - \varepsilon_j)}{(1-n_i)n_j}$$

$$= \delta_{ik} \delta_{jl} \frac{1}{(1-n_i)n_j}.$$

For $i \in$ hole, $j \in$ particle,

$$\frac{d}{dE} \left(\mathbf{\Pi}^0(i, j; k, l; E) \right)^{-1} = \delta_{ik} \delta_{jl} \frac{d}{dE} \left\{ -\frac{n_i(1-n_j)}{E + (\varepsilon_j - \varepsilon_i) - i\eta} \right\}^{-1} = \delta_{ik} \delta_{jl} \frac{d}{dE} (-1) \frac{E + (\varepsilon_j - \varepsilon_i)}{n_i(1-n_j)}$$

$$= \delta_{ik} \delta_{jl} \frac{-1}{n_i(1-n_j)}.$$

Define the diagonal matrix,

$$\nu = \begin{pmatrix} \frac{1}{(1-n_i)n_j} & \\ & \frac{-1}{n_i(1-n_j)} \end{pmatrix},$$

$$\mathbf{\Pi}^{\mathrm{RPA}} = \sum_{n \neq 0} \frac{\begin{pmatrix} \mathbf{X}^n \\ \mathbf{Y}^n \end{pmatrix} (\mathbf{X}^{n\dagger} \mathbf{Y}^{n\dagger})}{E - \varepsilon_n^\pi + i\eta} - \sum_{n \neq 0} \frac{\left(\begin{pmatrix} \mathbf{Y}^n \\ \mathbf{X}^n \end{pmatrix} (\mathbf{Y}^{n\dagger} \mathbf{X}^{n\dagger}) \right)^*}{E + \varepsilon_n^\pi - i\eta},$$

$$\mathrm{Im}\mathbf{\Pi}^{\mathrm{RPA}} = \sum_{n \neq 0} \begin{pmatrix} \mathbf{X}^n \\ \mathbf{Y}^n \end{pmatrix} (\mathbf{X}^{n\dagger} \mathbf{Y}^{n\dagger})(-\pi)\delta\left(E - \varepsilon_n^\pi\right) - \sum_{n \neq 0} \left(\begin{pmatrix} \mathbf{Y}^n \\ \mathbf{X}^n \end{pmatrix} (\mathbf{Y}^{n\dagger} \mathbf{X}^{n\dagger}) \right)^* \pi\delta\left(E + \varepsilon_n^\pi\right).$$

Thus

$$-\frac{1}{4\pi} \int_{-\infty}^{\infty} E \, dE \frac{d}{dE} \mathrm{ImTr} \left[\left(\mathbf{\Pi}^{RPA} \right) \frac{d}{dE} \left(\mathbf{\Pi}^0 \right)^{-1} \right]$$

$$= -\frac{1}{4\pi} \int_{-\infty}^{\infty} E \, dE \, \mathrm{Tr} \left[\sum_{n \neq 0} \begin{pmatrix} \mathbf{X}^n \\ \mathbf{Y}^n \end{pmatrix} (\mathbf{X}^{n\dagger} \mathbf{Y}^{n\dagger})(-\pi)\delta\left(E - \varepsilon_n^\pi\right) - \sum_{n \neq 0} \left(\begin{pmatrix} \mathbf{Y}^n \\ \mathbf{X}^n \end{pmatrix} (\mathbf{Y}^{n\dagger} \mathbf{X}^{n\dagger}) \right)^* \pi\delta\left(E + \varepsilon_n^\pi\right) \right] \nu$$

$$= \frac{1}{4} \sum_{n > 0} \left[\varepsilon_n^\pi \mathrm{Tr}(\mathbf{X}^{n\dagger} \mathbf{Y}^{n\dagger}) \nu \begin{pmatrix} \mathbf{X}^n \\ \mathbf{Y}^n \end{pmatrix} - \varepsilon_n^\pi \mathrm{Tr}(\mathbf{Y}^{n\dagger} \mathbf{X}^{n\dagger}) \nu \begin{pmatrix} \mathbf{Y}^n \\ \mathbf{X}^n \end{pmatrix} \right]$$

$$= \frac{1}{2} \sum_{n > 0} \varepsilon_n^\pi,$$

where we use the normalization condition for the RPA matrix eigenvalue problem, Eq. (121),

$$(\mathbf{X}^{n\dagger} \mathbf{Y}^{n\dagger}) \nu \begin{pmatrix} \mathbf{X}^n \\ \mathbf{Y}^n \end{pmatrix} = (\tilde{\mathbf{X}}^{n\dagger} \tilde{\mathbf{Y}}^{n\dagger}) \begin{pmatrix} \tilde{\mathbf{X}}^n \\ -\tilde{\mathbf{Y}}^n \end{pmatrix} = 1$$

$$(\mathbf{Y}^{n\dagger} \mathbf{X}^{n\dagger}) \nu \begin{pmatrix} \mathbf{Y}^n \\ \mathbf{X}^n \end{pmatrix} = (\tilde{\mathbf{Y}}^{n\dagger} \tilde{\mathbf{X}}^{n\dagger}) \begin{pmatrix} \tilde{\mathbf{Y}}^n \\ -\tilde{\mathbf{X}}^n \end{pmatrix} = -1.$$

Now consider the last term in Eq. (A21),

$$\frac{1}{4\pi}\int_{-\infty}^{\infty} dE\,\mathrm{Im}\mathrm{Tr}\left[\mathbf{\Pi}^0(E)\mathbf{U}_{ph}\right]$$

$$= -\frac{1}{4}\mathrm{Tr}\left[\begin{pmatrix}\tilde{\mathbf{X}}^{0,n}\\ \tilde{\mathbf{Y}}^{0,n}\end{pmatrix}(\tilde{\mathbf{X}}^{0,n\dagger}\tilde{\mathbf{Y}}^{0,n\dagger})\mathbf{U}_{ph} + \left(\begin{pmatrix}\tilde{\mathbf{Y}}^{0,n}\\ \tilde{\mathbf{X}}^{0,n}\end{pmatrix}(\tilde{\mathbf{Y}}^{0,n\dagger}\tilde{\mathbf{X}}^{0,n\dagger})\right)^{*}\mathbf{U}_{ph}\right]$$

$$= -\frac{1}{4}\left[(\tilde{\mathbf{X}}^{0,n\dagger}\tilde{\mathbf{Y}}^{0,n\dagger})\mathbf{U}_{ph}\begin{pmatrix}\tilde{\mathbf{X}}^{0,n}\\ \tilde{\mathbf{Y}}^{0,n}\end{pmatrix} + \left((\tilde{\mathbf{Y}}^{0,n\dagger}\tilde{\mathbf{X}}^{0,n\dagger})\mathbf{U}_{ph}\begin{pmatrix}\tilde{\mathbf{Y}}^{0,n}\\ \tilde{\mathbf{X}}^{0,n}\end{pmatrix}\right)^{*}\right]$$

$$= -\frac{1}{2}(\tilde{\mathbf{X}}^{0,n\dagger}\tilde{\mathbf{Y}}^{0,n\dagger})\mathbf{U}_{ph}\begin{pmatrix}\tilde{\mathbf{X}}^{0,n}\\ \tilde{\mathbf{Y}}^{0,n}\end{pmatrix}$$

$$= -\frac{1}{2}\mathrm{Tr}\,\mathbf{U}_{ph,frac}$$

$$= -\frac{1}{2}\sum_{ij}\langle ij|\,U_{ph}\,|ij\rangle_{frac}$$

$$= -\frac{1}{2}\sum_{ij}\sqrt{(1-n_i)n_j}\,\langle ij|\,U_{ph}\,|ij\rangle\,\sqrt{(1-n_i)n_j},$$

using

$$\int_{-\infty}^{\infty} dE\,\mathrm{Im}\mathbf{\Pi}^{0,N+\delta}(E) = -\pi\left[\begin{pmatrix}\tilde{\mathbf{X}}^{0,n}\\ \tilde{\mathbf{Y}}^{0,n}\end{pmatrix}(\tilde{\mathbf{X}}^{0,n\dagger}\tilde{\mathbf{Y}}^{0,n\dagger}) + \left(\begin{pmatrix}\tilde{\mathbf{Y}}^{0,n}\\ \tilde{\mathbf{X}}^{0,n}\end{pmatrix}(\tilde{\mathbf{Y}}^{0,n\dagger}\tilde{\mathbf{X}}^{0,n\dagger})\right)^{*}\right].$$

Finally,

$$\frac{1}{4\pi}\int_{-\infty}^{\infty} dE\,\mathrm{Im}\mathrm{Tr}\left[\ln(\mathbf{1}-\mathbf{\Pi}^0(E)\mathbf{U}_{ph}) + \mathbf{\Pi}^0(E)\mathbf{U}_{ph}\right]$$

$$= \frac{1}{2}\sum_{n>0}\varepsilon_n^{\pi} - \frac{1}{2}\sum_{a\in\mathrm{particle},\,j\in\mathrm{hole}}(\varepsilon_a-\varepsilon_j) - \frac{1}{2}\sum_{ij}\langle ij|\,U_{ph}\,|ij\rangle_f$$

$$= \frac{1}{2}\sum_{n>0}\varepsilon_n^{\pi} - \frac{1}{2}\mathrm{Tr}\mathbf{A},$$

which is the RPA correlation energy, Eq. (126).

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