The correlation energy as an explicit functional of the one-particle density matrix from a determinantal reference state

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Abstract

Using an approach based on many body perturbation theory, the correlation energy $E_{\text{co}}$ is expressed as an explicit functional of $\rho_1$, $v$, and $v_s$, where $\rho_1$ is the one-particle density matrix from the noninteracting, or reference, determinantal-state; $v$ is the external potential from the interacting, or target, state; $v_s$ is the (kernel of the) external potential from the noninteracting determinantal-state. In other words we have $E_{\text{co}}[\rho_1, v, v_s]$. Another possibility is the following explicit functional: $E_{\text{co}}[\rho_1, v_\text{co}, v_s]$, where $v_\text{co}$ is the (kernel of the) correlation potential from the noninteracting Hamiltonian. The proposed method can, in principle, be used to compute $E_{\text{co}}$ in a very accurate and efficient manner, since, like the Kohn–Sham approach, there are no virtual orbitals to consider. However, in contrast to the Kohn–Sham approach, $E_{\text{co}}$ is a known, explicit functional that can be approximated in a systematic manner. For simplicity, we only consider noninteracting closed-shell states and target states that are nondegenerate, singlet ground-states; so, in that case, $\rho_1$ denotes the spin-less one-particle density matrix from the determinantal reference state.
I. INTRODUCTION

The Kohn-Sham version of density functional theory has been very successful in the description of electronic structure for quantum chemistry and condensed matter physics.\textsuperscript{1,2,3,4,5,6,7} Unlike pure density functional approaches,\textsuperscript{1,2,8} the Kohn–Sham method uses a set of occupied orbitals from a noninteracting state, where this determinantal state shares its electron density $\rho$ with the target, or interacting, state $|\Psi\rangle$. In the Kohn–Sham approach, the kinetic energy (through the) first order is not an explicit functional of $\rho$, but, instead, this functional depends on the one-particle density matrix $\rho_1$ from the noninteracting, determinantal state. The Kohn–Sham approach requires as input the exchange-correlation functional $E_{xc}^{KS}$—or equivalently the exchange $E_x$ and correlation-energy $E_{co}^{KS}$ functionals(where $E_{xc}^{KS}$ is required to be an explicit functional of $\rho$). Unfortunately, $E_{xc}^{KS}$ is an unknown functional, and there is no systematic method to improve approximations.

The optimized potential method\textsuperscript{9,10,11,12,13,14,15} is a density functional approach that can convert a nonlocal operator into a local one, where the exchange-correlation functionals can depend on both the occupied and virtual orbitals. Unfortunately, this method lacks the efficiency of other Kohn–Sham approaches. Furthermore, the optimized potential method introduces functional that—in contrast to many wave function methods—are not invariant to a unitary transformation of either the occupied or virtual orbitals; the local potentials also depend on the orbital energies.

High levels of approximations—beyond the Kohn–Sham approaches—can be obtained by wave function methods,\textsuperscript{16,17,18,19} including the coupled cluster method, many-body perturbation theory, and configuration interaction. Often, however, these methods are much less efficient than the Kohn Sham approaches, where, typically, wave function methods consider a large number of 2-electron molecular integrals, depending on both the occupied and virtual orbitals, and these integrals must be computed and utilized in calculations involving large atomic-orbital basis sets.

In order to improve the efficiency of the wave function methods, especially in regards to their scaling with molecular size, perturbative methods have been developed based on localized molecular orbitals.\textsuperscript{20,21,22,23,24,25,26} An alternative approach uses a Laplace transform to remove the energy denominators in perturbation theory, yielding approaches involving correlation energy expressions that depend explicitly on the atomic-orbital basis set.\textsuperscript{27,28}
This method has also been used with the coupled cluster theory.\(^{29}\)

Our research interest is in the development of methods that bridge the gap between wave function approaches and Kohn–Sham density functional theory. However, these two different approaches already share some common features. For example, as mentioned above, Kohn–Sham introduces a determinantal wave function and treats the first-order kinetic energy in the same manner as in wave function methods, i.e., as a functional of the one-body density matrix from a determinant. Furthermore, hybrid density functionals\(^{30,31,32,33}\) including B3LYP\(^{30,34}\) introduce a component of the exact exchange—a functional of \(\rho_1\)—even though these approaches violate the Hohenberg–Kohn theorem\(^8\) by using the nonlocal exchange operator.

A simple generalization of the Kohn–Sham functionals involves using the exact exchange energy \(E_x\) (with its corresponding non-local operator) and, in addition, a correlation-energy functional that also depends on \(\rho_1\). Such an approach could probably be derived within a variant of the Kohn–Sham scheme. However, it is also reasonable to base such a formalism on wave function methods, since, for example, the correlation-energy, say \(E_{co}\), from wave function methods is an implicit functional of \(\rho_1\), and does not implicitly depend on the orbitals, even though there is an explicit dependence. (This is easily proven by noting that we have \(E_{co} = E - E_1[\rho_1]\), where \(E\) is the exact electron energy, and \(E_1\) is the first order energy that is determined by \(\rho_1\).) Furthermore, such a formalism can be based on any reasonable orbitals: Hartree–Fock, Brueckner, and natural, but there is probably no advantage to using Kohn–Sham orbitals. In addition, however, when considering a wave function approach, \(E_{co}\) also has a natural dependence on the external potential \(v\) from the interacting or target state \(|\Psi\rangle\). (This is easily proven from coupled cluster theory by noting the Fock operator \(\hat{F}\) appearance in the coupled equations and noting that \(\hat{F}\) depends on \(v\).) Therefore, it is reasonable to have \(E_{co}\) depending on both on \(v\) and \(\rho_1\). Since \(v\) is a known function defining the molecular structure, the inclusion of the \(v\) should not produce any difficulties.

Below we introduce an approach based on many body perturbation theory\(^{16,17,18,35}\) where the correlation energy \(E_{co}\) is expressed as an explicit functional of \(\rho_1\), \(v\), and \(v_s\), where \(\rho_1\) is the one-particle density matrix from the noninteracting, or reference, state; \(v\) is the external potential from the interacting state \(|\Psi\rangle\); \(v_s\) is the (kernel of the) external potential from the noninteracting state. In other words we have \(E_{co}[\rho_1, v, v_s]\). Here, the \(v_s\) explicit dependence appears because the individual diagrams from the perturbative expansion depend on
the zeroth-order Hamiltonian, or, equivalently, on \( v_s \), since—together with the number of
electrons—\( v_s \) defines the zeroth-order Hamiltonian. However, unless the perturbation expansion is truncated at some order, it is easily proven that \( \mathcal{E}_{\text{co}} \) does not implicitly depend on \( v_s \), since an exact \( \mathcal{E}_{\text{co}} \) does not depend of the zeroth-order Hamiltonian. (Infinite order summations, e.g., the coupled cluster method, also have \( \mathcal{E}_{\text{co}} \) not depending on \( v_s \).)

This method presented below can, in principle, be used to compute \( \mathcal{E}_{\text{co}} \) in an accurate and efficient manner, since, like the Kohn–Sham approach, there are no virtual orbitals to consider. However, in contrast to the Kohn–Sham approach, \( \mathcal{E}_{\text{co}} \) is a known, explicit functional that can be approximated in a systematic manner. Furthermore, in contrast to the optimized potential method, the functionals are invariant to a unitary transformation of occupied orbitals. The proposed method, like the efficient wave function methods mentioned above, removes the energy denominators by using Laplace transforms, as well as other techniques, to obtain the correlation energy as an explicit functional of \( \rho_1, v, \) and \( v_s \). For simplicity, we only consider noninteracting closed-shell states and target states that are nondegenerate, singlet ground-states; so, in that case, \( \rho_1 \) denotes the spin-less one-particle density matrix from the determinantal reference state.

Let us also mention that we have recently derived a generalization of the Kohn–Sham approach in which the correlation energy \( \mathcal{E}_{\text{co}} \) is assumed to be an explicit functional of \( v \) and \( \rho_1 \). In a similar Brueckner-orbital method, called reference-state one-particle density matrix theory, \( \mathcal{E}_{\text{co}} \) is also assumed to be an explicit functional of \( v \) and \( \rho_1 \), where for closed-shell systems, the local density approximation (LDA) and the LYP, BLYP, and B3LYP functionals was shown to be compatible with the method. In both of these two approach, errors from Coulomb self-interactions do not occur, nor the need to introduce functionals defined by a constraint search. By utilizing the method presented here, explicit forms of these two correlation-energy functionals can be obtained.

II. THE NONINTERACTING STATE

A determinantal state is a wave function that is an eigenfunction of a noninteracting Hamiltonian, say \( \hat{H}_{Nv_s} \), where \( \hat{H}_{Nv_s} \) has no electron-electron interaction terms. These noninteracting Hamiltonian \( \hat{H}_{Nv_s} \) are completely specified by the number of electrons \( N \) and
the kernel of an external operator, say $v_s$. Explicitly we have

$$\hat{H}_{v_s} = \sum_{i=1}^{N} \hat{F}_{v_s}(r_i),$$  \hspace{1cm} (1)

where

$$\hat{F}_{v_s} = -\frac{1}{2}\nabla^2 + \hat{v}_s,$$  \hspace{1cm} (2)

and the nonlocal operator $\hat{v}_s$—which we require to be spin-free—is defined by its kernel $v_s$, i.e., we have

$$\hat{v}_s\chi(r_1) = \int dr_2 v_s(r_1, r_2)\chi(r_2).$$  \hspace{1cm} (3)

Using second quantization, our noninteracting Hamiltonian, given by Eq. (1), becomes

$$\hat{H}_{v_s} = \sum_{ij} (i|\hat{F}_{v_s}|j) \hat{E}_{ij},$$  \hspace{1cm} (4)

where the spin-adapted excitation operator is given by

$$\hat{E}_{ij} = \sum_{\sigma} a_i^{\sigma\dagger} a_j^{\sigma\dagger},$$  \hspace{1cm} (5)

and the one-electrons integrals are spin-free and are written in chemist’s notation; these integrals use a spatial orbital set, say $\{\chi\}$; this set has the following form:

$$\psi_{i\sigma}(r, \omega) = \chi_i(r)\sigma(\omega); \quad \sigma = \alpha, \beta,$$  \hspace{1cm} (6)

where the spatial and spin coordinates, $r$ and $\omega$, can be denoted collectively by $x$, e.g.,

$$\psi_{i\sigma}(x) = \psi_{i\sigma}(r, \omega).$$  \hspace{1cm} (7)

It is well known that there is a one-to-one mapping between determinantal states and their one-particle density matrices, say $\gamma$. For a closed-shell state we have

$$\gamma(x_1, x_2) = \sum_{x \in \{\chi_o\}} \sum_{\sigma} \chi_x(r_1)\sigma(\omega_1)\chi_x^*(r_2)\sigma^*(\omega_2) = \sum_{x \in \{\chi_o\}} \chi_x(r_1)\chi_x^*(r_2)\delta_{\omega_1\omega_2},$$  \hspace{1cm} (8)

and the spin-less one-particle density-matrix is

$$\rho_1(r_1, r_2) = \sum_{\omega} \gamma(r_1, \omega, r_2, \omega) = 2 \sum_{x \in \{\chi_o\}} \chi_x(r_1)\chi_x^*(r_2),$$  \hspace{1cm} (9)

where the sum is over the occupied orbitals from Eq. (6); this set of orbitals is denoted by $\{\chi_o\}$. Comparing Eqs. (8) and (9) yields

$$\gamma(x_1, x_2) = \frac{1}{2}\rho_1(r_1, r_2)\delta_{\omega_1\omega_2}. $$  \hspace{1cm} (10)
Since our closed-shell determinantal states are determined by $\rho_1$, henceforth, these kets are denoted by $|\rho_1\rangle$.

Using Eq. (4) and the determinantal state $|\rho_1\rangle$, our eigenvalue problem can be written as

$$\hat{H}_{vs}|\rho_1\rangle = 2 \left( \sum_{w \in \{\chi_o\}} \epsilon_w \right) |\rho_1\rangle = \mathcal{E}_0|\rho_1\rangle,$$

(11)

where the set of occupied orbitals $\{\chi_o\}$ is defined by the lowest $N$ eigenstates of $\hat{F}_{vs}$,

$$\hat{F}_{vs}\chi_w = \epsilon_w \chi_w, \; \chi_w \in \{\chi_o\} \longrightarrow \rho_1,$$

(12)

and the right side indicates that these orbitals, from the set $\{\chi_o\}$, determine $\rho_1$. The unoccupied, or virtual, orbital set $\{\chi_u\}$ are also obtained from $\hat{F}_{vs}$:

$$\hat{F}_{vs}\chi_r = \epsilon_r \chi_r, \; \chi_r \in \{\chi_u\} \longrightarrow \rho_1,$$

(13)

where these orbitals also determine $\rho_1$, since, for a complete set of orbitals, the unoccupied set determines the occupied set; two sets of orbitals that differ by a unitary transformation are considered equivalent.

While there is no restriction placed upon $v_s$, normally it contains the external potential $v$ from the interacting state $|\Psi_{Nv}\rangle$, the Coulomb potential $\hat{J}$, and an additional term, the exchange-correlation potential $\hat{v}_{xc}$, that we also permit to depend on the one-particle density matrix:

$$\hat{v}_{xs} = v + \hat{J}_{\rho_s} + \hat{v}^{\rho_1}_{xc} = v + \hat{J}_{\rho_s} + \hat{K}_{\rho_1} + \hat{v}_{xc},$$

(14)

and the latter expression defines the correlation potential $\hat{v}_{xc}$, where $\hat{K}$ is the exchange operator, defined below; the Coulomb potential $\hat{J}$, given by

$$\hat{J}_{\rho_s}(r_1) = \int \rho_{s}^{-1}(r_2) d \rho_{s}(r_2),$$

(15)

depends on the electron density $\rho_s$ of the noninteracting state $|\rho_1\rangle$:

$$\rho_s(r) = \rho_1(r, r) = 2 \sum_{w \in \{\chi_o\}} \chi_w(r)\chi^*_w(r), \; \rho_1 \longrightarrow \rho_s,$$

(16)

and we use Eq. (9); the right side of this equation indicates that $\rho_s$ is determined by $\rho_1$.

The non-local operator $\hat{v}_{xc}$ can be identified as the exchange-correlation operator. If $|\rho_1\rangle$ is the Kohn-Sham noninteracting state, this operator is local and it implicitly depends only on
the density from $|\rho_1\rangle$ and the interacting state $|\Psi_{Nv}\rangle$. For Brueckner orbital theory,\textsuperscript{40,45} this operator is nonlocal and may depend on the external potential $v$. For Hartree–Fock theory, the correlation portion of $\hat{v}_{xc}$ is absent; so, in that case, $\hat{v}_{xc}^{\rho_1}$ is just the exchange operator $\hat{K}$, where the kernel of this operator is

$$K_{\rho_1}(\mathbf{r}_1, \mathbf{r}_2) = -\frac{1}{2}r_{12}^{-1}\rho_1(\mathbf{r}_1, \mathbf{r}_2). \tag{17}$$

For latter use, we also write down the expression for the Fock operator:

$$\hat{F}_{\rho_1} = -\frac{1}{2}\nabla^2 + v + \hat{J}_{\rho_s} + \hat{K}_{\rho_1}. \tag{18}$$

### III. THE INTERACTING STATE

Now consider an interacting system of electrons. The electronic energy, say $E_{Nv}$, for an eigenstate of an interacting Hamiltonian is determined by the number of electrons $N$ and the one-body external potential $v$. This must be the case, since the non-relativistic, electronic Hamiltonian is entirely specified by $N$ and $v$:

$$\hat{H}_{Nv} = \sum_{i} N\left( -\frac{1}{2}\nabla_i^2 + v(i) + \frac{1}{2} \sum_{i \neq j}^{N} r_{ij}^{-1} \right), \tag{19}$$

where $r_{ij}^{-1}$ is the electron-electron interaction operator. Furthermore, since each $N$ and $v$ yields a different ground state wave function $|\Psi_{Nv}\rangle$. Therefore, the ground state energies $E_{Nv}$, given by

$$E_{Nv} = \frac{\langle \Psi_{Nv} | \hat{H}_{Nv} | \Psi_{Nv} \rangle}{\langle \Psi_{Nv} | \Psi_{Nv} \rangle}, \tag{20}$$

are unique functionals of $N$ and $v$.

Using a second quantization approach, the Hamiltonian does not depend on $N$, and it can be expressed by

$$\hat{H}_v = \sum_{ij} (i|(-\frac{1}{2}\nabla^2)|j)\hat{E}_{ij} + \sum_{ij} (i|v|j)\hat{E}_{ij} + \frac{1}{2} \sum_{ijkl} (ij|kl)\hat{E}_{ijkl}, \tag{21}$$

where the symmetry-adapted excitation operators are given by Eq. (3) and

$$\hat{E}_{ijkl} = \sum_{\sigma\lambda} a^\dagger_{i\sigma} a^\dagger_{k\lambda} a_{l\lambda} a_{j\sigma}, \tag{22}$$

and the two electrons integrals are spin-free and are written in chemist’s notation.\textsuperscript{18}
IV. THE CORRELATION ENERGY AS IN EXPLICIT FUNCTIONAL OF \( v, \rho_1 \) AND \( v_s \)

Using many body perturbation theory, we partition our Hamiltonian into the zeroth order part and a perturbation \( V \):

\[
\hat{H}_v = \hat{H}_{v_s} + V_{\rho_1},
\]

where we choose \( \hat{H}_{v_s} \), from Eq. (1), as our zeroth-order Hamiltonian. Using Eqs. (2), (4), (21), and (23), we have

\[
V_{\rho_1} = \frac{1}{2} \sum_{ijkl} (ij|kl) \hat{E}_{ijkl} + \sum_{ij} (i|v|j) \hat{E}_{ij} - \sum_{ij} (i|v_s|j) \hat{E}_{ij}.
\]

The energy through the first order—the zeroth-order energy plus the correction from the 1st order—for many body perturbation theory is independent of the zeroth-order Hamiltonian. This energy functional, given by

\[
E_1[\rho_1, v] = \langle \rho_1 | H_v | \rho_1 \rangle,
\]

depends on the two functions: the external potential \( v \) and the one-particle density matrix \( \rho_1 \). Explicitly, this functional is given by

\[
E_1[\rho_1, v] = \int d\mathbf{r}_1 \left[ -\frac{1}{2} \nabla_1^2 \rho_1(\mathbf{r}_1, \mathbf{r}_2) \right]_{\mathbf{r}_2=\mathbf{r}_1} + \int d\mathbf{r}_1 v(\mathbf{r}_1) \rho(\mathbf{r}_1) + \frac{1}{2} \int \int r_{12}^{-1} d\mathbf{r}_1 d\mathbf{r}_2 \rho(\mathbf{r}_1) \rho(\mathbf{r}_2) - \frac{1}{4} \int \int r_{12}^{-1} d\mathbf{r}_1 d\mathbf{r}_2 \rho_1(\mathbf{r}_1, \mathbf{r}_2) \rho_1(\mathbf{r}_2, \mathbf{r}_1).
\]

In many-body perturbation theory, the electronic energy is given by an order-by-order expansion

\[
\mathcal{E} = \mathcal{E}_0 + \mathcal{E}_1 + \mathcal{E}_2 + \mathcal{E}_3 + \cdots,
\]

where the energy through the first order is

\[
E_1 = \mathcal{E}_0 + \mathcal{E}_1,
\]

and the correlation energy \( \mathcal{E}_{\text{co}} \) includes everything beyond the first order:

\[
\mathcal{E}_{\text{co}} = \mathcal{E} - E_1 = \mathcal{E}_2 + \mathcal{E}_3 + \cdots.
\]
In order to obtain the an order-by-order expansion of the electronic energy $E$, it is convenient to write the perturbation $V_{\rho_1}$, given by Eq. (24), in normal ordered form using $|\rho_1\rangle$ as the vacuum state:

$$V_{\rho_1} = V_{c\rho_1} + V_{1\rho_1} + V_{2\rho_1},$$

(30)

where the constant, one-, and two-body terms are given by

$$V_{c\rho_1} = E_1 - E_0,$$

(31)

$$V_{1\rho_1} = -\sum_{ij} (i|\hat{\nu}_{co}^\rho_1|j)\{\hat{E}_{ij}\}_\rho_1,$$

(32)

$$V_{2\rho_1} = \frac{1}{2} \sum_{ijkl} (ij|kl)\{\hat{E}_{ijkl}\}_\rho_1,$$

(33)

where the correlation potential is defined by Eq. (14), i.e.,

$$\hat{\nu}_{co}^\rho_1 = v_s - \hat{J}_{\rho_1} - \hat{K}_{\rho_1},$$

(34)

and $E_0$, $E_1$, $\hat{J}$, and $\hat{K}$ are given by Eqs. (11), (26), (15), and (17), respectively; the brackets $\{\cdots\}_\rho_1$ indicate that the excitation operators are in normal ordered form with respect to the vacuum state $|\rho_1\rangle$. Furthermore, subtracting Eq. (18) from (2) and using Eq. (34), we have

$$\hat{\nu}_{co}^\rho_1 = \hat{F}_{\rho_1} - \hat{F}_{\rho_1}.$$ 

(35)

Eq. (32) is the most convenient expression for $V_1$. However, we can also substitute Eq. (34) into Eq. (32), yielding individual diagrams from the perturbation expansion that depend explicitly on $v$ and $v_s$. Substituting Eq. (35) into Eq. (32) separates $V_1$ into the zeroth-order part $\hat{F}$ and the Fock-operator part $\hat{F}$. (Note that $\{\hat{F}\}_\rho_1$ is the one-body portion of the Hamiltonian.) While the individual terms from the perturbation expansion can depend on $v_s$ or $\hat{F}$, the correlation energy $E_{co}$, unless approximated from a truncated expansion, cannot depend on either $v_s$ or $\hat{F}$; we now prove that $E_{co}$ is an implicit functional of $v$ and $\rho_1$.

Consider the electronic energy $E$, determined by $v$ and $N$, while $E_1$ is an explicit functional of $v$ and $\rho_1$. Hence, the correlation energy, given by $(E_{co} = E - E_1)$, is determined by $v$, $\rho_1$, and $N$, or just $v$ and $\rho_1$, since $\rho_1$ determines $N$. Therefore, as mentioned above, at least for the ground state, the correlation energy is an implicit functional of $v$ and $\rho_1$, i.e., $E_{co}[v, \rho_1]$.

We now demonstrate that the individual perturbation terms, or diagrams, can be written as explicit functional of $v$, $v_s$ and $\rho_1$. 

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FIG. 1: The three diagrams from the second-order correlation-energy $\mathcal{E}_{\text{co}}$ and two other diagrams.

Generally speaking, perturbation theory expresses $\mathcal{E}_{\text{co}}$ as a functional of the occupied and unoccupied orbitals from $|\rho_1\rangle$, their orbitals energies $\{\epsilon\}$, and the one-body portion or the perturbation $V_1$, which, in our case is $-\hat{v}_{\text{co}}^\rho$, $(v - v_s + \hat{J}_{\rho_s} + \hat{K}_{\rho_1})$, or $(\hat{F} - \hat{F'})$, as indicated in Eqs. (32), (34), and (35). The correlation-energy diagrams, however, do not depend on the constant portion of the perturbation $V_c$; also, the two-body part $V_2$ is universal, since this operator is the same for all electronic systems.

Consider for the second-order (correction to the) energy, given by

$$\mathcal{E}_2 = \mathcal{E}_{2u} + \mathcal{E}_{2d} + \mathcal{E}_{2x},$$

where the Goldstone diagrams for these terms are given by the first three entries of Fig. 1, respectively. For the first term, we have

$$\mathcal{E}_{2u}[\chi_o, \chi_u, \epsilon, v_{\text{co}}^\rho] = 2 \sum_{w} \sum_{r} \frac{1}{\epsilon_w - \epsilon_r} (r|\hat{v}_{\text{co}}^\rho|w)(w|\hat{v}_{\text{co}}^\rho|r),$$

where this diagram depends explicitly on $v_{\text{co}}^\rho$—the kernel of $\hat{v}_{\text{co}}^\rho$—the orbital energies $\{\epsilon\}$, and both the occupied and unoccupied orbitals, $\{\chi_o\}$ and $\{\chi_u\}$. Writing out the integrations explicitly, we have

$$\mathcal{E}_{2u}[\chi_o, \chi_u, \epsilon, v_{\text{co}}^\rho] = 2 \sum_{wr} \int \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{1}{\epsilon_w - \epsilon_r} \hat{v}_{\text{co}}^\rho(\mathbf{r}_1)\chi_w(\mathbf{r}_1)\chi_w^*(\mathbf{r}_2)\hat{v}_{\text{co}}^\rho(\mathbf{r}_2)\chi_r(\mathbf{r}_2)\chi_r^*(\mathbf{r}_1).$$

In order to remove the energy denominator, we use the following Laplace transform:

$$\frac{1}{\epsilon_w - \epsilon_r} = \int_0^\infty dt e^{-t(\epsilon_w - \epsilon_r)},$$

giving

$$\mathcal{E}_{2u}[\chi_o, \chi_u, \epsilon, \hat{v}_{\text{co}}^\rho] =$$

$$2 \sum_{wr} \int \int d\mathbf{r}_1 d\mathbf{r}_2 \int_0^\infty dt_1 e^{t_1\epsilon_r}\chi_r^*(\mathbf{r}_1)\hat{v}_{\text{co}}^\rho(\mathbf{r}_1)e^{-t_1\epsilon_w}\chi_w(\mathbf{r}_1)\chi_w^*(\mathbf{r}_2)\hat{v}_{\text{co}}^\rho(\mathbf{r}_2)\chi_r(\mathbf{r}_2).$$

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Using Eqs. (12) and (13), and the observation that \( \hat{F}_{v_s} \) depends explicitly on the kernel \( v_s \), and, according to Eq. (21), \( \hat{v}_{co}^{\rho_1} \) depends explicitly on \( v \) and \( v_s \), we have

\[
\mathcal{E}_{2u}[\chi_o, \chi_w, v, v_s] = 2 \sum_{wr} \int d\mathbf{r}_1 d\mathbf{r}_2 \int_0^\infty dt_1 \left(e^{t_1 \hat{F}_{v_s}^* \chi_r^*(\mathbf{r}_1)} \hat{v}_{co}^{\rho_1}(\mathbf{r}_1) \left(e^{-t_1 \hat{F}_{v_s}^* \chi_w(\mathbf{r}_1)} \chi_w^*(\mathbf{r}_2) \hat{v}_{co}^{\rho_1}(\mathbf{r}_2) \chi_r(\mathbf{r}_2)\right)\right),
\]

where \( \hat{F}_{v_s}^* \) denotes \( \hat{F}_{v_s}(\mathbf{r}_i) \) and the round brackets \( \cdots \) serve to remind us that \( e^{t_1 \hat{F}_{v_s}^* \chi_r^*} \) acts exclusively upon \( \chi_r^*(\mathbf{r}_1) \) and \( e^{-t_1 \hat{F}_{v_s}^*} \chi_w(\mathbf{r}_1) \) acts upon \( \chi_w(\mathbf{r}_1) \). Note that, since \( \hat{v}_s \) and \(-\frac{1}{2} \nabla^2 \) do not commute, the exponential operator, defined by

\[
e^{t \hat{F}_{v_s}^* \chi_r^*} = \exp \left[t(-\frac{1}{2} \nabla^2 + \hat{v}_s)\right] = 1 + t \left(-\frac{1}{2} \nabla^2 + \hat{v}_s\right) + \frac{t^2}{2!} \left(-\frac{1}{2} \nabla^2 + \hat{v}_s\right) \left(-\frac{1}{2} \nabla^2 + \hat{v}_s\right) + \cdots,
\]

cannot separate into two factors.\(^{46}\)

\[
\exp \left[t(-\frac{1}{2} \nabla^2 + \hat{v}_s)\right] \neq \exp \left[t(-\frac{1}{2} \nabla^2)\right] \times \exp \left[t \hat{v}_s\right], \quad \text{if} \quad \left[-\frac{1}{2} \nabla^2, \hat{v}_s\right] \neq 0. \quad (43)
\]

In order to make our formulas less cluttered, especially when considering high order diagrams, we introduce a notation where the brackets are understood:

\[
\mathcal{E}_{2u}[\chi_o, \chi_w, v, v_s] = 2 \sum_{wr} \int d\mathbf{r}_1 d\mathbf{r}_2 \int_0^\infty dt_1 e^{t_1 \hat{F}_{v_s}^* \chi_r^*(\mathbf{r}_1)} \hat{v}_{co}^{\rho_1}(\mathbf{r}_1) \chi_w^*(\mathbf{r}_1) \chi_w(\mathbf{r}_2) \hat{v}_{co}^{\rho_1}(\mathbf{r}_2) \chi_r(\mathbf{r}_2),
\]

where \( \hat{F}_{v_s} \) is identical to \( \hat{F}_{v_s}^* \), except that it acts exclusively on \( \chi_r^* \); it does not act on the correlation operator \( \hat{v}_{co}^{\rho_1} \) (or its kernel \( v_{co}^{\rho_1} \)) or the complex conjugate function \( \chi_r^* \). Similarly, \( \hat{F}_{v_s}^* \) is identical to \( \hat{F}_{v_s} \), except that it acts exclusively on \( \chi_r \); it does not act on \( v_{co}^{\rho_1} \) or \( \chi_r^* \). The following identities clarify these definitions:

\[
e^{-t_1 \hat{F}_{v_s}^* \chi_r^*} = \chi_r^*(\mathbf{r}_1) \hat{v}_{co}^{\rho_1}(\mathbf{r}_1) \chi(\mathbf{r}_1) = \chi_r^*(\mathbf{r}_1) \hat{v}_{co}^{\rho_1}(\mathbf{r}_1) e^{-t_1 \hat{F}_{v_s}^*} \chi(\mathbf{r}_1), \quad (45)
\]

\[
e^{-t_1 \hat{F}_{v_s} \chi} = \chi(\mathbf{r}_1) \hat{v}_{co}^{\rho_1}(\mathbf{r}_1) \chi^*(\mathbf{r}_1) = \chi(\mathbf{r}_1) \hat{v}_{co}^{\rho_1}(\mathbf{r}_1) e^{-t_1 \hat{F}_{v_s}^*} \chi^*(\mathbf{r}_1). \quad (46)
\]

In order to further compress our notation, we define the following transformed correlation operator:

\[
\hat{v}_{co}^{\rho_1}(\mathbf{z}_i) = e^{t_i \hat{F}_{v_s}^*} \hat{v}_{co}^{\rho_1}(\mathbf{r}_i) e^{-t_i \hat{F}_{v_s}^*}, \quad (47)
\]

where \( \mathbf{z}_i \) is a combined index of \( \mathbf{r}_i \) and \( t_i \), i.e., \( \mathbf{z}_i = \mathbf{r}_i, t_i \). This notation yields

\[
\mathcal{E}_{2u}[\rho_1, \kappa_{\rho_1}, v, v_s] = \frac{1}{2} \int d\mathbf{r}_1 d\mathbf{r}_2 \int_0^\infty dt_1 \hat{v}_{co}^{\rho_1}(\mathbf{r}_1, \mathbf{r}_2) \hat{v}_{co}^{\rho_1}(\mathbf{r}_2) \kappa_{\rho_1}(\mathbf{r}_2, \mathbf{r}_1), \quad (48)
\]
where \( \rho_1 \) is given by Eq. (49), while its orthogonal complement, \( \kappa_{\rho_1} \), is given by

\[
\kappa_{\rho_1}(r_1, r_2) = 2 \sum_{r \in \{\chi_u\}} \chi_r(r_1)\chi^*_r(r_2),
\]

and the sum is over the unoccupied orbitals \( \{\chi_u\} \). For a complete set of basis functions, we have

\[
\delta(r_1 - r_2) = \sum_i \chi_i(r_1)\chi^*_i(r_2), \quad i \in \{\chi_o\} \cup \{\chi_u\},
\]

and therefore

\[
\delta(r_1 - r_2) = \frac{1}{2} \left( \rho_1(r_1, r_2) + \kappa_{\rho_1}(r_1, r_2) \right).
\]

So we can remove \( \kappa_{\rho_1} \) from Eq. (48), giving

\[
\mathcal{E}_{2u}[\rho_1, v, v_s] = \int \int dr_1 dr_2 \int_0^\infty dt_1 \tilde{v}^{v_1}_{\text{cop}} \rho_1(r_1, r_2)\tilde{v}^{\rho_1}_{\text{co}}(r_2)\delta(r_2 - r_1)
\]

\[
- \frac{1}{2} \int \int dr_1 dr_2 \int_0^\infty dt_1 \tilde{v}^{v_1}_{\text{cop}} \rho_1(r_1, r_2)\tilde{v}^{\rho_1}_{\text{co}}(r_2)\rho_1(r_2, r_1).
\]

Hence, we have \( \mathcal{E}_{2u} \) as an explicit functional \( v, v_s, \) and \( \rho_1 \).

In order to evaluate Eq. (52), one must handle the operator \( \exp(t\hat{F}) \) acting on the Dirac delta function \( \delta \), since the first term on the right side is given by

\[
\int \int dr_1 dr_2 \int_0^\infty dt_1 \tilde{v}^{v_1}_{\text{cop}} \rho_1(r_1, r_2)\tilde{v}^{\rho_1}_{\text{co}}(r_2)\delta(r_2 - r_1)
\]

\[
= \int \int dr_1 dr_2 \int_0^\infty dt_1 \tilde{v}^{\rho_1}_{\text{co}}(r_1) \left( e^{-t_1\hat{F}_{v_1}} \rho_1(r_1, r_2) \right) \tilde{v}^{\rho_1}_{\text{co}}(r_2) \left( e^{t_1\hat{F}_{v_1}} \delta(r_2 - r_1) \right).
\]

Using the expansion for \( e^{\hat{F}_{v_1}} \) given by Eq. (42), this factor will yield terms containing the Laplacian operator \( \nabla^2 \) acting on \( \delta \), i.e., \( \nabla^2 \delta \), as well as other higher order terms, e.g., \( \nabla^4 \delta \).

One way to handle these terms is by using a basis set expansion for \( \delta \), as in Eq. (50), where any complete basis can be used that satisfy the boundary conditions. Another possibility is to use one of the integral representations of the delta function, for example,

\[
\delta(r_1 - r_2) = \frac{1}{8\pi^3} \int e^{ik(r_1 - r_2)} dk.
\]

Now consider the second term of Eq. (36), given by the second diagram from Fig. 1, evaluating this diagram yields the following expression:

\[
\mathcal{E}_{2d}[\chi_o, \chi_u, \epsilon] = 2 \sum_{w \in \{\chi_o\}} \sum_{x \in \{\chi_o\}} \sum_{r \in \{\chi_u\}} \sum_{s \in \{\chi_u\}} \frac{1}{\epsilon_w - \epsilon_r + \epsilon_x - \epsilon_s} (rw|sx)(wr|xs),
\]
and this term can be written as

\[
E_{2d}[\chi_0, \chi_w, \epsilon] = 2 \sum_{ux} \sum_{rs} (\epsilon_w - \epsilon_r + \epsilon_x - \epsilon_s)^{-1} \times \int \int \int dr_1 dr_2 dr_3 dr_4 r_{12}^{-1} \chi^*_w(r_1) \chi_w(r_1) \chi^*_s(r_2) \chi_s(r_2) \chi^*_x(r_3) \chi_x(r_3) r_{34}^{-1} \chi^*_x(r_4) \chi_x(r_4).
\]

Using a generalization of Eq. (39), we have

\[
E_{2d}[\chi_0, \chi_w, \epsilon] = 2 \sum_{ux} \sum_{rs} \int \int \int dr_1 dr_2 dr_3 dr_4 \int_0^\infty dt_{12} \times e^{t_1 t_{12}} e^{t_2 t_{12}} e^{-t_{12} t_{w}} \chi^*_w(r_1) \chi_w(r_1) \chi^*_s(r_2) \chi_s(r_2) \chi^*_x(r_3) \chi_x(r_3) r_{34}^{-1} \chi^*_x(r_4) \chi_x(r_4).
\]

Using our notation, defined by Eqs. (47) and (48), and Eqs. (49) and (19), we obtain

\[
E_{2d}[\rho_1, v_s] = \frac{1}{8} \int \int \int dr_1 dr_2 dr_3 dr_4 \int_0^\infty \int_0^\infty dt_{12} \times (r_{12}^{v_s})^{-1} \rho_1(\mathbf{r}_1, \mathbf{r}_3) \kappa_{\rho_1}(\mathbf{r}_3, \mathbf{r}_1) \rho_1(\mathbf{r}_2, \mathbf{r}_4) \kappa_{\rho_1}(\mathbf{r}_4, \mathbf{r}_2) r_{34}^{-1},
\]

where the transformed electron-electron interaction term \((r_{12}^{v_s})^{-1}\) depends on the variables \(t_{12}, \mathbf{r}_1, \mathbf{r}_2\), and the function \(v_s\); this operator has the following form:

\[
\frac{1}{r_{12}^{v_s}} = e^{t_1 t_{12}} e^{t_2 t_{12}} e^{-t_{12} t_{w}} e^{t_{12} t_{w}} e^{-t_2 t_{w}} e^{-t_{12} t_{w}}.
\]

The 2d subscript indicates that \(E_{2d}\) correspond to a second order “direct” diagram. The second-order exchange term \(E_{2x}\), from Eq. (56), is represented by the third diagram of Fig. 1. This diagram can be evaluated in a similar way as the direct one \(E_{2d}\), giving

\[
E_{2x}[\rho_1, v_s] = -\frac{1}{16} \int \int \int dr_1 dr_2 dr_3 dr_4 \int_0^\infty \int_0^\infty dt_{12} \times (r_{12}^{v_s})^{-1} \rho_1(\mathbf{r}_1, \mathbf{r}_3) \kappa_{\rho_1}(\mathbf{r}_3, \mathbf{r}_1) \rho_1(\mathbf{r}_2, \mathbf{r}_4) \kappa_{\rho_1}(\mathbf{r}_4, \mathbf{r}_2) r_{34}^{-1}.
\]

Note that the \(E_{2d}\) and \(E_{2x}\) do not explicitly depend on the external potential \(v\).

In Fig. 1, the dummy indices that are used are denoted in the diagrams. For example, the first diagram has \(z_1\) for the first vertex and \(r_2\) for the second index, where these choices are indicated by 1 and 2 in the figure. In order to evaluate this diagram and obtain Eq. (56) directly, we start at the bottom vertex and go backwards: The bottom vertex gives a factor of \(-\nu_{12} z_1\); the hole line from vertex 1 to 2 gives a factor of \(\frac{1}{2} \rho_1(\mathbf{r}_1, \mathbf{r}_2)\); the top vertex gives...
the particle line from vertex 2 to 1 gives $\frac{1}{2}\kappa\rho_1(r_2, r_1)$. Furthermore, there is an additional factor of two for the loop, since the spin state is conserved on an orientated path. Similarly, the second two diagrams from the figure can be evaluated to give Eqs. (58) and (60), where in both diagrams, the lower interactions, with dummy indices $r_1, r_2$ and $t_{12}$, yield the operator $(\hat{r}_{12})^{-1}$. For the second diagram in the figure, the direct one $E_{2d_1}$, we have the following factors: a $\frac{1}{2}$, since the diagram is symmetric, a factor of $2 \times 2$ for the two loops, and a factor of $\frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} \times \frac{1}{2}$ for the two $\rho_1$ terms and two $\kappa$ terms. Putting this together gives $\frac{1}{2} \times 2 \times 2 \times \frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} = \frac{1}{8}$, in agreement with Eq. (58).

Now consider the fourth diagram in Fig. 1, where for convenience we denote this third order diagram by $E_{3d}^{hh}$, since this is a direct diagram where the middle interaction lies on two hole lines. Evaluating this diagram gives

$$E_{3d}^{hh} = 2 \sum_{wx} \sum_{rs} \sum_{yz} \frac{(yr|zs)(wy|xz)(rw|sx)}{(\epsilon_y - \epsilon_r + \epsilon_z - \epsilon_s)(\epsilon_w - \epsilon_r + \epsilon_x - \epsilon_s)},$$

where we have two energy denominators: One corresponding to the lowest interaction, given by $(\epsilon_w + \epsilon_x - \epsilon_r - \epsilon_s)$, and one for the middle interaction, given by $(\epsilon_y + \epsilon_z - \epsilon_r - \epsilon_s)$, where we denote the occupied orbitals by $w, x, y, z$ and the unoccupied orbitals by $r$ and $s$. Using the following identity:

$$\frac{1}{\epsilon_j \epsilon_i} = \int_{0}^{\infty} dt_2 e^{-t_2(\epsilon_j - \epsilon_i)} \int_{t_2}^{\infty} dt_1 e^{-t_1 \epsilon_i},$$

the product of the two energy denominator can be written as

$$\frac{1}{(\epsilon_y - \epsilon_r + \epsilon_z - \epsilon_s)(\epsilon_w - \epsilon_r + \epsilon_x - \epsilon_s)} = \int_{0}^{\infty} dt_{34} e^{-t_{34}(\epsilon_y - \epsilon_w + \epsilon_z - \epsilon_s)} \int_{t_{34}}^{\infty} dt_{12} e^{-t_{12}(\epsilon_w - \epsilon_r + \epsilon_x - \epsilon_s)}.$$
elements gives
\[
\langle rw|sx\rangle\langle wy|xz\rangle = \int \int \int d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 d\vec{r}_4 
\times \int_0^\infty dt_{34} \int_0^\infty dt_{12} \left( e^{t_{12} e_{12} s} e^{t_{12} w} e^{t_{12} w} \chi^*_w(\vec{r}_1)\chi_w(\vec{r}_1)\chi_w^*(\vec{r}_2)\chi_w(\vec{r}_2) \right) \]
\[
\times \left( e^{t_{34} e_{34} w} e^{t_{34} e_{34} w} e^{t_{34} e_{34} w} \chi^*_w(\vec{r}_3)\chi_w(\vec{r}_3)\chi_w^*(\vec{r}_4)\chi_w(\vec{r}_4) \right)
\]
\[
= \int \int \int d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 d\vec{r}_4 \int_0^\infty dt_{34} \int_0^\infty dt_{12} \times \left( \tilde{r}_{12}^{x_1} \chi^*_x(\vec{r}_1)\chi_x(\vec{r}_1)\chi_x^*(\vec{r}_2)\chi_x(\vec{r}_2) \right) \left( \tilde{r}_{34}^{y_2} \chi^*_x(\vec{r}_3)\chi_x(\vec{r}_3)\chi_x^*(\vec{r}_4)\chi_x(\vec{r}_4) \right),
\]
where we used Eq. (59). Comparing Eqs. (61) and (64), and using Eqs. (9) and (19), gives
\[
E^{hh}_{3d}[\rho_1, v_s] = \frac{1}{32} \int \int \int \int d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 d\vec{r}_4 d\vec{r}_5 d\vec{r}_6 \int_0^\infty dt_{34} \int_0^\infty dt_{12} \times \left( \tilde{r}_{12}^{y_1} \chi^*_x(\vec{r}_1)\chi_x(\vec{r}_1)\chi_x^*(\vec{r}_2)\chi_x(\vec{r}_2) \right) \left( \tilde{r}_{34}^{y_2} \chi^*_x(\vec{r}_3)\chi_x(\vec{r}_3)\chi_x^*(\vec{r}_4)\chi_x(\vec{r}_4) \right) \left( \tilde{r}_{56}^{y_1} \rho_1(\vec{r}_1, \vec{r}_3)\rho_1(\vec{r}_3, \vec{r}_5)\kappa_{\rho_1}(\vec{r}_5, \vec{r}_1)\rho_1(\vec{r}_2, \vec{r}_4)\rho_1(\vec{r}_4, \vec{r}_6)\kappa_{\rho_1}(\vec{r}_6, \vec{r}_2) \right).
\]

Note that in this diagram the two bottom interactions, \( r_{12}^{-1} \) and \( r_{34}^{-1} \), are transformed into \( \tilde{r}_{12}^{y_1} \) and \( \tilde{r}_{34}^{y_2} \), respectively, while the top interaction, \( r_{56}^{-1} \), is not transformed. Furthermore, the transformed interaction that is next to the top, \( \tilde{r}_{34}^{y_2} \), with the dummy index \( t_{34} \), gives an integration limit of 0 to \( \infty \), while the one below that, \( \tilde{r}_{12}^{y_1} \), with the dummy index \( t_{12} \), has an integration limit of \( t_{34} \) to \( \infty \). By considering higher-order diagrams, and by generalizing the identity given by Eq. (62), e.g. (19), it is easily shown that the following rules apply to all diagram: 1) A factor of \( \frac{1}{2} \rho_1 \) and \( \frac{1}{2} \kappa_{\rho_1} \) is given for each hole and particle line, respectively. 2) Interactions given by \( \tilde{v}_{\rho_1}(\vec{r}_i) \) and \( r_{ij}^{-1} \) are transformed into \( \tilde{v}_{\rho_1}(\vec{r}_i) \) and \( \tilde{r}_{ij}^{-1} \), unless they are the last, or uppermost, interaction. 3) The spatial dummy indices, \( \vec{r}_1, \vec{r}_2, \ldots \), are integrated over. 4) A \( t_i \) dummy index from \( \tilde{v}_{\rho_1}(\vec{r}_i) \) and a \( t_{ij} \) index from \( \tilde{r}_{ij}^{-1} \) are integrated over using the following rules to obtain their integration limits: i) If the interaction—either \( \tilde{v}_{\rho_1}(\vec{r}_i) \) or \( \tilde{r}_{ij}^{-1} \)—is the second from the top—the next to the last one—the integration limit is from 0 to \( \infty \). ii) For other interactions, the integration limit is from \( t_j \) to \( \infty \), if the interaction above it is \( \tilde{v}_{\rho_1}(\vec{r}_j) \), while, the integration limit is from \( t_{jk} \) to \( \infty \), if the interaction above it is \( \tilde{r}_{jk}^{-1} \). In addition, we also have the usual rules of symmetry and sign factors as well as a factor of two for each loop corresponding to a sum.
over each spin state, $\alpha$ and $\beta$. Also, according to Eq. (32), the one-body interaction has a negative sign associated with it, it is $-\tilde{v}_{c_0}$.

As a final example, consider the last diagram appearing in Fig. 1, where we denote this arbitrary (arb) fourth order diagram by $E_{\text{arb}}$. Using the rules above we get

$$E_{\text{arb}}[\rho_1, v, v_s] = -\frac{1}{32} \int \int \int \int \int \int \int \int \int \int dr_1 dr_2 dr_3 dr_4 dr_5 dr_6 dr_7 \int_0^\infty dt_5 \int_0^\infty dt_{34} \int_0^\infty dt_{57} \times (\tilde{v}_{d_3})^{-1} (\tilde{v}_{d_4})^{-1} \tilde{v}_{c_0} \int_0^{\infty} \rho_1(\mathbf{r}_1, \mathbf{r}_3) \rho_1(\mathbf{r}_3, \mathbf{r}_6) \kappa_{\rho_1}(\mathbf{r}_6, \mathbf{r}_1) \rho_1(\mathbf{r}_1, \mathbf{r}_2) \rho_1(\mathbf{r}_2, \mathbf{r}_4) \rho_1(\mathbf{r}_4, \mathbf{r}_7) \kappa_{\rho_1}(\mathbf{r}_7, \mathbf{r}_5) \kappa_{\rho_1}(\mathbf{r}_5, \mathbf{r}_2).$$

Hence, using the above rules for all diagram, and Eqs. 33) and 51)—for $\hat{\rho}_{c_0}$ and $\kappa_{\rho_1}$—yields the correlation energy $E_{\text{co}}$ as an explicit functional $\rho_1, v, v_s$, i.e., $E_{\text{co}}[\rho_1, v, v_s]$. The other two choices are $E_{\text{co}}$ as an explicit functional $\rho_1, v_{c_0}$ and $v_s$, or, using Eq. 35), $E_{\text{co}}$ as an explicit functional $\rho_1, v$, and $\hat{F}_{\rho_1}$, i.e., $E_{\text{co}}[\rho_1, v, \hat{F}_{\rho_1}]$, where the $v$ dependence arises from the Fock operator $\hat{F}_{\rho_1}$, using Eq. (18).

It is well known the the correlation energy cannot depend on the zeroth order Hamiltonian $\hat{F}_{\rho_1}$. Therefore, while the expansion $E_{\text{co}}[\rho_1, v, \hat{F}_{\rho_1}]$ has individual diagrams that explicitly depend of $\hat{F}_{\rho_1}$, the entire series does not. Certain infinite-order partial summations also yield results that are independent of a zeroth order Hamiltonian. For example, if all diagrams are included that correspond to a coupled cluster calculation, the final approximation of $E_{\text{co}}$ does not depend on the zeroth order Hamiltonian $\hat{F}_{\rho_1}$, that is, we have the following implicit functional: $E_{\text{co}}[\rho_1, v]$.

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