Reference–State One–Particle Density–Matrix Theory

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Abstract

A density-matrix formalism is developed based on the one-particle density-matrix of a single-determinantal reference-state. Unlike traditional density-functional-theory approaches, the \( v \)-representable problem does not appear in the proposed method, nor the need to introduce functionals defined by a constrained search; furthermore, the necessary conditions for a one-particle density matrix to come from a single determinant are known, so they can be expressed as constraints when minimizing variational-energy functionals. The correlation-energy functionals are not universal, in the sense that they depend on the external potential. Nevertheless, model systems can still be used to derive universal energy-functionals. For example, the Colle–Salvetti functional is shown to be compatible with the proposed method. In addition, the correlation-energy functionals can be partitioned into individual terms that are – to a varying degree – universal; yielding, for example, an electron gas approximation, where the gas in not assumed to be uniform. Variational and non-variational energy functionals are introduced that yield the target state when the reference state – or its corresponding one-particle density matrix – is constructed from Brueckner orbitals. Using many-body perturbation theory, diagrammatic expansions are given for the non-variational energy-functionals, where the individual diagrams explicitly depend on the one-particle density-matrix. Non-variational energy-functionals yield generalized Hartree–Fock equations involving a non-local correlation-potential and the Hartree–Fock exchange; these equations are obtained by imposing the Brillouin–Brueckner condition. The same equations – for the most part – are obtained from variational energy-functionals using functional minimizations, yielding the (kernel of) correlation potential as the functional derivative of correlation-energy functionals. Approximations for the correlation-energy functions are introduced, including a one-particle-density-matrix variant of the local-density approximation (LDA), a variant of the Lee–Yang–Parr (LYP) functional, and a variant of the correlation-energy functional used in the so-called B3LYP approach. A brief comparison with the exact SCF theory by Löwdin is presented.

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I. INTRODUCTION

Many variants of density functional theory (DFT) [1, 2, 3, 4, 5, 6] share common features with the Hartree–Fock approach. In particular, the Kohn–Sham method [7] uses orbital equations that appear similar, in certain respects, with the ones from Hartree–Fock theory. On the other hand, unlike the Hartree–Fock wavefunction, the Kohn-Sham determinantal state shares only a common density with the exact wavefunction, and is not considered an approximation of the ground-state. Furthermore, in contrast to the exchange potential from Hartree–Fock theory, the Kohn–Sham exchange-correlation potential is local.

DFT approaches that use hybrid functionals [8, 9, 10, 11] introduce a component of exact exchange-energy, where justification, in part, for this modification comes from the adiabatic connection [12, 13, 14, 15, 16], yielding an approach that, again, has more similarities with Hartree–Fock, especially since its energy functional yields a non-local potential – the Hartree-Fock exchange – that depends on the one-particle density matrix of the Kohn-Sham determinantal state. The most celebrated hybrid functional, B3LYP [8, 17], contains three parameters, two correlation-energy functionals, the Dirac-exchange functional (with a correction), and, of course, exact exchange. The LYP density functional [18] – a key component of B3LYP – is derived from the Colle–Salvetti correlation-energy functional [19], where this functionals depends on a one-particle density-matrix, say $\tilde{\gamma}$, where $\tilde{\gamma}$ is from the Hartree-Fock reference state, and not an exact eigenstate, indicating a further evolutionary step of DFT methods towards a Hartree-Fock generalization with inclusion of electron correlation.

In the Hartree–Fock Kohn–Sham approach [20], the exchange energy is treated in an exact manner and the non-local, Hartree–Fock exchange-potential appear in the orbital equations. A generalization of this approach by Lindgren and Salomonson [21] yields, in addition, a nonlocal correlation potential and orbitals that, they believe, are very similar to Brueckner orbitals. Other workers also suggest that Brueckner and Kohn-Sham orbitals are very similar [22].

Brueckner orbital theory [21, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37] is a generalization of Hartree–Fock theory that utilizes a single-determinantal state that has the maximum overlap with an exact eigenfunction [38, 39]. Below we use this formalism to develop a density-matrix theory, in which a variety of variational and non-variational energy-functionals are introduced that depend on the one-particle density-matrix, say $\gamma$. 
Unlike other approaches, where $\gamma$ is the one-particle density-matrix of an exact eigenfunction $^{40, 41, 42, 43, 44, 45}$, the introduced method – called *reference-state one-particle density-matrix theory* – has $\gamma$ arising from a single-determinantal reference state, where the energy-functionals yield the exact energy when $\gamma$ is the one from the Brueckner reference-state.

One advantage that this one-particle, density-matrix approach has over traditional density-functional formalisms – or one-particle density-matrix formalisms – is that there is no $v$-representable problem $^{1, 2, 46}$ nor the need to introduce functionals defined by a constrained search $^{43, 47, 48}$. Furthermore, the necessary conditions for a one-particle density matrix $\gamma$ to come from a single determinant are known, and they can be expressed as constraints when minimizing energy functionals that depend on $\gamma$ $^{49, 50}$.

Below, generalized Hartree–Fock equations are obtained containing the exact exchange-potential and a nonlocal correlation-potential, where these equations are obtained using the Brillouin-Brueckner condition – using non-variational energy functionals – and functional minimization – using variational functionals. Both variational and non-variational approached lead to the same correlation potential and generalized Fock-operator. (Correlation potentials from either approach are the same, in the sense that the (occupied) Brueckner-orbitals obtained from the *variational* correlation-potential differs only from the orbitals obtained from the *non-variational* one by unitary transformation.)

Using time-independent many-body perturbation theory $^{51, 52, 53, 54, 55, 56}$, diagrammatic expansions are given for the non-variational energy-functionals that are expressed in terms of orbitals and orbital energies. When restrictions are placed on the orbital energies, the individual diagrams are shown to explicitly depend on the one-particle density-matrix of the reference state. The diagrammatic expansions for the variational-energy functionals are presented elsewhere $^{57}$.

Kohn–Sham variants of DFT employ a universal exchange-correlation functional, independent of the external potential; approximations can be derived from model systems, where, in the vicinity of the model systems, the general form of the exchange-correlation functional is known. In contrasts, the correlation-energy functionals introduced below depend on the external potential, and are, therefore, in this sense, *not* universal. Nevertheless, as shown below, the correlation-energy functionals can be partitioned into individual terms that are – to a varying degree – universal; approximations can be derived from model systems. For example, the electron-gas correlation-energy can be used in an *electron gas approximation*,
where, unlike the local density approximation (LDA), the gas is not assumed to be uniform.

In addition, even without partitioning of the correlation-energy functionals – with the external-potential dependence intact – approximate functionals can still be derived from model systems. For example, as discussed below, the Colle–Salvetti functional[19] – derived from the helium atom – is a valid approximation within the proposed method.

II. OVERVIEW

Sec. V introduces four trial wavefunctions – say \(|\Psi_{\Phi}^{(\eta)}\rangle\), where \(\eta = I, II, III,\) and IV – that are defined with respect to a single-determinantal reference-state, say \(|\Phi\rangle\). The first trial-wavefunction \(|\Psi_{\Phi}^{(I)}\rangle\) is simply the target state of interest, say \(|\Psi\rangle\), with the single excitations removed. The second trial-wavefunction \(|\Psi_{\Phi}^{(II)}\rangle\) is defined with respect to the target state expressed by an exponential ansatz: \(|\Psi\rangle = e^{S}|\Phi\rangle\), where \(|\Psi_{\Phi}^{(II)}\rangle\) is generated by removing the single-excitation amplitudes \(S_1\) from the cluster-operator \(S\). All of the trial states \(|\Psi_{\Phi}^{(\eta)}\rangle\) – including the third and fourth ones defined below – share the property that they contain no single excitations; furthermore, they generate the target state of interest \(|\Psi\rangle\) when their reference states satisfies \(|\Phi\rangle = |\Theta\rangle\), where \(|\Theta\rangle\) is the determinantal state constructed from occupied Bruckner orbitals. In other words, we have \(|\Psi_{\Theta}^{(\eta)}\rangle = |\Psi\rangle\).

Using intermediate normalization, the exact energy of interest, say \(\mathcal{E}\), is just \(\langle \Phi | H | \Psi \rangle\), and it can be partitioned into two terms: the first-order energy, say \(E_1[\Phi]\) – given by \(\langle \Phi | H | \Phi \rangle\) – and the correlation energy, say \(\mathcal{E}_{\text{co}}[\Phi]\) – which, unlike \(\mathcal{E}\), is a functional of the reference state \(|\Phi\rangle\); these concepts are briefly review in Sec. III A.

Four non-variational energy-functionals, say \(E_\eta[\Phi]\), are defined in an analogous way as \(\mathcal{E}\): \(E_\eta[\Phi] = \langle \Phi | H | \Psi_{\Phi}^{(\eta)} \rangle\), where they yield the exact energy for the Bruckner reference-state: \(\mathcal{E} = E_\eta[\Theta]\), and these functionals can also be partitioned into two terms: \((E_\eta[\Phi] = E_1[\Phi] + E_{\text{co}}^{(\eta)}[\Phi])\), where \(E_{\text{co}}^{(\eta)}[\Phi]\) is the correlation-energy functional, and we have \((\mathcal{E}_{\text{co}}[\Theta] = E_{\text{co}}^{(\eta)}[\Theta])\); the details are presented in Sec. V.

Because of the one-to-one correspondence between the set of determinant states, say \(|\Phi\rangle\), and the one-particle density-matrices \(\gamma\), say \(\{\gamma\}\), the correlation energy, say \(\mathcal{E}_{\text{co}}[\gamma]\), and the correlation-energy functionals, say \(E_{\text{co}}^{(\eta)}[\gamma]\) – or any other functions and functionals of \(\gamma\) – can be transferred into ones that depend on the one-particle density-matrix \(\gamma\).
as discussed in Sec. VIII A, the correlation-energy and exact energy satisfy: 
\( E_{\text{co}}[\tau] = E_{\text{co}}^{(\eta)}[\tau] \) and \( (\mathcal{E} = E_{\eta}[\tau]) \), where \( \tau \) is the one-particle density matrix of the Brueckner reference-state \( |\Theta\rangle \).

Unlike the first-two trial wavefunctions, \( |\Psi^{(I)}\rangle \) and \( |\Psi^{(II)}\rangle \), that are generated by removing single-excitation amplitudes from the target state \( |\Psi\rangle \), the third and fourth trial wavefunctions, \( |\Psi^{(III)}\rangle \) and \( |\Psi^{(IV)}\rangle \), are obtained by solving the coupled-cluster theory\[56, 58, 60, 61, 62, 63, 64, 65\] and configuration interaction\[66, 67, 68, 69, 70, 71, 72\] equations, respectively, in an approximate way – by neglecting the single-excitation portions.

The coupled cluster formalism is briefly reviewed in Sec. III B. A transparent perturbative treatment of the coupled cluster theory is presented in Sec. III C that is useful to obtain a perturbative expansion for the third correlation-energy functional \( E_{\text{co}}^{(III)} \). (This approach is compared to Lindgren’s variant of the link diagram theorem in Sec. IIIE.) Sec. III D reviews Rayleigh-Schrödinger perturbation theory that can be used to generate the fourth correlation-energy functional \( E_{\text{co}}^{(IV)} \) when the linked diagram theorem is not invoked and the single-excitation subspace is neglected.

In Secs. VIII B and VIII C, diagrammatic expansions using many-body perturbation theory are presented for the correlation energy \( E_{\text{co}}[\gamma] \) and the correlation-energy functionals \( E_{\text{co}}^{(\eta)}[\gamma] \). The individual diagrams depend on the orbitals – both occupied and unoccupied – and the orbital energies – defined by the zeroth-order Hamiltonian. By using degenerate sets of occupied and unoccupied orbitals, and additional methods, it is demonstrated that diagrams can be defined that explicitly depend \( \gamma \).

In Sec. IX an approach based on many-body perturbation theory is introduced, where the perturbation is partitioned into terms that depend on the external potential, say \( v \), and the remaining portion that is \( v \) independent; the perturbation expansions for the correlation energy \( E_{\text{co}} \) and the correlation-energy functionals \( E_{\text{co}}^{(\eta)} \) mirrors this partitioning, yielding terms that depend on \( v \) and, the remainder, called the electron gas terms, that are \( v \) independent. The electron gas terms are the only terms that contribute to \( E_{\text{co}} \) and \( E_{\text{co}}^{(\eta)} \) for an electron gas and, in most other cases, are the dominant portions of \( E_{\text{co}} \) and \( E_{\text{co}}^{(\eta)} \); they are also universal functions – independent of the external potential. Atomic, diatomic and molecular terms are defined in an analogous way are are obtained by further partitioning the perturbation into potential terms from the individual nuclei and selectively partitioning the perturbation expansions for \( E_{\text{co}} \) and \( E_{\text{co}}^{(\eta)} \).
Using the electron gas terms, an *electron gas approximation* is proposed in Sec \( \text{X} \) that is an alternative to the LDA. Additional approximations are also considered in this Sec. including one that leads to the Colle–Salvetti functional \[19\].

Generalized Hartree–Fock equations are defined in Sec. \( \text{VII} \) where the exact Fock-operators, say \( \hat{F}^{(n)}_{\eta} \), generate the Brueckner orbitals, and these operators are defined by the trial wavefunctions \( |\Psi^{(n)}_{\eta}\rangle \) and the Brillouin-Brueckner condition, which is reviewed in Sec. \( \text{IV} \). In addition – from the one-to-one correspondence mentioned above – we can also write \( \hat{F}^{(n)}_{\tau} \); where, it is demonstrated that these operators are independent of \( \eta \); so, in addition, we can omit the \( \eta \) subscript and write \( \hat{F}_{\tau} \). Solving the generalized Hartree–Fock equations permit the determination of the Brueckner orbitals, and the one-particle density-matrix, \( \tau \), that is defined by these orbitals, permitting the determination of \( E \) and \( E_{\text{co}}[\tau] \), since, as mentioned above, they are given by \( E_{\eta}[\tau] \) and \( E_{\text{co}}^{(n)}[\tau] \), respectively; A correlation potential, say \( v_{\text{co}}^{\tau} \), is also defined, and satisfies the following identity: \( (\hat{F}_{\tau} = \hat{F}_{\tau} + v_{\text{co}}^{\tau}) \), where \( \hat{F}_{\tau} \) is the Fock operator, determined by \( \tau \); it is constructed from the Brueckner orbitals.

A variational formalism is presented in Sec. \( \text{XI} \) where energy functionals, say \( E_{\eta}[\gamma] \), are defined using the same trial wavefunctions as in the non-variational case: \( (E_{\eta}[\gamma] = \langle \Psi^{(n)}_{\gamma} | H | \Psi^{(n)}_{\gamma} \rangle \left[ (\langle \Psi^{(n)}_{\gamma} | \Psi^{(n)}_{\gamma} \rangle)^{-1} \right) \) where the exact energy is generated for the Brueckner-state one-particle density-matrix: \( (E = E_{\eta}[\tau]) \). These functionals are minimized subject to the constraint that the one-particle density-matrix comes from a single-determinantal state \( \gamma(|\Phi\rangle) \). The functional derivative of \( E_{\eta}[\gamma] \) – with respect to the one-particle density-matrix – generates \( \zeta^{(n)}_{\tau}(x_1, x_2) \), where these two-body functions are the kernels of generalized Fock operators, say \( \hat{\zeta}^{(n)}_{\tau} \), and it is demonstrated that these operators are independent of \( \eta \); in addition, these operators are – in a the sense mentioned in the introduction, Sec. \( \Pi \) – equivalent to the non-variational operators, \( \hat{F}_{\tau} \). A correlation potential, say \( \hat{v}_{\text{co}}^{\tau} \), is also obtained that is defined by its kernels which is given by the functional derivative of variational correlation-energy functionals, say \( E_{\text{co}}^{(n)}[\gamma] \). The electron-gas and Colle–Salvetti functionals, mentioned above, are valid within the variational approach, permitting the determination of approximate correlation potentials \( \hat{v}_{\text{co}}^{\tau} \) by functional differentiation.

A brief comparison with the Brueckner-orbital, *exact SCF theory* by Löwdin \[26\] and Kobe \[38\] is presented in Appendix \( \text{A} \).
III. PERTURBATION AND COUPLED CLUSTER THEORY

A. The exact and correlation energies

We seek solutions of the time-independent Schrödinger equation,

\[ H|\Psi\rangle = E|\Psi\rangle, \]

(1)

where \(|\Psi\rangle\) is an eigenstate of the Hamiltonian operator,

\[ H = \sum_{ij} [i|\hat{h}|j]a_i^\dagger a_j + \frac{1}{2} \sum_{ijkl} [ij|kl]a_i^\dagger a_k^\dagger a_l a_j, \]

(2)

and the integrals are written using chemist’s notation [70]:

\[ [i|\hat{h}|j] = [i|(-\frac{1}{2}\nabla^2)|j] + [i|v|j], \]

(3)

\[ [ij|kl] = \sum_{\omega_1\omega_2} \int \psi_{i1}^*(\mathbf{x}_1)\psi_{j1}(\mathbf{x}_1)\psi_{l2}^*(\mathbf{x}_2)\psi_{k2}(\mathbf{x}_2) \, d\mathbf{r}_1 d\mathbf{r}_2, \]

(4)

where the spatial and spin coordinates, \(\mathbf{r}\) and \(\omega\), are denoted collectively by \(\mathbf{x}\).

The wavefunction of interest \(|\Psi\rangle\) can be generated by a wave operator \(\Omega_\Phi\):

\[ \Omega_\Phi|\Phi\rangle = |\Psi\rangle, \]

(5)

where \(|\Phi\rangle\) is a determinantal reference-state.

The reference state \(|\Phi\rangle\) is completely defined by its occupied orbitals; we denote these orbitals by \(\{\psi_o \rightarrow \Phi\}\); the set of unoccupied orbitals – the virtual orbital set – is denoted by \(\{\psi_u \rightarrow \Phi\}\). The virtual set \(\{\psi_u \rightarrow \Phi\}\) also determines the occupied set, since the two sets are orthogonal, and the union of the two sets is a complete set. Hence, \(\{\psi_u \rightarrow \Phi\}\) also determines \(|\Phi\rangle\). Unless stated otherwise, two sets of either occupied or unoccupied orbitals that differ by a unitary transformation are considered equivalent.

We use the following orbital convention: Arbitrary orbitals are denoted by \(i\) and \(j\); occupied orbitals are denoted by \(w, x, \) and \(y\); virtual orbitals are denoted by \(r, s, \) and \(t\):

\[ \psi_w, \psi_x, \psi_y \in \{\psi_o \rightarrow \Phi\}, \]

(6a)

\[ \psi_r, \psi_s, \psi_t \in \{\psi_u \rightarrow \Phi\}, \]

(6b)

\[ \psi_i, \psi_j, \psi_k \in \{\psi_o \rightarrow \Phi\} \cup \{\psi_u \rightarrow \Phi\}. \]

(6c)
Explicitly, our spin-orbitals $\psi_i(x)$ have the following form:

$$\psi_i(x) = \chi_i(x) \sigma(\omega), \quad \sigma = \alpha \text{ or } \beta,$$

where the spin and spatial portions are given by $\chi_i(x)$ and $\sigma(\omega)$, respectively, and the spatial functions $\chi_i(x)$ are permitted to be unrestricted – two spin orbitals do not, in general, share the same spatial function.

In principle, $|\Phi\rangle$ can be any determinantal state that overlaps with the reference state: $(\langle \Phi | \Psi \rangle \neq 0)$. However, our interest is often in cases where the target state $|\Psi\rangle$ is a ground state that is well described by a closed-shell reference-state $|\Phi\rangle$, and the Hamiltonian is spin-free – it contains no spin coordinates. In these cases, instead of Eq. (7), we often use a spatially restricted set of orbitals, given by

$$\psi_{i\sigma}(x) = \chi_i(r) \sigma(\omega), \quad \sigma = \alpha, \beta,$$

so that $|\Phi\rangle$ is determined by a set of doubly-occupied spatial orbitals, denoted by $\{\chi_o \rightarrow \Phi\}$, where this set also determines the virtual set $\{\chi_u \rightarrow \Phi\}$. Two sets of orbitals that differ by a unitary transformation are considered, again, as equivalent.

By multiplying the Schrödinger Eq. (1) from the left by $\langle \Phi |$, and requiring intermediate normalization to be satisfied,

$$\langle \Phi | \Psi \rangle = \langle \Phi | \Omega_{\Phi} | \Phi \rangle = 1,$$

we get

$$E = \langle \Phi | H | \Psi \rangle = E_1[\Phi] + \mathcal{E}_{\text{co}}[\Phi],$$

where the first-order energy is

$$E_1[\Phi] = \langle \Phi | H | \Phi \rangle = \sum_{w \in \{\chi_o \rightarrow \Phi\}} [w]|(-\frac{1}{2}\nabla^2) + v + \frac{1}{2}(J_{\Phi} - K_{\Phi})|w],$$

and the Coulomb $J_{\Phi}(r)$ and exchange $K_{\Phi}(x)$ operators have their usual forms:

$$[i|J_{\Phi}|j] = \sum_{x \in \{\psi_o \rightarrow \Phi\}} [xx|ij],$$

$$[i|K_{\Phi}|j] = \sum_{x \in \{\psi_o \rightarrow \Phi\}} [x|jx];$$

furthermore, the correlation energy $\mathcal{E}_{\text{co}}[\Phi]$, given by

$$\mathcal{E}_{\text{co}}[\Phi] = \langle \Phi | H | \Psi_{Q_{\Phi}} \rangle,$$
is obtained from the correlation function:

$$|\Psi_{\Phi}Q\rangle = Q\Phi|\Psi\rangle,$$

(15)

where the orthogonal-space projector is

$$Q\Phi = 1 - |\Phi\rangle\langle\Phi|.$$

(16)

The first-order energy can also be written as

$$E_1[\Phi] = \langle\Phi|H|\Phi\rangle = (H)_{cl},$$

(17)

where the cl subscript indicates the closed portion – the fully contracted terms that, diagrammatically speaking, have no external free-lines [55, 56, 60, 61]. Appendix B presents partitioning or second-quantized operators into closed and open portions in a slightly different manner than is done by other authors.

Similar to the first-order energy, for the correlation energy we have

$$E_{co}[\Phi] = (H\chi\Phi)_{cl},$$

(18)

where the correlation operator $\chi\Phi$, defined by

$$\chi\Phi = \Omega\Phi - 1,$$

(19)

generates the correlation function $|\Psi_{\Phi}Q\rangle$ when operating on the reference state:

$$\chi\Phi|\Phi\rangle = |\Psi_{\Phi}Q\rangle.$$

(20)

The sum of Eqs. (17) and (18) gives the exact energy:

$$E = (H\Omega\Phi)_{cl}.$$

(21)

We also write down the expression for the exchange-correlation energy:

$$E_{xc}[\Phi] = E_{co}[\Phi] - E_x[\Phi],$$

(22)

where the exchange energy $E_x[\Phi]$ is the last term on the right side of Eq. (11):

$$E_x[\Phi] = \frac{1}{2} \sum_{w\in\{\psi_o\to\Phi\}} [w|K\Phi|w].$$

(23)
B. The linked cluster theorem

The wave operator $\Omega_\Phi$ can be expressed in an exponential form [56, 58, 59, 60, 61, 62, 63, 64, 65],

$$\Omega_\Phi = e^{S_\Phi} = 1 + S_\Phi + \frac{1}{2!} S^2_\Phi + \frac{1}{3!} S^3_\Phi + \cdots,$$  \hspace{1cm} (24a)

where the cluster operator $S_\Phi$ can be written as a sum of one-, two-, and higher-body terms,

$$S_\Phi = S^1_\Phi + S^2_\Phi + S^3_\Phi + \cdots,$$  \hspace{1cm} (24b)

and these amplitudes are defined by the following relations:

$$S^1_\Phi = \sum_{rw} s^\Phi_{rw} a^\dagger_r a^\dagger w,$$  \hspace{1cm} (25a)

$$S^2_\Phi = \frac{1}{2!} \sum_{rwsx} s^\Phi_{rwsx} a^\dagger_r a^\dagger s a^\dagger x a^\dagger w,$$  \hspace{1cm} (25b)

$$S^3_\Phi = \frac{1}{3!} \sum_{rwsxt} s^\Phi_{rwsxt} a^\dagger_r a^\dagger s a^\dagger t a^\dagger x a^\dagger w,$$  \hspace{1cm} (25c)

\vdots

which use the orbital convention given by Eqs. (6); furthermore, the coefficients are required to satisfy exchange symmetry:

$$s^\Phi_{rwsx} = s^\Phi_{sxrw},$$  \hspace{1cm} (26a)

$$s^\Phi_{rwsxty} = s^\Phi_{sxrwty} = s^\Phi_{rwtysx}, \cdots.$$  \hspace{1cm} (26b)

The cluster operator $S_\Phi$ and its amplitudes $S^\Phi_n$ are invariant to unitary transformations of the occupied or virtual orbitals [30].

Since $S_\Phi$ – given by Eqs. (24b) and (25) – is open, only connected (cn) portions contribute to the correlation- and exact-energies, $\mathcal{E}_{\text{co}}[\Phi]$ and $\mathcal{E}$, given by Eqs. (18) and (21). Therefore, we can write

$$\mathcal{E}_{\text{co}}[\Phi] = (H \chi_\Phi)_{\text{cl,cn}},$$  \hspace{1cm} (27)

$$\mathcal{E} = (H \Omega_\Phi)_{\text{cl,cn}},$$  \hspace{1cm} (28)

where the additional cn subscripts indicate that only the connected portions contribute – contractions in which all $S_\Phi$ amplitudes are connected together by $H$. 

Eq. (28) indicates that the closed part of \((H\Omega_{\Phi})_{cn}\) gives the energy of interest, \(E\); the open part is the mathematical statement of the linked-cluster theorem \([56, 60, 61, 62, 63, 64, 65]\):

\[
(H\Omega_{\Phi})_{op,cn} = 0.
\] (29)

Using the time-independent form of Wick’s theorem \([55, 56, 61, 73]\), the operator product \(H\Omega_{\Phi}\) can be written as a sum of zero-, one-, two- and higher-body excitations:

\[
H\Omega_{\Phi} = E + (H\Omega_{\Phi})_{1} + (H\Omega_{\Phi})_{2} + (H\Omega_{\Phi})_{3} + \cdots,
\] (30)

where the notation \((\ldots)_{n}\) indicates that the \(n\)-body term within the brackets \((\ldots)\) is normal-ordered with respect to the \(|\Phi\rangle\) vacuum state. Substituting this expression into Eq. (29), we get

\[
\sum_{n=1}^{\infty} [(H\Omega_{\Phi})_{n}]_{op,cn} = 0.
\] (31)

Since each term is linearly independent, the solution is

\[
[(H\Omega_{\Phi})_{n}]_{op,cn} = 0, \; n \neq 0.
\] (32)

This relation can be used to obtain the coupled-cluster equations, satisfied by the \(S_{\Phi}\) amplitudes, \(S_{\Phi}^{n}\) \([56, 58, 59, 60, 61, 62, 63, 64, 65]\).

C. Perturbation treatment of the linked cluster theorem

For Rayleigh-Schrödinger perturbation theory \([51, 52, 53, 54, 55, 56, 71, 74, 75]\), the wave- and cluster-operators are given by order-by-order expansions:

\[
S_{\Phi} = S_{\Phi}^{(1)} + S_{\Phi}^{(2)} + S_{\Phi}^{(3)} + \ldots,
\] (33a)

\[
\Omega_{\Phi} = \Omega_{\Phi}^{(0)} + \Omega_{\Phi}^{(1)} + \Omega_{\Phi}^{(2)} + \ldots,
\] (33b)

where

\[
\Omega_{\Phi}^{(0)} = 1.
\] (33c)
Substituting these relations into Eq. (24a) and equating each order, we get the following identities [56, 63]:

\[ \Omega^{(1)}_{\Phi} = S^{(1)}_{\Phi}, \]  
\[ \Omega^{(2)}_{\Phi} = S^{(2)}_{\Phi} + \frac{1}{2!} \left( S^{(1)}_{\Phi} \right)^2, \]  
\[ \Omega^{(3)}_{\Phi} = S^{(3)}_{\Phi} + S^{(1)}_{\Phi} S^{(2)}_{\Phi} + \frac{1}{3!} \left( S^{(1)}_{\Phi} \right)^3, \]  

where the order from each term is defined as a sum of the superscripts, e.g., \( S^{(1)}_{\Phi} S^{(2)}_{\Phi} \) is a third order term.

For a perturbative treatment, we partition the Hamiltonian into a zeroth-order Hamiltonian \( H_0 \) and a perturbation \( V \):

\[ H = H_0 + V, \]  

where we require the reference state \(| \Phi \rangle\) to be an eigenfunction of \( H_0 \), and a one-body operator:

\[ H_0 |\Phi \rangle = E_0 |\Phi \rangle, \]  
\[ H_0 = \sum_{ij} \epsilon_{ij} a_i^\dagger a_j. \]

The above zeroth-order Hamiltonian is defined by its matrix elements. We choose them by requiring the following relation to be satisfied:

\[ \epsilon_{ij} = \epsilon_{ji} = \epsilon_{ij}^*, \]  

where

\[ \epsilon_{\Phi}^* = 0, \]  
\[ \epsilon_{\Phi}^{*} = \langle \psi_w | \hat{f}^*_o | \psi_x \rangle, \]  
\[ \epsilon_{\Phi}^{*} = \langle \psi_r | \hat{f}^*_u | \psi_s \rangle, \]

and the one-body operators, \( \hat{f}^*_o \) and \( \hat{f}^*_u \), are determined by the reference state \(| \Phi \rangle\), but the dependence of \( \hat{f}^*_o \) and \( \hat{f}^*_u \) upon \(| \Phi \rangle\) is at our disposal; the orbital subspaces are, again, defined by Eqs. [38].
Using the above choice, our zeroth-order Hamiltonian becomes

$$H_\Phi^0 = \sum_{w,x \in \{\psi_o \to \Phi\}} \epsilon^p_{wx} a_w^\dagger a_x + \sum_{r,s \in \{\psi_u \to \Phi\}} \epsilon^p_{rs} a_r^\dagger a_s,$$

where the appended $\Phi$ superscript indicates that $H_\Phi^0$ now depends on the reference state $|\Phi\rangle$.

A linked diagram expansion for $\Omega_\Phi$ and $E_{co}[\Phi]$ is known to exist for a zeroth-order Hamiltonian that is a diagonal, one-body, operator \[51, 52, 53, 54, 55, 56, 71, 74, 75\]. A diagonal form for our one-body operator, $H_\Phi^0$, is obtained when we choose its orbital sets – $\{\psi_o \to \Phi\}$ and $\{\psi_u \to \Phi\}$ – to satisfy the following conditions:

$$\langle \psi_w | \hat{f}_{\Phi o} | \psi_x \rangle = \delta_{wx} \epsilon^p_w,$$

and

$$\langle \psi_r | \hat{f}_{\Phi u} | \psi_s \rangle = \delta_{rs} \epsilon^p_r,$$

where we denote these particular sets of orbitals by $\{\psi_o \leftarrow \Phi, \hat{f}_{\Phi o}\}$ and $\{\psi_u \leftarrow \Phi, \hat{f}_{\Phi u}\}$, indicating that they are uniquely determined by $|\Phi\rangle$ and their one-particle operator, $\hat{f}_{\Phi o}$ or $\hat{f}_{\Phi u}$.

Using these orbitals, $H_\Phi^0$ can be written as

$$H_\Phi^0 = \sum_{w \in \{\psi_o \leftarrow \Phi, \hat{f}_{\Phi o}\}} \epsilon^p_w a_w^\dagger a_w + \sum_{r \in \{\psi_u \leftarrow \Phi, \hat{f}_{\Phi u}\}} \epsilon^p_r a_r^\dagger a_r,$$

where our partitioning is

$$H = H_\Phi^0 + V_\Phi.$$

Since $H_\Phi^0$ is a second-quantized operator with no projection operators, it is appropriate to substitute the above partitioning into Eq. (29), yielding

$$- (H_\Phi^0 S_\Phi)_{op, cn} = (V_\Phi \Omega_\Phi)_{op, cn},$$

Substituting Eqs. (33) into (43), and equating each order, we have

$$- (H_\Phi^0 S_\Phi^{(n)})_{op, cn} = (V_\Phi \Omega_\Phi^{(n-1)})_{op, cn},$$

where $V_\Phi$ contributes unity to the overall order of the rhs. (In a sense, we have: $V_\Phi = V_\Phi^{(1)}$.)

Solving Eqs. (44) and (34) in an iterative and sequential manner generates a linked diagram expansion for $\Omega_\Phi$ and a connected expansion for $S_\Phi$, which is identical to the expansions obtained by Lindgen \[56, 63, 74\]. The procedure begins by using Eq. (33c), which gives $S_\Phi^{(1)}$ and $\Omega_\Phi^{(1)}$ from Eqs. (44) and (34a). Substituting $\Omega_\Phi^{(1)}$ back into Eq. (44) gives $S_\Phi^{(2)}$, permitting the calculation of $\Omega_\Phi^{(2)}$ from (34b), and so on. However, in order to
get the same diagrams as Lindgren, the factorization theorem \[52, 53, 56, 74, 76, 77, 78, 79\] must be exploited to unfactorize the disconnected products that appear on the right side on Eq. (34). The diagrammatic expansions for the correlations and exact energies, \(E_{\text{co}}[\Phi]\) and \(E\), are obtained from Eqs. (27) and (28). It is worth mentioning that these diagrammatic expansions are only obtained when the one-body, zeroth-order Hamiltonian \(H_0^\Phi\) is a diagonal operator, permitting the left side of Eq. (44) to be evaluated to give terms containing factors of orbital-energy differences, e.g., \((\epsilon_w^\Phi + \epsilon_y^\Phi - \epsilon_x^\Phi - \epsilon_s^\Phi)\).

Note that Eq. (44) can also be expressed by

\[
\left[ S_{\Phi}^{(n)}, H_0^\Phi \right] P_\Phi = Q_\Phi \left( V_\Phi \Omega_{\Phi}^{(n-1)} \right)_{\text{en}} P_\Phi,\tag{45}
\]

where the reference state projector is

\[
P_\Phi = |\Phi\rangle \langle \Phi|.	ag{46}
\]

Expression (45) is easily obtained from Eq. (44) by using the definition of an open operator, adding \((P_\Phi \left[ S_{\Phi}^{(n)}, H_0^\Phi \right] P_\Phi = 0)\), and using the following identity:

\[
Q_\Phi \left[ S_{\Phi}^{(n)}, H_0^\Phi \right] P_\Phi = -Q_\Phi \left( H_0^\Phi S_{\Phi}^{(n)} \right)_{\text{en}} P_\Phi.\tag{47}
\]

D. Rayleigh-Schrödinger perturbation theory and the Bloch Equations

Using Eqs. (5), (10), and (46), the Schrödinger Eq. (11) can be written

\[
H\Omega_\Phi |\Phi\rangle = \Omega_\Phi P_\Phi H\Omega_\Phi |\Phi\rangle.\tag{48}
\]

The operator form of this Eq. is the Bloch Eq. \[63, 74, 80, 81\]:

\[
H\Omega_\Phi P_\Phi = \Omega_\Phi P_\Phi H\Omega_\Phi P_\Phi,\tag{49}
\]

which yields Eq. (48) when multiplied by \(|\Phi\rangle\) from the right side. Substituting Eq. (35) into (49), and using (19) and (36), where \(H_0\) is Hermitian, gives a variant of the Bloch equation \[63, 74, 80, 81\]:

\[
(E_0 - H_0) \Omega_\Phi P_\Phi = Q_\Phi \left( V\Omega_\Phi - \Omega_\Phi P_\Phi V\Omega_\Phi \right) P_\Phi,\tag{50}
\]

where we have used the following identity:

\[
P_\Phi \left( V\Omega_\Phi - \Omega_\Phi P_\Phi V\Omega_\Phi \right) = 0,\tag{51}
\]
and this identity follows from intermediate normalization, given by Eq. (9), i.e., \((P_{\Phi} \Omega_{\Phi} P_{\Phi} = P_{\Phi})\).

For Rayleigh-Schrödinger perturbation theory, the wave-operator \(\Omega_{\Phi}\) is given by the order-by-order expansion (33b). Substituting this expression into Eq. (50) and equating the individual orders, gives

\[
(E_0 - H_0) \Omega^{(n)}_{\Phi} P_{\Phi} = Q_{\Phi} \left[ V \Omega^{(n-1)}_{\Phi} - \sum_{m=1}^{n-1} \Omega^{(n-m)}_{\Phi} P_{\Phi} V \Omega^{(m-1)}_{\Phi} \right] P_{\Phi},
\]

(52)

where the second term on the right side does not appear for \((n = 1)\).

E. The Linked diagram theorem

When the zeroth-order Hamiltonian is in the diagonal, one-body form, given by Eq. (41), it can be shown that the wave-operator \(\Omega_{\Phi}\) satisfies a linked diagram theorem (33b):

\[
(E_0 - H_0^0) \Omega_{\Phi} P_{\Phi} = Q_{\Phi} \left( V_{\Phi} \Omega_{\Phi} \right)_1 P_{\Phi},
\]

(53a)

where the individual orders, defined by Eq. (33b), satisfy

\[
(E_0 - H_0^0) \Omega^{(n)}_{\Phi} P_{\Phi} = Q_{\Phi} \left( V_{\Phi} \Omega^{(n-1)}_{\Phi} \right)_1 P_{\Phi},
\]

(53b)

and the additional \(l\) subscripts indicate that only the linked portions contribute – all disconnected terms are open.

In order to solve either of the above two Eqs, the wave operator \(\Omega_{\Phi}\) is written as a sum of one-, two-, and higher-body excitations,

\[
\Omega_{\Phi} = 1 + \Omega^\Phi_1 + \Omega^\Phi_2 + \Omega^\Phi_3 + \cdots,
\]

(54)

where

\[
\Omega^\Phi_1 = \sum_{rw} x^\Phi_{rw} a_r^\dagger a_w,
\]

(55a)

\[
\Omega^\Phi_2 = \frac{1}{2!} \sum_{rwsz} x^\Phi_{rwsz} a_r^\dagger a_s^\dagger a_z a_w,
\]

(55b)

\[
\Omega^\Phi_3 = \frac{1}{3!} \sum_{rwszty} x^\Phi_{rwszty} a_r^\dagger a_s^\dagger a_y^\dagger a_z a_w,
\]

(55c)
and Eqs. remain valid. In addition, we require our coefficients to have exchange symmetry:

\[ x_{\Phi} = x_{\Phi}, \]

\[ x_{\Phi} = x_{\Phi} = x_{\Phi}, \ldots \]  

The wave operator \( \Omega_{\Phi} \) and its \( n \)-body operators \( \Omega_{\Phi} \) are also invariant to a unitary transformation of either its occupied orbitals \( \{ \psi_o \rightarrow \Phi \} \) or its virtual orbitals \( \{ \psi_u \rightarrow \Phi \} \).

The linked diagram theorem provides an exponential form for the wave operator \( \Omega_{\Phi} \); comparing the two forms of the wave operator, Eqs. (24) and (54), the following identities are easily proven:

\[ \Omega_{\Phi} = S_{\Phi}, \]

\[ \Omega_{\Phi} = S_{\Phi} + \frac{1}{2} (S_{\Phi})^2, \]

\[ \Omega_{\Phi} = S_{\Phi} + S_{\Phi}S_{\Phi} + \frac{1}{3!} (S_{\Phi})^3, \]

:\

IV. BRILLOUIN-BRUECKNER CONDITION

Consider the Slater determinantal state, say \( |\Theta\rangle \), that satisfies the Brillouin-Brueckner condition (24, 26, 26, 38, 82, 83):

\[ \langle \Theta_{\psi} | H | \Psi \rangle = 0, \]

for any single excitation from \( |\Theta\rangle \):

\[ |\Theta_{\psi} \rangle = a_1^\dagger a_2 |\Theta\rangle, \]

where both the occupied and virtual orbitals determine the Brueckner determinantal-state \( |\Theta\rangle \):

\[ \psi_w \in \{ \psi_o \rightarrow \Theta \}, \]

\[ \psi_r \in \{ \psi_u \rightarrow \Theta \}. \]

Using Eqs. (61) and (58), it is easily demonstrated that the wavefunction \( |\Psi\rangle \) contains no single excitations from \( |\Theta\rangle \):

\[ \frac{1}{\epsilon} \langle \Theta_{\psi} | H | \Psi \rangle = \langle \Theta_{\psi} | \Psi \rangle = 0. \]
Since the states $|\Theta_w^r\rangle$ are linearly independent, the wavefunction satisfies the following condition:

$$P_{11}^\Theta |\Psi\rangle = 0.$$  \hspace{1cm} (62)

where the projector for the singly-excited states is

$$P_{11}^\Theta = \sum_{w\in\{\psi_o\rightarrow\Theta\}} \sum_{r\in\{\psi_u\rightarrow\Theta\}} |\Theta_w^r\rangle\langle \Theta_w^r| ,$$  \hspace{1cm} (63)

and this subspace is completely determined by $|\Theta\rangle$; $P_{11}^\Theta$ is also invariant to a unitary transformation of occupied, or virtual, orbitals \[30\].

Using Eqs. (61), (62) and (63), Eq. (58) can be generalized:

$$P_{11}^\Theta H (1 - P_{11}^\Theta) |\Psi\rangle = 0.$$  \hspace{1cm} (64)

The occupied set of orbitals $\{\psi_o\rightarrow\Theta\}$ that satisfy Eq. (64) are called Brueckner orbitals. However, since these orbitals are invariant to a unitary transformation, Eq. (64) actually defines the Brueckner-determinantal state $|\Theta\rangle$, since $|\Theta\rangle$ determines $P_{11}^\Theta$.

Note also the following identities:

$$\Omega_1^\Theta = 0,$$  \hspace{1cm} (65a)

$$S_1^\Theta = 0.$$  \hspace{1cm} (65b)

The first identity is obtained by substituting Eq. (5) into (62) and using (54) and (55) for $\Phi = \Theta$. The second identity uses either Eq. (57a) or Eqs. (24) and (25).

Since $S_1^\Theta$ is zero, we have

$$\Omega_\Theta = e^{-S_1^\Theta} \Omega_\Theta.$$  \hspace{1cm} (66)

Multiplying this equation from the right by $|\Theta\rangle$ and using Eq. (53) gives

$$|\Psi\rangle = e^{-S_1^\Theta} |\Psi\rangle.$$  \hspace{1cm} (67)

Substituting this equation into Eq. (58), and using Eq. (63), gives

$$P_{11}^\Theta H e^{-S_1^\Theta} |\Psi\rangle = 0.$$  \hspace{1cm} (68)

This equation is the Brillouin-Brueckner condition for coupled cluster theory \[30, 84\]. As in Eq. (64), the Brueckner orbitals that satisfy Eq. (68) are invariant to a unitary transformation, so Eq. (68) defines the determinantal state $|\Theta\rangle$, since $|\Theta\rangle$ determines $P_{11}^\Theta$ and $S_1^\Theta$. 

V. TRIAL WAVEFUNCTIONS AND ENERGY FUNCTIONALS

A. General Requirements

Consider four trial wavefunctions, denoted by $|\Psi^{(\eta)}_\Phi\rangle$, where $\eta = I, II, III, \text{ and } IV$. Each of these four states depends on the reference state $|\Phi\rangle$, satisfies intermediate normalization,

$$\langle \Phi | \Psi^{(\eta)}_\Phi \rangle = 1,$$

(69)

has no components within the singly-excited subspace,

$$|\Psi^{(\eta)}_\Phi\rangle = (1 - P_{11}^\Phi) |\Psi^{(\eta)}_\Phi\rangle,$$

(70)

and yields the exact state of interest when $|\Phi\rangle$ is the Brueckner determinantal-state:

$$|\Psi^{(\eta)}_\Theta\rangle = |\Psi\rangle.$$

(71)

From these trial wavefunctions $|\Psi^{(\eta)}_\Phi\rangle$, we can construct energy functionals:

$$E^{(\eta)}_\Phi[\Phi] = \langle \Phi | H | \Psi^{(\eta)}_\Phi \rangle = E_{1}[\Phi] + E^{(\eta)\text{co}}_\Phi[\Phi],$$

(72)

where the correlation (co) energy-functionals are given by

$$E^{(\eta)\text{co}}_\Phi[\Phi] = \langle \Phi | H | \Psi^{(\eta)}_{Q\Phi} \rangle,$$

(73)

the trial correlation-functions are

$$Q_{\Phi} |\Psi^{(\eta)}_\Phi\rangle = |\Psi^{(\eta)}_{Q\Phi}\rangle,$$

(74)

and $E_{1}[\Phi]$ is given by Eq. (11). Operating on Eq. (71) by $Q_{\Theta}$ and using Eqs. (15) and (74) we have

$$|\Psi^{(\eta)}_{Q\Theta}\rangle = |\Psi_{Q\Theta}\rangle.$$

(75)

Let us also define exchange-correlation (xc) energy-functionals:

$$E^{(\eta)\text{xc}}_\Phi[\Phi] = E^{(\eta)\text{co}}_\Phi[\Phi] - E_{x}[\Phi],$$

(76)

where the exchange energy $E_{x}[\Phi]$ is given by Eq. (23).

Eqs. (10), (71), and (72) indicate that the energy functionals $E_{\eta}[\Phi]$ yield the exact energy $E$ when the reference state $|\Phi\rangle$ is the Brueckner determinantal state $|\Theta\rangle$:

$$E = E_{\eta}[\Theta],$$

(77)
and from Eqs. (14), (22), (71), (73), and (76), the following identities are obtained for the correlation and exchange-correlation energies, $E_{\text{co}}[\Theta]$ and $E_{\text{xc}}[\Theta]$:

$$E_{\text{co}}[\Theta] = E_{\text{co}}^{(\eta)}[\Theta],$$

(78)

$$E_{\text{xc}}[\Theta] = E_{\text{xc}}^{(\eta)}[\Theta].$$

(79)

Substituting Eq. (71) into Eq. (64), and using Eq. (70) for $\langle \Phi | = \langle \Theta |$, gives the Brillouin-Brueckner condition for our trial wavefunctions:

$$P_{11}^{\Theta} H | \Psi_{\Theta}^{(\eta)} \rangle = 0.$$ 

(80)

We now define the explicit forms of these trial wavefunctions and give expressions for their correlation-energy functionals. Additional expressions for the correlation-functionals in terms of their wave-operator, or cluster-operator, amplitudes, e.g., $t_{\text{rwsx}}^{\phi}$, are given in Sec. VII; diagrammatic expressions are presented in Sec. VIII C.

**B. The first trial wavefunction**

The first trial-wavefunction is given by

$$| \Psi_{\phi}^{(1)} \rangle = (1 - P_{11}^{\phi}) | \Psi \rangle.$$ 

(81)

It follows from Eqs. (54) and (55) that $\Omega_1^{\phi}$ exclusively generates the singly-excited portion of the orthogonal space:

$$P_{11}^{\phi} \Omega_1^{\phi} | \Phi \rangle = \Omega_1^{\phi} | \Phi \rangle,$$

(82a)

$$P_{11}^{\phi} \Omega_n^{\phi} | \Phi \rangle = 0, \ n \neq 1.$$ 

(82b)

Therefore, this trial wavefunction can be written

$$| \Psi_{\phi}^{(1)} \rangle = (\Omega_{\phi} - \Omega_1^{\phi}) | \Phi \rangle.$$ 

(83)

Using this expression and Eq. (19), after substituting Eq. (74) into (73), yields the first correlation-energy functional:

$$E_{\text{co}}^{(\eta)}[\phi] = \left[ H \left( \chi_{\phi} - \Omega_1^{\phi} \right) \right]_{\text{cl}},$$ 

(84)

where we also used $(P_{\phi}(\chi_{\phi} - \Omega_1^{\phi})|\Phi\rangle = 0)$. 


C. The second trial wavefunction

The second trial-wavefunction is given by

$$|\Psi^{(II)}_\Phi\rangle = e^{-S^\Phi_1} |\Psi\rangle. \quad (85)$$

Using Eqs. (5) and (24a), this Eq. becomes

$$|\Psi^{(II)}_\Phi\rangle = e^{(S^\Phi_\Phi - S^\Phi_1)} |\Phi\rangle, \quad (86)$$

where we used the identity, given by

$$e^{-S^\Phi_1} \Omega_\Phi = e^{(S^\Phi_\Phi - S^\Phi_1)}, \quad (87)$$

and this relation follows from Eqs. (24), since $S^\Phi_\Phi$ and $S^\Phi_1$ commute [85].

Using Eq. (86) after substituting Eq. (74) into (73), gives the second correlation-energy functional:

$$E^{(II)}_{\text{co}}[\Phi] = \left[ H \left( e^{(S^\Phi_\Phi - S^\Phi_1)} - 1 \right) \right]_{\text{cl}}, \quad (88)$$

where we also used the following:

$$\langle \Phi|H P_\Phi e^{(S^\Phi_\Phi - S^\Phi_1)} |\Phi\rangle - \langle \Phi|H |\Phi\rangle = 0. \quad (89)$$

D. The third trial wavefunction

The third trial-wavefunction $|\Psi^{(III)}_\Phi\rangle$ can be generated by its wave-operator:

$$\hat{\Omega}_\Phi |\Phi\rangle = |\Psi^{(III)}_\Phi\rangle, \quad (90)$$

that can be expressed in an exponential form,

$$\hat{\Omega}_\Phi = e^{\hat{S}^\Phi_\Phi} = 1 + \hat{S}^\Phi_\Phi + \frac{1}{2!} \hat{S}^2_\Phi + \frac{1}{3!} \hat{S}^3_\Phi + \cdots, \quad (91a)$$

where $\hat{S}^\Phi_\Phi$ can be written as of sum $n$-body excitations, with the exclusion of a one-body operator:

$$\hat{S}^\Phi_\Phi = \hat{S}^\Phi_2 + \hat{S}^\Phi_3 + \cdots. \quad (91b)$$
The individual amplitudes are defined by the following equations:

\[
\hat{S}_2^\Phi = \frac{1}{2!} \sum_{rwsx} \hat{s}_{rwsx} a_r^\dagger a_s^\dagger a_x a_w,
\]

(92a)

\[
\hat{S}_3^\Phi = \frac{1}{3!} \sum_{rwsxty} \hat{s}_{rwsxty} a_r^\dagger a_s^\dagger a_t^\dagger a_y a_x a_w,
\]

(92b)

\[\vdots\]

Let us also mention that the orbital convention, Eqs. (6), remains valid; we also require the coefficients to possess exchange symmetry, as in Eqs. (26).

Using Eqs. (90) and (91a), after substituting Eq. (74) into (73), gives the third correlation-energy functional:

\[
E^{(iii)}[\Phi] = \left[ H \left( e^{\hat{S}_\Phi} - 1 \right) \right]_{cl},
\]

(93)

where we used the following:

\[
\langle \Phi | H P_\Phi e^{\hat{S}_\Phi} | \Phi \rangle - \langle \Phi | H | \Phi \rangle = 0.
\]

(94)

We define \( \hat{\Omega}_\Phi \) as a solution to the following variant of Eq. (29):

\[
(1 - P_{11}^\Phi) \left( H \hat{\Omega}_\Phi \right)_{op,cn} = 0,
\]

(95)

which defines the trial functional \( |\Psi_{\Phi}^{(iii)}\rangle \) using Eq. (90).

As in Eq. (30), the operator \( H \hat{\Omega}_\Phi \) can also be written as a sum of zero-, one-, two- and higher-body excitations:

\[
H \hat{\Omega}_\Phi = E_{\text{III}}[\Phi] + \left( H \hat{\Omega}_\Phi \right)_1 + \left( H \hat{\Omega}_\Phi \right)_2 + \left( H \hat{\Omega}_\Phi \right)_3 + \cdots,
\]

(96)

where we use the identity, given by

\[
E_{\text{III}}[\Phi] = \left( H \hat{\Omega}_\Phi \right)_{cl} = \left( H \hat{\Omega}_\Phi \right)_{0},
\]

(97)

and this relation follow from Eqs. (72) and (90). (See also Appendix B.)

Substituting Eq. (96) into Eq. (95) yields

\[
\left( H \hat{\Omega}_\Phi \right)_{op,cn} - \left[ \left( H \hat{\Omega}_\Phi \right)_1 \right]_{op,cn} = 0.
\]

(98)

Substituting expansion (96) into Eq. (98) and noting that each term is linearly independent, we have

\[
\left[ \left( H \hat{\Omega}_\Phi \right)_n \right]_{op,cn} = 0, \quad n \geq 2,
\]

(99)
and this relation can be used to obtain the coupled cluster equations for the $\hat{S}_\nu^\Phi$ amplitudes.

We now demonstrate that $|\Psi^{(III)}_\phi\rangle$ is a valid trial wavefunction: Eq. (71) and the other relations for Sec. (VA) are satisfied.

Consider a determinantal state, say $|\Theta'\rangle$, that we require to satisfy the following condition:

\[
P_{11}^{\Theta'} \left( H \hat{\Omega}_{\Theta'} \right)_{\text{op,cn}} = 0.
\]  

(100a)

Using Eq. (96), we can easily verify that the following conditions causes Eq. (100a) to be satisfied:

\[
\left[ \left( H \hat{\Omega}_{\Theta'} \right)_{1} \right]_{\text{op,cn}} = 0.
\]  

(100b)

Adding Eqs. (95) and (100a), for ($|\Phi\rangle = |\Theta'\rangle$), and comparing the result with Eq. (29), indicates that

\[
\hat{\Omega}_{\Theta'} = \Omega_{\Theta'},
\]  

(101)

and therefore we have

\[
|\Psi^{(III)}_{\Theta'}\rangle = |\Psi\rangle.
\]  

(102)

(Combining Eqs. (99) and (100b), and comparing the result with Eq. (32), also yields the above two Eqs.)

Multiplying Eq. (102) by $P_{11}^{\Theta'}$ and using Eqs. (90) and (91) gives

\[
P_{11}^{\Theta'} |\Psi\rangle = 0.
\]  

(103)

Comparing this Eq. with Eq. (62) indicate that $|\Theta'\rangle$ is the Brueckner state:

\[
|\Theta'\rangle = |\Theta\rangle.
\]  

(104)

Substituting this result into Eq. (102) indicates that Eq. (71) is satisfies. All other relations from Sec. (VA) are easily verified. For example, Eqs. (77), (78), and (79) follow from Eqs. (72) through (76).

Substituting Eq. (104) into Eqs. (100) yields the following identities:

\[
P_{11}^{\Theta} \left( H \hat{\Omega}_{\Theta} \right)_{\text{op,cn}} = 0,
\]  

(105a)

\[
\left[ \left( H \hat{\Omega}_{\Theta} \right)_{1} \right]_{\text{op,cn}} = 0.
\]  

(105b)
These equivalent relations are alternative representations of the Brillouin-Brueckner condition, since if they satisfied, then Eq. (91) is also satisfied. Note that \( \hat{\Omega}_\Phi \) does not possess a single-excitation operator, i.e., \( \hat{S}_1^{\Phi} \) is absent in Eq. (91b).

Using the definition of an open operator, Eqs. (93) and (105a) can be represented by the following:

\[
\tilde{Q}_\Phi \left( H \hat{\Omega}_\Phi \right)_{cn} P_\Phi = 0, \quad (106)
\]
\[
P_{11} \left( H \hat{\Omega}_\Phi \right)_{cn} P_\Phi = 0, \quad (107)
\]
where

\[
\tilde{Q}_\Phi = Q_\Phi - P_{11}^\Phi. \quad (108)
\]

As in Eqs. (33), the wave- and cluster-operators of interest are given by order-by-order expansions:

\[
\hat{S}_\Phi = \hat{S}^{(1)}_\Phi + \hat{S}^{(2)}_\Phi + \hat{S}^{(3)}_\Phi + \ldots, \quad (109a)
\]
\[
\hat{\Omega}_\Phi = \hat{\Omega}^{(0)}_\Phi + \hat{\Omega}^{(1)}_\Phi + \hat{\Omega}^{(2)}_\Phi + \ldots, \quad (109b)
\]
where \( \hat{\Omega}^{(0)}_\Phi = 1 \). Substituting these relations into Eq. (91a) and equating each order, we get similar identities as in Eqs. (34):

\[
\hat{\Omega}^{(1)}_\Phi = \hat{S}^{(1)}_\Phi, \quad (110a)
\]
\[
\hat{\Omega}^{(2)}_\Phi = \hat{S}^{(2)}_\Phi + \frac{1}{2} \left( \hat{S}^{(1)}_\Phi \right)^2, \quad (110b)
\]
and so so.

From Eq. (93), and using Eqs. (12) and (109) – as in the derivation of Eq. (44) – we have

\[
- (1 - P_{11}^\Phi) \left( H_{0}^{\Phi} \hat{S}^{(n)}_\Phi \right)_{op, cn} = \left( 1 - P_{11}^\Phi \right) \left( V_\Phi \hat{\Omega}^{(n-1)}_\Phi \right)_{op, cn}. \quad (111)
\]
Solving Eqs. (111) and (110) in an iterative and sequential manner generates a linked diagram expansion for \( \hat{\Omega}_\Phi \) and a connected expansion for \( \hat{S}_\Phi \). The diagrams representing \( F_{co}^{III}[\Phi] \) and \( \hat{S}^{(n)}_\Phi \) are discussed in Sec. VIII B and elsewhere [57], respectively.

Of the four trial wavefunctions \( |\Psi^{(n)}_\Phi\rangle \), the third one \( |\Psi^{(iii)}_\Phi\rangle \), we believe, is the most applicable; the fourth one is presented below for completeness.
E. The fourth trial wavefunction

The fourth trial wavefunction is a solution of the Schrödinger Eq. within the subspace that neglects the single-excited states:

\[
(1 - P_{11}^\Phi) H |\Psi^{(IV)}_\Phi\rangle = E_{IV}[\Phi] |\Psi^{(IV)}_\Phi\rangle. \tag{112}
\]

From the variational theorem, it follows that the above energy functional provides an upper bound to the exact energy:

\[
E_{IV}[\Phi] \geq \mathcal{E}. \tag{113}
\]

We now prove that the exact wavefunction and energy satisfy Eqs. (71) and (77), where (\(\eta = IV\)).

The proof uses the Schrödinger Eq. (1), which can be written

\[
P_{11}^\Theta H |\Psi\rangle + (1 - P_{11}^\Theta) H |\Psi\rangle = \mathcal{E} P_{11}^\Theta |\Psi\rangle + \mathcal{E} (1 - P_{11}^\Theta) |\Psi\rangle, \tag{114}
\]

where he have added and subtracted \(P_{11}^\Theta\) terms. Eqs. (58), (62), and (63) indicate that the first terms on the right and left sides vanish, so we have

\[
(1 - P_{11}^\Theta) H |\Psi\rangle = \mathcal{E} (1 - P_{11}^\Theta) |\Psi\rangle. \tag{115}
\]

Eqs. (71) and (77), for (\(\eta = IV\)), are obtained by comparing Eqs. (112) and (115), and using (70). All other relations from Sec. (VA) are easily verified.

As in the exact wavefunction of interest \(|\Psi\rangle\), the trial wavefunction \(|\Psi^{(IV)}_\Phi\rangle\) can be generated by a wave operator \(\tilde{\Omega}_\Phi\):

\[
\tilde{\Omega}_\Phi |\Phi\rangle = |\Psi^{(IV)}_\Phi\rangle, \tag{116}
\]

where \(\tilde{\Omega}_\Phi\) is similar to \(\Omega_\Phi\) – defined by Eqs. (54) and (55) – except that there is no excitation operator into \(P_{11}^\Phi\):

\[
\tilde{\Omega}_\Phi = 1 + \tilde{\Omega}_2^\Phi + \tilde{\Omega}_3^\Phi + \cdots, \tag{117}
\]

where

\[
\tilde{\Omega}_2^\Phi = \frac{1}{2!} \sum_{rwsz} \hat{x}_{rwsz} \hat{a}_r^{\dagger} \hat{a}_s \hat{a}_z \hat{a}_w, \tag{118a}
\]

\[
\tilde{\Omega}_3^\Phi = \frac{1}{3!} \sum_{rwszty} \hat{x}_{rwszty} \hat{a}_r^{\dagger} \hat{a}_s \hat{a}_t \hat{a}_y \hat{a}_z \hat{a}_w, \tag{118b}
\]

\vdots
Using Eq. (116), after substituting Eq. (74) into (73) gives the fourth correlation-energy functional:

$$E^{(IV)}_{co}[\Phi] = \left[ H \left( \tilde{\Omega}_\Phi - 1 \right) \right]_{cl},$$

(119)

where we added $$\langle \Phi | H P_\Phi (\tilde{\Omega}_\Phi - 1) | \Phi \rangle = 0 \rangle$$.

It is easily proven that $$\tilde{\Omega}_\Phi$$ is a solution to the following variants of Eqs. (33b) and (52):

$$\tilde{\Omega}_\Phi = 1 + \tilde{\Omega}_\Phi^{(1)} + \tilde{\Omega}_\Phi^{(2)} + \ldots,$$

(120)

$$(E_0 - H_0) \tilde{\Omega}_\Phi^{(n)} P_\Phi = \tilde{Q}_\Phi \left[ V \tilde{\Omega}_\Phi^{(n)} - \sum_{m=1}^{n-1} \tilde{\Omega}_\Phi^{(n-m)} P_\Phi V \tilde{\Omega}_\Phi^{(m-1)} \right] P_\Phi,$$

(121)

where $$\tilde{Q}_\Phi$$ is defined by Eq. (108), and we require $$H_0$$ to satisfy

$$P_{11}^\Phi H_0 (1 - P_{11}^\Phi) = 0.$$

(122)

VI. EXPRESSIONS FOR THE CORRELATION-ENERGY FUNCTIONALS:

Using Wick’s theorem [55, 56, 61, 73], the Hamiltonian can be separated in to zero-, one-, and two-body parts:

$$H = H_0^\Phi + H_1^\Phi + H_2^\Phi,$$

(123)

where

$$H_0^\Phi = \langle \Phi | H | \Phi \rangle = E_1[\Phi] = (H)_{cl},$$

(124a)

$$H_1^\Phi = \sum_{ij} [i|\tilde{F}_\Phi|j] \{ a_i^\dagger a_j \},$$

(124b)

$$H_2^\Phi = \frac{1}{2} \sum_{ijkl} [ij|kl] \{ a_i^\dagger a_k^\dagger a_l a_j \},$$

(124c)

where the Fock operator is given by

$$\tilde{F}_\Phi = -\frac{1}{2} \nabla^2 + v + J_\Phi - K_\Phi,$$

(125)

and the identities within Eqs. (124a) follow from Eqs. (11) and (17).

Substituting Eqs. (19) and (123) into (18), and using (54), yield an expression for the correlation energy:

$$\varepsilon_{co}[\Phi] = \left( H_1^\Phi \tilde{\Omega}_1^\Phi + H_2^\Phi \tilde{\Omega}_2^\Phi \right)_{cl},$$

(126)
and from Eqs. (124) and (55) we have
\[ E_{\text{co}}[\Phi] = \sum_{rw} x_{rw}^\Phi [w|\hat{F}_\Phi|r] + \frac{1}{2} \sum_{rwsx} x_{rwsx}^\Phi ([wr|xs] - [ws|xr]), \] (127)
where the coefficients are are assumed to have exchange symmetry, defined by Eq. (56).

As is the correlation-energy expression (18), the correlation-energy functionals, given by Eq. (73), can be written
\[ E_{\text{co}}(\eta)[\Phi] = (H\chi_\eta^\Phi)_{cl}, \] (128)
where the trial correlation-operators \( \chi_\eta^\Phi \) generate the trial correlation-functions:
\[ \chi_\eta^\Phi|\Phi\rangle = |\Psi_\eta^\Phi\rangle, \] (129)
and \( |\Psi_\eta^\Phi\rangle \) is given by Eq. (74). Comparing this definition with Eqs. (72) and (73), and using Eq. (124a), we have
\[ E_\eta[\Phi] = \langle \Phi|H (1 + \chi_\eta^\Phi)|\Phi\rangle = [H (1 + \chi_\eta^\Phi)]_{cl}. \] (130)

Comparing Eqs. (84), (88), (93), and (119) with (128), yields the following relations:
\[ \chi_\Phi^I = \chi_\Phi - \Omega_\Phi, \] (131a)
\[ \chi_\Phi^H = e^{(S_\Phi - S_\Phi^I)} - 1, \] (131b)
\[ \chi_\Phi^III = e^{\hat{S}_\Phi} - 1, \] (131c)
\[ \chi_\Phi^IV = \tilde{\Omega}_\Phi - 1. \] (131d)
Substituting Eqs. (18) and (128) into (78) for \(|\Phi\rangle = |\Theta\rangle\), we get
\[ \chi_\theta^\eta = \chi_\theta, \] (132)
and this expression indicates that any of the trial correlation-functions \( \chi_\theta^I, \chi_\theta^H, \chi_\theta^III \), and \( \chi_\theta^IV \) – can be used to obtain the Brueckner one, \( \chi_\theta \).

Substituting Eqs. (131) into Eq. (128), and using Eqs. (19), (54), (24), (91), (117), and (123), give expressions for the correlation energy functionals:
\[ E_{\text{co}}^{(i)}[\Phi] = (H_{2}^\Phi \Omega_{2}^\Phi)_{cl}, \] (133a)
\[ E_{\text{co}}^{(ii)}[\Phi] = (H_{2}^\Phi S_{2}^\Phi)_{cl}, \] (133b)
\[ E_{\text{co}}^{(iii)}[\Phi] = (H_{2}^\Phi \tilde{S}_{2}^\Phi)_{cl}, \] (133c)
\[ E_{\text{co}}^{(iv)}[\Phi] = (H_{2}^\Phi \tilde{\Omega}_{2}^\Phi)_{cl}. \] (133d)
Using Eqs. 55b, 25b, 92a, 118a, and 124c, the above energy functionals above can be evaluated, giving the following relations:

\[
E^{(I)}_{\text{co}}[\Phi] = \frac{1}{2} \sum_{rwsx} x^x_{rwsx} \left( [wr|xs] - [ws|xr] \right), \\
E^{(II)}_{\text{co}}[\Phi] = \frac{1}{2} \sum_{rwsx} s^x_{rwsx} \left( [wr|xs] - [ws|xr] \right), \\
E^{(III)}_{\text{co}}[\Phi] = \frac{1}{2} \sum_{rwsx} \tilde{s}^x_{rwsx} \left( [wr|xs] - [ws|xr] \right), \\
E^{(IV)}_{\text{co}}[\Phi] = \frac{1}{2} \sum_{rwsx} \tilde{x}^x_{rwsx} \left( [wr|xs] - [ws|xr] \right),
\]

where the coefficients are assumed to satisfy exchange symmetry, e.g., Eqs. (26) and (56).

For later use, we also mention that the correlation energy and the first correlation-energy functional, given by Eqs. (126) and (133a), can be written using the \( S \) amplitudes:

\[
E_{\text{co}}[\Phi] = \left( H^1_1 S^1_1 + \frac{1}{2} H^2_1 S^1_1 S^1_1 + H^2_2 S^2_2 \right)_{\text{cl}}, \\
E^{(I)}_{\text{co}}[\Phi] = \left( \frac{1}{2} H^2_2 S^1_1 S^1_1 + H^2_2 S^2_2 \right)_{\text{cl}},
\]

where we have used Eqs. (57a) and (57b).

**VII. EXACT FOCK OPERATORS**

Consider generalized, or exact, Fock operators \( \hat{F}^{(n)}_\Phi \), that are defined, in part, by the following matrix elements:

\[
\langle \psi_r | \hat{F}^{(n)}_\Phi | \psi_w \rangle = \langle \Phi_r | H | \Psi^{(n)}_\Phi \rangle; \quad \eta = I, II, III, IV,
\]

where the \( w \) and \( r \) orbitals are occupied and unoccupied within \( |\Phi\rangle \), respectively, as noted by Eqs. (6). By multiplying Eq. (80) from the left by \( \langle \Theta_r | \), using Eq. (63), and comparing the resulting relation to the above Eq., we have

\[
\langle \psi_r | \hat{F}^{(n)}_\Theta | \psi_w \rangle = 0,
\]

where the orbitals are defined by Eq. (60). When satisfied by all orbitals, this expression is equivalent to the Brillouin-Brueckner condition, given by Eq. (80). The operator form of Eq. (138) is

\[
\hat{K}_\Theta \hat{F}^{(n)}_\Theta \hat{\gamma}_\Theta = 0,
\]
where $\hat{\gamma}_\Phi$ is the one-particle, density-matrix operator for the determinantal-state $|\Phi\rangle$:

$$\hat{\gamma}_\Phi = \sum_{x \in \{\psi_\rightarrow \Phi\}} |\psi_x\rangle \langle \psi_x|; \quad (140)$$

$\hat{\kappa}_\Phi$ is the projector into the virtual-orbital subspace:

$$\hat{\kappa}_\Phi = \sum_{r \in \{\psi_u \rightarrow \Phi\}} |\psi_r\rangle \langle \psi_r|, \quad (141)$$

and the identity operator $\hat{I}$ can be expressed by

$$\hat{I} = \hat{\gamma}_\Phi + \hat{\kappa}_\Phi. \quad (142)$$

Multiplying Eq. (139) from the left and right by $\langle \psi_r|$ and $|\psi_w\rangle$ gives Eq. (138).

Since all of our generalized Fock operators – $\hat{F}_\Theta^{(I)}$, $\hat{F}_\Theta^{(II)}$, $\hat{F}_\Theta^{(III)}$, and $\hat{F}_\Theta^{(IV)}$ – satisfy Eq. (139), any one can be used to define an exact Fock operator $\hat{F}_\Theta$:

$$\hat{\kappa}_\Theta \hat{F}_\Theta \hat{\gamma}_\Theta = \hat{\kappa}_\Theta \hat{F}_\Theta^{(\eta)} \hat{\gamma}_\Theta = \hat{\kappa}_\Theta \hat{F}_\Theta^{(\nu)} \hat{\gamma}_\Theta, \quad (143)$$

and the Brillouin-Brueckner condition, Eq. (139), becomes

$$\hat{\kappa}_\Theta \hat{F}_\Theta \hat{\gamma}_\Theta = 0. \quad (144)$$

Using Eq. (142), this Eq. can be written as

$$\left(\hat{I} - \hat{\gamma}_\Theta\right) \hat{F}_\Theta \hat{\gamma}_\Theta = 0. \quad (145)$$

Since $\hat{\gamma}_\Theta$ is idempotent,

$$\hat{\gamma}_\Theta \hat{\gamma}_\Theta = \hat{\gamma}_\Theta, \quad (146)$$

Eq. (145) can be written as

$$\left(\hat{F}_\Theta \hat{\gamma}_\Theta - \hat{\gamma}_\Theta \hat{F}_\Theta\right) \hat{\gamma}_\Theta = 0. \quad (147)$$

By requiring $\hat{F}_\Theta$ to be, at least in part, Hermitian:

$$\hat{\gamma}_\Theta \hat{F}_\Theta \hat{\kappa}_\Theta = 0, \quad (148)$$

yields the following identity:

$$\left(\hat{F}_\Theta \hat{\gamma}_\Theta - \hat{\gamma}_\Theta \hat{F}_\Theta\right) \hat{\kappa}_\Theta = 0. \quad (149)$$
Adding together Eqs. (147) and (149), and using Eq. (142), indicates that \( \hat{\gamma}_\Theta \) and \( \hat{F}_\Theta \) commute:

\[
\left[ \hat{F}_\Theta, \hat{\gamma}_\Theta \right] = 0. \tag{150}
\]

Eq. (150) is a generalization of the one obtained for Hartree-Fock theory \([2, 49, 50]\).

Note that for any reference state, say \( |\Phi'\rangle \), we can find a corresponding state, \( |\Phi\rangle \), in which the following relation is satisfied:

\[
\hat{\kappa}_{\Phi} \hat{F}_\Theta (\eta) \hat{\gamma}_{\Phi} = 0. \tag{151}
\]

Solving this expression in an iterative and self-consistent-field manner leads to the Brillouin-Brueckner condition, Eq. (144), being satisfied, since when \( (|\Phi\rangle = |\Phi'\rangle) \), we have \( (|\Phi\rangle = |\Theta\rangle) \).

Consider now the following application of the identity operator:

\[
\hat{I} \hat{F}_\Phi |\psi_w\rangle = \hat{F}_\Phi |\psi_w\rangle = \sum_{x \in \{\psi_o \rightarrow \Phi\}} \varepsilon_{xw}^\phi |\psi_x\rangle + \sum_{r \in \{\psi_u \rightarrow \Phi\}} \varepsilon_{rw}^\phi |\psi_r\rangle, \tag{152}
\]

where

\[
\varepsilon_{ij}^\phi = \langle \psi_i | \hat{F}_\Phi | \psi_j \rangle. \tag{153}
\]

Setting \( (\Phi = \Theta) \), and using Eq. (138), gives exact Hartree–Fock Eqs:

\[
\hat{F}_\Theta |\psi_w\rangle = \sum_{x \in \{\psi_o \rightarrow \Theta\}} \varepsilon_{xw}^\Theta |\psi_x\rangle, \tag{154}
\]

where the orbital \( |\psi_w\rangle \) is from the set \( \{\psi_o \rightarrow \Theta\} \).

Returning to Eq. (137), inserting the identity operator – defined by Eq. (16) – we have

\[
\langle \psi_r | \hat{\mathcal{F}}^{(n)}_\Phi | \psi_w \rangle = \langle \Phi_w | H | \Phi \rangle + \langle \Phi_w | H | \Psi_{\Phi q}^{(n)} \rangle, \tag{155}
\]

where the trial-correlation functions \( |\Psi_{\Phi q}^{(n)}\rangle \) are given by Eq. (74); the first term on the right side of Eq. (155) is the off-diagonal block of the Fock-operator \( \hat{F}_\Phi \):

\[
\langle \psi_r | \hat{F}_\Phi | \psi_w \rangle = \langle \Phi_w | H | \Phi \rangle, \tag{156}
\]

where is \( \hat{F}_\Phi \) defined by Eq. (126). Substituting Eqs. (150) and (129) into (155), we have

\[
\langle \psi_r | \hat{\mathcal{F}}^{(n)}_\Phi | \psi_w \rangle = \langle \psi_r | \hat{\gamma}_\Phi | \psi_w \rangle + \langle \Phi_w | H \chi_{\Phi}^{\phi} | \Phi \rangle + \langle \psi_r | (\hat{F}_\Phi)_{\Phi} | \psi_w \rangle + \langle \psi_r | (H \chi_{\Phi}^{\phi})_{\Phi} | \psi_w \rangle, \tag{157}
\]

where

\[
\varepsilon_{ij}^\phi = \langle \psi_i | \hat{\gamma}_\Phi | \psi_j \rangle. \tag{153}
\]
where we use the more restrictive definition of an open (op) operator, presented in Appendix B.

Setting \( \Phi = \Theta \), and using Eqs. (132) and (138), gives another variant of the Brillouin-Brueckner condition:

\[
\left( \hat{F}_\Theta + (H\chi)_1 \right)_{\text{op}} = 0,
\]

where this expression acts within the one-body sector of the Hilbert space, even though the subscript op indicates the open portion – defined by the \( n \)-body sector.

Now let the second term on the right side of Eq. (155) define the off-diagonal block of correlation potentials \( v_{\text{co}}^\eta(x) \), given by

\[
\langle \psi_r | v_{\text{co}}^\eta | \psi_w \rangle = \langle \Phi_r | H | \psi_{\Phi}^{(\eta)} \rangle.
\]

Similarly, exchange-correlation potentials \( v_{\text{xc}}^\eta(x) \) are defined, in part, by

\[
\langle \psi_r | v_{\text{xc}}^\eta | \psi_w \rangle = \langle \psi_r | v_{\text{co}}^\eta | \psi_w \rangle - \langle \psi_r | K_\Phi | \psi_w \rangle.
\]

Using Eqs. (155), (156), and (159), and with no loss of generality, our exact Fock operators \( \hat{F}_\phi^{(\eta)} \) can be written

\[
\hat{F}_\phi^{(\eta)} = \hat{F}_\Phi + v_{\text{co}}^\eta.
\]

Multiplying Eq. (161) from the left and right by \( \langle \psi_r | \) and \( | \psi_w \rangle \), and using the one-body partitioning method of Eqs. (B8), gives

\[
\langle \psi_r | \hat{F}_\phi^{(\eta)} | \psi_w \rangle = \langle \psi_r | (\hat{F}_\Phi)_{\text{ex}} | \psi_w \rangle + \langle \psi_r | (v_{\text{co}}^\eta)_{\text{ex}} | \psi_w \rangle.
\]

Comparing Eq. (157) with (162), and using (139), we have

\[
(v_{\text{co}}^\eta)_{\text{ex}} = [(H\chi_\Phi^\eta)_1]_{\text{op}},
\]

and the Brillouin-Brueckner condition (158) becomes

\[
\left( \hat{F}_\Theta \right)_{\text{ex}} = 0,
\]

where

\[
\hat{F}_\Theta = \hat{F}_\Theta + v_{\text{co}}^\eta,
\]

and the \( \eta \) superscript is suppressed, since, in general we have

\[
(v_{\text{co}}^\eta)_{\text{ex}} = (v_{\text{co}}^\eta)_{\text{ex}} = (v_{\text{co}}^\eta')_{\text{ex}}.
\]
The remaining matrix elements of $v_{\eta}^{\Phi} - |\psi_w|v_{\eta}^{\Phi}|\psi_x\rangle$ and $\langle \psi_r|v_{\eta}^{\Phi}|\psi_s\rangle$ – are at our disposal. By defining these matrix elements in a manner that is independent of $\eta$, but dependent on $|\Phi\rangle$, $v_{\eta}^{\Phi}(x)$ and $\hat{F}_{\eta}$ are completely, and unambiguously determined; our exact Fock operator can be diagonalized:
\[ \hat{F}_{\eta}\psi_i^{\Phi}(x) = \varepsilon_i^{\Phi}\psi_i^{\Phi}(x), \] (167)
where orbital energies $\varepsilon_i^{\Phi}$ can be defined to give exact ionization potentials and electron affinities – exact Koopman’s theorems [21, 57]. In addition, since the operators, $\hat{f}_{\alpha}^\Phi$ and $\hat{f}_{\alpha}^{\Phi}$, that give the zeroth-order Hamiltonian $H_0^{\Phi}$, and the exact Fock operators, $\hat{F}_{\Phi}^{(\eta)}$, are not mutually exclusive, one tempting choice is
\[ \hat{f}_{\alpha}^\Phi = \hat{f}_{\alpha}^{\Phi} = \hat{F}_{\Phi}^{(\eta)}. \] (168)

By using the diagrammatic expansion for $\chi_{\eta}^{\Phi}$, and Eq. (163), a diagrammatic expansion for $(v_{\eta}^{\Phi})_{ex}$ can be obtained that is a subset of the open one-body diagrams of $H_{\chi}^{\Phi}$ [57].

VIII. REFERENCE–STATE ONE–PARTICLE DENSITY–MATRIX THEORY

A. Functionals of the one-particle density-matrix $\gamma$

There is a one-to-one correspondence between the set of determinant states, $\{|\Phi\rangle\}$, and their one-particle density-matrices [2, 50], $\{\gamma\}$, where these density-matrices are given by [49, 86, 87, 88, 89]
\[ \gamma(x, x') = \sum_{w \in \{\psi_o \rightarrow \Phi\}} \psi_w(x)\psi_w^*(x'). \] (169)
Because of this correspondence, determinantal states are uniquely determined by their one-particle density-matrix: $|\Phi(\gamma)\rangle$; functionals, or functions, that depend on $|\Phi\rangle$, can be written as ones depending on $\gamma$. For example, the total energy $E$, Eq. (10), and our energy functionals $E_{\eta}[\Phi]$, Eq (172), can be written
\[ E = E_1[\gamma] + E_{co}[\gamma], \] (170)
\[ E_{\eta}[\gamma] = E_1[\gamma] + E_{co}^{(\eta)}[\gamma], \] (171)
where, in addition, our trial wavefunctions $|\Psi_{\Phi(\gamma)}^{(\eta)}\rangle$ can be denoted by $|\Psi_{\gamma}^{(\eta)}\rangle$. 
For simplicity, we require the external potential $v(r)$ to be a spin-free operator, so the first-order energy can be written as

$$E_1[\gamma] = \int \left[ -\frac{1}{2} \nabla_r^2 \gamma(x, x') \right]_{x=x'} dx + \int v(r) \gamma(x, x) dx + E_3[\gamma] - E_x[\gamma], \quad (172)$$

where the Coulomb and exchange energies are

$$E_3[\gamma] = \frac{1}{2} \int \int r_{12}^{-1} \gamma(x_1, x_1) \gamma(x_2, x_2) dx_1 dx_2, \quad (173)$$

$$E_x[\gamma] = \frac{1}{2} \int \int r_{12}^{-1} \gamma(x_1, x_2) \gamma(x_2, x_1) dx_1 dx_2. \quad (174)$$

(As in Eq. (1), an integration over $x_i$ actually implies a summation over the spin variable $\omega_i$ and an integration over the spatial portion $r_i$.)

Similarly, the one-body operators $\hat{F}_\phi^{(o)}$, Eq. (161), can be written

$$\hat{F}_\gamma^{(o)} = \hat{F}_\gamma + v_c^{\gamma_o}, \quad (175)$$

where, instead of Eq. (125), the Fock operator is given by

$$\hat{F}_\gamma = -\frac{1}{2} \nabla^2 + v + J_\gamma - K_\gamma, \quad (176)$$

and the Coulomb $J_\gamma$ and exchange $K_\gamma$ operators satisfy:

$$J_\gamma \phi(x_1) = \int r_{12}^{-1} \gamma(x_2, x_2) \phi(x_1) dx_2, \quad (177)$$

$$K_\gamma \phi(x_1) = \int r_{12}^{-1} \gamma(x_1, x_2) \phi(x_2) dx_2. \quad (178)$$

In addition, the identity operator, given by Eq. (142), can be written

$$\hat{I} = \hat{\gamma} + \hat{\kappa}_\gamma, \quad (179)$$

where the density-matrix operator $\hat{\gamma}$ is defined by its kernel, $\gamma(x, x')$ [89]:

$$\hat{\gamma} \phi(x) = \int \gamma(x, x') \phi(x') dx', \quad (180)$$

and $\kappa_\gamma(x, x')$ is the kernel of the virtual-space projector:

$$\hat{\kappa}_\gamma \phi(x) = \int \kappa_\gamma(x, x') \phi(x') dx', \quad (181)$$
where

\[ \kappa_\gamma(x, x') = \sum_{r \in \{\psi_u \to \gamma\}} \psi_r(x) \psi_r^*(x'), \quad (182) \]

and \( \hat{\kappa}_\Phi \) is given by Eq. (141). Similarly, the one-particle density-matrix for the Brueckner state, say \( \tau(x, x') \), and its density-matrix operator, say \( \hat{\tau} \), are given by the following expressions:

\[ \tau(x, x') = \sum_{w \in \{\psi_o \to \Theta\}} \psi_w(x) \psi_w^*(x'), \quad (183) \]

\[ \hat{\tau} \phi(x) = \int \tau(x, x') \phi(x') \, dx', \quad (184) \]

where we have

\[ |\Theta\rangle = |\Phi(\tau)\rangle. \quad (185) \]

Since the one-particle density-matrix, \( \hat{\tau} \), also satisfies

\[ \hat{\tau} = \hat{\gamma}_\Theta, \quad (186) \]

where \( \hat{\gamma}_\Theta \) is given by Eq. (140), the Brillouin-Brueckner condition, given by Eq. (141), and its complex conjugate, given by Eq. (148), become

\[ \hat{\kappa}_\tau \hat{F}_\tau \hat{\tau} = 0, \quad (187a) \]

\[ \hat{\tau} \hat{F}_\tau \hat{\kappa}_\tau = 0; \quad (187b) \]

the commutation condition, given by Eq. (150), can be written

\[ [\hat{F}_\tau, \hat{\tau}] = 0; \quad (188) \]

the exact Hartree–Fock Eq. (154) is

\[ \hat{F}_\tau |\psi_w\rangle = \sum_{x \in \{\psi_o \to \tau\}} \varepsilon_{xw}^\tau |\psi_x\rangle, \quad (189) \]

where the occupied orbital, \( |\psi_w\rangle \), is from \( \{\psi_o \to \tau\} \); furthermore, the other Brillouin-Brueckner condition, Eq. (164), can be written as

\[ (\hat{F}_\tau)_{ex} = 0, \quad (190) \]

where Eq. (165) becomes

\[ \hat{F}_\tau = \hat{F}_\tau + \nu_{co}^\tau. \quad (191) \]
In the following subsections, we illustrate how the correlation energy and correlation-energy functionals, \( E_{\text{co}}[\gamma] \) and \( E_{\text{co}}^{(\eta)}[\gamma] \), can be obtained from perturbation theory, in which all terms (or diagrams) explicitly depend on \( \gamma \). (An explicit expression for the first-order energy, \( E_1[\gamma] \), is given by Eq. (172).)

**B. The correlation energy as a functional of the one-particle density matrix: \( E_{\text{co}}[\gamma] \)**

Consider the normal-ordered form of the Hamiltonian \( H \), given by Eqs. (123) and (124), where we choose to represent this operator using the following orbital sets: \( \{\psi_\sigma \rightarrow \gamma, \hat{f}_\sigma \} \) and \( \{\psi_\nu \rightarrow \gamma, \hat{f}_\nu \} \), and both sets are introduced in Sec. III C. Since the one-body portion of the Hamiltonian \( H_1^\gamma \) is determined by the Fock operator \( \hat{F}_\gamma \), it seems appropriate to use the following notation:

\[
H_1^\gamma = \{\hat{F}_\gamma\},
\]

or, equivalently, the expression \( \{\hat{F}_\gamma\} \) is defined by the following procedure: Obtain the Fock operator \( \hat{F}_\gamma \) for the one-particle Hilbert space, given by Eq. (176); write this operator in its second quantized form using the true vacuum state \(|\rangle\); re-write \( \hat{F}_\gamma \) using normal ordering with respect to the new vacuum state, \(|\Phi(\gamma)\rangle\): \( \hat{F}_\gamma = (\hat{F}_\gamma)_{\text{cl}} + \{\hat{F}_\gamma\} \); the uncontracted term is \( \{\hat{F}_\gamma\} \). In other words, \( \{\hat{F}_\gamma\} \) is the uncontracted term when the operator \( \hat{F}_\gamma \) is written in normal ordered form using Wick's theorem \[55, 56, 61, 73]\.

Using this notation, we also write

\[
H_2^\gamma = \{r_{12}^{-1}\},
\]

where, again, \( r_{12}^{-1} \) is written in second quantization using the true vacuum state \(|\rangle\) – given by the second term on the right side of Eq. (2) – and then it is re-written using normal-ordering with respect to the new vacuum state; the uncontracted term is \( \{r_{12}^{-1}\}_\gamma \), where the additional \( \gamma \)-subscript from \( \{\ldots\}_\gamma \), serves to remind us that the vacuum state is \(|\Phi(\gamma)\rangle\).

(This \( \gamma \) subscript is suppressed in Eq. (192a): The vacuum state is understood, since \( \gamma \) determines \( \hat{F}_\gamma \).)

The correlation energy \( E_{\text{co}} \) is determined by the one- and two-body parts of the Hamiltonian, \( \{\hat{F}_\gamma\} \) and \( \{r_{12}^{-1}\}_\gamma \). However, the individual orders of the perturbation expansion for \( E_{\text{co}} \), also depends, in addition, on the zeroth-order Hamiltonian, given by Eq. (11); this operator...
can be written as

\[ H_0^\gamma = \hat{O}_\gamma + \hat{u}_\gamma, \]  

(193)

where these terms – \( \hat{O}_\gamma \) and \( \hat{u}_\gamma \) – are the occupied and unoccupied portions of \( H_0^\gamma - (H_0^\gamma)_{oc} \) and \( (H_0^\gamma)_{un} \) – and are given by the following:

\[ \hat{O}_\gamma = \sum_{w \in \{\psi_o \rightarrow \gamma, \hat{f}_o\}} \epsilon_w \, a_w^\dagger a_w, \]  

(194a)

\[ \hat{u}_\gamma = \sum_{r \in \{\psi_u \rightarrow \gamma, \hat{f}_u\}} \epsilon_r \, a_r^\dagger a_r. \]  

(194b)

Using this notation, our zeroth-order Hamiltonian in normal-ordered form can be written as

\[ H_0^\gamma = E_0[\gamma] + \{\hat{O}_\gamma\} + \hat{u}_\gamma, \]  

(195)

where \( \hat{u}_\gamma \) is already normal-ordered; the constant term \( E_0[\gamma] \) is the zeroth-order energy of \( |\Phi(\gamma)\rangle \):

\[ H_0^\gamma |\Phi(\gamma)\rangle = E_0[\gamma] |\Phi(\gamma)\rangle, \]  

(196)

and is given by

\[ E_0[\gamma] = \sum_{w \in \{\psi_o \rightarrow \gamma, \hat{f}_o\}} \epsilon_w. \]  

(197)

Note that the first-order and the correlation energies, \( E_1[\gamma] \) and \( \mathcal{E}_{co} \), do not depend the zeroth-order energy \( E_0[\gamma] \).

The perturbation \( V_\gamma \), defined by Eqs. (12), can also be written in normal-ordered form:

\[ V_\gamma = V_1^\gamma + V_2^\gamma, \]  

(198)

where, from Eqs. (124), (124a), (192), and (195), the individual terms are given by the following expressions:

\[ V_1^\gamma = E_1[\gamma] - E_0[\gamma], \]  

(199a)

\[ V_2^\gamma = \{\tilde{F}_\gamma\} - \{\tilde{O}_\gamma\} - \hat{u}_\gamma, \]  

(199b)

\[ V_2^\gamma = \{r_{12}^{-1}\}_\gamma. \]  

(199c)

The one- and two-body parts of \( H \) are given by Eqs. (124b) and (124c), and are equal to \( \{\tilde{F}_\gamma\} \) and \( \{r_{12}^{-1}\}_{12} \), as indicated by Eqs. (192). The Goldstone diagrammatic representation
of these operators can be written in the following manner:

\[
\{ \hat{F}_\gamma \} = H_1^\gamma = \begin{array}{c}
\vrule height 3ex width 0.5ex
\end{array},
\]

\[ (200a) \]

\[
\{ r_{12}^{-1} \} = H_2^\gamma = \begin{array}{c}
\vrule height 3ex width 0.5ex
\end{array}.
\]

\[ (200b) \]

The one-body part of the perturbation \( V_1^\gamma \) is usually represented by a single diagrammatic operator. However, for our purposes, it is convenient to use separate diagrammatic operators for the three terms on the right side of Eq. (199b), where \( \{ \hat{F}_\gamma \} \) is presented by Eq. (200a). Since the other two terms are diagonal, it is appropriate is simply represent them as (unfilled) arrows:

\[
-\{ \hat{O}_\gamma \} = \begin{array}{c}
\vrule height 3ex width 0.5ex
\end{array},
\]

\[ (201a) \]

\[
-\hat{u}_\gamma = \begin{array}{c}
\vrule height 3ex width 0.5ex
\end{array}.
\]

\[ (201b) \]

In contrast, hole- and particle-lines, by themselves, are represented by filled arrows: \( \cdot \) and \( \cdot \).

As a slight alternative to the usual approach to evaluate the diagrams of the correlation energy \( E_{co} \), we associate a hole line corresponding to a \( w \)-occupied orbital with a \( \psi_w(x_1)\psi_w^*(x_2) \) factor; we associate a particle line corresponding to an \( r \)-unoccupied orbital with a \( \psi_r(x_2)\psi_r^*(x_1) \) factor, where \( x_1 \) and \( x_2 \) denote the dummy integration variables that arise from the vertices. Using this convention, the sole diagram involving the Fock operator \( \hat{F}_\gamma \) from second-order perturbation theory can be evaluated in the following manner:

\[
(\varepsilon_{rw}^\gamma)^{-1} \int d\mathbf{x}_1 d\mathbf{x}_2 \left( \hat{F}_{\gamma_1\gamma_w}(\mathbf{x}_1, \mathbf{x}_2) \right) \cdot \hat{F}_{\gamma_2\gamma_r}(\mathbf{x}_2, \mathbf{x}_1),
\]

\[ (202) \]

where

\[
\varepsilon^\gamma_{rw} = \epsilon^\gamma_w - \epsilon^\gamma_r,
\]

\[ (203) \]

and the repeated indices \( r \) and \( w \) are summed over; \( \hat{F}_{\gamma_i} \) denotes the Fock operator \( \hat{F}_\gamma \) given by Eq. (176) – acting upon \( (\mathbf{x}_i) \); the term \( (\hat{F}_{\gamma_i} \cdots) \) indicates that \( \hat{F}_{\gamma_i} \) exclusively acts
within the brackets; furthermore, the \( w \)th component of the (one-particle) density-matrix \( \gamma \) is denoted by

\[
\gamma_w(x_1, x_2) = \psi_w(x_1)\psi_w^*(x_2); 
\]

(204a)

the \( r \)th orthogonal-component of \( \gamma \) is denoted by

\[
\gamma_r(x_1, x_2) = \psi_r(x_1)\psi_r^*(x_2),
\]

(204b)

where, for a complete set of orbital states, we have [54]

\[
\delta(x_1 - x_2) = \sum_w \gamma_w(x_1, x_2) + \sum_r \gamma_r(x_1, x_2),
\]

(205)

which is a shorthand notations for

\[
\delta(x_1 - x_2) = \delta(r_1 - r_2)\delta_{\omega_1\omega_2}.
\]

(206)

In order to further compress our notation, we use the convention that all repeated dummy indices are integrated over and restrict the Fock operator \( \hat{F}_\gamma \) to exclusively act upon the first index of any two-body function, i.e., \( \hat{F}_\gamma, \alpha'(x_j, x_i)\alpha(x_i, x_j) = \alpha'(x_j, x_i)\hat{F}_\gamma\alpha(x_i, x_j) \);

Eq. (202) can then be written as

\[
= (\varepsilon_{rw}^\gamma)^{-1}\hat{F}_\gamma\gamma_w(x_1, x_2)\hat{F}_\gamma\gamma_r(x_2, x_1),
\]

(207a)

and the other two diagrams from second-order perturbation theory have the following forms:

\[
= \frac{1}{2}(\varepsilon_{rw}^\gamma)^{-1}r_{12}^{-1}r_{34}^{-1}\gamma_w(x_1, x_3)\gamma_r(x_3, x_1)\gamma_x(x_2, x_4)\gamma_s(x_4, x_2),
\]

(207b)

\[
= -\frac{1}{2}(\varepsilon_{rw}^\gamma)^{-1}r_{12}^{-1}r_{34}^{-1}\gamma_w(x_1, x_3)\gamma_r(x_3, x_2)\gamma_x(x_2, x_4)\gamma_s(x_4, x_1),
\]

(207c)

where

\[
\varepsilon_{rw}^\gamma = \varepsilon_{rw}^\gamma + \varepsilon_{sx}^\gamma.
\]

(208)

The diagonal terms arising from the zeroth-order Hamiltonian, given by \( -\{\hat{O}_\gamma\} \) and \( -\hat{u}_\gamma \), and represented by Eqs. (201), first appear in third order. For example, the following two
diagrams can be obtained by inserting $-\{\hat{O}_\gamma\}$ and $-\hat{u}_\gamma$ into the diagram on the left side of Eq. (207a):

\[
\begin{aligned}
\psi &= -\frac{(-\epsilon_w)}{(\epsilon_{rw})^2}\hat{F}_{\gamma_1\gamma_w}(x_1, x_2)\hat{F}_{\gamma_2\gamma_r}(x_2, x_1), \\
\kappa &= \frac{(\epsilon_r)}{(\epsilon_{rw})^2}\hat{F}_{\gamma_1\gamma_w}(x_1, x_2)\hat{F}_{\gamma_2\gamma_r}(x_2, x_1).
\end{aligned}
\tag{209a}
\]

The hole-line operator $\{\hat{O}_\gamma\}$ generates an additional hole line when inserted into a diagram and, therefore, a factor of $-1$ is included when diagram (209a) is evaluated, where this factor cancels the $-1$ factor from $-\epsilon_w$. Since this type of cancellation always occurs, as an alternative, we associate a factor of $\epsilon_w$ for $\{\hat{O}_\gamma\}$ insertions, and treat $\{\hat{O}_\gamma\}$ vertices as ones that do not generate additional hole lines; $\hat{u}_\gamma$ is associated with a $-\epsilon_r$ factor. Keep in mind, also, that these operators generate an additional energy-denominator factor, e.g., $\epsilon_{rw}$, when inserted into a diagram.

One advantage of partitioning the one-body part of the perturbation $V_\gamma^1$ into individual components, as indicated by Eq. (199b), is that it yields correlation-energy diagrams that explicitly depend on the Fock operator $\hat{F}_\gamma$. Furthermore, an overall dependence of the correlation energy $E_{\text{co}}$ on the one-particle density matrix $\gamma$ becomes, to a certain extent, transparent, by using Eqs. (204), (169), and (182), yielding the following identities:

\[
\begin{aligned}
\gamma(x_1, x_2) &= \sum_w \gamma_w(x_1, x_2), \\
\kappa(x_1, x_2) &= \sum_r \gamma_r(x_1, x_2),
\end{aligned}
\tag{210}
\]

and note that $\kappa_\gamma$ depends, explicitly, on $\gamma$:

\[
\delta(x_1 - x_2) = \gamma(x_1, x_2) + \kappa_\gamma(x_1, x_2),
\tag{212}
\]

where the operator form of this relation is Eq. (179).

The individual diagrams depend, in part, on each of the $\gamma_w$ components, given by Eq. (204a), and the orthogonal components $\gamma_r$, given by Eq. (204b). In addition, each diagram depends on the set of orbital energies $\{\epsilon^{\gamma}\}$, which are at our disposal. In order to
make each diagram an explicit functional of the one-particle density matrix $\gamma$, we choose all occupied orbitals to be degenerate, with energy $\epsilon_0^\gamma$; also, we choose all unoccupied orbitals to be degenerate, with energy $\epsilon_u^\gamma$. With these choices, the zeroth-order Hamiltonian, given by Eq. (41), becomes

$$H_0^\gamma = \epsilon_0^\gamma \sum_{w \in \{ \psi_o \rightarrow \gamma, \hat{f}_o \}} a_w^\dagger a_w + \epsilon_u^\gamma \sum_{r \in \{ \psi_u \rightarrow \gamma, \hat{f}_u \}} a_r^\dagger a_r, \quad (213)$$

and since this operator is invariant to a unitary transformation of occupied or unoccupied orbitals, it no longer depends on $\hat{f}_o^\gamma$ and $\hat{f}_u^\gamma$ – any set of orbitals defining $\gamma$ is appropriate – so we can write

$$H_0^\gamma = \epsilon_0^\gamma \sum_{w \in \{ \psi_o \rightarrow \gamma \}} a_w^\dagger a_w + \epsilon_u^\gamma \sum_{r \in \{ \psi_u \rightarrow \gamma \}} a_r^\dagger a_r. \quad (214)$$

It is easily proven that all perturbative orders, except for the zeroth-order, depend on the orbital-energy difference $\epsilon^\gamma$, given by

$$\epsilon^\gamma = \epsilon_0^\gamma - \epsilon_u^\gamma, \quad (215)$$

and not on the individual orbital-energies, $\epsilon_0^\gamma$ and $\epsilon_u^\gamma$. Therefore, we can choose ($\epsilon_u^\gamma = 0$), and so our only parameter is $\epsilon^\gamma$. With this choice we have

$$H_0^\gamma = \epsilon^\gamma \hat{N}_\gamma, \quad (216)$$

where $\hat{N}_\gamma$ is the number operator for the occupied orbitals,

$$\hat{N}_\gamma = \sum_{w \in \{ \psi_o \rightarrow \gamma \}} a_w^\dagger a_w, \quad (217)$$

and it gives the total number of occupied orbitals when acting on a single determinant. In the one-particle Hilbert space, this operator is the projector for the occupied subspace – spanned by $\{ \psi_o \rightarrow \gamma \}$ – or, the one-particle density-matrix operator:

$$\hat{N}_\gamma = \sum_{w \in \{ \psi_o \rightarrow \gamma \}} |\psi_w^\gamma\rangle\langle \psi_w^\gamma| = \hat{\gamma}. \quad (218)$$

Using the above two expressions, let us generalize the definition of $\hat{\gamma}$:

$$\hat{\gamma} = \sum_{w \in \{ \psi_o \rightarrow \gamma \}} a_w^\dagger a_w, \quad (219)$$
and write the zeroth-order Hamiltonian in a simplified form, given by

\[ H_0^\gamma = \varepsilon_\gamma \hat{\gamma}. \] (220)

By normal-ordering this expression, we have

\[ H_0^\gamma = \varepsilon_\gamma N_\gamma + \varepsilon_\gamma \{ \hat{\gamma} \}, \] (221)

where \( N_\gamma \) is the number of particles within \( |\Phi(\gamma)\rangle \), and from Eq. (195), we get the following identities:

\[ E_0[\gamma] = \varepsilon_\gamma N_\gamma, \] (222)

\[ \{ \hat{O}_\gamma \} = \varepsilon_\gamma \{ \hat{\gamma} \}, \] (223)

\[ \hat{u}_\gamma = 0; \] (224)

furthermore, our zero- and one-body portion of the perturbation, Eqs. (199a) and (199b), have the following modified forms:

\[ V_c^\gamma = E_1[\gamma] - \varepsilon_\gamma N_\gamma, \] (225a)

\[ V_1^\gamma = \{ \hat{F}_\gamma \} - \varepsilon_\gamma \{ \hat{\gamma} \}. \] (225b)

Eq. (224) indicates that the unoccupied operator, \( \hat{u}_\gamma \), represented by Eq. (201b), does not appear in the expansion of the correlation-energy \( E_{\infty}; \{ \hat{O}_\gamma \} \), represented by Eq. (201a) and given by \( \varepsilon_\gamma \{ \hat{\gamma} \} \), is associated with a factor of \( \varepsilon_\gamma \). Each diagram now becomes an explicit functional of \( \gamma \) and \( \kappa \). For example, the second-order diagrams can be written in the following manner:

\[ = \varepsilon_\gamma^{-1} \hat{F}_{\gamma_1}(x_1, x_2) \hat{F}_{\gamma_2}(x_2, x_1), \] (226)

\[ = \frac{1}{4} \varepsilon_\gamma^{-1} r_{12}^{-1} r_{34}^{-1} \gamma(x_1, x_3) \kappa_\gamma(x_3, x_1) \gamma(x_2, x_4) \kappa_\gamma(x_4, x_2), \] (227)

\[ = -\frac{1}{4} \varepsilon_\gamma^{-1} r_{12}^{-1} r_{34}^{-1} \gamma(x_1, x_3) \kappa_\gamma(x_3, x_2) \gamma(x_2, x_4) \kappa_\gamma(x_4, x_1), \] (228)
where $\kappa_\gamma$ is given by Eq. (212).

In order to remove the explicit dependence on $\kappa_\gamma$, we first note that the kernel of the Fock operator is given by [2]:

$$F_\gamma(x_1, x_2) = \delta(x_2-x_1) \left[ -\frac{1}{2} \nabla^2 + v(r_2) \right] + \delta(x_2-x_1) \int r_{23}^{-1} \gamma(x_3, x_3) \, dx_3 - r_{12}^{-1} \gamma(x_1, x_2),$$

or we can use its matrix representation from a complete basis set:

$$F_\gamma(x_1, x_2) = \sum_{ij} \psi_i(x_1) \langle \psi_i | \hat{F}_\gamma | \psi_j \rangle \psi_j^*(x_2).$$

In any case, we use the following identity:

$$\hat{F}_\gamma \alpha(x_1, x_2) = \int d x_3 \, F_\gamma(x_1, x_3) \alpha(x_3, x_2),$$

and

$$= \varepsilon_\gamma^{-1} F_\gamma(x_1, x_3) \gamma(x_3, x_2) F_\gamma(x_2, x_4) \kappa_\gamma(x_4, x_1).$$

Using Eq. (212), this term becomes

$$\varepsilon_\gamma^{-1} F_\gamma(x_1, x_3) \gamma(x_3, x_2) F_\gamma(x_2, x_4) \kappa_\gamma(x_4, x_1) =$$

$$\varepsilon_\gamma^{-1} \left[ F_\gamma(x_1, x_3) \gamma(x_3, x_2) F_\gamma(x_2, x_4) \delta(x_4-x_1) - F_\gamma(x_1, x_3) \gamma(x_3, x_2) F_\gamma(x_2, x_4) \gamma(x_4, x_1) \right].$$

The first term on the right side reduces to

$$\varepsilon_\gamma^{-1} F_\gamma(x_1, x_3) \gamma(x_3, x_2) F_\gamma(x_2, x_4) \delta(x_4-x_1) = \varepsilon_\gamma^{-1} F_\gamma(x_1, x_3) \gamma(x_3, x_2) F_\gamma(x_2, x_4),$$

where $F_\gamma(x_2, x_1)$ is given by Eq. (230), and not by Eq. (229), since this form of the Fock kernel contains the laplacian $\nabla^2$, which is only defined when acting upon a function. As a possible alternative, the term on the left side of Eq (234) can be treated using the Fock kernel, given by Eq. (229), and a representation of delta function that is convenient to differentiate. This approach is probably more efficient, since it avoids the sums over the one-particle basis that appears in the matrix representation of the Fock kernel, Eq. (230).

The substitution for $\kappa_\gamma(x_4, x_1)$ in Eq. (233) is applicable for any diagram. For example, consider the second order (correction to the) energy, denoted by $E_2[\gamma]$, that is given by a sum of the right sides of Eqs. (232), (227), and (228); where, using Eq. (212), it can be written as a explicit functional of $\gamma$: 
\[
E_2[\gamma] = \varepsilon_{\gamma}^{-1} \left[ F_\gamma(x_1, x_2)\gamma(x_2, x_3)F_\gamma(x_3, x_1) - F_\gamma(x_1, x_2)\gamma(x_2, x_4)F_\gamma(x_3, x_1) \right]
\]

\[
+ \frac{1}{4} \varepsilon_{\gamma}^{-1} \left[ r_{12}^{-2} \gamma(x_1, x_1)\gamma(x_2, x_2) - 2r_{12}^{-1}r_{13}^{-1} \gamma(x_1, x_1)|\gamma(x_2, x_3)|^2 + r_{12}^{-1}r_{34}^{-1} |\gamma(x_1, x_3)|^2 |\gamma(x_2, x_4)|^2
\right.

\[
- r_{12}^{-2} |\gamma(x_1, x_2)|^2 + 2r_{31}^{-1}r_{12}^{-1}\gamma(x_1, x_2)\gamma(x_2, x_3)\gamma(x_3, x_1) - r_{13}^{-1}r_{24}^{-1}\gamma(x_1, x_2)\gamma(x_2, x_3)\gamma(x_3, x_4)\gamma(x_4, x_1) \right].
\]

The individual terms from Eq. (235), as well as higher-order terms, can be represented by diagrams, where we write the Fock kernel in the following manner:

\[
F_\gamma(x_1, x_2) = \begin{cases} \hline \xrightarrow{\gamma} \xrightarrow{\gamma} \\ \gamma \end{cases},
\]

and the two terms from Eq. (233) are given by

\[
\begin{align*}
34 & = -\varepsilon_{\gamma}^{-1} F_\gamma(x_1, x_2)\gamma(x_2, x_3)F_\gamma(x_3, x_4)\gamma(x_4, x_1), \\
34 & = \varepsilon_{\gamma}^{-1} F_\gamma(x_1, x_2)\gamma(x_2, x_3)F_\gamma(x_3, x_4)\delta(x_4, x_1).
\end{align*}
\]

These diagrams are evaluated by following the arrows in a backwards direction, where the circled arrow in Eq. (237a) indicates that this line is not a particle line, but a hole one with an additional factor of $-1$. This convention conforms to the one used for folded diagrams in valence-universal multireference perturbation theory [53, 56, 74, 78, 79]. The $\delta$–line in Eq. (237b) yields a $\delta(x_4, x_1)$ factor; the integration over the $x_4$ can be performed, as in Eq. (234), and the resulting diagram can be represented by

\[
\begin{cases} \hline \xrightarrow{\gamma} \xrightarrow{\gamma} \\ \gamma \end{cases} = \varepsilon_{\gamma}^{-1} F_\gamma(x_1, x_2)\gamma(x_2, x_3)F_\gamma(x_3, x_1),
\]

where the sole purpose of the above internal line without an arrow is to preserve the dummy index – in this case $x_1$ – for the two vertices it connects.

The diagrams from Eqs. (238) and (237a) correspond to the first two terms on the right side of Eq. (235); the other terms are given by the diagrams from Fig. 1. The mirror-image
diagrams (b) and (c) are equivalent, or non-distinct. Therefore, one of them can be omitted if a factor of 2 is included when evaluating the other one. Similarly, diagrams (f) and (g) are also non-distinct, so one can be omitted. Higher-order, correlation-energy $E_{co}$ diagrams are obtained in a similar way.

It is well known that $E_{co}$ is given by the set of connected diagrams, when (at least some of) the exclusion principle violating (EPV) diagrams are included [51, 52, 53, 54, 55, 56, 71, 72, 73]. Diagrams (a) through (f) in Fig. 2 present examples of diagrams that contribute to $E_{co}$. (Diagram (g) is disconnected and does not contribute.) When orbital degeneracy is not imposed, the hole and particle lines in these diagrams correspond to $\gamma_w$ and $\gamma_r$, respectively. However, by imposing orbital degeneracy, as indicated by Eq. (220), and using Eq. (212), these diagrams can be converted into ones that explicitly depend on $\gamma$, where the arrows representing the particle lines are either deleted or circled, in all unique ways. Additional diagrams containing the $-\varepsilon_\gamma \{\hat{\gamma}\}$ (or $-\{\hat{O}_\gamma\}$) interactions are generated by adding unfilled arrows, as represented by Eqs. (201a) and (223), and including a factor of $\varepsilon_\gamma$ for each one appearing in a diagram, as well as the appropriate energy-denominators. For example, the following sixth-order diagram is generated from diagram (a) from Fig. 2:

\[
\begin{align*}
\frac{1}{16} \varepsilon_\gamma^{-3} \gamma(x_1, x_2) \gamma(x_2, x_3) \gamma(x_3, x_4) \gamma(x_4, x_5) F_\gamma(x_5, x_6) \gamma(x_6, x_1),
\end{align*}
\]

where the dummy index from the left-bottom vertex is $x_1$. The above diagram contains four hole-lines, one loop, and a circled particle-line, yielding, overall, a factor of $+1$. In addition, each one of the two unfilled-arrow interactions give a factor of $\varepsilon_\gamma$, and an energy-denominator factor of $2\varepsilon_\gamma$ – since both interactions appears within a double excitation – so overall a factor of $(2\varepsilon_\gamma)^{-1}\varepsilon_\gamma$, or $\frac{1}{2}$, is obtained for each of these interactions; in general,
an unfilled-arrow interaction gives a factor of $\frac{1}{n}$ when appearing on a $n$–body excitation. In the above diagram, an additional factor of $\frac{1}{4}\varepsilon^{-3}$ also appears from the remaining three energy-denominators.

A discussion of perturbative convergence when imposing orbital degeneracies is presented in Appendix C.

C. The correlation-energy functionals $E^{(q)}_{\text{co}}[\gamma]$

We now briefly discuss the diagrammatic representation of the correlation-energy functionals $E^{(q)}_{\text{co}}$; the details are given elsewhere [57]. The diagrams for $E^{(q)}_{\text{co}}$ are a subset of the correlation-energy $E_{\text{co}}$ diagrams. Therefore, we continue to use the diagrams from Fig. 2 as examples, where, as mentioned previously, these diagrams can be converted into ones that explicitly depend on $\gamma$; additional diagrams containing $-\varepsilon_{\gamma}\{\hat{\gamma}\}$ interactions are easily generated from the ones in the figure.

Comparing Eqs. (135) and (136), we see that the $E^{(I)}_{\text{co}}$ diagrams that contribute to $(H^*_1 S^*_1)_{\text{cl}}$, or $(\{\hat{F}_\gamma\} S^*_1)_{\text{cl}}$, do not contribute to $E^{(I)}_{\text{co}}$, where these diagrams have a final interaction, associated with $H^*_1$, and a single-excitation below this last interaction, associated with $S^*_1$. Diagram (a) from Fig. 2 is an example of a $(H^*_1 S^*_1)_{\text{cl}}$ diagram.

Eqs. (136) and (133b) indicate that the $E^{(II)}_{\text{co}}$ diagrams are a subset of the $E^{(I)}_{\text{co}}$ diagrams, where diagrams contributing to $(\frac{1}{2}H^*_2 S^*_1 S^*_1)_{\text{cl}}$ do not contribute to $E^{(II)}_{\text{co}}$. Diagram (b) in Fig. 2 is an example of a $(\frac{1}{2}H^*_2 S^*_1 S^*_1)_{\text{cl}}$ diagram [56, 74]; when the top $H^*_2$ interaction is removed, the resultant diagram is disconnected – it possessing two pieces, where, using the factorization theorem, it is easily demonstrated that each of these fragments contribute to $S^*_1$. In general, any $E^{(II)}_{\text{co}}$ diagrams diagram that generates a disconnected diagram by removing its top interaction is not a $E^{(II)}_{\text{co}}$ diagram, and the resulting disconnected diagram contributes to $\frac{1}{2}S^*_1 S^*_1$. 

FIG. 2: Examples of $E_{\text{co}}$ and $E^{(q)}_{\text{co}}$ diagrams.
It is easily shown that the $E_{\text{co}}^{(\text{III})}$ diagrams are a subset of the $E_{\text{co}}^{(\text{II})}$ diagrams [57]. In general, any $E_{\text{co}}^{(\text{II})}$ diagram that has an intermediate single-excitation does not contribute to $E_{\text{co}}^{(\text{III})}$. An example is given by diagram (c) in the figure. This diagram possesses a single-excitation that appears in the second order. In other words, if we remove the top-two interactions, a second-order, single-excitation diagram is produced.

Another type of $E_{\text{co}}^{(\text{II})}$ diagram that does not contribute to $E_{\text{co}}^{(\text{III})}$ is diagram (d). If we remove the top two interactions from this diagram we obtain a disconnected diagram comprised of two fragments – one fragment being a third-order single-excitation diagram and the other one being a first-order double-excitation diagram. In general, if we remove any of the top interaction of a $E_{\text{co}}^{(\text{II})}$ diagram and obtain a disconnected diagram, in which one or more fragments are single-excitation diagrams, the (parent) $E_{\text{co}}^{(\text{II})}$ diagram does not contribute to $E_{\text{co}}^{(\text{III})}$.

Diagrams (e) and (f) contribute to $E_{\text{co}}^{(\text{II})}$. Diagram (e) is connected in each order; diagram (f) is disconnected in the second order, but both fragments are double-excitation diagrams.

By including certain EPV diagrams, disconnected diagram can be excluded from the set of diagrams that contribute to the first three correlation-energy functionals: $E_{\text{co}}^{(\text{I})}$, $E_{\text{co}}^{(\text{II})}$, and $E_{\text{co}}^{(\text{III})}$. However, disconnected diagrams, like diagram (g), do contribute to $E_{\text{co}}^{(\text{IV})}$; the set of diagrams representing $E_{\text{co}}^{(\text{IV})}$ excludes diagrams with intermediate single-excitations, and this omission removes certain disconnected diagrams that are needed to invoke the factorization theorem and obtain a linked diagram expansion.

IX. TREATMENT OF THE EXTERNAL POTENTIAL

A. External potential dependence on $E_{\text{co}}^{(\text{I})}$ and $E_{\text{co}}^{(\text{II})}$

Density functional theory employs a universal exchange-correlation functional, independent of the external potential, permitting approximations to be derived from model systems, where, in the vicinity of the model systems, the general form of the exchange-correlation functional is known. In contrasts, our correlation-energy functionals depend on the external potential $v(\mathbf{r})$: $E_{\text{co}}^{(\text{I})}[\gamma, v]$, and are, therefore, in this sense, not universal. Nevertheless, by partitioning $E_{\text{co}}^{(\text{I})}[\gamma, v]$ into individual terms that are – to a varying degree – universal, we can also obtain approximations from model systems.
In order to pursue this approach, and partition $E^{(\gamma)}_{\text{co}}[\gamma, v]$, we first partition the Fock-operator, given by Eq. (176), into two terms:

$$\hat{F}_\gamma = \hat{F}^g_\gamma + v,$$

where $\hat{F}^g_\gamma$ is the Fock operator for an electron gas:

$$\hat{F}^g_\gamma = -\frac{1}{2} \nabla^2 + J_\gamma - K_\gamma,$$

and this operator is independent of the external potential $v$. Using this partitioning, the one-body part of the perturbation $V^\gamma_1$, given by Eq. (199b), can be written as

$$V^\gamma_1 = \{\hat{F}^g_\gamma\} + \{v\} - \{\hat{o}_\gamma\} - \hat{u}_\gamma,$$

where the normal-ordered, uncontracted portions of $\hat{F}^g_\gamma$ and $v$ have the following forms:

$$\{\hat{F}^g_\gamma\} = \sum_{i,j} [i|\hat{F}^g_\gamma|j]\{a_i^\dagger a_j\},$$

$$\{v\} = \sum_{i,j} [i|v|j]\{a_i^\dagger a_j\}.$$

The correlation energy and our correlation-energy functionals, $E^{(\gamma)}_{\text{co}}[\gamma, v]$ and $E^{(\eta)}_{\text{co}}[\gamma, v]$, have a dependence on the external potential $v$ that arises, exclusively, from the $\{v\}$ contribution to $V^\gamma_1$, as indicated in Eq. (242). In the diagrammatic treatment presented in Sec. VIII B, $V^\gamma_1$ is partitioned into three terms, given by Eq. (199b). We now consider an approach where we partitioned it into the four terms, given by Eq. (242).

The diagrammatic representations of $-\{\hat{o}_\gamma\}$ and $-\{\hat{u}_\gamma\}$ are given by Eqs. (201); the other two terms from Eq. (242) use the following:

$$\{\hat{F}^g_\gamma\} = \odot \quad \text{and}$$

$$\{v\} = \odot.$$

For simplicity, in this section, we consider diagrammatic examples that do not distinguish between the various functionals, do not contain $-\{\hat{o}_\gamma\}$ and $-\{\hat{u}_\gamma\}$ insert, and do not explicitly depend on $\gamma$. For example, diagrams (a) through (d) in Fig. 3 are simple examples of
fourth-order diagrams that contain the \( \{ \hat{F}_\gamma^g \} \) and \( \{ v \} \) operators. These diagrams contribute to the correlation energy \( \mathcal{E}_{co}[\gamma, v] \), and any of the correlation-energy functionals \( E_{co}[\gamma, v]^{(n)} \). Diagram (e) is the corresponding diagram that uses the \( \{ \hat{F}_\gamma \} \) operator, given by Eq. (200a).

All four diagrams, (a) through (d), can be obtained from diagram (e) by replacing the \( \{ \hat{F}_\gamma^g \} \) operators with the \( \{ \hat{F}_\gamma \} \) and \( \{ v \} \) operators in all unique ways; the sum of diagrams (a) through (d) is equal to diagram (e). In general, all diagrams containing \( \{ \hat{F}_\gamma^g \} \) and \( \{ v \} \) can be obtained from the \( \{ \hat{F}_\gamma \} \) diagrams by using this approach. A similar procedure can be used when adding an additional perturbation [56].

**B. Electron gas terms**

Note that the diagrams from Fig. 3 can be partitioned into one that does not depend on the external potential \( v \), diagram (a) in the figure, and the remaining ones that do depend on \( v \). This is a general result when using the partitioned Fock operator \( \hat{F}_\gamma \), given by Eq. (240); therefore, the correlation energy \( \mathcal{E}_{co}[\gamma, v] \), and the correlation-energy functionals \( E_{co}[\gamma, v]^{(n)} \), can be divided in the following manner:

\[
\mathcal{E}_{co}[\gamma, v] = \mathcal{E}_{co}^{(0)}[\gamma] + \mathcal{E}_{co}^{(1+)}[\gamma, v],
\]

\[
E_{co}^{(n)}[\gamma, v] = E_{co}^{(n,0)}[\gamma] + E_{co}^{(n,1+)}[\gamma, v],
\]

where \( \mathcal{E}_{co}^{(0)}[\gamma] \) and \( E_{co}^{(n,0)}[\gamma] \) are universal functionals of \( \gamma \), independent of the external potential; they are given by the sum of diagrams that do not contain \( \{ v \} \) inserts; including diagram (a) in the figure, and the second-order Coulomb and exchange diagrams, given by Eqs. (207b) and (207c). The remaining diagrams of \( \mathcal{E}_{co}[\gamma, v] \) and \( E_{co}^{(n)}[\gamma, v] \) contribute to \( \mathcal{E}_{co}^{(1+)}[\gamma, v] \) and \( E_{co}^{(n,1+)}[\gamma, v] \), respectively, including diagrams (b) through (d) in the figure.

We refer to \( \mathcal{E}_{co}^{(0)}[\gamma] \) and \( E_{co}^{(n,0)}[\gamma] \) as electron-gas terms, since, for an electron gas, \( v \) is...
constant, so \( \{v\} \) is zero, and we have the following:

\[
\begin{align*}
\mathcal{E}_{\text{co}}[\gamma] &= \mathcal{E}_{\text{co}}^{(0)}[\gamma], \\
E_{\text{co}}^{(0)}[\gamma] &= E_{\text{co}}^{(0,0)}[\gamma].
\end{align*}
\]  

(electron gas)

(247a)

From Eq. (78), the terms on the left sides of Eqs. (247) are equal when \( \gamma \) is the one-particle density-matrix for the Brueckner state; hence, we have

\[
E_{\text{co}}^{(\eta,0)}[\tau_g] = \mathcal{E}_{\text{co}}^{(0)}[\tau_g],
\]

(248)

where \( \tau_g \) is the Brueckner-state one-particle density-matrix for an electron gas. For future use, we denote the correlation energy of an electron gas by \( \mathcal{E}_{\text{co}}^{(\text{gas})}[\gamma] \); explicitly, we have

\[
\mathcal{E}_{\text{co}}^{(\text{gas})}[\gamma] = \mathcal{E}_{\text{co}}[\gamma, v], \text{ for } v = \text{constant},
\]

(249)

so, using Eq. (247a), Eq. (248) can be written as

\[
E_{\text{co}}^{(\eta,0)}[\tau_g] = \mathcal{E}_{\text{co}}^{(\text{gas})}[\tau_g].
\]

(250)

C. Atomic and molecular terms

In order to further generalize Eqs. (246), we partition the external potential into its individual components:

\[
v = \sum_m v_m,
\]

(251)

where \( v_m(r) \) is the external potential from the \( m \)th nuclear point-charge at \( \mathbf{R}_m \):

\[
v_m(r) = -\frac{Z_m}{|\mathbf{R}_m - \mathbf{r}|},
\]

(252)

and we choose the following diagrammatic representation for this operator:

\[
\{v_m\} = m:\quad .
\]

(253)

Using the decomposition of \( v \), given by Eq. (251), the one-body part of the perturbation \( V_1^\gamma \), Eq. (242), becomes

\[
V_1^\gamma = \{\hat{F}_g\} + \sum_m \{v_m\} - \{\hat{O}_\gamma\} - \{\hat{u}_\gamma\},
\]

(254)
permitting us to generalize Eqs. (246) in the following manner:

\[
E_{\text{co}}^{(\gamma,v)} = E_{\text{co}}^{(0)}[\gamma,v] + \sum_m E_{\text{co}}^{(1)}[\gamma,v_m] + E_{\text{co}}^{(2+)}[\gamma,v], \tag{255a}
\]

\[
E_{\text{co}}^{(\eta)}[\gamma,v] = E_{\text{co}}^{(\eta,0)}[\gamma] + \sum_m E_{\text{co}}^{(\eta,1)}[\gamma,v_m] + E_{\text{co}}^{(\eta,2+)}[\gamma,v], \tag{255b}
\]

where the atomic terms, \(E_{\text{co}}^{(1)}[\gamma,v_m]\) and \(E_{\text{co}}^{(\eta,1)}[\gamma,v_m]\), depend on \(v_m\); they are the sum of all diagrams that contain one or more \(\{v_m\}\) inserts, but have no inserts from other external-potential components, say \(\{v_n\}\), where \((n \neq m)\). For example, diagrams (b), (c), and (d) from Fig. 4 contribute to \(E_{\text{co}}^{(1)}[\gamma,v_m]\) and \(E_{\text{co}}^{(\eta,1)}[\gamma,v_m]\). These diagrams are generated from the corresponding diagrams in Fig. 3 by replacing all the external-potential inserts, \(\{v\}\), given by Eq. (245b), with the individual components, \(\{v_m\}\), given by Eq. (253).

The remaining diagrams contribute to \(E_{\text{co}}^{(2+)}[\gamma,v]\) and \(E_{\text{co}}^{(\eta,2+)}[\gamma,v]\). These diagrams have two or more inserts from different external-potential components, e.g., diagrams with both \(\{v_m\}\) and \(\{v_n\}\) inserts, where \((m \neq n)\). Diagram (a) in the figure is an example of a \(E_{\text{co}}^{(2+)}[\gamma,v]\) or \(E_{\text{co}}^{(\eta,2+)}[\gamma,v]\) diagram. Diagram (e) is also a \(E_{\text{co}}^{(\eta,2+)}[\gamma,v]\) diagram, unless \((m = n = p)\), where it then contributes to \(E_{\text{co}}^{(1)}[\gamma,v_m]\) and \(E_{\text{co}}^{(\eta,1)}[\gamma,v_m]\).

For an atomic system we only have a single nucleus, and we get

\[
\begin{align*}
E_{\text{co}}[\gamma,v] &= E_{\text{co}}^{(0)}[\gamma] + E_{\text{co}}^{(1)}[\gamma,v_m], \quad \text{(atomic systems)} \quad (256a) \\
E_{\text{co}}^{(\eta)}[\gamma,v] &= E_{\text{co}}^{(\eta,0)}[\gamma] + E_{\text{co}}^{(\eta,1)}[\gamma,v_m]. \quad (256b)
\end{align*}
\]

The atomic terms, \(E_{\text{co}}^{(1)}[\gamma,v_m]\) and \(E_{\text{co}}^{(\eta,1)}[\gamma,v_m]\), are – for a range of systems – universal functionals: They contribute to \(E_{\text{co}}[\gamma,v]\) and \(E_{\text{co}}^{(\eta)}[\gamma,v]\) for any system with a nuclei with a charge of \(Z_m\). Note that two atomic tems, say \(E_{\text{co}}^{(1)}[\gamma,v_m]\) and \(E_{\text{co}}^{(1)}[\gamma,v_{m'}]\), are the same functionals when they are from the same nuclei \((Z_m = Z_{m'})\), but they are expressed from different nuclear locations, since we have \((\mathbf{R}_m \neq \mathbf{R}_{m'})\).
Factoring $Z_m$ from the diagrams, we get the following expansions:

\begin{align}
\mathcal{E}^{(1)}_{\text{co}}[\gamma, v_m] &= Z_m \mathcal{E}^{(1)}_{\text{co}(1)}[\gamma] + Z_m^2 \mathcal{E}^{(1)}_{\text{co}(2)}[\gamma] + Z_m^3 \mathcal{E}^{(1)}_{\text{co}(3)}[\gamma] + \ldots, \\
E^{(n,1)}_{\text{co}}[\gamma, v_m] &= Z_m E^{(n,1)}_{\text{co}(1)}[\gamma] + Z_m^2 E^{(n,1)}_{\text{co}(2)}[\gamma] + Z_m^3 E^{(n,1)}_{\text{co}(3)}[\gamma] + \ldots,
\end{align}

where $\mathcal{E}^{(1)}_{\text{co}(i)}[\gamma]$ and $E^{(n,1)}_{\text{co}(i)}[\gamma]$ are universal functionals, independent of $Z_m$; they are given by the sum of all diagrams with $i$ inserts of $\{v_m\}$, with $(Z_m = 1)$. For example, diagrams diagrams (b) and (c) from Fig. 4 contribute to $\mathcal{E}^{(1)}_{\text{co}(1)}[\gamma]$ and $E^{(n,1)}_{\text{co}(1)}[\gamma]$, for $(Z_m = 1)$, since they have a single insert; diagram (d) contributes to $\mathcal{E}^{(1)}_{\text{co}(2)}[\gamma]$ and $E^{(n,1)}_{\text{co}(2)}[\gamma]$; diagram (e) contributes to $\mathcal{E}^{(1)}_{\text{co}(3)}[\gamma]$ and $E^{(n,1)}_{\text{co}(3)}[\gamma]$, if $(n = p = m)$.

Further generalizing Eqs. (255), we have the following external-potential expansions:

\begin{align}
\mathcal{E}_{\text{co}}[\gamma, v] &= \mathcal{E}^{(0)}_{\text{co}}[\gamma] + \sum_m \mathcal{E}^{(1)}_{\text{co}}[\gamma, v_m] + \sum_{m>n} \mathcal{E}^{(2)}_{\text{co}}[\gamma, v_m, v_n] + \ldots, \\
E^{(n)}_{\text{co}}[\gamma, v] &= E^{(n,0)}_{\text{co}}[\gamma] + \sum_m E^{(n,1)}_{\text{co}}[\gamma, v_m] + \sum_{m>n} E^{(n,2)}_{\text{co}}[\gamma, v_m, v_n] + \ldots,
\end{align}

where the diatomic terms, $\mathcal{E}^{(2)}_{\text{co}}[\gamma, v_m, v_n]$ and $E^{(n,2)}_{\text{co}}[\gamma, v_m, v_n]$, depend on $v_m$ and $v_n$; they are the sum of all diagrams that contain one or more $\{v_m\}$ and $\{v_n\}$ inserts, but have no inserts from other external-potential components, say $\{v_p\}$, where $(p \neq m)$ and $(p \neq n)$. They are universal functionals for any system with one or more nuclei with charges of $Z_m$ and $Z_n$, but, in addition, they also depend on the molecular geometry – the distance between the charges. Diagrams (a) from Fig. 4 is one example. By factoring the $Z_m$ and $Z_n$ terms from the diagrams, analogous expansions, as in Eqs. (257), can also be obtained. Triatomic and molecular terms are defined in a similar manner.

X. APPROXIMATIONS

The diagrammatic methods presented in Sec. VIII and in the previous section, gives explicit expansions for the functionals $\mathcal{E}_{\text{co}}[\gamma, v]$ and $E^{(n)}_{\text{co}}[\gamma, v]$, and for the terms on the right side of Eq. (258). However, in the approximations we consider below, we often assume that these functionals can be expressed in a more simplified form, for example, as integrals involving the coordinates of only two electrons:

\begin{align}
\mathcal{E}_{\text{co}}[\gamma, v] &= \frac{1}{2} \int \int \mathcal{G}_{\text{co}}(x_1, x_2) \, dx_1 \, dx_2, \\
E^{(n)}_{\text{co}}[\gamma, v] &= \frac{1}{2} \int \int G^{(n)}_{\text{co}}(x_1, x_2) \, dx_1 \, dx_2,
\end{align}
where the integrands, $G_{co}(x_1, x_2)$ and $G^{(n)}_{co}(x_1, x_2)$, explicitly depends upon $\gamma(x_1, x_2)$, $\gamma(x_2, x_1)$, $v(r_1)$, and $v(r_2)$, and can include gradients or higher-order derivatives, e.g., $\nabla^2 \gamma(x_1, x_2)$.

If $E^{(0)}_{co}$ and $E^{(n,0)}_{co}$ are known for a model, one-particle, density-matrix, say $\gamma_m$, then possible approximations are the following:

$$E^{(0)}_{co}[\gamma] = E^{(0)}_{co}[\gamma_m](\gamma_m = \gamma),$$  \hspace{1cm} (260)

$$E^{(n,0)}_{co}[\gamma] = E^{(n,0)}_{co}[\gamma_m](\gamma_m = \gamma).$$ \hspace{1cm} (261)

If $\gamma_m$ is equal to, or similar to, the Brueckner-state one-particle density-matrix for an electron gas $\tau_g$, then, from Eqs. (250) and (261), we get the following approximation:

$$E^{(n,0)}_{co}[\gamma] \approx E^{(gas)}_{co}[\tau_g](\tau_g = \gamma).$$ \hspace{1cm} (262)

If periodic boundary conditions are used, the Brueckner orbitals are known to be plane waves \[2, 54, 85, 90, 91\], so $\tau_g$ is known. Because of conservation of momentum, there are many diagrams that are absent in the $E^{(gas)}_{co}[\tau_g]$ expansion \[54, 85, 90, 91\], but, in general, these diagrams appear in the expansion of $E^{(gas)}_{co}[\gamma]$. Since, apparently, all of these excluded-diagrams are also excluded in the $E^{(III,0)}_{co}[\gamma]$ expansion, the above approximation, Eq. (262), is probably most appropriate for ($\eta = III$):

$$E^{(III,0)}_{co}[\gamma] \approx E^{(gas)}_{co}[\tau_g](\tau_g = \gamma).$$ \hspace{1cm} (263)

For systems with a non-constant external potential, $E^{(n,0)}_{co}[\gamma]$ is, in many instances, the dominant portion of $E^{(n)}_{co}[\gamma, v]$. In that case, we can neglect all terms except the electron gas one from Eq. (258b), and using Eq (263), we get the following electron-gas approximation:

$$E^{(III)}_{co}[\gamma] \approx E^{(gas)}_{co}[\tau_g](\tau_g = \gamma),$$ \hspace{1cm} (264)

where, in this approximation, the dependence on $v$ is neglected.

Eq. (264) shares many similarities with the LDA of density-functional theory \[1, 2, 7\], where this approach constructs approximate energy-functional from expressions derived from a uniform electron gas. If periodic boundary conditions are used, the Brueckner orbitals (and the Hartree–Fock ones) are known to be plane waves \[54, 91\], so $\tau_g$ is known. If, in addition to requiring the volume to be infinitely large, the number of particles becomes infinite, a uniform electron gas is obtained. In this limiting case, the density of the Brueckner
reference-state $|\Theta\rangle$, say $\rho_{ug}$, is identical to the density of the target state $|\Psi\rangle$, both being a constant; the correlation energy of a uniform electron gas, say $E^{(\text{gas})}_{\text{co}}(\rho_{ug})$, is a function of this density, not a functional [54, 85, 90, 91]. In the LDA a functional is constructed using the function $E^{(\text{gas})}_{\text{co}}(\rho_{ug})$ divided by the number of electrons – the correlation energy per particle. An analogous approach may be necessary when constructing the functional $E^{(\text{gas})}_{\text{co}}[\tau_g]$, although the one-particle density matrix for an electron gas is not a constant [2, 54, 91]. Furthermore, when evaluating the diagrams for $E^{(\text{gas})}_{\text{co}}(\rho_{ug})$, as in the random phase approximation (RPA) [54, 85, 90, 91], the summations over the occupied, plane-wave states are replaced by integrals. For an exact treatment of $E^{(\text{gas})}_{\text{co}}[\tau_g]$, this approach cannot be used, and, mathematically speaking, this is the difference between $E^{(\text{gas})}_{\text{co}}[\tau_g]$ and $E^{(\text{gas})}_{\text{co}}(\rho_{ug})$.

In using the above electron gas approximation, Eq. (264), or other similar approximations, especially for atoms or molecules, one must take into consideration the boundary conditions imposed on the wavefunction. For example, if the wavefunction for an electron gas is required to vanish at the end points of a cube – and the cube has a finite size – this may lead to an electron gas functional $E^{(\text{gas})}_{\text{co}}[\tau_g]$, that explicitly depends on the boundary conditions. However, probably in many cases, this explicit dependents can be transformed, or contained within $\tau_g$, since $\tau_g$ also depends on the boundary conditions.

We have, so far, used the external-potential expansions, Eqs. (258), to obtain approximate functionals. An alternative approach is obtained, if $E^{(n)}_{\text{co}}[\gamma, v]$ is known for some system, say the helium atom, in the vicinity of some one-particle density-matrix, say the Brueckner one. In that case, the following prescription yields an approximate correlation-energy functional:

$$E^{(n)}_{\text{co}}[\gamma, v] \approx E^{(n)}_{\text{co}}[\tau_{ne}, v_{ne}](\tau_{ne}=\gamma, v_{ne}=v),$$

(265)

where $\tau_{ne}$ is the Brueckner, one-particle, density-matrix for the helium atom, and $v_{ne}$ is the external potential for this system, where using Eq. (78), we have

$$E^{(n)}_{\text{co}}[\gamma, v] \approx E_{\text{co}}[\tau_{ne}, v_{ne}](\tau_{ne}=\gamma, v_{ne}=v),$$

(266)

In the limit of $\rho \rightarrow \tau_x$, necessarily, many terms from $E_{\text{co}}[\tau_x, v_x]$ must vanish, where $v_x$ is the external potential associated with the Brueckner one-particle density matrix, $\tau_x$. Since, apparently, all of these vanishing-diagrams are also excluded in the $E^{(III,0)}_{\text{co}}[\gamma, v_x]$ expansion, most probably, the above approximation, Eq. (266), is most appropriate for ($\eta = \text{III}$).
Furthermore, since the Brueckner density matrix $\tau_{ne}$ is approximately equal to the Hartree–Fock one, say $\tilde{\tau}_{ne}$, we can write

$$E^{(\text{III})}_{\text{co}}[\gamma, v] \approx E_{\text{co}}[\tilde{\tau}_{ne}, v_{ne}](\tilde{\tau}_{ne}=\gamma, v_{ne}=v).$$

(267)

Using the expansion for $E_{\text{co}}$, given by Eq. (258a), and neglecting all terms except the electron gas one, we get

$$E^{(\text{III})}_{\text{co}}[\gamma, v] \approx E^{(\text{w})}_{\text{co}}[\tilde{\tau}_{ne}](\tilde{\tau}_{ne}=\gamma).$$

(268)

The above approximation assumes that the terms arising from the helium potential $v_{ne}$ are small; therefore, including them in the following way should yield only a small error:

$$E^{(\text{III})}_{\text{co}}[\gamma] \approx E_{\text{co}}[\tilde{\tau}_{ne}, v_{ne}](\tilde{\tau}_{ne}=\gamma).$$

(269)

A well known approximation for $E_{\text{co}}[\tilde{\tau}_{ne}, v_{ne}]$ is given by Colle and Salvetti functional [18, 19], say $E_{\text{co}}^{\text{cs}}[\tilde{\tau}_{ne}]$; so we have

$$E^{(\text{III})}_{\text{co}}[\gamma] \approx E_{\text{co}}^{\text{cs}}[\tilde{\tau}_{ne}](\tilde{\tau}_{ne}=\gamma),$$

(270)

where we have suppressed any mention of $v_{ne}$, since this functional has no explicit dependence on the external potential. However, this functional can still possess an implicit dependence on $v_{ne}$, since, for example, its four empirical parameters are determined by using data from the helium atom. An improved functional, perhaps, can be obtained by appending a potential dependence on these parameters and using the approximation given by Eq. (267).

We also mention that the correlation potentials $v_{co}^\tau$ can be treated in a similar manner as the correlation-energy functionals $E_{\text{co}}^{(n)}[\gamma, v]$, since they also depend on the external potential: $v_{co}^\tau[v]$; Equations, or approximations, analogous to Eqs. (258b), (257b), (264), and (265), are easily defined. However, we now pursue a different approach, permitting correlation potentials to be obtained as functional derivatives of variation correlation-energy functionals.

**XI. VARIATIONAL FORMALISM**

We now introduce variational energy-functionals $\tilde{E}_{\eta}^\gamma$. By functional differentiating these functionals with respect to the one-particle density-matrix $\gamma$, generalized Fock operators are obtained. These operators – denoted by $\hat{\zeta}^{(\eta)}_\tau$ – satisfy the same Brillouin-Brueckner and
commutation relations, Eqs. (187a) and (188), as the corresponding non-variational ones, \( \hat{F}^{(n)} \).

Using our trial wavefunctions from Sec. (V), we can construct variational energy-functionals:

\[
\bar{E}_\eta[\gamma] = \frac{\langle \Psi^{(n)} | H | \Psi^{(n)} \rangle}{\langle \Psi^{(n)} | \Psi^{(n)} \rangle} = E_1[\gamma] + \bar{E}^{(n)}_{\eta}[\gamma],
\]

(271)

where the first-order energy \( E_1[\gamma] \) is given by Eq. (172), our variational correlation-energy functionals are

\[
\bar{E}^{(n)}_{\eta}[\gamma] = \frac{\langle \Psi^{(n)} | (\{ \hat{F} \} + \{ r^{-1} \}_{12} ) \Psi^{(n)} \rangle}{\langle \Psi^{(n)} | \Psi^{(n)} \rangle},
\]

(272)

and we have used Eqs. (123), (124a) and (192). We also define exchange-correlation (xc) energy-functionals:

\[
\bar{E}^{(n)}_{x}[\gamma] = \bar{E}^{(n)}_{\eta}[\gamma] - E_x[\gamma],
\]

(273)

The exact energy is also given by

\[
\mathcal{E} = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} = E_1[\gamma] + \frac{\langle \Psi | (\{ \hat{F} \} + \{ r^{-1} \}_{12} ) | \Psi \rangle}{\langle \Psi | \Psi \rangle}.
\]

(274)

Comparing this Eq. to Eq. (110) gives

\[
\mathcal{E}_{\eta}[\gamma] = \frac{\langle \Psi | (\{ \hat{F} \} + \{ r^{-1} \}_{12} ) | \Psi \rangle}{\langle \Psi | \Psi \rangle},
\]

(275)

From the variational theorem, the fourth-trial wavefunctions are equal:

\[
E_{iv}[\gamma] = E_{iv}[\gamma],
\]

(276)

and we have

\[
\bar{E}^{(iv)}_{\eta}[\gamma] = E^{(iv)}_{\eta}[\gamma].
\]

(277)

From the variational theorem, we also have

\[
\bar{E}_\eta[\tau] \geq \mathcal{E},
\]

(278)

where Eqs. (111), (274), (275), (276), (277), and (22) give the following equalities that appear for the Brueckner one-particle density-matrix \( \tau \):

\[
\mathcal{E} = \bar{E}_\eta[\tau] = E_\eta[\tau],
\]

(279)

\[
\mathcal{E}_{\eta}[\tau] = \bar{E}_{\eta}^{(n)}[\tau] = E_{\eta}^{(n)}[\tau],
\]

(280)

\[
\mathcal{E}_{x}[\tau] = \bar{E}_{x}^{(n)}[\tau] = E_{x}^{(n)}[\tau],
\]

(281)
where the latter relations use Eqs. (77), (78), and (79); Eqs. (278) and (279) indicate that
the minimization of $\bar{E}_\eta[\gamma]$ occurs at $\tau$.

We now pursue, in a formal way, the minimization of $\bar{E}_\eta[\gamma]$, using an approach that is
similar to the procedure used by Parr and Yang [2] in their treatment of Hartree–Fock theory,
where $\bar{E}_\eta[\gamma]$ is subject to the constraint that the one-particle density-matrix comes from a
single-determinantal state $\gamma(|\Phi\rangle)$. This condition is imposed by requiring the one-particle
density-matrix $\gamma$ to have a trace equal to the number of electrons $N_\gamma$, and that it is also
idempotent [49, 50]:

$$
\int \int \gamma(x_3, x_4)\delta(x_4 - x_3) \, dx_3 \, dx_4 = N_\gamma,
$$

(282)

$$
\int \gamma(x_3, x_5)\gamma(x_5, x_4) \, dx_5 = \gamma(x_3, x_4).
$$

(283)

The normalization constraint, Eq. (282), insures that $\gamma$ can be constructed from $N_\gamma$ orbitals;
Eq. (283) insures that the density-matrix operator $\hat{\gamma}$ – when acting within the one-particle
Hilbert space – is a projector into the occupied subspace, as indicated by Eq. (169), where
$\gamma$ serves as the kernel of the one-particle density-matrix operator $\hat{\gamma}$, Eq. (180).

Using the above constraints, the variational problem is expressed by

$$
\delta \mathcal{L}(\gamma)|_{\tau} = 0,
$$

(284)

where

$$
\mathcal{L}(\gamma) = \bar{E}_\eta[\gamma] - \beta \left[ \int \int \gamma(x_3, x_4)\delta(x_4 - x_3) \, dx_3 \, dx_4 - N_\gamma \right]
$$

$$
- \int \int d x_3 \, d x_4 \, \alpha(x_4, x_3) \left[ \int \gamma(x_3, x_5)\gamma(x_5, x_4) \, dx_5 - \gamma(x_3, x_4) \right],
$$

(285)

and where $\alpha$ and $\beta$ are the Lagrangian multipliers. Eq. (284) is satisfied when the functional
derivative of $\mathcal{L}$ vanishes:

$$
\left. \frac{\delta \mathcal{L}(\gamma)}{\delta \gamma(x_2, x_1)} \right|_{\tau} = 0,
$$

(286)

where the definition of the functional derivative is

$$
\delta \mathcal{L}(\gamma) = \int \int \frac{\delta \mathcal{L}(\gamma)}{\delta \gamma(x_2, x_1)} \delta \gamma(x_2, x_1) \, dx_1 \, dx_2.
$$

(287)
Substituting Eq. (285) into (286), yields
\[
\zeta^{(n)}(x_1, x_2) - \int dx_3 \left[ \tau(x_1, x_3) \alpha(x_3, x_2) + \alpha(x_1, x_3) \tau(x_3, x_2) \right] + \alpha(x_1, x_2) - \beta \delta(x_1 - x_2) = 0, \tag{288}
\]
where
\[
\zeta^{(n)}(x_1, x_2) = \left. \frac{\delta \bar{E}_\eta[\gamma]}{\delta \gamma(x_2, x_1)} \right| \tau. \tag{289}
\]
Let the two-body functions, \( \alpha(x_1, x_2) \) and \( \zeta^{(n)}(x_1, x_2) \), serve as kernels of operators, \( \hat{\alpha} \) and \( \hat{\zeta}^{(n)}; \) explicitly, we have
\[
\hat{\alpha} \phi(x_1) = \int \alpha(x_1, x_2) \phi(x_2) \, dx_2, \tag{290}
\]
\[
\hat{\zeta}^{(n)} \phi(x_1) = \int \zeta^{(n)}(x_1, x_2) \phi(x_2) \, dx_2. \tag{291}
\]
Using this notation, the operator form of Eq. (288) is given by
\[
\hat{\zeta}^{(n)} - \hat{\tau} \hat{\alpha} - \hat{\alpha} \hat{\tau} + \hat{\alpha} - \beta = 0, \tag{292}
\]
where \( \hat{\tau} \) is defined by Eq. (134).

The identity operator \( \hat{I} \), defined by Eq. (179), or expressed by
\[
\hat{I} = \hat{\tau} + \hat{\kappa}, \tag{293}
\]
can be used to obtain the following relation:
\[
\hat{\alpha} - \hat{\tau} \hat{\alpha} - \hat{\alpha} \hat{\tau} = \hat{I} \left( \hat{\alpha} - \hat{\tau} \hat{\alpha} - \hat{\alpha} \hat{\tau} \right) \hat{I} = \hat{\kappa} \hat{\alpha} \hat{\kappa} - \hat{\alpha} \hat{\tau}, \tag{294}
\]
which we substitute into Eq. (292); this procedure gives
\[
\hat{\zeta}^{(n)} - \hat{\tau} \hat{\alpha} \hat{\tau} + \hat{\kappa} \hat{\alpha} \hat{\kappa} - \beta = 0, \tag{295}
\]
and yields the following requirements:
\[
\hat{\kappa} \hat{\zeta}^{(n)} \hat{\kappa} = 0, \tag{296a}
\]
\[
\hat{\tau} \hat{\zeta}^{(n)} \hat{\tau} = 0, \tag{296b}
\]
where we have dropped the \( \eta \) superscript since, for \( (\gamma = \tau) \), all operators are equal within these blocks:
\[
\hat{\kappa} \hat{\zeta}^{(n)} \hat{\kappa} = \hat{\kappa} \hat{\zeta}^{(n)} \hat{\kappa} = \hat{\kappa} \hat{\zeta}^{(n)} \hat{\kappa}, \tag{297a}
\]
\[
\hat{\tau} \hat{\zeta}^{(n)} \hat{\tau} = \hat{\tau} \hat{\zeta}^{(n)} \hat{\tau} = \hat{\tau} \hat{\zeta}^{(n)} \hat{\tau}. \tag{297b}
\]
Eq. (296a) is yet another representation of the Brillouin–Brueckner condition; comparing Eqs. (187) and (296) give

\[
\hat{\kappa}_\tau \hat{\nu}_{\tau} = \hat{\kappa}_\tau \hat{F}_\tau, \tag{298a}
\]

\[
\hat{\kappa}_\tau \hat{\nu}_{\tau} = \hat{\kappa}_\tau \hat{F}_\tau, \tag{298b}
\]

and it is easily verified that the commutation relation, Eq. (188), also holds for the variational one-body operators \(\hat{\zeta}_\tau\):

\[
\left[ \hat{\zeta}_\tau, \hat{\tau} \right] = 0. \tag{299}
\]

An alternative to the exact Hartree–Fock Eq. (189) is

\[
\hat{\zeta}^{(\eta)}_{\tau} |\psi_w\rangle = \sum_{x \in \{\psi_\eta \rightarrow \tau\}} \xi^{\tau \eta}_{xw} |\psi_x\rangle, \tag{300}
\]

where the appended \(\eta\) superscripts appear since the occupied-block matrix-elements \(\xi^{\tau \eta}_{xw}\), perhaps, depend on \(\eta\). However, we can redefine the variational operators \(\hat{\zeta}^{(\eta)}_{\tau}\) to remove this dependence, since Eqs. (296) still holds. In any event, we assume that \(\hat{\zeta}^{(\eta)}_{\tau}\) is independent of \(\eta\) and choose orbitals that diagonalize \(\xi^{\tau}_{xw}\), giving a generalized Hartree-Fock Eq. that is an alternative to Eq. (167):

\[
\hat{\zeta}_\tau \hat{\psi}^T_{\tau}(x) = \xi^{\tau}_{\eta} \hat{\psi}^T_{\eta}(x). \tag{301}
\]

Substituting Eq. (271) into (289) for \((\tau = \gamma)\) gives

\[
\zeta^{(\eta)}_{\tau}(x_1, x_2) = F_{\gamma}(x_1, x_2) + \nu^{\gamma \eta}_{co}(x_1, x_2), \tag{302}
\]

where \(F_{\gamma}(x_1, x_2)\) and \(\nu^{\gamma \eta}_{co}(x_1, x_2)\) are the kernel of the Fock operator \(\hat{F}_{\gamma}\) – defined by Eq. (229) – and variational correlation-potentials \(\nu^{\gamma \eta}_{co}\):

\[
F_{\gamma}(x_1, x_2) = \frac{\delta E_{1}[\gamma]}{\delta \gamma(x_2, x_1)}, \tag{303}
\]

\[
\nu^{\gamma \eta}_{co}(x_1, x_2) = \frac{\delta E_{co}^{(\eta)}[\gamma]}{\delta \gamma(x_2, x_1)}. \tag{304}
\]

The operator form of Eq. (302) is

\[
\hat{\zeta}^{(\eta)}_{\tau} = \hat{F}_{\gamma} + \hat{\nu}^{\gamma \eta}_{co}. \tag{305}
\]

Substituting this Eq. into Eq. (297) indicates that we have

\[
\hat{\kappa}_\tau \hat{\nu}^{\gamma \eta}_{co} = \hat{\kappa}_\tau \hat{\nu}^{\gamma \eta}_{co} \hat{\tau} = \hat{\kappa}_\tau \hat{\nu}^{\gamma \eta}_{co} \hat{\tau}, \tag{306a}
\]

\[
\hat{\tau} \hat{\nu}^{\gamma \eta}_{co} \hat{\kappa}_\tau = \hat{\tau} \hat{\nu}^{\gamma \eta}_{co} \hat{\kappa}_\tau = \hat{\tau} \hat{\nu}^{\gamma \eta}_{co} \hat{\kappa}_\tau. \tag{306b}
\]
Substituting Eqs. (305) and (191) into (298) and using the two above definitions, yields

\[ \hat{K}_\tau \hat{v}_{\cot} \hat{T} = \hat{K}_\gamma v_{\cot} \hat{T}, \]  
(307a)

\[ \hat{T} \hat{v}_{\cot} \hat{K}_\tau = \hat{T} v_{\cot}^* \hat{K}_\tau. \]  
(307b)

In order acquire to the kernels of the generalized Fock operators \( \zeta^{(\eta)}(x_1, x_2) \), given by Eq. (302), it is necessary obtain the functional derivatives of \( E_{1}[\gamma] \) and \( \bar{E}_{\cot}^{(\eta)}[\gamma] \), as indicated by Eq. (303) and (304). The functional derivative for \( E_{1}[\gamma] \) can be evaluated using Eqs. (172), (173), and (174), yielding Eq. (229). The functional derivative of the diagrammatic terms of \( \bar{E}_{\cot}^{(\eta)}[\gamma] \) can also be obtained; the details are presented elsewhere [57]. Here we only mention that by imposing the same occupied and virtual orbital degeneracies as in Sec. VIII B, each diagram in the expansion is given by a product of one-particle density-matrices, and can, therefore, be differentiated in the same manner as in the treatment of \( E_{1}[\gamma] \). After the functional derivative is taken, the nondegeneracy of the orbitals can be restored, since the entire expansion is invariant to the choice of orbital energies, but this removes the explicit dependence on \( \gamma \) for each term.

It is easily demonstrated that an analogous external-potential expansion, as given in Eq. (258a), also holds:

\[ \bar{E}_{\cot}^{(\eta)}[\gamma, v] = \bar{E}_{\cot}^{(\eta,0)}[\gamma] + \sum_m \bar{E}_{\cot}^{(\eta,1)}[\gamma, v_m] + \sum_{m>n} \bar{E}_{\cot}^{(\eta,2)}[\gamma, v_m, v_n] + \ldots \]  
(308)

Furthermore – by using, Eqs. (279), (280) and (281) – all approximations presented in Sec. X are valid when \( \bar{E}_{\cot}^{(\eta)} \) is replaced by \( \bar{E}_{\cot}^{(\eta)}[\gamma] \). For example, consider the electron-gas approximation, Eq. (264), and the Colle–Salvetti functional, Eq (270):

\[ \bar{E}_{\cot}^{(\text{III})}[\gamma] \approx E_{\cot}^{\text{(gas)}}[\tau_g|\tau_g=\gamma], \]  
(309)

\[ \bar{E}_{\cot}^{(\text{III})}[\gamma] \approx E_{\cot}^{\text{CS}}[\tilde{\tau}_h|\tilde{\tau}_h=\gamma]. \]  
(310)

Assuming both approximations are reasonable ones, we can use a linear combination of the two:

\[ \bar{E}_{\cot}^{(\text{III})}[\gamma] \approx a_c E_{\cot}^{\text{CS}}[\tilde{\tau}_h|\tilde{\tau}_h=\gamma] + (1 - a_c) E_{\cot}^{\text{(gas)}}[\tau_g|\tau_g=\gamma], \]  
(311)

where \( a_c \) is an empirical parameter. This Eq. is an alternative to the B3LYP functional [8, 17], which uses analogous correlation-energy functionals: They use the LYP correlation-energy functional [18], derived from Colle–Salvetti one \( E_{\cot}^{\text{CS}} \), and a uniform-electron-gas functional, derived from the RPA [92]; they set \( a_c = 8.1 \).
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APPENDIX A: VARIATIONAL BRUECKNER-ORBITAL FORMALISMS

In the exact SCF theory by Löwdin \cite{26}, an orbital variation of an energy functional is used to derive the Brillouin–Brueckner condition. By using a slight modification of Kobe’s formulation \cite{38}, Löwdin’s energy-functional can be written in the following manner:

\[ E_\eta[\Theta, \Phi] = \langle \Phi | \hat{H}_\text{eff}^\Theta | \Phi \rangle = \langle \Phi | (H_0^\Theta + t^\Theta) | \Phi \rangle \]

(A1)

where \( t^\Theta \), or \( V_{\Theta} \Omega_{\Theta} \), is the reaction operator, which we also define above by the effective Hamiltonian \( \hat{H}_\text{eff}^\Phi \); by definition, this operator satisfies the following relation:

\[ \mathcal{E} = \langle \Phi | \hat{H}_\text{eff}^\Phi | \Phi \rangle = \langle \Phi | H \Omega_{\Phi} | \Phi \rangle = \langle \Phi | H (1 + \chi_{\Phi}) | \Phi \rangle \]

(A2)

and it acts only within the one-dimensional reference-space, with projector \( P_{\Phi} \): \( \hat{H}_\text{eff}^\Phi = P_{\Phi} \hat{H}_\text{eff}^\Phi P_{\Phi} \); the wave operator \( \Omega_{\Phi} \) and correlation operator \( \chi_{\Phi} \) are given by Eqs. (5) and (19). As in valence-universal multireference perturbation theory \cite{56, 74, 75, 78, 79, 93, 94}, \( \hat{H}_\text{eff}^\Phi \) can be written as a sum of constant, one-, two- and higher-body excitations, where the vacuum state is at our disposal.

By varying the occupied orbitals from the reference state \( | \Phi \rangle \), i.e., \( \{ \psi_o \to \Phi \} \), Löwdin and Kobe derived a form of the Brillouin–Brueckner condition, indicating that the above functional \( E_\eta[\Theta, \Phi] \) – when \( \hat{H}_\text{eff}^\Theta \) is held constant – satisfies a variational condition that yields the exact energy at the extremum: \( \mathcal{E} = E_\eta[\Theta, \Theta] \), where the reference state is the Brueckner one, \( | \Theta \rangle \). A modified version of Löwdin and Kobe’s formulation involving a one-particle density matrix approach, instead of an orbital one, is easily derived \cite{57}.
A generalization of Löwdin and Kobe’s theory, by Brueckner and Goldman, minimizes the following functional: $E_\eta[\Phi, \Phi]$, given by the right side of Eq. (A2). Such an approach has been criticized, since this functional is invariant to the reference state $|\Phi\rangle$, and its a constant – the exact energy $\mathcal{E}$; also, if an approximate $\hat{H}_{\text{eff}}^\Phi$ is used, the energy functional does not satisfy the Rayleigh-Ritz principle, as pointed out by Brandow. This method leads to the so-called rearrangement potential that arises from the variation of the term involving the reaction operator $t^\Phi$. (For further references regarding the rearrangement potential and an historical account of Brueckner orbital theory, see the bibliography notes within Kobe’s article.)

Another variant of the energy functional $E_\eta[\Phi, \Phi]$, replaces the correlation operator $\chi_\Phi$ with $\chi^\Phi_\Theta$ in the right side of Eq. (A2); this energy functional is simply the non-variational one $E_\eta[\Phi]$, as indicated by Eq. (130). Löwdin and Kobe’s exact SCF theory is obtained by using $\chi^\Phi_\Theta$ and not permitting it to vary, where from Eq. (132) we have ($\chi^\Phi_\Theta = \chi_\Theta$).

APPENDIX B: PARTITIONING OF SECOND QUANTIZED OPERATORS

Any second quantized operator, say $\hat{O}$, can be partitioned into open (op) and closed (cl) portions with respect to a single- or multi-reference space. In our case, where the reference space is only spanned by a single-determinantal state, the closed portion of $\hat{O}$, say $\hat{O}_{\text{cl}}$, is simply a constant – as in Eqs. (17) and (18) – and is given by the fully contracted part of $\hat{O}$, where the operator is written in normal-ordered form with respect to the reference state $|\Phi\rangle$. Explicitly, we have

$$\hat{O}_{\text{cl}} = \hat{O}_0 = \langle \Phi | \hat{O} | \Phi \rangle,$$

where the 0 subscript indicates the zero-body term.

The open portion of $\hat{O}$, say $\hat{O}_{\text{op}}$, is usually defined as the remaining portion; it is given by the one-, two- and higher-body terms, where, again, the operator is written in normal-ordered form. However, for our purposes, we use a more restrictive definition for $\hat{O}_{\text{op}}$, and define it by the following conditions:

$$\hat{O}_{\text{op}} |\Phi\rangle = Q_\Phi \hat{O} |\Phi\rangle,$$

$$\hat{O}_{\text{op}} Q_\Phi = 0.$$
We define the remaining portion, $\hat{O}_{re}$, by the following:

$$\hat{O} = \hat{O}_{cl} + \hat{O}_{op} + \hat{O}_{re}, \quad (B4)$$

so the following identities are satisfied:

$$(\hat{O}_{cl} + \hat{O}_{op})|\Phi\rangle = \hat{O}|\Phi\rangle, \quad (B5)$$

$$\hat{O}_{re}|\Phi\rangle = 0. \quad (B6)$$

The remaining portion $\hat{O}_{re}$ has at least one hole or particle annihilation-operator. $\hat{O}_{op}$ has at least one pair of hole-particle creation-operators and no hole or particle annihilation-operators. In terms of diagrams, $\hat{O}_{re}$ has at least one external line below the vertex; $\hat{O}_{op}$ has no lines below the vertex and at least one pair of externals lines above it; $\hat{O}_{cl}$ has no external free-lines.

As an alternative to the above normal-ordered partitioning, we find it convenient to partition one-body operators, say $\hat{h}$,

$$\hat{h} = \sum_{ij} \hat{h}_{ij}, \quad (B7)$$

into the following four components:

$$\hat{h} = \hat{h}_{ex} + \hat{h}_{de} + \hat{h}_{oc} + \hat{h}_{un}, \quad (B8a)$$

where the excitation (ex), de-excitation (de), occupied (oc), and unoccupied (un) parts are given by the following expressions:

$$\hat{h}_{ex} = \sum_{w} h_{rw} a_{r}^{\dagger} a_{w}, \quad (B8b)$$

$$\hat{h}_{de} = \sum_{w} h_{wr} a_{w}^{\dagger} a_{r}, \quad (B8c)$$

$$\hat{h}_{oc} = \sum_{w} h_{wx} a_{w}^{\dagger} a_{x}, \quad (B8d)$$

$$\hat{h}_{un} = \sum_{r} h_{rs} a_{r}^{\dagger} a_{s}. \quad (B8e)$$

and the orbitals are defined with respect to a reference state $|\Phi\rangle$, as indicated by Eqs. (6). Note that the open and excited portions are identical:

$$\hat{h}_{ex} = \hat{h}_{op}. \quad (B9)$$
APPENDIX C: DISCUSSION OF PERTURBATIVE CONVERGENCE WHEN USING ORBITAL DEGENERACIES

Our primary reason for choosing orbital degeneracies within the occupied and virtual subspaces is that it provides a means of obtaining an explicit dependence on the one-particle density-matrix $\gamma$ for the individual perturbative terms (the diagrams) that represent the correlation energy $E_\gamma$ and correlation-energy functionals $E_\gamma(\gamma)$. While this choice greatly restricts the zeroth-order Hamiltonian, it can still yield convergent series for ground states, as long as the parameter $\varepsilon_\gamma$ is chosen to be sufficiently large, and negative, so that the dominant configurations do not become intruder-states from the presence of small-energy denominators or incorrect energy ordering, as in the case for multireference perturbation theory. However, because of incorrect energy-ordering it is probably not possible to generate convergent expansions for excited states. However, infinite-order summation methods can be attempted, or the series can be asymptotically convergent.

Consider a suitable partitioning method, like, for example, Møller–Plesset, Epstein–Nesbet, or maximum radius of convergence perturbation theory. Any of these approaches generate a separate energy-denominator for each orthogonal-space state $|q\rangle$, say $\Delta_q = E_\Phi^q - E_0^q$, where $E_\Phi^q$ and $E_0^q$ are the, respective, zeroth-order energies. Since small energy-denominators can yield convergence problems, a reasonable choice for $2\varepsilon_\gamma$ is given by the maximum $\Delta_q$ within the doubly-excited subspace:

$$\varepsilon_\gamma = \frac{1}{2} \max_{|q\rangle \in \{|\Phi_{\omega s}\rangle\}} \Delta_q,$$

where the search is over all orthogonal-space states $\{|q\rangle\}$ from within the set of double excited-states $\{|\Phi_{\omega s}\rangle\}$ that arise from a reasonable set of orbitals, e.g., from the $\{\varphi_o \leftarrow \Phi, \hat{F}_o\}$ and $\{\varphi_u \leftarrow \Phi, \hat{F}_u\}$ sets. (Some modification is necessary for Møller–Plesset, since this method is restricted to Hartree–Fock orbitals, e.g., choose $H_0$ to be given by Eqs. (39), (38c) and (38d), where $\hat{F}_o^s = \hat{F}_o^u = \hat{F}_\Phi$.)

At least for ground states, we anticipate that perturbative expansions using orbital degeneracies can often converge, but, perhaps, at a slow rate. On the other hand, this deficiency is partially compensated by a greater computational efficiency, since, for example, costly two-electron integral-transformations can be avoided. Furthermore, approximations that involve...
infinite-order summations are often invariant to the choice of $H_0$ – and hence $\varepsilon_\gamma$ – including the coupled cluster method that can be viewed as an infinite-order partial-summation method \[56, 63\].

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